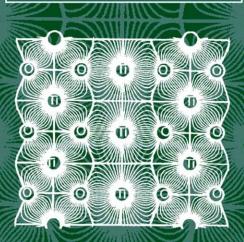
The Chemical Bond in Inorganic Chemistry

The Bond Valence Model

I. David Brown



INTERNATIONAL UNION OF CRYSTALLOGRAPHY
OXFORD SCIENCE PUBLICATIONS

INTERNATIONAL UNION OF CRYSTALLOGRAPHY MONOGRAPHS ON CRYSTALLOGRAPHY

IUCr BOOK SERIES COMMITTEE

A. A. Chernov, *Russia*P. Coppens (*Chairman*), *USA*G. R. Desiraju, *India*

J. Drenth, The Netherlands

A. M. Glazer, UK

J. P. Glusker, USA

J. R. Helliwell, UK

IUCr Monographs on Crystallography

- 1 Accurate molecular structures: their determination and importance A. Domenicano and I. Hargittai, editors
- 2 P. P. Ewald and his dynamical theory of X-ray diffraction D.W.J. Cruickshank, H. J. Juretschke, and N. Kato, editors
- 3 Electron diffraction techniques, Volume 1 J. M. Cowley, editor
- 4 Electron diffraction techniques, Volume 2 J. M. Cowley, editor
- 5 The Rietveld method R. A. Young, editor
- 6 Introduction to crystallographic statistics
 U. Shmueli and G. H. Weiss
- 7 Crystallographic instrumentation L. A. Aslanov, G. V. Fetisov, and J. A. K. Howard
- 8 Direct phasing in crystallography: fundamentals and applications C. Giacovazzo
- The weak hydrogen bond in structural chemistry and biologyG. R. Desiraju and T. Steiner
- 10 Defect and microstructure analysis by diffraction R. L. Snyder, J. Fiala, and H. J. Bunge
- 11 Dynamical theory of X-ray diffraction A. Authier
- 12 The chemical bond in inorganic chemistry
 L. David Brown

IUCr Texts on Crystallography

- 1 The solid state: from superconductors to superalloys
 A. Guinier and R. Jullien, translated by W. J. Duffin
- **2** Fundamentals of crystallography
 - C. Giacovazzo, editor
- 4 X-Ray charge densities and chemical bonding P. Coppens
- 5 The basics of crystallography and diffraction, second edition C. Hammand

IUCr Crystallographic Symposia

- 1 Patterson and Pattersons: fifty years of the Patterson function J. P. Glusker, B. K. Patterson, and M. Rossi, editors
- 2 Molecular structure: chemical reactivity and biological activity J. J. Stezowski, J. Huang, and M. Shao, editors
- 3 Crystallographic computing 4: techniques and new technologies N. W. Isaacs and M. R. Taylor, editors
- 4 Organic crystal chemistry
 J. Garbarczyk and D. W. Jones, editors
- 5 Crystallographic computing 5: from chemistry to biology D. Moras, A. D. Podjarny, and J. C. Thierry, editors
- 6 Crystallographic computing 6: a window on modern crystallography H. D. Flack, L. Parkanvi, and K. Simon, editors
- 7 Correlations, transformations, and interactions in organic crystal chemistry D. W. Jones and A. Katrusiak, editors

The Chemical Bond in Inorganic Chemistry

The Bond Valence Model

I. DAVID BROWN

Department of Physics and Astronomy
McMaster University
Hamilton
Ontario



OXFORD

Great Clarendon Street, Oxford OX2 6DP

Oxford University Press is a department of the University of Oxford. It furthers the University's objective of excellence in research, scholarship, and education by publishing worldwide in

Oxford New York

Auckland Cape Town Dar es Salaam Hong Kong Karachi Kuala Lumpur Madrid Melbourne Mexico City Nairobi New Delhi Shanghai Taipei Toronto

With offices in

Argentina Austria Brazil Chile Czech Republic France Greece Guatemala Hungary Italy Japan Poland Portugal Singapore South Korea Switzerland Thailand Turkey Ukraine Vietnam

Oxford is a registered trade mark of Oxford University Press in the UK and in certain other countries

> Published in the United States by Oxford University Press Inc., New York

> > © Oxford University Press 2002

The moral rights of the author have been asserted Database right Oxford University Press (maker)

First published 2002 First published in paperback 2006

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, without the prior permission in writing of Oxford University Press, or as expressly permitted by law, or under terms agreed with the appropriate reprographics rights organization. Enquiries concerning reproduction outside the scope of the above should be sent to the Rights Department, Oxford University Press, at the address above

You must not circulate this book in any other binding or cover and you must impose the same condition on any acquirer

A catalogue record for this title is available from the British Library

Library of Congress Cataloging in Publication Data

Brown, I. David (Ian David)

The chemical bond in inorganic chemistry: the bond valence model / I. David Brown. (International Union of Crystallography monographs on crystallography; 12)

1. Chemical bonds–Mathematical models.

2. Inorganic compounds.

I. Title II. Series. OD461.B837 2002 541.2′24–dc21 2001036457

Typeset by Newgen Imaging Systems (P) Ltd., Chennai, India
Printed in Great Britain
on acid-free paper by
Biddles Ltd., King's Lynn

ISBN 0-19-850870-0 978-0-19-850870-0 ISBN 0-19-929881-5 (Pbk.) 978-0-19-929881-5 (Pbk.)

Preface

This book describes the bond valence model, an increasingly popular description of acid—base bonding, particularly in fields such as materials science and mineralogy where solid state inorganic chemistry is important. The text is aimed at two groups of readers, those who are teaching chemical bonding in acid—base systems, and those who are researching in fields, ranging from physics to molecular biology, in which such bonding is involved. The model derives from Pauling's concept of electrostatic valence which, in recent years, has evolved into a simple but highly predictive model. It is essentially empirical. Its theorems have not yet been derived from quantum mechanics, but its presentation of chemical bonding is complementary to the quantum mechanical approaches. The essential simplicity of the model makes it useful in situations that are too complex to be adequately treated by more fundamental theories.

The reader is advised to avoid bringing too many preconceptions about the nature of chemical bonding to a reading of this work. While there are rather too many models of chemical bonding in existence, the bond valence model represents their common features reduced to their simplest mathematical form. The model should be judged on its own terms: how well does it predict acid-base chemistry and how effective are the insights it provides? Attempts to formulate the model in terms of the traditional concepts of chemistry, covalent versus ionic bonding, resonance Lewis structures, or electronic orbitals (except as discussed in Chapter 8), only make it more complex and less predictive. The model works best when it is kept simple. I have, therefore, only introduced concepts where they are needed to account for the observed phenomena, and the concepts are all precisely defined. The result is a simple but quantitatively rigorous model that describes many of the phenomena of inorganic and other acid-base bonding. It requires a minimum of computing (a pocket calculator, pencil, and paper usually suffice) and the basic concepts can readily be grasped by secondary school students.

The model itself is developed in Part I and its applications to inorganic chemistry are described in Part II. Part III is devoted to an analysis of inorganic solids, showing how the unique character of solid state chemistry derives from the conflict between the constraints of chemistry and those of three-dimensional space. Part IV surveys the wide range of problems to which the model has been applied, from condensed matter physics, through mineralogy and soil science, to catalysis and molecular biology. The book ends with a comparison between the bond valence model and other descriptions of chemical bonding, and includes a discussion of why such a simple model works so well.

vi PREFACE

This book started as a series of lectures which Prof. Schenk invited me to give to the Chemistry Department of the University of Amsterdam in 1994. Many people have helped in developing the ideas presented in this book, often in lively discussions over midmorning cups of coffee. These people are too numerous to list here, but I thank them all for their contributions which are referred to at the appropriate places in the text. I would particularly like to acknowledge three people whose influence was instrumental in introducing me to the important ideas described in these pages. They are my research supervisor, Jack Dunitz, whose unconventional, but always correct, approach to research has inspired many besides myself, Bob Shannon, who introduced me to Pauling's electrostatic valence principle, and Hans Burzlaff, who convinced me of the importance of symmetry and spatial restrictions in understanding the chemistry of solids. To these three I wish to dedicate this work.

11 April 2001 I. D. B

Contents

Pr	ologue	1
1	Historical introduction 1.1 Introduction 1.2 Chemical bonds 1.3 The ionic model 1.4 Quantum mechanics 1.5 The symmetry model 1.6 Topological models 1.7 Pauling's electrostatic valence model	3 3 3 5 6 6 6 7 8
I	Theory	11
2	The ionic bond 2.1 Introduction 2.2 Crystal energy and the Coulomb field 2.3 How are the atom fragments chosen? 2.4 The Madelung field of a crystal 2.5 Bond networks and bond graphs 2.6 Coordination number 2.7 Conclusions	13 13 14 15 17 20 23 25
3	The bond valence model 3.1 Experimental bond valences and bond lengths 3.2 Empirical network equations 3.3 The bond valence model 3.4 The distortion theorem 3.5 Bond networks with non-bipartite graphs	26 26 28 31 33 34
II	Chemistry	41
4	Anion and cation bonding strengths 4.1 Bond graphs and coordination number 4.2 Anion bonding strength 4.3 Cation bonding strength 4.4 The valence matching principle	43 43 45 47 49

viii CONTENTS

	4.5	Hard and soft acids and bases	50			
	4.6	Applications of the valence matching principle	51			
5	Liqu	ids	53			
	5.1	Introduction	53			
	5.2	Cation and anion bonding strength of water	53			
	5.3	Reactions of cations with water	55			
	5.4	Reactions of anions with water	57			
	5.5	Aqueous solubility	59			
	5.6	Aqueous solutions of soft ions	62			
	5.7	Non-aqueous solutions and melts	62			
6	Cation coordination number					
	6.1	Introduction	64			
	6.2	Anion-anion repulsion	64			
	6.3	The strength of the anions	69			
	6.4	Other factors	70			
	6.5	Applying the different effects	72			
7	Hydrogen bonds					
	7.1	Introduction	75			
	7.2	The role of anion–anion repulsion	76			
	7.3	The normal hydrogen bond	80			
	7.4	Strong hydrogen bonds	81			
	7.5	Weak hydrogen bonds	83			
	7.6	The structural chemistry of hydrogen bonds	84			
	7.7	Other types of hydrogen bonds	86			
	7.8	Assigning experimental bond valences to hydrogen bonds	87			
8	Elec	tronically distorted structures	90			
	8.1	The origins of electronic distortion	90			
	8.2	Non-bonding valence shell electrons	93			
	8.3	Transition metals	98			
		8.3.1 Jahn–Teller distorted cations	99			
		8.3.2 Transition-metal cations with empty or near-empty d shells	100			
	8.4	Conclusions	104			
9	Physical properties of bonds					
	9.1	Introduction	105			
	9.2	Bond lengths and bond angles	106			
	9.3	Bond force constants and thermal vibrations	110			
	9.4	Thermal expansion	113			
	9.5	The variation of R_0 with temperature	118			

CONTENTS

ix

III	Soli	Solids				
10	Space and space groups					
	10.1	Introduction	121			
	10.2	The crystal lattice and translational symmetry	122			
	10.3	Space groups	125			
	10.4	Special positions	126			
	10.5	Matching the special positions to the chemistry	129			
	10.6	The symmetry of bonded neighbours	130			
	10.7	Summary	133			
11	Modelling inorganic structures					
	11.1	The problem of <i>a priori</i> modelling	134			
	11.2	Determining the topology	135			
		11.2.1 Space-based approaches	136			
		11.2.2 Chemistry-based approaches	140			
		11.2.3 Valence maps	157			
	11.3	Refining the geometry	160			
	11.4	Modelling defect structures	161			
	11.5	Modelling glasses	162			
	11.6	Summary	162			
12	Lattice-induced strain					
	12.1		164			
	12.2	Structures with lattice-induced strain	166			
	12.3	Relaxation of lattice-induced strains	168			
		12.3.1 Relaxation of the geometry	168			
		12.3.2 Relaxation by defects	169			
		12.3.3 Electronic relaxation	170			
		12.3.4 Relaxation of symmetry—displacive phase transitions 12.3.5 Changing the bond	171			
		graph—reconstructive phase transitions	172			
	12.4	Incommensurate structures	174			
	12.5	Summary	177			
IV	App	plications and implications	179			
13	Applications					
1.7	13.1 Introduction					
	13.2 Crystallography					
		13.2.1 Structure solution	181 181			
		13.2.2 Analysis of crystal structures	184			
	13.3	Physics	186			
		13.3.1 Perovskite-related solids	186			

x CONTENTS

		13.3.2	Electrical properties	188
		13.3.3	Magnetic properties	191
		13.3.4	Grain boundaries	192
	13.4	Miner	193	
		13.4.1	Soil chemistry	194
		13.4.2	Zeolites	196
		13.4.3	Glasses	197
	13.5	Chem		197
		13.5.1	E .	197
		13.5.2	*	198
		13.5.3	5	200 201
	13.6	13.5.4 Biolog	• •	201
	13.0	13.6.1	Enzymes	203
		13.6.2	Calcium and sodium binding by proteins	203
	13.7	Datab		206
14	Cher	207		
	14.1	Why i	s the bond valence model so robust?	207
		14.1.1	The attractive force	207
		14.1.2	The repulsive force	209
	14.2		pody potential models	210
	14.3		roperties of the bond graph	210
	14.4 14.5		ewis electron-pair model are cations different from anions?	211 213
	14.6		al models	215
	14.7		on density models	216
	14.8		opology of the Madelung field	220
	14.9		usions	220
Δn	pendi	ces		223
	•			223
			nd valence parameters	224
		_	ce group spectra	233
•			ution of the network equations	240
			ion and anion bonding strengths	244
			erences to the ICSD and the CSD	247
	erence			253 271
List of symbols				
Ind	.ex			273

Prologue



Historical introduction

1.1 Introduction

Of all the concepts used in chemistry, that of the chemical bond is one of the most useful and, at the same time, one of the most difficult. It is useful because it helps us to understand the structures of compounds and their properties, and it is difficult because it is not easy to relate it to the physical theories, such as quantum mechanics, that underlie chemistry. This is not to say that people have not attempted to find a connection between the chemical bond and quantum mechanics. The Lewis (1923) electron pair model and the orbital overlap model (Coulson 1961) are, perhaps, among the better known attempts, but all are *a posteriori* rationalizations, trying to explain the properties of the empirical nineteenth-century chemical bond in terms of twentieth-century physical concepts. It is unlikely that, left to themselves, theoretical chemists in the twentieth century would have ever created the idea of a chemical bond had not the concept already been central to the language of structural chemistry. To this day the chemical bond remains largely an empirical concept.

As an empirical concept, the chemical bond was fully developed by the end of the nineteenth century (Partington 1964, chapter 17). Even though the discovery of the electron at the turn of the century changed the way we think about bonds, it has added little to the model's predictive power. The only significant addition made during the twentieth century has been a knowledge of the actual lengths of the bonds and angles between them.

Partly because, in the twentieth century, we have insisted on interpreting the chemical bond in terms of the quantum mechanical properties of electrons, we have failed to exploit the essential simplicity of the traditional bond model. According to this model, an atom has a certain bonding power, called its valence. The atom shares its valence among the bonds that it forms, the portion received by a particular bond being regarded as a measure of the bond's strength. The relation between the strength of a bond and the valence of the atom lies at the heart of all chemical bond models such as the bond model widely used in organic chemistry and the bond valence model described in these pages.

1.2 Chemical bonds

Although the idea of an attractive interaction that holds the various particles of matter together can be traced back to Greek times, it was not until the early



Fig. 1.1. A portion of the infinite structure of NaCl (18189).

nineteenth century that the concept became usefully predictive. It derived from Dalton's atomic hypothesis (Thompson 1807), in which a limited number of types of atom were assumed to associate together to form the compounds familiar to chemists. While it soon became clear that electricity was involved in the forces by which atoms were attracted to each other, no model of chemical bonding based on Coulomb's law was possible at that time, and it was some decades before the chemical bond model as we now know it was developed (Partington 1964, chapter 16). The model treated compounds as composed of atoms connected by a network of bonds. Neither the nature of the atoms nor the nature of the bonds was known at the time, but the model proved so remarkably effective in organizing the enormous variety of known organic compounds, that by the end of the century the model could even account for stereoisomerism. This was sufficient to convince most chemists of the reality of both atoms and bonds.

In the early twentieth century, advances in atomic physics confirmed the existence of atoms, and the discovery of X-ray diffraction revealed the precise arrangements of these atoms, confirming in a striking manner the geometric predictions of the bond model in organic chemistry. However, there were a number of problems. Neither X-ray diffraction, nor any other of the techniques developed at the time were able to demonstrate the physical existence of bonds. While the theoretical developments of the twentieth century have revealed much about the nature of chemical bonding, they have been much less successful in describing this bonding in terms of the localized interactions that we call bonds. Further problems arose when the structures of inorganic crystals were examined since these did not follow the rules that worked for organic chemistry. Instead of NaCl (18189¹) forming a diatomic molecule as the bond model predicted, each atom was found to be part of an infinite array of atoms lying on a cubic lattice, each atom being surrounded at equal distances by six neighbours of the opposite kind (Fig. 1.1). There was no indication of the diatomic molecule

¹ Each compound mentioned in this book is followed by its collection code (number) in the Inorganic Crystal Structure Database (Bergerhoff *et al.* 1983) or its refcode (letters) in the Cambridge Crystallographic Database (Allen *et al.* 1979). A reference to the original paper describing the structure of the compound is listed under this code in the literature references in Appendix 5.

predicted by the bond model. Similar results were found for other inorganic solids. The failure of the bond model that worked so well for organic chemistry to provide useful structural predictions in these cases led to its abandonment in inorganic chemistry.

1.3 The ionic model

There were several attempts to develop alternative bonding models for inorganic solids but none of these met with the same success as the bond model for organic compounds. Born and his colleagues (Born and Landé 1918; Madelung 1918; Born and Mayer 1932) took a physicist's approach when they proposed the *ionic model* in which the atoms were considered to be charged spheres, cations carrying positive charge and anions carrying negative charge, held together to form a solid by the electrostatic attractions between them. The potential energy, U, between any pair of atoms was expressed as the sum of two terms: an attractive Coulomb potential generated from the charges on the atoms, and a short-range, generally repulsive, potential that became important only when atoms came into contact (eqn (1.1)):

$$U = U_{\text{electrostatic}} + U_{\text{repulsive}}.$$
 (1.1)

The correct arrangement of the atoms in the solid was assumed to be the one that minimized this potential energy summed over all pairs of atoms in the crystal. The particular virtue of this model is that the long-range attractive part of the potential can be calculated exactly using classical electrostatic theory while the unknown short-range repulsive part can be modelled empirically. Born and Landé (1918) proposed an inverse power law for $U_{\rm repulsive}$, but later Born and Mayer (1932) suggested that an exponential expression was more in keeping with the predictions of the newly developed quantum mechanics.

The ionic model was able to account for many of the properties of simple salts such as the alkali metal halides, but ran into difficulties with more complex structures, partly because of the difficulty of determining the correct form of the repulsive potential, and partly because of the difficulty of summing the slowly converging electrostatic potential. The latter problem was solved for NaCl by Madelung (1918) with more general methods being subsequently developed by Ewald (1921) and Bertaut (1952). In recent years the introduction of computers has allowed both these difficulties to be overcome, and it is now possible to use the ionic model to make quantitative predictions of the properties of most inorganic compounds (Catlow 1997). However, the procedures require care in selecting the correct form for $U_{\text{repulsive}}$ and involve extensive computer resources. While the model gives good numerical predictions, it lacks the intuitive insights that are the strength of the traditional chemical bond model.

1.4 Quantum mechanics

The ultimate description of chemical bonding lies in quantum mechanics and the solution of the Schrödinger equation for the crystal. Although this equation can be exactly solved only for two particles, increasingly sophisticated approximate methods have been developed which provide excellent values for both the energy and the electron density distributions in crystals. However, such calculations are cumbersome for analysing and predicting complex chemical structures. The computing requirements are even more demanding than those of the ionic model, and quantum mechanics also lacks the essential simplicity of the traditional chemical bond model.

A promising simplification has been proposed by Bader (1990) who has shown that the electron density in a molecule can be uniquely partitioned into atomic fragments that behave as open quantum systems. Using a topological analysis of the electron density, he has been able to trace the paths of chemical bonds. This approach has recently been applied to the electron density in inorganic crystals by Pendás *et al.* (1997, 1998) and Luaña *et al.* (1997). While this analysis holds great promise, the bond paths of the electron density in inorganic solids are not the same as the more traditional chemical bonds and, for reasons discussed in Section 14.8, the electron density model is difficult to compare with the traditional chemical bond models.

Other simplified quantum treatments, such as the Lewis electron pair and orbital overlap models, have proved useful in teaching and they give qualitative predictions of the structures of molecular compounds, but they become unwieldy when applied to solids. They have not proved to be particularly helpful in the description of the complex structures found in inorganic chemistry and have therefore not been widely used in this field.

1.5 The symmetry model

In the early years of the twentieth century, an alternative approach to understanding inorganic structure was proposed by Niggli (1918) and Shubnikov (1922), who advocated using the recently developed theory of space group symmetry. They recognized that most inorganic compounds do not form finite molecules but exist only as crystals. The translational symmetry that generates a three-dimensional crystal from a basic building block requires that every crystal must belong to one of only 230 possible space groups. Such a requirement places considerable restrictions on the arrangements of atoms that can be present in the building block.

For example, if two atoms that are related by a plane of mirror symmetry move onto that plane, they fuse to become a single atom. Thus atoms that lie on elements of symmetry (special positions) will occur less frequently in the building block than ones that lie on positions with no symmetry. The higher the

site symmetry of the atom, the smaller its multiplicity, i.e. atoms occupying sites of high symmetry appear less frequently in the building block than atoms occupying sites of low symmetry. The composition is thus determined by the multiplicities of the special positions available to the atoms. Niggli and Shubnikov argued that it should be possible to determine the structure of a compound by finding which of the 230 space groups have special positions with multiplicities that correspond to the known composition of the compound. The power of this approach was demonstrated by Niggli who used it to show that, based strictly on geometric arguments, there are only four possible cubic structures having the chemical formula AB, thus accounting for the large number of different binary compounds that adopt the NaCl (18189), CsCl (22173), sphalerite (60378) or NaTl structures. However, as in the case of the ionic model, this initial success could not be repeated with more complex structures.

Subsequent workers have explored other ways in which symmetry can be used to restrict, or at least to describe, inorganic crystal structures. Lima de Faria and Figueiredo (1975) have arranged the space groups in hierarchical order according to their symmetry and have classified inorganic structures according to where they occur in this hierarchy. Parthé (1996) and Bergerhoff *et al.* (1999) have used space group symmetry as a way of identifying isostructural compounds. While these approaches are useful in exploring the restrictions that the three-dimensional world places on possible structures, they can never provide a complete description since they are based solely on the geometric properties of space and ignore the chemistry that gives each element its distinctive properties.

1.6 Topological models

The mathematical theory of topology is the basis of other approaches to understanding inorganic structure. As mentioned in Section 1.4 above, a topological analysis of the electron density in a crystal allows one to define both atoms and the paths that link them, and any description of structure that links pairs of atoms by bonds or bond paths gives rise to a network which can profitably be studied using graph theory.

Graph theory has been used to explore structures, such as organic molecules and alumino-silicate minerals, in which the bonds are all of similar strength. Many minerals are built around frameworks composed of SiO₄ and AlO₄ tetrahedra sharing corners. The ways in which such tetrahedra can be connected has led to attempts to enumerate and classify all possible alumino-silicate minerals. It is not difficult to show that the number of possible structures that can be made out of even a limited number of tetrahedra is extremely large, but it is the aim of this type of analysis to discover which topologies are most likely to correspond to stable structures. While such an approach is useful in rationalizing the large number of known silicate structures (Liebau 1985; Smith 1988),

it becomes awkward when different types of coordination polyhedra are present, or when the bonds differ greatly in strength.

1.7 Pauling's electrostatic valence model

In 1929 Pauling brought a chemist's intuitive perspective to the problem of describing the structures of inorganic compounds. In a seminal paper, Pauling (1929) lists five principles that determine the structures of complex ionic crystals. These principles are qualitative, but they summarize in a concise way much of the empirical information that was available to him about the structures of inorganic solids, particularly minerals. Because these principles have been widely used in the analysis of complex inorganic structures and since they form the starting point for the development of the bond valence model, they are worth quoting here in full:

- I. A coordinated polyhedron of anions is formed about each cation, the cation—anion distance being determined by the radius sum and the coordination number of the cation by the radius ratio.
- II. In a stable coordination structure the electric charge of each anion tends to compensate the strength of the electrostatic valence bonds reaching to it from the cations at the centers of the polyhedra of which it forms a corner; that is, for each anion

$$\zeta = \sum_i z_i / v_i = \sum_i s_i$$

[ζ = anion charge, z = cation charge, v = cation coordination number, s = (Pauling) bond strength.]

- III. The presence of shared edges, and particularly shared faces, in a coordinated structure tends to decrease its stability; this effect is large for cations with large valence and small coordination number, and is especially large in case the radius ratio approaches the lower limit of stability of the polyhedron.
- IV. In a crystal containing different cations those with large valence and small coordination number tend not to share polyhedron elements with each other.
- V. *The rule of parsimony*. The number of essentially different kinds of constituents in a crystal tends to be small.

These principles are phrased in the language of the ionic model, but they provide a simpler and more explicit description of stable structures than that given by the ionic model's energy minimization principle. Among the important ideas captured by Pauling's rules are those of local charge neutrality, the definition of electrostatic bond strength, and the rule of parsimony which is closely

related to the principle of maximum symmetry introduced in Chapter 3. The year following the publication of Pauling's rules, Bragg (1930) showed that they could be represented pictorially by Faraday's lines of electrostatic field which link the cations to their neighbouring anions. Because the energy of an electrostatic field is lowest when the lines of field are shortest, it follows that the equilibrium structure will be one which places cations and anions in intimate contact with each other.

As more accurate information became available on the structures of inorganic solids, a correlation was noticed between the length of a bond and its strength (Pauling 1947; Byström and Wilhelmi 1951; Zachariasen 1954). Donnay and Allmann (1970) showed that Pauling's second rule becomes quantitatively exact around both the cations and the anions if the electrostatic bond strengths are calculated from the bond lengths rather than from the charge and coordination number, an idea that was subsequently expanded by Brown and Shannon (1973). Donnay and Allmann coined the term *bond valence* to differentiate this new quantity from Pauling's bond strength, and since then bond valences have been extensively used in modelling and analysing crystal structures. The properties of bond valences have been summarized in a number of simple quantitative rules generally known as the *bond valence model* described in detail in Section 3.3. Recent reviews of the model have been given by Brown (1981, 2000), O'Keeffe (1989), Trömel (1992), and Urusov and Orlov (1999).

Theoretical aspects of the bond valence model have been discussed by Jansen and Block (1991), Jansen *et al.* (1992), Burdett and Hawthorne (1993), and Urusov (1995). Recently Preiser *et al.* (1999) have shown that the rules of the bond valence model can be derived theoretically using the same assumptions as those made for the ionic model. The Coulomb field of an ionic crystal naturally partitions itself into localized chemical bonds whose valence is equal to the flux linking the cation to the anion (Chapter 2). The bond valence model is thus an alternative representation of the ionic model, one based on the electrostatic field rather than energy. The two descriptions are thus equivalent and complementary but, as shown in Section 2.3 and discussed further in Section 14.1.1, both apply equally well to all types of acid—base bonds, covalent as well as ionic.

This book is divided into four parts. Part I provides a theoretical derivation of the bond valence model. The concept of a localized ionic bond appears naturally in this development which can be used to derive many of its properties. The remaining properties, those dependent on quantum mechanics, are, as in the traditional ionic model, fitted empirically. Part II describes how the model provides a natural approach to understanding inorganic chemistry while Part III shows how the limitations of three-dimensional space lead to new and unexpected properties appearing in the inorganic chemistry of solids. Finally, Part IV explores applications of the model in disciplines as different as condensed matter physics and biology. The final chapter examines the relationship between the bond valence model and other models of chemical bonding.



Theory



The ionic bond

2.1 Introduction

The particular virtue of the ionic model is that it divides the potential energy of a crystal into two components, a long-range Coulomb potential that is responsible for the attraction that holds the crystal together, and a short-range potential which contains all the remaining forces, principally the repulsion that prevents the atoms from collapsing into each other (eqn (1.1)). The Coulomb potential can be calculated using classical electrostatic theory and the short-range potential is generally treated empirically by defining a classical potential that reproduces the experimental measurements, or that best represents the quantum mechanical potential between two isolated atoms. In this way, the model can be used without the need to solve the Schrödinger equation for the complex system under study, considerably simplifying the calculations. Catlow (1997) surveys the many ways in which this traditional semi-classical ionic model has been used.

One aspect of the ionic model that often causes conceptual problems is its apparently improbable assumption that a crystal can be treated as an array of formal ionic point charges. As is shown in Section 2.3, this assumption is not nearly as restrictive as it appears. It is valid for a surprisingly wide variety of inorganic salts, ceramics, and minerals, even those such as silicates, whose Si–O bond clearly has a strong covalent character. The model does, however, have its limitations since this assumption excludes those systems, such as metals and organic molecules, in which the atoms formally remain electrically neutral. While the model does not cover all types of chemical bonding, it can be used to provide a quantitative description of the structure and properties of a remarkably large group of materials.

In the traditional approach to the ionic model, the potential energy, U in eqn (1.1), is calculated for a given configuration of atoms and the equilibrium structure sought by adjusting the atomic positions to minimize this energy. There are, however, alternative ways to develop the model and one of these, presented in this chapter, uses the electrostatic field rather than the electrostatic energy. Bragg (1930) first pointed out that the electrostatic interaction between cations and anions can be represented by Faraday's lines of field, but this idea has only recently been fully explored (Preiser *et al.* 1999). In Section 2.4, the electrostatic field is shown to partition itself naturally into localized bond-like fragments whose properties are explored both theoretically and, in Chapter 3,

experimentally. This leads to a chemical bond model which is complementary to the traditional energy description of the ionic model, and which provides a more intuitive way of understanding and modelling the structures and properties of inorganic compounds.

2.2 Crystal energy and the Coulomb field

In the ionic model, the energy of an inorganic solid is assumed to be the sum of all the potentials, U_{ij} , between atoms i and j. These consists of two terms, a classical electrostatic potential, $U_{ij,\text{electrostatic}}$, determined by the charges on the atoms, and a quantum mechanical term, $U_{ij,\text{Fermi}}$, that includes the repulsion that prevents individual atoms from collapsing into each other as well as any residual contributions from covalent bonding (eqn (2.1)):

$$U_{ij} = U_{ij,\text{electrostatic}} + U_{ij,\text{Fermi}}.$$
 (2.1)

 $U_{ij,\text{electrostatic}}$ can be derived from the electrostatic fields, E_i , generated by the individual atoms, i, and these fields can in turn be represented as the sum of the three terms shown in eqn (2.2):

$$E_i = E_{i,\text{mono}} + E_{i,\text{mult}} + E_{i,\text{local}}. \tag{2.2}$$

In this equation $E_{i,\text{mono}}$, given by eqn (2.3), is the field generated by the point ionic charge, Q_i , which is assumed to reside at the centre of the atom:

$$E_{i,\text{mono}} = Q_i / 4\pi\epsilon_0 r^2. \tag{2.3}$$

Here r is the distance from the atom centre. In this book the units are chosen so that Q_i is measured in electron charges (= valence units) and ε_0 is set equal to 1.0. According to Gauss' theorem, if the electron density of the atom is spherically symmetric, $E_{i,\text{mono}}$ gives a fully correct description of the field generated by the atom in the region outside the atom itself, i.e. in the region where the electron density of the atom has fallen to zero.

If the electron density is not spherically symmetric, the field outside the atom can again be correctly reproduced by adding as many point multipoles as necessary to the original point charge, Q_i . These contribute the term $E_{i,\text{mult}}$ which can be exactly calculated if the sizes and orientations of the multipoles are known. The multipoles give rise to a field that drops off rapidly with distance and is, in any case, small relative to the field produced by Q_i . Even though they may make a significant contribution to the field in the immediate neighbourhood of the atom, the multipoles make a negligible contribution at distances of more than a few hundred pm from the centre of the atom (Bouhmaida *et al.* 1997). In this book, the multipole terms are ignored except where explicitly

mentioned, e.g. in Chapter 8 which describes the structural chemistry of atoms with non-spherical electron density.

 $E_{i,\text{mono}}$ and $E_{i,\text{mult}}$ thus reproduce the exact electric field outside the atom as determined by the distribution of electrons within the atom. To obtain the correct field inside the atom requires the addition of the term $E_{i,\text{local}}$ which can be calculated if the electron density distribution is known. For present purposes it is sufficient to note that $E_{i,\text{local}}$ is, by definition, zero outside the atom and therefore can have no long-range effect on the structure. All the long-range influences are therefore carried by $E_{i,\text{mono}}$ and, to a much lesser extent, $E_{i,\text{mult}}$.

The total electric field in the crystal is obtained by adding together the electrostatic fields produced by all the individual atoms in the crystal. At any particular point, it will have contributions from the $E_{i,\text{mono}}$ of all the atoms, i, in the crystal, but only the immediately neighbouring atoms will contribute $E_{i,\text{mult}}$ and $E_{i,\text{local}}$ terms. The energy associated with these last two terms can therefore be combined with U_{Fermi} into a short-range potential, leaving only $E_{i,\text{mono}}$ to describe the long-range effects. The total energy of the crystal is thus given by U_{total} in eqn (2.4):

$$U_{\text{total}} = U_{\text{Madelung}} + U_{\text{local}},$$
 (2.4)

where U_{Madelung} is the Madelung energy related to the Madelung field, E_{Madelung} , given by eqn (2.5):

$$E_{\text{Madelung}} = \sum_{i} E_{i,\text{mono}}$$
 (2.5)

and U_{local} is the energy associated with the fields $\sum_i E_{i,\text{local}}$ and $\sum_i E_{i,\text{mult}}$ as well as the potential $\sum_{ij} U_{ij,\text{Fermi}}$. In the traditional ionic approach, U_{local} is calculated by summing short-range interatomic potentials represented by an empirical analytical function with parameters fitted to the properties of the system. Since all the long-range interactions are included in the Madelung term, U_{Madelung} , they are correctly represented by the field E_{Madelung} which in turn depends only on the magnitudes and positions of the monopole charges, Q_i .

The ionic theory thus has the advantage of isolating the quantum and other effects that are difficult to calculate into the potential $U_{\rm local}$ which is treated empirically (Section 3.1). The long-range effects which are important for crystal chemistry are then given by the Madelung term which can be readily calculated using classical electrostatic theory.

2.3 How are the atom fragments chosen?

Before examining the properties of the Madelung field, it is necessary to show that it is possible to partition the electron density of the crystal into atoms that

obey the assumptions of the model. The point charges, Q_i , are assumed to be at the positions of the nuclei of the atoms they represent, but it is less clear what value should be assigned to Q_i because the atoms are extended and their electron densities overlap. It is therefore necessary to find some way of partitioning the electron density between the different atoms. There are many ways of doing this, and each will result in a different set of values for Q_i .

Whatever method is chosen, the resulting atoms must satisfy the following criteria if the ionic model is to be used:

- 1. Every part of the electron density of the crystal must belong to at least one atom. The definition of atoms must ensure a complete coverage of the space occupied by the crystal in order to ensure electroneutrality. However, atoms may overlap, since the electron density in an overlap region can be partitioned in any convenient way between the overlapping atoms.
- 2. The partitioning must ensure an appropriate assignment of charges, Q_i . As shown in Section 9.2, the ionic model works for a wide variety of different choices of Q_i , the only constraint being that the charges contributing to each type of bond are treated consistently. It is therefore only a matter of convenience that Q_i is set equal to the formal charge, V_i .
- 3. Consistent with the above constraints, the partitioning should be chosen so as to minimize $E_{\rm mult}$. This specifies how the electron density in overlap regions is to be partitioned and supports the assumption that $E_{\rm mult}$ can usually be reduced to the level at which it can be ignored.

These conditions allow considerable flexibility in the way the electron density of an atom is chosen. The most physically plausible partitioning is the 'Atoms in Molecules' partitioning based on the topology of the electron density (Section 14.7, Bader 1990; Pendás *et al.* 1997). This is a unique partitioning of space into polyhedral atomic fragments that behave as open quantum systems. Although multipoles are needed to describe the fields produced by the polyhedral fragments, the orders of the multipoles are generally no smaller than the number of faces on the polyhedron and their contributions are therefore small. Although this partitioning gives physically meaningful charges, they can only be calculated by solving the Schrödinger equation for the whole system which removes any practical advantage this particular partitioning may offer.

Spherical atoms can be selected with radii sufficient to enclose the required charge. In this partitioning, most cations, being small and comprising only the nucleus and core electrons, have a spherical electron density. The anions, which must be large enough to include all the valence electrons, will overlap and the partitioning of charge in the overlap region can be used to minimize the size of $E_{\rm mult}$. Again, if multipole terms are needed, their order will normally be comparable to the coordination number and their influence can be neglected. It should therefore be possible in all cases to find a partitioning of the electron

¹ This section may be omitted on first reading.

density into atoms that satisfies the above criteria and at the same time allows the atomic charges to be set equal to the formal ionic charges.²

Because it is not necessary to know the exact atomic charges, we set them equal to the formal ionic charges, V_i . These are determined by assuming that all anions have a closed shell configuration. Although many cations also have closed shells, electroneutrality sometimes requires cations to have partially filled valence shells. It is beyond the scope of this book to discuss in detail how formal charges (atomic valences) are assigned since this is treated in most general chemistry texts.

2.4 The Madelung field of a crystal

Consider the electrostatic field, $E_{\text{Madelung}} = \sum_{i} E_{i,\text{mono}}$ (eqn (2.5)), created by an infinite array of positive and negative point charges placed at the positions of each of the atoms in a crystal. As has been pointed out by Bragg (1930), the lines of field that represent E_{Madelung} will not extend far in space because at an energy minimum the lines of field will be as short as possible. Looked at from another point of view, the lines of field must remain short since their paths are not allowed to cross. All the lines of field starting at a positive point charge will therefore terminate on the nearest shell of negative point charges and vice versa. The collection of all the lines joining the two charges i and j defines a region in space that represents the electrostatic link between them. Further, the boundaries that separate the links are necessarily boundaries that are not crossed by electric flux. Thus E_{Madelung} directly partitions space into a collection of localized link regions separated by zero-flux boundaries. An exact picture of the lines of the Madelung field in the (110) section of rutile (TiO₂, 202240) that contains the Ti⁴⁺ and O²⁻ ions is shown in Fig. 2.1 with the zero-flux boundaries shown as thick lines (Preiser et al. 1999).

These link regions, which we can identify with chemical bonds, are characterized by the electrostatic flux, Φ_{ij} defined by eqn (2.6), that links the two ions i and j:

$$\Phi_{ij} = \int E_{\text{Madelung}} \, dA, \qquad (2.6)$$

where the integration is taken over any cross-sectional area of the bond. These fluxes must obey Gauss' law (eqn (2.7)) around each ion:

$$\sum_{i} \Phi_{ij} = \oint E_{\text{Madelung}}. \, \mathrm{d}A = Q_{i}, \tag{2.7}$$

where the sum is taken over all bonds connected to Q_i and the integration is taken over any closed surface surrounding Q_i .

² Section 14.1 gives an alternative view of why the choice of the atomic charge is not critical.

Surprisingly, the localization of the Madelung field into bonds as shown in Fig. 2.1 is quite compatible with the long-range nature of the electrostatic force. The mechanism for the long-range interaction is through the application of Gauss' law around each intermediate atom. As shown in Fig. 2.2, the removal of an ${\rm O}^{2-}$ ion from the top right-hand part of the perfect lattice shown in Fig. 2.1 results in a redistribution of the flux. The flux that originally terminated on the missing ${\rm O}^{2-}$ ion now terminates on charges in the second neighbour shell but, in order to accommodate this new flux, the charges of the second neighbour shell must shed flux to the fourth neighbour shell and so on. Thus a ripple of flux relaxation spreads out from any change made in the lattice, the

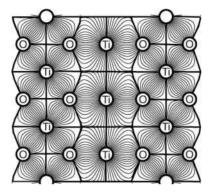


Fig. 2.1. A representation of the Madelung field of rutile (TiO₂, 202240) in the (110) plane $\{(x, y, z); x + y = 1\}$. The light lines represent the field lines, the heavy lines show the zero-flux boundary that partitions space into bonds (from Preiser *et al.* 1999).

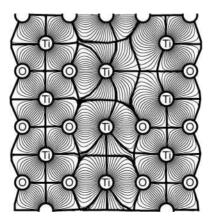


Fig. 2.2. The Madelung field of the same projections as Fig. 2.1 with one O^{2-} ion removed from the top right showing the rearrangement of the flux lines (from Preiser *et al.* 1999).

long-range effects being mediated through a redistribution of the flux around the intervening atoms in accordance with Gauss' theorem. Thus the partitioning of the Madelung field into localized bonds is quite compatible with its long-range influence.

The law of conservation of energy, which states that the sum of the potential differences around any closed loop is zero, can also be applied to this system if the potential differences between the ions can be calculated. To determine these, it is convenient to recognize that each bond acts as a capacitor, C_{ij} , with the atoms acting as the plates that carry the charges and the bond providing the field linking them. This capacitor then supports the potential difference, P_{ij} , according to the capacitor eqn (2.8):

$$P_{ij} = \frac{q_i}{C_{ij}},\tag{2.8}$$

where q_i is the charge that terminates the flux lines. According to Gauss' theorem,

$$q_i = \Phi_{ij}. \tag{2.9}$$

Combining eqns (2.8) and (2.9) gives eqn (2.10):

$$P_{ij} = \frac{\Phi_{ij}}{C_{ii}}. (2.10)$$

Since the law of conservation of energy requires that the sum of the potentials, P_{ii} , around any closed loop be zero,

$$0 = \sum_{\text{loop}} P_{ij} = \sum_{\text{loop}} \frac{\Phi_{ij}}{C_{ij}},\tag{2.11}$$

where each loop is composed of a number of bonds and the flux of each bond is taken as positive or negative according to the direction in which it is traversed. It is positive if the bond is traversed from anion to cation and negative if traversed in the opposite direction.

Calculating the values of the bond capacitances presents a number of problems. Firstly, since the electric potential is singular at a point charge, the potential difference between a point positive and a point negative charge is infinite and C_{ij} is zero for all links. This singularity can be avoided by replacing each point charge by a small closed equipotential shell and distributing the charge Q_i over its surface in such a way as to leave the external field unchanged. The bonds are now bounded at their ends by that portion of the charged equipotential surface on which their field lines start or terminate. These portions of the equipotential surfaces therefore act as the plates of the capacitor and carry the charge q_i . For this arrangement, C_{ij} and P_{ij} are finite and, in principle, calculable.

The values of C_{ij} , of course, depend on which equipotential surface is used to represent the ion. Since these surfaces can be arbitrarily chosen, it might be supposed that all the values of C_{ij} can also be arbitrarily chosen. However, the number of ions is always less than the number of bonds. If there are N_a ions in the array, it is only possible to assign arbitrary values of C_{ij} to $N_a - 1$ bonds, those in the spanning tree described in Section 2.5 below. For the remaining bonds, those that close the loops in the network, a knowledge of the bond topology alone is insufficient to determine C_{ij} . To find these values of C_{ij} , the geometry of the array, i.e. the positions of the ions, must also be known.

If all values of C_{ij} are known, the distribution of flux between the bonds can be calculated by solving eqns (2.7) and (2.11) since they contain only the parameters Q_i and C_{ij} . Unfortunately, the values of C_{ij} cannot be determined a priori, since they depend on a knowledge of the interatomic distances which are determined by the mutual repulsion of the ions and hence by the electron density distribution. This problem is taken up in Chapter 3 where it is shown that, for a large number of equilibrium structures, the values of C_{ij} can all be set equal. As C_{ij} is common to all the terms in (2.11), it can be cancelled, allowing eqns (2.7) and (2.11) to be solved.

2.5 Bond networks and bond graphs

The fact that all the long-range Coulomb forces in a crystal are correctly described by the electrostatic bond fluxes, Φ_{ij} , means that it is possible to represent the Madelung field of a molecule or a crystal as a network of bonds (Beevers and Schwarz 1935). In mathematical language a network consists of an array of nodes which are connected by links. Translated into chemical terms a bond network consists of an array of atoms which are connected by bonds. The important properties of this network are the valences of the atoms and the fluxes of the bonds. These, combined with a knowledge of the topology of the network (the description of the way the atoms are connected), provide a complete representation of the properties of the Madelung field, hence of the long-range bonding forces in the crystal.

The topology of such a network can be represented in several different ways. An algebraic representation is the $N_a \times N_a$ connectivity or adjacency matrix,

³ In the mathematical theory of networks 'valence' is defined as the number of links terminating at a node, and it was in this sense that the term was introduced into chemistry. However, chemists were later forced to distinguish between a chemical valence (bonding power) and a coordinative valence (number of bonds). They chose to keep the term 'valence' for the chemical valence and introduced the term 'coordination number' for the coordinative valence. This book follows the chemical convention. The term 'valence' is always used in the sense of bonding power unless otherwise stated, and 'coordination number' is used to indicate the number of bonds.

⁴ The reader's attention is drawn to the discussion in Sections 14.3 and 14.4 which shows that all chemical bond models are equivalent because they all reduce to this same topological description. The derivation here is based on the ionic model because it is the simplest and most convincing.

where N_a is the number of atoms in the network. The elements of this matrix all have the value of zero except where a bond exists between the column atom and the row atom. An example of a connectivity matrix is given for the molecule B_2H_6 (1312) in Table 2.1. An alternative representation of the topology is the bond graph, a diagram in which the bonds are represented by lines and the atoms by the nodes, as shown for B_2H_6 in Fig. 2.3.

Bond graphs are familiar in organic chemistry where they are called molecular diagrams. The network of an organic molecule contains a finite number of atoms and bonds, and, because bonded atoms are always neighbours in three-dimensional space, such a bond graph can easily be drawn as a two-dimensional projection of the three-dimensional molecular structure.

It is impossible to draw bond graphs in this way for the majority of inorganic compounds which exist only as crystals, because the bond network is effectively infinite and contains around 10²⁴ atoms. However, because a crystal contains translational symmetry, the nearest neighbour topological properties of the bond network are all contained in the small repeating unit from which the crystal is generated. It is possible to extract this unit from the network in order to represent the network by a finite bond graph. This is done by removing the atoms of one formula unit from the network. In the NaCl (18189) network shown in Fig. 1.1, the formula unit contains just one Na⁺ ion and one Cl⁻ ion. Removing this unit from the network requires the breaking of five bonds around each ion, but the broken bonds occur in symmetry related pairs which can be reconnected within the formula unit to form a closed, finite bond graph which correctly reproduces the nearest neighbour topology of the original

	B 1	B2	H1	H2	Н3	H4	H5	Н6
B1	0	0	1	1	1	0	1	0
B2	0	0	1	1	0	1	0	1
H1	1	1	0	0	0	0	0	0
H2	1	1	0	0	0	0	0	0
H3	1	0	0	0	0	0	0	0
H4	0	1	0	0	0	0	0	0
H5	1	0	0	0	0	0	0	0

Table 2.1 Connectivity table for B₂H₆

0

H6

0

0

0

0

Fig. 2.3. The bond graph of B_2H_6 (1312).

network (Fig. 2.4). Such a finite bond graph provides sufficient information about the connectivity of the network to allow eqns (2.7) and (2.11) to be solved.

The finite bond graph of an inorganic crystal differs in a second important respect from the familiar bond graph of organic chemistry. In the latter, the presence of two lines connecting the same pair of atoms indicates a double bond. There is only one bond between the two atoms but that bond has double the strength of a bond represented by a single line. For inorganic compounds, each line in the finite bond graph represents a separate connection between two different atoms. For example, the six lines connecting the Na⁺ and Cl⁻ ions in the finite bond graph of NaCl shown in Fig. 2.4 do not represent a sextuple bond, but rather six separate bonds between one Na⁺ ion and six different but symmetry related Cl⁻ ions. A less trivial example is the finite bond graph of CaCrF₅ (10286) shown in Fig. 2.5. In this example the Cr³⁺ ion is six coordinate, the Ca²⁺ ion seven coordinate, and the fluorine ions F1⁻, F2⁻, and F3⁻ each have a different coordination environment.

As mentioned in Section 2.4, in the ionic model the chemical bond is an electrical capacitor. It is therefore possible to replace the bond network by an equivalent electric circuit consisting of links which contain capacitors as shown in Fig. 2.6. The appropriate Kirchhoff equations for this electrical network are eqns (2.7) and (2.11). It is thus possible in principle to determine the bond fluxes for a bond network in exactly the same way as one solves for the charges on the capacitors of an electrical network. While solving these equations is simple in principle providing the capacitances are known, the calculation itself can be



Fig. 2.4. The bond graph of NaCl (18189). The heavy line represents the spanning tree (Appendix 3). Compare this graph with the infinite three-dimensional network shown in Fig. 1.1.

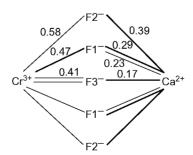


Fig. 2.5. The bond graph of CaCrF₅ (10286). The heavy lines indicate one of many possible choices of the spanning tree (Appendix 3). The numbers are the experimental bond fluxes (vu) taken from Table 3.1.

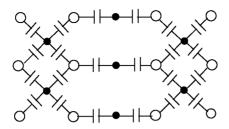


Fig. 2.6. The equivalent circuit for the section of rutile (TiO_2) shown in Fig. 2.1. The filled circles are Ti^{4+} , the open circles are O^{2-} .

somewhat involved if done by hand. Various approaches taken to solving these equations are described in Appendix 3.

2.6 Coordination number

The concept of coordination number, i.e. the number of bonds formed by an ion, is important in structural chemistry, but it is a concept that has defied precise definition. Most chemists would agree on the coordination number to be assigned for the majority of cation environments, but none of the attempts to provide a rigorous definition has been particularly successful in cases where the coordination number is ambiguous. The more rigorous the definition, the less well it corresponds to chemical intuition. However, the Madelung field provides a definition that is based on the electrostatic linkages between atoms and therefore directly reflects the contribution of each bond to the cohesion energy of the crystal.

Definition of coordination number. The coordination number of an ion is the number of ions to which it is linked by electrostatic flux.

There is generally good agreement between the conventional coordination numbers and those derived from the Madelung field, because both correspond to the number of neighbouring ions that are in direct contact (Preiser *et al.* 1999). However, the Madelung field sometimes contains bonds to second nearest neighbours that would not normally be considered chemically bonded. Most of these long bonds, here called *tertiary bonds*, ⁵ have small fluxes ($< 0.05 \, \mathrm{vu}^6$) and therefore make only a minor contribution to the chemical bonding.

⁵ The term *secondary bond* was used by Alcock (1972) to describe the longer bonds that occur in the electronically distorted cation environments described in Chapter 8, particularly those around atoms with stereoactive lone pairs. The term *tertiary bond* has been used here to avoid confusion with Alcock's secondary bonds.

 $^{^6}$ vu = valence unit. One valence unit is equal to the charge of one electron or the flux generated by the charge of one electron.

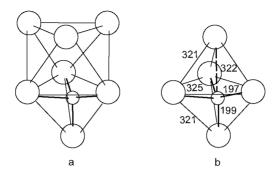


Fig. 2.7. Comparison of the primary and tertiary bonding around Zn^{2+} (small circle) in (a) the sphalerite structure and (b) the wurtzite structure. In (b) the distances (in pm) are those found in ZnO (67454).

Many of the tertiary bonds reported by Preiser *et al.* (1999) are likely artefacts of their calculations since these were based on the use of formal ionic charges. Substituting a more physically reasonable value for the formal ionic charge will reduce the total flux starting at the cation and eliminate many of the tertiary bonds around the highly charged cations where most tertiary bonds were found. However, there are some cases where tertiary bonds undoubtedly do occur and these can provide important information about the crystal chemistry.

One example is the tertiary bond found in the wurtzite structure of ZnO (67454). All members of the Zn chalcogenide series crystallize with structures based on the close packing⁷ of the chalcogenide ions, with Zn²⁺ occupying half the tetrahedral cavities. The higher members, ZnSe and ZnTe (31840), crystallize with the cubic sphalerite structure while ZnO crystallizes with the hexagonal wurtzite structure. ZnS (60378, 67453) is known in both forms.

In the sphalerite structure the anions form a cubic close packed array. The structure has a single adjustable parameter, the cubic cell edge. The O^{2-} ions are too small for them to be in contact in this structure (see Fig. 6.4) so ZnO adopts the lower symmetry hexagonal wurtzite structure which has three adjustable parameters, the a and c unit cell lengths and the z coordinate of the O^{2-} ion, allowing the environment around the Zn^{2+} ion to deviate from perfect tetrahedral symmetry. In the sphalerite structure the ZnX_4 tetrahedron shares each of its faces with a vacant octahedral cavity (one is shown in Fig. 2.6(a)), while in the wurtzite structure one of these faces is shared with an empty tetrahedral cavity which places an anion directly over the shared face as seen in Fig. 2.6(b). The primary coordination number of Zn^{2+} in sphalerite is 4 and there are no tertiary bonds, but in wurtzite, which has the same primary coordination number, there is an additional tertiary bond with a flux of 0.02 vu through the face shared with the vacant tetrahedron.

⁷ For a discussion of close packing, see Section 11.2.1.2.

Crystallographic symmetry requires the primary coordination around Zn^{2+} in the sphalerite structure to be exactly tetrahedral. In the wurtzite structure this restriction is removed. The Zn^{2+} coordination in ZnO is distorted slightly towards a five-coordinate trigonal bipyramid as shown by the bond lengths in Fig. 2.7(b), the opening up of the shared face being made possible by the smaller size of the O^{2-} ions. The distortion is quite small, so it is still appropriate in all these compounds to consider Zn^{2+} as having a primary coordination number of 4 (average flux = 0.50 vu) with the wurtzite structure being stabilized in the case of ZnO by the formation of an additional tertiary bond of flux 0.02 vu.

A fuller discussion of the factors that determine the coordination number of the cation (including Zn^{2+}) can be found in Chapter 6.

2.7 Conclusions

This chapter shows that the ionic model can not only be presented in terms of chemical bonds characterized by their electrostatic flux, but also that the improbable assumptions of the model are satisfied by the wide range of compounds that conform to the following two conditions:

- 1. The chemical bonding can be completely described in terms of localized bonds between neighbouring atoms. This condition excludes only metals and aromatic compounds where the bonding is provided by delocalized electrons.
- 2. The bonds have a cation at one end and an anion at the other. This excludes the majority of organic compounds but does not exclude the polar bonds that many organic compounds form. The model thus covers the bonds found in inorganic compounds, their solutions, and melts, but it also extends to acid—base bonds found in other systems, particularly the important aqueous chemistry of living organisms.

The bond valence model

3.1 Experimental bond valences and bond lengths

The ionic model divides the forces acting on atoms into an electrostatic component that can be calculated using classical electrostatic theory and a short-range component that is determined empirically. The previous chapter explored the properties of the classical electrostatic field. This chapter explores the properties of the empirically determined short-range force which is represented in the electrostatic model by the bond capacitance, C_{ij} , defined in eqn (2.8). Rather than try to determine the values of C_{ij} directly, it is better to step back and look at the way in which the bond valence model developed historically. Its connection with the electrostatic model of Chapter 2 will then become apparent.

The concept of bond valence, which, as will be shown below, is the same as the bond flux derived in Chapter 2, grew out of attempts to refine Pauling's 'principles determining the structures of complex ionic crystals' (Section 1.7). In this empirical evolution of Pauling's model, both the electrostatic and short-range components were developed simultaneously. Only later did it become apparent that it was also possible to derive the properties of the electrostatic component independently using the ionic theory.

When Pauling published his 'Principles' in 1929, the absence of computers and the rudimentary knowledge of bonding geometry made the calculation of bond fluxes impossible except in trivial cases. The best that could be done for complex structures was to approximate the bond flux by a *bond strength*, defined as the ratio of the cation's valence to its coordination number. In effect all the bonds formed by a cation were assumed to have the same flux. Pauling's second law (Section 1.7), which can be paraphrased as 'the sum of the bond strengths around each anion is equal to the anion's valence', is therefore only an approximation to Gauss' law (eqn (2.7)). Deviations as large as 1.0 valence unit (vu) sometimes occurred (Baur 1970).

As improvements in X-ray diffraction techniques led to a better knowledge of bonding geometry, it became clear that there was a relationship between the length of a bond and its strength. This led Pauling (1947), followed by Byström and Willhelmi (1951), Zachariasen (1954), Donnay and Allmann (1970), Pyatenko (1973), and Brown and Shannon (1973), to show that assigning bond strengths on the basis of bond lengths resulted in a more exact fulfilment of Pauling's second law. To avoid confusion with Pauling's definition of bond

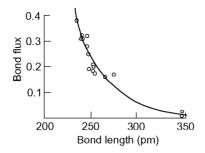


Fig. 3.1. The line shows correlation between bond valence and bond length for Ca–O bonds given by eqn (3.1). The circles represent bond fluxes calculated from the Madelung field (Preiser *et al.* 1999).

strength, the quantity determined from the bond length is called the *experimental* bond valence, represented in this book by the upper case letter S.

The correlation found empirically between the valence and length of a bond is shown by the line in Fig. 3.1 for Ca–O bonds. Similar correlations are found for other bond types. For most bonds this correlation can be approximated by a simple two-parameter expression such as eqn (3.1) or (3.2):

$$S_{ij} = \exp\left(\frac{R_0 - R_{ij}}{B}\right),\tag{3.1}$$

$$S_{ij} = \left(\frac{R_{ij}}{R_0}\right)^{-N},\tag{3.2}$$

where R_{ij} is the length of the bond between atoms i and j, and S_{ij} is its experimental valence. R_0 , B, and N are parameters that are chosen to ensure that the sums of the bond valences around all the ions (cations as well as anions) in a large number of well-determined structures are the same as their atomic valences or formal charges. The parameters B and N determine the slope of the curve shown in Fig. 3.1, and R_0 , which varies with the nature of the two ions forming the bond, is the length of a bond of unit valence. For many bonds in oxides, B is found to be close to 37 pm with somewhat larger values expected for more polarizable ions. N tends to increase from around 4 to 6 with increasing atomic number. Although both equations describe the correlation equally well, eqn (3.1) is preferred because the exponential function has useful mathematical properties and best reflects the repulsive potential between atoms. The relative constancy of B is also an advantage. Appendix 1 discusses the practical problem of determining the bond valence parameters and describes some of the other functions that have been proposed to represent this correlation. This appendix also gives a partial list of bond valence parameters for eqn (3.1). A more comprehensive list is available on the web site http://www.ccp14.ac.uk/ccp/ web-mirrors/i d brown/bond valence parm/

Equations (3.1) and (3.2) are, however, only approximations. In practice the bond valence falls to zero at a finite distance somewhere between 300 and 400 pm depending on the bond type, and at short distances the curve becomes very steep as can be seen for H–O bonds in Fig. 7.1. As a result, eqns (3.1) and (3.2) both overestimate the valences of very weak bonds and underestimate the valences of very strong bonds.

The experimental uncertainties in the measured bond lengths ensure that the sum of experimental bond valences around any particular ion will never exactly equal the atomic valence and, as shown in later chapters, there are cases where this discrepancy gives important information about the crystal chemistry, but the *valence sum rule*, which states that the sum of experimental bond valences around each atom is equal to the atomic valence (V_i in eqn (3.3)), is much better obeyed than Pauling's second rule.

$$V_i = \sum_j S_{ij}. (3.3)$$

The similarity between eqns (2.7) and (3.3) (given the equality of Q_i and V_i) is a necessary but not sufficient condition that bond fluxes, Φ_{ij} , and bond valences, S_{ij} , are the same. A theoretical proof of their equality is not possible, but it can be demonstrated by comparing the bond valences calculated using eqn (3.1) (the line in Fig. 3.1) with bond fluxes calculated from the Madelung fields in particular compounds (the points in Fig. 3.1). This figure shows that the flux and bond valence are essentially the same for Ca–O bonds and similar agreement is found for other types of bond provided that electronic anisotropies of the kind discussed in Chapter 8 are not present (Preiser *et al.* 1999).

Equations (3.1) and (3.2) therefore give information about the short-range repulsive forces that prevent the ions from collapsing into each other. They give an indication of how close two ions can approach when linked by a given flux: the larger the flux, the closer the ions are pulled together. Fitting the parameters R_0 , B, and N empirically has several advantages. It provides a simple correlation, it avoids the need for quantum mechanical calculations, and it automatically compensates for a number of other systematic effects as discussed in Section 14.1.2.

3.2 Empirical network equations

A second empirical observation related to the short-range forces of the ionic model is the observation that in many crystals the experimental bond valences also obey eqn (3.4) (Brown 1987b):

$$0 = \sum_{\text{loop}} S_{ij},\tag{3.4}$$

where the summation is over the bond valences around any closed loop in the bond network having regard for the direction in which the loop is traversed, S_{ij} being taken as positive if the bond is traversed from the anion to the cation and negative otherwise.

Equations (3.3) and (3.4) have become known respectively as the *valence sum* rule and the *loop*, or *equal valence*, rule, and are known collectively as the *network equations*. Equation (3.4) represents the condition that each atom distributes its valence equally among its bonds subject to the constraints of eqn (3.3) as shown in the appendix to Brown (1992a). The two network equations provide sufficient constraints to determine all the bond valences, given a knowledge of the bond graph and the valences of the atoms. The solutions of the network equations are called the *theoretical bond valences* and are designated by the lower case letter s. Methods for solving the network equations are described in Appendix 3.¹

In many compounds, the experimental bond valences, S, and the theoretical bond valences, s, are both found to be equal to the bond fluxes, Φ , within the limits of experimental uncertainty. This is an empirical observation that is not required by any theory. For this reason, and because there are occasions when the differences between them are significant and contain important information about the crystal chemistry, it is convenient to retain a different name for each of these three quantities to indicate the ways in which they have been determined. The bond flux is determined from the calculation of the Madelung field, the theoretical bond valence is calculated from the network equations (3.3) and (3.4), and the experimental bond valence is determined from the observed bond lengths using eqn (3.1) or (3.2).

It is observed that the experimental and theoretical bond valences have similar values in compounds in which there are no perturbing factors such as the anisotropic electron density associated with lone electron pairs (Chapter 8) or steric strains of the kind found in most perovskite-related compounds (Chapter 12). Structures in which the experimental and theoretical bond valences differ by an average of less than 0.05 vu are therefore called *unstrained structures*, the value of 0.05 vu being chosen to accommodate the experimental uncertainties typically present in *S.* Compounds that do not satisfy this condition are generically referred to as *strained structures* and are discussed in Chapters 8 and 12. For the present, the discussion will be restricted to unstrained structures unless otherwise specified. Typical of these are CaCO₃ (both calcite (100676) and aragonite (15198)), TiO₂ (both rutile (202240) and anatase (9852)), ZnS (both sphalerite (60378) and wurtzite (67453) forms), NaClO₄ (200405), β -Ga₂O₃ (34243), CaSO₄ (16382), and CaCrF₅ (10286). As an example, Table 3.1 compares the bond fluxes with the experimental and theoretical bond valences

¹ Rutherford (1998) and Rao and Brown (1998) have proposed other ways of applying the principle of maximum symmetry (rule 3.1) to the problem of calculating the theoretical valences as mentioned in Appendix 3.

3()							
Bond	Φ (vu)	s (vu)	S (vu)	R _{theor} (pm)	R _{exper} (pm)	s - S (vu)	$\Delta R \text{ (pm)}$
Cr-F3	0.41	0.41	0.41	199	194	-0.05	5
Cr-F1	0.47	0.48	0.47	193	192	-0.01	1
Cr-F2	0.58	0.61	0.58	184	185	0.01	-1
Ca-F3	0.17	0.18	0.17	248	250	0.01	-2
Ca-F1	0.26	0.26	0.29	234	229	-0.04	5
Ca-F1	0.23	0.26	0.23	234	239	0.03	-5
Ca-F2	0.39	0.39	0.39	219	221	0.02	-2

Table 3.1 A comparison of the bond fluxes, Φ , theoretical bond valences, s, and experimental bond valences, S, and the corresponding bond lengths, R, in CaCrF₅(10286)

The differences in the two observed bond lengths for Ca-F1 bonds can be attributed to steric effects discussed in Section 12.3.5.

and bond lengths in CaCrF₅, the compound whose bond graph is shown in Fig. 2.5.

The network equations (3.3) and (3.4) invite comparison with the Kirchhoff equations (2.7) and (2.11). By choosing the ionic charge, Q_i , in eqn (2.7) to be the same as the atomic valence, V_i , in eqn (3.3), and recognizing that in unstrained structures Φ_{ij} is equal to s_{ij} , it follows from eqn (2.11) that $\sum_{loop} s_{ij}/C_{ij} = 0$ which, when compared with eqn (3.4), means that the capacitances in eqn (2.11) must cancel, i.e. they must all be equal. This greatly simplifies the model, since it means that

for unstrained structures at equilibrium all bonds have the same bond capacitance.²

For unstrained compounds the quantum mechanical component of the ionic model is described entirely by the empirical bond valence parameters, R_0 and B, and an explicit knowledge of the bond capacitances is not needed.

In cases where the experimental and theoretical bond valences are different, the bond capacitances do not cancel, but the experimental bond valences continue to give a good estimate of the bond flux (Preiser *et al.* 1999). In these cases, discussed in Chapters 8 and 12, the theoretical bond valences can be used to determine a reference bond length against which the sizes of the strains in the observed bond lengths can be measured.

Although the empirical eqns (3.3) and (3.4) can be justified by their similarity with eqns (2.7) and (2.11) which have been derived using the ionic model, they are not restricted to ionic bonds. The formation of a chemical compound results in the pairing of the unpaired valence electrons drawn from the two bonded

² Tertiary bonds (Section 2.6) are excluded. Where they are real, they have very small capacitances and therefore should not be included in the bond network used to solve the network equations. Tertiary bonds are not found among the traditionally assigned chemical bonds.

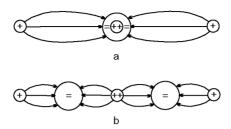


Fig. 3.2. A conceptual view of two monovalent cations (small circle with + sign) bonding a single divalent anion (small circle with + sign surrounded by large circle with pairs of - signs). (a) an ionic view in which the bonding electrons reside on the anion. (b) a covalent view in which the bonding electron pairs are located in the bonds. Note that the bond flux does not depend on whether the electrons pairs reside on the anion or are located in the bond.

atoms. In an ionic bond, these pairs all reside on the anions and the flux of a bond is equal to the number of the electron pairs associated with it. The electron pairs do not, however, have to reside on the anions, which is where they are assumed to be in the ionic limit. They can just as readily reside in the middle of the bond since, as shown in Fig. 3.2, the position of the electron pairs makes no difference to the flux linking the two atoms. Equation (3.3) is therefore obeyed in covalent as well as ionic compounds, provided one interprets V_i as the number of unpaired electrons in the valence shell of atom i, and s_{ij} as the number of electron pairs associated with the bond between atoms i and j.

Surprisingly, therefore, the same topological equations (3.3) and (3.4), provide a description of both ionic and covalent bonding. It does not therefore matter whether a bond is considered to be ionic or covalent in character since both have the same bond valence description. This leads to the important corollary: *the bond valence model cannot distinguish between ionic and covalent bonding*. Within the model, the terms 'ionic bond' and 'covalent bond' are without any formal significance.

3.3 The bond valence model

In Chapter 2 it was shown that the Madelung field of a crystal is equivalent to a capacitive electric circuit which can be solved using a set of Kirchhoff equations. In Sections 3.1 and 3.2 it was shown that for unstrained structures the capacitances are all equal and that there is a simple relationship between the bond flux (or experimental bond valence) and the bond length. These ideas are brought together here in a summary of the three basic rules of the bond valence model, Rules 3.3, 3.4, and 3.5.

First, however, it is appropriate to introduce the *Principle of maximum symmetry*, an important heuristic that underlies the bond valence model and its application.

Rule 3.1 (Principle of maximum symmetry.) As far as allowed by the chemical and geometric constraints, all atoms and all bonds in a compound will be chemically and geometrically indistinguishable.

In NaCl (18189), this principle would require all atoms to be identical. Clearly this symmetry is already broken by the constraint imposed by the chemical formula which requires half the atoms to be Na⁺ and half Cl⁻. However, all the Na⁺ ions are indistinguishable from each other, and the same is true for the Cl⁻ ions. The bonds likewise, six for each formula unit, are also equivalent in the bond graph (Fig. 2.4). The crystal structure (Fig. 1.1) is then determined by applying the principle of maximum symmetry to the constraints imposed by three-dimensional space as described in Section 11.2.2.4. The crystal structure is thus uniquely determined by the principle of maximum symmetry and the chemical and spatial constraints.

In more complex compounds, particularly ternary and quaternary compounds, it is often not possible to maintain the equivalence of all atoms of the same element because they are required to form different numbers of bonds. For example, in the bond graph of $CaCrF_5$ (10286) shown in Fig. 2.5, Cr^{3+} can only have its expected coordination number of six if one of the five F^- ions forms two bonds to Cr^{3+} . The equivalence of the remaining four F^- ions is broken by the spatial constraints (Section 12.3.5).

The principle of maximum symmetry can be justified by recognizing that the free energy of any symmetric system must necessarily be either a maximum or a minimum with respect to small shifts that break that symmetry, since shifts in opposite directions will produce identical changes in the energy. Thus equilibrium structures will tend to adopt the most symmetric configuration that corresponds to a minimum in the free energy.

The principle of maximum symmetry has a useful corollary:

Rule 3.2 (Corollary). The breaking of symmetry is always the consequence of an identifiable chemical or spatial constraint.

Any time the symmetry is lower than expected, a search for the cause of the broken symmetry will reveal the constraints that are at work in the system.

While the principle of maximum symmetry is a heuristic with wide scientific application, Rules 3.3 to 3.5 define the bond valence model. They have each been discussed before but are brought together here for convenience.

Rule 3.3 (Valence sum rule (eqn (3.3)). The sum of the valences of all the bonds formed by an ion is equal to the valence of the ion.

Since the bond valence is the same as the bond flux, this is the same as Gauss' law given by eqn (2.7). In every bond network the atomic valences can always be

distributed between the bonds in at least one way that obeys this rule providing the compound satisfies two conditions:

Condition 3.1. The stoichiometry must obey the electroneutrality principle, namely that the sum of all the atomic valences (formal ionic charges), having regard to their sign, is zero.

Condition 3.2. The bond graph must be bipartite as described in Section 3.5, i.e. all of the bonds must connect a cation, e.g. Na^+ , to an anion, e.g. Cl^- .

The valence sum rule is not, in general, sufficient to determine the distribution of the valence among the various bonds, but the principle of maximum symmetry suggests that the distribution will be the most symmetric one that is consistent with the valence sum rule. The condition that makes the bond valences most nearly equal is the *loop*, or *equal valence rule*.

Rule 3.4 (Equal valence rule (eqn (3.4)). The sum of bond valences around any loop in the bond network, having regard to the direction of the bond, is zero.

This rule is obeyed by unstrained structures and is equivalent to eqn (2.11), the law of conservation of energy, if the capacitances are all set equal.

Rules 3.3 and 3.4, through the corresponding network equations (3.3) and (3.4), can be solved (see Appendix 3) to give theoretical bond valences which, for unstrained structures, are equal to the bond fluxes and experimental bond valences. Taken together, Rules 3.3 and 3.4 are equivalent to the statement:

The valence of each atom is distributed as uniformly as possible among the bonds that it forms.

The correlation between bond length and bond valence corresponds to the third rule of the bond valence model.

Rule 3.5 (Bond length-bond valence correlation (eqns (3.1) or (3.2)). *Increasing the bond valence between two ions reduces the distance between them as shown in Fig. 3.1.*

This empirical correlation has been discussed in Section 3.1.

3.4 The distortion theorem

There is a useful theorem relating to coordination spheres that derives from the shape of the bond valence—bond length correlation shown in Fig. 3.1.

Rule 3.6 (Distortion theorem). For any ion, lengthening some of its bonds and shortening others, keeping the bond valence sum the same, will always increase the average bond length.

The proof of this theorem based on eqn (3.1) is given by Allmann (1975) who shows that the increase in average bond length, ΔR , in the distorted

environment of an ion is given by

$$\Delta R = B\{\ln\langle S\rangle - \langle \ln(S)\rangle\},\tag{3.5}$$

where the angle brackets indicate averages over all the bonds formed by the ion. Since the first term in the curly brackets is the logarithm of the arithmetic mean of the bond valences, and the second term is the logarithm of the geometric mean, and since the arithmetic mean is always equal to or larger than the geometric mean, ΔR must be positive or, when all the bonds are the same length, zero.

The theorem can also be understood by referring to Fig. 3.1. If a Ca^{2+} ion is at the centre of an octahedron of O^{2-} ions, it forms six bonds of 0.33 vu and, according to Fig. 3.1, each Ca–O bond has a length of 237 pm. If the Ca^{2+} ion is displaced, so as to increase the valence of three bonds to 0.53 vu and decrease the valence of the other three to 0.13 vu, the valence sum remains unchanged, but three bonds have been shortened to 220 pm and the other three lengthened to 272 pm, the average bond length being increased from 237 to 246 pm. By distorting the environment of Ca^{2+} , the average bond length has been increased by 9 pm, but the bond valence sum remains unchanged.

The distortion theorem can be expressed in an alternative form:

Rule 3.6a (An alternative statement of the Distortion theorem). For any ion, lengthening some of its bonds and shortening others, keeping the average bond length the same, will always increase the valence sum.

This statement of the distortion theorem can be demonstrated in the same way as the previous statement, but it leads to an interesting corollary:

Rule 3.7 (Corollary). If an ion is placed in an environment in which the average bond length is too long, i.e. in a cavity which is too large for the ion, the environment will distort in such a way as to increase the lengths of some bonds and decrease the lengths of others in order to raise the bond valence sum to the expected value.

Typically, the ion will move off-centre in its coordination sphere (see Chapter 12), but distortions which preserve a centre of symmetry, such as the Jahn–Teller distortion discussed in Section 8.3.1, are also possible.

3.5 Bond networks with non-bipartite graphs

Hitherto it has been assumed that the bond graph is bipartite, i.e. bonds only occur between a cation and an anion with no cation—cation or anion—anion bonds present. While the majority of inorganic compounds have bipartite bond graphs, there are a few, such as mercurous and peroxy compounds, that contain homoionic bonds. It is easy to see that there can be no electric flux linking two cations or two anions, so the ionic model predicts that no bond will exist between them.

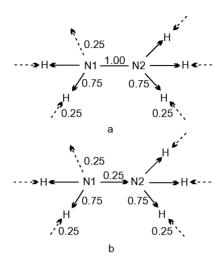


Fig. 3.3. (a) Expected bond valences in $NH_2 \cdot NH_3^+$. No chemically reasonable assignment of bond valences will give equal integer valence sums at both nitrogen atoms. (b) An alternative treatment of the N-N bond that ignores the N-N bonding electron pair but gives correct valence sums (of -2) on the two nitrogen atoms.

The practical problem created by homoionic bonds is illustrated by the hydrazinium ion, N₂H₅⁺, shown in Fig. 3.3(a). If the H⁺ atoms are treated as cations carrying a formal charge of +1, the N atoms must each have a formal charge of -2 if the hydrazinium ion is to have a net charge of +1. This leaves each N atom with an unpaired electron which is used to form an N-N electron pair bond. Whether one ignores the N-N bond or whether one counts it as having a bond of valence 1.0, it is mathematically impossible for the valence sums around both N atoms to be equal, nor is it possible for both sums to be integers. Assuming that each H⁺ ion forms a hydrogen bond as described in Chapter 7, so that the five N-H bonds each have a valence of 0.75 vu, and that N1 accepts a hydrogen bond of 0.25 vu as shown in Fig. 3.3(a), the sum of the N-H bond valences around N1 is 1.75 vu and around N2 is 2.25 vu. There is no reasonable chemical way of adjusting these valence sums, either by strengthening or weakening the N-H bonds, or by assigning a valence to the N-N bond, that will make these sums equal, let alone allow them to be equal to the integer 2 or 3.

However, we do not need to abandon the bond valence model for those few inorganic compounds which contain homoionic bonds since there are a number of ways of adapting the model depending on the nature of the structure. If the two cations or two anions that form the bond are equivalent by symmetry, as the two ${\rm Hg}^{2+}$ cations are, for example, in the tetragonal crystals of ${\rm Hg}_2{\rm Cl}_2$ (65441, Fig. 3.4), the normal rules still apply. In this compound the two ${\rm Hg}^{2+}$

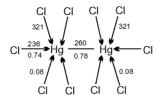


Fig. 3.4. The environment of the Hg_2^{2+} cation as observed in $\mathrm{Hg}_2\mathrm{Cl}_2$ (65441). Bond valences are shown in the lower part of each figure and bond lengths (in pm) in the upper part.

ions are equivalent by crystallographic symmetry and both Hg^{2+} ions have an observed valence sum of 1.84 vu which is close to the expected value of 2.00 vu. The symmetry ensures that both Hg^{2+} ions contribute the same number of valence electrons to the Hg–Hg bond, a condition which lies at the heart of the ionic model.

However, if the atoms are not related by symmetry, the normal rules break down. The homoionic N–N bond in the hydrazinium ion is an electron pair bond, but one in which N1 contributes 1.25 and N2 0.75 electrons. How can we apply the bond valence model in such cases where no solution to the network equations is possible? One approach is to isolate the non-bipartite portion of the graph into a complex pseudo-atom. Thus in the hydrazinium ion the homoionic bond and its two terminating N atoms are treated as a single N_2^{4-} pseudo-anion which forms six bonds with a valence sum equal to the formal charge of -4.

The trifluoroacetate ion CF₃CO₂ (Fig. 3.5(a)) is similar (Brown 1980b). F and O² are both anions so the two C atoms are both formally cations, each with a valence of +4. As before, we treat the C-C unit as a single pseudocation, C₂⁶⁺ reserving one electron pair for the C-C bond. It is instructive to compare this with the closely related acetate ion, $[H_3^+C^{4-}-C^{4+}O_2^{2-}]^-$, whose graph is bipartite (Fig. 3.5(b)). In the acetate ion the valence of the C–C bond is determined by the valences of the C-H and C-O bonds, hence ultimately by the strengths of the external bonds that the H⁺ and O^{2 -} atoms form as discussed in Section 9.2. In most acetates the C-C distance is 151 pm corresponding to a valence of 1.10 vu. Where the external bonds are strong, the C-O and C-H bonds are weaker, thus strengthening the C-C bond and shortening it in some compounds to as little as 144 pm. Where the external bonds are weak, the opposite effect is seen and the C-C bond increases in length to 154 pm. In contrast, the C-C bond in the trifluoroacetate ion is insensitive to its environment and never varies significantly from the single bond length of 154 pm. The contributions of the two C atoms to the electron pair bond may be vary, but the total number of electrons in the bond is fixed (Section 14.1.1).

A homoionic bond that needs a different treatment is the cation—cation bond formed by a cation with a stereoactive lone electron pair, a situation modelled in more detail in Section 8.2. An example of this kind of bond is the Cu–N bond

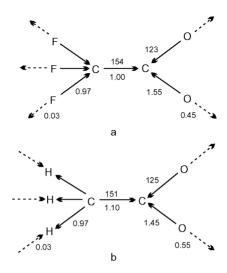


Fig. 3.5. Typical experimental bond valences in (a) the trifluoroacetate anion and (b) the acetate ion (Brown 1980b). Bond valences are shown in the lower part of each figure and bond lengths (in pm) in the upper part.

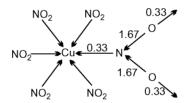


Fig. 3.6. Expected structure and bond valences of the $Cu(NO_2)_6^{4-}$ ion.

found in $\text{Cu}(\text{NO}_2)_6^{4-}$ (Fig. 3.6). Both Cu^{2+} and N^{3+} are nominally cations, but N^{3+} has a lone electron pair occupying one of its sp^2 orbitals. In this case, N^{3+} acts through its lone pair as an anion towards Cu^{2+} while acting as a cation towards O^{2-} . If the net formal charge of -4 on the complex anion is divided equally between the 12 peripheral O^{2-} ions, each will carry a formal charge of 4/12=0.33 vu with which to form external bonds. The remaining 1.67 vu of negative valence on each O^{2-} ion is used to form a bond to N^{3+} . Since N^{3+} forms two such bonds, it will be overbonded, with the bond valence sum equal to $2\times 1.67=3.33$ vu. However, the overbonding can be reduced if N^{3+} acts as an anion through its lone electron pair to form a bond of 0.33 vu to Cu^{2+} . Taking account of the direction of the bonds (from anion to cation), the valence sum at N^{3+} becomes $2\times 1.67-0.33=3.00$ vu as required by the valence sum rule.

A slightly different example is the metal-ligand bond formed by the S^{4+} atom of the bipartite molecule dimethylsulphoxide, dmso = $(CH_3)_2SO$, shown in

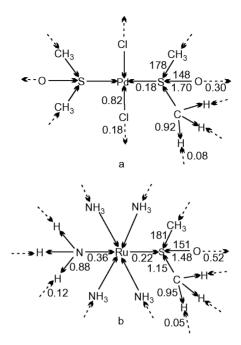


Fig. 3.7. Structures of dmso complexes: (a) $PdCl_2dmso_2$ (PDDMSX), (b) $[Ru(NH_3)_5dmso]^{2+}$ (DMSARU). Bond valences are shown in the lower part of each figure and bond lengths (in pm) in the upper part.

Fig. 3.7 (Brown 1987a). Dmso normally coordinates to transition-metal cations through O²⁻, but with some of the later transition metals it coordinates through the lone pair of electrons on S⁴⁺ (Section 8.2). However, there is an important difference between this and the previous case. The N-Cu bond is a σ donor bond from N³⁺ to Cu²⁺, but S⁴⁺ has vacant d orbitals that can also accept a π bond from the filled non-bonding d orbitals found in the late transition metals. The metal-S bond is strictly represented by two bonds, a σ bond directed from S^{4+} to the metal, and a π bond directed from the metal to S^{4+} . The fluxes in these two bonds almost cancel, so the net flux of the bond is small, typically less than 0.2 vu, even though the bond itself may be quite strong. Although the net valence of the metal-S bond does not therefore correlate with the bond length, it can be found by ensuring correct bond valence sums around both S⁴⁺ and the metal. The two examples shown in Fig. 3.7, PdCl₂(dmso)₂ (PDDMSX) and Ru(NH₃)₅dmso²⁺ (DMSARU), represent two opposite extremes. The direction of the arrow on the metal-S bond indicates the direction of the net electron transfer (opposite to the directions of the electrostatic flux lines). The bond transmits the influence of the electron donating or withdrawing character of the transition-metal complex to dmso resulting in an observable

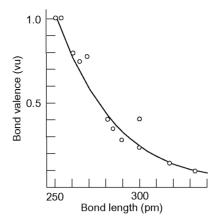


Fig. 3.8. Correlation between bond valence and bond length for Hg–Hg bonds. The circles represent observed values (Brown *et al.* 1984).

difference in the geometry of the dmso molecule and the strengths of the bonds formed by its hydrogen and oxygen atoms.

The bonding in the hydrazinium and trifluoroacetate ions can also be described in a similar way. Since each atom of the N-N or C-C bond contributes a different number of electrons (valence) to the bond, one can show the net valence transfer by means of an arrow as shown in Fig. 3.3(b). The valence sum rule is obeyed by this graph but at the expense of ignoring the electron pairs that provide the primary bond between the two N atoms. As in the case of dmso, the bond valence of the N-N bond in Fig. 3.3(b) shows only the net electron transfer, not the total number of electron pairs that contribute to the bond. The bond valence does not, therefore, correlate with the bond length.

In most of these cases the homoionic bond can be assigned a valence, but this does not always correlate with bond length as the examples of the trifluoroacetate ion and S-bonded dmso show. However, a correlation is expected for $\text{Cu}(\text{NO}_2)_6^{4-}$ and has been found for Hg-Hg bonds. In addition to the well-known mercurous ion (Hg_2^{2+}) , cations such as Hg_3^{2+} , Hg_4^{2+} , $(\text{Hg}^{0.35+})_{\infty}$ (infinite chains), and $(\text{Hg}^{0.33+})_{\infty}$ (infinite sheets) are also known. The Hg-Hg bonds in these cations show a considerable variation in length which correlates well with the bond valence, as shown in Fig. 3.8 (Brown *et al.* 1984).



II

Chemistry



Anion and cation bonding strengths

4.1 Bond graphs and coordination number

In applying the rules developed in Chapter 3 to understand and predict the properties of inorganic compounds, it is necessary to know which particular atoms are connected by bonds, i.e. one must know the bond graph. In simple cases it is possible to predict the bond graph from first principles using the procedure described in Section 11.2.2.1, but in other cases, one must be content to work with something less than a full knowledge of the graph.

Even if the connectivity is not known, one can predict many properties if one can make a reasonable estimate of the coordination number. Chapter 6 describes the different factors that determine the coordination number, but at this point in the discussion it is sufficient, and simpler, to work with coordination numbers that are determined experimentally.

The coordination number of a cation is defined as the number of bonds that it forms. Although it was shown in Section 2.6 that the number of bonds is uniquely defined by the partitioning of the Madelung field, extensive calculation is needed to extract this information. It is, therefore, convenient to use a simpler, if more arbitrary, definition.

There have been many attempts to define coordination number using a simple criterion to decide when two atoms are bonded (Brunner and Laves 1970). Rules have been proposed based on bond lengths, ionic radii, and topological properties such as the Voronoi partitioning of space, but none has proved entirely satisfactory. In this book the coordination number is determined by setting an arbitrary, though reasonable, lower threshold for the experimental bond valence (Altermatt and Brown 1985).

Rule 4.1 (An operational definition of a bond). A bond exists between a cation and an anion if its experimental bond valence is larger than $0.04 \times$ the cation valence.

While this definition is arbitrary it is appropriate because it is based on chemical as well as geometric considerations and, like other definitions, it agrees with the conventional assignment in cases where there is no dispute. The definition can be justified for use with the bond valence model since any true bond that is excluded by this definition contributes at most only 4 per cent to the cation bond valence sum, and generally much less given that eqn (3.1) tends to overestimate the valence of weak bonds.

Cation coordination numbers using Rule 4.1 as a criterion have been determined for some 14000 cation environments (Brown 1988a). Some cations, such as S⁶⁺, are known with only one coordination number (4 in this case), but others, such as Cs⁺, can be found with every coordination number between 3 and 12. Whatever the total range, the frequency distribution of the coordination number for a given cation usually peaks close to the average. It is therefore convenient to take the average observed coordination number as a characteristic chemical property of the cation.

Average cation coordination numbers vary slightly depending on the anion. Most cations have similar coordination numbers when bonded to ${\rm O}^{2-}$ and ${\rm F}^-$ and generally smaller coordination numbers when bonded to larger anions, but monovalent cations have similar coordination numbers with all monovalent anions (halogens) and smaller coordination numbers with divalent anions (chalcogens). The average observed coordination numbers used in this book are those to ${\rm O}^{2-}$ unless otherwise stated. They are referred to as *ideal coordination numbers* and are listed in Appendix 4.

Ideal coordination numbers for anions can, in principle, be determined in a similar way but it is difficult to find many examples of an anion surrounded by only one kind of cation. In the alkali halides, Cl^- is six coordinated by each of the smaller alkali metal atoms, but is eight coordinated by Cs^+ . An ideal coordination number of 7 can therefore be chosen. The coordination numbers around O^{2-} in stable compounds range between 2 and 6 with an average close to 4 and similar values are found for F^- .

With a knowledge of the ideal coordination numbers expected for each of the ions, one can explore the crystal chemistry of a compound without prior knowledge of its structure or even its bond graph. It is not even necessary that the compound exist in order to explore its chemistry and to discover whether it is likely to be stable, and if so, what its properties might be.

The coordination numbers observed in a crystal are expected to be close to the ideal value. Both Na⁺ and Cl⁻ have ideal coordination numbers close to 6, so it is not surprising to find that in crystals of NaCl both ions are six coordinate. The situation is different for CsCl since the ideal coordination number of Cs⁺ surrounded by Cl⁻ is 10.4 (Brown 1988a). A compromise is needed since both atoms are required to have the same coordination number. The observed value for CsCl is 8, which is close to the average of the ideal coordination numbers (10 and 7) of the two ions. The mismatch is more severe for Na₂O since the two Na⁺ ions would be expected to form a total of $2 \times 6 = 12$ bonds but the single O²⁻ ion would normally form only four bonds. The coordination number of Na⁺ must be greatly decreased and that of O²⁻ increased. The average of 12 and 4 is 8, suggesting that O^{2-} should be eight coordinate which requires that Na⁺ be only four coordinate. These are the coordination numbers found in the antifluorite structure adopted by Na₂O (60 435). With both ions adopting coordination numbers far from the ideal, Na₂O is unstable with respect to the formation of other compounds in which both ions can adopt a more normal

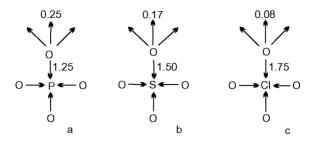


Fig. 4.1. Anion bonding strengths of (a) PO_4^{3-} , (b) SO_4^{2-} , and (c) ClO_4^{-} .

coordination. Both the Na⁺ and O²⁻ ions in Na₂O therefore tend to react with molecules such as water or carbon dioxide that can provide them with coordination numbers closer to the ideal.

4.2 Anion bonding strength

 P^{5+} , S^{6+} , and Cl^{7+} all have ideal coordination numbers of 4 resulting in the formation of the oxyanions PO_4^{3-} , SO_4^{2-} , and ClO_4^- (Fig. 4.1). The valence of the P–O bonds is 5/4=1.25 vu leaving each O^{2-} ion with a valence of 0.75 vu for forming external bonds. Similarly, the valence of the S–O bonds is 1.50 vu leaving only 0.50 vu for forming external bonds. The valence expected for each of the external bonds formed by these complex anions can be calculated if the coordination numbers of the O^{2-} ions are known. If in PO_4^{3-} the O^{2-} ions are six coordinate, each would form one O–P bond of 1.25 vu and five external bonds of 0.75/5=0.15 vu. This is the weakest bond that PO_4^{3-} is expected to form. The strongest, formed when the O^{2-} ions are only two coordinate, is 0.75 vu. If nothing is known about the compound in which the phosphate group occurs, the best guess would be that the O^{2-} ions have their ideal coordination number of 4 (Fig. 4.1(a)). The three external bonds would then each have a valence of 0.75/3=0.25 vu. A similar exercise applied to the SO_4^{2-} ion (Fig. 4.1(b)) shows that it will form bonds with valences between 0.10 and 0.50 vu with a most probable value of 0.50/3=0.17 vu. Similarly ClO_4^- will form bonds with a most probable valence of 0.08 vu (Fig. 4.1(c)).

The most probable valence for the external bonds of an anion is called the *anion bonding strength*, s_a , and is defined by eqn (4.1):

$$s_{\rm a} = V_{\rm a}/\nu_{\rm a} \quad (V_{\rm a} < 0), \tag{4.1}$$

 $^{^{1}}$ The number, 0.75 vu, is sometimes called the formal charge on the O atoms, but it should not be confused with either the formal ionic charge (=-2 for all O^{2-} ions) or the charges on the O atoms calculated by quantum mechanics. Quantum mechanical charges are usually larger than -0.75 (depending on how the calculation is performed) since they include ionic contributions to the P-O bonds as well as to the external bonds. Quantum mechanics does not allow one to separate the internal and external bond contributions.

where ν_a is the ideal anion coordination number. The extreme values are referred to as the maximum and minimum anion bonding strengths.

Bonding strengths can be calculated for other anions in the same way, namely by dividing the valence available for external bonds by the number of external bonds formed. This can be done either atom by atom as done above, or for the anion as a whole. For example, SO_4^{2-} has a formal charge (valence available for external bonds) of -2.0 and it is expected to form $4 \times 3 = 12$ external bonds. Its anion bonding strength is therefore 2/12 = 0.17 vu, the same value as calculated above. A listing of anion bonding strengths is given in Appendix 4 and some typical values are shown on the right-hand side of Fig. 4.2. Maximum and minimum anion bonding strengths can be calculated in the same way by assuming O_2^{2-} coordination numbers of 2 and 6 respectively.

When calculating the bonding strengths of oxyanions, it is normal to assume that each oxygen atom will form a total of four bonds, but there are some occasions when this is clearly inappropriate. If the oxygen atom is bridging between two strongly bonding cations as, for example, in $S_2O_7^{2-}$ (= $O_3S-O-SO_3$), the two S-O bridging bonds cannot have valences as large as 1.50 vu as found in SO_4^{2-} . Since the valence sum around the oxygen cannot be greater than 2.0 vu, the bridging S-O bonds must have valences of 1.0 vu or less, leaving the bridging oxygen little or no valence for forming external bonds. In this case the coordination number of O^{2-} is unlikely to be greater than 2. If one of the terminal O^{2-} ions is protonated, as in HSO_4^- , it forms two relatively strong bonds, one to the H^+ ion and one to S^{6+} . In this case it is usually better to assume a smaller coordination number such as 2 or 3 for the oxygen. The method of calculating the bonding strengths of protonated anions is described in more detail in Section 5.4.

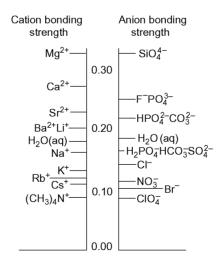


Fig. 4.2. Comparison of cation and anion bonding strengths for selected ions.

Anions with larger bonding strengths are better able to bind H^+ so it is no surprise that there is a correlation between bonding strength and pK_a , the equilibrium constant that measures the ability of an anion A^- to attach an H^+ ion in the reaction:

$$A^- + H^+ \rightarrow AH$$
.

Anions like PO_4^{3-} that have a relatively large anion bonding strength (0.25 vu) are able to form stronger bonds to H^+ and therefore will have a correspondingly large pK_a . Those like ClO_4^- , which have a small anion bonding strength (0.08 vu), can only bond H^+ ions with extreme difficulty and so have a low pK_a (Fig. 4.3). Since Lewis bases are ions that donate electrons to the bonds they form, anions with a large bonding strength are also strong Lewis bases. The bonding strength is therefore a direct measure of an anion's *Lewis base strength*. Anions are referred to in this book as *strong* or *weak anions* according to whether they have large or small bonding strengths.

4.3 Cation bonding strength

One can calculate *cation bonding strengths*, s_c , in the same way as anion bonding strengths by dividing the valence (or formal ionic charge) of a cation by its ideal coordination number, ν_c (eqn (4.2)):

$$s_{\rm c} = V_{\rm c}/\nu_{\rm c} \quad (V_{\rm c} > 0),$$
 (4.2)

 Si^{4+} has a valence of +4 and is normally four coordinate so that its bonds have a valence of 4/4 = 1.0 vu. Al^{3+} has a valence of 3 and occurs in both four- and six-coordination. It can form bonds of either 3/4 = 0.75 vu (as in AlPO₄, 201773)

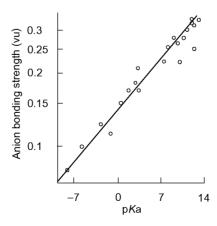


Fig. 4.3. Anion bonding strength plotted as a function of pK_a .

or 3/6 = 0.50 vu (as in Al_2O_3 , 75559), but since Al^{3+} is more often surrounded by six than by four oxygen atoms, its ideal coordination number is 5.27 and its cation bonding strength is 3/5.27 = 0.57 vu. Mg^{2+} is usually found in six coordination giving it a cation bonding strength of 2/6 = 0.33 vu. Cation bonding strengths are listed in Appendix 4 and a selection is shown on the left-hand side of Fig. 4.2. As with anions, the terms *strong* and *weak cation* refer to cations with large or small bonding strengths respectively.

Just as the bonding strength of an anion is a measure of its Lewis base strength, so the bonding strength of a cation is a measure of its Lewis acid strength. For this reason, cation bonding strengths correlate with electronegativity, increasing as one moves upwards and to the right in the periodic table. Many different scales of electronegativity have been proposed based on a wide variety of different properties. Figure 4.4 shows the correlation between the cation bonding strength and Pauling's (1960, p. 93) scale of electronegativity based on the dipole moments of diatomic molecules, while Fig. 4.5 shows the correlation with a more recent scale proposed by Allen (1989) based on the

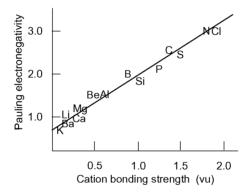


Fig. 4.4. Pauling electronegativity versus cation bonding strength.

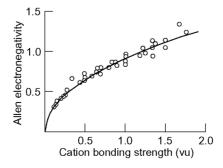


Fig. 4.5. Allen spectroscopic electronegativity versus cation bonding strength.

spectroscopic properties of free atoms. Given the widely differing bases for these three scales, the surprise is not so much that they differ in detail as that their overall agreement is so good. Although they show differences for the transition-metal atoms, the three scales agree on the relative ordering of the main group elements, particularly when allowance is made for non-bonding valence electrons (Brown and Skowron 1989). These similarity arises because each of these scales ultimately derives from the ratio of the charge of the atomic core to its radius, this ratio being a measure of the electric potential at the surfaces of the core, the place where all the chemistry occurs.

4.4 The valence matching principle

The cation bonding strength is an estimate of the valence of the bonds formed by a cation, and the anion bonding strength is an estimate of the valence of the bonds formed by an anion. The most stable bond between the two will occur when the bonding strength of the cation is equal to the bonding strength of the anion. This result is summarized by the *Valence matching principle*, which states:

Rule 4.2 (Valence matching principle). The most stable compounds are formed between cations and anions that have the same bonding strength.²

The bonding strengths of several cations and anions are compared in Fig. 4.2 which shows which cations and anions have similar bonding strengths and thus form stable compounds. For example, Mg²⁺ and SiO₄⁴⁻ both form bonds with valences of 0.33 vu and so readily bond to each other to form Mg₂SiO₄(26374), the mineral forsterite believed to form a large portion of the earth's mantle. Similarly, PO_4^{3-} ($s_a = 0.25$ vu) is well matched with Ca^{2+} ($s_c = 0.27$ vu) to form the mineral whitlockite (23598), but it is poorly matched with K^+ ($s_c = 0.13 \text{ vu}$). Even though K₃PO₄ has a stoichiometrically correct formula, it is relatively unstable because of its poor valence match. K₃PO₄ is, in fact, deliquescent. It reacts with water to form the H₂PO₄ ion and hydroxyl, a result that can readily be deduced using the bond valence model as shown in Chapter 5. Similarly Si₃(PO₄)₄, while stoichiometrically correct, is not stable because of the poor match between the cation and anion bonding strengths ($s_c = 1.00$, $s_a = 0.25$ vu). An alternative but equivalent way of demonstrating the instability of this compound is to note that even if all the O²⁻ atoms were only two coordinate, which is the lowest coordination number found for O²⁻ in solids, there would still be 16 Si-O bonds in the formula unit. Since there are only three Si⁴⁺ ions, the average Si⁴⁺ coordination number would

² Stability is a relative term. Almost all chemical compounds are at best metastable, there being other chemical combinations (usually with other elements) that have lower free energies. A chemical compound is therefore only stable if there is no mechanism for it to proceed to a more stable configuration. For example some compounds that are stable when dry, react with water when moist to form a system of lower free energy as discussed in Chapter 5.

be 16/3 = 5.33, forcing two of the three Si^{4+} ions to be six coordinate, a coordination adopted by Si^{4+} only under extreme conditions.

Although the most stable compounds are found when the bonding strengths of the cation and anion are exactly equal, a certain degree of mismatch is allowed. As a general rule, compounds can exist if the ratio of the two bonding strengths does not exceed 2.0. While it may be possible to prepare materials that are more poorly matched, it requires heroic methods and the resulting compounds are generally unstable.

4.5 Hard and soft acids and bases

Pearson (1973) divided Lewis acids (cations) and Lewis bases (anions) into two classes which he called hard and soft, reflecting the ease with which they can be polarized. He pointed out that hard acids tend to form compounds with hard bases, and soft acids with soft bases. The hard cations and anions are those from the top of the periodic table in which the excited states that are required to polarize the electron density lie well above the ground state and are thus inaccessible. Hard cations behave as relatively hard spheres and have a simple crystal chemistry with a limited range of coordination numbers. On the other hand, soft ions are those that occur lower in the periodic table, with cations centred around Groups 11 and 12 (Au³⁺, Hg²⁺) and anions centred around Group 17 (I⁻). These ions have many low-lying excited levels that can be stabilized by suitable changes in their environment. Soft ions are characterized by having a more variable structural chemistry and can be found with different coordination numbers and geometries, sometimes with strongly directed bonds as discussed in Chapter 8. Although a number of different scales of hardness and softness have been proposed, the concept has been difficult to quantify and is most useful when it is used qualitatively.

Soft ions can adopt a number of different coordination environments, and which one is adopted depends sensitively on the available low-lying excited states and the chemical environment. Tl^+ for example, which has a pair of valence electrons not used in bonding, behaves like a normal hard cation in its binary halides, falling neatly between K^+ and Rb^+ in the alkali metal sequence, but in Tl_3BO_3 (10196) it behaves quite differently, forming three strong Tl-O bonds arranged along three of the sides of a triangular pyramid. According to the valence matching principle, K_3BO_3 should be quite unstable since the bonding strengths of K^+ (0.13 vu) and BO_3^{3-} (0.33 vu) are very poorly matched. If Tl^+ always behaved like a hard alkali metal, Tl_3BO_3 should be equally unstable but this is not the case. Unlike K^+ , Tl^+ is a soft cation and can rearrange its electron density so as to match the bonding strength of the anion as discussed in Section 8.2. Thus the characteristic of soft ions is that they display a much wider range of bonding strengths than hard ions. For this reason the soft cations are shown with a range of bonding strengths in Appendix 4.

It is instructive, for example, to compare the structural chemistry of Mg^{2+} and Zn^{2+} which have identical charges and similar sizes. Mg^{2+} is hard and rarely occurs in other than six coordination (bonding strength of 0.33 vu), but, because Zn^{2+} has a filled d shell which can readily mix with the electrons of the valence shell, it is soft and is found equally often in four- and six-coordination (bonding strength between 0.33 and 0.50, average 0.40 vu, see Section 6.5). A more complete discussion of the behaviour of soft cations is given in Chapter 8.

4.6 Applications of the valence matching principle

Many examples of the valence matching principle will be found in the following chapters, but a couple of examples are given here to illustrate its power.

We often ask the question 'Why does such and such a compound exist?' but more rarely do we ask the question 'Why does such and such a compound not exist?', yet the answer to the second question may be more revealing than the answer to the first. A number of years ago, Dent-Glasser (1979) published a paper entitled 'Non-existent silicates' in which she noted that there were many stoichiometrically allowed silicate structures that had never been observed. In particular she pointed out that the alkali metals rarely formed orthosilicates such as Na₄SiO₄, and transition metals rarely formed highly condensed silicates such as NiSi₄O₉. Dent-Glasser's list of known silicates is shown in Fig. 4.6

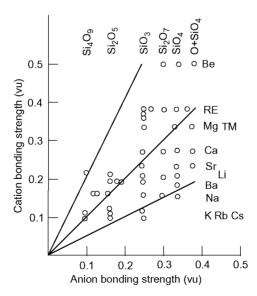


Fig. 4.6. Known silicates plotted as a function of anion and cation bonding strengths. The lines correspond to the s_c/s_a ratios of 2.0, 1.0, and 0.5.

plotted as a function of their anion and cation bonding strengths. The known silicates all cluster around the line that represents the best valence match. Those silicates with an s_c/s_a ratio greater than 2.0 or less than 0.5 are the ones that do not exist because the poor valence matching would require that the ions adopt coordination numbers far from their ideal values.

Hawthorne (1994) has expanded on this idea to suggest that the silicate mineral that forms as a particular magma solidifies is determined by which cations are present. It is easy to see from Fig. 4.6 that a rock containing strongly bonding transition-metal cations will crystallize with equally strongly bonding meta- or orthosilicate anions, while one containing only weakly bonding alkali metals will crystallize with equally weakly bonding condensed silicate anions.

An example from a quite different field is the observation by Plenio (Plenio 1998; Plenio and Hermann 1998) that fluorinated macrocyclic molecules are much better chelating agents for Cs⁺ than the more common macrocycles that use O and N as their coordinating atoms, even though organic O and N are much stronger bases than organic F. This unexpected result is readily understood in terms of the valence matching principle which predicts that a weak cation like Cs⁺ will form better bonds with a weak base like –CF than with the stronger bases that are used to chelate stronger cations like K⁺ and Na⁺.

Liquids

5.1 Introduction

It is now time to show how the ideas developed in the previous chapters can be applied to real chemical systems. Apart from a few simple gases, the materials we come across in everyday life are either solids or liquids. A proper understanding of the chemistry of the solid state requires some appreciation of the role of symmetry in crystals and is therefore deferred to Part III. This chapter explores the use of bond valences to understand the simpler chemistry of liquids. Most of this chapter is devoted to the chemistry of aqueous solutions because water is not only the solvent of choice for polar systems but also the most common solvent in our environment.

5.2 The cation and anion bonding strength of water

The process by which a solid is dissolved in water is a chemical reaction of which eqn (5.1) is a typical example:

$$MgSO_4 + 6H_2O \longrightarrow Mg(H_2O)_6^{2+} + SO_4^{2-}$$
 (5.1)

In order to understand why this reaction occurs, it is first necessary to determine the cation and anion bonding strengths of water. To calculate these requires, in turn, an understanding of the unique properties of the hydrogen ion. A full discussion of hydrogen bonding is deferred to Chapter 7, but for the present it is sufficient to know that $\mathrm{H^+}$ ions bond asymmetrically between two anions, here assumed to be $\mathrm{O^{2-}}$ unless otherwise specified. Typically $\mathrm{H^+}$ forms a bond of 0.8 vu with one oxygen atom and a bond of 0.2 vu with the other, though the degree of asymmetry varies somewhat with the chemical context.

An isolated water molecule does not form any hydrogen bonds since there are no nearby anions to act as acceptors. Therefore the bond between O^{2-} and H^+ has a valence of 1.0 vu (Fig. 5.1(a)). However, in condensed phases each water molecule forms hydrogen bonds with four neighbouring molecules (Fig. 5.1(b)). The valence of the bond between O^{2-} and H^+ within the molecule is reduced from 1.0 to 0.8 vu and a new weak bond of 0.2 vu is formed between the hydrogen of one molecule and the oxygen of a neighbour. Each water molecule bonds to two neighbours through H^+ (as the hydrogen bond donor) and to two

54 LIQUIDS

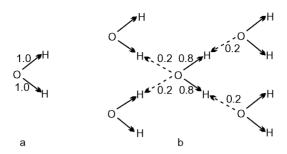


Fig. 5.1. The structure of water showing the expected bond valences: (a) an isolated water molecule, (b) water in the liquid or solid state.

other neighbours through O^{2-} (as the hydrogen bond acceptor). The water molecule therefore behaves as both a cation and an anion: the hydrogen acting as a cation with a bonding strength of $0.2\,\mathrm{vu}$ and the oxygen acting as an anion with a bonding strength also of $0.2\,\mathrm{vu}$. In liquid water the hydrogen bonds are labile, they tend to be bent and consequently a little weaker than in the solid as discussed in Section 7.5. Therefore the effective bonding strengths of water molecules in the liquid phase are a little smaller and can be taken as $0.17\,\mathrm{vu}$.

According to the valence matching rule, water molecules will readily bond to each other since their cation and anion bonding strengths are equal, but they can also bond to other anions and cations that have appropriate bonding strengths. Although the ideal valence of the weak side of the hydrogen bond in water is around 0.17 vu, some variation is possible. In practice water forms donor hydrogen bonds with valences anywhere in the range from 0.10 to 0.25 vu by suitable adjustment of the strengths of the bonds formed by the oxygen. Any anion with a bonding strength between 0.10 and 0.25 vu can therefore accept a hydrogen bond from water, and any cation with a bonding strength between 0.1 and 0.5 vu can bond to the oxygen, the maximum bonding strength of 0.5 vu corresponding to a three-coordinate oxygen atom and the formation of strong hydrogen bonds (Fig. 5.2(c)). Compounds whose ions have bonding strengths lying in these ranges can dissolve in water as discussed in Section 5.5 below.

¹ It is interesting to compare H₂O with HF, NH₃ and CH₄. If HF forms one donor hydrogen bond of 0.2 vu and F is taken as four coordinate, HF has an anion bonding strength of 0.2/3 = 0.07 vu. Similarly, if NH₃ forms three donor hydrogen bonds of 0.2 vu, it can form only one bond to a cation and thus has an anion bonding strength of $3 \times 0.2/1 = 0.6$ vu. These molecules can form bonds to both anions and cations but they are poorly matched to themselves. With $s_c/s_a = 0.33$, HF has a boiling point of 293 K, lower than the boiling point of water, 373 K, where the ratio is 1.0 and the match is perfect. For NH₃, s_c/s_a is 3.0 and the boiling point is again lower, 240 K. The ratios of s_c/s_a for HF and NH₃ both lie outside the normal limits for stability (Section 4.4) and, unlike H₂O, both are unstable in the presence of water. Finally, CH₄ has no possibility of bonding to cations, so it is unable to form hydrogen bonds. Its boiling point is only 109 K. The high anion bonding strength of NH₃ makes it an excellent ligand for coordinating to the three-valent six-coordinate cations (s_c = 0.5 vu) found in the transition-metal series.

5.3 Reactions of cations with water

Any cation in liquid water will be surrounded by water molecules oriented with the oxygen atom facing the cation (Fig. 5.2). The number of water molecules in the coordination sphere will normally be close to the ideal coordination number expected for the cation (Appendix 4) but if the hydrated complex is to be stable, the bonding strength of the cation must match that of the water molecule. This is best illustrated by examples.

First consider the cation Na^+ whose ideal coordination number is 6.4 and whose bonding strength (0.16 vu) closely matches that of liquid water. In this case we expect the complex $Na(H_2O)_6^+$ to be formed. However, this is not the whole story. Since the Na-O bonds have valences comparable to the hydrogen bonds found in the bulk water, they are, like the hydrogen bonds of water, labile at room temperature. We therefore expect the complex to be fluxional, with additional water molecules attaching themselves to Na^+ and other water molecules breaking away on a timescale comparable to the fluctuations in the bonds between the water molecules themselves. In addition, to satisfy the valence sum rule, each of the coordinated oxygen atoms must either form a bond to a second Na^+ ion or act as the acceptor of a hydrogen bond with the surrounding water. Clearly there are many possible configurations, including, at high Na^+ concentrations, the formation of Na^+-H_2O clusters similar to the

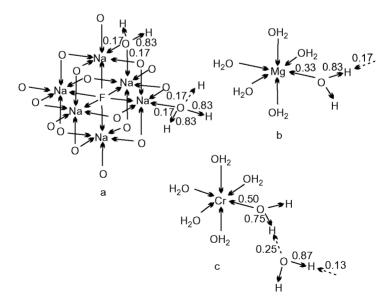


Fig. 5.2. Hydration spheres around cations showing the expected bond valences: (a) $Na_6F(H_2O)_{18}^{5+}$ cluster, (b) $Mg(H_2O)_6^{2+}$, (c) $Cr(H_2O)_6^{3+}$. Note the strong hydrogen bonds to the second coordination sphere in (c).

56 LIQUIDS

 $[Na_6F(H_2O)_{18}]^{5+}$ cluster (Fig. 5.2(a)) found in $[Na_6F(H_2O)_{18}]Na(PO_4)_2 \cdot H_2O(2156)$. In solution, therefore, Na^+ forms a hydrated complex that is labile and not well characterized.

 ${
m Mg^{2+}}$ also surrounds itself with six water molecules (Fig. 5.2(b)) but, since the Mg-O bonds must have valences of $2/6=0.33\,{
m vu}$, the oxygen atoms of the coordinated water molecules will be only three coordinate, forming one bond to ${
m Mg^{2+}}$ of 0.33 vu and two bonds to ${
m H^+}$, each of 0.83 vu. The coordinated water molecules will therefore form donor hydrogen bonds of $1-0.83=0.17\,{
m vu}$ to other water molecules or anions. Because the Mg-O bonds have a valence of 0.33 vu, twice that of the hydrogen bonds between water molecules, they are less labile and, even in solution, the ${
m Mg(H_2O)_6^{2+}}$ ion is a stable, well-characterized species forming donor hydrogen bonds with a cation bonding strength of 0.17 vu to anions and other water molecules.

Consider now the trivalent cation Cr^{3+} (Fig. 5.2(c)). This too is six coordinated by water, giving the Cr–O bonds a valence of 3/6 = 0.50 vu leaving only 0.75 vu each for the two O–H bonds. Consequently the coordinated water forms donor hydrogen bonds with a valence of 0.25 vu to water molecules in the second hydration sphere. These hydrogen bonds are considerably stronger than those found in the surrounding water and consequently the $Cr(H_2O)_6^{3-}$ complex has a bound second coordination sphere containing a further 12 water molecules (Caminiti *et al.* 1978; Blenzen *et al.* 1997).

Cations with charges of +4 would, if six coordinate, form cation—O bonds of 0.67 vu resulting in the first hydrated coordination sphere forming donor hydrogen bonds with valences of 0.33 vu. Such strong hydrogen bonds are only known when they are stabilized by an acceptor that is a strongly bonding anion. In the weakly bonding environment of water they are not stable. In such cases it is more favourable for at least one of the H^+ ions to detach from the coordinated water molecule, leaving a complex with the generic formula $M(H_2O)_{6-n}$ (OH) $_n^{4-n}$. Clearly a variety of arrangements is possible, depending on the value of n, the number of H^+ ions lost. This number will, in turn, depend on the pH of the solution, since the higher the pH, the higher the value of n. In all cases the MO_6 core will be stable and remain an identifiable species in solution.

Cations with still larger charges or lower coordination numbers lose progressively more and more H^+ ions until with P^{5+} typically only one or two are left, $(PO_2(OH)_2)^-$ or $(PO_3OH)^{2-}$, and with S^{6+} none are left $(SO_4^{2-}, Fig. 4.1(b))$. At this stage these are no longer thought of as deprotonated hydrated cations but as oxyanions or protonated oxyanions.

With very weakly bonding cations such as Cs^+ ($s_c = 0.11$ vu), the water molecules are only loosely bound and hence are labile. Such cations cannot form bonds strong enough to satisfy the anion bonding strength of water, with the result that the water molecules in contact with Cs^+ form weaker hydrogen bonds than those in the bulk. The Cs^+ ion therefore disrupts the organized structure of the water molecules, a feature that causes Cs^+ to be called a 'structure breaking' cation. By contrast, strong cations bind water molecules and create a strongly

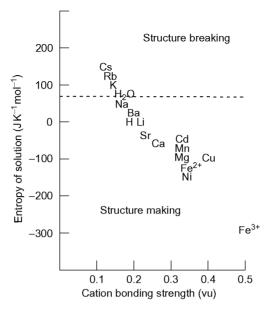


Fig. 5.3. Standard molar entropy of solution as a function of cation bonding strength. By convention the entropy of H^+ is taken as zero but H_2O would be a more natural choice in this figure.

ordered structure in the adjacent water which can extend from the first to the second coordination sphere as the bonding strength of the cation increases (Fig. 5.2(c)). These cations are referred to as 'structure making' cations. The terms 'structure making' and 'structure breaking' are assigned on the basis of the entropy of solution of the cation, a quantity which correlates well with cation bonding strength as shown in Fig. 5.3. The entropy of the H⁺ ion is conventionally taken to be zero on these scales, but as shown in Section 7.6, H⁺ is a relatively strong cation that causes an ordering of the adjacent water molecules. A better choice for the zero of entropy would be the water molecule itself whose entropy of solution is similar to that of Na⁺, the least disruptive of the cations.

5.4 Reactions of anions with water

Anions bind to water through the hydrogen atom. For example, SO_4^{2-} has an anion bonding strength of 0.17 vu which is the same as the cation bonding strength of water (Fig. 4.2). We therefore expect the sulphate ion to accept 12 hydrogen bonds of 0.17 vu and to be surrounded by a coordination sphere containing 10-12 water molecules, allowing that some of the water molecules may form two hydrogen bonds to the anion (Fig. 5.4(a)). As in the case of Na⁺, this coordination sphere will be labile.

58 LIQUIDS

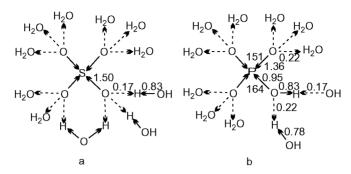


Fig. 5.4. Possible hydration spheres around anions showing the expected bond valences: (a) around SO_4^{2-} , (b) around $(PO_3OH)^{2-}$ (the predicted P-O bond lengths in pm are also shown to the left of the bond).

Anions that are stronger bases, such as PO_4^{3-} , are expected to form stronger hydrogen bonds (0.25 vu), but they can also reduce their anion bonding strength by protonation, i.e. by binding an H+ ion. Calculating the anion bonding strength of a protonated ion is more complex than calculating it for an unprotonated ion. While the coordination number of most O²⁻ ions in an oxyanion can be taken as 4, the large valences of the O-P and O-H bonds nearly saturate the valence of O²⁻, leaving only enough valence for one extra weak bond. Thus (PO₃OH)²⁻, for example, can accept three hydrogen bonds at each of the three terminal oxygen atoms but only one at the hydroxyl group for a total of 10 bonds as shown in Fig. 5.4(b). The calculation is further complicated because the hydrogen of the OH^- group carries a formal charge of +0.17electrons with which it forms a donor hydrogen bond of 0.17 vu. In order to maintain the net charge of -2 on the complex anion, the oxygen atoms must carry between them an effective charge of 2.17 electrons. The anion bonding strength of the oxygen atoms in $(PO_3OH)^{2-}$ is therefore 2.17/10 = 0.22 vu. Consequently (PO₃OH)²⁻ accepts hydrogen bonds that are weaker than those formed by PO_4^{3-} (0.25 vu) but still stronger than those in the surrounding water $(0.17 \, vu)$.

Adding a second hydrogen atom to give $(PO_2(OH)_2)^-$ results in even weaker hydrogen bonds. Using the same procedure, the bonding strength of this anion is $(1.00+2\times0.17)/8=0.17$ vu, which is the same as that of water. This is therefore the species expected in neutral aqueous solution. PO_4^{3-} ions, when dissolved in water, extract H^+ ions from the water until they form a protonated anion with the same bonding strength as the surrounding water molecules. Consequently the solvent is enriched in OH^- explaining why solutions of tribasic phosphates such as K_3PO_4 are alkaline.

Changing the pH of the water affects the equilibrium between the various protonated forms. In solutions with a high pH, the PO_4^{3-} ion $(s_a=0.25 \text{ vu})$ is stabilized because the excess OH^- ions $(s_a=(1+0.17)/3=0.39 \text{ vu})$ are a better

match for any available H⁺ ions ($s_c = 0.8 \text{ vu}$). In solutions with a low pH, there are excess H⁺ ions (more correctly H(H₂O)₃⁺ ions, Section 7.6) which favour the formation of phosphoric acid, PO(OH)₃. At low pH it is also possible to protonate the sulphate ion to form SO₃(OH)⁻ with an anion bonding strength of 1.17/10 = 0.12 vu. As shown in Fig. 4.3, the anion bonding strength correlates with p K_a , the pH at which an anion protonates.

Protonating an anion changes its internal structure as illustrated in Fig. 5.4(b) which shows the bond valences and P–O bond lengths expected in (PO₃OH)²⁻ if all the acceptor hydrogen bonds have the same valence. The P–O_{terminal} bonds have valences of 1.36 vu corresponding to a length of 151 pm but the P–OH bond has a valence of only 0.95 vu corresponding to a length of 164 pm. This example shows how the bond valence model readily predicts the distortion from tetrahedral geometry that occurs when a phosphate ion is protonated, a topic discussed further in Section 9.2.

Anions with a small anion bonding strength such as ClO_4^- ($s_a = 0.083$ vu, Fig. 4.1(c)) can only be protonated under extreme acid conditions. Because of its small bonding strength, ClO_4^- can only form hydrogen bonds that are much weaker than those in the surrounding water. As shown in Section 7.5, such bonds are generally bent, allowing the formation of further very weak hydrogen bonds with O...H distances ranging from 260 to 320 pm. Weakly basic anions in aqueous solution are therefore expected to form a range of very weak hydrogen bonds, an effect seen in the shift of the OH stretching vibrations to higher frequencies in aqueous perchlorate solutions (Brink and Falk 1970).

5.5 Aqueous solubility

The previous sections showed what happens to particular cations and anions when dissolved in water. These ideas are now brought together to show what happens when an inorganic solid is brought into contact with water.

Dissolving a solid in water is a chemical reaction typically represented by eqn (5.2):

$$AB + (n+1)H_2O = A(H_2O)_n^+ + HB + OH^-.$$
 (5.2)

We can identify four different situations depending on the relative bonding strengths of A^+ and B^- . The first occurs if the cation and anion are well matched and both have large bonding strengths, e.g. Mg^{2+} and SiO_4^{4-} ($s_a = s_c = 0.33$ vu, Fig. 4.2). In this case there is no reaction with water, since the match between the two ions is better than the match between either of them individually and water. The solid is insoluble and, if the ions find themselves in solution together, they precipitate out as Mg_2SiO_4 (26374), the insoluble mineral, forsterite, which is a major constituent of the earth's mantle. Such compounds have positive free energies of solution.

60 LIQUIDS

A second situation occurs when the two ions are well matched but have bonding strengths that are relatively small so that each ion is also well matched with water, e.g. $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ ($s_\mathrm{c} = 0.16\,\mathrm{vu}$, $s_\mathrm{a} = 0.14\,\mathrm{vu}$). In this case both the solution and the solid will be equally stable. The solid, in this case common salt, readily dissolves in water, but as readily recrystallizes when the water is removed. Its free energy of solution is close to zero.

More interesting are the cases where the two ions are poorly matched, since they may both be able to form better bonds with water than they can with each other. Such compounds have negative free energies of solution meaning that they are readily soluble. In cases where the mismatch is large, the compound can even be deliquescent, able to pull water out of the atmosphere. Consider first the case where a weak anion, e.g. SO_4^{2-} , is bonded to a strong cation, e.g. Mg²⁺· MgSO₄ lies at the limit of stability with the bonding strength of Mg²⁺ (0.33 vu) twice that of the sulphate ion (0.17 vu). As discussed above, water can bond to Mg^{2+} to give the hydrated cation $Mg(H_2O)_6^{2+}$, which, like SO_4^{2-} , has the right bonding strength (0.17 vu) to bond to solvent water molecules. Anhydrous MgSO₄ (16759) is therefore hygroscopic and readily dissolves in water. Further, both $Mg(H_2O)_6^{2+}$ and SO_4^{2-} are stable entities in solution and, since both have the same bonding strength, the solid that recrystallizes from neutral aqueous solution is the hydrate. Although the hexahydrate is known, the most stable hydrate is the heptahydrate, epsomite, whose formula can be written Mg(H₂O)₆SO₄·H₂O (29384), with the seventh water molecule occupying an otherwise empty cavity between the ions. Similar arguments apply to other compounds formed between a strongly bonding cation and a weakly bonding anion. All tend to form hydrates and their anhydrous salts are hygroscopic or deliquescent depending on how poor the match is.

Compounds in which a weakly bonding cation, e.g. Na^+ ($s_\mathrm{c}=0.16\,\mathrm{vu}$), is bonded to a strongly bonding anion, e.g. $\mathrm{CO_3^{2-}}$ ($s_\mathrm{a}=0.22\,\mathrm{vu}$), are also soluble for the same reason, though the reaction with water is different. In this case the cation has the right bonding strength to bond to water, but the anion must extract $\mathrm{H^+}$ from the water in order to lower its anion bonding strength. Following the arguments given in Section 5.4, protonation of $\mathrm{CO_3^{2-}}$ reduces its anion bonding strength from $2/9=0.22\,\mathrm{vu}$ to $1.17/7=0.17\,\mathrm{vu}$, the value needed to form well-matched bonds with water. Because of the poor valence match between cation and anion, $\mathrm{Na_2CO_3}$ reacts with water converting $\mathrm{CO_3^{2-}} + \mathrm{H_2O}$ to $\mathrm{HCO_3^{-}} + \mathrm{OH^{-}}$. The model therefore explains why $\mathrm{Na_2CO_3}$ (60311, washing soda) readily dissolves in water to give an alkaline solution, and why NaHCO₃ (18183, baking soda) is the solid that crystallizes from neutral solution.

Figure 5.5 shows the variation of the free energies of solution of several halides as a function of the bonding strength of the cation. Positive free energies correspond to insoluble compounds and negative free energies to either soluble, hygroscopic, or deliquescent compounds. Among the halide anions, only F^- , with its relatively large anion bonding strength (0.25 vu), forms insoluble salts, the most insoluble being formed with Ca^{2+} ($s_c = 0.27$ vu) with which it is well

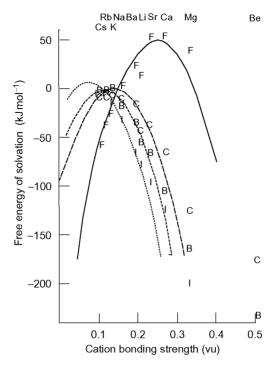


Fig. 5.5. Free energies of solution (Johnson 1968, p. 70) of alkali metal and alkaline earth halides as a function of cation bonding strength. F = fluorides, C = chlorides, B = bromides, and I = iodides. The lines represent eqn (5.3), the solid line is for F^- , the broken line for CI^- , the dense dotted line for Br^- , and the light dotted line for I^- .

matched. Both MgF₂ and BaF₂, being less well matched, are more soluble than CaF₂, a periodic anomaly that the bond valence model nicely predicts. The relationship between the free energy of solvation (ΔG) and the difference in the bonding strengths ($s_c - s_a$) can be expressed as a power series:

$$\Delta G = \Delta G_0 + A(s_c - s_a)^2 + \cdots$$
 (5.3)

where $A=-5585\,\mathrm{kJ\,mol}^{-1}\,\mathrm{vu}^{-2}$, and $\Delta G_0=+50\,\mathrm{kJ\,mol}^{-1}$ for F⁻, $0\,\mathrm{kJ\,mol}^{-1}$ for Cl⁻, Br⁻, and $+8\,\mathrm{kJ\,mol}^{-1}$ for I⁻. The first two terms of eqn (5.3) (shown by the lines in Fig. 5.5) reproduce the observed free energies of solvation reasonably well providing the mismatch is not too large. Cl⁻, Br⁻, and I⁻, whose anion bonding strengths lie close to the range of possible hydrogen bond strengths, form only soluble salts with alkali metals and alkaline earths, but the iodides of even weaker cations such as N(CH₃)⁺₄ ($s_c=0.08\,\mathrm{vu}$) should be much less soluble.

62 LIQUIDS

5.6 Aqueous solutions of soft ions

Soft ions as defined in Section 4.5 behave somewhat differently in aqueous solutions. MgBr₂ contains the hard cation Mg²⁺, but the ions are poorly matched ($s_c = 0.33$ vu, $s_a = 0.10$ vu, Fig. 5.5). It is therefore deliquescent, picking up moisture from the atmosphere with the formation of a hydrated Mg²⁺ ion as discussed in Section 5.3. The salt that crystallizes from this solution is $Mg(H_2O)_6Br_2$. The soft cation Zn^{2+} has the same size and charge as Mg^{2+} and a similar bonding strength ($s_c = 0.40 \text{ vu}$) but, according to Pearson (1973), it should show a preference for bonding to the soft anion, Br⁻. One might therefore expect ZnBr₂ to precipitate out of solution. However, in this case there is a competition between the Zn-Br bonds stabilized by the softness of the two ions and the Zn-O bonds whose ions form a better match. In solution Zn²⁺ bonds to both H₂O and Br⁻, in the latter case forming polymeric complexes such as the dimer $Zn_2Br_6^{2-}$. Thus the compound that crystallizes from aqueous ZnBr₂ solutions is Zn(H₂O)₆(Zn₂Br₆). A saturated solution of ZnBr₂, whose composition is not very different from that of the solid, contains polymeric strings of $(ZnBr_2)_n$ which make the solution highly viscous, a behaviour quite different from that of MgBr₂.

5.7 Non-aqueous solutions and melts

The ideas presented above can also be applied to non-aqueous liquids such as NH₃ and (CH₃)₂SO (dimethylsulphoxide = dmso), high temperature fluxes, and melts. All these materials have both cationic and anionic character but in some cases, e.g. NH₃ and dmso, the cation and anion bond strengths are not well matched, a difference that can often be exploited. For example, dmso has an anion bonding strength (through O) of 0.20 vu and a cation bonding strength (through $-CH_3$) of 0.07 vu (Brown 1987a). It can bind to moderately strong cations, such as Cd²⁺ or Zn²⁺, to form complexes with very weak external bonds (s_c =0.06 vu, Fig. 5.6). It is therefore possible to dissolve a strong cation in a weakly polar or non-polar solvent in which it would normally be insoluble, by complexing it with dmso which, like the coordinated water in aqueous solution, acts as a transformer, matching the bonding strength of the cation to that of the solvent. Dmso is the agent of choice when it is necessary to dissolve strong cations in non-polar solvents.

Although we tend to think of liquid solvents as something found only at room temperature, they are also found at higher temperatures, though here they are usually called fluxes and are often binary salts such as CaF₂. Solids can be prepared from these fluxes, as they can from the melts themselves, by cooling. The valence matching principle can be used to predict what might happen. At a high enough temperature a flux or melt has a low viscosity because all bonds are labile. As the temperature approaches the freezing point of one of the

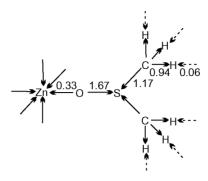


Fig. 5.6. Part of the structure of the $Zn(dmso)_6^{2+}$ complex showing the expected bond valences

components, the stronger well-matched ions start to form stable bonds and complex ions appear. If these complexes remain discrete, the viscosity of the solution remains low, but if they show a tendency to polymerize, the solution becomes viscous. Further cooling results in further bonds becoming stable and a solid phase appears.

This effect is illustrated by silicate magmas discussed in Section 4.6. Those that contain strong cations such as $\mathrm{Ca^{2+}}$ or $\mathrm{Mg^{2+}}$ will induce the formation of strong silicate anions such as $\mathrm{SiO_4^{4-}}$ ($s_c = 0.33\,\mathrm{vu}$) leading to the eventual crystallization of compounds like $\mathrm{Mg_2SiO_4}$, but those magmas that contain only weak cations such as the alkali metals will encourage the formation of weak silicate anions such as $\mathrm{Si_2O_5^{2-}}$ ($s_a = 0.17\,\mathrm{vu}$) where the $\mathrm{SiO_4^{4-}}$ units polymerize, leading to the eventual crystallization of compounds such as $\mathrm{Na_2Si_2O_5}$ as shown in Fig. 4.6. Before this happens, the presence of polymeric silicate ions in the melt will cause the magma to become viscous. Consequently alkaline silicate magmas are more viscous than those containing alkaline earths or transition metals.

Cation coordination number

6.1 Introduction

The cation coordination number was defined in Section 2.6 as the number of anions to which the cation is linked by electrostatic flux. This number can be approximated using the operational definition of a bond given by Rule 4.1, but a prior knowledge of the structure is needed in order to determine the coordination number by either of these two methods. For a proper understanding of crystal chemistry, and particularly for modelling a structure *ab initio* (Chapter 11), one needs to be able to predict in advance what coordination number any given cation will adopt. This in turn requires a review of the various factors that determine just how many bonds a cation will form in a particular compound. Among these factors are the repulsion between the ligands (the anions to which the cation is bonded), the bonding strength of the anions, the hardness or softness of the cation, spatial constraints, and symmetry (O'Keeffe and Hyde 1984; Brown 1988a, 1995).

This chapter focuses primarily on the influence of anion–anion repulsion and on the anion bonding strength. The other factors are described briefly in Section 6.4 but are developed in more detail in later chapters. The special case of H^+ is discussed in Chapter 7 and effects that depend on details of the electronic structure of the cation are treated in Chapter 8. The influence of space and symmetry are discussed in Part III. For simplicity, unless otherwise stated, the discussion is confined to compounds in which the anion is oxygen or an oxyanion. Any conclusions will be applicable, *mutatis mutandis*, to other kinds of anion.

Cations are found with a range of coordination numbers. For some, such as N^{5+} , the range is narrow, essentially only one coordination number being known (Fig. 6.1(a)). For others, such as Cs^+ , the range is broad covering coordination numbers from 3 to 14 (Fig. 6.1(c)). Most cations, for example Zn^{2+} whose distribution is shown in Fig. 6.1(b), lie between these two extremes, but in each case there is a tendency for the distribution to peak near the middle. Any theory of crystal chemistry must be able to explain this variation and provide a reliable estimate for the coordination number found in a particular compound.

6.2 Anion-anion repulsion

The occurrence of different coordination numbers is traditionally explained by a model in which atoms are treated as hard spheres. Each cation is then assumed

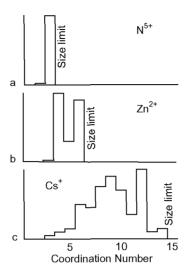


Fig. 6.1. Coordination number distributions around (a) N⁵⁺, (b) Zn²⁺, and (c) Cs⁺.

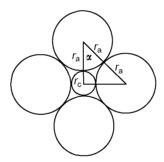


Fig. 6.2. A diagram showing the definitions of anion and cation radii and the angle α .

to be surrounded by the maximum possible number of anions in order to form the most densely packed structure. The factor that determines the coordination number in this picture is the ratio of the radius of the cation to that of the anion as expressed by Pauling's first rule (Section 1.7, Fig. 6.2). In an ideal tetrahedron, for example, the ratio of the O-O to cation-O distance is 1.63 which occurs when the cation:anion radius ratio is 0.224 (Table 6.1). For an ideal octahedron the ratio of O-O to cation-O distance is 1.42, corresponding to a cation:anion radius ratio of 0.414. The cation:anion radius ratio therefore determines how many anions can be placed around a given cation. If this ratio lies between 0.224 and 0.414, only tetrahedral coordination is possible. For octahedral coordination the ratio must be at least as large as 0.414.

There are several problems with this simplistic model, not the least being the difficulty of determining good values for the radii. Typically the radii are

Coordination number	Radius ratio $r_{\rm c}/r_{\rm a}$	$R_{ m OO}/R_{ m MO}$	$\cos \alpha$
2 (line)	0	2.00	1.00
3 (triangle)	0.134	1.73	0.87
4 (tetrahedron)	0.224	1.63	0.81
6 (octahedron)	0.414	1.42	0.71
8 (cube)	0.732	1.15	0.58
12 (cuboctahedron)	1.000	1.00	0.50

Table 6.1 Radius ratios for regular coordination (see Fig. 6.2)

determined from observed bond distances, but which distance is to be used? Different bond lengths are often found between the same pair of atoms even in the same coordination sphere, and the average bond length varies systematically with the coordination number (Shannon and Prewitt 1969; Shannon 1976). How then can one use radii to determine the coordination number if the radii themselves depend on the coordination number? Further, bond distances cannot give absolute radii, only the differences between the radii. For example, the difference between the K-O and Na-O bond distances is equal to the difference between the radii of K^+ and Na^+ ions, but an absolute value of either radius can only be found if the absolute value of one ion is arbitrarily assumed. By convention the radius of the O^{2-} ion is taken as 140 pm since this corresponds to the O-O distance of 280 pm frequently found in crystals. A more serious problem with the hard-sphere model is that it predicts a single coordination number for each ion pair and is therefore unable to account for the behaviour of cations such as Cs^+ which are observed with a wide range of coordination numbers.

Given these problems, the surprise is that the hard-sphere model works so well. Figure 6.3 shows that the agreement between the ideal coordination number and the coordination numbers predicted using the six-coordinate radii of Pauling (1960) is much better than might be expected, though there are a significant number of cations with ideal coordination numbers smaller than predicted and a few cases where the coordination number is larger.

One reason for the failure of the radius ratio rules is that ions do not behave like hard spheres. Even those that are hard in the Pearson (1973) sense can still be compressed. This is clearly seen in the way the bond length varies with the bond valence. If cation—anion bonds can be compressed, so can the distance between the O^{2—} ions in the first coordination sphere. The stronger the cation—anion bonds, therefore, the closer the anions in the first coordination sphere can be pulled together (Shannon *et al.* 1975).

It is possible to explore how closely the oxygen atoms can be brought together by comparing the O–O distances in observed coordination spheres with the O–O distances expected in coordination spheres that are not observed because they bring the ligands too close together. For example, the O–O distance in the known NO_3^- ion can be compared to the O–O distance that would be expected in the unknown NO_3^{3-} ion. It is easy to calculate this distance using the bond

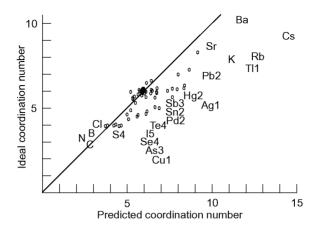


Fig. 6.3. Ideal (average observed) coordination number versus predicted coordination number for various cations. The predicted coordination numbers are calculated using the ratios of the Pauling (1960) six-coordinate radii by interpolating coordination numbers between the values given in Table 6.1. Most cations are represented by points, selected cations are shown by their chemical symbol and, where necessary, oxidation state.

valence model even for unknown cation environments. It is first necessary to calculate the N–O distance from its expected bond valence. In NO_4^{3-} the N–O bond would have a valence of 5/4=1.25 vu which corresponds to a bond length of 135 pm (eqn (3.1)). If the ion is tetrahedral as expected, the O–O distance is readily calculated to be 218 pm. A similar calculation shows that the O–O distance in NO_3^- is 215 pm. It may seem surprising that the O–O distance should be larger in the unknown NO_4^{3-} ion than in the observed NO_3^- ion, but the bonds in NO_3^- are much stronger (1.67 vu compared to 1.25 vu) and are able to pull the O atoms much closer together than is possible in the more weakly bonded four-coordinate complex.

A further factor tending to stabilize NO_3^- is the smaller angle, α , between the N-O bond and the O-O vector, resulting in the attractive bonding force having a larger component along the O-O direction (Fig. 6.2). The factor therefore that determines how close the two oxygen atoms can brought is the effective valence, s', defined by eqn (6.1):

$$s' = s \cos \alpha, \tag{6.1}$$

where s is the valence of the two cation—O bonds. Values of $\cos \alpha$ for the regular coordination polyhedra are given in Table 6.1.

Figure 6.4 shows the effective valence as a function of O–O distance for a variety of known and unknown cation environments, the unknown environments being shown in italics. The observed environments, shown in bold type, mostly lie to the right of the solid line which is given by eqn (6.2). This line can therefore be taken as the closest distance that two oxygen atoms can approach

each other for a given effective valence.

$$s' = \exp(R_0 - R_{\min})/b.$$
 (6.2)

In eqn (6.2) $R_0 = 220$ pm, b = 34 pm, and R_{\min} is the smallest O-O distance that can be achieved with an effective valence of s'. The maximum coordination number that can be observed must therefore satisfy the inequality (6.3) obtained from eqns (6.1) and (6.2):

$$R_{\text{OO}} \ge R_{\text{min}} = R_0 - b \ln(s \cos \alpha). \tag{6.3}$$

Here $R_{\rm OO}$ is the O-O distance expected in the given coordination polyhedron. There are some anomalies in Fig. 6.4, particularly for cations with s' < 0.2 vu, and it is instructive to ask why these occur. There are several possible reasons. If a given pair of oxygen atoms is bonded to more than one cation, the effective valence is the sum of the effective valences of each of the cation-O bonds, reducing the minimum length of the O-O contact, an effect that has not been taken into account in preparing Fig. 6.4. For example, a weak cation may be chelated by NO_3^- ions so that the shared O-O edges are only 215 pm long rather

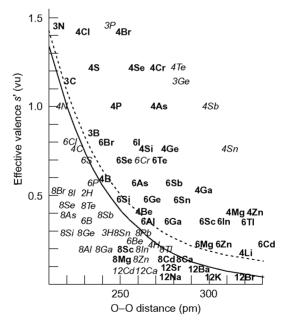


Fig. 6.4. Effective valence, s' versus O–O distance for various regular MO_n coordination environments. Coordination environments shown in bold are known, those in italics are not known. The solid line represents the observed R_{\min} given by eqn (6.3). The broken line represents $R_{\text{unstrained}}$, the distance at which the anion–anion repulsion becomes negligible.

than the 290 pm that might otherwise be expected. With some O–O distances being much shorter than expected, more O^{2-} ions can be included in the coordination sphere around the weak cation. This effect accounts, for example, for the presence of eight-coordinated Sc^{3+} in $Sc(NO_3)_3urea_4$ (20201). Figure 6.4 is calculated for regular coordination, but some weak cations have irregular coordination environments and, according to the distortion theorem (Rule 3.6), any distortion from regular coordination results in an increase in the average bond length which leads to the possibility of a higher coordination number. Finally, materials prepared at high pressure, such as $MgSiO_3$ (200139) with eight-coordinated Mg^{2+} , may have higher than expected coordination numbers since pressure can force the ligands closer together. In a number of cases more than one of these effects is present. The eight coordination around Mg^{2+} in the garnet $MgAl_2Si_3O_{12}$ (71892) is stabilized both by sharing faces with AlO_6 octahedra and by Mg^{2+} being displaced from the centre of its polyhedron.

Not all the anomalies occur around the weaker cations. For instance, on the basis of size alone, one would expect to find Cr^{6+} in six coordination but it is only ever found tetrahedrally coordinated. The absence of any observed examples of octahedral coordination around Cr^{6+} is the result of an electronic instability discussed in Section 8.3.2.

Anion-anion repulsion places an upper limit on the coordination number that a cation can adopt but, since the O²⁻ ions do not behave like hard spheres, the size of the limiting O-O distance depends on the effective valence of the bonds. Either Fig. 6.4 or eqn (6.3) can be used to decide whether or not a particular coordination number is physically possible.

6.3 The strength of the anions

The relative sizes of the cation and anion are not the only determinant of the coordination number; the bonding strength of the anion also plays an important role and explains how the same cation can display different coordination numbers in different compounds.

Since all the bonds in an inorganic compound with a bipartite graph start at a cation and end at an anion, they must obey the *Coordination number rule*.

Rule 6.1 (Coordination number rule). The total number of bonds formed by all the cations in a compound equals the total number of bonds formed by all the anions.

Although this rule is self-evident and has been known for some time (see, for example, O'Keeffe and Hyde (1984) and references therein), its importance is still not widely appreciated. According to the coordination number rule, compounds that are anion rich, or in which the anions have large coordination numbers, will favour the adoption of high coordination numbers by the cation. Consider the two compounds $Cs_2Cr_3O_{10}$ (22030) and $Cs_2Sn_2O_3$ (24392). The first contains the trichromate ion consisting of a chain of three corner-sharing

 ${\rm CrO_4}$ tetrahedra. The two bridging ${\rm O^2^-}$ ions are fully saturated and cannot form bonds to ${\rm Cs^+}$, but the remaining eight terminal ${\rm O^2^-}$ ions can each form three external bonds (assuming a coordination number of 4 for oxygen). The anion thus forms $3\times 8=24$ external bonds requiring that both ${\rm Cs^+}$ ions be 12 coordinate as observed. In the second compound, each of the ${\rm O^{2^-}}$ ions form two of their four bonds with ${\rm Sn^{2^+}}$ leaving them only two bonds for ${\rm Cs^+}$. The ${\rm Sn_2O_3^{2^-}}$ anion therefore forms $2\times 3=6$ bonds, and since these are shared between two ${\rm Cs^+}$ ions, each will be only three coordinate. The coordination of oxygen can be increased to a maximum of 6, but this only increases the ${\rm Cs^+}$ coordination from 3 to 6. A higher coordination number is not possible. In the observed structure one ${\rm Cs^+}$ is three coordinate, the other six coordinate.

The coordination number rule is closely related to the valence matching principle (Rule 4.1) since the bonding strength of an ion varies inversely with its coordination number. The two rules can, therefore, be used interchangeably to explore the variations in coordination number. In the above example the bonding strength of the $Cr_3O_{10}^{2-}$ ion is given by the ratio of the charge to the expected number of bonds, $2/24=0.08\,\mathrm{vu}$. It requires 12 bonds of this strength to give the correct valence sum around Cs^+ again leading to the prediction of 12 coordination. The bonding strength of $Sn_2O_3^{2-}$ is $2/6=0.33\,\mathrm{vu}$. Only three bonds of this strength are needed to satisfy the valence of Cs^+ . The trichromate ion is weak and well matched to Cs^+ so $Cs_2Cr_3O_{10}$ is a stable compound, but $Cs_2Sn_2O_3$ is poorly matched and is hygroscopic. From this example one can see how weakly bonding anions lead to high cation coordination numbers and strongly bonding anions lead to low cation coordination numbers.

The alkali halides provide another interesting example. Na⁺ has a bonding strength of 0.16 vu and Cl⁻ 0.14 vu. The average of 0.15 vu corresponds to a coordination number close to 6 which is the maximum number of Cl⁻ ions that can be packed around Na⁺. The larger Cs⁺ ion has a bonding strength of 0.11 vu giving an average for CsCl (22173) of 0.125 vu corresponding to a coordination number of 8, but the high anion bonding strength of F⁻ (0.25 vu) in CsF leads to an average bonding strength of 0.18 vu, clearly favouring the six-coordinate NaCl structure over the eight-coordinate CsCl structure found for the other caesium halides. If one used size arguments alone, one would expect that Cs⁺ should display its highest coordination number in CsF because Cs⁺ is the largest alkali metal and F⁻ is the smallest halogen. The smaller coordination number that is observed is a consequence of the larger anion bonding strength of F⁻.

6.4 Other factors

There are at least three other factors that have a smaller but important effect on the final choice of coordination number: symmetry, the softness of the ions, and spatial constraints.

¹ The reason why the coordination number is 6 and not 7 is discussed in Section 6.4 below.

The principle of maximum symmetry (Rule 3.1) results in most simple compounds adopting high symmetry crystal structures. In these cases the available coordination numbers are restricted by crystallographic symmetry. In Section 11.2.2.4 it is shown that the ions in compounds with the formula AB are restricted to the coordination numbers 4, 6, or 8 unless constraints are present that destroy the cubic symmetry. For lower symmetry structures the restrictions are less severe, but the geometries associated with the coordination numbers 5, 7, 9, 10, and 11 require that there be at least two different angles between adjacent bonds and that at least two of the bonds not be related by symmetry. Only in cation environments with coordination numbers 2, 3, 4, 6, 8, and 12 is there a point group that permits all the bonds, and the angles between adjacent bonds, to be equivalent. According to the principle of maximum symmetry, the latter coordination numbers are favoured, as can be seen in the distributions plotted in Fig. 6.1. The frequency with which the coordination numbers 4 and 6 are found around spherically symmetric ions is therefore a direct consequence of the principle of maximum symmetry.²

In Section 4.5 it was shown that the bonding strengths of soft cations are less well defined than those of hard cations since they are able to form stable compounds with anions having a wider range of anion bonding strengths. Consequently they also display a wider range of coordination numbers. Thus the soft Zn²⁺ cation is found in four and six coordination in contrast to the similar, but hard, Mg²⁺ cation which is usually found only in 6-coordination. Most hard cations either display only a single coordination number or their coordination numbers lie in a narrow range, but there are some important exceptions. The broken line in Fig. 6.4 lies 0.08 vu above the solid line and the space between them defines a region in which the R_{OO} distances are only marginally stable. The broken line can be referred to as R_{unstrained} since O-O distances to the right of this line do not influence the choice of coordination number. O-O distances between $R_{\text{unstrained}}$ and R_{min} are found, but their coordination environments tend to be destabilized by O-O repulsion. While four-coordinate B³⁺, six-coordinate Si⁴⁺, and six-coordinate Al⁶⁺, which lie between these lines, are all known, these three cations are also frequently found with a smaller coordination number even though they are all hard. For example, Al³⁺ has a repulsion-limited bonding strength of 0.57 vu which corresponds to the unfavourable coordination number of 5. For this reason, Al³⁺ is more usually found in four rather than five coordination, but six coordination can be stabilized, e.g. in Al₂O₃ (75559) where the

² The one-electron s, p, and d orbitals frequently used to explain observed stereochemistries are a convenient but arbitrary means of decomposing the electron density into spherical harmonics. They represent nothing more than a suitable basis set for a quantum mechanical calculation. When assigned solely on the basis of the observed geometry, they convey no very profound information about the bonding processes at work. It is much simpler and more informative to say that an atom is tetrahedrally coordinated than to say that it is sp³ hybridized, just as it is easier to say that it forms three equatorial or two axial bonds than to say it is sp² or sp hybridized, respectively. Only in the case of the electronically distorted ions discussed in Chapter 8 does an orbital description provide a meaningful rationale for the observed stereochemistry.

six-coordinate corundum structure has a higher symmetry than is possible for a four-coordinate structure (Section 11.2.2.4).

Spatial constraints can also influence the coordination number and can often explain, for example, why the same cation can occur with more than one coordination number in the same crystal. However, a full treatment of spatial constraints requires an understanding of crystallographic symmetry, so further discussion is deferred to Part III which deals with the chemistry of extended three-dimensional solids.

6.5 Applying the different effects

The primary constraint on the coordination number is the anion—anion repulsion. Clearly this determines the maximum possible coordination number and, for hard cations, this is normally the coordination number that is observed. However, if the cation is soft or if the maximum possible coordination number gives rise to very small bonding strengths, other coordination numbers may be found as discussed in Section 6.3. A number of examples will illustrate how these various factors work together.

 $\mathrm{Cs^+}$ has such a small bonding strength that Fig. 6.4 does not provide a reliable indication of its maximum coordination number, though a value of 14 is probably not far wrong. With a coordination number this large, the $\mathrm{Cs-O}$ bonds would have a valence of 0.07 vu, smaller than the bonding strength of any of the anions shown in Fig. 4.2. The primary determinant of the coordination number of $\mathrm{Cs^+}$ is therefore not the anion-anion repulsion but the anion bonding strength. As indicated in the example discussed in Section 6.3, $\mathrm{Cs^+}$ is well matched to weak anions with which it forms stable compounds having large $\mathrm{Cs^+}$ coordination numbers, but it can also form compounds with stronger anions giving rise to smaller $\mathrm{Cs^+}$ coordination numbers, though the larger the anion bonding strength, the more ill-matched and unstable the compound becomes. Poorly matched compounds such as $\mathrm{Cs_2Sn_2O_3}$ can be prepared only under stringently anhydrous conditions.

Figure 6.1(c) shows that the distribution of coordination numbers observed around Cs⁺ largely reflects the distribution of anion bonding strengths weighted towards the weaker anions (higher coordination numbers). The average observed (ideal) coordination number of 9.2 corresponds to a bonding strength of 0.11 vu, though one could argue that, since there are very few anions weaker than Cs⁺, these observations are heavily biased towards smaller coordination numbers and hence larger bonding strengths. According to this argument the true bonding strength of Cs⁺ should be closer to 0.07 vu. However, it is more useful to determine the bonding strength on the basis of what is actually observed rather than what might be observed if a wide range of very weak anions were available. It is interesting to note that the average observed coordination number for Ba²⁺ (10.2) is larger than that of Cs⁺ (9.2) even though

Ba²⁺ itself is considerably smaller.³ The reason for this anomaly lies in the higher charge on Ba²⁺ which gives it a bonding strength (0.20 vu) that ensures that its coordination number distribution is not skewed by the distribution of the bonding strengths of the available anions.

At the other end of the scale from Cs⁺ are the strongly bonding cations such as N⁵⁺ whose size-limited coordination number of 3 ensures a minimum cation bonding strength of 1.67 vu, a value which greatly exceeds the bonding strength of the strongest anion, O^{2-} ($s_a = 0.50$ vu). Because the cation bonding strength of N⁵⁺ is always greater than any possible anion bonding strength, the cation coordination number is determined only by anion-anion repulsion. The only possible complex that can be formed with oxygen is NO₃ since all the complex oxyanions have even smaller bonding strengths. Even then the O²⁻ ion must make all the adjustments. Instead of all its bonds having the same valence, as would be expected from the principle of maximum symmetry, O²⁻ must form one very strong bond (1.67 vu) to N^{5+} and several very weak bonds (0.11 vu) to other cations. Such a large mismatch between the bonding strengths of N⁵⁺ and O²⁻ suggests that the nitrate ion should be highly unstable, but there is no easy mechanism by which the stress caused by the mismatch can be relieved. The reaction with water which, for weaker cations, leads to a better valence match clearly will not work here. The stress can be relieved only by a major rearrangement of the bonding around N^{5+} (e.g. the formation of N_2) which is why NO_3^- , and similar strongly bonded complex anions such as ClO_4^- , are good oxidizing agents and why, in the presence of suitable materials, they can decompose explosively into compounds that provide better valence matches.

Most cations lie between the extremes represented by N^{5+} and Cs^+ . Typical of these is Zn^{2+} , a moderately soft cation which has an ideal coordination number of 4.98 and a corresponding cation bonding strength of 0.40 vu. The maximum regular coordination number allowed by anion—anion repulsion is 6 (Fig. 6.4) corresponding to a bond valence of 0.33 vu. This suggests that Zn^{2+} will not form stable compounds with anions having a bonding strength less than 0.33/2 = 0.17 vu (cf. Fig. 4.6). The poor match with the weak perchlorate anion $(0.083 \, \text{vu})$, for example, means that anhydrous $Zn(ClO_4)_2$ is deliquescent, picking up water from the atmosphere to form the more stable hydrate, $Zn(H_2O)_6(ClO_4)_2$ (100218) in which Zn^{2+} has its maximum coordination of 6 and each H^+ ion forms two weak hydrogen bonds (Section 7.5) ensuring a well-matched and stable structure.

For the best match to the bonding strength of O^{2-} ($s_a = 0.50$ vu), Zn^{2+} should display a coordination number of 4 as is found in ZnO (67454). Although Mg^{2+} is similar in size and charge to Zn^{2+} , the same argument does not apply since Mg^{2+} is hard and is normally found only with its maximum coordination

 $^{^3}$ Shannon and Prewitt (1969) give the 10-coordinate radius of Ba^{2+} as 152 pm compared to 181 pm for $\mathrm{Cs}^+.$

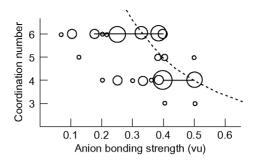


Fig. 6.5. Coordination number versus anion bonding strength for Zn^{2+} . The areas of the circles are proportional to the number of known Zn^{2+} environments. The solid lines represent the predictions of the model, the broken line shows the coordination number Zn^{2+} would have to adopt for a perfect valence match.

number of 6. The consequence is that while ZnO adopts the four-coordinate wurtzite structure (see Section 2.6), MgO (9863) adopts the six-coordinate NaCl structure.

Figure 6.5 shows how the coordination number of Zn²⁺ varies with the bonding strength of the anion. The areas of the circles in this figure are proportional to the number of known environments and the solid lines show the coordination numbers expected (six coordination between 0.17 and 0.40 vu and four coordination between 0.40 and 0.50 vu, five coordination being rarely found because of its low symmetry). Since 6 is the size-limited coordination number, lowering the anion bonding strength below 0.33 vu does not increase the coordination number. Instead, the compounds become increasingly mismatched and unstable, and the number of known compounds decreases.

Hydrogen bonds

7.1 Introduction

Since water is a constituent in a great many inorganic solids, and is involved in all chemical reactions performed in aqueous solutions, H⁺ is the most widely distributed of all cations. When present, it usually plays a pivotal role in the chemistry, whether in the solid or the liquid state (Chapter 5). It is therefore important that its behaviour and the origin of its unusual properties be properly understood.

The crystal chemistry of the H^+ ion is so anomalous that it is usually considered to be qualitatively different from other cations, yet its anomalous properties can be derived in a perfectly rational way by assuming that H^+ is, in principle, no different from other cations except for its small size. H^+ is the only cation where the anion–anion repulsion predicts a maximum regular coordination number of less than 2, as can be seen in Fig. 6.4, where the point for regular two-coordinate H^+ (s'=0.5 vu) lies well to the left of the R_{\min} line. However, as shown in Section 7.2 below, it is impossible for a cation to be only one coordinate in a condensed phase because there will always be nearby ions capable of forming bonds. H^+ must be at least two coordinate and, since H^+ is too small for regular two coordination, it must, according to the corollary of the distortion theorem (Rule 3.7), adopt a distorted environment. Asymmetric two coordination is therefore the typical environment expected and found around H^+ .

The combination of an H^+ cation asymmetrically bonded to its two ligands is called a hydrogen bond. The hydrogen bond is often represented by the bonding scheme $X'-H\ldots X$ ($X, X'=O^{2-}, N^{3-}, C^{4-}, F^-, Cl^-, Br^-, I^-,$ etc.) where the strongly bonded X' anion is called the hydrogen bond donor and the weakly bonded X anion is called the hydrogen bond acceptor. In this description of a hydrogen bond, the H^+ ion is seen as the glue that holds the two anions together. Since it is the strength of the weaker side of the hydrogen bond that determines how strongly X' and X are bound to each other, a hydrogen bond that is described as 'strong' is one in which the $H\ldots X$ bond is stronger than normal. Strengthening the $H\ldots X$ bond, however, requires weakening the X'-H bond. Similarly a weak hydrogen bond is one in which the $H\ldots X$ bond is weaker than normal, and the X'-H bond correspondingly stronger. As in previous chapters, the discussion in this chapter will focus on the hydrogen bonds formed by O^{2-} ions, but hydrogen bonds involving other anions behave in a qualitatively similar way. Some of the differences are discussed in Section 7.7.

Because of its importance in many fields of chemistry and biology, the hydrogen bond has been the subject of many studies, both theoretical and experimental. In order to simplify the problem, the theoretical studies often focus on isolated molecules or pairs of molecules, but such systems are not always good models for the hydrogen bonds found in solids and liquids where cooperative effects can be important. For example, if an –OH group acts as a hydrogen bond donor, the O–H bond is weakened and the oxygen atom is then able to act as the acceptor of a second hydrogen bond. Hydrogen bonds therefore often form chains in which the strength of one bond is enhanced by the presence of the next hydrogen bond along the chain. Any break in the chain will result in a weakening of all the remaining bonds.

Kroon et al. (1975) combined the results of a careful theoretical study with an analysis of the geometries of the hydrogen bonds in a large number of organic crystals, concluding that the principal contribution to the energy was electrostatic. The geometry of hydrogen bonds in organic crystals has been surveyed by Taylor and Kennard (1984). More recently several elegant statistical analyses of different varieties of hydrogen bond, again mostly in organic crystals, have been published by Steiner (Steiner and Saenger, 1992, 1994; Steiner, 1995a,b, 1997, 1998a,b; Desiraju and Steiner 1999). The emphasis on organic crystals results in part from the importance of hydrogen bonding in biological processes, and in part from the simpler crystal chemistry of organic molecules where the hydrogen bonds are more likely to be ordered. However, the character of a hydrogen bond is the same whether it appears in an organic or an inorganic compound.

An examination of the stereochemistry of the H⁺ ion is complicated by a number of factors. Because it has no electron core, hydrogen is difficult to locate using X-rays which are scattered by electrons. In earlier structure determinations its presence was often ignored because it made no contribution to the X-ray diffraction pattern and could not therefore be located. Even when H⁺ is included in the model, its position can rarely be accurately determined and in any case the centre of its electron density is usually displaced from the nucleus towards the donor anion by around 20 pm. Accurate positions of the H⁺ nuclei can be found using neutron diffraction which has provided sufficient information to reveal the essential characteristics of hydrogen bond geometries, but in many of the structures determined by X-ray diffraction the positions of the H⁺ cations have had to be inferred from the positions of their neighbouring anions.

7.2 The role of anion-anion repulsion

Large uncertainties in our knowledge of the lengths of H–X bonds means that there are bound to be uncertainties in the determination of experimental bond valences, a problem that is made worse by the inability of eqns (3.1) and (3.2) to give a good description of the bond valence—bond length correlation over the

extended range of bond lengths observed around H⁺. The best way of determining the true correlation is to calculate the bond fluxes (Section 2.4) for structures determined by neutron diffraction. These are shown by the points in Fig. 7.1. The heavy line, which is drawn so as to represent this correlation, differs from the exponential function of eqn (3.1) in three important ways. Firstly, it reaches zero at a finite distance (310 pm), secondly, it is much steeper at short distances (the slope is almost infinite), and thirdly, it displays an unusual bulge in the middle of its range. One expects the valence to drop to zero at a finite distance, since it is a weakness of both egns (3.1) and (3.2) that they predict finite (even if small) valences for all distances, not just for those distances that represent bonds. It is also not surprising that at very short distances the repulsion will increase much faster than either eqn (3.1) or (3.2) would predict since neither equation properly takes into account the strong core repulsion at short distances. These are features that are shown by all bond valence-bond length correlations. Equations (3.1) and (3.2) are approximations that are only valid over the relatively short range of bond lengths normally observed.

The bulge in the centre of the bond flux—bond length correlation in Fig. 7.1 is, however, unexpected and is quite unlike the behaviour shown by any other cation (cf. Fig. 3.1). As pointed out below, the reason for this bulge is the repulsion between the donor and acceptor O²⁻ ions. The bulge is an artefact of anion-anion repulsion and is not intrinsic to the H–O bond itself. The thin line in Fig. 7.1 represents a reasonable interpolation between the two ends of the bond flux-bond length curve and indicates the correlation that might be expected if there were no anion-anion repulsion.

Figure 7.2 shows the relationship between the effective valence, s' (eqn (6.1)), of an O-H...O hydrogen bond and its O...O distance in a way that can be

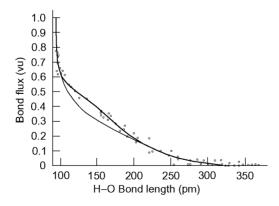


Fig. 7.1. Bond flux—bond length correlation for H–O bonds. The points correspond to fluxes calculated from structures determined by neutron diffraction. The heavy line is drawn through these points. The thin line is a smooth interpolation between the two ends of the heavy line and represents the correlation that would be expected in the absence of O–O repulsion.

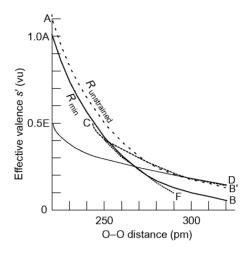


Fig. 7.2. The effective valence, s', as a function of O–O distance (R_{OO}). AB is R_{min} and A'B' is $R_{unstrained}$ from Fig. 6.4; ED shows the distance expected for a linear hydrogen bond uncorrected for O–O repulsion (based on the thin line of Fig. 7.1); CD shows the distance expected for a linear hydrogen bond corrected for O–O repulsion (based on the heavy line of Fig. 7.1); CF is the minimum value of R_{OO} observed for maximally bent hydrogen bonds (based on the broken line in Fig. 7.4).

compared with Fig. 6.4, the solid and open dotted lines being the same in both figures. For a linear O-H... O bond, the effective valence, s', is the same as the valence, S_h , of the weaker H...O bond since this is the bond responsible for keeping the two O²⁻ ions in contact. The point E on the left-hand side of Fig. 7.2 marks the O...O separation expected for a symmetrically two-coordinate H⁺ ion if the anion-anion repulsion is ignored, i.e. it is calculated from the thin line in Fig. 7.1. This distance is considerably shorter than the value of R_{\min} (point C) calculated for s' = 0.5 using eqn (6.3), indicating that the highest possible regular coordination number of H⁺ must be less than 2. However, while a coordination number of one may be possible in the gas phase, it is not possible in a condensed phase as the following argument shows. Suppose the H+ ion is bonded to just one O²⁻ ion, the combination would create a local dipole which will attract other anions. The H⁺ ion would therefore have a number of additional anion neighbours (perhaps at longer distances), but since these nonbonded neighbours are attracted to the H⁺ ion by the electrostatic field, they must be connected to it by electrostatic flux. Thus, according to the definition of a bond given in Section 2.6, they will, in fact, be bonded. Any attempt to create a singly bonded cation will result in at least one, and possibly more, additional bonded neighbours even if the additional bonds are weak. Since the distortion theorem (Rule 3.6) predicts that displacing the H⁺ ion away from the centre of a symmetrical hydrogen bond will increase the average H–O bond length, thereby allowing the O²⁻ ions to move further apart, the only bonding environment

available to an H⁺ ion is one that is distorted and has a coordination number of at least 2.

It is possible to treat this distortion quantitatively. If S_h is the valence of the weak $H \dots O$ bond formed by two-coordinated H^+ , the valence of the strong O-H bond must be $1-S_h$ if the bond valence sum at H^+ is to be 1.0 vu. The valences of both the O-H and the $H \dots O$ bonds, and hence their lengths, thus depend only on the parameter, S_h .

If the hydrogen bond is also linear, i.e. the O–H ... O angle is 180° , then the O ... O distance is equal to the sum of the two H–O distances. In this case, the O ... O distance is also a function of S_h which, for a linear hydrogen bond, is the same as the effective valence, s', that pulls the O^{2-} ions together (Section 6.2). In the absence of anion–anion repulsion, one would expect the O–O distance in a linear hydrogen bond to follow the line ED in Fig. 7.2 calculated using the thin interpolated line of Fig. 7.1. For s' > 0.25 vu, this lies to the left of the R_{\min} suggesting that hydrogen bonds with s' > 0.25 vu should not exist.

However, under appropriately constrained conditions, symmetric hydrogen bonds are known (Section 7.4), but not with the predicted O–O distance of 220 pm (point E). Since the shortest O–O distance allowed by the anion–anion repulsion is 244 pm (point C), the O–H bonds are stretched from 110 to 122 pm and, because they are stretched, the valence sums at H⁺ are less than 1.0 vu and the bonds are constrained to be linear.

According to the corollary to the distortion theorem (Rule 3.7), the valence sum at H^+ can be increased by displacing H^+ towards one of the O^{2-} ions. However, moving the H^+ ion off-centre also decreases S_h and, hence, s'. Consequently as the bond becomes more asymmetric, R_{\min} also increases. For 0.5 > s' > 0.4 vu, the strains are reduced but are still large and the observed O-O distance (line CD calculated from the heavy line in Fig. 7.1) lies close to R_{\min} . Once S_h falls below 0.4 vu, the stresses in the bond start to diminish as CD moves to the right of R_{\min} . The bonds are still strained because the O-O distance still lies to the left of R_{\max} and the line son, although some variation in the $O-H \dots O$ geometry is allowed, the O-O distance is constrained to lie between the line CD (linear bonds) and the line CF which shows the shortest O-O distance observed in maximally bent hydrogen bonds (taken from the broken line in Fig. 7.4). As expected, CF closely follows R_{\min} . Once CD joins the unstrained line ED (s'=0.2 vu), the repulsion between the two O^{2-} ions disappears. This point defines the geometry of the most symmetric unconstrained hydrogen bond.

Figure 7.3 displays these same results in a different way by plotting S_h , rather than s', against the O-O distance. Although S_h is the same as s' for linear hydrogen bonds, it is not the same if the bonds are bent. Since the O-O distance

¹ The term 'strain' is used in this chapter in a different sense from its use in the rest of the book where it refers to the difference between the theoretical and experimental bond lengths (Section 3.2). In this chapter it refers to the difference between the observed bond distance and the distance that would be expected in the absence of O–O repulsion.

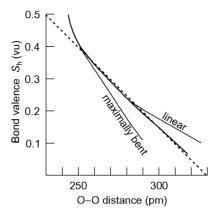


Fig. 7.3. The hydrogen bond valence, S_h , as a function of O–O distance. The heavy line shows the most probable distance, the light lines indicate the range of permitted values depending on the O–H...O angle. The straight broken line is calculated from eqn (7.1) and is a linear fit to the heavy line for $S_h < 0.4$ vu.

depends on the O-H...O angle as well as on S_h , Fig. 7.3 shows three possibilities. The light lines represent the limits found when the bond is linear (upper), and when the bond is maximally bent (lower), while the heavy line shows the most likely value of R_{OO} based on the frequencies shown in Fig. 7.4. The bonds are linear for $S_h > 0.4$ vu, but bonds weaker than this can be bent. However, the most likely bond remains linear as long as $S_h > 0.2$ vu, the point where the line CD in Fig. 7.2 meets the line ED. The linear hydrogen bond with $S_h = 0.2$ vu is the most symmetrical arrangement for which the bond is not strained by anion—anion repulsion. This is the configuration that is expected for a normal hydrogen bond.

Surprisingly, Fig. 6.4 shows that tetrahedral four-coordinate H^+ should be less strained than linear two-coordinate H^+ because its $H \dots O$ bonds are much weaker and longer. Although neither regular three- nor four-coordinated H^+ has been reported, distorted three- and four-coordinated H^+ environments are frequently found with weakly bonding anions as discussed in Section 7.5.

7.3 The normal hydrogen bond

A normal hydrogen bond is defined as one in which the distortion is just enough to remove the strain caused by anion—anion repulsion. A normal hydrogen bond therefore comprises a strong O–H bond with a valence of 0.8 vu and length 97 pm, and a weak H...O bond with a valence of 0.2 vu and length 190 pm. The bond is linear with an O–H...O bond angle of 180° giving an O...O distance of 287 pm. This is the bonding geometry expected for a hydrogen bond if no other constraints are present.

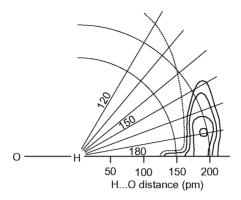


Fig. 7.4. The frequency of observed O-H...O geometries projected onto the plane of the three atoms. The O-H bonds lie on the horizontal axis. The contours show the probability of finding the acceptor O²⁻ ion, each contour representing a doubling of the probability relative to the contour below. The broken line shows the closest approach observed for acceptor O atoms (adapted from Brown 1976a).

Figure 7.4 shows the observed geometries of O-H...O hydrogen bonds expressed as their frequency of occurrence projected onto the plane of the three atoms. The contour intervals are on a logarithmic scale with each contour representing double the frequency of the contour below. The highest frequency is found at the geometry of the normal hydrogen bond.²

The normal hydrogen bond is formed between a strong anion with a maximum bonding strength close to $0.8\,\mathrm{vu}$ and a weak anion with a bonding strength of $0.2\,\mathrm{vu}$. Therefore, unlike other cations, the H^+ ion has two cation bonding strengths, one of $0.8\,\mathrm{vu}$ (to the donor anion) and one of $0.2\,\mathrm{vu}$ (to the acceptor anion).

7.4 Strong hydrogen bonds

The normal hydrogen bond is assumed to be the conformation with the lowest energy, but other conformations are possible if the additional energy required to produce them can be recovered elsewhere in the structure. Strong hydrogen bonds are more symmetric, shorter and, as discussed above, involve significant stretching of the H–O bonds since the O...O distance cannot be less than R_{\min} . The stronger the bond, the more closely the observed O...O distance approaches R_{\min} .

Strong hydrogen bonds can be divided into two classes, the very strong hydrogen bonds with $0.5 > S_h > 0.4$ vu which are necessarily linear, and those

² The apparent shift of the maximum away from the linear O-H...O geometry is an artefact of projecting around the cylindrical axis. If this graph were plotted in the three dimensions of real space, the maximum would be seen to lie on the horizontal axis.

with $0.4 > S_h > 0.2$ vu which are normally linear but may be bent as long as $R_{\rm OO} > R_{\rm min}$. However, any bending of a strong hydrogen bond costs energy as long as $R_{\rm OO} < R_{\rm unstrained}$ and only occurs if this energy can be recovered by other changes in the structure.

Strong hydrogen bonds tend to be found between anions that have bonding strengths lying in the range between 0.2 and 0.8 vu since such anions favour forming H–O bonds that lie in the strained region. The phosphate ion $(s_a=0.25\,\mathrm{vu},\,s_a(\mathrm{max})=0.75\,\mathrm{vu})$ is one example. In KH₂PO₄ (68696, 201373) hydrogen bonds link phosphate ions that are chemically equivalent. The observed geometry of the hydrogen bond lies between two extremes. At one extreme is the symmetric structure shown in Fig. 7.5(a) in which both the phosphate ions and the hydrogen ions have regular coordination. This arrangement is destabilized by the highly strained hydrogen bond. At the other extreme is the structure with a normal hydrogen bond shown in Fig. 7.5(c). This structure is destabilized by the large asymmetry induced in the PO₄³⁻ ion. The observed structure, shown in Fig. 7.5(b), is a compromise between these two extremes, the energy required to form the strong hydrogen bond being balanced against the energy needed to distort the phosphate ion.

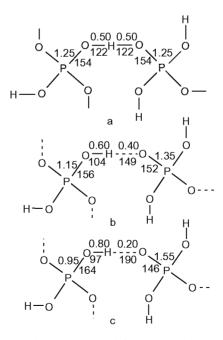


Fig. 7.5. Bond valences and lengths expected for KH_2PO_4 (68696, 201373) (a) assuming the principle of maximum symmetry, (b) observed structure, (c) assuming normal hydrogen bonds. Note that in addition to the bonds shown, each O^{2-} ion receives a valence of 0.25 vu from K^+ .

Fig. 7.6. The bond graph of oxalic acid dihydrate (OXACDH04) showing the observed bond valences. This graph shows the correct connectivity, but is not a three-dimensional molecular diagram.

Oxalic acid dihydrate (OXACDH04) is an example in which the presence of a strong hydrogen bond is required by the bond graph shown in Fig. 7.6. There are three hydrogen ions in the half-formula unit, all of which bond to the water oxygen, O_w . Either all three hydrogen atoms are attached to O_w , in which case O_w forms an H_3O^+ ion and three strong hydrogen bonds ($S_h=0.33\,vu$), or, as observed, two hydrogen atoms are attached to O_w and the third to the oxalic acid molecule. Since the water molecule acts as an acceptor to one hydrogen bond but as a donor to the other two, the acceptor bond must be twice as strong as the donor bonds. The compromise is that the donor hydrogen bonds are slightly weaker ($S_h=0.17\,vu$), and the acceptor bond considerably stronger ($S_h=0.34\,vu$), than normal.

In a few cases, particularly when the two anions are chemically equivalent or when steric constraints force the two anions close together as in certain organic molecules, the hydrogen bond can be symmetric. The hydrated H^+ ion, $H_5O_2^+$, discussed in Section 7.6, is one example, but such cases are rare since they involve considerable strain in the H–O bonds.

7.5 Weak hydrogen bonds

Weaker (more asymmetric) hydrogen bonds are formed with anions having a bonding strength significantly less than 0.2 vu, for example, the perchlorate ion, ClO_4^- , with a bonding strength of 0.08 vu. The anion's small bonding strength ensures that it can only form weak hydrogen bonds. Because the H^+ ion is displaced even further from the centre of the bond than normal, such bonds are no longer constrained to be linear and the internal pressure in the crystal usually keeps the O^{2-} ions in contact. Typically the O-O distance is equal to $R_{\rm unstrained}$, and in any case it is longer than $R_{\rm min}$, leading to $O-H\ldots O$ angles in the range $130^{\circ}-160^{\circ}$ (Fig. 7.4).

Decreasing the O–H…O angle exposes the H^+ ion to other neighbouring anions with which it can form one or more additional very weak bonds ($S_h < 0.05 \, \text{vu}$, $H \dots O > 250 \, \text{pm}$ with O–H …O angles $< 130^\circ$). While such very weak bonds individually make only a small contribution to the valence sums, in compounds such as the perchloric acid hydrates they are so numerous that

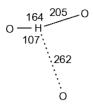


Fig. 7.7. The hydrogen ion environment in $Li(H_2O)_3ClO_4$ (1914). The distances are in pm, the angles in degrees.

proper bond valence sums can only be obtained if these very weak bonds are included (Brown 1976b).

 ${\rm Li(H_2O)_3ClO_4}$ (1914) contains a typical weak hydrogen bond. Its geometry is shown in Fig. 7.7. The Li⁺ ion is coordinated by six water molecules whose H⁺ ions form one weak hydrogen bond ($S_h = 0.13\,{\rm vu}$) with one of the three basal oxygen atoms of the perchlorate ion and a second very weak hydrogen bond ($S_h = 0.04\,{\rm vu}$) with the apical oxygen. The weak H...O bond has a length 205 pm, significantly longer that found in a normal hydrogen bond, and the observed O-H...O angle of 164° is close to the angle of 159° that would be expected from Fig. 7.4. The very weak bond has a length of $262\,{\rm pm}$ with an O-H...O angle of only 107° . Since the three basal oxygen atoms of the ${\rm ClO}_4^-$ ion each form two H...O bonds of valence 0.13 vu and the apical oxygen forms six H...O bonds of valence $0.04\,{\rm vu}$, each perchlorate oxygen receives 0.25 vu from the hydrogen bonds allowing the ${\rm ClO}_4^-$ ion to retain its regular tetrahedral geometry. If the very weak bonds are ignored, the bond valence sum at the apical ${\rm O}^{2-}$ is only $1.75\,{\rm vu}$, much smaller than expected.

Weak hydrogen bonds are also found in places where the O-H...O angle is constrained to be less than 180°, since bending the bond causes R_{OO} to be lengthened. The hydrogen bonds in liquid water are therefore weaker than those in ice since in ice all the bonds are straight, but in the liquid, the disorder and mobility of the water molecules ensures that the hydrogen bonds are all more or less bent and therefore weaker. For this reason it was assumed in Chapter 5 that the bonding strength of liquid water is only 0.17 vu.

7.6 The structural chemistry of the hydrogen ion

A consequence of the asymmetry of the hydrogen bond is that the H^+ ion behaves both as a strong cation to the donor anion and as a weak cation to the acceptor anion. Unlike most other cations, H^+ is able to form a link between anions of very different bonding strength. It thus plays a unique role in chemistry, particularly in the chemistry of aqueous solutions. Compounds that contain hydrogen bonds often form bond graphs that exploit this intrinsic asymmetry. The six Ni–O bonds in Ni(H_2O)₆SO₄ (69127, Fig. 7.8), for example,

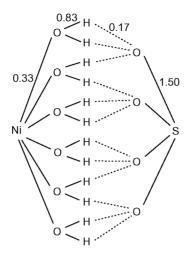


Fig. 7.8. Bond graph of Ni(H₂O)₆SO₄ (69127) showing the bond valences.

have a valence of 0.33 vu which gives the NiO_6^{10-} group a bonding strength of 0.56 vu making it a strong anion. The sulphate group, with a bonding strength of 0.17 vu, is a relatively weak anion. H⁺ provides a uniquely suitable link between these two very disparate anions, using the strong anion as its hydrogen bond donor and the weak anion as its acceptor. If, as would be expected from the principle of maximum symmetry, hydrogen bonds were always symmetric, H⁺ would have a bonding strength of 0.5 vu and Ni(H₂O)₆SO₄ would be unstable because of the poor valence match. The constraint of anion-anion repulsion, which breaks the symmetry of the hydrogen bond, has therefore important consequences for the chemistry of H⁺, allowing the formation of compounds that would otherwise be impossible. Conversely, compounds that would be predicted to be stable by the principle of maximum symmetry are destabilized by the anion-anion repulsion. If it were not for the repulsion between the O^{2-} ions, water would be a hard quartz-like mineral in which all the O-H bonds had a valence of 0.5 vu. It is the asymmetry of the hydrogen bond that causes the H⁺ ions to bond more strongly to one O²⁻ than the other, thus causing solid water to break into the weakly linked H₂O molecules of the liquid water we know.

A particularly interesting question is what happens to free H⁺ ions when placed in water. The large cation bonding strength (0.8 vu) of H⁺ is not well matched to water whose anion bonding strength is only 0.2 vu. If stronger bases, such as PO_4^{3-} , are present in solution, H⁺ will preferentially bond to them as discussed in Section 5.4, but in the absence of stronger bases, H⁺ will attach itself to a water molecule to form the H₃O⁺ ion. This forms three donor hydrogen bonds with $S_h = 0.33$ vu, making them stronger (and shorter) than normal (Fig. 7.9(a)). If one of the hydrogen atoms in H₃O⁺ forms a symmetric bond with another water molecule, the H₅O₂⁺(= H₂OHOH₂⁺) ion is formed (Fig. 7.9(b)). This ion has a

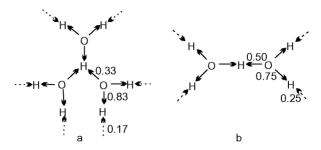


Fig. 7.9. Structure of the hydrated H⁺ ion: (a) H(H₂O)₃, (b) H(H₂O)₂.

bonding strength (0.25 vu) which is more closely matched to water, but this reduction in bonding strength is only obtained at the cost of forming an internal symmetric hydrogen bond. Other configurations are possible, but any hydrated proton complex must have at least six terminal hydrogen atoms (e.g. $H_7O_3^+$, Fig. 7.9(a)) if it is to have a bonding strength matching that of water. Within the water complex surrounding the H^+ ion, the bonds will all be stronger than normal. The ways in which the strains are shared between these internal bonds may fluctuate and at any particular time will be determined by the environment in which the hydrated H^+ ion finds itself. The H^+ ion thus generates its own structured hydration sphere and is properly represented by $H(H_2O)_3^+$. It thus has a lower entropy of solution than H_2O (see Fig. 5.3) and is classified as a structure forming ion.

7.7 Other types of hydrogen bond

The discussion has so far focused on O-H...O hydrogen bonds because these are the most common and best understood, but the same principles apply to the other X'-H...X hydrogen bonds where X' and X can be C^{4-1} , N^{3-1} , O^{2-1} , F^{-1} , Cl⁻, Br⁻, and I⁻ or even a transition metal (Brammer et al. 1995). Changing the anion does not change the nature of the hydrogen bond but does change the numerical values. Unfortunately, detailed graphs comparable to Figs 7.1–7.3 are not available for anions other than O^{2-} , but within the series F^- , O^{2-} , N^{3-} , and C⁴⁻ the size of the anion increases by about 8 pm between one element and the next. F⁻ is the smallest and the symmetric F-H-F bond (length 227 pm) is found in the stable FHF⁻ ion because the F...F repulsion is smaller than the O... O repulsion. Consequently the normal F-H...F bond is more symmetric and shorter (251 pm in solid HF) than the normal O-H... O bond. Conversely, the symmetrical N-H-N bond is not known and the normal N-H... N bond is more asymmetric and longer (around 300 pm). The normal C-H...X hydrogen bonds are highly asymmetric and even longer (C...O around 310 pm) with S_h less than 0.06 vu. Interestingly, the -CH group does not form a single weak H...X bond but generally two, three, or more very weak bonds because at a distance of 310 pm it is possible to surround the -CH group with several O^{2-} ions. For many years it was believed that C-H...X bonds did not exist, but recently Steiner (1995b, 1997) has convincingly demonstrated their reality by showing that there is a significant (if small) increase in the length of the C-H bond as the length of the H...O bond decreases. The differences in the structure and basicity (p K_a) of the CH_3COO^- and CF_3COO^- ions discussed in Section 9.2 can be attributed in part to the acidic character of the methyl group measured by its ability to form hydrogen bonds.

The chemistry of the ammonium ion, NH₄⁺, provides another important example of hydrogen bonding. Because of its tetrahedral symmetry, NH₄ sometimes behaves like a spherically symmetrical monovalent cation such as K⁺ or Rb⁺. Thus, at high temperatures, NH₄Br (60679) crystallizes with the NaCl structure adopted by both KBr and RbBr. The ammonium ion is rotating so the hydrogen atoms have no fixed positions and NH₄ is surrounded by six Br⁻ ions at a distance of 345 pm. At room temperature, NH₄Br (24916), unlike either KBr or RbBr, transforms to the CsCl structure which places eight Br ions around the ammonium ion at the corners of a cube. The ammonium ion is now able to orient itself so that its four H⁺ ions point directly at four of its eight Br⁻ neighbours. However, the ammonium ion is still disordered, because there are two equivalent ways of orienting the tetrahedral NH₄ ion and both of these arrangements are found with equal frequency. As expected for a larger coordination number, the bond distance is slightly longer (352 pm) than in the high temperature phase. Below room temperature the structure transforms to NH₄Br(III) (26579) with the ammonium ion freezing out in one of the two orientations. Four N-H...Br bonds are now shortened to 350 pm, while the four N..Br distance that are not hydrogen bonded are lengthened to 365 pm. NH₄F (9872) takes the formation of hydrogen bonds a stage further and adopts a structure in which each NH₄⁺ ion has only four close neighbour F⁻ ions with which it forms strong, and therefore strained, hydrogen bonds.

The unique character of NH_4^+ allows it to behave at times like an alkali metal similar in size to K^+ or Rb^+ having coordination numbers in the range 6–10, and at other times to express its hydrogen bond character by forming four bonds at the corners of a tetrahedron. Which of these occurs depends on the bonding strength of the anion. Stronger anions such as F^- ($s_a = 0.25$ vu) favour a lower coordination number which results in an ordering of the hydrogen bonds, but weaker anions such as Br^- ($s_a = 0.10$ vu) favour a larger coordination number and hence disordered H^+ ions. Garcia-Rodríguez *et al.* (2000) have analysed the bonds formed by the ammonium ion and have proposed a set of bond valence parameters that can be used if the ammonium cation is treated as an alkali metal.

7.8 Assigning experimental bond valences to hydrogen bonds

For the reasons discussed in Section 7.1, there are a number of factors that make the assignment of experimental bond valences to hydrogen bonds particularly difficult. These include the inability of X-ray diffraction to locate the position of the H⁺ ion accurately, the systematic displacement of the electron density of hydrogen towards the donor anion, the extended range of observed H–O bond lengths which precludes the use of an analytical expression such as eqn (3.1) or (3.2), and the effects of anion–anion repulsion.³

If an accurate position for the H^+ ion has been determined by neutron diffraction, Fig. 7.1 can be used to find the experimental bond valence of the $\mathrm{H}\ldots\mathrm{O}$ bond but it cannot be used to calculate the valence of the donor bond since the $\mathrm{O}\mathrm{-H}$ bond length is insensitive to bond valence. The valence of the $\mathrm{O}\mathrm{-H}$ bond is best assigned by subtracting the valences of the acceptor bonds from the atomic valence, 1.0 vu, of H^+ (see Table 13.2 for an example).

If the observed structure has been determined by X-ray diffraction, one has a choice of two methods, one that is useful if approximate H⁺ positions are known and the other when the H⁺ positions are not known. If approximate positions of the H⁺ ions have been determined by X-ray diffraction, the X'(donor)-H distance not only has a large standard uncertainty but is systematically too short. Better H⁺ positions can be calculated for normal or weak hydrogen bonds by increasing the O-H distance to around 97 pm (100 pm for N-H and longer still for C-H bonds) since the X'(donor)-H distance is insensitive to its valence. Distances for the H...O(acceptor) bonds can then be calculated and Fig. 7.1 used to determine their valences. This calculation corrects for the shortening of the O-H bond and gives a better estimate of the position of the H⁺ nucleus than is possible from X-ray diffraction measurements. The remaining uncertainty in the position of the H⁺ ion is not a problem since even a large uncertainty in the length of the weak H...O bonds will result in only a small uncertainty in the bond valence. The valence of the donor X'-Hbond is then determined as before by differences.

If the positions of the H⁺ ions are not known, one can make use of the observed distances between the donor and acceptor anions to search for potential hydrogen bonds. Donnay and Allmann (1970) have shown that it is possible to identify which atoms are donors and which are acceptors by considering the deficiency in the bond valence sums when the contributions of the hydrogen bonds are ignored. Donor anions will have a deficiency of around 0.8 vu while those with a smaller deficiency are likely acceptors. Identifying neighbouring donor and acceptor anions usually allows the hydrogen bond

³ The curves shown in Fig. 7.1 can be approximated by more complex analytical expressions. The sum of two exponentials gives a reasonable (though not perfect) fit to the thin line but this does not take account of the anion-anion repulsion. Alig *et al.* (1994) obtained good valence sums around H⁺ in O–H...O hydrogen bonds using eqn (3.1) with $R_0 = 91.4$ pm and B = 40.4 pm, but they did not check whether this also gave good sums around the O²⁻ ions. Steiner and Saenger (1994) found that using $R_0 = 92.8$ pm and B = 39.3 pm reproduces the geometry of O–H...O hydrogen bonds reasonably well except for very strong and very weak bonds, but they do not recommend using these parameters for quantitative work. It is also possible to fit the heavy line in Fig. 7.1 by three different sets of parameters, one for each of the three distinct regions of the curve as discussed in Appendix 1.

scheme to be reconstructed. Baur (1972) has proposed an electrostatic method of calculating where the H^+ ions are located in such crystals, but it is not necessary to go to these lengths since reasonably accurate bond valences can be found from a knowledge of just the O...O distances using the heavy line in Fig. 7.3. This provides a good approximation to the most probable value of S_h and, for valences less than 0.4 vu, the heavy line follows the simple linear eqn (7.1):

$$S_{\rm h} = 330 - R_{\rm OO}/200. \tag{7.1}$$

However, since S_h also depends on the O–H...O angle, eqn (7.1) must be used with care, particularly for the weaker bonds where the angles are more variable. As in the previous method, the valence of the donor bond is assigned by differences.

In assigning valences to hydrogen bonds, care needs to be taken to include all the interactions formed by the $\mathrm{H^+}$ ion. Even though there may be one relatively strong $\mathrm{H...X}(\mathrm{acceptor})$ bond, there can be several additional interactions which, although individually very weak ($S < 0.05\,\mathrm{vu}$), when taken together may account for a significant contribution to the total valence. Multiple acceptors are frequently found among the weak bases, e.g. $\mathrm{ClO_4^-}$ and $\mathrm{Br^-}$, and around weak acids, e.g. $-\mathrm{C-H^+}$. Any $\mathrm{H...O}$ distance less than 310 pm should be considered as bonding provided that the $\mathrm{O-H...O}$ angle is greater than 90°.

It is unfortunate that the process of assigning bond valences to hydrogen bonds cannot be easily programmed into a computer, but the extra time needed for the manual assignment of these valences is usually worth the effort because of the critical role hydrogen bonds play in the cohesion and properties of many inorganic solids. A knowledge of their valences sheds valuable light on their role in the crystal chemistry.

Electronically distorted structures

8.1 The origins of electronic distortions

While it is appropriate to treat most ions as spherically symmetric as was done in Chapter 2, there are a few ions, such as those with stereoactive non-bonding electron pairs, whose electronic ground state in a crystal is far from symmetric. Such ions must be modelled by adding either point dipoles or point quadrupoles to the point charges. The electrostatic field calculated using only the point charges is referred to here as the *Madelung field*. The corresponding field calculated using both point charges and point multipoles is referred to as the *Coulomb field*. This chapter shows how the electronic asymmetries arise, how they can be modelled and what effect they have on the structure.

The hard ions described in Section 4.5 are found mostly near the top of the periodic table. They are characterized by having a large energy gap between their spherically symmetric ground states and their first excited state. This makes it difficult for the electrons to polarize and results in the atoms having a rigid spherically symmetric electron density. On the other hand, the soft ions, found towards the bottom and right of the periodic table, have excited states close enough to the ground state that they can be stabilized by small changes in the environment. Such ions are easily polarized, and their low-energy asymmetric states are often stabilized by, and in turn can stabilize, a suitably distorted arrangement of the ligands.

Soft cations that display electronically induced distortions are conveniently grouped into classes according to the origin of their asymmetry. Best known of these are the main group cations in low oxidation states, the so-called *lone-pair cations*, in which one or more pairs of electrons in the valence shell are not directly involved in bonding. Transition-metal cations also undergo a variety of distortions, the Jahn–Teller distortion shown by Cu²⁺ and Mn³⁺ being the best known, and the distortion observed around octahedral V⁵⁺ being the most dramatic. Other electronically driven distortions are found around Hg²⁺ and around I in its various low oxidation states.

The asymmetry found in the electron density of these soft ions can be modelled by adding one or more point multipoles to the point charge used to

¹ The Coulomb field defined here is not to be confused with the physical Coulomb field calculated using the full electron density. The Coulomb field used here is based on point charges and point multipoles, not on extended electron densities.

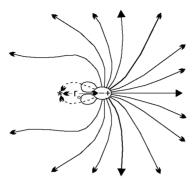


Fig. 8.1. The Coulomb field of a monopole and a dipole. The star indicates the point of zero field. The heavy lines represent the surface that divides the flux into two equal portions.

represent the ion. The field produced by the multipoles is relatively short ranged, contributing mostly to the flux linking the ion to its immediate neighbours. The Coulomb field thus consists of the Madelung field determined by the point charges, and a multipole field determined by the point multipoles. The order of the multipole is determined by the nature of the electronic states involved, a state without a centre of symmetry, for example, possessing an electric dipole. The orientation of the multipole is determined by any pre-existing tendency of the coordination polyhedron to distort, since it is energetically favourable for different distortion mechanisms to reinforce each other. The size of the multipole depends on the extent of the asymmetry in the electron density.

No flux calculations involving multipoles have yet been performed so a quantitative discussion is not possible, but the effects can be explored in a qualitative way. As an example, consider the effects of adding a point dipole, the lowest order multipole, to the point charge of a cation. The resultant field is shown in Fig. 8.1. Because the dipole is electrically neutral the net flux leaving the cation is determined entirely by the size of the point charge, but the dipole changes the way in which this flux is distributed. It increases the flux density around the positive pole and decreases it around the negative pole, generating stronger, and therefore shorter, bonds on the side facing the positive pole, and weaker, longer bonds on the side facing the negative pole. This is equivalent to shifting the ion within its coordination sphere in the direction of the positive pole as illustrated in Fig. 8.2(b).

Although the field of the dipole itself does not extend much beyond its immediate neighbourhood, the displacement of the ion relative to its ligands will alter the Madelung field, and so indirectly contribute to long-range effects. The Madelung field, which is correctly calculated if the distorted geometry is known, still gives a good approximation to the Coulomb field everywhere in the crystal except in the immediate neighbourhood of the non-spherical ion.

Before one can calculate the bond flux directly, both the magnitude and the orientation of the multipole must be determined, and these are generally not

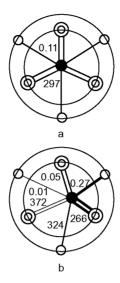


Fig. 8.2. Projection of the O^{2-} environment of TI^{+} when (a) undistorted and (b) at maximum distortion. Bond valences are shown in the top half of each diagram and bond lengths in pm below.

known. However, the experimental bond valence, which in other compounds is known to be equal to the flux, is expected to give a good approximation to the flux even in cases where an electronic distortion is present. The influence of the dipole can be seen by comparing the fluxes calculated using only the Madelung field in the lone-pair molecule I_2O_5 (78387), shown by the circles in Fig. 8.3, with the empirically determined bond valence—bond length correlation for I^{5+} –O bonds, shown by the line. The Madelung fluxes of the strong bonds are lower, and of the weak bonds higher, than the experimental bond valences, but if the flux had been calculated using the Coulomb field rather than the Madelung field, i.e. if the dipole field had been included in the calculation of the flux, the points would have been shifted closer to the line since the dipole would have strengthened the field in the region where the bonds are short and weakened it in the region where the bonds are long.

The theoretical bond valence, which is calculated using the equal valence rule (3.4), clearly gives a very poor estimate of both the flux and the experimental bond valence since in these compounds the valence is not equally distributed between the bonds. Nevertheless, it provides a useful reference against which to measure the strain introduced by the electronic asymmetry.²

² The bond strain in this chapter, as in most other places in this book, is defined as the difference between the observed bond lengths and the bond lengths calculated from the theoretical bond valences. A bond strain index that measures this strain is defined in eqn (12.1).

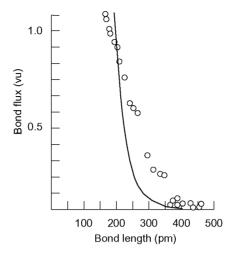


Fig. 8.3. Bond flux versus bond length in I_2O_5 . The points are the Madelung fluxes (calculated without the dipole by Preiser *et al.* 1999). The line represents the empirical bond valence—bond length correlation which is expected to be close to the true flux.

There is an alternative way of calculating the bond flux using the Kirchhoff equations ((2.7) and (2.11)) in place of the network equations ((3.3) and (3.4)), the problem in this case being to determine the appropriate bond capacitances which are not now all equal. Where the multipole produces a shorter bond, a larger capacitance is needed, and conversely where the multipole produces a longer bond, a smaller capacitance is needed. Transferable bond capacitances have been successfully used to model the asymmetries in d⁰ transition metal environments as discussed in Section 8.3.2 below.

The remaining sections of this chapter examine particular classes of cations that show electronically induced distortions. Section 8.2 explores the distortions caused by lone pairs and Section 8.3 explores the distortions found in transition metals.

8.2 Non-bonding valence-shell electrons

One of the best known examples of electronically induced distortion is the steric effect of the non-bonding valence-shell electrons found in main group cations in low oxidation states, cations such as S⁴⁺, N³⁺, and Sn²⁺, in which one or more pairs of valence electrons are not involved in chemical bonding. Such non-bonding electrons are popularly known as *lone pairs* because they occur as localized spin-paired electrons.

The distortion produced by the lone pairs is traditionally described using the Valence Shell Electron Pair Repulsion Model (VSEPR model) (Gillespie and Hargittai 1991), which assumes that each pair of electrons in the valence shell is

localized in a way that minimizes the repulsion between them. Bonding electron pairs point towards the ligands they bond, but the non-bonding lone pairs point to a region in which there is no ligand. In this model the environment of the cation is described in terms of a regular coordination polyhedron (tetrahedron, trigonal bipyramid, or octahedron) in which the lone pair points to an apex which is not occupied by a ligand. Thus the geometry around a Tl^+ cation that forms three bonds is described as a tetrahedron with one site occupied by the lone pair (cf. Fig. 8.4(a)). The geometry around an Sn^{2+} cation that forms four bonds is described by a trigonal bipyramid with the lone pair occupying an equatorial position, while that around an Xe^{6+} cation that forms five bonds is described by an octahedron, again with one apex occupied by a lone pair. This model gives a remarkably simple and accurate description of the geometry of isolated MX_n complexes, so much so that Galy *et al.* (1975) were able to show that the lone pair occupies a well-defined volume whose centre is displaced about 100 pm from the cation nucleus.

In crystals the bonding around main group cations containing lone pairs is more complex because the short bonds described by the VSEPR model are frequently accompanied by a series of longer bonds close to the region occupied by the lone pair (Fig. 8.4(b)). These weaker bonds are conventionally called secondary bonds in contrast to the short bonds which are referred to as primary (Alcock 1972). The environments of lone-pair ions in the solid are more conveniently treated by considering them as octahedra which are distorted by having the cation displaced towards a face, edge, or apex (Brown 1974). For cations near the top of the periodic table the displacements may be so large that the secondary bonds make no significant contribution to the bonding, which is the case shown in Fig. 8.4(a). Atoms lower in the periodic table show smaller displacements (Fig. 8.4(b)) or even no displacement at all (Fig. 8.4(c)), i.e. they have perfectly regular environments in which the lone pair is described as stereoinactive and is considered to occupy an unhybridized s orbital.

Displacement of the cation towards a face gives three primary and three secondary bonds and is favoured by low-valence cations such as Tl⁺. Cations with intermediate valence, e.g. Sn²⁺, tend to move towards an edge giving four primary and two secondary bonds while high-valence cations such as Xe⁶⁺ favour displacement towards a corner to give five primary bonds (one strong

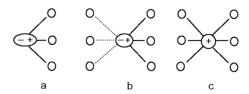


Fig. 8.4. Environments of cations with non-bonding valence electrons: (a) SO_3^{2-} , (b) SbO_3^{-} as found in solids, (c) PbS_6 in PbS (38293). Primary bonds are shown with solid lines, secondary bonds with broken lines.

apical and four medium strength equatorial bonds). Since secondary bonds avoid lying directly over the lone pair, the bonding around Xe^{6+} usually involves two or three secondary bonds arranged around the lone-pair direction. In each of these cases the primary bonding corresponds to the VSEPR description and the secondary bonds fill the area around the lone pair.

A simple orbital picture can be used to describe these distortions. The lone pair can occupy either an sp³ hybridized orbital or an unhybridized s orbital. Around cations from the upper half of the periodic table it usually occupies an sp³ orbital where the four valence-shell electron pairs (three bonding and one lone pair) are arranged at the corners of a tetrahedron giving rise to three primary bonds as described by the VSEPR model. Cations from lower in the table can also show this configuration but are sometimes found with the lone pair occupying a pure s orbital which can then be treated as part of the core, giving a spherically symmetric electron density. Intermediate states of hybridization are also possible and frequently found.

In the ionic model, the bonding electrons are all assigned to the anions, but the lone pair remains on the cation in accordance with the assumptions made in Section 2.3. The asymmetry caused by a lone pair occupying an sp³ hybrid orbital can be represented by a dipole whose magnitude depends on the degree of hybridization. This in turn is determined by the bonding strength of the ligands as discussed below. For weak ligands the dipole may even be zero, corresponding to the lone pair occupying a symmetric s orbital.

The dipole will orient itself in such a way as to enhance any pre-existing distortion arising, e.g. from asymmetries in the bond graph or steric strains, an arrangement that minimizes the strain energy. If there is no pre-existing distortion the lone pair will, if sufficiently stereoactive, result in a spontaneous breaking of the symmetry, in which case the dipole may be oriented along any of the directions that were equivalent under the symmetry that has been broken.

No quantitative treatment of the lone pair using an electric dipole has yet been reported, but a semiquantitative treatment is possible. Figure 8.1 shows the Coulomb field around a positive point charge, V, and point dipole, D. The positive direction of the axis is taken along the positive pole of the dipole. At large distances the point charge dominates the field, but at short distances the field is strongly perturbed by the dipole. As shown in the figure the near-field flux lines are shifted towards the positive axis while along the negative axis there is a region in which the field is reversed. The point at which the field changes sign is marked by an asterisk in Fig. 8.1. The distance, r_0 (given by eqn (8.1)), between this point and the nucleus is a characteristic scaling distance of the field:

$$r_0 = 2D/V. (8.1)$$

Consider the maximum distortions observed in the MO_2 and MO_3 groups listed in Table 8.1 (M=a cation from Group 15 or 16). If there were no dipole, the ions would be planar with an O-M-O angle of 120° (180° in the case of

	Bond lengths (pm) M-O primary	Bond lengths (pm) M-S-O secondary	Angle O-M-O (degrees)	Bond valences S_p (vu) primary	Bond valences $S_{\rm s}$ (vu) secondary
$\overline{\mathrm{NO_2^-}}$	126		115	1.50	
PO_3^{3-}	165	318	99	1.00	0.02
$\mathrm{AsO_3^{3-}}$	179	305	98	1.00	0.03
$\mathrm{SbO_3^{3-}}$	198	292	96	0.98	0.08
BiO_3^{3-}	220	255	84	0.75	0.29
SO_3^{2-}	155	343	104	1.36	0.01
SeO_3^{2-}	173	282	96	1.24	0.06
${\rm TeO_3^{2-}}$	200	290	94	0.94	0.08

Table 8.1 Typical geometries of selected lone-pair cations in their most distorted form

 NO_2^-). When the dipole is present the flux lines, hence the ligands, are shifted towards the positive axis, leading to a reduction in the O-M-O angle. This reduction in NO_2^- is limited by the repulsion between the O^{2-} ions whose separation cannot be less than R_{\min} . This, taken from Fig. 6.4, is 213 pm and corresponds to the observed O-M-O angle of 115°. In this case the non-existence of NO_3^{3-} , as well as the geometry of NO_2^- , are both determined by anion-anion repulsion. For all the other ions, the O-O distance exceeds R_{\min} so the geometry is primarily determined by other factors.

Because of the shift in the flux lines, one might expect the ligands to lie in the plane represented in Fig. 8.1 by the heavy line which divides the flux into two equal portions. This plane is given (in polar coordinates r, θ) by eqn (8.2):

$$\cos \theta = -r/r_0 + ((r/r_0)^2 + 1)^{1/2}.$$
 (8.2)

If the ligands lie in this plane, the values of θ and r are their coordinates. Since these can be determined from the observed geometry, eqn (8.2) can be solved for r_0 which, using eqn (8.1), can be used to determine the dipole moment, D. However, this calculation ignores two effects, namely, the anion-anion repulsion which will tend to increase θ , and the presence of secondary bonds which use a portion of the flux from the negative side of the dipole and so tend to decrease θ . Both these effects can be seen in Table 8.1. The large angle in NO_2^- is determined by anion-anion repulsion as described above, the small angle in BiO_3^{3-} is determined by the presence of significant secondary bonding. After allowing for these effects the ideal O-M-O angle is seen to be about 100° corresponding to $r_0 \sim 200$ pm. For Group 15 cations this gives $D \sim 300$ electron pm, equivalent to a 150 pm separation between the nucleus and a lone-pair charge of two electrons, a distance comparable to the 100 pm found by Galy et al. (1975). For Group 16, the results are more variable but are consistent

with a similar r_0 and a larger dipole moment, in agreement with the observation of Galy *et al.* (1975) that the distance between the nucleus and lone pair in these complexes is increased to 125 pm.

The presence of the reversed field along the negative axis permits cations with stereoactive lone pairs to bond to other cations using the lone pair as an electron donor, but only if the bond to the second cation is shorter than r_0 . This accounts for the ability of cations near the top of the periodic table to bond to other cations through their lone pairs as discussed in Section 3.5, e.g. N^{3+} bonding to Cu^{2+} in $Cu(NO_2)_6^{4-}$, S^{4+} in $NH_4Co(SO_3)_2(NH_3)_4 \cdot 3H_2O$ (36406) and dimethyl-sulphoxide, and P^{3+} in $Pt(PO_3)_4^{2-}$. Copper also forms complexes with AsO_3^{3-} and possibly also very weak complexes with Se^{4+} and Ge^{2+} .

Table 8.1 lists the most highly distorted geometries found around lone-pair cations of Groups 15 and 16, but compounds with smaller distortions, or with no distortion at all, are also known. For example, the cation environments in TlCl (29107), PbS (38293), and K₂TeCl₆ (26127) all have cubic symmetry and therefore the dipole has zero moment. The size of the moment in any particular compound is determined by the bonding strength of the counterion. This is illustrated by the crystal chemistry of Tl⁺ which, in different compounds, can show either no displacement, a displacement leading to three primary and no secondary bonds, or to any configuration in between (Brown and Faggiani 1980). In TlNO₃ (75253, anion bonding strength 0.11 vu) and TlCl (29107, anion bonding strength 0.14 vu), the environment of Tl⁺ is fully symmetric and the cation behaves like an alkali metal similar in size to Rb⁺ (bonding strength 0.12 vu), but in Tl₃BO₃ (10196, anion bonding strength 0.33 vu) the non-bonding pair is fully stereoactive and Tl⁺ forms the pyramidal arrangement of three bonds of valence 0.33 vu predicted by the VSEPR model and shown in Fig. 8.4(a).

Figure 8.5 shows the correlation between the dipole moment, as indicated by the coordination number, and the counterion bonding strength. Where Tl⁺ adopts its maximum coordination number, i.e. where its coordination number is limited only by anion-anion repulsion, Tl⁺ has a bonding strength of 0.11 vu, similar to Rb⁺, and can bond to relatively weak anions such as NO₂ or Cl⁻. In this case, the ligands are in contact and fill the surface of the coordination sphere so the bonding is necessarily symmetric, the cation is at the centre of the sphere and the dipole has zero moment (Fig. 8.4(c)). Where Tl⁺ bonds to anions with a larger bonding strength, it will form fewer and stronger bonds. It can accomplish this by shifting its lone pair away from the nucleus to create a dipole which forces the flux lines towards the positive axis. This decreases the number of primary bonds and increases their flux (Fig. 8.4(b)). By forming only three primary bonds, Tl⁺ can match the bonding strength of anions as strong as BO₃⁻ (Fig. 8.4(a)). Any anions, therefore, with bonding strengths lying between 0.11 and 0.33 vu can bond to Tl⁺, the size of the dipole moment adjusting to ensure a good bonding strength match with the anion. This can also be seen in Fig. 8.5 which shows the way the observed coordination numbers cluster around the line that represents a perfect match with the bonding strength of the counterion.

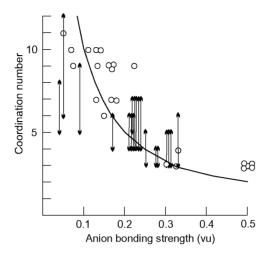


Fig. 8.5. Tl⁺ coordination number versus anion bonding strength. The curved line represents the coordination number expected if the valence of the Tl–O bonds is equal to the anion bonding strength. The circles are observed coordination numbers. The vertical lines mark the primary coordination number (bottom arrows) and the total coordination number (top arrow) for environments that contain both primary and secondary bonds.

One consequence of the ability of Tl⁺ to vary its electronic configuration in response to its environment is that it can adopt a cation bonding strength anywhere in the range from 0.11 to 0.33 vu. Unlike the similar sized but hard Rb⁺ ion, which only forms stable bonds with weak anions, Tl⁺ is soft and can form stable compounds with both strong and weak anions (Section 4.5).

The ligands of a lone-pair cation lie on the surface of a sphere. When Tl⁺ is surrounded by weakly bonding oxyanions, it lies at the centre of the sphere, forming nine bonds of 297 pm each (0.11 vu, Fig. 8.2(a)). When it bonds to strongly bonding anions, as in Tl₃BO₃, Tl⁺ moves about 70 pm away from its centre to form three primary bonds of 266 pm (0.33 vu), and six secondary bonds of 324–372 pm (Fig. 8.2(b)). In the process the radius of the coordination sphere increases from 297 to 322 pm in accordance with the distortion theorem (Rule 3.6).

8.3 Transition metals

In transition metals the electrons in the d shell are not directly involved in bonding and therefore should be considered part of the cation core. If the d shell is completely full, it will be spherically symmetric and no distortion is expected. For partial fillings the core may or may not be symmetric, but even if it is not symmetric, the asymmetry may not be large enough to cause any distortion in

the environment since the d shell is somewhat shielded from the environment by the valence shell. There are two important ways in which the d shell can lead to distortions, either if the d electrons are in a degenerate energy level where the degeneracy can be removed by a distortion of the environment of the transition metal, or if empty d orbitals can mix with filled orbitals on either the transition metal or its ligands. These two cases will be discussed separately.

8.3.1 Jahn-Teller distorted cations

The best known transition-metal cation distortions are those found around Cu²⁺ and Mn³⁺, systems that have partially filled d shells with a degenerate ground state. According to the Jahn–Teller theorem, any degenerate electronic system will spontaneously distort in such a way as to remove the degeneracy (Dunitz and Orgel 1960). The distortions around Cu²⁺ have been extensively studied and may play a role in the superconductivity found in some copper oxides (Section 13.3.2), while the distortions around Mn³⁺ play an important role in the potentially useful magnetoresistive properties of LaMnO₃ (Section 13.3.3).

When a transition-metal cation is surrounded by an octahedral arrangement of ligands, the five d-shell orbitals split into a triplet, t_{2g} , and a doublet, e_g , state (Fig. 8.6(a) and (b), i and ii). The electrons in the triplet state are localized in the region between the ligands and have little effect on the stereochemistry but those in the doublet state point directly at the ligands and thus lie higher in energy than the t_{2g} electrons. The presence of electrons in the e_g orbitals tends to destabilize the octahedral bonding. If the doublet is only partially filled, the

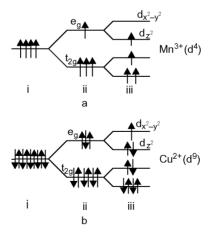


Fig. 8.6. Energy levels showing the Jahn–Teller splitting in octahedrally coordinated transition metal cations: (a) d^4 (Mn³⁺), (b) d^{10} (Cu²⁺). The energy levels are shown (i) in a spherical field, (ii) in a regular octahedral field, and (iii) in a tetragonally distorted octahedral field.

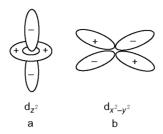


Fig. 8.7. Perspective views of the e_g orbitals: (a) d_{g^2} orbital and (b) $d_{g^2-g^2}$ orbital.

state will be degenerate since the odd electron or hole can occupy either of the two orbitals that form the doublet. One of these orbitals is the $d_{x^2-y^2}$ orbital (Fig. 8.7(b)) which points at the four ligands in the equatorial plane, the other is the d_{z^2} orbital (Fig. 8.7(a)) which points to the two axial ligands. The degeneracy is removed by lengthening the bonds opposite the filled orbital and shortening the bonds opposite the empty orbital. In practice, the distortion is always found to shorten the four equatorial bonds and to lengthen the two axial bonds, i.e. the electrons preferentially fill the d_{z^2} orbital for reasons discussed by Burdett (1980).

Since the d orbitals have quadrupolar character, this distortion must be modelled using a point electric quadrupole with the shape of the d_{z^2} orbital oriented with a negative pole along the z axis and the positive pole in the x-y equatorial plane (Fig. 8.7(a)). No fluxes have been calculated for Jahn–Teller distorted cations, either with or without the quadrupolar contribution but, as in the other cases, the experimental bond valences are expected to provide a good approximation to the bond fluxes.

The distortions shown by Mn³⁺ ions with four d electrons (Fig. 8.6(a)) and Cu²⁺ ions with nine d electrons (Fig. 8.6(b)) do not vary greatly from compound to compound, suggesting that the quadrupole moment is the same in all the compounds of a given cation. As in other cases, the orientation of the quadrupole is determined by any predisposition of the Cu²⁺ or Mn³⁺ environment to distort as a result of other influences (e.g. the connectivity of the bond graph or steric strains as found, for example, in La₂CuO₄ discussed in Section 12.3.3). This suggests that it might be possible to model the distortion using the Kirchhoff equations ((2.7) and (2.11)) with a set of standard capacitances as has been done for the d⁰ systems as described in Section 8.3.2.

8.3.2 Transition-metal cations with empty or near-empty d shells

According to conventional wisdom transition metals with empty d shells should have spherically symmetric electron densities since there are no d electrons available to cause a distortion. They should therefore have regular coordination environments but, surprisingly, the largest electronic distortions are shown by six-coordinate d^0 or d^1 cations. Transition-metal cations with empty d shells

include Sc^{3+} , Ti^{4+} , V^{5+} , Nb^{5+} , Cr^{6+} , and Mo^{6+} . The observed distortions arise because, under suitable conditions, the empty d orbitals can mix with both the filled p orbitals of the ligands and the filled core orbitals of the transition metal. When the oxidation state of the transition metal is small (e.g. Sc^{3+}), the empty d orbitals are high in energy, there is little mixing and no electronic asymmetries are observed. As the oxidation state increases and the d orbitals are less screened from the nucleus, their energy is lowered to the point where it becomes comparable to the energy of the filled orbitals, allowing the orbitals to mix and the electron density to polarize.

Unlike the simple electronic structures of Mn³⁺ and Cu²⁺ in which the d orbitals are influenced only by the crystal field, the electronic states of d⁰ and d¹ transition-metal cations involve the mixing of the d orbitals with those of the core and the ligands. A simple analysis similar to that presented for the Jahn–Teller distortion is not possible. However, it appears that where mixing occurs, the formation of a bond between the transition metal and one of its ligands polarizes the core electrons of the transition metal away from the bond, tending to destabilize any bond trans to the primary bond (Gillespie and Robinson 1996). Thus, the effect of the distortion in all cases can be described as an attempt to remove any centre of symmetry that may be present. Tetrahedral coordination, having no centre of symmetry, remains regular, but regular octahedral coordination is destabilized. The centre of symmetry is removed by the transition metal being displaced towards a face, edge, or corner of the octahedron.

The polarization of the core electrons of the transition metal induces a parallel polarization of the electrons on the ligands as shown in Fig. 8.8, both polarizations being allowed by mixing filled orbitals on the metal and ligand with the empty d orbitals. This type of distortion lends itself to the formation of metal-ligand chains with alternating long and short bonds, $-\mathbf{M} = \mathbf{O} - \mathbf{M} = \mathbf{O} + \mathbf{$

On the basis of size alone, all first row transition metals would be expected to have regular octahedral coordination. This is found to be the case for the early

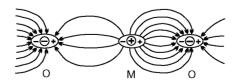


Fig. 8.8. Schematic view of the flux lines induced by the dipole on the d^0 transition metal (the central atom) in the -O-M-O- system (M= transition metal).

 d^0 transition metals where the d electron levels are much higher in energy than the filled orbitals, but as one progresses along the period, the energy of the d orbitals is lowered producing an increase in both the distortion and destabilization of octahedral coordination. The latter effect can be seen in the decrease in the ideal (average observed) coordination numbers given in Appendix 4 for the first row d^0 transition-metal cations, dropping from 6.2 for Sc^{3+} through 6.0 for Ti^{4+} , 4.6 for V^{5+} to 4.0 for Cr^{6+} . The latter cation is never found octahedrally coordinated even though this is easily permitted on the basis of size as can be seen in Fig. 6.4.

Although Ti⁴⁺ is almost always octahedrally coordinated, it is often found displaced from the centre of its coordination sphere, as for example in BaTiO₃ (23759, Fig. 10.4), where, even though the distortion is driven by the lattice strains discussed in Chapter 12, it is stabilized by a favourable electronic state. Even when Ti⁴⁺ possesses a crystallographic centre of symmetry as in SrTiO₃ (201256), it is probable that it is dynamically distorted (Abramov *et al.* 1995). By contrast, Sn⁴⁺, which is similar in size to Ti⁴⁺, is found in octahedral environments that are rarely distorted. Tetrahedral Ti⁴⁺ is known in Ba₂TiO₄ (2625) but in very few other compounds.

In V⁵⁺, the element next to Ti⁴⁺ in the periodic table, the mixing has increased to the point where regular tetrahedral coordination is the preferred geometry but highly distorted octahedral environments are also common (Schindler *et al.* 2000). According to the principle of maximum symmetry, one might expect ZnV₂O₆ (30880) to adopt the same symmetric structure as the isoelectronic ZnSb₂O₆ (30409) which crystallizes with the trirutile structure whose bond graph is shown in Fig. 8.9(a), but by adopting the less symmetric graph shown in

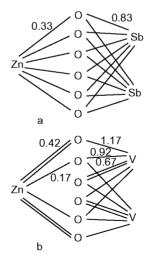


Fig. 8.9. Bond graphs of (a) $\rm ZnSb_2O_6$ (30409) and (b) $\rm ZnV_2O_6$ (30880) showing the theoretical bond valences.

Fig. 8.9(b), ZnV_2O_6 is able to crystallize with the brannerite structure whose theoretical bond valences, calculated from the network equations ((3.3) and (3.4)) and shown in Fig. 8.9(b), already predict an out-of-centre distortion for the V^{5+} ion. ZnV_2O_6 thus adopts a bond graph that supports the electronically induced distortion. In this case the adoption of a lower symmetry bond graph is favoured because it is able to reduce the bond strain.

The distortion around six-coordinated Cr⁶⁺, the next cation in the periodic table, is so much larger than that around V⁵⁺ that the two weakest cation—ligand bonds have effectively disappeared, reducing the coordination number to 4. The coordination around Cr⁶⁺ is always tetrahedral, though one can sometimes observe two residual weak bonds in compounds such as CrO₃ (16031) which crystallizes with chains of corner-linked CrO₄ tetrahedra packed in such a way that two very long octahedral bonds (lengths 322 and 334 pm) can still be identified (Fig. 8.10).

The stereochemistry of d^0 transition-metal cations has been modelled using the Kirchhoff equations ((2.7) and (2.11)) of the equivalent electrical network in place of the network equations ((3.3) and (3.4)). This requires the assignment of capacitances to each bond to reflect the expected distortion. Two quantities define this distortion, the orientation and the magnitude of the dipoles. Kunz and Brown (1995) modelled these by using large capacitances for bonds that were expected to be strong and small capacitances for bonds that were expected to be weak. They showed that the electronic distortion orients itself so as to enhance the intrinsic distortion arising from asymmetries in the bond graph and the repulsions between neighbouring cations. They assigned a capacitance $C_{\rm max}$ to any bond lying within 65° of the intrinsic distortion vector. Bonds trans to these were assigned a capacitance $C_{\rm min}$ and all other bonds a capacitance of 1.0. With the values given in Table 8.2, Kunz and Brown could reproduce the experimental bond valences in a variety of compounds using just two transferable capacitances.

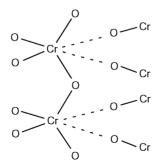


Fig. 8.10. The arrangement of chains in CrO_3 (16031) showing the residual octahedral coordination around Cr^{6+} .

	. ,	~	
	$C_{ m max}$	$C_{ m mid}$	$C_{ m min}$
Ti ⁴⁺	1.3	1.0	0.7
Ta ⁵⁺ Nb ⁵⁺ V ⁵⁺	1.3	1.0	0.7
Nb^{5+}	1.4	1.0	0.6
V^{5+}	1.6	1.0	0.7, 0.1*

Table 8.2 Capacitances assigned to d⁰ transition-metal cations by Kunz and Brown (1995) in arbitrary units

8.4 Conclusions

A cation that shows an electronically driven distortion falls into the category of soft cations capable of showing a range of bonding strengths, but the nature of the distortion depends on the electronic structure of the ion. Bond valences in these systems can be modelled by the addition of a point dipole or quadrupole to the ion or its neighbours, or by the choice of appropriate bond capacitances in the Kirchhoff equations of the equivalent electrical circuit. The multipoles (or capacitances) must be oriented so as to reinforce any pre-existing distortion. For transition metals, the magnitude of the multipole does not depend on the local environment, but this is not true of the magnitudes of the dipoles representing lone pairs which can vary over a wide range depending on the bonding strength of the counterion.

The equal valence Rule 3.4 is clearly violated in these compounds so that the theoretical bond valence does not give a good prediction of the experimental bond valence. It can, however, be used to calculate a bond strain, i.e. the amount by which the electronic effects change the bond lengths. Even though the equal valence rule is not obeyed, the valence sum rule (3.3) still applies since the multipoles contribute no net charge to the ion. Compounds that show electronic strain typically have a large bond strain index (BSI defined in eqn (12.1)) which measures the failure of the equal valence rule and a small global instability index (GII defined in eqn (12.2)) which measures the failure of the valence sum rule. On the other hand, the lattice induced strains discussed in Chapter 12 tend to give a large GII and a small BSI.

^{*}For V^{5+} two different values of C_{\min} were needed. The smaller value is used for the bond trans to the bond making the smallest angle with the distortion vector.

Physical properties of bonds

9.1 Introduction

The concept of a chemical bond has proven so powerful that many properties have been ascribed to it, often in the absence of any experimental evidence. If the concept of a bond could be rigorously derived from theory, it would then also be possible to derive the properties associated with it, but in the absence of such a theoretical justification, it is necessary to rely on empirical evidence to discover what properties, if any, can be reliably associated with a chemical bond.

Chapter 2 provides a semi-theoretical derivation of the concept of a bond based on the ionic model and suggests that the key property of a bond is its flux or valence. Any other property that legitimately belongs to a bond should therefore be expressible in terms of the bond flux. The difficulty is that the flux is not the same for all bonds between the same pair of ions, but depends on three distinct features of the bond's environment. Firstly, it depends on the formal charges or valences of the two atoms that define the bond since increasing the formal charge increases the flux. Secondly, it depends on the relative positions of the terminal atoms, since bringing the atoms closer together increases the flux. Thirdly, it depends on the way in which all the atoms in the compound are bonded to each other (the graph of the bond network) since the fluxes must satisfy the Kirchhoff equations (2.7) and (2.11). The consequence is that every bond that is not related by crystallographic symmetry is unique and displays a unique set of properties. This can be seen by the fact that, even though bond length is a measurable bond property, not all Na-O bonds, for example, have the same length. The length depends on the bond flux (or bond valence) which has its own unique value for every Na-O bond. However, since the bond valence can be predicted given the bond graph, the properties of each individual bond should also be predictable.

Energy is often treated as if it were a bond property on the assumption that the total stabilizing energy of a compound can be divided into energies associated with each bond (see, for example, eqn (13.5)). Even if this is true, it is almost impossible to establish the relationship between the energy and the valence of a bond as the following thought experiment shows. Supposing one adds an atom to an existing collection of bonded atoms in, say, a molecule or a small crystallite. New bonds will be formed and, if energy is a bond property, the change in the energy of the molecule or crystallite should be equal to the sum of the energies of the new bonds. But the creation of these new bonds draws flux

from the existing bonds and thus changes their energy. Therefore, when an atom is added to an existing collection of bonded atoms, it is not just the energies of the newly formed bonds that need to be taken into account, but also the changes in the energies of all the other bonds. Even if energy is a good bond property, its relationship to the bond valence is difficult to determine since the only measurement one can make, namely the change in the total energy, involves changes in the energies of all the bonds in the sample. Until a clear relationship between valence and energy has been demonstrated, it is safer to assume that energy is not a good bond property.

There are, fortunately, several properties that do correlate well with the bond valence as discussed below. They include the bond length and its thermal expansion as well as a bond force constant that can be used for a semi-quantitative analysis of the Raman and infrared spectra of crystals.

9.2 Bond lengths and bond angles

As shown in the earlier chapters of this book, there is a good correlation between the valence and the length of a bond as given specifically by eqn (3.1). This is an empirical equation with two fitted parameters, R_0 , which depends on the sizes of the two bonded atoms, and B which gives an indication of the softness of the bond, larger values corresponding to a softer repulsion between the terminal atoms.

These parameters are found by fitting the bond valence to experimentally observed bond lengths. It is this empirical fitting that gives the model its robustness, since the fitted parameters automatically compensate for a number of systematic effects. As an example, suppose that the true charge, q, of a cation differs from the formal charge, V, by a factor k as given by eqn (9.1):

$$q = kV. (9.1)$$

Then the true fluxes, ϕ , of the bonds formed by the cation will differ from the bond valences, S, in the same proportion (eqn (9.2)):

$$\phi = kS. \tag{9.2}$$

Hence eqn (3.1) can be written as

$$\phi = kS = k \exp((R_0 - R)/B) = \exp(((R_0 + B \ln k) - R)/B). \tag{9.3}$$

This shows that the only effect of using the wrong set of charges is to increase the value of R_0 by $B \ln(k)$. Fitting the value of R_0 empirically therefore automatically compensates for an inappropriate choice of ionic charge. The value of k does not even have to be the same for all bonds, only for the bonds that use the same value

of R_0 . The charges on the anions are determined by the fluxes they receive, so whatever value of k is used, the crystal remains electrically neutral. There is therefore no necessity for the assumed charges to be close to the actual charges, since any reasonable values can be used providing they are used consistently, that is to say the same value of k should apply to all the bonds between a given cation and anion (say, 0.95 for Na–O bonds and 0.25 for S⁶⁺–O bonds). It follows therefore that the bond valence model does not depend on a knowledge of the actual bond charges since any error in the choice of the charge is automatically compensated by the empirically fitted value of R_0 , a fact which justifies the convenient use of formal ionic charges and, incidentally, shows that the bond valence model cannot directly be used to determine the true ionic charges.

In addition to containing information about the size of the electron core, R_0 therefore also includes hidden information about the formal charges on the atoms as well as other systematic effects such as π bonding and the effects of thermal motion on the apparent bond length (Section 9.4). The only information that the user needs to know is that R_0 applies to all the bonds between the same pair of ions (see also the discussion in Section 14.1.2).

The transferability of R_0 between the bonds of a given pair of ions has been demonstrated for most bonds but there is at least one exception which illustrates what happens in the few cases where the character of the bond depends on factors other than the bond valence itself. The exception is found for the bonds between transition metals and ligands bonding through N. Here the length of the bond depends not only on the bond valence but also on the ability of N to form π bonds. The N atom in the isothiocyanate ligand (–NCS) forms two orthogonal sets of π bonds which can interact with d orbitals on the metal. This results in a stronger bond than is formed when, for example, N is part of an ammonium group (–NH₃) where such π bonding is not possible. Even when the metal–N bond has the same bond valence, the ability of N to take part in π bonding is an additional factor in determining the bond length. Different values of R_0 are therefore needed according to the coordination number of N. The more π bonds the N atom can form, the smaller the value of R_0 (See *et al.* 1998; Shields *et al.* 2000).

As pointed out above, the bond flux depends on the connectivity of the compound, that is, on the bond graph. This means that the length of a bond depends not only on its immediate environment, but also on the structure of the whole crystal or molecule of which the bond is part. Thus anions such as PO_4^{3-} , which ideally are perfect tetrahedra, will often be distorted when they appear in crystals. However, this distortion can normally be predicted via the network equations provided the graph of the bond network is known.

¹ If very different values of k are used for different cations, there will be some small changes in the distribution of flux. In particular, choosing a small k for highly charged ions such as S^{6+} or Cl^{7+} will reduce the number of tertiary bonds that are found during flux calculations (Section 2.6). For this reason, and for the reason that tertiary bonds play a negligible role in bonding, they are conveniently treated as artefacts of the calculation and ignored.

Even if the full network is not known, it is possible to estimate the distortion if some of the neighbours of the bond are known. Ideally the phosphate ion, PO₄³⁻, has the four O₂²⁻ ions arranged at the corners of a regular tetrahedron. Each bond has a valence of 1.25 vu and a length of 153 pm, and all the angles between the bonds are 109°. In a liquid or solid, the O₂²⁻ ions form a number of external bonds in addition to the bond to phosphorous. If one of the O₂²⁻ ions forms a large number of external bonds, or if one of these bonds is intrinsically strong, the corresponding P-O bond will be weakened. For example, if the phosphate group is protonated and the hydrogen ion forms an O-H bond of 0.8 vu, the P-OH bond cannot have a valence larger than 1.2 vu, meaning that the protonated P-O bond is lengthened from 153 pm to at least 155 pm. The lengthening will be even greater if the oxygen also bonds to other cations as is frequently observed (see Sections 5.3 and 7.4).

In most tetrahedral complexes, the change in the bond length is accompanied by changes in the bond angles (Murray-Rust *et al.* 1975). Because stronger bonds have larger fluxes they form larger angles at the cation, causing the strongly bonded ligands to move away from each other and weakly bonded ligands to move closer together. The angles between the bonds in a tetrahedral complex are given by eqn (9.4) (Brown 1980*a*):

$$\theta = 109.5 + 180x - 652x^2. \tag{9.4}$$

In this equation $x = [(S_1 + S_2)/2V] - 0.25$ and measures the extent to which the valences, S_1 and S_2 , of the two bonds that define the angle θ deviate from the ideal value of V/4, where V is the cation valence. Equation (9.4) is the simplest function that gives a regular tetrahedron when all four bonds are equal and a regular planar triangle when one of the bonds is removed (S=0). When eqn (9.4) is applied to the observed dihydrogen phosphate ion, $H_2PO_4^-$ shown in Fig. 7.5(b), it predicts that the OH-P-OH angle is reduced from 109° to 107 (107)° and the O-P-O angle increased to 112 (113)°, the values in parenthesis being those observed in KH₂PO₄ (68696, 201373).

An alternative way of viewing this distortion is to imagine the cation moving off-centre in a rigid ligand environment though, according to the distortion theorem, the radius of the ligand sphere will increase slightly, particularly when the displacement is large. This description is similar to that given for the electronically driven distortion around Tl⁺ shown in Fig. 8.2. The origin of the distortion in these two cases is different, but the effect on the geometry is the same.

The acetate ion, $\mathrm{CH_3COO}^-$, is an example of a more complex anion whose geometry is affected by its environment (Brown 1980b). Although organic, the acetate ion has a bipartite graph and so can be analysed using the bond valence model. According to the principle of maximum symmetry (Rule 3.1), the single ionic charge is shared equally between the two O^{2-} ions, giving each oxygen a bonding strength (for external bonds) of $0.5/3 = 0.17\,\mathrm{vu}$. To ensure the correct valence sums around O^{2-} , the C–O bonds must each have a valence of 1.50 vu

as shown in Fig. 9.1(a). The carboxylate C is then treated as a cation with a valence of +4 vu and the methyl C is treated as an anion with a valence of -4 vu. The C-C and C-H bonds each have a valence of 1.0 vu, i.e. they are single bonds in the terminology of organic chemistry.

In crystals and polar solutions, the methyl group is surrounded by anions with which it forms significant, if weak, hydrogen bonds. Each methyl H^+ ion forms several of these bonds, contributing a total valence of about 0.03 vu to each H^+ atom. The valence of the C–H bonds is therefore reduced to 0.97 vu and the valence of the C–C bond increased to about 1.10 vu, corresponding to the observed C–C bond length of 151 pm, a distance which is significantly shorter than the C–C single bond length of 154 pm. The C–O bonds are correspondingly weakened from 1.50 vu (124 pm) to 1.45 vu (125 pm), enhancing the bonding strength of each O^{2-} atom to 0.55/3 = 0.18 vu. The effect of the weakly acidic methyl H^+ atoms is thus to increase the basicity (anion bonding strength) of O^{2-} from 0.17 to 0.18 vu, to shorten the C–C bond and lengthen the C–O bonds as shown in Fig. 9.1(b). Corresponding changes are seen in the bond angles as described above.

With an anion bonding strength of 0.18 vu, the acetate ion is well matched to water, hence acetates are soluble. However in the presence of a strong cation, both oxygen atoms can form a single external bond as strong as 0.55 vu. Still stronger cations, such as Si^{4+} with a bonding strength of 1.00 vu, can be bonded by redistributing the bond flux between the two C–O bonds, making one of them longer and the other shorter as shown in Fig. 9.1(c). In extreme cases such as the acetonium ion, $\mathrm{CH_3C(OH)}_2^+$, the effect of bonding a strong cation (H⁺) to both the oxygen atoms is to strengthen (and shorten) the C–C bond and make the methyl hydrogens even more acidic as shown in Fig. 9.1(d). Since the acetonium ion will only form in strongly acid solutions, the consequences of lowering the pH of an acetate solution are readily seen to be the formation of stronger O–H . . . O hydrogen bonds, the shortening of the C–C bond, and increasing the methyl group acidity.

It is interesting to compare the acetate ion with the non-bipartite trifluoro-acetate ion discussed in Section 3.5. Here the methyl hydrogen, which is a Lewis acid, is replaced with the Lewis base, fluorine. Because the F^- ions are treated as anions, both carbon atoms are cationic and the graph is no longer bipartite. However, about 0.10 vu of the total trifluoroacetate ionic charge of -1.00 is carried by the three fluorines, lowering the charge on the oxygen atoms and reducing their bonding strength to 0.45/3 = 0.15 vu (Fig. 9.1(e)). As a result, the trifluoroacetate ion has a lower pK_a and the C-O bonds are stronger (1.55 vu) and shorter (123 pm) than in the acetate ion. Because the bond graph is not bipartite, it is impossible to assign a valence to the C-C bond that satisfies the valence sum around both C atoms, but a valence of 1.00 vu gives valence sums whose mean is 4.00 vu. The C-C bond is observed to have a length of 154 pm, exactly equal to the length of a single C-C bond, a distance which, unlike the C-C distance in the acetate ion, does not change as the external

environment of the ion is altered. The nature of this C-C bond is further discussed in Section 14.1.1.

9.3 Bond force constants and thermal vibrations

The dynamical behaviour of the atoms in a crystal is described by the phonon (sound) spectrum which can be measured by inelastic neutron spectroscopy, though in practice this is only possible for relatively simple materials. Infrared and Raman spectra provide images of the phonon spectrum in the long wavelength limit but, because they contain relatively few lines, these spectra can only be used to fit a force model that is too simple to reproduce the full phonon spectrum of the crystal. Nevertheless a useful description of the bond dynamics can be obtained from such force constants using the methods described by Turrell (1972).

In the simple Urey-Bradley force field which is commonly used to interpret vibrational spectra, each bond is assumed to behave like a harmonic spring and is assigned a spring force constant. Additional force constants are needed for the bond angles, or, alternatively, for the distances between the non-bonded atoms that define the bond angles. Because the bond stretching force constants are an order of magnitude larger than the angle force constants, the latter can sometimes be ignored.

Fig. 9.1. Structures of the acetate ion showing bond valences (above the bond) and bond lengths (in pm below the bond); (a) the ideal structure of the isolated ion; (b) the structure normally observed in the solid state; (c) the structure observed when bonded to a strong cation (Si); (d) the structure observed for the diprotonated acetate ion; (e) the structure of the trifluoroacetate ion normally observed in the solid state.

A selection of bond stretching force constants, G, taken from the literature is plotted in Fig. 9.2 as a function of the bond valence, S. What is surprising is not that there is some scatter (this is expected from the crudeness of the Urey–Bradley force field) but that an expression such as eqn (9.5) gives such a good fit:

$$G = aS - b(1 - \exp(-aS/b)).$$
 (9.5)

Equation (9.5) is designed to give a quadratic fit at S=0 and a linear fit for S>1 vu. The constants a and b, which correspond to the solid line in Fig. 9.2, are $450 \,\mathrm{N\,m^{-1}\,vu^{-1}}$ and $140 \,\mathrm{N\,m^{-1}}$ respectively. To make explicit the extent of the uncertainty introduced by the scatter, two limiting broken lines are also shown, the upper having $a=505 \,\mathrm{N\,m^{-1}\,vu^{-1}}$ and $b=100 \,\mathrm{N\,m^{-1}}$, and the lower having $a=405 \,\mathrm{N\,m^{-1}\,vu^{-1}}$ and $b=200 \,\mathrm{N\,m^{-1}}$.

The amplitude, A, of the thermal motion of a bond is a property directly related to the stretching force constant, G, since the vibrational energy of a harmonic bond is given by eqn (9.6):

$$Energy = GA^2/2. (9.6)$$

In the classical approximation, which is sufficiently accurate at room temperature and above, the mean square amplitude of vibration of a bond, $\langle A^2 \rangle$, at

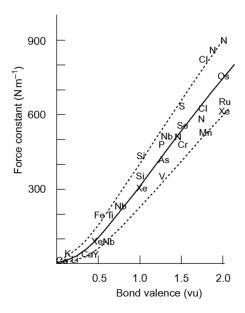


Fig. 9.2. Force constants determined from infrared and Raman spectroscopy as a function of bond valence. The bonds are between the cation shown and (mostly) O^{2-} . The lines represent the fit given by eqn (9.5).

a temperature, T, is related to the energy by the Boltzmann equation (9.7):

$$\langle A^2 \rangle = \int (A^2 \exp(-GA^2/2kT) \, dA / \int \exp(-GA^2/2kT) \, dA = kT/G, \quad (9.7)$$

where k is the Boltzmann constant and the integration is taken over all values of A.

 $\langle A^2 \rangle$ cannot be measured directly, but the mean square amplitudes of vibration of the individual atoms, U, can be found using X-ray or neutron diffraction. $\langle A^2 \rangle$ can be determined from U only if we know both the amplitudes of the atomic vibrations along the direction of the bond and how they are correlated. While the amplitudes are readily measured, the correlations between their motions are unknown. There are, however, two limiting cases, the first when the bond connecting the two atoms is strong and rigid so the atoms always move in phase, and the second when bond is weak so that the atomic motions are uncorrelated.

In the rigid bond limit $\langle A^2 \rangle$ is, by definition, identically zero regardless of the amplitude of the atomic motion since the bond length never changes. Rosenfield *et al.* (1978) have used this property to identify rigidly bonded groups of atoms by looking for pairs of atoms whose atomic displacements are identical along the bond vector. Rigid bonds are typically found in strongly bonded complexes such as SO_4^{2-} , PO_4^{3-} and SiO_4^{4-} .

Uncorrelated motion is most likely to be found when the bonds are weak, for example, when the cation is a large alkali metal. In this case the mean square amplitude, $\langle A^2 \rangle$, is given by the sum of the components of the atomic displacement parameters, U, of the two atoms along the bond direction, that is,

$$(U_{\text{cation}} + U_{\text{anion}}) \cdot \mathbf{r} \equiv U_{\text{uncor}}, \tag{9.8}$$

where r is a unit vector in the direction of the bond (Busing and Levy 1964).

Because the absolute value of $U_{\rm uncor}$ measured in a crystal depends on the amplitude of the zero point motion and includes contributions from static disorder, it is more appropriate to compare how $\langle A^2 \rangle$ and $U_{\rm uncor}$ vary with temperature. Differentiating eqn (9.7) with respect to temperature gives eqn (9.9):

$$d\langle A^2 \rangle / dT = k/G. \tag{9.9}$$

Figure 9.3 compares $d\langle A^2 \rangle/dT$ calculated from eqns (9.9) and (9.5) (shown by the solid line), with $dU_{\rm uncor}/dT$ obtained from X-ray diffraction experiments using eqn (9.8) (shown by the circles). Both are plotted against bond valence, the broken lines corresponding to the limits shown in Fig. 9.2. As expected, for weak bonds the values of $dU_{\rm uncor}/dT$ closely follow the theory given by eqn (9.9)

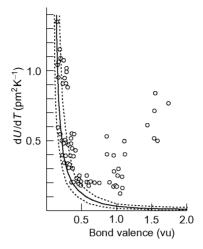


Fig. 9.3. Rate of increase of the mean square amplitude of thermal vibration with temperature plotted as a function of bond valence. The circles represent the sum of uncorrelated atomic displacements along the bond direction, the lines represent the expected bond vibrational amplitudes calculated from eqn (9.9).

but for strong and rigid bonds dU_{uncor}/dT is, as expected, a poor estimate of $d\langle A^2\rangle/dT$ which tends to zero in the rigid bond limit.

9.4 Thermal expansion

The expansion that occurs when a solid is heated is the net result of two effects, the expansion of bonds caused by the anharmonic potential between bonded atoms, and the contraction (or expansion) in the distance between second nearest neighbours caused by the increased bending of the bond angles. Both effects are related to the increase in the amplitude of the atomic vibrations: vibrations along the direction of the bond causing bond expansion and vibrations perpendicular to the bonds causing bond bending. The relationship between the thermal expansion of bonds and bond valences has been examined by Megaw (1939), Hazen and Finger (1982), and Brown *et al.* (1995, 1997).

The distortion theorem (Rule 3.6) can be used to predict the thermal expansion of a bond since the theorem is based on the curvature in the bond valence—bond length graph which, in turn, reflects the anharmonic potential between the atoms. Suppose an atom is at the centre of a regular coordination sphere, i.e. all of its bonds have the same length, $R_{\rm e}$. As the temperature is raised, the atom will vibrate around its equilibrium position with an increasingly large amplitude. At any instant the atom will be displaced from the centre of its coordination sphere and, according to the distortion theorem, the average of its bond lengths is increased.

To make the model quantitative, imagine that at a particular time a given bond has the length R' given by eqn (9.10):

$$R' = \langle R \rangle + \delta R, \tag{9.10}$$

where $\langle R \rangle$ is the time-averaged bond length. $\langle R \rangle$ is, in general, different from $R_{\rm e}$ since the average bond length is expected to increase with temperature. δR will fluctuate, at some times being positive and at others negative, but with an average value of zero.

The instantaneous bond valence, S', is given by eqn (9.11):

$$S' = \exp((R_0 - R')/B) = \exp((R_0 - \langle R \rangle/B)) \exp(-\delta R/B). \tag{9.11}$$

The last term can be expanded as a Taylor series in $\delta R/B$ providing that $\delta R/B$ is small. Ignoring higher-order terms and taking the time average gives eqn (9.12), recognizing that the time average of δR is zero and that the valence sum is independent of temperature so that the time average of S' is the same as S calculated from the length $R_{\rm e}$.

$$S = \exp((R_0 - \langle R \rangle)/B)(1 + \langle \delta R^2 \rangle/2B^2). \tag{9.12}$$

Substituting for S from eqn (3.1) and combining the exponents gives eqn (9.13):

$$\exp((\langle R \rangle - R_e)/B) = 1 + \langle \delta R^2 \rangle / 2B^2. \tag{9.13}$$

Here $\langle R \rangle - R_e = \Delta R$ is the thermal expansion of the bond and, by expanding the left-hand side of eqn (9.13) as a power series in ΔR and ignoring higher-order terms, one gets eqn (9.14):

$$\Delta R = \langle \delta R^2 \rangle / 2B. \tag{9.14}$$

As the temperature increases, the mean square amplitude of vibration, $\langle \delta R^2 \rangle$, increases, and with it the average bond length. Recognizing that $\langle \delta R^2 \rangle$ in eqn (9.14) is the same as $\langle A^2 \rangle$ in eqn (9.7), the two equations can be combined to give the expression for the thermal expansion of a bond shown in eqn (9.15):

$$dR/dT = k/(2BG) = (0.186/G) \text{ pm K}^{-1}$$
 (9.15)

for B = 37 pm and G (in N m⁻¹) given by eqn (9.5). This expression is shown by the solid line in Fig. 9.4 and, with a few exceptions discussed below, the observed bond expansions averaged over each coordination sphere (shown by the circles) lie between the broken lines that correspond to the uncertainties in the determination of the force constants.

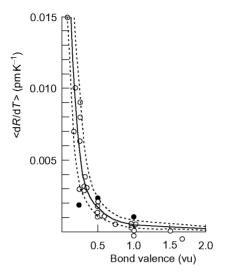


Fig. 9.4. The thermal expansion of bonds averaged over each coordination sphere as a function of bond valence. The circles are measured values, the lines represent eqn (9.15). The filled circles are for grossular (24944) discussed in the text.

Equation (9.15) can be written in terms of α , the coefficient of linear thermal expansion (eqn (9.16)):

$$\alpha = (1/R)(dR/dT) = (0.186 \times 10^{-12})/Rp \, S \, {}^{\circ}K^{-1},$$
 (9.16)

where G has been written as pS, p being a quantity which increases with S as can be seen from Fig. 9.2. However, R decreases with S at almost the same rate so that the product Rp remains constant at around 4.6×10^{-8} in the SI units of eqn (9.15). Thus, the coefficient of thermal expansion of a bond can be written as

$$\alpha = (4.0 \times 10^{-6})/S \,{}^{\circ}K^{-1}, \tag{9.17}$$

which is identical to the empirical expression by which Hazen and Finger (1982, p. 136) were able to fit a large number of observed average thermal expansions of cation polyhedra to their Pauling bond strength.

In structures containing bonds constrained by the lattice as described in Chapter 12, the lattice stresses may also affect the expansion of individual bonds, though the average expansion of the bonds in a given coordination sphere is usually correctly given by eqn (9.15) or (9.17) (Brown *et al.* 1997). One example will serve to show the effect of the lattice on thermal expansion. The mineral grossular, $Ca_3Al_2Si_3O_{12}$ (24944), adopts the garnet structure in which AlO_6

octahedra share corners with $\mathrm{SiO_4}$ tetrahedra to form a complex three-dimensional framework. Within this framework are cavities occupied by the $\mathrm{Ca^{2+}}$ ions. The thermal expansion of the crystal is determined entirely by the expansion of the framework since the $\mathrm{Ca-O}$ bonds cannot expand any faster than the cavity in which the $\mathrm{Ca^{2+}}$ ions are located. The framework expansion is in turn determined by the expansion of the Al–O bonds since the Si–O bonds are essentially rigid. The thermal expansion of the bonds in grossular, shown as filled circles in Fig. 9.4, is therefore constrained to be no larger than the expansion of the Al–O bonds ($S=0.5\,\mathrm{vu}$). The expansion of $\mathrm{Ca-O}$ bond ($S=0.25\,\mathrm{vu}$) is the same as that of the Al–O bond and only about one-third of the value that would otherwise be expected.

While it is possible to derive a simple expression for the thermal expansion of a bond, it is much more difficult to use this result to determine the thermal expansion of a solid. For a simple solid such as NaCl (18189), the macroscopic thermal expansion of the crystal is closely related to the thermal expansion of the bonds, but for more complex structures the motion of the atoms transverse to the bond is also important. Although these transverse vibrations generally give rise to a thermal contraction, their influence is more complex than the thermal expansion of the bonds. Consider the simple system in which an O²⁻ ion forms two collinear bonds to Si⁴⁺ as shown in Fig. 9.5(a). Because the Si-O bonds are strong, they have negligible thermal expansion and can be treated as rigid. However, the O^{2-} ion will undergo a transverse vibration causing it to be displaced from the linear position. This will pull the Si⁴⁺ ions closer together and cause a shortening of the Si... Si distance as shown in Fig. 9.5(b). In most crystals, the mean square transverse amplitude, $\langle A_i^2 \rangle$, of such bridging oxygen atoms is larger than the corresponding amplitude parallel to the bond because the transverse motion is much less restricted than motion along the bond. Figure 9.5(b) shows that if the true length of the Si-O bond is R, the apparent

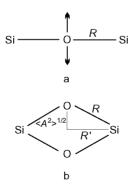


Fig. 9.5. (a) Transverse vibration of the O²⁻ ion in linear Si-O-Si; (b) the average displaced structure of a linear Si-O-Si bond showing how the displacement leads to an apparent bond shortening.

length, R', at a particular temperature is given by

$$R^{\prime 2} = R^2 - \langle A_{\rm t}^2 \rangle. \tag{9.18}$$

For small displacements, the bond shrinkage is $\langle A_t^2 \rangle / 2R$. From eqn (9.9) this leads to a thermal contraction of

$$dR/dT = -k/2RG_t, (9.19)$$

where $G_{\rm t}$ is the force constant for transverse vibrations. The apparent negative thermal expansion shown by some of the strong bonds in Fig. 9.4 can be attributed to the contraction caused by transverse vibrations.

If the Si–O–Si bond is already bent, the transverse motion will cause both expansion and contraction of the apparent bond length depending on the direction in which the $\rm O^{2-}$ ion is displaced (Fig. 9.6(a)), but on average there will be a net contraction. What is more important from a structural point of view is the possibility that the $\rm O^{2-}$ ion will be able to flip to the symmetrically related position on the opposite side of the Si–Si vector as shown in Fig. 9.6(b). This leads to a disorder of the $\rm O^{2-}$ ion around the Si–Si vector which, since it increases the entropy, will be favoured at high temperatures. The result may be a phase change to a structure with higher crystallographic symmetry and a much larger apparent contraction of the Si–O bonds.

From these examples, it is clear that the amplitude of the thermal motion transverse to the bonds will affect the thermal properties of the solid, but in ways that depend on details of the particular structure. It is therefore impossible to provide a universal model for the effects of the transverse thermal motion, the combinations of thermal expansion and thermal contraction must be considered individually for each structure. For most materials the combination results in a net thermal expansion, but there are a few compounds that show a net thermal contraction in one or more directions (Evans 1999).

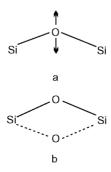


Fig. 9.6. (a) Transverse vibration of the O²⁻ ion in bent Si-O-Si; (b) the disordered bent Si-O-Si bond found at high temperatures.

9.5 The variation of R_0 with temperature

The above analysis of thermal expansion can be used to derive an expression for the variation in the bond valence parameter, R_0 , with temperature. The tabulated values given in Appendix 1 have been obtained from structures measured at relatively low temperatures (200–300 K) and are clearly inappropriate for use when analysing structures determined at much higher temperatures. The bond valence parameters can, however, easily be corrected for temperature by noting that at a higher temperature the bond valence will not change even though the bond has expanded by an amount ΔR . Consequently at higher temperatures eqn (3.1) can be written as

$$S = \exp(((R_0 + \Delta R) - (R + \Delta R))/B), \tag{9.20}$$

where $R + \Delta R$ is the bond length measured at the higher temperature. Thus R_0^T , the value of R_0 to be used at temperature T, is given by (9.21):

$$R_0^T = R_0 + \Delta R = R_0 + (dR/dT)\Delta T.$$
 (9.21)

Here $\Delta T = T - T_{\rm RT}$, $T_{\rm RT}$ being room temperature (~ 300 K). Values of ${\rm d}R/{\rm d}T$ as a function of S can be calculated using eqn (9.15) or read from the solid line shown in Fig. 9.4.

III

Solids



Space and space groups

10.1 Introduction

Parts I and II of this book focused on the chemistry of inorganic compounds but only briefly considered how the atoms might arrange themselves in space to form a solid. The spatial constraints imposed by anion—anion repulsions were discussed in Section 6.2, but in Part III of this book we look at the much more stringent constraints that appear when atoms come together to form a crystal. As will become apparent, these constraints play an extremely important role in the chemistry of inorganic solids.

One of the principal differences between the chemistry of inorganic and organic compounds is that organic compounds generally form discrete molecules whose bonding network is finite in extent. Organic compounds are defined by the structures of their molecules which are stable and remain intact even when the solid is melted or dissolved. A solution of sugar contains the same sugar molecules that were present before the solid was dissolved, and the same molecules will be present when the sugar is recrystallized. On the other hand, when an inorganic compound is melted or dissolved, the bonds are broken and the individual atoms dispersed. NaCl dissolved in water no longer contains Na-Cl bonds, only hydrated Na+ and Cl- ions separated by intervening water molecules. When the solid is recrystallized, each atom has a different set of neighbours than it had before dissolution. Consequently it makes no sense to define an inorganic compound in terms of a molecular structure as no molecules are present. The only way they can be characterized is by the structures of their crystalline solids. Without a crystal there is no compound. It is meaningless to ask if a solution containing Na⁺, Ca²⁺, Cl⁻, and CO₃²⁻ ions is a solution of NaCl and CaCO3 or a solution of Na2CO3 and CaCl2. Only when the crystals have been formed can one refer to an inorganic compound by its chemical formula.

For a crystal to be formed, both the laws of chemistry and the laws of crystallography must be simultaneously satisfied. The chemistry of inorganic compounds cannot therefore be understood without some understanding of crystallography which is the science of how atoms can be arranged in space.¹

¹ Not all solids are crystalline but the majority of inorganic compounds form crystals. Although the ideas developed in the next few chapters refer to crystals, many of them can also be applied to amorphous solids.

The laws of crystallography describe the constraints that restrict the number of ways in which atoms can be bonded to each other in three-dimensional space, particularly, but not exclusively, when they are arranged in an infinite ordered array as found in crystals. Where the laws of crystallography and the laws of chemistry lead to incompatible predictions, a compound cannot be formed, though if the incompatibility is small enough the differences may be accommodated by small violations, particularly of the laws of chemistry. These violations often lead to instabilities, and the instabilities in turn may result in the crystal having unusual properties. It is the conflict between the chemical and crystallographic laws that makes the physics and chemistry of inorganic solids an unexpectedly fertile field for study. Properties such as superconductivity, ferroelectricity, non-stoichiometry, ionic conduction, and the stabilization of unusual oxidation states all have their origin in the conflicting requirements of chemistry and space.

The laws of crystallography are formalized in space group theory which is concisely summarized in the various volumes of International Tables for Crystallography, particularly Vol. A (1996). The basic elements of this theory are covered in most texts on crystallography. This chapter introduces only those aspects of the theory that are essential for understanding the subsequent chapters of this book. Those familiar with space group theory will find some familiar material here, but they will also find some important results that are not discussed in the standard texts (Brown 1997).

10.2 The crystal lattice and translational symmetry

An ideal crystal consists of a group of atoms repeated throughout space at the points of an infinite regular three-dimensional lattice, R(l, m, n), generated from a set of three non-coplanar vectors, a, b, and c (known as the lattice parameters), according to eqn (10.1):

$$\mathbf{R} = l\mathbf{a} + m\mathbf{b} + n\mathbf{c},\tag{10.1}$$

where (l, m, n) is a set of any three integers. A two-dimensional example of such a lattice is illustrated by the wallpaper pattern shown in Fig. 10.1 where the points of the lattice occur at the intersections of the horizontal and vertical lines. The vectors a, b and c in a crystal define a parallelepiped, known as the *unit cell* (outlined in bold in Fig. 10.1), which contains all the information about the arrangement of atoms in the crystal since the unit cells are all identical and pack together like building blocks to fill space. The set of vectors R(l, m, n) represents the translational symmetry elements of the crystal, since translating the crystal by any of the possible vectors R(l, m, n) leaves the crystal unchanged. The presence of the crystal lattice greatly simplifies the description of a solid, since only the structure of one unit cell needs to be described.

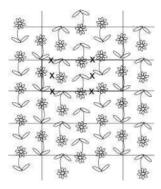


Fig. 10.1. Illustration of a two-dimensional repeating pattern. The repeating unit cell, outlined with heavy lines, contains four symmetry-related flowers. The thin lines outline the lattice of translational symmetry. X marks the intersection of a two-fold axis with the plane of the page.

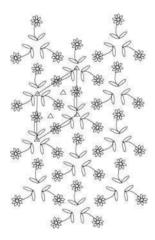


Fig. 10.2. Wallpaper design with a three-fold axis perpendicular to the plane of the page (shown by triangles). The unit cell is outlined. All the flowers are related by symmetry.

The presence of the crystal lattice, however, imposes severe constraints on the arrangement of the atoms within the unit cell. This will be familiar to anyone who has hung a patterned wallpaper such as one of those shown in Figs 10.1 or 10.2. Once the first piece of wallpaper has been hung, the position of the next piece must be chosen so that the pattern flows seamlessly from one piece to the next. This can be seen in Fig. 10.1 where the vertical lines mark the edges of the sheet of wallpaper. Such matching is only possible if the wallpaper pattern has been properly designed. If a flower is divided so that one-half appears on the left-hand side of the sheet, the matching half must appear on the right and must be designed so that the seam is not visible once two adjacent pieces of wallpaper

are in place. This puts a severe constraint on the designer who must ensure that the design flows without a break across the edges of the paper. The corresponding three-dimensional problem of matching the six faces of the unit cell in a crystal is clearly even more restrictive. Each cell shares faces with six neighbouring unit cells, and since the bonding between the atoms is continuous throughout the crystal, opposite faces of the unit cell must exactly match.

An example of how such restrictions work in three dimensions is provided by the perovskite structure shown in Figs 10.3 and 10.4. Crystals of $BaTiO_3$ (23759) are composed of an alternation of the BaO and TiO_2 layers shown

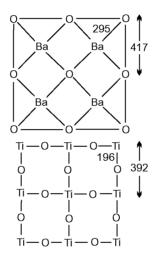


Fig. 10.3. The BaO and TiO₂ layers that compose BaTiO₃. The ideal bond lengths and the corresponding cell lengths are shown in pm.

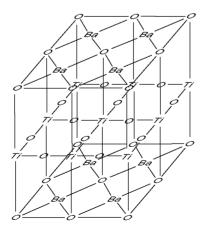


Fig. 10.4. The structure of BaTiO₃ (23759) is composed of an alternation of the layers of BaO and TiO₂ shown in Fig. 10.3.

in Fig. 10.3. If the layers are to form a crystal, the size of the repeating pattern in both layers must be the same, i.e. each layer must have the same lattice parameters. But the repeat distances are determined by the lengths of the Ba-O and Ti-O bonds respectively. These can be calculated from chemical considerations using the network equations, (3.3) and (3.4). Since Ba²⁺ is 12 coordinate, the Ba-O bonds are expected to have valences of 2/12 = 0.17 vu and lengths (from eqn (3.1)) of 295 pm giving a repeat distance of 417 pm for the BaO layer, while the Ti-O bonds formed by the six-coordinate Ti⁴⁺ atom are expected to have valences of 4/6 = 0.67 vu and lengths of 196 pm, giving a repeat of 392 pm for the TiO₂ layer. The two layers are therefore predicted on chemical grounds to have different sizes as shown in Fig. 10.3. Clearly, the only way in which these layers can exist in the same crystal (see Fig. 10.4) is for the Ti-O bonds to be stretched and the Ba-O bonds to be compressed. In the case of BaTiO₃ the strains required to bring the layers to a common repeat distance are sufficient to destabilize the structure. According to the corollary to the distortion theorem (Rule 3.7), the tension in the TiO₂ layer can be relieved by Ti⁴⁺ moving away from the centre of its octahedron. Since all the Ti⁴⁺ ions move in the same direction, this distortion results in BaTiO₃ having an electric dipole moment which can be reversed by an applied electric field, a phenomenon known as ferroelectricity. The resultant large dielectric constant (~10³) makes BaTiO₃ an ideal material for use in capacitors as discussed in Section 13.3.2. This is an example of an unusual physical property which is directly attributable to the constraints of three-dimensional space. The perovskite structure is discussed further in Section 13.3.1.

10.3 Space groups

Space groups describe the different symmetries that a crystal can adopt. To understand the influence of these symmetries on structure, it is useful to pursue the analogy of the wallpaper a little further. The basic repeating design corresponds to the unit cell of the crystal. It is repeated down the length of the wallpaper and, when the wallpaper is hung, it is also repeated across the wall. In some wallpapers, particularly those with geometric designs, the unit cell may have internal symmetry. This is seen in the pattern shown in Fig. 10.1 where the flower is shown both reflected and rotated to create four symmetry-related flowers within the unit cell. It can also be seen in Fig. 10.2 where the three flowers are related by a three-fold rotation symmetry around the points marked with a triangle in one of the unit cells. When internal symmetry is present, the contents of the crystal are completely specified by a portion of the unit cell known as the *asymmetric unit* (the flower in Figs 10.1 and 10.2) since the rest of the unit cell, hence the crystal, can be generated by applying the appropriate symmetry operations.

The complete set of these operations constitutes a mathematical group, G, which, in three dimensions, is known as a *space group*. The symmetry operations

consist of inversions and rotations. Inversion symmetry means that the structure is unchanged if every atom at x, y, z is replaced by an atom at -x, -y, -z. An n-fold rotation axis means that rotating the crystal by $360/n^{\circ}$ around this axis brings the structure into coincidence with itself. In Fig. 10.1 the intersections of the two-fold rotation axes with the plane of the paper are marked by an X within the outlined unit cell. It is easy to see that rotating this pattern by $360/2 = 180^{\circ}$ around any of the X's, or rotating the pattern in Fig. 10.2 by $360/3 = 120^{\circ}$ around any of the triangles, leaves the pattern unchanged. The presence of symmetry restricts the possible arrangements of atoms in a crystal because the symmetry applies to the lattice as well as to the contents of the unit cell.

Only certain symmetry operations are possible in crystals composed of identical unit cells. In three dimensions these are one-, two-, three-, four- and six-fold rotations and each of these axes combined with inversion through a centre to give $\bar{1}$, $\bar{2}$ (= m, mirror plane), $\bar{3}$, $\bar{4}$, and $\bar{6}$ operations. Five-fold rotations and rotations of order 7 and higher, while possible in a finite molecule, are not compatible with a three-dimensional lattice.

In addition, some of the above operations can be combined with translations to give glide planes and screw axes. These symmetry elements are not used in this book, except for a brief mention in Section 11.2.2.5, but are included here for completeness. Screw axes (n_p) are created by combining each of the n-fold rotations with a p/n translation (where p is an integer less than n) along the rotation axis. Glide planes are created by combining the mirror plane $(\bar{2} = m)$ with translations of one-half a lattice translation in the plane. In Fig. 10.1 the different flowers in the unit cell are related by glides.

Only 230 different arrangements of these symmetry operations are possible in three-dimensional space and the properties of the corresponding 230 space groups are listed in International Tables for Crystallography, Vol. A (1996) supplemented by the information given in Appendix 2. Every crystalline solid must necessarily satisfy the constraints imposed by one of these space groups even if it is only P1, the space group that has no internal symmetry.

The symmetry operations, G, of the space group acting on an atom placed at an arbitrary point in space will generate a set of m_G equivalent atoms in the unit cell. Operation of the lattice translations, R, acting on this set generates an infinite array of such atoms, with the finite set of m_G atoms being repeated at each point on the lattice. This is illustrated in Fig. 10.1 in which $m_G = 4$ and each of the rectangles defined by the horizontal and vertical lines represents a unit cell that is identical with the one outlined with heavy lines.

10.4 Special positions

An atom that is repeated m_G times in the unit cell is said to occupy a general position in the crystal, but an atom that lies on a symmetry element such as a mirror plane will be repeated less frequently because the symmetry operation of

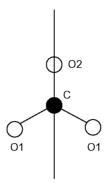


Fig. 10.5. A CO₃ group lying on a mirror plane perpendicular to the page (shown by the vertical line). The two atoms O1 are related by the mirror plane. C and O2 lie on the mirror plane and have site symmetry m (C_s).

this element (in this case the mirror) merely transforms the atom into itself. This is shown for a CO₃²⁻ ion in Fig. 10.5, where the C and O2 atoms lie on a mirror plane perpendicular to the page. These two atoms occur only once while O1 occurs twice, the second O1 atom being related to the first by the mirror plane. Atoms such as C and O2 are said to occupy special positions which are characterized by their point symmetry (in this case m or C_s)² and by their multiplicity, i.e. the number of times an atom placed at that position appears in the unit cell. The two atoms labelled O1 are in general positions related by the mirror plane. They have multiplicity, $m_G = 2$ and no symmetry in their environment (site symmetry = $1 (C_1)$). The atoms labelled C and O2 lie on the mirror plane and have a multiplicity of $m_G/2 = 1$ and a site symmetry of m (C_s) since the environment to the right of C and O2 is the mirror image of the environment to the left. The properties of both the general and special positions for all space groups are listed in International Tables for Crystallography Vol. A (1996), where each general or special position is designated by a letter, known as the Wyckoff letter. The general and special positions are therefore collectively referred to as Wyckoff positions.

Not all symmetry operations generate special positions, only those, such as rotations and inversions, that contain no translational element. We will therefore ignore glide planes and screw axes in the following discussion. The remaining (non-translational) symmetry elements generate a portion of the unit cell, in general larger than the asymmetric unit but smaller than the unit cell, called here the *non-translational unit*. The multiplicities, m_N , used in this chapter and Appendix 2 refer to this unit, whereas the multiplicities, m_G , given in

² The Hermann-Mauguin symmetry symbols widely used by crystallographers are used here to describe point groups as well as space groups as they are easier to interpret than the Schönflies symbols used in spectroscopy. For point groups, the equivalent Schönflies symbol is given in parenthesis.

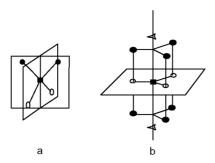


Fig. 10.6. Examples of site symmetries. In (a) the central atom (shown by the square) has site symmetry mm2 (C_{2v} , $m_S = 8$, $m_W = 1$). The two unique ligands (shown by filled and open circles respectively) that form a tetrahedron must lie on the mirror planes ($m_S = 2$, $m_W = 2$). In (b) the central atom has site symmetry $\bar{6} = 3/\text{m}$ (C_{3h} , $m_S = 6$, $m_W = 1$). It may have two ligands that lie on the three-fold axis (shown by triangles, $m_S = 3$, $m_W = 2$), three that lie on the mirror plane (shown by open circles, $m_S = 2$, $m_W = 3$) and six that lie in general positions (shown by filled circles, $m_S = 1$, $m_W = 6$).

International Tables for Crystallography Vol. A (1996) refer to the full unit cell and are integral multiples of m_N .

The symmetry elements that intersect at a Wyckoff position determine its site symmetry. For example, a Wyckoff position that lies on the intersection of two mirror planes has mm2 (C_{2v}) symmetry (Fig. 10.6(a)) while one that lies at the intersection of a mirror plane and a three-fold rotation axis along its normal has 3/m (C_{3h}) symmetry (Fig. 10.6(b)). An atom lying on a general position has no symmetry other than a one-fold axis which is represented by the symbol 1 (C_1).

The symmetry operations of the non-translational unit form a group N which, when applied to an atom in a general position, will generate the m_N equivalent atoms of the non-translational unit. The group of operations N acting on an atom occupying any Wyckoff position can be factored into two subgroups, S and W, where the group S transforms the atom into itself and is thus the point group that describes the site symmetry of the Wyckoff position, and the group W generates m_W equivalent atoms, where m_W is the multiplicity of the Wyckoff position in the non-translational unit. The order of S, m_S , is the number of times that the operations of S transform the atom into itself. Since W * S = N,

$$m_W \times m_S = m_N \tag{10.2}$$

an immediate corollary of which is:

Rule 10.1. In a given space group, all the Wyckoff positions with the same multiplicity, m_W , have site symmetries of the same order, m_S .

³ The symbol 3/m is used here because it is descriptive of the two operations that are being discussed. Conventionally this point group is designated by the equivalent Hermann–Mauguin symbol $\bar{6}$.

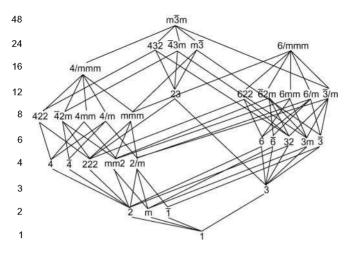


Fig. 10.7. The crystallographic point groups arranged according to their order, m_S , shown on the left, and linked to show sub- and supergroup relations (adapted from International Tables for Crystallography Vol. A, (1996) Table 10.3.2).

A second corollary is:

Rule 10.2. The order of the site symmetry of any Wyckoff position is in inverse proportion to its multiplicity.

International Tables for Crystallography, Vol. A (1996) gives the site symmetries, S, of all the Wyckoff positions. It does not give their multiplicities in the non-translational unit, m_W , so these are given for each space group in Appendix 2. The 32 site symmetries compatible with crystallographic symmetry are shown in Fig. 10.7 together with lines linking sub- and supergroups.

10.5 Matching the special positions to the chemistry

In 1922 Shubnikov proposed his *fundamental law of crystal chemistry* which drew attention to the relationship between the frequencies with which atoms appear in the chemical formula and the multiplicities of the Wyckoff positions they occupy. A similar relationship had been pointed out earlier by Niggli (1918). A more powerful version of Shubnikov's law that reflects the role of symmetry as well as multiplicity can be stated as:

Rule 10.3. Since all the atoms in the chemical formula must exist on one or other of the Wyckoff positions of a crystal, the multiplicity of an occupied Wyckoff position must correspond to the frequency with which the corresponding atom appears in the chemical formula, and the site symmetry of the Wyckoff position must correspond to a possible symmetry of the atom's bonded environment.

In order to simplify the search for a space group that matches the chemical formula, Galiulin and Khachaturov (1994) proposed to use the spectrum of a space group, a number consisting of 10 digits, each digit being the maximum number of atoms that can be placed in Wyckoff positions that have nontranslational multiplicities of 1, 2, 3, 4, 6, 8, 12, 16, 24, and 48 respectively. Thus the spectrum of the space group $Pm\bar{3}m$ is $(2020^{**}0^{**})$ (see Appendix 2), meaning that the space group allows two different atoms to be placed in Wyckoff positions of multiplicity 1 and another two to be placed in Wyckoff positions of multiplicity 3 but none in positions of multiplicity 2, 4, or 16. The * indicates that an indeterminate number of atoms can be placed on Wyckoff positions having multiplicities of 6, 8, 12, 24, and 48 because these positions lie on mirror planes or rotation axes which can accommodate more than one atom on the same special position. The Wyckoff positions of multiplicity 24, for example, all lie on mirror planes, each of which can accommodate several atoms depending on the size of the unit cell. The general position is always the position with the highest multiplicity: in Pm³ m it is the position with multiplicity 48.

The spectra of all 230 space groups are given in Appendix 2. They are listed in order of decreasing symmetry, grouped together according to the non-translational multiplicities of the general positions, m_N , which represents the order of the non-translational unit of the space group. Within each group, the space groups are listed in the reverse order to that found in International Tables for Crystallography, Vol. A (1996). This arrangement, which gives a different ordering from that found in International Tables, is chosen because it is particularly convenient to use when searching for the matching space group that has the highest symmetry (Rule 3.1) as discussed in Section 11.2.2.4.

10.6 The symmetry of bonded neighbours

In Chapter 6 it was shown that the coordination number adopted by a given cation is determined *inter alia* by the repulsion between its ligands. The arrangement that minimizes this repulsion is normally the one with the highest symmetry. For six coordination it is the octahedron which has the highest possible crystallographic site symmetry, $m\bar{3}$ m (O_h with $m_S=48$, Fig. 10.7). For four coordination it is the tetrahedron which has the site symmetry $\bar{4}3$ m (T_d with $m_S=24$). Other high-symmetry arrangements are the 12-coordinate cuboctahedron ($m\bar{3}$ m), the three-coordinate triangle ($\bar{6}2$ m (D_{3h}) with $m_S=12$), and the eight-coordinate cube ($m\bar{3}$ m). Although the cube is the eight-coordination environment with the highest symmetry, the square antiprism (4 mm (C_{4v}), $m_S=8$) minimizes the repulsion between ligands but at the cost of lowering the symmetry. Other coordination numbers such as 5, 7, and 9 are encountered less frequently since they can only be accommodated by

low-symmetry environments in which the ligands cannot all be crystallographically equivalent.

When a cation occupies a Wyckoff position of particularly high symmetry, its bonded neighbours may also be required to lie on special positions. For example, a cation that occupies a site of m $\bar{3}$ m symmetry for which $m_S = 48$ would have 48 neighbours if the neighbours occupied a general position. This is clearly impossible since, as shown in Chapter 6, few cations have coordination numbers higher than 12. If the cation is octahedrally coordinated, it has only six neighbours and each neighbour must therefore have a site symmetry of order at least 48/6 = 8. This requires that they be placed on the three four-fold axes which pass through the cation and that they have a site symmetry of at least 4 mm (C_{4v}). Their site symmetry may be higher than this if, for example, they also lie on a mirror plane that does not pass through the cation site, but it cannot be lower than 4 mm. Figure 10.6(b) illustrates the simpler case of a triangle of neighbours (open circles) around a cation (rectangle) at a site of $\bar{6}$ (C_{3h}) symmetry which has $m_S = 6$. Since there are only three open circle ligands, they must have site symmetry of order 6/3 = 2. The only possibility is that they lie on the mirror planes as shown in Fig. 10.6(b). The symmetry relations implied by these constraints for cations with triangular, tetrahedral, and octahedral coordination are summarized in Tables 10.1-10.3 which list the minimum site symmetries and multiplicities that the neighbours of a cation can have when the cation occupies a site of given crystallographic symmetry.

Table 10.1 Subgroups for trigonal planar coordination

Central atom		Ligand site symmetry and	
Order	Site symmetry	multiplicity	
12	62 m	$mm2^3$	
6	32	2^{3}	
6	$\bar{6} (= 3/m)$	m^3	
6	3 m	m^3	
4	2/m	$2+1^{2}$	
4	mm2	$mm2 + m^2$	
3	3	1^3	
2	2	$2+1^{2}$	
2	m	$m + 1^2$	
1	1	1 + 1 + 1	

Column 1 gives the order of the site symmetry of the central 3-coordinate atom. Column 2 gives the site symmetry of the central atom. Column 3 gives the minimum site symmetry of the ligands, the superscript giving the number of symmetry related ligands with this site symmetry. The ligand symmetry may be higher than that shown if the ligand also lies on symmetry elements that do not intersect the position of the central atom.

 Table 10.2
 Subgroups for tetrahedral coordination

Central atom		Ligand site symmetry and	
Order	Site symmetry	multiplicity	
24	43 m	3m ⁴	
12	23	3 ⁴	
8	$\bar{4}2\mathrm{m}$	m^4	
6	3m	$3m + m^3$	
4	$\bar{4}$	14	
4	222	14	
4	mm2	$m^2 + m^2$	
3	3	$3+1^{3}$	
2	2	$1^2 + 1^2$	
2	m	$m + m + 1^2$	
1	1	1+1+1+1	

See Table 10.1.

 Table 10.3
 Subgroups for octahedral coordination

Central atom		Ligand site symmetry and	
Order	Site symmetry	multiplicity	
48	m3 m	4mm ⁶	
24	432	4^6	
24	$m\bar{3}$	$\mathrm{mm}2^6$	
16	4/mmm	$4\mathrm{mm}^2+\mathrm{mm}2^4$	
12	$\bar{3}2\mathrm{m}$	m^6	
12	23	2^{6}	
8	$\bar{4}2\mathrm{m}$	$mm2^2 + 2^4$	
8	$\bar{4}2\mathrm{m}$	$mm2^2 + m^4$	
8	422	$4^2 + 2^4$	
8	4 mm	$4^2 + m^4$	
8	4/m	$4^2 + m^4$	
8	mmm	$mm2^2 + m^4$	
8	mmm	$mm2^2 + mm2^2 + mm2^2$	
6	32	1^{6}	
6	$\frac{\bar{3}}{4}$	1^6	
4	$\bar{4}$	$2^2 + 1^4$	
4	4	$4+4+1^{4}$	
4	222	$2^2 + 1^4$	
4	222	$2^2 + 2^2 + 2^2$	
4	mm2	$mm2 + mm2 + 1^4$	
4	mm2	$m^2+m^2+m^2$	
4	2/m	$m^2 + 1^4$	
4	2/m	$m^2 + m^2 + 2^2$	
3	3	$1^3 + 1^3$	
2 2	2	$2+2+1^2+1^2$	
2	m	$m+m+m+m+1^2$	
2	m	$m + m + 1^2 + 1^2$	
1	1	1+1+1+1+1+1	

See Table 10.1.

SUMMARY 133

10.7 Summary

The principle of maximum symmetry requires that the crystal structure adopted by a given compound be the most symmetric that can satisfy the chemical constraints. We therefore expect to find high-symmetry environments around atoms wherever possible, but such environments are subject to constraints such as the relationship between site symmetry and multiplicity (eqn (10.2)) and the constraint that each atom will inherit certain symmetries from its bonded neighbours. The problems that arise when we try to match the symmetry that is inherent in the bond graph with the symmetry allowed by the different space groups are discussed in Section 11.2.2.4.

Modelling inorganic structures

11.1 The problem of a priori modelling

The problem of modelling the structure of an inorganic crystal is first to determine which chemically possible structures are compatible with three-dimensional space and then to determine which of these has the lowest free energy. With all our extensive knowledge of crystal structure and interatomic forces, it is surprising that our ability to predict crystal structures from first principles is still so limited, but the large number of compounds that are known to exist with more than one structure (polymorphic compounds) indicates that many structures must have similar energies and that it will be difficult to determine which is the most stable under a given set of conditions. If we had a quick way of calculating the energy of any given configuration of atoms, we could, in principle, calculate the energy for all possible configurations, but the number of such configurations that we would need to examine, even for relatively simple structures, is prohibitively large. We must therefore look for ways that take us directly to the most likely candidate structures.

There are three distinct steps in modelling a crystal. The first step is to determine the *topology* or *structure*, that is the approximate arrangement of the atoms in space as indicated by the way atoms are bonded to each other. The second is to refine the *geometry*, i.e. to determine the exact positions of the atoms and the distances between them. The third step is to compare different structures with the same composition to determine their *relative stability*.

In certain favourable cases it is possible to determine the topology of the crystal from first principles, but no general solution has been found. In practice trial topologies are assumed because they are known or thought to exist. Only the second step, refining the geometry, can be performed with any reliability and several methods are available. These include minimization of the energy calculated using quantum mechanics or semi-classical two-body potentials, or the minimization of the difference between the modelled and predicted bond valences. The third step, comparing the relative stabilities of competing structures, is difficult because the energy differences between different structures are frequently smaller than the accuracy with which the energies can be calculated (see, for example, Woodward 1997b).

This chapter reviews some of the different approaches that can be taken to modelling. The subject is large enough to deserve a book of its own, so the treatment here is necessarily brief. Emphasis is given to those methods that make use of bond valences. Other techniques are described briefly with references given to more comprehensive treatments.

11.2 Determining the topology

Although there is no single way in which the topology, or structure, of an inorganic crystal can be determined, there are a few principles that underlie many of the methods that are used (O'Keeffe and Hyde 1982). Some of these may seem self-evident but, since they can easily be overlooked, there is an advantage in making them explicit.

The first rule is the *Principle of electroneutrality* (Rule 11.1) which restricts the chemical composition of inorganic compounds to those in which the net charge is zero. In the context of the bond valence model this rule can be stated as:

Rule 11.1 (Principle of electroneutrality). Since the sum of all atomic valences is zero, the sum of the atomic valences of the cations is equal to the sum of the atomic valences of the anions.

The second principle is a rule that is derived from the properties of the bond graph and is known as the *Coordination number rule* (Rule 6.1). An alternative statement of the rule from that given in Section 6.3 is:

Rule 6.1 (Coordination number rule). Since each bond starts on a cation and ends on an anion, the sum of the coordination numbers of the cations equals the sum of the coordination numbers of the anions, and both are equal to the total number of bonds in the formula unit.

For a compound with the generic formula A_aX_x this leads to the corollary:

Rule 11.2 (Corollary 1). The ratio of the average coordination number of the cations, $\langle N_a \rangle$, to the average coordination number of the anions, $\langle N_x \rangle$, is the same as the ratio of the number of anions, x, to the number of cations, x.

This is expressed algebraically by eqn (11.1):

$$\langle N_a \rangle / \langle N_x \rangle = x/a.$$
 (11.1)

This result can be used to see whether an assumed cation coordination number leads to an acceptable anion coordination number. For example, if Al^{3+} in Al_2O_3 is six coordinate, the O^{2-} ions will be four coordinate but if Al^{3+} is four coordinate, the O^{2-} ions will be only 2.67 coordinate on average. The principle of maximum symmetry favours the first choice as the second requires at least two different types of O^{2-} ion.

A second corollary can be stated (cf. O'Keeffe and Hyde 1984):

Rule 11.3 (Corollary 2). Compounds that have a high anion content will stabilize high cation coordination numbers.

The third principle is the *Principle of maximum symmetry* that plays a major role in deciding between different possible structures as the example given under Rule 11.2 shows. This principle has been previously given as Rule 3.1:

Rule 3.1 (Principle of maximum symmetry). As far as allowed by chemical and geometric constraints, all atoms and all bonds in a compound will be chemically and geometrically indistinguishable.

The fourth principle is the *Principle of close packing* (Rule 11.4) which relates to the distribution of cations and anions:

Rule 11.4 (Principle of close packing). Like ions tend to lie on close packed lattices, since this arrangement minimizes their repulsive energy when they are confined to a fixed volume.

Close packing, which is described in more detail in Section 11.2.1.2, gives not only the densest packing of spheres but also represents the arrangement of lowest energy when an array of like charges is confined to a fixed volume. This rule not only applies separately to the cations and the anions in ceramics, it also applies to the arrangement of the atoms in a metal. One consequence is that the same cation lattices are found in both metals and in ceramic materials (O'Keeffe and Hyde 1985).

A final principle is *Shubnikov's fundamental law of crystal chemistry* (Rule 10.3) paraphrased as:

Rule 10.3 (Shubnikov's fundamental law). Atoms will occupy Wyckoff positions in the crystal that are compatible in both multiplicity and symmetry with the bond graph.

This rule is the basis of the space group method discussed in Section 11.2.2.4.

The derivation of the topology is the first and most important step in modelling, since once we know the topology we know also the bond network, the unit cell size, and the space group (or at least one of its supergroups). The following sections explore some of the ways crystal topologies have been modelled. They are discussed under two broad classes, depending on whether they start by specifying the spatial constraints or the chemical constraints.

11.2.1 Space-based approaches

The ultimate space-based approach is to explore systematically every possible spatial arrangement of the atoms in the formula unit and to determine which has the lowest energy. The energy may be calculated using quantum mechanics, but it is more usual in complex solids to use two-body potentials where the

calculation is classical and much simpler (Catlow 1997). It is, however, impractical to examine every possible configuration that the atoms might adopt so a strategy is needed to find a route that leads directly to the energy minimum.

Two possible space-based schemes are the random structure approach and the lattice method. In the first, the atoms are placed in random positions to form an initial structure containing no chemical information. The configuration of the atoms is then altered in such a way as to better match a pre-selected set of chemical or physical constraints. In the second approach the cations and anions are separately arranged on lattices that minimize the electrostatic repulsions between the (like) ions. The lattices are then merged by placing the anion lattice in the cavities of the cation lattice and vice versa.

11.2.1.1 Random structure approaches

In these methods, the desired target structure is characterized by one or more desirable properties such as a low potential energy. A number of random trial structures are proposed and a cost function is calculated. The cost function measures how far the current configuration is from having the desired properties. The goal in all these methods is therefore to lower the cost function by changing the configuration of atoms until the global minimum is reached. The energy is an obvious choice for the cost function but involves extensive computation since the summation has to include every atom pair in the (infinite) crystal. An alternative is to use an empirical cost function that involves only nearest neighbours. Such a function might be designed, for example, to prevent atoms from overlapping, to favour the expected coordination number, or to minimize the difference between the bond valence sum and the atomic valence. Empirical cost functions are particularly useful in the early stages when a large number of configurations must be examined.

The difficulty with this procedure is that simple refinement routines, such as simplex or least squares, lead only to the nearest minimum in the cost function which is unlikely to be the global minimum. The refinement procedure therefore has to be one that randomly samples different parts of configuration space so as to be able to reach different minima, ultimately selecting the global minimum. Two refinement methods have been proposed, simulated annealing and the genetic algorithm.

In simulated annealing the atoms are made to simulate the random motions they would undergo during a period of annealing at high temperature. This is followed by lowering the notional temperature through the freezing point. In practice small random changes are made to the atomic positions at each step in the calculation. Any configuration that lowers the cost function is accepted but those that raise it are generally rejected. In order to explore a wide range of configurations, changes which increase the cost function are not automatically rejected but, with a certain probability, are accepted. The process is then iterated to convergence with the probability of the rejection of an increased cost

function being steadily raised in order to simulate a gradual reduction in temperature. Pannetier *et al.* (1990) have described simulated annealing using a cost function based on the deviations of the bond valence sums from the atomic valence, with an additional term to represent the repulsion experienced by like ions when they get too close together. They found that they could reproduce the observed structures of a number of moderately complex compounds. In some cases, they found that different structures could be obtained for the same compound by varying the cooling conditions, but even so they were not always able to reproduce the observed structure, presumably because, in these cases, a more sophisticated cost function or annealing procedure is needed.

Woodley *et al.* (1999) have described an alternative approach to finding the global minimum using a genetic algorithm. A number of arbitrary trial structures constitute the first (parent) population and these are combined in pairs to form a new generation of child structures, each child inheriting characteristics from both its parents. The children are then allowed to breed a third generation, with breeding preference being given to the fittest children, i.e. those having the lowest cost function. The procedure maintains genetic diversity in the population by cross-breeding as well as by creating occasional mutations designed to reach configurations not contained in the original parent population. Because of the bias given toward the fitter structures, the population gradually converges towards the most fit structure, i.e. the structure with the lowest cost function. This method has been used to successfully derive a number of simple structures.

Even though these methods have shown some success, they require that the box containing the trial structure have cyclic boundary conditions to keep the calculations to a manageable size. This imposes an artificial translational symmetry on the structure. If the results are to converge to the observed structure, the box should either have the size and shape of the observed unit cell or else it should be sufficiently large that a small crystal can spontaneously form within it.

Random structure methods have proved useful in solving structures from X-ray powder diffraction patterns. The unit cell can usually be found from these patterns, but the normal single-crystal techniques for solving the structure cannot be used. A variation on this technique, the reverse Monte Carlo method, includes in the cost function the difference between the observed powder diffraction pattern and the powder pattern calculated from the model (McGreevy 1997). It is, however, always necessary to include some chemical information if the correct structure is to be found. Various constraints can be added to the cost function, such as target coordination numbers or the deviation between the bond valence sum and atomic valence (Adams and Swenson 2000b; Swenson and Adams 2001).

11.2.1.2 Lattice models

These methods start with models that already contain some physical information. The cations and anions are separately arranged on two lattices having



Fig. 11.1. A close packed layer of atoms. A indicates the position of the atoms in this layer, B and C are possible positions for atoms in adjacent layers.

translational repeat distances that correspond to the unit cell of the crystal. For hard ions, the arrangement that minimizes the electrostatic energy of each lattice (given a fixed volume) is one that is close packed. There are two basic arrangements of close packed lattices, face centred cubic (FCC) and hexagonal close packed (HCP) as described below. Each of these lattices has cavities (cages in topological notation) which provide ideal sites for the counterion. The aim is to find mutually compatible cation and anion lattices such that the ions in one lattice map onto the cage points of the other and vice versa. The difficulties arise in trying to match the stoichiometry and to ensure that the cages of one lattice provide the correct coordination number for the ions on the other lattice.

Close packed structures are generated by stacking two-dimensional hexagonal (honeycomb) nets of atoms over each other so that the atoms of one net lie over the centre of a triangle of atoms on the net below (points B and C in Fig. 11.1). Since there are two such triangles for each atom in the net, there are two possible positions in which the next net can be placed. If the position of the first net is labelled A, then the next net can occupy either the position labelled B or the position labelled C in Fig. 11.1. Any stacking sequence of these layers is allowed providing that no two adjacent nets share the same letter. An infinity of different sequences is thus possible but the principle of maximum symmetry predicts that only those of high symmetry, e.g. with short repeat sequences, will normally be observed. The HCP lattice has the shortest possible sequence containing only two layers (ABABAB) but it can only be mapped into a space group of relatively low symmetry (P63/mmc) requiring three variable parameters. The FCC lattice has a slightly longer sequence of three layers (ABCABCABC) but can be mapped into a high-symmetry cubic space group $(Fm\bar{3}m)$ with only one variable parameter (the unit cell length). Thus both FCC and HCP lattices are expected to be found under appropriate circumstances and both are examined here.

The FCC lattice has three cage points, one surrounded by an octahedron of ions, the other two surrounded by tetrahedra. An FCC lattice of counterions can be placed so as to occupy any one of these three cages. Placing an FCC anion

¹ As has been pointed out by O'Keeffe and Hyde (1985), the cation lattices of many of these structures are found in the structures of metal crystals, the delocalized conduction electrons, which provide the cohesive force, concentrating in the cages where their potential energy is lowest (Zuo *et al.* 1999). These low potential cages therefore also provide good sites for anions.

lattice at the octahedral cage points of an FCC cation lattice gives the NaCl (18189) structure with six-coordinate Na⁺ and Cl⁻ (Fig. 1.1). Placing it at one of the tetrahedral cage points gives the sphalerite (ZnS, 60378) structure with four-coordinate Zn²⁺ and S²⁻. Placing FCC anion lattices on both the tetrahedral cage points of an FCC cation lattice gives the fluorite structure (CaF₂, 29008) with four-coordinate F⁻ and eight-coordinate Ca²⁺. Since the tetrahedral and octahedral cage points share faces, it is generally not possible to place anion lattices simultaneously at both octahedral and tetrahedral cage points.

The HCP lattice has two tetrahedral cage points and two octahedral cage points. The octahedral cage points share faces in columns along the hexagonal axis so only half of them can usually be occupied. Similarly, the two tetrahedral cages also share faces and cannot both be occupied. Placing an anion HCP lattice at one tetrahedral cage point of the cation HCP lattice gives the wurtzite (ZnO, 67454) structure (see Section 2.6 and Fig. 2.7).

Compounds of stoichiometry AX_2 with six-coordinated A require (according to eqn (11.1)) that X be three coordinate. Since none of the close packed lattices have cage points with three coordination, these structures are less simple. The rutile (202240) and anatase (202242) forms of TiO_2 are based on HCP and FCC lattices of Ti^{4+} respectively, but fitting the O^{2-} ions into positions of three coordination results in distortions that lower the symmetry. An alternative derivation of these structures is described in Section 11.2.2.4 below.

Not all structures are based on close packed lattices. Ions that are large and soft often adopt structures based on a primitive or body centred cubic lattice as found in CsCl (22173) and α -AgI (200108). Others, such as perovskite, ABO₃ (Fig. 10.4), are based on close packed lattices that comprise both anions and large cations. The larger and softer the ions, the more variations appear, but the lattice packing principle can still be used. Santoro *et al.* (1999, 2000) have shown how close-packing considerations combined with the use of bond valences can give a quantitative prediction of the structure of BaRuO₃ (10253).

The ions do not have to be simple ions. The same principles apply to the packing of complex ions though identification of the atoms that make up the complexes requires prior chemical knowledge and so properly belongs under the heading of chemical-based methods. A discussion of lattices of complex ions is deferred to Section 11.2.2.2.

The lattice approach has also been used for the systematic description of inorganic crystal structures (Wells 1975, pp. 119–55; Hyde and Andersson 1989, pp. 6–49), but the method is not just geometric and descriptive. It has a sound physical basis and can therefore be used for structure modelling.

11.2.2 Chemistry-based approaches

Chemistry-based approaches start by postulating a structure that satisfies the rules of chemistry and then look for ways in which this structure can be mapped into three-dimensional space. The chemical constraints are the ones that

determine which atoms are nearest neighbours and therefore determine the short-range order. The long-range order is determined primarily by spatial constraints. The question that needs to be answered is how can the bond graph be expanded to form an extended bond network in three-dimensional space? In the space-based approaches described in Section 11.2.1, both long- and short-range orderings are developed simultaneously, but in the chemistry-based approaches the short-range order is developed first through the construction of a bond graph of the kind introduced in Section 2.5. This is then expanded into an infinite network in three-dimensional space if such an expansion is possible. If there is more than one such expansion, the principle of maximum symmetry will determine which network will be observed. If there is no such expansion, the compound does not exist.

Central to the chemistry-based approaches is the Hierarchical principle (Hawthorne 1985) which states:

Rule 11.5 (Hierarchical principle). When generating a chemical structure, the strongest bonds are formed first, followed by the others in decreasing order of their valence.

This principle is appropriate for modelling because it follows the chemical process by which solids are formed in nature. The process can be divided into three stages. The pre-crystallization stage occurs while the compound is still in the form of a liquid melt or solution. As the liquid cools, the first species to appear are strongly bonded finite complexes or molecules. At this stage the weaker bonds are still labile so the complexes and molecules, while retaining their integrity, remain free to move through the liquid.

The second stage occurs when the complexes and ions are connected by weaker bonds into a rigid infinite network. This is the stage that determines the long-range order in the solid, and hence determines its space group and lattice parameters. This step may, in some cases, occur in two or three steps if the network is initially infinitely connected only in one or two dimensions, requiring further cooling to generate the full three-dimensional network. Linking the complexes in only one or two dimensions gives rise to viscous liquids as discussed in Sections 5.6 and 5.7.

The third stage is the post-crystallization stage when the weakest bonds are formed. Since the solid has already crystallized at this stage, these weak bonds must accommodate themselves to the existing bond network. This stage is not independent of the second stage, since the structure formed when the compound solidifies must have cavities capable of accommodating the weakly bonding ions. Thus the weak ions may influence the choice of the long-range structure, but ultimately they find themselves in cavities which do not necessarily provide ideal bonding conditions.

A good example of these three stages is provided by garnet which has the generic formula $A_3B_2(XO_4)_3$ and which crystallizes in a high-symmetry cubic structure. Typical examples are $Mg_3Al_2(SiO_4)_3$ (71892) and $Ca_3Al_2(SiO_4)_3$

(24944). The Si-O bonds (1.00 vu) form at stage 1, the long-range order (stage 2) occurs when the Al-O bonds (0.50 vu) form since these link the SiO₄ groups into a three-dimensional network. The resulting structure contains eight-coordinate cavities whose size is fixed by the Al-O and Si-O bonds. The cavities are too small for Ca²⁺ which must be compressed to fit in the available space (its bond valence sum is 2.51 vu), but they are too large for Mg²⁺ (its bond valence sum is 1.72 vu). In accordance with the predictions of the distortion theorem, Mg²⁺ moves away from the centre of the cavity and is found disordered over a number of possible sites surrounding the cavity centre.

The weak cations therefore may determine some of the characteristics of the network, as was pointed out for silicate minerals in Section 4.6, but their local environments, specifically the connections they form in the bond graph, are determined by the anions that form the surface of the cavity. While those parts of the bond graph that correspond to the first two stages of crystallization are primarily driven by chemistry and may reasonably be predicted *a priori* from chemical considerations alone, the bonds formed at the third stage cannot be predicted without a knowledge of the three-dimensional topology generated during crystallization.

The three stages of bond formation are not present in all compounds. Binary compounds like NaCl (18189) only show the second stage, the stage which all materials must undergo when they solidify. Since inorganic compounds can only be characterized by the structures of their crystalline solids, the second stage determines which compounds can exist.

11.2.2.1 Creating the bond graph

The first step in any chemical approach to crystalline structure is to determine the short-range order, i.e. which atoms are bonded. The most convenient way of doing this is by means of the bond graph described in Section 2.5. In many cases all or most of the bond graph can be determined from first principles, since, except for the weakest bonds created in the post-crystallization stage, the bond graph is determined by the rules of chemistry, particularly the hierarchical principle (Rule 11.5), the valence matching principle (Rule 4.2), and the principle of maximum symmetry (Rule 3.1).

To construct a bond graph, the atoms of the formula unit are listed and their bonding strengths determined using the methods described in Sections 4.2 and 4.3. According to the hierarchical principle bonds are then drawn between the cations and anions that have the largest bonding strengths, the bonding strengths serving as targets for the valences of the bonds while at the same time maintaining the highest symmetry. The first set of bonds drawn will link some of the atoms into complexes, frequently anionic complexes such as SO_4^{2-} or molecules such as H_2O . The atoms forming the complex are then replaced by the complex itself which is inserted at the appropriate place in the list according to its bonding strength. The process is then repeated until all the bonds have been

$$\begin{array}{c} 2.88 \\ \text{Na} & \begin{array}{@{}@{}@{}@{}@{}} & \text{CI} \\ (m\overline{3}m) & (m\overline{3}m) \\ 22 & \\ \end{array}$$

$$\begin{array}{c} 3.56 \\ \text{Cs} & \begin{array}{@{}@{}@{}@{}} & \text{CI} \\ (m\overline{3}m) & (m\overline{3}m) \\ 22 \\ \end{array}$$

$$\begin{array}{c} b \\ \text{Zn} & \begin{array}{@{}@{}@{}@{}} & \text{O} \\ (\overline{4}3m) & (\overline{4}3m) \\ 22 \\ \end{array}$$

Fig. 11.2. Bond graphs of (a) NaCl (18189), (b) CsCl (22173), and (c) ZnO (67454). In this and other bond graphs in the chapter, the spectrum and the highest possible crystallographic site symmetry allowed by the graph is shown but these site symmetries may not be mutually compatible.

assigned, or at least those bonds necessary to define the three-dimensional framework formed at stage $2.^2$

A simple example is given by the construction of the bond graph of NaCl (18189) described in Chapter 3. Creating the bond graph in this case is straightforward since there is only one cation and one anion (Fig. 11.2(a)). The only question is, how many bonds should be drawn between them? Na⁺ has a cation bonding strength of 0.16 vu and Cl has an anion bonding strength of 0.14 vu (Appendix 4). The two ions are well matched and will form either 6 (=1/0.16) or 7 (=1/0.14) bonds with each other. The principle of maximum symmetry favours six coordination since, as shown in Section 10.5, it is not possible for seven bonds to be symmetrically equivalent in a crystal. NaCl is therefore predicted to have the bond graph in which each Na⁺ cation forms bonds to six Cl⁻ anions and vice versa. The bond graphs for CsCl (22173, Fig. 11.2(b)) and ZnO (67454, Fig. 11.2(c)) can be drawn in the same way, taking into account the different bonding strengths of Cs and Zn (Section 6.5). Bond graphs of binary compounds with coordination numbers greater than 8 cannot be mapped into three-dimensional space and therefore such compounds cannot exist, coordination numbers of 5 and 7 are unlikely according to the principle of maximum symmetry and coordination numbers of 2 and 3 do not give infinitely connected three-dimensional structures.

² It may not always be possible to assign the weak bonds formed, e.g. by alkali metals both because they are numerous and because their connections are determined more by the constraints of three-dimensional space than by the principle of maximum symmetry.

The perovskite SrTiO₃ (210256) contains two kinds of cation. The cation bonding strengths of Sr²⁺ (0.23 vu) and Ti⁴⁺ (0.67 vu), taken from Appendix 4, indicate that the strongest bonds will be formed by Ti⁴⁺, which is well matched to O²⁻ with an anion bonding strength of 0.5 vu. According to the hierarchical principle, the Ti-O bonds will be formed first. The cation bonding strength of Ti⁴⁺ suggests a coordination number of 6 while the O²⁻ bonding strength suggests a coordination number of 8. A coordination number of 6 can result in a higher-symmetry environment since it maintains the equivalence of the three O²⁻ atoms, so two bonds are drawn between Ti⁴⁺ and each of the three O²⁻ ions, giving each bond a valence of 0.67 vu (Fig. 11.3 where Sr²⁺ is represented by A and Ti⁴⁺ by B). At this point the Ti⁴⁺ and O²⁻ ions are linked to form the TiO_3^{2-} complex anion whose bonding strength can be calculated by dividing its charge (-2) by the number of bonds the O^{2-} ions are expected to form with Sr^{2+} . Assuming that each O^{2-} ion forms four bonds, two to Ti^{4+} and two to Sr^{2+} , the bonding strength of the complex is $2/(3 \times 2) = 0.33$ vu since there are three atoms, each of which can form two external bonds of 0.33 vu. Although not related to the construction of the bond graph, it is worth noting that each of the three O²⁻ ions bonds to two different Ti⁴⁺ ions suggesting even at this stage that the TiO₃ complex is connected into a three-dimensional network of corner shared octahedra. Other arrangements, such as a chain of face-sharing octahedra, are also consistent with the graph and are found in some barium titanates where they are favoured by spatial constraints.

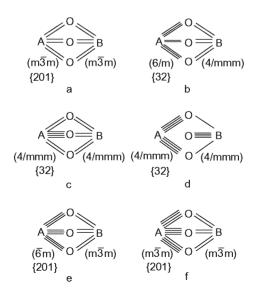


Fig. 11.3. Possible bond graphs of ABO₃ with 6-coordinate B, (a) 6-coordinate A, (b) 8-coordinate A, (c) a second graph for 8-coordinate A, (d) a third graph for 8-coordinate A, (e) 9-coordinate A, (f) 12-coordinate A.

The bonding strength of TiO₃²⁻ thus favours six coordination around Sr²⁺ but the bonding strength of Sr²⁺ favours nine coordination so the correct choice of coordination number is not obvious. A selection of possible bond graphs is shown in Fig. 11.3. Eight coordination is not favoured since it destroys the equivalence of the three O atoms (Figs 11.3(b), (c), and (d)). Six, 9 and 12 coordination retain this equivalence, but 9 coordination (Fig. 11.3(e)), which is close to the expected coordination number for Sr²⁺, does not allow the Sr-O bonds to be crystallographically equivalent since a site symmetry of order 9 is not possible in crystals (Fig. 10.7). Six and 12 coordination (Figs 11.3(a) and (f)) both correspond to possible high crystallographic symmetries but, as shown below, only for 12 coordination is it possible to find a space group in which all Sr-O bonds remain equivalent. On the other hand, neither 6 nor 12 coordination is favoured by the bonding strengths. The choice is not obvious and all six of the graphs shown in Fig. 11.3 can be found among the ABX₃ compounds depending on the relative sizes of the different ions.

Chemical considerations favour eight coordination for Sr^{2+} , but which of the graphs, Figs 11.3(b), (c), or (d), is the most symmetric? Rao and Brown (1998) proposed that the entropy, defined by eqn (11.2), can be used as a measure of the degree of symmetry in these cases:

$$Entropy = -\sum s_{ij} \ln(s_{ij}). \tag{11.2}$$

In this equation s_{ij} is the ideal bond valence calculated using the network equations, (3.3) and (3.4), and the summation is over all the bonds in the graph. Interestingly the entropy of a particular graph depends not only on its topology but also on the atomic valences of the ions, since the values of s_{ij} are sensitive to the ionic charges. Rao and Brown found that the entropy of the graph in Fig. 11.3(b) is marginally larger than that of Fig. 11.3(c) for $A^+B^{5+}O_3$ (2.988 and 2.981 respectively) and $A^{2+}B^{4+}O_3$ compounds (4.384 and 4.354 respectively), but that for $A^{3+}B^{3+}O_3$ compounds the highest entropy graph is the one shown in Fig. 11.3(d) (5.021 against 4.997 and 4.932 for Figs 11.3(b) and (c) respectively). These values are sufficiently similar that none of the graphs can be summarily ruled out. Consequently all three are further developed in the Section 11.2.2.4 which discusses how to find the space group that can best accommodate these graphs.

11.2.2.2 Fundamental building blocks

The fundamental building block approach is similar to the lattice model described in Section 11.2.1.2 but uses the chemical information derived from the bond graph to define complex ions. The crystal structure is assumed to be composed of building blocks constructed of the strongly bonded groups of atoms formed during stage 1 of crystallization (or possibly stage 2 if the blocks are composed of infinite chains or sheets). They usually carry a positive or negative charge and pack together in a way that brings cationic and anionic blocks into contact.

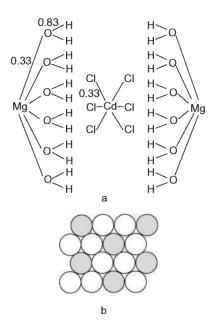


Fig. 11.4. (a) The bond graph of $[Mg(H_2O)_6]_2CdCl_6$ (26368) in which the H...Cl bonds have not been assigned, (b) close packed layers. The open circles are cations, the filled circles are anions.

A simple example is provided by the structures of $[Mg(H_2O)_6]_2CdX_6$ where X = Cl (26368) and Br (49915) (Brown and Duhlev 1991). The bond graph can easily be completed to the end of stage 1 as shown for the chloride in Fig. 11.4(a). Completing the graph to show the hydrogen bonds between H and Cl is not possible because there are too many similar ways in which these connections can be made and the observed structure will depend on the packing of the three fundamental building blocks, two blocks of $[Mg(H_2O)_6]^{2+}$ and one of $CdCl_6^{4-}$. Both types of block have approximately the same size and can therefore be expected to form a close packed array in which each ion has 12 neighbouring ions. In order to provide the largest number of contacts between cations and anions, the complex anion should be surrounded only by complex cations. From eqn (11.1) it is clear that if each anion has 12 cation neighbours, each cation will have, on average, six anion neighbours. The remaining six neighbours must therefore be cations. With this information it is easy to see that the close packed layers must have the structure shown in Fig. 11.4(b).

The two most likely stackings of these layers would appear to be HCP and FCC as discussed in Section 11.2.1.2. Unfortunately the two-layer HCP stacking does not preserve the crystallographic three-fold axis and necessarily leads to an orthorhombic or monoclinic structure. The three-layer FCC stacking permits the space group to be $R\bar{3}$ which gives site symmetries of $\bar{3}$ to Cd^{2+} and

 ${
m Mg}^{2+}$ respectively. It is however possible to maintain the three-fold symmetry of the hexagonal layer with the sequence AA. While this does not give a close packed array, it is permitted when the ions are large and may be favoured if it leads to a high-symmetry structure. In this stacking, each ion has eight neighbours. However, to ensure the maximum contact between anions and cations alternate layers must be shifted. By placing the anions of one layer over the cations of the layer below an AA' stacking is achieved in the space group P31c, preserving the three-fold axis and giving each cation, on average, four anion and four cation neighbours. It is not obvious whether the AA' or FCC structure has the highest symmetry and in practice both are observed. The AA' stacking is found when X = Cl and the FCC stacking when X = Br.

In this example the two complexes have high internal symmetry and this symmetry allows a high-symmetry space group to be adopted. Complexes of lower symmetry necessarily crystallize in a space group of lower symmetry even though the underlying lattice may still be the same.

Cation-centred complexes as found in the example above are those most often encountered, but anion-centred building blocks also exist in, for example, H_2O and OPb_4^{6+} . The latter complex is stabilized by its stereoactive lone pair (Section 8.2) which allows a strong Pb-O bond of 0.50 vu to form with the central O^{2-} anion. The remaining bonds formed by Pb $^{2+}$ are weaker and serve to link the OPb_4^{6+} complex with neighbouring anions (Krivovichev and Filatov 1999).

The building blocks need not be discrete complexes but may be infinitely connected in either one or two dimensions. In their study of the crystal chemistry of lead—antimony sulphides, Skowron and Brown (1994) showed that the allowed packings of infinitely long NaCl-type ribbons of (Pb,Sb)S correctly accounted for eight of the nine observed phases and qualitatively indicated their relative stability. They also predicted a further four phases that might exist with a limited stability range.

In addition to modelling, fundamental building blocks are frequently used to analyse classes of crystal structures in cases where it is possible to recognize a strongly bonded complex whose surfaces give rise to characteristic modes of inter-block bonding (Hawthorne 1985; Ferraris *et al.* 1997; Leonyuk *et al.* 1999). The method can, however, only be applied to systems in which the bonding within the blocks is significantly stronger than the bonding between blocks. In this sense, the method has limited applicability. Nevertheless, the placing of fundamental building blocks on simple lattices in order to generate trial structures is a powerful and well-tried technique in modelling that has been successfully used even in the modelling of organic crystals (Williams 1996).

11.2.2.3 Polyhedral linkage

An alternative approach is to use the bond graph to propose a coordination polyhedron for each of the cations and to generate the full structure by examining the different ways in which these polyhedra can link together to form an infinite framework.

One of the simplest cases is that of silica, SiO_2 whose bond graph is shown in Fig. 11.5. Si^{4+} is almost invariably found at the centre of a tetrahedron of O^{2-} ions and, according to eqn (11.1), the O^{2-} ion must therefore be two coordinate. This means that the structure of silica is most probably composed of corner linked SiO_4 tetrahedra, given that the tetrahedra are unlikely to share edges and faces. Because of the importance of silica and the minerals derived from it, much work has been focused on the different ways in which tetrahedra can be corner linked to form infinite networks in three dimensions. The problem is not a trivial one, because the networks of highest symmetry have linear Si-O-Si bonds leading to three-dimensional networks with large cavities and very low densities. The energy of such a network can be reduced if the density is increased by collapsing the network. The question is, what are the possible three-dimensional networks and how can one select the network most likely to be observed?

It is possible to simplify the description of three-dimensional networks derived from silica by replacing each SiO₄ tetrahedron by a node. The result is a network in which each node forms four links (through the four shared corner O²⁻ ions) to adjacent nodes (Fig. 11.6). Such a network is called a four-connected net. The goal is then to determine all possible arrangements of these four-connected nets that can be mapped into three-dimensional space. Sato and Uehara (1997) have shown that although there is only one graph for the nearest neighbour nodes around a given Si atom, there are many thousands of graphs generated when the second-nearest neighbours are added. The total number of possible graphs is thus impossibly large. Fortunately, only a few hundred of these are observed in nature. The object is to discover the principles nature uses to select them.

Many of the four-connected three-dimensional networks have been tabulated by Smith (1988) and can be used to describe the materials based on silica. These



Fig. 11.5. Bond graph of SiO₂.

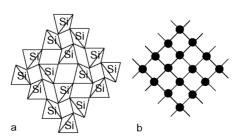


Fig. 11.6. Silicate networks. (a) silicate tetrahedra linked to form a framework, (b) a simplified four-connected network representing the silicate framework.

include a wide range of minerals in which some of the Si⁴⁺ is replaced by Al³⁺ and the charge compensated for by inserting weakly bonding cations, such as alkali metals or alkaline earths, into the cavities of the network. In this network approach, the weaker cations are initially ignored and attention is focused on the strongly bonded alumino-silicate four-connected framework.

Not all alumino-silicate networks are fully four coordinated. Some contain additional O^{2-} ions resulting in some of the O^{2-} ions forming only one bond to the network. Such networks are necessarily anionic (they have an excess of O^{2-}), even more so if some of the Si^{4+} is replaced by Al^{3+} . Figure 4.6 shows that there is a correlation between the anion bonding strength of a silicate network, which depends on the amount of excess O^{2-} , and the bonding strength of the additional weak cations. The valence matching principle thus plays a role in determining which of the three-dimensional networks should be considered for a particular composition (Hawthorne 1985).

Even so, the attempts to enumerate all possible four-connected three-dimensional nets shows that the expansion of even such a simple bond graph as that of SiO₂ is far from trivial. A more profitable approach has been to list and describe those networks that are commonly found, or seem likely to be found, in nature (O'Keeffe *et al.* 2000). Thus the more pragmatic terminology introduced by Liebau (1985, pp. 76ff.) is frequently used to describe the structures of minerals.

In this network description of minerals, the alumino-silicate four-connected network is seen as the framework that supports the structure. Any other cations that are needed to balance the charge are found in cavities within the network. But cations are not the only species that can occupy these cavities. Large cavities can be stabilized by the inclusion of neutral species such as water or other molecule of crystallization. If the cavities are linked into channels, it becomes possible to diffuse molecules into or out of the cavities without destroying the framework. Materials with this property are called zeolites and have important technological applications as water softeners (Ca²⁺ in the water exchanges for Na⁺ in the zeolite), as molecular sieves used for selectively absorbing hydrocarbons according to their size, or as catalysts (because of their high specific internal surface). Because of the large number of possible networks that the alumino-silicates can adopt, many different zeolite frameworks have been found or synthesized (Meier and Olson 1992). The enumeration of four-connected three-dimensional networks has made an important contribution to the study of these technologically important materials.

In spite of the importance of four-connected nets, there are many inorganic materials that contain higher coordination polyhedra linked through shared corners, edges, or sometimes faces. In general it is not profitable to enumerate all the possible topologies. The bond graph gives exact information about the coordination number of each of the polyhedra and some information about the ways in which they are linked. Face sharing is generally not favoured as it brings the central atoms too close together, particularly for

polyhedra of low coordination number, but corner and edge sharing are both frequently found.

Schlegel diagrams are a useful way to explore how these polyhedra can be linked (Hoppe and Köhler 1988). They consist of the outline of the coordination polyhedron projected onto a flat surface in a way that avoids any overlapping lines. The lines in Figs 11.7(b) and (c) represent the edges of an octahedron viewed down a three-fold axis but with the nearest face expanded in a way that allows one to view all the other faces of the octahedron from the inside. Like an animal skin that is opened up, the three-dimensional shell of the octahedron is forced to lie in a two-dimensional plane. The open circles represent the corners of the octahedron and the lines represent the edges. The bond graph of TiO₂ in Fig. 11.7(a) shows that Ti⁴⁺ is six coordinated and an octahedral coordination polyhedron is assumed. Figures 11.7(b) and (c) shows the Schlegel diagrams for the rutile and anatase forms of TiO₂. Both show the projected outline of the octahedron around Ti⁴⁺ but they also give information about the way in which the octahedra are linked. This is done by placing the central atom of a connected octahedron (shown by the filled circles) over a face (when the octahedra share faces), an edge (when they share edges), or attached to a corner (when they share corners).

These diagrams make it possible to examine systematically the different ways in which the polyhedra can link in three dimensions. The bond graph shows that all the ${\rm O}^{2-}$ ions are three coordinate which means that each vertex of the Schlegel diagram must be connected to two other octahedra, through either face, edge, or corner sharing. Ignoring the possibility of face sharing, there are three kinds of vertex, those that share corners with two other octahedra, those that share a corner and an edge, and those that share two edges. The number of possible Schlegel diagrams is thus restricted. Vertices with three shared edges,

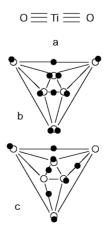


Fig. 11.7. Schlegel diagrams for TiO_2 : (a) bond graph, (b) Schlegel diagram for rutile, (c) Schlegel diagram for anatase. See the text for an explanation.

for example, are not allowed. The various possibilities can be systematically explored. There are only seven ways to combine edges and corners that satisfy the constraints, and for each of these there is a strictly limited number of topologies—only one if all the octahedra are corner linked, or two if all the octahedra are linked by shared edges. The number of possible Schlegel diagrams for TiO₂ is thus limited to around 12 and, keeping in mind that the principle of maximum symmetry implies that all the polyhedra in a structure will, if possible, have the same diagram, one can explore the three-dimensional networks in a systematic way. Figure 11.7(b) shows that the Schlegel diagram for rutile has two opposite shared edges indicating that the octahedra are linked into edgeshared columns, while Fig. 11.7(c) shows that in anatase it is adjacent edges that are shared. The Schlegel diagram can then be used to explore how the edgeshared columns might be linked together. Schlegel diagrams can prove a valuable tool in restricting the number of configurations that need to be examined.

11.2.2.4 The space group method

Another approach to expanding the bond graph into a three-dimensional network is to find the highest symmetry space group into which the bond graph can be mapped, a procedure which will generally find the correct structure if a high-symmetry structure is possible (Brown 1997). If no high-symmetry structure can exist, as is frequently the case, the method is instructive in indicating the nature of the restrictions that three-dimensional space places on possible expansions of the bond graph.

This approach is based on Shubnikov's fundamental law of crystal chemistry (Rule 10.3) which states that the space group must be one in which the atoms in the bond graph can be mapped onto Wyckoff positions having matching multiplicities and site symmetries. Implicit in this mapping is that the symmetry of the space group cannot be higher than that of the bond graph.

The first step is to identify the symmetry inherent in the bond graph. The graph gives information only about nearest neighbours, so the search for symmetry needs to focus on the symmetry of the three-dimensional coordination environments of each of the atoms in the graph. A site symmetry is assigned to each ion assuming that each ion adopts the highest possible crystallographic symmetry. However, there are three important spatial restrictions that these site symmetries must obey if they are to be mapped into a three-dimensional space group:

- 1. The site symmetry of each atom must be one of the 32 crystallographic point groups shown in Fig. 10.7, since these are the only point groups compatible with three-dimensional space groups.
- 2. The product of the multiplicity and the order of the site symmetry of an atom must be the same for all atoms in the structure (eqn (10.2)).
- 3. If the number of bonds formed by an atom is less than the order of its site symmetry, the ligands must share some symmetry elements with the central atom as shown in Tables 10.1–10.3.

Any 6- or 12-coordinate ion in the graph is initially assumed to have the site symmetry $m\bar{3}m$ (O_h) if all the ligands are equivalent in the bond graph. If they are not all equivalent, then one must choose a lower site symmetry that is compatible with this inequivalence. Similarly an ion with four equivalent ligands is assumed to be tetrahedrally coordinated with site symmetry $\bar{4}3m$ (T_d). The constraints 1-3 above are then examined to ensure that all have been satisfied. If they are, then one can look in Appendix 2 to find a matching space group using the procedure described below. If they are not, the symmetry of one or more atoms must be lowered until all the constraints are satisfied.

The identification of a space group that matches the multiplicity and symmetry is only the first step in finding a space group that can accommodate the bond graph. There are then three further conditions that must then be satisfied:

- 4. It must be possible to place the atoms on the selected special positions of the space group so that their bonds match those in the bond graph.
- 5. The resulting structure must be one that is chemically plausible. For example, coordination polyhedra that share faces usually bring the cations too close together, and arrangements that are connected in only one or two dimensions need to be carefully examined since the columns or layers will be held together only by Van der Waals bonds. Such bonding can be found between softer ions such as Cl⁻ or Br⁻ but is generally rare between hard ions such as F⁻ or O²⁻.
- 6. It must be possible to choose parameters for the unit cell and atomic coordinates that reproduce as closely as possible the ideal bond lengths calculated using the network equations (3.3) and (3.4), without bringing any atoms into too close contact.

If a matching space group is found, there may be a choice of Wyckoff positions with the correct multiplicity and site symmetry. If sites of lower symmetry are occupied, there will be positional coordinates that need to be chosen. It may be necessary to test several different atomic arrangements to determine whether or not an embedding of the graph with reasonable bond lengths is possible. Any of these constraints may make it impossible for a structure to exist in a given space group, but a systematic check of all the possibilities is difficult in low-symmetry structures. If no satisfactory space group can be found at a given symmetry level, either a lower symmetry space group must be sought, a different bond graph must be constructed or, if neither of these work, the compound is not able to exist.

So that the method can be fully understood, the rest of this section works through a number of examples in some detail. Readers who are not interested in these details may skip to the next section.

The structure of NaCl (18189) can readily be obtained by noting that both ions are six coordinate and are expected to have octahedral environments

with $m\bar{3}m$ symmetry (Fig. 11.2(a)). The spectrum³ of the bond graph is $\{2000000000\}$, or more simply $\{2\}$, since there are two atoms with multiplicity of 1 in the formula unit. From Appendix 2 it is easily seen that two space groups, $Fm\bar{3}m$ and $Pm\bar{3}m$, have the right site symmetries and match this spectrum, but only $Fm\bar{3}m$, which is the observed space group of NaCl, allows the mapping of a six-coordinate graph. $Pm\bar{3}m$ can accommodate the eight-coordinated graph of Fig. 11.2(b) and is the space group of CsCl (22173).

For ZnO (67454, Fig. 11.2(c)) both atoms can be tetrahedrally coordinated and have site symmetry $\bar{4}2m$ (T_d). The spectrum is again $\{2\}$ and the first match found in Appendix 2 is Fd $\bar{3}m$, but this structure can be eliminated on chemical grounds (constraint 5) since it gives Zn–Zn and O–O distances that are the same as the Zn–O distances. The next match is F $\bar{4}3m$ which is the space group of sphalerite, ZnS (60378). For reasons discussed in Section 2.6, ZnO adopts the lower-symmetry wurtzite structure. It is left as an exercise to show that wurtzite (67454) with space group P6 $_3mc$, is the next most symmetric structure after F $\bar{4}3m$ that can accommodate the graph of Fig. 11.2(c) and satisfy the six constraints listed above.

Less trivial examples are the various bond graphs of ABO₃ shown in Fig. 11.3. The six-coordinate B cation is assumed to have site symmetry m3m $(O_h, m_s = 48)$, but this site symmetry is only possible in the bond graphs shown in Figs 11.3(a), (e), and (f) where all the bonds are equivalent. Because the ligands are not all equivalent in Figs 11.3(b), (c) and (d), the highest symmetry possible around B is 4/mmm (D_{4h}, $m_s = 16$). On the other hand, the site symmetries of the cation A are different for each of the graphs shown. In Fig. 11.3(a), where A is six coordinate, in Fig. 11.3(d) where it is eight coordinate and in Fig. 11.3(f) where it is 12 coordinate, site symmetry $m\bar{3}m$ (O_h, $m_s = 48$) is theoretically possible. In Fig. 11.3(b), A is eight coordinate, but not all the ligands are equivalent. They fall into two groups of six and two (three bonds are formed to each of two equivalent O²⁻ ions, so all six bonds, which in three dimensions will be to six different ligands, may be equivalent). The highest possible symmetry environment is the hexagonal bipyramid with site symmetry 6/m (C_{6h} , $m_s = 12$). In Fig. 11.3(c) the coordination number of A is also 8 and the ligands also break into two groups, but in this case there are four bonds in each group. The highest symmetry environment is a tetracapped tetrahedron with site symmetry 43m (T_d , $m_s = 24$). In Fig. 11.3(e) where A is nine coordinate, the ligands are equivalent but the highest symmetry environment in a crystal corresponds to a tricapped trigonal prism with site symmetry $\bar{6}2m$ (D_{3h}, $m_s = 12$). In this case, even though the ligands are equivalent in the bond graph, there is no crystallographic site symmetry that allows all the bonds to be equivalent. In $\bar{6}2m$ the

³ The spectrum of a bond graph is constructed in the same way as the spectrum of a space group described in Section 10.5. It indicates the number of atoms in the bond graph that have the corresponding multiplicities. Trailing zeros are usually omitted. For a space group to be compatible with a given bond graph, each term in the spectrum of the space group should be at least as large as the corresponding term in the spectrum of the bond graph.

bonds are broken into two symmetry distinct groups of six and three, the latter lying either on mirror planes or two-fold axes that pass through the A site.

However, within each of the bond graphs, the site symmetries discussed above are not always mutually compatible. Equation 10.2 shows that there is a relationship between the order of the site symmetry and the multiplicity. Since both A and B have the same multiplicity (they each appear just once in the formula unit), they must have site symmetries of the same order (see Fig. 10.7). This condition is satisfied only for Figs 11.3(a) and (f) whose cations can both be assigned the site symmetry $m\bar{3}m$ (O_h, $m_s = 48$) as discussed above. The spectrum in both cases is {201} (A and B have multiplicity of 1 while O²⁻ has multiplicity of 3) and the only space group that matches these conditions is Pm3m (Appendix 2). There are two ways of distributing the atoms over the different sites, but both lead to the same structure, that shown in Fig. 10.4, in which B is six coordinate and A is 12 coordinate. This structure corresponds to the bond graph of Fig. 11.3(f) and meets all the conditions except number 6. It has only one free parameter (the unit cell edge) and requires that the length of the A-O bond be $\sqrt{2}$ times the length of the B-O bond. Only for a particular choice of cations will the chemical lengths predicted using the network equations (3.3) and (3.4), satisfy this condition, so this structure, while having the highest symmetry, is expected to occur only for a small number of compounds. SrTiO₃ (201256) is one of these, but the condition is not satisfied for either BaTiO₃ (23759) or CaTiO₃ (62149) which adopt different, though related, structures as described for BaTiO₃ in Section 10.2.

Finding the space group for the graph of Fig. 11.3(a) is more difficult. There are quite a number of matches to be found in Appendix 2, but all the cubic structures can be discounted as they give six coordination around only one of the cations. In space groups of non-translational order 12 the three hexagonal and three trigonal matches require one of the sites to be only three coordinate. There are no matches for a space group with a non-translational order of 8 or 4. There are several promising possibilities in space groups of order of 6, but these give columns of face-sharing octahedra which are chemically unlikely. It is not until one reaches an order of 3 that one can find a plausible structure in R3, the ilmenite structure (FeTiO₃, 67046) which is found for a number of compounds where both A and B are six coordinate, but even this requires the A and B octahedra to share one face. What looked like an excellent candidate for a highsymmetry structure turns out to be unable to crystallize in a space group that can provide the cations with a site symmetry higher than 3, and even in this case the face sharing of octahedra results in strains in the bonds, the three bonds to the shared face being longer than the other three, even though the O²⁻ ions are crystallographically equivalent and the bond graph predicts regular octahedral coordination.

In the nine-coordinate graph of Fig. 11.3(e) all the O^{2-} ions are chemically equivalent but the A-O bonds cannot all be crystallographically equivalent as there is no crystallographic site symmetry of order 9. The highest possible

symmetry, the tricapped trigonal prism, has site symmetry $\bar{6}2m$ (D_{3b}), but this requires six of the A–O bonds to be crystallographically distinct from the other three.⁴ The order of 62m is 12, therefore the order of the site symmetry of B must also be 12 which gives candidate site symmetries of $\bar{3}$ m (D_{3d}) and 23 (T) (Table 10.3). Since all the O^{2-} ions are equivalent in the bond graph, the spectrum is {201}. Appendix 2 is thus searched for space groups listed under order 12, spectrum $\{201\}$ and site symmetries of $\bar{6}2m$ (for A) and either $\bar{3}m$ or 23 (for B). There are two hits, P6₃/mmc and P6₃/mcm, but both allow only three coordination around A. No space group has a spectrum of {201} in the space groups of order 8. In order 6, B must have site symmetry 32 (D_3) or $\bar{3}$ (C_{3i}) and A must have site symmetry 3m (C_{3v}), 32 (D_3) or $\bar{6}$ (C_{3h}), the latter two symmetries permitting a tricapped trigonal prism. Since A has site symmetries of order 6. O^{2-} will have a site symmetry with $m_s = 2$, i.e. it must have 2 (C₂), or m (C_s) site symmetry since it must share these symmetry elements with the facecapping ligands. If the site symmetry of A is 3m, these three of the ligands will lie on one of the three mirror planes that include the three-fold axis passing through A, if it is 32 they must lie on the two-fold axes but if it is $\bar{6}$ they must lie on the mirror plane perpendicular to the three-fold axis (Table 10.1). There are 10 space groups in Appendix 2 that match. A close examination of these shows that the first four, P4₁23, P6c2, P62c, and P6₃22, cannot accommodate the bond graph, the latter, for example, can have octahedral coordination around B but A can then only be placed on a site of three or 12 coordination. Only with the fourth matching group, R3c, is it possible to find an embedding for the bond graph. This is the space group found for many perovskites in which A is smaller than the cubic cavity into which it is placed. The cavity distorts so that 6 of the 12 A-O distances become shorter and three become so long that they no longer contribute to the bonding, leaving A nine coordinate.

Finally we consider the eight-coordinate graphs. Figure 11.3(b) shows the graph with the highest entropy for structures with mono- and divalent A (Section 11.2.2.1). The spectrum of this graph is $\{31\}$ since there are now two chemically distinct O^{2-} ions, one with a multiplicity of 1, the other of 2. The highest possible symmetry for A is the rather unlikely hexagonal bipyramid of order 12. The order of the site symmetry of B cannot therefore be greater than 12, but the only two compatible site symmetries of this order for an octahedron are, from Table 10.3, $\bar{3}$ m (D_{3d}) and 23 (T), neither of which permit two of the ligands to be different from the other four. Going to lower symmetry, site symmetries of order 8 are not possible as 8 is not a submultiple of 12, and site symmetries of order 6 again require all ligands to be equivalent as can again be seen from Table 10.3. The highest site symmetries from Table 10.3 which allow the six ligands to be split into a group of two and a group of four are found in

 $^{^4}$ Even though the A–O bonds are not all equivalent, it is still possible for all three O^2- atoms to be crystallographically equivalent. For example, each O^2- atom may form two A–O bonds of one kind and one of a second kind. This would satisfy the requirements of the A site symmetry of $\bar{6}2m$ and still leave all the O^2- atoms equivalent.

order 4 ($\bar{4}(S_4)$, 4 (C_4), 222 (V), mm2 (C_{2v}), 2/m (C_{2h})) and the last three are also compatible with an eight-coordination split into 2+2+4 groups. This split is compatible with the bond graph since not all the bonds between symmetry-related atoms need themselves be related by symmetry. The number of space groups in Appendix 2 that meet these conditions is quite large and their symmetry is low. It is not profitable to examine each of these to find which allow a suitable mapping of the bond graph, but it is clear that any perovskite with an eight-coordinate A cation having the bond graph of Fig. 11.3(b) will have a structure of low symmetry, probably not higher than orthorhombic. This graph is found in a large number of distorted perovskites with the orthorhombic space group Pnma (Woodward 1997a).

A second eight-coordinate bond graph is shown in Fig. 11.3(c). Although this graph has a lower entropy, it can be mapped into a space group of higher symmetry and for this reason may be preferred. It is left as an exercise for the reader to show that this space group is I4/mcm. A number of compounds are known with this structure but none in which A and B are trivalent cations, since for these cations, the graph of Fig. 11.3(c) has a significantly smaller entropy than that of Fig. 11.3(b).

The highest entropy graph for eight-coordinate A^{3+} cations is that shown in Fig. 11.3(d). This can be mapped into the space group P4/mmm but only if the B cations share four edges in the equatorial plane, an arrangement that brings the B cations rather too close. This structure is not known for any of the A^{3+} perovskites but it is known for NH₄HgCl₃ (15962) where it is stabilized by two chemical properties of the compound: the electronic polarizability of Hg²⁺ helps to stabilize the large tetragonal distortion needed to keep the Hg²⁺ ions well separated, and the tetrahedral arrangement of H⁺ ions around N³⁻ helps to stabilize the cubic eight coordination of the ammonium ion (Section 7.7).

11.2.2.5 Weakly bonded structures

The approaches described in the previous sections work well in cases where a good match is possible between the chemical and crystallographic symmetry, where the strongly bonded coordination polyhedra are linked into strongly bonding frameworks, or where the fundamental building blocks have high symmetry so that the lattice model can be used, but in many other cases a different strategy is needed.

The problem becomes particularly acute for organic molecules which are irregular in shape and are held together by weaker interactions such as Van der Waals forces and hydrogen bonds. A method that shows some promise is the use of packing groups proposed by Gao and Williams (1999). As shown in Chapter 10, the symmetry operations of the space group can be split into two subgroups: those that give the site symmetry of a special position and those that generate the set of equivalent special positions in the unit cell. An alternative way of splitting the symmetry operations of the space group is to split them into

a subgroup that contains the operations of the point group of the formula unit (molecule) and those that generate the other formula units in the crystal-lographic unit cell. The latter group of operations constitute the packing group since they describe the way in which the formula units pack.

According to the principle of maximum symmetry one would expect to find only one formula unit in the unit cell, but the shape of the formula unit does not often lend itself to efficient packing by simple translation. Better packing can usually be achieved if adjacent formula units have different orientations. Such freedom is allowed by screw axes and particularly by glide planes. The two most frequently found space groups in inorganic crystals are the monoclinic $P2_1/c$ and the orthorhombic Pnma, both of which have glide planes. For the same reason, $P2_1/c$ is also the most frequently found space group among organic crystals (Brock and Dunitz 1994). The use of packing groups has still to be developed into a workable model, but they hold considerable promise for use in modelling, particularly if it becomes possible to determine *a priori* which translational symmetry elements allow formula units to pack efficiently.

11.2.3 Valence maps

The valence map is a device that is useful for exploring the space available to an ion when most of the structure is known. It can be used to find diffusion paths or to locate the most favourable sites for those atoms that form bonds in the post-crystallization phase after the three-dimensional bonding network has been established. The method was first proposed by Waltersson (1978) who used it to find the sites of the Li⁺ ions in various Li₂WO₄ phases where the relatively weak scattering of the Li⁺ ions made them difficult to locate by X-ray diffraction. He placed an Li⁺ ion at an arbitrary point in the unit cell and calculated the lengths of the bonds it would form to the neighbouring O²⁻ ions. From these distances he calculated the bond valence sum around the Li⁺ ion using eqn (3.1) or (3.2). The Li⁺ ion was then moved to other positions in the cell and the calculation repeated to generate a map of the bond valence sum that an Li⁺ ion would have if placed at any given point in the crystal.⁵

The valence map for F^- in the (110) plane through fluorite, CaF_2 (29008), is shown in Fig. 11.8 to illustrate the technique. In this map all the F^- ions have been removed leaving only Ca^{2+} ions in place. An F^- ion is then moved systematically through the crystal along the points of a grid, at each point its valence sum being calculated. Places where the valence sum is equal to 1.00 vu are places that can accommodate F^- ions. Such places are found at the regular

 $^{^5}$ In practice it is necessary to block the sites of those cations such as W^{6+} , whose positions are already known, by ensuring that the valence sums become large if the Li^+ ion gets too close. This can be done by using eqn (3.1) to assign a fictitious valence to distances between the cation whose position is being sought, Li^+ in this case, and those such as W^{6+} whose positions are already known. The bond valence parameters should be designed to give large valences for short distances but negligible values beyond about 150 pm.

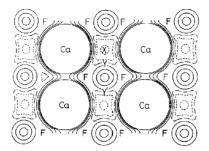


Fig. 11.8. The valence map of a (110) section through CaF_2 showing possible locations for F^- ions. The 1.0 vu contour is shown with a dot and dash line. Contours less than 1.0 vu are shown with a broken line, those larger than 1.0 vu with a solid line. The contour interval is 0.2 vu. Contours above 1.8 vu have been omitted for clarity. Atomic positions are shown by the element symbol (one F has been omitted to show the contours at this site). X, Y, and Y' are proposed sites for an interstitial F^- ion as discussed in the text.

site of the F⁻ ions (indicated by the letters F in Fig. 11.8 where one letter F has been omitted to reveal details of the valence map at this point), but there is also a contour of 1.00 vu (dash-dot line) surrounding the cavity between the Ca²⁺ ions. Originally it was proposed that an interstitial F⁻ ion might occasionally be found at the centre of one of these cavities (at the point marked X), but such interstitials have been found to be displaced from the centre of the cavity at the sites labelled Y and Y' which lie on the 1.00 vu contour. The valence sum at X is less than 0.6 vu and the distortion theorem (Rule 3.6) would predict an offcentre displacement from this site. The valence map provides a visual display of the predictions of the theorem. Once the position of the interstitial atom has been identified, the bonds it forms can be found and the network equations can be used to find the relaxation that occurs in the bonds that surround the defect (Brown 1988b).

Valence maps may alternatively be presented in a way which gives a direct impression of the atom's probability density function, a function which indicates the probability of finding the atoms at a particular point in space. This is calculated by inverting the valence function using eqn (11.3):

$$p_i = \left(\sum_j s_{ij}/V_j\right)^{-N}. (11.3)$$

Raising $\sum s_{ij}$ to an inverse power has the effect of converting minima into maxima, and the division by the atomic valence gives p_i a value of 1.0 at an ideal location. If N is set equal to 16, the maxima become quite sharp and the resultant p_i map contains peaks that, under suitable conditions, resemble the probability density function for the atom at room temperature as shown for

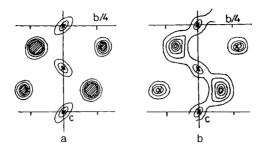


Fig. 11.9. The valence map of Mg_2SiO_4 transformed to simulate the probability distribution function of Mg^{2+} at (a) room temperature, (b) high temperature. The shaded areas have values larger than 1.0.

the $\mathrm{Mg^{2+}}$ ions in olivine, $\mathrm{Mg_2SiO_4}$ (26374), in Fig. 11.9(a). Three different peaks are seen in this figure. Two, marked with a cross, are occupied by $\mathrm{Mg^{2+}}$, the third is vacant. The smaller peaks that lie on the c axis have maxima of 1.0 and represent quite faithfully the probability density function of Mg1 at room temperature. The other two peaks have maxima larger than 1.0 and represent holes that are too large to comfortably accommodate an $\mathrm{Mg^{2+}}$ ion. The larger of the two peaks represents a vacant hole, but the smaller is occupied by $\mathrm{Mg2}$. However, $\mathrm{Mg2}$ is not found at the centre of the hole, indicated by the maximum in p_i , but is displaced to one side where the value of p_i is close to 1.0. As in the example of the interstitial site in $\mathrm{CaF_2}$, this valence map provides a visual representation of the distortion theorem.

Figure 11.9(b) shows that when p_i is calculated with N=8, it resembles a high-temperature probability density function. The peaks are broader and two of them are linked by bridges along the c direction, the direction of easy Mg^{2+} diffusion. Figure 11.9(b) suggests a diffusion mechanism in which $\mathrm{Mg1}$, but not $\mathrm{Mg2}$, moves between its regular sites via the vacant hole in the structure.

A different method of displaying diffusion paths has been used by Adams (1996) who has plotted a three-dimensional view of the structure showing the lowest contour surface that provides a continuous path through the crystal. Figure 11.10 shows these paths for the mobile Ag^+ ions in the ionic conductor α -AgI (200108). In examining the diffusion paths of Ag^+ in various crystalline and glassy oxygen complexes of silver iodides, Adams and Swenson (2000*a*) find a direct correlation between the volume enclosed by this contour, the ionic conductivity and the activation energy for diffusion.

Valence maps are not restricted to inorganic materials but can be used in any situation where acid-base bonding is involved. For example, Nayal and Di Cera (1994) have used valence maps to locate the sites of Ca²⁺ ions on the surfaces of Ca-binding proteins as described in Section 13.6.2.

A program for calculating bond valence maps has been published by Gonzáles-Platas et al. (1999).

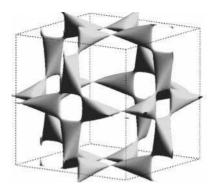


Fig. 11.10. The lowest isovalent contour in α -AgI that permits diffusion through the crystal. I⁻ ions (not shown) occur at the cell corners and cell centre. Reproduced with permission from Adams and Swenson (2000b).

11.3 Refining the geometry

If the topology of a structure is known, there are various ways in which the geometry can be refined. The generally accepted method is to refine the coordinates by minimizing the energy. The energy may be calculated by solving the Schrödinger equation, a method used mostly for isolated molecules but recently extended for use with crystals. It gives geometries close to those observed particularly for light atoms. Heavy atoms, where relativistic effects are important, still present computational problems. While the calculations require considerable computing power, they provide details of the electron density distribution and the properties that depend on it. The method has only recently been applied to inorganic crystals and has not yet been sufficiently explored to discover all its advantages and limitations. These methods lie beyond the scope of this book, and the reader is referred to Payne *et al.* (1992) for further details.

A simpler method of finding the geometry minimizes the energy calculated using effective two-body potentials. This is a classical or semi-classical approach depending on how the potentials are determined. Using appropriately determined potentials the method gives refined atomic positions that also lie within a few pm of the observed values. It has been used to explore the structures of surfaces and defects which are not easy to measure. Since it is not as computer intensive as the quantum mechanical methods, it has been widely used in materials science for exploring inorganic structures and the properties that depend on structure. Further accounts of this approach are given by Burnham (1990) and Catlow (1997).

The bond valence model may also be used to refine the structure since it is based on the same assumptions as the two-body potential method. The network equations (3.3) and (3.4), can be used to predict the theoretical bond valences as soon as the bond graph is known. From these one can determine the expected bond

lengths using eqn (3.1) or (3.2). It is not necessary at this stage to know the threedimensional structure since, as the example of Table 3.1 shows, the bond lengths predicted using the network equations can be quite close to the observed bond lengths providing there is no spontaneous electronic distortion of the kind discussed in Chapter 8 or lattice induced strain of the kind discussed in Chapter 12.

These expected bond lengths can be used as targets in a distance-least-squares (DLS) program (Villiger 1969) which finds the set of atomic coordinates that best reproduces the target bond lengths. Alternatively, one can refine against the theoretical bond valences or one can minimize the deviations from the network equations. In distance-valence-least-squares (DVLS, Sato 1982; Kroll *et al.* 1992), the sums of ionic radii are used as target distances, but the distortions that are introduced by the bond connectivity are satisfied by requiring that the bond valence sums around each atom be equal to the atomic valence.

While there are several ways in which targets for the bonds lengths can be set, setting targets for the bond angles, or equivalently the non-bonded distances, is more difficult. Unfortunately, these are needed in any refinement to prevent two anions or two cations from occupying the same space. For tetrahedra, target angles given by eqn (9.4) can be used. Non-bonding constraints are incorporated in DVLS as target bond angles, but anion—anion and cation—cation distances could be used instead, giving them zero weight if the calculated distance exceeds the target. Pannetier *et al.* (1990), in their simulated annealing, used a Coulomb potential and O'Keeffe (1991a) used an exponential repulsive function to keep like ions apart. The form of the non-bonded term is not critical, providing it is sufficient to prevent adjacent non-bonded atoms from occurring in the same space. If the structures are not subject to the strains described in Chapters 8 and 12, these techniques give atomic positions that lie within a few pm of the observed positions.

Bond valences can be used in conjunction with other techniques, particularly powder diffraction where, for example, light atoms are difficult to refine in the presence of heavy atoms. Adding the chemical constraints of the bond valence model can stabilize the refinement, particularly in the case of superstructures that have high pseudo-symmetry (Thompson *et al.* 1999).

The refinement of geometries using bond valences has the advantage of computational simplicity. The network equations allow rapid calculation of the ideal bond lengths. Its principal disadvantages are that it does not give a direct measure of the energy, and the network equations only describe equilibrium geometries. Only qualitative estimates of the relative stabilities of different structures are possible.

11.4 Modelling defect structures

Many inorganic compounds are not stoichiometric, but have atoms missing or additional atoms occupying interstitial sites or substituting for other atoms.

Such defects can give rise to unusual physical and chemical properties as discussed more fully in the following chapters. Here it is worth pointing out that bond valences can be used to explore the local environments around defects which are difficult to observe using the standard techniques of X-ray and neutron diffraction.

The bond valence model does not necessarily give an unambiguous description of the environment of a defect but it can be used to test whether a proposed model is chemically plausible by checking that the bond valence sums around all the atoms are reasonable. Figure 11.8 shows how a valence map can be used to find possible positions for interstitial F⁻ in CaF₂ (Frenkel defect) but it cannot say which of the positions on the 1.0 vu contour will be occupied. Once a position has been chosen, standard refinement techniques can be used to determine how the neighbouring atoms relax (Brown 1988b). Hughes et al. (1997) have used the bond valence model to show how substituting a rare earth ion for calcium in the mineral titanite promotes the creation of antiphase boundaries where the direction of displacement of the Ti⁴⁺ ions in their octahedra is reversed. Hawthorne (1997) has used the model to discuss possible local arrangements of impurities in amphiboles in relation to the distribution of Al³⁺ ions in the alumino-silicate framework. Brese et al. (1999) have used Monte Carlo methods with a cost function based on the network equations to model diffusion in Cu doped ZnS. Further examples of the modelling of defects are given in Chapters 12 and 13.

11.5 Modelling glasses

Glasses are solids that lack crystalline order and their structures are therefore much harder to determine and model. Individual atoms are found with a wide range of environments, but the valence sum rule is still expected to be obeyed, giving promise that modelling of glass structure is possible. Swenson and Adams (2001) have used the bond valence model in conjunction with the reverse Monte Carlo simulation of glass diffraction patterns to produce plausible models for glassy mixtures of AgI and Ag oxysalts. Brown *et al.* (1995, pp. 382ff.) have combined bond valence methods with X-ray absorption spectroscopy to examine the structures of silicate glasses and melts. In these complex structures, the experimental techniques need to be supplemented by a simple model of crystal chemistry to ensure a realistic picture of the structure is obtained. The bond valence model is ideal for this purpose.

11.6 Summary

No single method can predict all crystal structures and many crystal structures cannot be predicted by any technique currently available. Structure modelling SUMMARY 163

remains more of an art than a science, but a variety of methods have been mentioned in this chapter, ranging from the brute force methods that use the power of computers to explore a wide range of possible structures to those in which all prior chemical and physical knowledge is used to finesse a structure. Much more work is needed before we can replace experimental methods of structure determination with simple theory.

Lattice-induced strain

12.1 The origins of lattice-induced strain

The unit cell of a particular compound is often composed of chemically distinct units, the fundamental building blocks described in Section 11.2.2.2. If these blocks are infinitely extended in one or two dimensions, they will possess a translational symmetry whose repeat distance will be determined by the lengths of the strong bonds within the blocks. Since the length of these bonds can be calculated using the network equations ((3.3) and (3.4)), the ideal translational repeat of the block can also be calculated. For example, La₂NiO₄ (65917) shown in Fig. 12.1 is composed of a stack of alternating NiO₂ and (LaO)₂ layers similar to the TiO₂ and BaO layers shown in Fig. 10.3. The double layer (LaO)₂ has the NaCl structure with translation distances within the layer equal to 365 pm ($\sqrt{2}$ times the ideal La–O bond length calculated to be 258 pm using the methods described in Chapter 3). Similarly the single NiO₂ layer has an ideal translation distance of 412 pm (twice the calculated Ni–O bond length of 206 pm). In this example, the

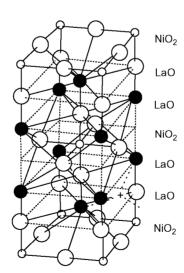


Fig. 12.1. The structure of La_2NiO_4 (65917) showing how the structure is composed of $(LaO)_2$ and NiO_2 layers. The + sign marks the position of the interstitial O^{2-} ion. The large open circles represent O^{2-} , the small open circles Ni^{2+} and the filled circles La^{3+} .

(LaO)₂ and NiO₂ layers, which constitute the two fundamental building blocks, have different ideal translations, and without some adjustment they cannot be stacked to form a crystal in which all components have the same lattice spacing. If the two blocks are to coexist in a single crystal, this incommensuration must be resolved.

There are two essentially different ways in which this can be done. If the bonding between the blocks is weak compared to the bonding within the blocks, each block may retain its own characteristic translation. The resulting crystal is then a composite of two finely interleaved crystals, each with a different lattice spacing. Such crystals are not common, but are by no means unknown as shown by the example of (EuS)_{1.725}NbS₂ illustrated in Fig. 12.2. If the ratio of the lattice spacings of the two blocks is close to a rational fraction, the crystal will form a supercell whose length is equal to the lowest common multiple of the individual block translations, i.e. if one block has a lattice spacing of 300 pm and the other a lattice spacing of 400 pm, the crystal will have a supercell with a spacing of 1200 pm. More generally, the ratio of the translation vectors of the two blocks will not be a rational number, in which case the crystal is incommensurate as discussed in Section 12.4.

On the other hand, if the blocks are strongly bonded to each other as they are in La₂NiO₄, the atoms in one block will be forced to remain in register with their

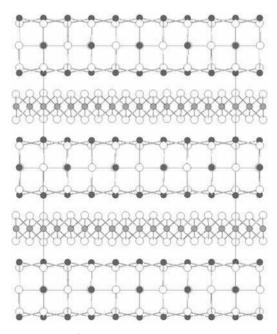


Fig. 12.2. Packing of the $(EuS)_3^+$ and $(NbS)_2^-$ layers in $(EuS)_{1.725}NbS_2$ viewed parallel to the layers and perpendicular to the incommensurate direction. Black circles are Eu, grey circles are Nb, and open circles are S. Reproduced with permission from Cario *et al.* (1999).

neighbours in the adjacent block. The two blocks will be constrained to have the same lattice spacing, requiring that one block, (LaO)₂, be stretched while the other, NiO₂, is compressed. Necessarily this results in some bonds being stretched and others being compressed. The crystal acts like a Procrustean bed, forcing its building blocks to share a common lattice spacing. The strains that result from such mismatched blocks are called *lattice-induced strains* (Wegner and O'Keeffe 1988).

12.2 Structures with lattice-induced strain

Lattice-induced strains clearly cause the bonds to violate the network equations and their presence may be indicated by a large value of the *bond strain index* (BSI) defined in eqn (12.1) (Preiser *et al.* 1999, σ_3 in table 1):

$$BSI = \langle (S - s)^2 \rangle^{1/2}, \tag{12.1}$$

where S is the experimental bond valence calculated from the observed bond length and s is the theoretical bond valence calculated from the network equations. The angle brackets $\langle \ \rangle$ indicate an average taken over all bonds in the formula unit. If the value of the BSI for a particular crystal is greater than 0.05 vu, the structure can be regarded as strained. However, lattice mismatch is not the only, or even the principal, cause of bond strain. The electronic instabilities discussed in Chapter 8, or the anion—anion repulsions discussed in Sections 6.2 and 7.2, also lead to large values of the BSI. Since the lowest energy will be achieved when all sources of strain work together, it is not uncommon for a particular strain to have several causes. For example, the tendency of an ion to show electronic distortion will make it easier for the environment of that ion to distort in response to a lattice-induced strain as was noted for BaTiO₃ in Section 10.2.

A second and complimentary measure of lattice strain is the *global instability* index (GII) defined by Salinas-Sanchez et al. (1992) using eqn (12.2):

$$GII = \left\langle \left(\sum_{j} S_{ij} - V_{i}\right)^{2} \right\rangle^{1/2}, \tag{12.2}$$

where the average here is over all the atoms in the formula unit. This measures the extent to which the valence sum rule is violated. Values of the GII less than 0.05 vu suggest that little or no strain is present while values greater than about 0.20 vu indicate a structure that is so strained as to be unstable. Such large values of the GII are rarely found in properly determined crystal structures. Where a crystal structure has a GII much larger than 0.20 vu, there is reason to suppose that the reported crystal symmetry is too high and that the real crystal has relaxed in one of the ways discussed below.

An interesting example of the use of the GII is provided by compounds with the formula Ln_2BaCuO_5 (72165, Ln=rare earth) studied by Salinas-Sanchez

et al. (1992). These have a complex structure that involves the packing of ${\rm Ln^{3+}}$, ${\rm Ba^{2+}}$, and ${\rm CuO_5^{8-}}$ ions. Only for ${\rm Ln^{3+}} = {\rm Tm^{3+}}$ do all the pieces have the right size to fit together without strain. Replacement of ${\rm Tm^{3+}}$ with other rare earth ions causes the structure to become strained as indicated by the GII shown in Fig. 12.3 where it is plotted against the rare earth ionic radius. For these compounds the GII is closely approximated by eqn (12.3):

$$GII = 0.058 + 10^{-3} \Delta r^2, \tag{12.3}$$

where Δr is the amount (in pm) by which the radius of the rare earth differs from that of Tm³⁺. For ions larger than Sm³⁺, the GII is predicted to exceed the stability limit of 0.20 vu and it is significant that the Nd³⁺ and La³⁺ compounds both crystallize with a different structure. Similar results have been found for Ln₂Cu₂O₅ (69328) compounds (Garcia-Muñoz and Rodríguez-Carvájal 1995).

Typically lattice-induced strain results in the bonds around one cation being stretched and the bonds around another cation being compressed as found in BaRuO₃ (10253) by Santoro *et al.* (1999, 2000). When this happens, the valence sum rule will be violated around the cations in question but the valence still distributes itself as uniformly as possible among the bonds, so that the experimental bond valences determined from the bond lengths remain as close as possible to the theoretical bond valences. For this reason the BSI is typically smaller than the GII for lattice-induced strains, though the opposite is true for compounds with electronically induced strain where the valence sum rule remains well obeyed.

If possible, the lattice-induced strain will relax in such a way as to minimize both strain indices as illustrated in the following sections by the structure of

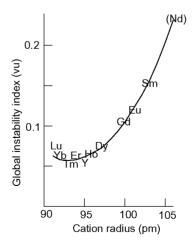


Fig. 12.3. The variation of the observed GII versus rare earth ionic radius in Ln_2BaCuO_5 (Ln = rare earth). The line corresponds to eqn (12.3). Nd_2BaCuO_5 has a different structure, the value shown is calculated from eqn 12.3.

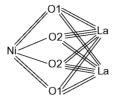


Fig. 12.4. Bond graph of La₂NiO₄.

La₂NiO₄ (Brown 1992a). Its bond graph, shown in Fig. 12.4, indicates that all the bonds have theoretical bond valences of $0.33\,\mathrm{vu}$. As described above, this means that the natural lattice spacing of the $(\mathrm{LaO})_2$ layer is 365 pm, while the natural lattice spacing of the NiO₂ layer is 412 pm. Since the layers are strongly bonded to each other, they remain in register and are therefore strained. Assuming that they adopt a common spacing close to the mean (388 pm), the NiO₂ layer must be compressed until the Ni–O bonds are only 194 pm instead of 206 pm and the $(\mathrm{LaO})_2$ layers must be stretched until the La–O bonds are 277 pm long instead of 258 pm. For this structure the GII = 0.47 and the BSI = 0.07. The large value of GII clearly indicates an unstable structure which relaxes in one or more of the ways described in the following section.

12.3 Relaxation of lattice-induced strain

Any crystal, in which some bonds are stretched and others compressed as a result of lattice induced strain, will relax so as to ensure that the network equations are as well satisfied as possible under the given geometric constraints. There are a large number of ways in which this relaxation can occur. The lattice-induced lengthening (or shortening) of some bonds around a given ion will be compensated by the shortening (or lengthening) of the unstrained bonds so as to preserve the valence sum rule. Where the bonds formed by an ion are stretched, the ion may move off-centre in its coordination sphere in accordance with the distortion theorem (Rule 3.6). Compressed layers may buckle while interstitial ions or vacancies may be introduced into a stretched layer. If there are atoms that can adopt different oxidation states, electrons may be transferred from a cation that is being compressed (so as to raise its oxidation state, hence shorten its bonds) to a cation that is being stretched (so as to lower its oxidation state and lengthen its bonds). Finally, it may be necessary for the structure to adopt a bond graph of lower symmetry. The particular modes of relaxation adopted will depend on the nature of the structure and, for a given structure, can often be predicted.

12.3.1 Relaxation of the geometry

In many structures, it is possible to change the lengths of unstrained bonds in order to compensate for the stretching and compression required to make the

structure commensurate. In La₂NiO₄ this is achieved by changing the lengths of the interlayer bonds to compensate for the changes that must occur within the layers. Ni²⁺ has four compressed equatorial bonds in the NiO₂ layer. These must be shortened from 206 pm (S=0.33 vu) to 194 pm (S=0.46 vu) to keep the layers commensurate. To compensate and ensure the correct valence sum at Ni²⁺, the two axial bonds perpendicular to the layers should have valences of only 0.08 vu corresponding to lengthening the bonds to 259 pm. This axial O²⁻ ion forms five bonds to La³⁺ in addition to the weak Ni–O bond. Four of these must be stretched to 277 pm (S=0.20 vu) to make the layers commensurate. This leaves a valence of 1.12 vu (1.29 vu if the buckling of the LaO layer is taken into account) for the single remaining La–O bond directed perpendicular to the layer. The length of this bond is therefore predicted to be reduced to 207 pm. This (hypothetical) structure is constrained to satisfy the valence sum rule (GII = 0) and it can be geometrically fitted into three-dimensional space, but its BSI of 0.29 indicates that the distortions, especially around La³⁺, are too large to be stable. Further relaxation is required.

12.3.2 Relaxation by defects

A second mode of relaxation is the incorporation of defects into the stretched layer. Interestingly, insertion of extra O^{2-} ions on interstitial sites, or the formation of La^{3+} vacancies, both help to relax the stretched layers as shown in Fig. 12.5. An interstitial anion will form additional bonds to the cation thus increasing its bond valence sum, while removing a cation allows the anions to which it was bonded to relax towards the neighbouring cations, shortening the bonds, and increasing their bond valence sums. Both kinds of defects are found in La_2NiO_4 which, if prepared in air, will automatically incorporate extra O^{2-} to give the composition of $La_2NiO_{4.18}$, adding just enough oxygen to ensure the correct valence sums around La^{3+} . The interstitial O^{2-} is located between the two LaO layers in a place where it can bond to four different La^{3+} ions

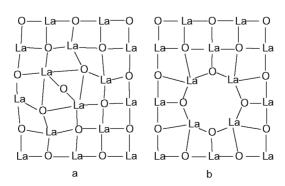


Fig. 12.5. Relaxation of the LaO layer of La_2NiO_4 by (a) an O^{2-} interstitial or (b) an La^{3+} vacancy.

(marked by + on Fig. 12.1), but it is necessary to occupy only a small fraction of these sites. The interstitial O^{2-} ions can easily move between these sites and can adopt many different ordered arrangements giving rise to interesting superstructures (Otero-Diaz *et al.* 1992).

12.3.3 Electronic relaxation

Strains can also be relieved by changing the oxidation states of cations that can adopt more than one oxidation state. Cations in stretched layers can accommodate themselves to longer bonds by reducing their oxidation state, since this will lower the valences of their bonds. Similarly cations that are in compressed layers will tend to increase their oxidation state so as to increase the bond valence and shorten the bonds. This is a mechanism that can be used to stabilize unusual oxidation states.

The addition of 0.18 interstitial O^{2-} ions to the formula unit of La₂NiO₄ requires that the oxidation state of Ni²⁺ be increased to +2.36. Given that the equatorial Ni–O bonds have a length of 194 pm and therefore a bond valence of 0.46 vu, this increase in the oxidation state of Ni allows the axial bond valences to be increased from 0.08 to 0.26 vu reducing the length of the Ni–O_{axial} bonds from 259 pm to the more acceptable value of 215 pm. This in turn reduces the valence required for the axial La–O bond by 0.18 vu which, together with the extra valence contributed by the interstitial O^{2-} , reduces the distortion around La³⁺ to an acceptable level. It is difficult to calculate the BSI and GII for this compound since one needs to know how the interstitial O^{2-} ions are ordered within the LaO double layer, but clearly the BSI will be considerably reduced from the value 0.29 vu that it had before the introduction of the defect and subsequent electronic relaxation. This form of the structure is stable and is the form normally found when the material is prepared in air.

The relaxation of La_2NiO_4 to $La_2NiO_{4.18}$ illustrates a couple of important points. Firstly, the defect and electronic modes of relaxation necessarily work together since the change in oxidation state of Ni^{2+} is directly related to the amount of interstitial O^{2-} present. This simultaneous relaxation of both the stretched and the compressed layers is a feature found in many, if not all, of the observed mechanisms for relaxing lattice-induced strain. Secondly, the lattice-induced strain is directly responsible for the crystallization of a stable compound with a fixed, but irrational, composition, involving a fixed, but non-integral, oxidation state for nickel.

 La_2CuO_4 has a structure and crystal chemistry virtually identical to that of La_2NiO_4 with a couple of important exceptions. Firstly, all octahedrally coordinated Cu^{2+} compounds show a spontaneous electronic distortion (the Jahn–Teller distortion described in Section 8.3.1) by which the two axial bonds become longer and the four equatorial bonds become shorter. The distortion observed in La_2CuO_4 is usually attributed to this effect, but the observation of the same distortion in La_2NiO_4 shows that the driving force in both compounds

is the lattice-induced strain. The only difference is that the lattice-induced distortion in La_2CuO_4 is further stabilized by the Jahn–Teller effect.

The second difference between the nickel and copper compounds is that La₂CuO₄ is a superconductor, being the first of the CuO₂ layer compounds in which superconductivity was observed. The lattice-induced strain is a necessary condition for superconductivity since it stabilizes the higher oxidation state needed to provide the superconducting carriers as discussed in Section 13.3.2.

The electronic relaxation of lattice strain is an important factor in many other superconducting copper oxides. In the most famous compound in the series, $Ba_2YCu_3O_{6+\delta}$, there are two layers containing copper. One is the superconducting CuO_2 layer, the other is a similar layer which is heavily depleted in oxygen, CuO_{δ} . The strains that arise between these and the BaO layer result in the transfer of electrons between the two different types of copper atom, depending on the value of δ . By annealing the material in atmospheres containing different amounts of oxygen, it is possible to tune the oxidation states of the copper ions and hence to tune the superconducting properties of the material (Brown 1991b).

12.3.4 Relaxation of symmetry—displacive phase transitions

The geometric relaxation described in Section 12.3.1 occurs by redistributing the bond valence between the bonds until GII and BSI both have acceptable values, but in some cases this relaxation is restricted by symmetry. In the case of perovskite, the cubic symmetry of the archetypal ABO₃ structure (Fig. 10.4) does not allow any of the bonds to relax unless the symmetry is lowered. Thus true cubic perovskites are rare since they can only exist if the A and B ions are exactly the right size. Most perovskites have a reduced symmetry that allows the bonds to relax. For compounds in which the A–O bonds are stretched, the relaxation takes the form of a rotation of the BO₆ octahedra and results in a reduction of the coordination number of A. The various relaxed structures based on different expected coordination numbers were modelled in Section 11.2.2.4.

Relaxation by loss of symmetry can also be seen in the structures adopted by La_2NiO_4 when it is prepared in the absence of oxygen, thus preventing the absorption of interstitial O^{2-} ions. At high temperatures, the crystal has tetragonal symmetry, i.e. the two in-plane axes are identical by symmetry and the La, Ni, and oxygen atoms all lie on a four-fold axis (the oxygen atoms are those in the $(LaO)_2$ layer). As the temperature is reduced, the four-fold symmetry is lost and the compressed NiO_2 layers buckle. This has the effect relaxing both the compressed NiO_2 layer and the stretched $(LaO)_2$ layer. The buckling of the NiO_2 layer allows the equatorial Ni-O bonds to be longer without changing the size of the lattice translation, and at the same time it displaces the axial oxygen atoms from the four-fold axis, thus distorting the environment around La^{3+} . This, according to the distortion theorem (Rule 3.6), increases the valence sum at La^{3+} without changing the average bond length.

Buckling of the ${\rm NiO_2}$ layers occurs by the rotation of the ${\rm NiO_6}$ octahedra, either around an equatorial Ni–O bond or about the bisector of two equatorial bonds, giving rise to two different structures (with space groups P4₂/ncm and Bmab respectively). The structure found at room temperature (Bmab) has GII = 0.23 and BSI = 0.15, that found at low temperature (P4₂/ncm) has GII = 0.21 and BSI = 0.15. In both cases the rotation of the octahedra proceeds only far enough to produce a stable structure, but not far enough to fully relax all the strains, an interesting example of the principle of maximum symmetry which requires the symmetry to be broken only to the extent that the constraints can be satisfied.

Although these structures all have different space groups from the parent tetragonal structure (I4/mmm) shown in Fig. 12.1, the differences between them are small, the atoms are only slightly displaced from the positions they would occupy in the high-symmetry archetype. The transitions between these different structures are called displacive phase transitions and are frequently observed in strained structures as the temperature is changed. At high temperatures, crystals of La₂NiO₄ have the higher symmetry of the archetype (I4/mmm) but they also have a high GII (0.28) and BSI (0.20). However, I4/mmm is only the macroscopic symmetry of the crystal. The local symmetry around individual atoms is lower. The NiO₂ layers are still buckled, but the rotations of the NiO₆ octahedra are dynamic, with different rotations occurring at different times and in different parts of the crystal. The higher symmetry only appears when the displacements are averaged over the whole crystal. As the temperature is reduced, the rotations freeze out and the crystal goes through a phase transition to a lower-symmetry structure. The topology (bond graph) generally remains unaltered during a displacive phase transition, only the bond lengths changing, though if the changes in bond length are large enough, some bonds may be broken and new ones formed.

12.3.5 Changing the bond graph—reconstructive phase transitions

Reconstructive phase transitions occur when major changes are made in the topology, i.e. when the bond graph is reorganized. The transitions usually observed in structures with lattice-induced strain are displacive and often second order (no latent heat). Reconstructive transitions arise when two quite different structures with the same composition have similar free energies. Unlike the displacive transitions they involve the dissolution of one structure and the recrystallization of a quite different structure. These phase transitions possess a latent heat and often display hysteresis.

Conceptual reconstructive transitions can be valuable in modelling in cases where a proposed high-symmetry structure is so excessively strained that a drastic rearrangement of the bonds is needed. As an example consider the high-symmetry bond graph of $CaCrF_5$ (10286, Fig. 12.6(a)) drawn by connecting Cr^{3+} to each of the five F^- ions, with one bond doubled to give the expected six

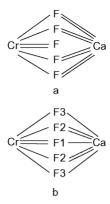


Fig. 12.6. Bond graph of CaCrF₅ (a) tetragonal archetype, (b) observed monoclinic structure.

coordination around Cr3+. This makes one of the F- ions unique but the remaining four are still symmetrically equivalent. Ca²⁺ is then expected to form two bonds to each of these four F⁻ ions to match the ideal coordination number of 8. This graph can be easily mapped into the high-symmetry tetragonal space group P4/mmm using the method described in Section 11.2.2.4 (Fig. 12.7(a)). In this structure, chains of corner-linked CrF₆ octahedra run along the unique axis with Ca²⁺ ions occupying the channels between the chains. The problem with this structure is that, given the predicted Ca-F bond length (236 pm), the F ions from different chains are brought much too close to each other (194 pm), while the F⁻ ions in adjacent octahedra of the same chain are too far apart (383 pm). The relaxation conceptually occurs in two stages. First, the chains buckle by rotating the octahedra in alternate directions until the F⁻ ions in adjacent octahedra are just touching (Fig. 12.7(b)), then planes of chains shear so that the octahedra of one chain fit into spaces between the octahedra of the adjacent chain to give the monoclinic structure (C2/c) shown in Fig. 12.7(c). In the process, several Ca-F bonds are broken and new ones formed, so the structure adopts the lower-symmetry bond graph shown in Fig. 12.6(b) (Brown 1992b). In the real structure the two Ca-F2 bonds are not related by crystallographic symmetry and have slightly different distances as a result of lattice-induced strain. Details of the predicted and observed geometries are given in Table 3.1.

In this compound the tetragonal structure is not known. It is introduced into the modelling process as the archetype that corresponds to the bond graph predicted using the methods of Section 11.2.2.1. However, the stretching of the Ca–F bonds and compressing of the Cr–F bonds needed to form this structure is so large that it can be relaxed only by a reorganization of the bond graph itself. Even though the observed symmetry is low, the principle of maximum symmetry is not violated because the constraints acting on the system do not permit the formation of a structure with higher symmetry.

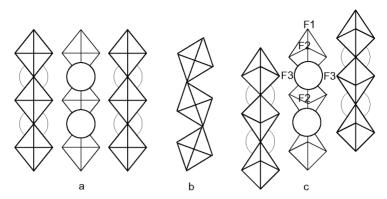


Fig. 12.7. (a) Tetragonal structure of the CaCrF₅ archetype, (b) buckled CrO₅ chain, (c) observed monoclinic structure viewed perpendicular to the projection shown in (b). The octahedra represent the CrF₆ groups, the circles represent Ca²⁺.

12.4 Incommensurate structures

Where the individual blocks that compose the crystal are only weakly bonded to each other, the result may be an incommensurate composite structure such as $(\text{EuS})_{1.725}(\text{NbS}_2)$ shown in Fig. 12.2 (Cario *et al.* 1999). Crystals of this compound consist of alternating cationic $(\text{EuS})_3^+$ and anionic $(\text{NbS})_2^-$ layers. The $(\text{EuS})_3$ layer has the NaCl structure with an ideal cubic lattice parameter of 576 pm, calculated for a six-coordinate mixture of $\text{Eu}^{3+} + 2\text{Eu}^{2+}$. The NbS₂ layer is composed of two hexagonal close packed sheets of S^{2-} ions with Nb^{3.42+} filling the octahedral holes between them (Section 11.2.1.2). This layer can be described by a centred cell having the ideal dimensions 576×332 pm (assuming $R_0 = 214$ pm in eqn (3.1)). The 576 pm cell dimension of the NbS₂ layer matches 576 pm cell dimension of the (EuS)₃ layer. In the other direction however, the two layers have different and incommensurate translation vectors, 576 and 332 pm for (EuS)₃ and NbS₂ respectively. In this direction each layer maintains its own periodicity, with the result that the compound has a fixed but non-integral stoichiometry.

This has a number of interesting consequences. One is that the oxidation state of Nb is lowered from the ideal value of +3.5 to +3.425. A second consequence is that each Eu^{2+} ion at the surface of the (EuS)₃ layer has a different environment since each sees a different part of the NbS₂ layer. Some Eu^{2+} ions lie directly over an S^{2-} ion and form a very short Eu-S bond, while others lie between the S^{2-} ions and form two or more longer bonds. Not surprisingly, the bond valence sums around the Eu^{2+} ions, as well as around the S^{2-} ions of the NbS₂⁻ layer, show considerable variation depending on the relative positions of the layers at any given point in the crystal.

This variation can be reduced if each layer relaxes so as to ensure that the valence sums around all ions deviate as little as possible from the expected atomic valence. This is achieved by displacing the ions from their ideal positions in a way that follows the positions of the atoms in the adjacent layer. Such displacements can be described by a displacement wave with a wave vector directed along the incommensurate axis, the wavelength in the (EuS)₃ layer being equal to the lattice translation of the NbS₂ layer, and the wavelength in the NbS₂ layer being equal to the lattice translation of the (EuS)₃ layer. When account is taken of these displacements, the bond valence sums around Eu are close to their expected value as shown in Fig. 12.8 which plots the valence sum experienced by the Eu³⁺ and Eu²⁺ ions as the (EuS)₃ and NbS₂ layers slide past each other.

A second example of an incommensurate composite structure is given by $Hg_{2.82}AsF_6$ (6029). In this compound, shown in Fig. 12.9, the octahedral AsF_6^- ions form a compact array which contains two mutually perpendicular sets of channels through which are threaded chains of metallically bonded Hg atoms. The chains act as cations in which each Hg atom carries a formal charge of +0.35 vu (to balance the charge on the anions) leaving 1.65 electrons with which it forms metallic bonds of length 267 pm to its two Hg neighbours in the chain (see Fig. 3.8). The composition of this compound is determined by a balance between structural chemistries of the two independent components. On the one hand is the charge (-1) and spacing (754 pm) of the AsF_6^- framework, on the other the relationship between the charge and spacing of the atoms in the Hg metallic chain. As in (EuS)_{1.725}(NbS₂) the two components are incommensurate because the interaction between them is weak relative to the interactions within each component itself and, also as in (EuS)_{1.725}(NbS₂), each component is

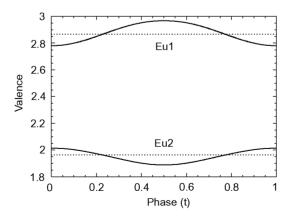


Fig. 12.8. The bond valence sums calculated around Eu²⁺ (Eu2) on the surface of the EuS layer and Eu³⁺ (Eu1) inside the layer as a function of the position along the incommensurate wave (phase t). Reproduced with permission from Cario *et al.* (1999).

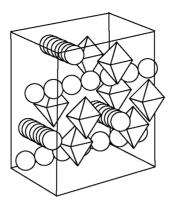


Fig. 12.9. The structure of $Hg_{3-\delta}AsF_6$. The octahedra represent the AsF_6^- ions, the rows of circles represent the chains of Hg atoms.

modulated with a displacement wave having a wavelength equal to the lattice translation of the other component.

Hg_{2.82}AsF₆ has a number of interesting properties. The metallic character of the mercury chains ensures that Hg_{2.82}AsF₆ is an electron conductor and, close to absolute zero, it becomes superconducting. The incommensuration between the chains and the AsF₆ lattice also ensures that the Hg atoms can diffuse easily through the crystal. All possible environments of AsF₆ ions around Hg are found at some point or another along the chain, so the average bonding of the Hg atoms does not change as the chain slides though the channel. For every Hg atom whose bonding energy increases there is another Hg further down the chain whose bond energy decreases by the same amount. Thus there is no activation barrier to diffusion which makes it easy to grow large crystals. Crystals nucleate on the surface of a drop of mercury placed in a liquid SO₂ solution of AsF₅, and mercury diffuses through the channels to the growing surface which reaches out into the solution. The result is the appearance of large, flat golden metallic crystals extended along the two directions of the Hg channels. On cooling, the AsF₆ lattice contracts faster than the Hg chains, with the result that small droplets of mercury are squeezed out onto the surface of the crystal. Hg_{2.82}AsF₆ is, however, exceedingly sensitive to moisture which limits the extent to which its unusual properties can be exploited (Gillespie et al. 1985; Datars et al. 1985).

Not all incommensurate structures are composite. It is possible to have incommensurate modulations in a structure composed of a single infinite building block, particularly if a weak cation fits rather loosely into a hole in a flexible framework. The polyhedra that compose the framework tend to twist to give the cation a distorted environment. These twists can often be described by a wave with a wavelength that may or may not be commensurate with the lattice translation of the crystal. If it is commensurate, the twisting is described as

producing a superstructure, if it is not, it is described as producing an incommensurate modulated structure. The mellilite family of structures, which have the generic formula $A_2MN_2O_7$, consist of a framework of linked MO_4 and NO_4 tetrahedra (M=Si, Ge; N=Zn, Co) with holes that contain $A=Ca^{2+}$ or Sr^{2+} . The holes are rather too large for Ca^{2+} ions but are about right for Sr^{2+} . The compounds containing Sr^{2+} therefore have relatively small GIIs (eqn (12.2)) (0.17 vu for $Sr_2ZnGe_2O_7$ (39159)) but those containing Ca^{2+} have GIIs that are much greater (0.29 vu for $Ca_2ZnGe_2O_7$ (69387)). Thus it is not surprising to find that the Sr^{2+} compounds adopt the high-symmetry tetragonal archetype structure while the Ca^{2+} compounds adopt an incommensurately modulated structure of lower symmetry (Armbruster *et al.* 1990; Bagautdinov *et al.* 2000).

These examples illustrate how fundamental building blocks that are only weakly bonded to each other can give rise to incommensurate structures, and how such structures relax by generating waves of small displacements that ensure conformance to the valence sum rule around all atoms. An excellent and full account of modulated structures has recently been published by Withers *et al.* (1998) where many further details of these fascinating materials can be found.

12.5 Summary

The examples discussed in this chapter show that there are many different ways in which lattice-induced strain can be relaxed or accommodated, the particular mode depending on the properties of the elements and the structures involved. Many of these compounds have unusual properties resulting from non-integral stoichiometry, the presence of non-integral oxidation states, or the spontaneous breaking of symmetry, all of which are the direct consequence of lattice-induced strain.

Lattice-induced strains are characterized by large values of the GII because the environments around some atoms are stretched and around other atoms are compressed but, since the valence is still distributed as uniformly as possible among the bonds, the BSI remains small. This contrast with the electronically driven distortions discussed in Chapter 8 where the GII is small (the valence sum rule is obeyed) but the BSI is necessarily large.

There are, obviously, no compounds to illustrate lattice-induced strains with $GII \gg 0.2$ vu. Such structures are unstable and cannot exist, but if it is possible to model structures of any arbitrary composition using the methods described in Chapter 11, it is possible to determine which compositions give rise to stable structures and which ones do not. A systematic exploration of different compositions occurring between a group of elements would then lead to an understanding of the phase diagram. For example, on the basis of a few simple rules, Skowron and Brown (1994) were able to predict most of the structures in the Pb-Sb-S phase diagram and their relative stabilities (Section 11.2.2.2).

The set of all observed structures is necessarily a highly biased selection of all conceivable structures, but any proper model of chemical bonding in inorganic solids should be able to account for the structures that do not exist as well as for those that do.

IV Applications and implications



Applications

13.1 Introduction

The previous chapters have described the bond valence model and shown how it can be used to understand many aspects of the crystal chemistry of inorganic compounds, but the model has found application in many other fields ranging from metals to proteins. This chapter does not pretend to be a comprehensive review of the uses to which bond valences have been put. Rather it is intended to give a flavour of the wide range of problems that can be treated using the model, presented from the point of view of the scientific issues that need to be addressed rather than from the point of view of the model itself. It is apparent that these applications extend well beyond the inorganic systems within which the model was developed, but the common feature is that all involve some form of acidbase bonding.

The applications have been organized according to the scientific disciplines to which they most closely relate, but many are interdisciplinary and could equally well appear under more than one heading. Cross references are given to places where a particular theme can also be found discussed under another discipline heading.

13.2 Crystallography

Applications discussed in this section are those that have traditionally been considered fields of crystallography, namely the determination and analysis of crystal structures.

13.2.1 Structure solution

As described in Chapter 11, bond valences can play a role in modelling but, since most crystal structures can still not be predicted *ab initio*, diffraction methods remain the most common and reliable technique for determining the structures of those compounds that can be prepared as single crystals large enough for study by X-ray or neutron diffraction.

Where a material can only be prepared as a fine crystalline powder, powder diffraction methods are needed, and for these the determination of the phases of the diffraction peaks is more problematic. Often a good model structure is

needed to allow a comparison between the measured and calculated diffraction pattern. As mentioned in Section 11.2.1.1, there have been a number of attempts to produce model structures *ab initio* using simulated annealing (Pannetier *et al.* 1990) and genetic algorithms (Woodley *et al.* 1999). These methods often make use of lattice parameters obtained from the powder diffraction pattern, though in principle this is not necessary. A more powerful technique is to combine the chemical information supplied by the bond valence model with the observed diffraction pattern using reverse Monte Carlo methods. In this approach the cost function contains the discrepancy between the observed and calculated powder pattern as well as the differences between the atomic valences and the corresponding bond valence sums (Swenson and Adams 2001).

Once the basic structure has been determined, bond valences can be used to resolve a number of problems of interpretation. Diffraction experiments can identify the location of each atom, but cannot identify its oxidation state. In most structures the oxidation state is determined by the requirements of electroneutrality (Rule 11.1), but in some structures more than one assignment is possible. Bond valence sums can usually resolve this ambiguity.

A classic and particularly interesting example is the distribution of Fe^{2+} and Fe^{3+} between the octahedral and tetrahedral sites in the spinel, magnetite, Fe_3O_4 (65340). The average oxidation state of iron in spinel is 2.67 but the ions can be arranged with either Fe^{2+} on the tetrahedral site and $2Fe^{3+}$ on the two octahedral sites (normal spinel), Fe^{2+} on an octahedral site and $2Fe^{3+}$ split between the tetrahedral and octahedral sites (inverse spinel), or some mixture of these characterized by an inversion parameter which measures the proportion of the inverse structure present. The relative amounts (p_1 and p_2) of each cation on a given site can be determined using eqns (13.1) and (13.2) which are readily derived by setting the weighted bond valence sum equal to the average charge and solving for p_1 :

$$p_1 = \left(\sum S_2 - V_2\right) / \left[(V_1 - V_2) - \left(\sum S_1 - \sum S_2\right) \right]$$
 (13.1)

and

$$p_2 = 1 - p_1, (13.2)$$

where V_1 and V_2 are the atomic valences, and ΣS_1 and ΣS_2 are the corresponding bond valence sums at the cation site calculated from the observed bond lengths. ΣS_1 is calculated assuming that the site is fully occupied by the cation with valence V_1 (Fe²⁺) and ΣS_2 by assuming that the site is fully occupied by the cation with valence V_2 (Fe³⁺). The results for Fe₃O₄ are shown in Table 13.1. The observed bond lengths (column 2) are used to calculate the valences, S, of the bonds in the tetrahedral and octahedral sites assuming the cation is all Fe²⁺ (column 3) or all Fe³⁺ (column 4). These are substituted into eqns (13.1) and (13.2) to determine the proportions, p_1 and p_2 , of Fe²⁺ and Fe³⁺ on each site (column 5 and 6) from which the degree of inversion, i (column 7),

Site	Length (pm)	$S(\mathrm{Fe}^{2+})$ (vu)	$S(\mathrm{Fe}^{3+})$ (vu)	$p(Fe^{2+})$	$p(Fe^{3+})$	i
T	188.9	0.658	0.704	0.227	0.773	0.77
O	206.0	0.414	0.443	0.412	0.588	0.81

Table 13.1 Fe^{2+} and Fe^{3+} distribution in Fe_3O_4 (65340)

T = tetrahedral site, O = octahedral site. p gives the proportion of the ion on the site. The last column gives the inversion parameter, i.

can be determined. The independent values of the inversion parameters calculated for the two sites are in good agreement with each other, giving confidence that the true inversion parameter is close to 0.79. Kubayashi *et al.* (1998) have confirmed the presence of Fe³⁺ on the tetrahedral site using XANES. The method can be used to explore the contents of any site that contains a cation in two different oxidation states and has been used to determine the charge distribution in vanadium oxides (Åsbrink 1980; Brown 1978) and copper oxide superconductors, though in the latter case allowance has also been made for the lattice-induced strain discussed in Chapter 12 (Brown 1991*b*).

A number of crystals undergo a charge ordering (charge disproportionation) transition as the temperature is lowered, often associated with transition to an insulating or ordered magnetic state. The bond valence sums can be used to determine the distribution of cation valence states below the transition as shown, for example, in NaV_2O_5 by van Smallen and Lüdecke (2000), in rare earth nickelates by Alonso *et al.* (2000), and in CaFeO₃ by Woodward *et al.* (2000).

Equations (13.1) and (13.2) can also be used to explore the disorder that occurs when two different ions occupy the same crystallographic site since there is nothing in the above analysis that requires both cations to belong to the same chemical element. In this case, it is the effective occupation numbers of the two ions rather than the oxidation states that are calculated, p_1 measuring the probability of finding an atom of element 1, and p_2 measuring the probability of finding an atom of element 2, on the given site.

Occupation numbers can also be determined using X-ray diffraction since the observed electron density is the average electron density of the different ions occupying the site. If the scattering powers (atomic numbers) of the ions are very different, it is easy to determine the occupation number using diffraction methods, but if the two ions have a similar number of electrons, for example if they are adjacent in the periodic table, such as Al^{3+} and Si^{4+} or Pb^{2+} and Bi^{3+} , X-ray diffraction is unable to distinguish between them. However, the bond lengths will be different, because atoms adjacent in the periodic table usually have different oxidation states and so can be distinguished by their bond valence sums. Skowron and Brown (1990) used this method to determine the distribution of Sn^{2+} and Sb^{3+} over the various cation sites in $Sn_4Sb_6S_{13}$ (26332).

Equations (13.1) and (13.2) can be used when only two species occupy a given site but sometimes several different species are found to occupy the same site, particularly in minerals. In this case it is necessary to use all available evidence

to determine the site occupations. Wright *et al.* (2000) have written the program OccQP which optimizes the occupation numbers using a weighted combination of electron density, chemical composition, and bond valence sums. They have shown that it is possible to determine the distribution of as many as 12 cation species over the 5 crystallographic sites in dravite tourmaline.

Hydrogen bonding plays a vital role in the cohesion and properties of many crystals but the geometry of hydrogen bonds is poorly determined using X-ray diffraction for the reasons discussed in Section 7.8. Donnay and Allmann (1970) have shown how a knowledge of the valences of the remaining bonds in the crystal can be used to reconstruct the hydrogen bonding scheme and a recent example of the technique can be found in the paper by Adams *et al.* (1993). Details of this technique are given in Section 7.8 and will not be repeated here except to point out that the bond valence model treats hydrogen just like any other cation providing that the repulsion between the donor and acceptor anions is taken into account.

Particularly interesting is the application of bond valences to the determination of superstructures. Crystals with lattice-induced strain frequently relax by displacing the atoms in a way that leads to the breakdown of the translational symmetry and the formation of a superstructure (Section 12.4). While the substructure can generally be determined unambiguously using standard X-ray diffraction methods, there are usually several modes of distortion that are compatible with the observed superstructure peaks and it is not easy to determine which is correct. Withers *et al.* (1991) systematically explored the possible relaxations of $\mathrm{Bi_4Ti_3O_{12}}$ (16488) and used the bond valence sums around each of the atoms to deduce the proper relaxation. The correct structure has a global instability index (GII, eqn (12.2)) of 0.19 vu compared with 0.26 vu for the incorrect structure previously reported.

Diffraction methods are not the only way of determining structure. Other techniques that sometimes make use of bond valences include NMR discussed in Section 13.5.1 and EXAFS discussed in Section 13.6.1.

13.2.2 Analysis of crystal structures

Once a crystal structure has been determined, it is customary to analyse the results from a chemical perspective. For inorganic compounds, one of the best ways is to calculate the valences of the bonds using eqn (3.1) or (3.2) to convert the rather precise information available in the bond lengths into bond valences. Although length and valence both measure the strength of a bond, the valences are independent of atomic size and can distinguish between the strong and weak bonds in a crystal. They thus identify which bonds are important in determining the structure. This is well illustrated by ZnSb₂O₆ (30409, Fig. 8.9). Zn²⁺ and Sb⁵⁺ ions both form bonds to O²⁻ with lengths of around 210 pm, but the ions themselves are very different in size. Calculation of the bond valences quickly draws attention to the greater strength of the Sb-O bonds (0.83 vu) relative to Zn-O (0.33 vu), indicating that they play a much more important role in

determining the structure. Bond valences also give a quantitative explanation of the loss of tetrahedral symmetry of oxyanions such as PO_4^{3-} when placed in an environment of lower symmetry as described in Section 9.2.

The most common application of bond valences has been to test whether a proposed structure complies with the normal rules of crystal chemistry by comparing the bond valence sums with the atomic valence. Many reports of structure determinations routinely include a listing of the bond valences since bond valence sums that agree with the atomic valences can be taken as primae facie evidence of a correct structure. An example of such an analysis is shown in Table 13.2. The valence sum will immediately identify an incorrectly assigned oxidation state (see Section 13.7 for its use in detecting errors in structural databases) but, even if the oxidation state is correct, a valence sum that is too small may indicate that some bonds or atoms, such as water of crystallization. have been overlooked. Low valence sums around some cations and high valence sums around others is the signature of lattice-induced strain (Chapter 12) which should be confirmed by a careful analysis of the bond strains and their modes of relaxation. The GII (eqn (12.2)) and the bond strain index (BSI, eqn (12.1)) can be used to test whether the strain is large enough to cause the compound to relax to a lower symmetry or to a modulated structure. If either of these values are greater than 0.2 vu, the diffraction pattern should be examined for evidence of superstructures. A large GII is an indication of lattice-induced strain (Chapter 8) while a large BSI is an indicator of electronic strain (Chapter 8). Hunter et al. (1999) used bond valences to show how the expansion or contraction of the unit cell of yttrium stabilized zirconia was a natural consequence of the changes in bond length on substitution for Zr^{4+} . In particular they were able to show why substitution by the smaller cation Sn⁴⁺ leads to expansion of the unit cell.

Table 13.2 Observed bond lengths (pm), bond valences (vu) and bond valence sums (vu) for Li₂SO₄·H₂O (62089)

	Li1	Li2	S	H1	H2	Sum
O1	191		146	203		
	0.30		1.54	0.15		1.99
O2		194, 195	148	282		
		0.28,0.27	1.48	0.04		2.07
O3	196, 198		148			
	0.26, 0.25		1.49			2.00
O4	200	195	148	278	290	
	0.24	0.27	1.49	0.05	0.03	2.08
O5		190		93	91, 216	
		0.31		(0.76)	(0.82),0.15	2.04
Sum	1.05	1.12	6.00	(1.00)	(1.00)	

Valences in parentheses were determined by assuming that the valence sum around H is 1.00 (see Section 7.8).

13.3 Physics

Condensed matter physicists are interested in the electrical, magnetic, and mechanical properties of solids. Many of the electrical and all of the magnetic properties depend on the behaviour of electrons whose properties are not explicitly described by the bond valence model. Normal metallic conduction is a property of delocalized electrons which do not satisfy the bond valence model requirement that the bond graph be bipartite (condition 3.2). Similarly, magnetic properties depend on the magnetic coupling between the unpaired spins of electrons, a property which also lies beyond the scope of the model. However, both are influenced by the underlying chemical structure which can be usefully analysed using bond valences. The model has a more direct application to physical properties such as ferroelectricity and ionic conduction, which depend only on the motions of ions, and on mechanical properties which depend on defects in the crystal structure.

Physicists prefer to test their theories against observations made on simple crystals such as those with structures of the NaCl (18189, Fig. 1.1) and perovskite (ABO₃, Fig. 10.4) type. Although these two structure-types are adopted by many different compositions, both have cubic symmetry and a single free crystallographic parameter, the unit cell edge, which simplifies the theory. The properties of compounds with the NaCl structure are straightforward, but the perovskite structure turns out to be anything but simple because the single free parameter must be consistent with the lengths of both the A-O and the B-O bonds. In general, one free parameter cannot be made to satisfy two constrains at the same time, so compounds belonging to the perovskite family always show some degree of lattice-induced strain and most of them relax to structures having lower symmetry and therefore more degrees of freedom. Further complexities can be found among the perovskite-related layer structures in which layers of perovskite-like structure alternate with layers of NaCl-like structure as in La₂NiO₄ (65917, Fig. 12.1). As a result, the perovskite family of structures possesses a rich and complex crystallography which, because of the need to relax the lattice-induced strain, gives rise to a variety of interesting physical properties. Not surprisingly, many of the applications of bond valences in physics are directed to understanding the physical properties of the perovskite family of compounds. For this reason, Section 13.3.1 provides an introduction to the perovskite structures. Later sections focus on particular properties, many of them also found in the perovskite system.

13.3.1 Perovskite-related solids

In Chapter 12 the layered perovskite, La₂NiO₄ (65917), was used as an example of a structure which displays lattice-induced strain. This compound is typical of the large class of perovskite-related structures. All show some degree of lattice-induced strain and, because the mechanism of relaxation depends on the details

PHYSICS 187

of the composition and structure, the perovskites as a class show many unusual physical and chemical properties that can be conveniently analysed using bond valences.

The parent perovskite structure shown in Fig. 10.4 consists of alternating layers of composition AO and BO₂, as for example in BaTiO₃ (23759) and CaTiO₃ (62149). It is also possible to have several AO layers between each BO₂ layer providing each AO layer is sheared by half a unit cell from the adjacent AO layers, as shown for La₂NiO₄ in Fig. 12.1. This permits a wide range of structures with an even wider range of compositions to be prepared. Which compositions are possible depend on how well the structure can accommodate the bonding requirements of the atoms A and B.

In a perovskite¹ in which all the anion (O²⁻) sites are occupied, the coordination number of the cation depends on the layer in which the cation is found and its adjacent layers. The B cation is always six coordinate because only AO layers can neighbour a BO₂ layer. In the triple sequence AO-AO-AO, the central A cation is also six coordinate (as in NaCl), but in the sequence AO-AO-BO₂ it is 9 coordinate while in the sequence BO₂-AO-BO₂ it is 12 coordinate. However, many perovskites have systematically missing ions, which extends the range of possible coordination numbers from a low of 2 to a high of 12, providing a coordination number to match the requirements of almost any cation in the periodic table (Brown 1991a). The effective coordination number of an A cation can also be reduced by rotating the BO₆ octahedra, giving rise to the low-symmetry perovskites that were modelled in Sections 11.2.2.1 and 11.2.2.4 (see also Woodward 1997a,b).

However, selecting a layer sequence that gives the correct coordination number is only one of the conditions that needs to be met. In general, two other conditions must also be satisfied. The composition must be electroneutral and the bond lengths calculated from theoretical bond valences must lead to a set of layers that are commensurate or nearly so, that is, all the layers must have the same lattice spacings. Figure 13.1 shows the lattice spacing expected for a number of cations as a function of their typical coordination number. Using this figure it is possible to design different compounds by choosing AO and BO₂ layers with similar lattice spacings together with layer sequences that provide the appropriate coordination numbers.

Whatever composition and structure is chosen, a perfect match between the lattice spacings of the different layers is virtually impossible to achieve. Thus all perovskites show some evidence of lattice-induced strain. Section 13.3 describes some of the ways in which these strains can be relaxed, and the more effective the method of relaxation, the greater the amount of mismatch that can be accommodated. Since many relaxation mechanisms have already

 $^{^{1}}$ The term 'perovskite' is used here loosely to comprise all the structures based on sequences of AO and BO₂ layers.

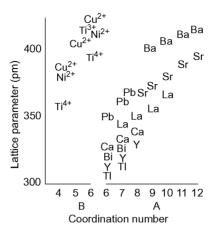


Fig. 13.1. The lattice parameter of a perovskite layer as a function of its cation coordination number. Cations in the BO_2 layers are shown on the left, those in the AO layers are shown on the right.

been illustrated in Chapter 12 using the example of La₂NiO₄, only one further example will be given here.

Appendix 4 shows that Tl^{3+} favours a coordination number of 6 suggesting that it would be found in the layer sequence $AO-TlO-AO.^2$ However, the lattice spacing of a TlO layer is much smaller than any of the other AO or BO_2 layers shown in Fig. 13.1, so the Tl-O bonds within the layer must be stretched. This stress is relaxed in part by reducing the oxidation state of some of the Tl^{3+} ions to Tl^+ , and in part by shortening the two interlayer (axial) Tl-O bonds. The first relaxation results in an increase in the oxidation state of other cations in the structure (typically Cu^{2+} increased to Cu^{3+}). The second gives rise to a flattening of the octahedral environment of Tl^{3+} which, since Tl^{3+} is a relatively hard cation, is not easily stabilized by an electronic rearrangement as would, for example, be possible around Bi^{3+} . Hg^{2+} , on the other hand, is soft and often spontaneously adopts a flattened octahedral environment. Mercury analogues of the thallium layer compounds such as $HgBa_2Ca_2Cu_3O_8$ (75896) are therefore well known and relatively stable.

13.3.2 Electrical properties

By analogy with ferromagnetism, ferroelectricity is the property by which a crystal has a permanent electric dipole moment which can be reversed by the application of an electric field. The perovskite BaTiO₃, in which the BaO layers are compressed and the TiO₂ layers stretched (see Fig. 13.1), is a ferroelectric

 $^{^2}$ If Tl^{3+} were to occur in a BO_2 layer which also provides six coordination, the lattice spacing within the layer would be 452 pm, much too large to match to any available A cations.

PHYSICS 189

because the Ti⁴⁺ ions move off-centre in accordance with the predictions of the distortion theorem (Rule 3.6). This displacement is favoured by the electronic instability of Ti⁴⁺ in an octahedral environment (Section 8.3.2) as discussed in Section 10.2. The high crystallographic symmetry of the Ti⁴⁺ site in the unrelaxed structure means that the off-centre shift must break the symmetry and therefore can occur in one of several different directions. Whichever way it shifts, neighbouring Ti⁴⁺ ions must shift in the same direction in order to keep the bond valence sums constant around O²⁻. As a result, the crystal acquires a net electric dipole. An external electric field can then be used to reverse the directions in which the Ti⁴⁺ ions are shifted, reversing the direction of polarization. BaTiO₃ is thus a ferroelectric, a property shared by several other perovskites with large A cations (Thomas 1989). Ferroelectrics are used in electric capacitors (because of their large effective dielectric constant) and in electric memory chips (because their polarization can be switched).

Ferroelectric perovskites with Pb²⁺ substituted for Ba²⁺, and Nb⁵⁺ or Ta⁵⁺ plus a divalent cation substituted for Ti⁴⁺, are known as relaxors because the high degree of disorder results in a softening of the sharp dielectric anomalies found in BaTiO₃, making relaxors suitable for a number of important applications in the electronics industry. A typical relaxor has the composition $Pb(B1_{1/3}B2_{2/3})O_3$ with $B1 = Mg^{2+}$ or Zn^{2+} and $B2 = Ta^{5+}$ or Nb^{5+} . Because of the small size of the Zn^{2+} ions, the zinc niobate compound lies just below the limit of stability and can only be prepared if larger ions are included as impurities. Bond valences can be used to determine how much impurity is needed to reach stability. In principle, one could use the GII (eqn (12.2)) to answer this question, but the real structure is disordered and it is therefore impossible to calculate accurate bond valences. However, the conditions for stability can be explored by examining the bond valence sums in a notional cubic structure having the same composition and unit cell volume. The valence sums calculated in this way will be different from those calculated for the real structure and will therefore give an unrealistic measure of the oxidation states, but they allow the different compositions to be ordered according to the degree of mismatch and they are easy to calculate. In the above example, the valence sums around all the atoms in the notional cubic structure are too low since in the real crystal both the A and B cations lie off-centre in their coordination spheres which, according to the distortion theorem, increases their valence sum. In the notional cubic structure the stability limit is found to occur when the valence sum around O^{2-} is 1.74 vu as shown in Fig. 13.2. Wakiya et al. (1997) have shown that the addition of just enough of the larger cation to bring the O²⁻ valence sum up to this value is sufficient to stabilize the compound.

Many layer-perovskites with Cu as the B cation are superconductors at relatively high temperatures ($\sim 100 \, \text{K}$). Although the mechanism of superconductivity is not well understood, a necessary condition is that the oxidation state of the copper ion be around +2.2. In many compounds, such as the well-known YBa₂Cu₃O₇ (63324) this is achieved naturally through the relaxation of

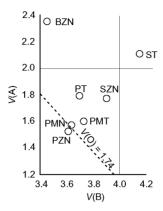


Fig. 13.2. Bond valence sum V(A) versus V(B) for $A(B1_{1/3}B2_{2/3})O_3$ compounds using an idealized cubic perovskite model. The line V(O) = 1.74 vu represents the stability limit. P = Pb, S = Sr, B = Ba, N = Nb, T = Ta, M = Mg, Z = Zn.

the lattice strain as discussed for La_2CuO_4 in Section 12.3.3. More usually the oxidation state of copper is tuned by the inclusion of impurity cations having a different oxidation number, or by adjusting the oxygen content by annealing the material in atmospheres with different oxygen partial pressure. A bond valence analysis provides information on both the extent of the lattice-induced strain and the effective oxidation state of the Cu ions (Tallon 1990; Tanaka *et al.* 1990; Brown 1991*b*; Karppinen and Yamauchi 1999).

Electrical conduction occurs by the movement of charged particles. The bestknown carriers are the free electrons found in metals, but currents can also be carried by charged ions under appropriate conditions. This is the normal mode of conduction in polar liquids where the mobility of all the atoms allows the ions to move with little resistance under the influence of an electric field. However, in most ionic solids the ions are fixed which makes them good insulators, but the structures of some solids contain channels in which the ions can move relatively freely. Such materials, known as solid electrolytes or ionic conductors, have important applications in batteries and fuel cells where the conducting electrodes need to be separated by electronic insulators through which ions can flow under the influence of a chemical potential. This flow generates an electric current which is then used to drive electrical devices. The condition for ionic conduction is that the structure contains channels in which the conducting ions are weakly bound. For example, Hg_{2.86}AsF₆ (6029, Fig. 12.9) described in Section 12.4 is both an ionic conductor and an electronic conductor since the Hg cations are free to move through the channels under the influence of an external field.

An ideal tool to study the mechanism of ionic conduction is the valence map described in Section 11.2.3 since this locates all the points in the crystal at

PHYSICS 191

which the migrating ion has a valence sum equal to its formal charge. The valence map for an ionic conductor has shallow saddle points between the sites occupied by the conducting ions, the values of the valence sum along the conducting pathways always remaining close to the atomic valence of the conducting species (Fig. 11.9).

One important system of ionic conductors is based on α -AgI (200108), often combined with varying amounts of other silver compounds such as Ag₄P₂O₇ or Ag₂MoO₄ to provide glassy or crystalline solid electrolytes. The conduction paths in the parent α -AgI found using the valence map closely follow the Ag⁺ probability density function found by neutron diffraction (Garrett *et al.* 1982), and similar paths have been traced in the 4:1 divanadate complex (Adams 1996). The lowest valence that gives an infinitely connected isovalent surface in a crystal defines a conduction pathway whose enclosed volume is a direct measure of the activation energy for conduction (Adams and Maier 1998; Adams and Swenson 2000*a*). Such a surface is shown for α -AgI in Fig. 11.10. The same approach can be used to explore the nature of the conduction paths in glassy structures using models of the structure obtained by a reverse Monte Carlo fitting of the structure to its diffraction pattern (Swenson and Adams 2001). Since ionic conduction is a special case of ionic diffusion, these techniques can also be used to explore diffusion as described in Section 11.2.3.

13.3.3 Magnetic properties

The perovskite AMnO₃, where A is La³⁺ with an admixture of divalent cations (6148), displays unusually large magnetoresistance and could become an important material in the heads used for reading magnetic memories. Manganese occurs in a mixture of Mn³⁺ and Mn⁴⁺ oxidation states, the former showing a tetragonal Jahn-Teller distortion (Section 8.3.1) because it has a single electron in the eg level (Fig. 8.6(a)). This electron can hop between Mn atoms but, because its spin is coupled to the spin of the remaining 3d electrons, it can only move between manganese atoms that have parallel spins. Thus the mobility of the electron, and hence the electrical conductivity, depends on the material being ferromagnetic. In turn, the presence of conduction helps to stabilize the ferromagnetic ordering. According to the distortion theorem, when the cation A is small, the MnO₆ octahedra rotate to provide a distorted environment for A, but this rotation weakens the ferromagnetic coupling and narrows the electron conduction band. When A becomes small enough, both the ferromagnetism and the electronic conduction simultaneously collapse, but both can be restored by application of a strong enough magnetic field. Compounds at this critical composition show extremely large variations in magnetoresistance (change of electrical resistivity with applied magnetic field) as the temperature and magnetic field are changed, an effect known as 'colossal magnetoresistance' (CMR). This behaviour is also influenced by two other factors, the inhomogeneities introduced by the random occupation of A sites by

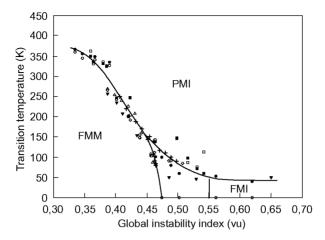


Fig. 13.3. The phase diagram of $A_{0.33}A'_{0.67}MnO_3$ (A = divalent cation, A' = rare earth) as a function of temperature and the global instability index of the idealized perovskite structure. The points show the observed transition temperatures in various compounds. FMM = ferromagnetic metal, PMI = paramagnetic insulator, FMI = ferromagnetic insulator (from Rao *et al.* 1998).

divalent and trivalent cations of different sizes, and by the tendency of the Jahn–Teller distortions around the Mn³⁺ ions to order at higher Mn³⁺ concentrations. As in the case of the Pb²⁺ perovskites discussed in Section 13.3.2, the disorder makes it difficult to calculate the bond valence sums for the real structure, but they can be calculated for the notional cubic structure of the same composition. Rao *et al.* (1998, 1999) used the GII (eqn (12.2)) of a notional cubic structure, in which the Mn–O bonds were given their ideal length, as an order parameter for normalizing the phase diagrams of a wide range of CMR-related compounds (Fig. 13.3).

13.3.4 Grain boundaries

Most materials consist of small randomly oriented crystallites (grains) and, since the bonding in the boundaries between these grains is weaker than in the crystallites, it is the grain boundaries that determine mechanical properties. Browning, Pennycook, and their colleagues have recently explored the nature of these boundaries in a number of simple oxides using high-resolution Z-contrast scanning electron microscopy to locate the positions of atoms, combined with electron energy loss spectroscopy (EELS) to identify the chemical species present in the interface. They used bond valences to construct plausible grain boundary models that are consistent with their observations. They show that the 24° [001] tilt–grain interface in MgO (9863) consists of a string of dislocations which use Ca²⁺ impurity atoms to reduce the strain caused by the failure

of the valence sum rule in the boundary region (Yan *et al.* 1998; Browning *et al.* 1999). Similar interfaces in SrTiO₃ (201256) consist of a series of simple dislocations which saturate the interface at a tilt angle of 10° after which the dislocations become more complex and broader (McGibbon *et al.* 1994, 1996; Browning and Pennycook 1996; Browning *et al.* 1998b). The same behaviour is seen in the structurally related superconductor, YBa₂Cu₃O_{7- δ} (63324), where a bond valence modelling of the interface shows that the valences of the Cu atoms drop from +2.3 vu in the bulk to as low as +1 vu at the centre of the interface, a condition which quenches the superconductivity (Section 13.3.2). As the interfacial angle is increased, the region containing Cu⁺ becomes wider and the distance through which the superconducting electrons need to tunnel becomes larger. In this way Browning *et al.* (1998*a*) were able to account for the exponential decrease in the critical current observed as the interface angle of a grain boundary is increased.

O'Keeffe (1991b) has used bond valences to model the coherent interface that occurs between the semiconductors Si and MSi₂ with M = Ni or Co (27139). Although these systems contain Si-Si bonds and therefore do not obey the assumptions of the bond valence model (condition 3.2), the mathematical formalism of the model still works because of the high symmetry. As both Si-Si and Si-Ni bonds are found in NiSi₂, the cubic structure is strained (cf. BaTiO₃ in Section 13.3.2) and this strain affects the structure of the interface. Of the six possible interfacial structures examined, the two with the lowest BSI eqn (12.1) are those that are believed to occur in NiSi₂ and CoSi₂ respectively, and in both cases the strain introduced at the interface is correctly predicted.

13.4 Mineralogy

In the traditional topological approach to aluminosilicate minerals, the AlO₄ and SiO₄ tetrahedra are treated as forming covalently bonded frameworks, with the remaining atoms ionically bonded in the cavities (Liebau 1985, pp. 52ff.). Since all bonds are divided into the strong bonds that form the framework and the weak bonds formed by the interstitial ions, this approach runs into difficulties when relatively strongly bonded interstitial ions (such as octahedrally bonded Al³⁺) are present. The hierarchical approach recognizes that such a simple division into strong and weak bonds is not always appropriate and that in many minerals there is a continuum of bond strengths ranging from the strong Si–O bonds (1.0 vu) to the weak bonds formed by large alkali cations (~0.1 vu). The process of constructing a mineral starts with the formation of the strong bonds and continues with the formation of increasingly weaker bonds until the whole structure has been formed as discussed in Section 11.2.2.

The systematics of mineral structure have been explored using bond valences in a number of papers by Hawthorne (1985, 1992b (review), 1994, 1997) and Eby and Hawthorne (1993) who have applied the hierarchical principle (Rule 11.5)

to the description of mineral structures. There are many ways in which the strongly bonded aluminosilicate framework can be arranged to form either finite or infinite complexes and the one that is found in a particular mineral is the one that provides the correct bonding strength to match the other cations that are present. According to the valence matching rule (Rule 4.2), the presence of strongly bonding cations such as transition metals (bonding strength ~ 0.33 vu) results in the formation of strongly bonding $\mathrm{SiO_4^{4^-}}$ complexes, while the presence of weakly bonding alkali metals results in the formation of weakly bonding condensed framework silicates as illustrated in Fig. 4.6. In later papers Hawthorne has extended these ideas to phosphate minerals (Hawthorne 1998) and to an examination of the role of water in mineral structures (Hawthorne 1992a).

Wu and Farges (1999) have made use of eqn (9.17) relating bond valence to the coefficient of thermal expansion to confirm that it is possible to resolve the different thermal expansions of the long and short Th–O bonds in thorite (α -ThSiO₄) from XAFS spectra measured between room temperature and 1700 K. They also use this relation to estimate the anharmonic corrections needed for the bond lengths determined from XAFS (Brown *et al.* 1995, pp. 358–9).

13.4.1 Soil chemistry

Soils are composed of finely ground mineral crystals, typically minerals with structures that are strongly bonded in two dimensions and consequently offer easy planes along which the crystals can cleave. Weather and water grind these crystals to a fine powder consisting of thin plates with large exposed surfaces, allowing the crystals to bind to each other, to water or to other chemical species depending on which atoms are exposed on the surface. When such minerals are a major constituent in the soil, they form clays which are plastic when water can bond to the surfaces and hard when the surfaces bond directly to each other. A knowledge of the surface properties of soil minerals is therefore needed in order to understand the properties of soils that are important in agriculture, engineering, and waste management, including the problems of soil remediation, and the ability of soils to hold water or to bind nutrients or toxins.

The surfaces of minerals are created either during crystal growth or subsequently through cleavage of the crystals. Determining the crystal habit and surface properties of a face prepared during growth is difficult since it depends on the growth condition and is largely kinetically controlled, but the process by which crystals break along cleavage planes can be predicted by looking for those planes that break the weakest set of bonds or that leave surfaces with the smallest residual charge. In most cases the same set of planes will satisfy both these criteria. As a practical criterion, cleavage planes are assumed to be those that break the smallest total bond valence per unit area. The valence of the broken bonds then represents the bonding strength of the surface, and the

difference between the bonding strengths of the surface cations and anions gives a measure of the residual charge on the surface (Koretsky *et al.* 1998).

To fully understand the properties of a surface, one needs to know both the bonding strength of each potential binding site as well as its surface density and depth below the surface. In an aqueous environment such as is usually found in soils, water will bond to all surfaces, with oxygen bonding to the surface cations and hydrogen bonding to the surface anions. Either way, the exposed surface contains a mixture of O, OH, and OH₂ groups. The number of bound H⁺ ions depends on the pH of the soil, and the degree of protonation at a given site determines its ability to bond to other cations (Bleam 1993 and references therein).

The proton affinity of different sites in soil minerals can be determined from the degree of over- or underbonding of the surface oxygen ions as measured by their valence sum. A surface O²⁻ ion bonded internally to three octahedrally coordinated Al³⁺ ions has a bond valence sum of 1.5 vu assuming all the Al-O bonds have equal valences. This degree of underbonding suggests that the oxygen will accept two or three hydrogen bonds from adjacent water molecules or that it will bind a cation with a bonding strength of 0.5 vu or less. If this O²⁻ is protonated (i.e. is an OH⁻ group), it has a valence sum of 2.3 vu and is overbonded. In such a configuration the O²⁻ ion is unable to bind any cations but the high degree of overbonding suggests that this species will only be found at low pH and will form strong hydrogen bonds (Section 7.4). Similar arguments suggest that an O²⁻ bound to a single Al³⁺ will be doubly protonated (i.e. will be a water molecule) and, with a valence sum of 2.1 vu, will form moderately strong hydrogen bonds. The best site for binding a weak cation is an O²⁻ ion bonded to two Al³⁺ ions and one proton since this will have a valence sum of 1.8 vu, giving it a bonding strength of 0.2 vu.

Hiemstra *et al.* (1996) have used valence sums of this kind to explore the proton affinities of the different surface sites in various oxides and hydroxides of Si, Ti, Fe, and Al. In some crystals, particularly of the hydroxides, the bonding around the cation is irregular so that the bonding strength of the surface atoms depends on the particular strengths of the metal—O bonds. An analysis of the surface of the goethite form of FeOOH (28247) shows that each crystallographically distinct O²⁻ site on the surface has a different bonding strength and therefore a different proton affinity. As expected, O²⁻ ions bonded to a single Fe³⁺ ion are generally protonated and those bonding to three Fe³⁺ ions are generally unprotonated. Over the pH range normally encountered, only one of the five crystallographically distinct O²⁻ sites is able to adsorb or desorb H⁺ (Venema *et al.* 1998). Bond valence modelling of the Fe³⁺ clay mineral, ferrihydrite, combined with the measurements of the X-ray absorption near-edge structure (XANES), reveals differences in the surface hydration depending on whether the clay is wet or dry (Manceau and Gates 1997).

Bargar *et al.* (1997*a*,*b*,*c*) have explored the affinity of the surface oxygen atoms in aluminum and iron oxides and hydroxides for Pb(II) and Co(II) using

bond-valence modelled structures to interpret the results of surface X-ray absorption fine structure (XAFS) measurements which give information about the distances to atoms neighbouring the Pb or Co adatom. They are able to show that Pb(II), which can form relatively strong bonds of 0.50 vu, and Co(II), which forms weaker bonds of 0.33 vu (Appendix 4), tend to bind to different sites and that, for a given cation, some crystallographic faces have better bonding sites than others.

Rohrer and Rohrer (1994) used Monte Carlo simulation with a bond valence cost function to show that Al³⁺ dissolved in MgO migrates to the surface of the crystal where it helps to passivate the active surface base sites.

Xia et al. (1997a,b) have used bond valences to model the coordination environment of transition metals and Pb(II) complexed to humic, fulvic, and other soil acids that consist of a mix of oxygen-containing organic species capable of coordinating metal atoms. They compared the XAFS spectra calculated for a model complex with the spectra measured from real samples and conclude that the metal atoms form inner-shell complexes, i.e. they bond directly to the organic acids rather than indirectly through the formation of a hydrated metal complex. Other examples of the use of bond valences to model surfaces are given below in Section 13.5.3.

The fine size of soil particles makes the determination of their bulk structure difficult since it is generally impossible to obtain crystals large enough for single crystal measurements. Thus X-ray absorption spectroscopy (XAS) provides information not generally available by other means even for the bulk materials. Manceau *et al.* (1998) have made use of the sheet-like character of clay minerals to prepare oriented films of Garfield nontronite on which they made oriented extended X-ray absorption fine structure (EXAFS) measurements with polarized X-rays. In order to compare these results with theory, they needed a good model structure which they obtained using the Distance Valence Least Squares (DVLS) program of Kroll *et al.* (1992) described in Section 11.3. In this way they were able to model the distortions in the archetype structure of smectic clay minerals caused by incommensurations between the ideal structures of the octahedral and tetrahedral layers.

13.4.2 Zeolites

The bond valence model can be applied to the structure of zeolites, though the many different structures adopted by the aluminosilicate framework are better described using simple topological models, since all the links between AlO_4 and SiO_4 tetrahedra that make up these frameworks can be treated as equivalent and the bond valence model adds little to this description. However, it is possible to use bond valences to look for potential binding sites for the interstitial cations and water molecules that occupy the channels in the framework. The surfaces of the channels can be analysed in the same way as the exterior surfaces of mineral crystals (Section 13.4.1) by assigning varying bonding strengths to the O^{2-} ions

that line the surface, and this, combined with valence maps (Section 11.2.3), provides fairly severe restrictions on possible cations and cation sites.

13.4.3 *Glasses*

Bond valences can be used to study the structure of glasses as well as crystals, though since glasses possess no long-range order, they present a different set of problems. Swenson and Adams (2001) have used bond valences in conjunction with a reverse Monte Carlo method to derive possible models of glass structures from X-ray diffraction patterns. X-ray absorption spectroscopy (XANES, XAFS, EXAFS) has been used to study cation environments in glasses and melts as well as on surfaces (Section 13.4) and in enzymes (Section 13.6.1). In these applications bond valences are used to generate structural models that are consistent with the observed spectra. The solubilities of different impurities in the glass can be examined by seeing which impurities have the best valence match with the model structure (Brown *et al.* 1995 and references therein).

13.5 Chemistry

Bond valences can be used as part of the systematic examination of a series of related structures or compounds as has been done by Efremov (1990) for lanthanum molybdates and tungstates. They can also be used for the systematic modelling of a sequence of structures. Duhlev *et al.* (1991) used bond valences and hard–soft relations to show which compounds can be expected in the system $MX_2-M'X_2-H_2O$ where M and M' are divalent cations and X is a halogen, while Skowron and Brown (1994) used bond valence arguments to show which compounds are possible in the phase diagram of the PbS–Sb₂S₃ system. Bond valences have also been used in more specialized applications as described in the following sections.

13.5.1 Nuclear magnetic resonance

Nuclear magnetic resonance (NMR) measures the resonant frequencies of nuclei in an externally applied magnetic field. Since the field at the nucleus also contains a contribution from the internal field provided by the crystal, the frequency of each nucleus is shifted by an amount that depends on the local environment of the resonating atom. Measurement of this chemical shift has long proved a powerful tool for analysing the structure of liquids and, with the recent development of the magic angle spinning (MAS), chemical shifts can now be measured with comparable accuracy in solids.

Since atoms in different environments experience different chemical shifts, measuring the chemical shift can give information about the local environments of the atoms. The measurements can be interpreted empirically but in many

cases the chemical shift can be calculated directly from a knowledge of the positions of the neighbouring atoms. The chemical shift of ²⁹Si depends on how many corners the SiO₄ group shares with other SiO₄ groups and provides information on the nature of the silicate complexes present. Sherriff and Grundy (1988) showed that the chemical shift can be calculated from the distance and orientation of the bonds between the ligand O²⁻ ions and the second neighbour cations, provided the influence of each bond is weighted by its bond valence, i.e. the number of valence electrons associated with the bond. Labouriau *et al.* (1998) have applied this method to understanding the ²⁹Si chemical shifts observed in titanosilicates.

Koller *et al.* (1994) have shown that the chemical shift of 23 Na is related to the sum of the bond valence sums around each O^{2-} ligand divided by the cube of the Na–O distance. They also modelled the quadrupole coupling constant by calculating the electric field gradient at the Na⁺ nucleus in various minerals and inorganic crystals and found good agreement using an ionic charge calculated with the aid of eqn (13.3):

$$q = -\left(2 - \sum f_{ij}\right),\tag{13.3}$$

where f_{ij} is the covalency of a bond related to the bond valence by eqn (13.4) (Brown and Shannon 1973):

$$f_{ij} = AS_{ij}^M. (13.4)$$

In this equation A and M are fitted constants that are the same for all ions having the same electron core. Skibsted *et al.* (1996, 1998) have used this method for calculating the quadrupole coupling constants of 133 Cs and 51 V.

Gründemann *et al.* (1999) have analysed the structures of transition-metal hydrides and show that the H–H bond can be assigned a valence that obeys the valence sum rule and is directly proportional to the NMR coupling constant between the H atoms. Klein *et al.* (1999) have used NMR to study the cooperative transfer of H atoms around the triple hydrogen bond ring in 4-nitropyrazole using bond valences to explore the shortening of the N...N distances as the hydrogen bonds move through the symmetric transition state (Section 7.4).

13.5.2 Transition-metal complexes

Most transition-metal cations can adopt several different oxidation states depending on the method of preparation and the compound in which they find themselves, but which oxidation state they adopt in a particular compound is not always clear from the chemical formula or from the nature of the bonding environment. Providing that the oxidation state is not zero, the bond valence model can help because the metal-ligand bond can usually be described as an

acid-base bond even when the organic components of the ligand do not lend themselves to treatment by bond valences.

There are several reasons why transition-metal complexes are less amenable than inorganic compounds to the application of the bond valence model. Firstly, the ligands that surround the metal atoms frequently do not have bipartite graphs. They may, for example, contain rings with odd numbers of atoms. This means that the network equations ((3.3) and (3.4)) cannot be applied. The bipartite condition is, however, usually satisfied around the transition metal itself (except when the metal is in a very low oxidation state) and it is also satisfied by a number of common ligands, e.g. NH₃, Cl⁻, CH₃COO⁻. When only bipartite ligands are present, the full bond valence model can be used, but for ligands with non-bipartite graphs, e.g. CF₃COO⁻, aromatic systems and systems with odd-membered rings, the bond valence model will not, in general, work unless the whole ligand is treated as a pseudo-atom capable of forming both acid and base bonds as discussed in Section 3.5.

A second problem is the widespread occurrence of compounds in which several different anionic elements bond to the metal (heteroleptic compounds). Most inorganic compounds have homoleptic coordination, i.e. the cation is bonded to only one kind of anion, making the determination of the bond valence parameters relatively simple (Appendix 1). Homoleptic coordination is much less common among the transition-metal complexes. As described in Appendix 1, bond valence parameters for a variety of transition metals to O, N, C, Cl, S, and P have been determined using heteroleptic systems although the values obtained are often less reliable than those obtained from homoleptic systems.

A third problem is the existence of high- and low-spin states for some transition metals. This is not a problem in inorganic oxides which are almost invariably high spin, but for other ligands it is necessary to use different bond valence parameters for the different spin states. Recent work (See *et al.* 1998; Shields *et al.* 2000) also suggests that different bond valence parameters may be needed for the same ligand atom in different environments. For example, the bonds between a metal and N are shorter if N forms only one bond within its ligand (e.g. $N \equiv C$) than if it forms two or three bonds (e.g. $N \equiv C$) than if it forms two or three bonds (e.g. $N \equiv C$), this is a consequence of differences in π bonding that are not reflected in the bond valence.

In spite of these difficulties, there have been a number of determinations of bond valence parameters for use in transition-metal complexes. In most cases the bond valence parameters determined for oxides work well with transition-metal complexes, but care is needed when the metal can be found in different spin states or the ligand allows different degrees of π bonding.

In spite of these difficulties the bond valence model has been used to check the oxidation state assignments of transition-metal complexes in the Cambridge Crystallographic Database (Allen *et al.* 1979; Palenik 1997*b*; Shields *et al.* 2000). Even though each structure determination undergoes rigorous checking before

being entered into the database, the calculation of bond valence sums has revealed a number of errors, including the discovery of hydrogen atoms whose presence had not previously been suspected. The method has also been used to show, for example, that the copper atoms in $[(LCu)_2(\mu-O_2)]X_2$ complexes have an oxidation state of +3 rather than the more usual +2 (Mahapatra *et al.* 1996).

13.5.3 Heterogeneous catalysis

Transition metals play an important role in heterogeneous catalysis where reactions occur on the surfaces of metal or oxide crystals. Typical of these metals are V or Mo which exist in oxides with tetrahedral, tetragonal pyramidal, or octahedral coordination and which can change their oxidation states with minimal changes in their coordination environment. As in the case of soil minerals (Section 13.4.1), bond valences can be used to determine the bonding strength of the anions on the surface, by noting how far the valence sums around the surface O^{2-} ions fall short of 2.00 vu.

Andersson (1982) has given a qualitative, though detailed, discussion of the catalytic activity of various vanadium oxides, recognizing the tendency of the adsorbed ${\rm O}^{2-}$ ions to increase the surface concentration of oxygen and thus to oxidize the surface vanadium atoms to ${\rm V}^{5+}$. Ziółkowski (1983*a*) has proposed a quantitative model for the oxygenation of propylene on the (201) and (20 $\bar{2}$) surfaces of ${\rm Mn(V,Mo)_2O_6}$ brannerite (24418), assuming that the bonding strengths of the surface atoms are inversely proportional to their bond valence sum. He has also explored the oxygenation and deoxygenation as well as hydrogenation and dehydrogenation of various organic species on the surfaces of ${\rm MoO_3}$ (35076) by assuming that the final products are the ones which give the best agreement between the bond valence sums and the atomic valence (Ziółkowski 1983*b*; Ziółkowski and Wiltowski 1984). In later work Ziółkowski and Dzienbaj (1985) have proposed a linear relationship between bond valence, *s*, and bond energy, *E*:

$$E = Js, (13.5)$$

where J is a constant (typically around $100 \,\mathrm{kCal\,mol^{-1}\,vu^{-1}}$) that depends on the atoms forming the bonds.³ Using this result, he has presented his earlier studies in terms of bond energies (Ziółkowski 1986) and calculated surface enthalpies. Although these are in qualitative agreement with the few experimental results available, the predictions suffer from the difficulty of correcting for surface relaxation (Ziółkowski 1988).

A somewhat different kind of catalytic surface, a monolayer of vanadium grown on both the rutile and anatase forms of TiO₂ (202240, 202242), has been modelled by Depero (1993) who uses bond valences to show which sites will be

³ But see the discussion in Section 9.1.

favoured by vanadium and how V can bind a chemisorbed oxygen in such a way as to allow for easy electron transfer.

Bond valences have been applied to the examination of layers of oxygen, sulphur, or halogen adsorbed onto a pure metal substrate, either to analyse the observed structures or to assist in the building of models needed for the interpretation of low energy electron diffraction (LEED) measurements (Mitchell et al. 1986). When two monolayers of oxygen are adsorbed onto the (0001) surface of Zr, half the oxygen atoms lie on the surface and half lie in tetrahedral sites below the first Zr layer. The different layers, starting at the surface, follow the sequence (O1–Zr1–O2–Zr2–Zr3–Zr4–) in which the first three or four layers represent a surface oxide film which can be modelled using bond valences. The bond valence sums around O1 and O2 are 2.07 and 1.82 vu respectively, while Zr1 has a valence sum of 3.43 vu, reasonably close to the value of 4 expected for an oxide film. The valence sum around Zr2 is only 0.45 vu, consistent with its transitional character between oxide and metal (Wang et al. 1997).

13.5.4 Esterification and hydrolysis

An ester is a compound formed between an acid RO₂H and an alcohol or oxyanion R'OH by the elimination of water according to the reaction:

$$RO_2H + R'OH \longrightarrow RO_2R' + H_2O.$$
 (13.6)

The ester RO_2R' can be thought of as the compound formed from the Lewis base, RO_2^- , and the Lewis acid, R'^+ , and its stability will be determined by the similarity of their cation and anion bonding strengths.

The bonding strengths of the two components can be calculated in the following way. For both components the hydrogen atom is removed and valences are assigned to the bonds within each complex based on the assumption that the net (negative) charge is distributed equally among all the terminal O atoms present as shown for adenosine diphosphate (ADP, ADENDP) in Fig. 13.4. This charge is taken as the anion bonding strength of the species RO⁻ and the valence of the R-O bond is taken as the cation bonding strength for the species

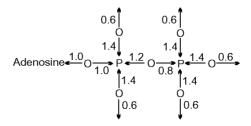


Fig. 13.4. Assignment of bonding strengths in adenosine diphosphate (ADP).

 R^+ (Table 13.3). Note that the base strength and acid strength for a given species R add up to 2.0, the valence of O^{2-} . Small corrections need to be made to allow for the Lewis acidity of carbon-bonded H atoms which have the effect of increasing the negative total charge by 0.03 for each H atom bonded to an α -carbon and 0.02 for each H atom bonded to a β -carbon. The corrected bonding strengths are shown in parentheses in Table 13.3.

The water is assumed to be eliminated by breaking the weakest O–H and R–O bonds in the two reacting species. The stability of the resulting ester is given by the ratio of the cation bonding strength to the anion bonding strength. The most stable esters are formed when this ratio is close to 1.0 and, using the observation from Fig. 4.6 that silicates with a bonding strength ratio greater than 2 are unstable, compounds with ratios larger than 2 are expected to be readily hydrolysed. Figure 13.5 shows that the bonding strength ratios for esters correlate with the free energy of hydrolysis. Of particular interest is the biologically important conversion of ADP to adenosine triphosphate (ATP, ADENTP) by reaction with $HOPO_3^{2-}$. The bonding strength ratio is 2 indicating that ATP is on the edge of stability. As is observed in many biological

Table 13.3 Bonding strengths of organic acids and bases

R	R ⁺ bonding strength	RO ⁻ bonding strength
CH ₃ -	1.0 (0.91)	1.0 (1.09)
C_2H_5-	1.0 (0.88)	1.0 (1.12)
Ph-	1.0 (0.96)	1.0 (1.04)
AdenosineO(PO ₂)O(PO ₂)-	1.4	0.6
CH ₃ CO-	1.5 (1.45)	0.5 (0.55)
O_3P-	1.25	0.75

Values in parentheses are corrected for the influence of carbon-bonded H.

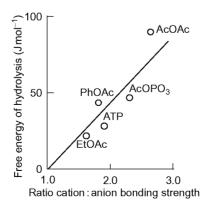


Fig. 13.5. Free energy of hydrolysis versus the raiton of cation to anion bonding strength. Ac = acetyl, acetate, Ph = phenyl, Et = ethyl, ATP = adenosine triphosphate.

BIOLOGY 203

systems, nature has selected a system that is on the verge of instability, thus allowing it to be controlled by small changes in the ambient conditions (see Section 13.6.1).

13.6 Biology

Biological chemistry takes place in the aqueous environment of the body of an animal or plant. Therefore, in spite of the fact that the molecules involved are largely organic in nature, the chemistry is essential acid—base chemistry and therefore a good candidate for the application of the bond valence model, as the example of adenosine triphosphate discussed in the previous section (Section 13.5.4) shows. This section illustrates a number of other ways in which the model has been used in biological systems.

13.6.1 *Enzymes*

Enzymes are proteins designed to catalyse particular biochemical reactions by binding the reacting molecule (the substrate) and deforming it such a way as to lower the activation energy for the reaction. In many enzymes a transition-metal atom is involved in this process because such a metal can readily bind the N or O atoms of the substrate and, by changing its oxidation state or the lengths of its bonds, the metal can act as a reservoir for the exchange of electrons with the substrate.

While X-ray diffraction is now routinely used to determine the structures of proteins, the geometries obtained are not yet sufficiently accurate for a quantitative application of the bond valence model and in any case the transition state for the enzymic reaction is, by definition, difficult to stabilize and examine. Other techniques, such as EXAFS and infrared spectroscopy, applied to substrates that are designed to mimic the geometry of the transition state, are used to give information about the local environment of the metal. Although these techniques can give more precise information about the bond lengths and sometimes the oxidation state, they do not give accurate information about the number and arrangement of the ligands. The bond valence model can play an important role in complementing the experimental information to provide a reliable description of the geometry before, during and after the reaction.

The EXAFS spectrum of a metal atom in a protein gives the lengths of the bonds between the metal and its ligand atoms with sufficient accuracy to calculate their bond valences. In principle it can also determine the number of each type of bond that the metal forms, but the results are much less reliable. However, calculation of the bond valences sum for the possible environments allows one to determine not only the coordination number but also the oxidation state of the metal atom (Thorp 1992; Hati and Datta 1995; Scarrow *et al.* 1996; Bell *et al.* 1997; Clark-Baldwin *et al.* 1998; Dooley *et al.* 1998).

Garner *et al.* (1996) used bond valences to help find good binding sites for metal atoms and Thorp (1998) has proposed a method of predicting the changes in bond length that can be expected with a change in oxidation state, based on minimization of the reorganization energy, a method that is closely related to the principle of maximum symmetry (Rule 3.1).

Bond valences can also be used to model the structural changes that occur during the enzyme reaction. Xiang *et al.* (1996) postulate a mechanism for the reaction of cytidine deaminase based on the conservation of the bond valence sum around the Zn²⁺ atom. The lengthening of a Zn–S bond by a small change in conformation of the protein increases the valence of the Zn–O(H) bond, facilitating the transfer of the H⁺ ion to a neighbouring carboxylate group which, in turn, releases its own H⁺ to the nitrogen of the cytidine substrate. Simultaneously the (Zn)O atom, having lost its H⁺ ion and therefore having a large unsatisfied bonding strength, removes the NH₂ group from the cytidine, thereby completing the substitution of –H for –NH₂. The key step in this mechanism is the change in the protein conformation which lengthens the Zn–S bond allowing the Zn²⁺ to act as a valence (or electron) buffer. This is another example of a system close to an instability where a small change in the ambient conditions triggers a reaction (see Section 13.5.4).

Deng et al. (1993, 1998) and Ray et al. (1993) have used V⁵⁺ as an analogue of P⁵⁺ in an attempt to model the transition state of the hydrolysis of phosphodiesters by ribonuclease A since V⁵⁺ is assumed to adopt the expected five coordination more readily than P⁵⁺. Examination of the vibrational spectrum of the vanadate analogue indicates that the terminal V–O bonds are only slightly weakened when bonded to the protein. A quantitative bond valence analysis effectively rules out two proposed mechanisms that involve the protonation of the terminal O atoms.

13.6.2 Calcium and sodium binding by proteins

While transition metals are usually incorporated close to the active site of an enzyme in order to support the catalytic activity, alkali metals and alkaline earth ions are usually bound close to the protein surface. Glusker (1991) has reviewed the structural aspects of cations bonding to proteins. Most cations can be readily seen in crystal structure determinations using X-ray diffraction because they have an electron density that is significantly different from that of the carbon, nitrogen, and oxygen atoms that compose the protein and the surrounding water. Sodium is an exception, since the Na⁺ ion contains the same number of electrons as a water molecule, and forms bonds to oxygen that are similar in length to the hydrogen bonds between the water molecules themselves. It is not easy to decide whether a particular atom revealed by X-ray diffraction is a water molecule or a sodium atom. Nayal and Di Cera (1996) used bond valence sums to distinguish between these two possibilities. They checked over 300 000 water molecules that had been reported in 2742 protein

BIOLOGY 205

crystal structures by calculating the valence sums for each on the assumption that the atom was sodium. Because water molecules form fewer bonds (typically four) than sodium (typically six or seven), they give a lower bond valence sum than an Na⁺ ion when the valences are calculated in this way. Most of the atoms had valence sums less than 0.6 vu, but 64 had sums greater than 1.0 vu and these were presumed to be Na⁺. There is no independent way of checking whether this is correct but all were found to be bonded to one or more O atoms in the protein, to have coordination environments typical of Na⁺ and to occur in the same place in multiple determinations of the same protein. In one case, the Na⁺ could be replaced by Rb⁺ at the same site. The circumstantial evidence is strong that this is a reliable method of distinguishing between Na⁺ cations and water molecules and the method has subsequently been adopted by others (Shui *et al.* 1998).

In an earlier paper, Nayal and Di Cera (1994) used valence maps (Section 11.2.3) to find suitable sites for bonded Ca²⁺ ions. Ca²⁺ valence maps were calculated for 32 known calcium-binding proteins in regions close to at least three protein oxygen atoms. In a traditional valence map, one would expect to find a minimum with a valence of 2.0 vu at a cation site, but since the water molecules were not included in the calculation, these valence maps are interpreted in a different way. The site of a Ca²⁺ ion far from the surface of the protein has a valence sum of zero on this map because all its bonds are to water molecules. Potential binding sites, on the other hand, will have several appropriately arranged neighbouring protein O atoms. Typical valence sums that Nayal and Di Cera found in this map were around 0.4 vu except close to known Ca²⁺ sites where, in over 90 per cent of the cases, the valence map had a value greater than 1.4 vu. Further, 87 per cent of the grid points with valences of this size were found to lie within 100 pm of a Ca²⁺ atom. This use of valence maps is thus an elegant way of locating potential binding sites for Ca²⁺ or any other cation. The program VALE written by Naval and Di Cera has been used by Lu et al. (1998) to locate the site of the Ca²⁺ ion that controls the behaviour of the muscle protein titin. As mentioned in Section 13.6.1, a similar method was used by Garner et al. (1996) to find potential metal atom sites in enzymes.

Not all biological problems involve macromolecules. Cisplatine (cisdichlorodiaminoplatinum(II)) is an effective anticancer drug, but ensuring its delivery to the active site in a patient involves knowing what chemical transformations it might undergo along the way. This requires a good understanding of its aqueous chemistry (Lock 1980). Cisplatine was known to form a variety of aquo and bridged hydroxy species in silver nitrate solution, but these species could never be isolated as solids. The valence matching rule was used to show that water coordinated to Pt²⁺ would necessarily form relatively strong hydrogen bonds and, since no suitable acceptors existed in the solid, the aquo ligands would not be stable on crystallization. Similarly Lock argued that the large anion bonding strength of the hydroxy group could only be satisfied by bonding to two Pt²⁺ ions, accounting for the high degree of polymerization

in solution. This understanding of the aqueous chemistry of coordinated platinum was important in the design of drugs targeted to reach the active site in the patient.

13.7 Databases

A bond valence analysis of entries taken from structural databases can be used to check their quality. Palenik (1997b) and Shields *et al.* (2000) have used them to check the assigned oxidation states and to detect errors that were missed by more traditional checking methods in the Cambridge Structural Database (Allen *et al.* 1979) but, surprisingly, bond valences have been little used for quality control in the Inorganic Crystal Structure Database (Bergerhoff *et al.* 1983) though some accessing software now routinely calculates bond valences as well as bond lengths.

Many users would like to search the Inorganic Crystal Structure Database for sets of 'similar' structures. However, the term 'similar' is usually not well enough defined to be useful as a search query. Some series of high-symmetry compounds have identical structures (e.g. compounds with the NaCl structure) and these are easy to retrieve by a variety of search strategies, but where the structures are not identical, it is difficult to specify the nature of the similarity. Most of the strategies so far developed rely on similar compounds having either the same stoichiometry or crystallizing in the same space group (Bergerhoff et al. 1999; Burzlaff and Malinovsky 1997; Parthe 1996), but neither of these restrictions is a necessary condition for similarity. The perovskite family of structures discussed in Section 13.3.1 provides a good example of similar structures that crystallize in different space groups according to the mode of relaxation (Woodward 1997a) and these often have compositions involving more than one chemical species on either the A or B sites. An alternative strategy based on the comparison of bond graphs might not pick up all similar structures, though it should prove more flexible than requiring either identical stoichiometry or identical space groups. A bond valence approach to this problem has yet to be developed.

Chemical implications of the bond valence model

14.1 Why is the bond valence model so robust?

It is appropriate to ask why an empirical model with such a poor theoretical foundation is able to give such a good account of chemical structure. The answer lies in the way the attractive and the repulsive forces between the atoms are described, as discussed in the next two sections.

14.1.1 The attractive force

The attractive force arises from the valence electrons. Depending on the nature of the bond, these are found either in the region between the bonded atoms (for covalent bonds) or localized on the anions (for ionic bonds). The development of the model described in Chapter 2 was based on the ionic model in which the valence electrons were assumed to be located on the anions. The bonding in this case arises from the electrostatic attraction between cations and anions, which is represented by the electrostatic flux, or bond valence, linking them as shown schematically for an anion and two cations in Fig. 3.2(a). The flux lines terminate on the electrons that give the anion its charge but, since each of these electrons is paired with one of the valence electrons of the anion, the total number of electrons involved in the bond is twice the number of electrons that have been transferred from the cation, both ions contributing equal numbers of electrons to the bond. The bond flux is therefore also equal to the number of valence electron pairs that form the bond. This number is not, of course, necessarily an integer, since each bonding electron pair is spread over a finite volume and may contribute to more than one bond.

Suppose that the electron pairs associated with a bond are now moved from the anion into the middle of the bond so that they are shared equally between the anion and cation, forming a covalent bond as shown in Fig. 3.2(b). The number of electron pairs in the middle of each bond is still equal to the bond flux as can be seen in the figure. The anion now carries a net positive charge equal in magnitude to its original negative charge, since it has contributed one valence electron to the bond for every valence electron contributed by the cation. The electrostatic flux now connects both the cation and the anion with the bonding electron pairs but the number of flux lines linking the two atoms remains

unchanged; it is exactly the same as it was when the electrons were located on the anion. Moving the bonding electrons from the anion into the bond does not therefore change the bond flux or the bond valence. The location of the electrons in the bond therefore makes no difference to the value of the bond valence. Whether the bond is covalent or ionic, the degree of covalency or ionicity has no direct effect on the bond valence.

One can even go a further step and transfer all the bonding electrons to the cation but even this does not change the bond valence. Thus the bond valence model works just as well when the cation and anion charges are reversed, indicating that the model is perfectly symmetric with respect to the interchange of positive and negative charge, a point taken up again in Section 14.5.

From this argument one can deduce that the model works equally well for covalent and ionic bonds, which means that one does not have to worry about which model, ionic or covalent, is the appropriate one to use in a particular situation. But the argument leads to a more surprising conclusion, namely, that the bond valence model cannot, in principle, distinguish between ionic and covalent bonds. In the framework of the bond valence model the terms 'ionic' and 'covalent' have no significance. They are only meaningful in models that depend on how the valence electrons are distributed within the bond and, as shown above, the bond valence depends only on the number of bonding electrons, not their distribution. However, even though the bond valence model gives no direct information about the degree of covalency, there is reason to believe that weak bonds are more ionic and strong bonds more covalent, so that the bond valence can be used as an indirect measure of covalency as given by eqn (13.4) (Brown and Shannon 1973).

Instead of developing the bond valence model from the ionic extreme, it could in principle have been developed assuming covalent bonds in which a certain (non-integral) number of electron pairs reside within the bond itself and attract the positively charged ionic cores of the two terminal atoms. This development of the model is not as straightforward as the one given in Chapter 2, because there is no easy way of determining the number of electron pairs associated with each bond. However, this approach is the basis for the bond model in organic chemistry where all the bonds are assumed to involve an integral number of electron pairs, and it can be used to understand how bonds are formed between two anions or two cations as discussed in Section 3.5. Unless these two bonded atoms are related by symmetry, they do not necessarily contribute the same number of electrons to the bond. Thus in the trifluoroacetate ion CF₃CO₂ discussed in Section 9.2, the central C-C bond receives different contributions from the two C atoms, because the -CF₃ group carries part of the negative charge of the ion and therefore contributes more electrons to the C-C bond than the carbon of the -CO₂ group. The pair of electrons forming the bond will receive different fluxes from the two carbon atoms so that predicting the properties of the bond becomes more difficult. However, the average flux (of 1.0 vu) agrees well with the observed bond length, and both the average flux and the bond length remain unchanged as charge is transferred from the oxygen to the fluorine atoms (Brown 1980b). The only thing that changes is the contribution each C atom makes to the bond. In cases where the two atoms are equivalent by symmetry, the bond valence model works because the symmetry requires that each atom make equal contributions to the bond even though the bond graph is not bipartite.

14.1.2 The repulsive force

The second force that is important in the model is the repulsion between atoms in contact. This force determines the length of the bond for a given bond valence according to eqn (3.1). The robustness of this equation lies in the fitting of the parameters R_0 and B to observed distances, thereby compensating for a number of systematic effects that affect the lengths of all the bonds. The example of an inappropriate choice of atomic valence was discussed in Section 9.2. The apparent shortening of the bonds by the thermal vibrations of the ions perpendicular to the bond (Section 9.4) is also taken into account because all the bonds of a given type are subject to a similar shortening, so fitting the bond valence parameters to the experimental measurements automatically compensates for this effect.

The same is true of the influence of the repulsion between non-bonded ligands. In Section 6.2 it was shown that the strong N–O bonds in the NO_3^- ion bring the ligand O^{2-} ions much closer together than would be possible if the N–O bonds were weaker. In turn, the strong repulsion between the O^{2-} ions causes the N–O bonds to be stretched and therefore longer than they would be if the ligand repulsion were not present. However, all N–O bonds are subject to a similar strain, and any variation in this strain will be a function of the bond valence. The effects of ligand repulsion are thus also compensated by the use of fitted bond valence parameters.

Another systematic effect is the influence of π bonding which might be expected to shorten the bonds formed by certain transition-metal cations, since the electrons involved in π bonding to the d shell are not included among the valence electrons measured by the bond valence, but again, since all the bonds between the same pair of ions will normally be affected in the same way, they will all be subject to a similar shortening which, if it varies at all, will vary with the bond valence. The important exception, which serves to show that this shortening is significant and cannot always be ignored, was discussed in Section 9.2. Where the same pair of bonded atoms have π -bond character that is different in kind, different values of R_0 may be needed. For example -N=C=S can form π bonds to transition metals, but $-NH_3$ cannot. The two types of metal-N bond do not have the same π -bond character and therefore different fitted bond valence parameters are needed (see, for example, the values given for Co-N bonds in Appendix 1).

The robustness of the bond valence model derives, therefore, from two factors: the independence of the bond valences from the location of the bonding electrons, and the use of fitted values for the bond valence parameters which automatically compensates for systematic changes in the bond length produced by other effects.

14.2 Two-body potential models

As pointed out in Chapter 2, the bond valence model is an accurate representation of the ionic model developed in terms of the electrostatic field. Traditionally the ionic model has been developed in terms of the electrostatic energy. The energy is calculated using a two-body potential composed of two terms, one representing the Coulomb potential and the other representing the effects of interatomic repulsions and van der Waals forces. The second potential is short range and is only important between nearest neighbours, but the Coulomb potential is long range and must be summed over all pairwise interactions in the crystal. This form of the ionic model has had considerable success in calculating the structures and properties of inorganic compounds (Catlow 1997) but it is based on precisely the same assumptions as the bond valence model. The two models are therefore exactly equivalent, differing only in the form of the empirical short-range potential, which in the bond valence model is assumed to have the simple form of eqn (3.1) or (3.2). Each model has its advantages and disadvantages. The two-body potential model can be used to calculate the energy and properties of a solid for any configuration, but it is computer intensive since calculation of the Coulomb energy requires summation over all the ion pairs. The bond valence model is intuitive and requires only simple calculations, but does not yield the energy-related properties.

14.3 The properties of the bond graph

The way in which the bond valence model takes into account the long-range Coulomb interactions is through the bond network and its solution using the network equations (3.3) and (3.4). By means of these two equations, which correspond to the law of charge conservation and the principle of maximum symmetry, both the short-range and long-range interactions are described in terms of localized bonds. The fact that the Coulomb field, which provides the stabilizing energy in these systems, can be expressed in terms of a local bond model means that at equilibrium the atoms arrange themselves so that each atom is screened by its neighbours from the influence of more distant atoms.

The graph of the bond network is simple and contains all the necessary chemistry. It is fully defined by the atomic valences and the connections between

nearest neighbours. The latter are essentially determined by the coordination number which is limited by the relative sizes of the atoms. Thus the chemistry of acid-base bonding can be reduced to two properties, the number of valence electrons and the relative sizes of the ions. These are the only concepts normally needed to account for the chemical structure and many of the properties of acid-base compounds. It is no surprise that many other quantities used in chemistry, such as electronegativity, are directly or indirectly related to size and valence (see, for example, Figs 4.3–4.5), or that ultimately all chemical models can be reduced to the same simple topological description as demonstrated in the following sections.

14.4 The Lewis electron-pair model

The electron-pair model proposed by Lewis (1923) has proved popular with generations of chemistry teachers since it expresses the charge conserving electron counting rules in a simple graphical form. All bonds in this model are assumed to be formed by electron pairs, with the two bonded atoms each normally contributing one electron. A Lewis structure is represented by a graph in which each electron pair is indicated by a line connecting the two bonded atoms (Fig. 14.1). Where two or more electron pairs connect the same two atoms, the bond is represented by two or more lines (double or multiple bonds). Thus the total number of lines on the graph is equal to the total number of electron pairs shared between the atoms. In order to avoid partially filled valence shells, it is sometimes necessary to leave atoms with a net charge

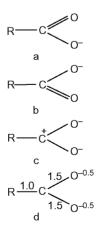


Fig. 14.1. Lewis structures of the carboxylate ion. (a) and (b) Two equivalent symmetry breaking structures. (c) An alternative Lewis structure. (d) The average of (a) and (b) which preserves the inherent symmetry of the ion.

indicated by the appropriate number of + or - signs attached to the atoms. The bond created by a shared electron pair is often described as a covalent bond while bonding that results from the net atomic charges is considered to be ionic and not directly treated by the model. The result is that all chemical bonds are classified as being either covalent or ionic, a concept which has had the unfortunate consequence of implying that covalent and ionic bonds must be treated using two different and incompatible bonding models.

In spite of the strength of the Lewis model as a teaching tool, it runs into several difficulties when applied to anything but the simplest systems. The first is that most Lewis structures violate the principle of maximum symmetry. For example, in the carboxylate ion, the simplest Lewis structure of RCOO⁻, shown in Fig. 14.1(a), destroys the equivalence of the two O atoms, since the carbon atom forms a double bond with one and a single bond with the other. To complete the valence electron shell, the latter has to carry a full negative charge as shown in Figs 14.1(a) or (b). Such asymmetry is observed when the carboxylate ion is bonded to a strong counterion such as Si⁴⁺ as in (CH₃COO)₄Si (SIACET), but in most compounds both the C-O bonds are the same length as expected from the principle of maximum symmetry (Brown 1980b). Only by enumerating and averaging all the equivalent Lewis structures can a graph be obtained that maintains the equivalence of the two O atoms, a process which has been given the unfortunate name of resonance, suggesting that the different Lewis structures are in some form of dynamic equilibrium. In the case of the carboxylate ion, averaging the two equivalent structures shown in Figs 14.1(a) and (b) gives the structure shown in Fig. 14.1(d) in which the number of electron-pair bonds (the resonant bond number) is 1.5 for both C–O bonds leaving a formal charge of -0.5 electrons on each O atom. This is exactly the bond valence and residual atomic valence predicted by the bond valence model for an isolated carboxylate ion (Section 9.2), but the bond valence model achieves this description directly without invoking covalency, ionicity, or resonance. When Lewis proposed his model, the electron was considered indivisible and resonance was the only mechanism by which an electron-pair bond could be shared between more than one pair of atoms. The later introduction of wave mechanics removed this difficulty since each electron is now known to occupy a finite volume which may be shared between more than one bond. If this had been realized earlier, the Lewis model might have developed in a different and simpler way.

A second problem presented by the Lewis model is the question of which Lewis structures to include in the average. One can draw other Lewis structures, such as that shown in Fig. 14.1(c), in addition to the two obvious structures shown in Figs 14.1(a) and (b). In fact there are an infinite number of possible Lewis structures, though only a few represent reasonable bonding models. How far should one go in dreaming up possible (though physically implausible) structures? Should the average be a weighted average and if so, how does one determine the weights? Two criteria can be used to limit the number of

structures considered. One criterion is to reject all structures that contain atoms with residual charge (strictly only applicable for neutral molecules), the other is to reject all structures containing atoms with partially filled valence shells. Unfortunately, these criteria are often mutually exclusive. The problem is further complicated in inorganic compounds by the infinite nature of the bond network which requires, in principle, a doubly infinite set of Lewis structures, explaining why the Lewis model is rarely used in analysing real, complex structures, whatever its virtues may be in introducing the concept of a chemical bond to neophyte chemists. Nevertheless Boisen et al. (1988) have made the effort to average all possible Lewis structures in a number of minerals by making a few reasonable assumptions to restrict the size of the calculation. They enumerated the Lewis structures by restricting the search to a finite cluster of uncharged atoms, the atoms on the outside of the cluster being given properties that approximate their bonding to the extended crystal beyond. After a lengthy calculation they showed that the resonance bond numbers correlate with bond length in exactly the same way as the bond valence, i.e. the resonance bond number and the bond valence are precisely the same.

The reason for this equality is not far to seek. Each Lewis structure that contains no residual atomic charge is a bond network that obeys the valence sum rule providing that the Lewis structure has a bipartite graph. However, in general individual Lewis structures violate the principle of maximum symmetry. This symmetry can be reincorporated by averaging over the full set of equivalent Lewis structures. The result is a bond graph with a set of resonance bond numbers that obey both the valence sum rule and the principle of maximum symmetry. Since the resulting Lewis bond graph is the same as that of the bond valence model, the resonant bond numbers satisfy the same network equations as the bond valences. The underlying topology of both models is therefore the same and it is only a matter of personal preference which model one uses. The bond valence model has the advantage of simplicity, both conceptual and computational, but the Lewis model is a convenient way of illustrating the principles of shared electron bonds and can, with some effort, be used to derive bond valences (Tytko 1999).

14.5 Why are cations different from anions?

The bond graph used in the bond valence model is a bipartite graph, meaning that all the atoms are either cations or anions and that bonds are found only between a cation and an anion. There is nothing in the bond valence model that suggests that the properties of cations are in any way different from those of anions apart from the difference in the sign of the charge. The model is completely symmetric with respect to the interchange of positive and negative charge: changing positive charge into negative charge and vice versa does not change any of the predictions of the model. Yet every chemist knows that

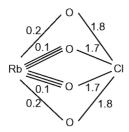


Fig. 14.2. Bond graph of RbClO₄ (63363) showing the bond valences.

cations and anions behave quite differently. While the equal valence rule predicts that coordination environments will be equally regular around both cations and anions, in practice the coordination around cations is found to be much more regular than that around anions. This is illustrated by the structure of RbClO₄ (63363) whose bond graph is shown in Fig. 14.2. The bonds around Cl⁷⁺ are all similar having valences close to 1.75 vu. Those around Rb⁺ are again similar with bond valences close to 0.15 vu, but the bonds around O²⁻ are very different, ranging from 0.1 to 1.8 vu. This is an extreme case but many other examples can be found where the bonding around the cations is more symmetric than that around the anions. There are very few cases where the anion has a more symmetric environment than the cation.

This asymmetry is not inherent in the bond valence model, which treats cations and anions entirely equivalently. It lies in the chemical nature of the anions and cations themselves. In the case of $RbClO_4$ the asymmetry is driven by the large valence of the Cl^{7+} cation, but anions rarely have valences greater than -2 or -3, because the looseness with which each additional valence electron is bound makes highly charged anions unstable. By contrast, the removal of electrons to form cations results in a shrinkage of the ion as its charge increases making the ion more compact.

Because the valence electrons of highly charged anions are spread over a large volume, they readily overlap with the valence electrons of neighbouring anions, resulting in the formation of band structures with semiconducting or metallic properties. In such compounds one can no longer identify localized bonds and the bond valence model can no longer be used.

The symmetry between cations and anions in the bond valence model can best be seen in the compounds of the alkali metals and alkaline earths where the cation valences are similar to those of the anions. Binary compounds such as NaCl (18189), CsCl (22173), and ZnO (67454) are invariant under the interchange of the cations and anions since both kinds of ions occupy equivalent sites. For compounds such as CaF_2 (29008) which crystallizes with the fluorite structure, changing the signs of ions gives the antifluorite structure adopted by the alkali metal oxides such as Na_2O (60435). Although the antifluorite

structures are less stable because of poor valence matching, there is a perfect charge inversion symmetry between the structure and its anti-structure.

Asymmetry only arises when cations with larger valences are present. The cation with the largest valence forms the strongest bonds and dominates the structure as illustrated by the example of RbClO₄. The Cl–O bonds take the valence they need to create a symmetrical ClO_4^- complex ion, leaving only a small residual valence available to the Rb⁺ ion which, however, still manages to adopt a relatively symmetric environment. The oxygen ion also adopts the most symmetrical environment available to it given the large difference in the bonding strengths of the Rb⁺ and Cl^{7+} ions.

14.6 Orbital models

In the bond valence model quantum effects are treated classically by including them in the interatomic repulsion described by eqn (3.1) or (3.2). There are, however, a number of cases where quantum effects are directly responsible for deviations from the higher symmetry that would otherwise be expected. Such electronically distorted structures were discussed in Chapter 8.

Electronic distortions are seen in two situations: when there are valence electrons that are not involved in bonding, and when there are unfilled core orbitals (specifically d orbitals) that have energies similar to the valence electrons. These situations cannot properly be treated using a classical model and a full treatment requires the solution of the quantum mechanical equations. However, simplified orbital models can often give a good indication of when such distortions will occur and what form they will take. The bond valence model, being classical in character, does not include an explicit orbital description but treats electronic distortions in an *ad hoc* manner by adding point dipoles and quadrupoles to the ionic point charge as needed. However, an orbital description is helpful in determining what kind of multipoles should be included.

When non-bonding valence electrons are present, the VSEPR model (Gillespie and Hargittai 1991) provides a simple explanation which correctly predicts the geometries of isolated molecules, but it is less effective in describing the behaviour in solids where secondary bonds are present. Both VSEPR and the bond valence model give only a semi-quantitative treatment, but the bond valence model is able to explain under what conditions the stereoactivity of the lone electron pair will be suppressed.

The situation for atoms with unfilled d shells is more complex. The orbital models are able to indicate where distortions induced by degenerate or near-degenerate states are likely to occur and what kind of distortion might be expected, but a quantitative treatment requires a knowledge not only of the first neighbours of the transition metal, but also of the full chemical context in which the metal finds itself. The bond valence model can help to provide this context,

though the only bond valence treatment worked out in any detail is for d⁰ transition metals (Kunz and Brown 1994).

In cases where there are no electronically driven distortions, the orbital description provides no better account of the chemistry than the bond valence model. Rather it tends to make an essentially simple situation more complex. For example, consider the phosphate and nitrate anions, PO_4^{3-} and NO_3^{-} . In orbital models the P atom is described as sp^3 hybridized and the N atom as sp^2 hybridized, but these descriptions are just representations of the spherical and cylindrical harmonics appropriate to the observed geometries. They provide no explanation for why P is four but not three coordinate, or why N is three but not four coordinate. The bond valence account given in Chapter 6 is simpler, more physical, and more predictive. The orbital description is merely a rather complicated way of saying that the ions obey the principle of maximum symmetry but implying that the constraints are related in some unspecified way to the properties of one-electron orbitals rather than to the ionic sizes.

14.7 Electron density models

An approach to chemical bonding that is currently attracting attention is that based on an analysis of electron densities calculated from quantum mechanics or measured using X-ray diffraction. Since the electron density shows how the electrons are distributed, it gives a better physical picture of the nature of chemical bonding than other models. It has been admirably described by Bader (1990) and, for inorganic solids, by Pendás *et al.* (1997, 1998) and Luaña *et al.* (1997), but it is only necessary here to give a brief account of the approach to show why it is difficult to relate its concepts to those of the bond valence model.

The electron density is a continuous function that is experimentally observable, hence uniquely defined, at all points in space. Its topology can be described in terms of the distribution of its critical points, i.e. the points at which the electron density has a zero gradient in all directions. There are four kinds of critical point which include maxima (A) usually found near the centres of atoms, and minima (D) found in the cavities or cages that lie between the atoms. In addition there are two types of saddle point. The first (B) represents a saddle point that is a maximum in two directions and a minimum in the third, the second (C) represents a saddle point that is a minimum in two direction and a maximum in the third. One can draw lines of steepest descent connecting the maxima (A) to the minima (D), lines whose direction indicates the direction in which the electron density falls off most rapidly. Of the infinite number of lines of steepest descent that can be drawn there exists a unique set that has the property that, in passing from the maximum to the minimum, each line passes successively through a B and a C critical point. This set forms a network whose nodes are the critical points and whose links are the lines of steepest descent connecting them.

In an infinite solid this set of critical points obeys a number of theorems, the chief being the Euler equation (eqn (14.1)):

$$a - b + c - d = 0, (14.1)$$

where *a*, *b*, *c* and *d* are the numbers of A, B, C, and D critical points respectively in any infinite three-dimensional network. The topology of the critical point network of the electron density is, in general, insensitive to small changes in the electron density and hence it is insensitive to small changes in the bonding geometry. However, if a large change is made in the position of an atom, a point is reached where the topology changes discontinuously. At such a catastrophe point, critical points are destroyed or created, corresponding to the breaking or making of network links, but the number of critical points in the new topology, like that in the old, still obeys Euler's equation (eqn (14.1)).

One consequence of the insensitivity of the topology to the details of the electron density is that one does not need to know the exact electron density in order to determine its topology. It is sufficient, for example, to use the proatom density, namely the electron density obtained by placing free atoms or free ions at the observed atomic positions in the crystal. The topology is therefore not sensitive to the relaxation of the electrons that occurs on compound formation.

The topology of the critical point network of the electron density can be analysed in at least two different ways, each representing a particular chemical viewpoint. One way is to use the critical point network to partition space into atomic fragments. This description is based on a subset of the original network that contains only the links between the D and C critical points. These define the edges of a set of space filling polyhedra that have a D critical point at each vertex and a C critical point at the position of maximum electron density along each edge as shown in Fig. 14.3. Each polyhedron contains one A critical point,

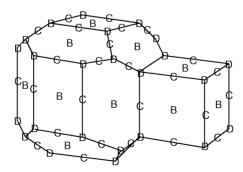


Fig. 14.3. Atomic fragments in LiF. The A points (not marked) lie at the centres of the two polyhedra, Li $^+$ in the cube and F $^-$ in the larger polyhedron. For clarity, some C points are omitted. The angled faces are the surfaces between F $^-$ ions.

corresponding to an atomic centre, and each of the polyhedral faces contains one B critical point at its electron density maximum. Each polyhedron thus represents an atom and the whole space of the crystal is divided into atomic fragments that share faces with a finite number of neighbouring atomic fragments. The surfaces that separate them are zero-flux surfaces, i.e. they represent surfaces at which the electron density is a minimum along any line connecting the two atomic centres.

Since the electron density is a continuous function across the interatomic surface, the two atoms that form the surface must have the same distribution of electrons over this face. The most stable structures will be those which require the least amount of redistribution of electron density when the free atoms come together, that is, they will be formed between atoms that have similar surface electron densities. This idea is related to the valence matching principle (Rule 4.2) which states that the most stable bonds are formed between ions that have similar bonding strengths. The bonding strength is thus related to the surface electron density of the ion.

An alternative way of describing the critical point network is to consider only the links connecting the A and B critical points. Since each B critical point is linked to only two A points (a consequence of it being a minimum along only one direction), the resulting network can be described as a network having nodes only at the atoms, A, with the B critical points at the electron density minimum on the lines connecting them. The links in this network are often described as bond paths and the point B as a bond critical point, but the word 'bond' in this context is used in its topological sense of a link between two nodes rather than in the sense of a chemical bond. Although this network may be similar to the bond network defined in Section 2.5, the two are not the same and, in order to avoid confusion, the electron density 'bond' network is here referred to as a 'B network' and the links between the A nodes are referred to as 'B paths'. The term 'bond' will continue to be used to describe the electrostatic links between atoms derived in Chapter 2.

These two topological descriptions of the electron density, one in terms of atomic fragments, the other in terms of the B network, are equivalent but complementary since every face of the polyhedral atomic fragment has a B path passing through it at the B critical point. One may use whichever of these topological descriptions is the most convenient for a particular purpose. In real space the B path is not necessarily a straight line since it follows the line of steepest descent in the electron density from A to B. Similarly the surface between the atomic fragments is not necessarily planar. If the electron density changes, the shape of the B paths and interatomic surfaces may change, even though the topology (the network connectivity) remains the same. By definition, a stable structure lies far from the catastrophe points where critical points are destroyed or created.

The B network derived from the electron density topology links all atoms that share faces. Although the B links are all topologically equivalent, only those

between cations and anions correspond to the bonds of the bond network described in Section 2.5. The remainder, those between two anions or between two cations, correspond to what are traditionally referred to as non-bonding contacts. While the distinction between bonds and non-bonding contacts is irrelevant in the electron density model, it is essential in the bond valence model, since the valence electrons are assumed to be associated only with the cation—anion links, that is, with the bonds. In a bipartite bond graph there are no valence electrons associated with the cation—cation and anion—anion contacts. When solving the network equations ((3.3) and (3.4)), it is only the bond links that are used.

In the electron density model it is common to use the electron density or its Laplacian at the B critical point as an indicator of the type of B path that is formed. A large electron density or negative Laplacian at this point indicates a concentration of electrons in the middle of the B path, corresponding to a covalent bond. A small electron density or positive Laplacian, on the other hand, suggests that few electrons are concentrated in the middle of the B path. Bader (1990) refers to these as closed shell interactions. Such interactions are indicative of either an ionic bond or a van der Waals bond (nonbonding contact), but the properties of the B critical points do not distinguish between these chemically distinct interactions. Thus, although both the electron density and the bond valence models can be represented by a network of links between atoms in contact, the bond valence model distinguishes between bonds (either ionic or covalent) on the one hand and non-bonding contacts (van der Waals) on the other, while the electron density model distinguishes between covalent bonds on the one hand, and ionic and van der Waals bonds on the other. If, however, one allows that the bond valence is a measure of the degree of covalency as suggested in Section 14.1.1, then one would expect the electron density at the B point to correlate with the bond valence, as has been observed in theoretical calculations by Gibbs et al. (1998) in minerals and by Alkorta et al. (2000) in bonds to carbon. It is hardly surprising that the electron density at the B critical point would increase as the atoms are brought closer together, since the shorter the interatomic distance the closer the B point is to the electron density maximum of each of the atoms. One therefore needs to be careful in assigning special significance to the electron density at the B critical point.

A closer comparison of bond valence and electron density models is not possible because of the different underlying assumptions of the models. The forces in the bond valence model act between structureless point atoms, but the forces in the electron density model are exerted by electrons on nuclei and vice versa. This basic difference makes it difficult to compare the two models in greater detail. They are best seen as complementary, the electron density model providing important information about the nature of the bonding between the atoms, the bond valence model providing a simple tool for predicting structure and properties, particularly in cases where the structure is complex.

14.8 The topology of the Madelung field

The topology of the Madelung field of the ionic model can also be described in terms of critical points, but these points do not occur at the same places as those of the electron density. The lines of electrostatic field (flux lines) described in Chapter 2 are the lines of steepest descent in the electric potential field. The maxima (A critical points) in the Madelung potential field occur at the positions of the cations and the minima (D critical points) at the positions of the anions. The topology is thus different from that derived from the electron density where all atoms are found at A critical points. However, the mathematical theorems are the same. Space can be divided into polyhedra using the same constructions as were used for the electron density. If the D critical points (anions) are chosen as the vertices, one gets a partitioning of space into cation-centred fragments, but if instead the A critical points (cations) are chosen as the vertices one gets a partitioning into anion-centred fragments. These partitionings lead to the cation and anion lattices discussed in Section 11.2.1.2 and help to show the complementarity of these lattices.

Alternatively if all four kinds of critical point are chosen as vertices, one gets a partitioning into fragments which each contain the flux lines of a single bond. The surfaces of the bond fragment are zero flux surfaces, i.e. no field lines cross into or out of the bond fragment. In this interpretation, each bond occupies a finite space and every point in space belongs to one and only one bond.

14.9 Conclusions

There have been a number of attempts to provide a physical justification for the bond valence model. Jansen and Block (1991) and Jansen *et al.* (1992) have given a critical derivation starting from the Born-Meyer (1932) equation. Preiser *et al.* (1999) have developed the model in terms of the Madelung field. Burdett and Hawthorne (1993) have produced a justification based on an orbital description, while Urusov (1995) has provided a semi-empirical groundwork based on an eclectic selection of physical models. Whatever kind of theoretical justification one wishes to use, the bond valence model provides a simple and robust account of chemical bonding. The full quantum mechanical calculations, while they describe accurately the distribution of electrons, and so give information about the nature of chemical bonding, involve extensive computation and do not easily yield the insights that are needed to understand the complex interactions found in most crystals or large molecules. The bond valence and quantum mechanical approaches are thus complementary. They provide different kinds of information and are most useful in different situations.

¹ This field is not the physical electrostatic field observed in the crystal because the ionic model takes no account of the distribution of electrons within the atom. The distributed charge of the atom is replaced by a single point charge at its centre.

There are simple underlying principles that govern structural chemistry, of which the principle of maximum symmetry is one. Another is the notion that the chemical properties of an atom are determined by the potential at the surface of its electron core, the potential that the valence electrons experience. This potential is proportional to the ratio of the atom's charge to size, and it is no surprise that this ratio determines such varied atomic quantities as bonding strength, acid and base strength, and electronegativity.

When atoms are brought together to form a compound, it is the electrostatic field that provides the cohesion whether the bonds are ionic or covalent. Although this field is long range and results in a significant force being exerted between well-separated atoms, it is fully described by the localized bond flux linking neighbouring atoms, the long-range effects being automatically taken into account by the network equations. It is therefore possible to describe chemistry in terms of localized chemical bonds whose properties can be predicted from the topology of the bond network.

Finally, a chemical compound must satisfy the constraints of three-dimensional space. The physical and chemical properties of a solid or liquid are determined by the interplay between the constraints of chemistry described, for example, by the bond valence model, and the constraints of space. Ultimately it is the ability of a chemical structure to be mapped into three-dimensional space that determines whether or not it exists.

While more physically based models provide a picture of the underlying forces that lead to chemical bonding, the bond valence model reduces the rules of chemistry to their simplest mathematical form. In this form it is able to provide insights into the behaviour of the many complex systems found in acid—base chemistry.



Appendices

Appendix 1

Bond valence parameters

A1.1 Introduction

Pauling (1947) first suggested using eqn (3.1) to associate bond valences (bond numbers or bond strengths) to interatomic distances in metals and alloys. Byström and Wilhelmi (1951) then applied the same relation to oxides. Subsequently Zachariasen (1954) and Zachariasen and Plettinger (1959) published graphical correlations for U-O bonds. Clark et al. (1969) determined bond valences for Si-O bonds by expressing the bond distance as a third degree power series in S with four fitted parameters, though Perloff (1970) found a simple linear relation worked for Cr-O and Mo-O bonds. Donnay and Allman (1970) used eqn (3.2) with a linear extrapolation to S = 0 at a finite value of R to locate hydrogen bonds in minerals. Equation (3.2) was also adopted by Brown and Shannon (1973) to produce a systematic listing of bond valence parameters. Since then there have been many determinations of bond valence parameters for both egns (3.1) and (3.2) (Brown 1981) as well as more limited listings of parameters for some of the other relations discussed in Section A1.3 below. A listing of published parameters for use in eqn (3.1) can be found at http://www.ccp14.ac.uk/ccp/web-mirrors/i d brown/bond valence parm/ and a shorter selected list of bond valence parameters is given in Table A1.1.

The bond length-bond valence relationship is a measure of the repulsion between ions. Equation (3.1) is based on the exponential Born-Meyer (1932) repulsion potential and eqn (3.2) on the earlier power law of Born and Landé (1918). Both equations contain two fitted parameters which is the minimum number needed to give a reasonable fit over the limited ranges of bond lengths normally found. Both give equally good fits, though eqn (3.1) is generally preferred because of its more robust mathematical properties and the approximate constancy of the parameter B. Neither equation describes the relationship particularly well over an extended range of bond lengths, but these are encountered in only a few cases such as the O-H bonds discussed in Chapter 7.

A1.2 Determination of bond valence parameters

This section discusses the determination of the bond valence parameters used in eqns (3.1) and (3.2) though the principles can be applied to the other expressions discussed in Section A1.3. Since there is no exact theoretical derivation of the correlation between bond valence and bond length, the bond valence

Table A1.1 Selected bond valence parameters for eqn (3.1)

Cation	Anion	R_0 (pm)	B (pm)
$\overline{\mathrm{Ag}^{+}}$		238	37
$A1^{3+}$	O^{2-}	162	37
As^{5+}	\mathbf{F}^{-}	162	37
B^{3+}	O^{2-}	137.1	37
Ba^{2+}	O^{2-}	228.5	37
Ba ²⁺ C ⁴⁺	O^{2-}	139	37
Ca^{2+}	F^-	184.2	37
Ca ²⁺	O^{2-}	196.7	37
Ca^{2+} Cd^{2+}	${ m Br}^-$	249	37
Cd^{2+}		237	37
Cl ⁷⁺	O^{2-}	163.2	37
Co ²⁺	N ³⁻ (two coordinate)	170	37
Co ²⁺	N^{3-} (three coordinate)	177	37
Cr ³⁺	F	165.7	37
Cr^{3+}	O^{2-}	172.4	37
Cr ⁶⁺	O^{2-}	179.4	37
Cs ⁺	C1 ⁻	279.1	37
Cs ⁺	O^{2-}	241.7	37
Cu ⁺	O^{2-}	161	37
Cu ²⁺	${ m O}^{2-}$	167.9	37
Cu ³⁺	O^{2-}	174	37
Er ³⁺	S ²⁻	246	37
Eu ³⁺	O^{2-}	207.4	37
Fe ²⁺	O^{2-}	173.4	37
Fe ³⁺	O^{2-}	175.4	37
Ga ³⁺	O^{2-}	173.9	37
Ge ⁴⁺	O^{2-}	173.0	37
Hg ²⁺	Cl ⁻	228	37
Hg^{2+}	F ⁻	228 217	37
пg I ⁵⁺	O^{2-}	200.3	37
K ⁺	Cl ⁻	200.3 251.9	37
K ⁺	O^{2-}		37
La ³⁺	O^{2-}	213.7	
La 2+	O^{2-}	217.2	37
Mg^{2+} Mn^{3+}	O^2	169.3	37
Mn ^s	O^{2}	176.0	37
Mo ⁶⁺	O^2	190.7	37
N ⁵⁺	O^2 O^{2-}	136.1	37
NH ₄ ⁺	O-	222.6	37
NH ₄ ⁺	F ⁻	212.9	37
NH_4^+	Cl ⁻	261.9	37
Na ⁺	Cl ⁻	215	37
Na ⁺	F ⁻	167.7	37
Na ⁺	O^{2}	180.3	37
Nb^{5+}	O^{2}	191.1	37

226 APPENDIX 1

Table A1.1 (Continued)

Cation	Anion	R_0 (pm)	<i>B</i> (pm)
Ni ²⁺	O ²⁻	165.4	37
P^{5+}	O ^{2 –} S ^{2 –} Cl [–]	161.7	37
Pb^{2+}	S^{2-}	254.1	37
Pd^{2+}	Cl ⁻	253	37
Rb^+	O^{2-} O^{2-} O^{2-} O^{2-} O^{2-} O^{2-}	226.3	37
Ru ⁵⁺	O^{2-}	190	37
S ⁴⁺	O^{2} –	164.4	37
S^{6+}	O^{2-}	162.4	37
Sb ⁵⁺	O^{2}	194.7	37
Sc^{3+}	O^{2}	184.9	37
Si ⁴⁺	$O^{2} O^{2} O^{2} O^{2} O^{2} O^{2}-$	162.4	37
Sn ²⁺	O^{2}	194	37
Sr^{2+}	O^{2-}	211.8	37
Te ⁴⁺ Ti ⁴⁺	Cl ⁻	237	37
Ti ⁴⁺	O^{2}	181.5	37
T1 ⁺	O^{2} –	212.4	37
Tm ³⁺ V ⁵⁺ Y ³⁺	O^{2}	200.0	37
V^{5+}	O^{2-}	180.3	37
Y^{3+}	O^{2} –	201.9	37
Yb^{3+}	O^{2}	196.5	37
Zn^{2+}	O^{2-}	170.4	37
Zn^{2+}	S^{2-}	209	37
Zn^{2+}	Te ²⁻	245	37

Mostly taken from Brown and Altermatt (1985) and Brese and O'Keeffe (1991). (A complete set is available at http://www.ccp14.ac.uk/ccp/web-mirrors/i_d_brown/bond_valence_parm/)

parameters, R_0 , and B or N, must be determined empirically using experimentally determined bond lengths.

In principle the bond valence parameters could be obtained by comparing the experimental bond valences, S, determined using an initial set of bond valence parameters, against the theoretical bond valences, s, calculated using the network eqns (3.3) and (3.4). These initial values could then be refined to minimize the differences given by the expression (A1.1):

$$\sum_{i} (s_{ij} - S_{ij})^2. \tag{A1.1}$$

This method has not so far been used but should work well providing that only structures with unstrained bonds are used.

The normal procedure is to refine the bond valence parameters by minimizing the difference between the atomic valence and the sum of the bond valences around cations with only one kind of ligand (expression (A1.2)):

$$\sum_{i} \left(V_i - \sum_{j} S_{ij} \right)^2. \tag{A1.2}$$

Since there are two bond valence parameters to be determined, at least two cation environments are needed. In practice it is best to use at least 20-30 environments if these are available. Even so, there are a number of hazards. If all the cations in the sample have the same coordination number and an average bond valence of 1.0 vu, B necessarily refines to infinity (N refines to 0), but even when different coordination numbers are present there is a strong correlation between B (or N) and R_0 . The ambiguities caused by this correlation can be resolved by calculating the valence sums around the anions as well as the cations, but this is difficult to do in a systematic way since the anions usually bond to more than one type of cation. A further uncertainty is introduced by the choice of the maximum bonding distance since including longer distances in the coordination sphere systematically increases B and decreases R_0 (Adams 2001). In the list prepared by Brown and Altermatt (1985), and by inference the list based on it prepared by Brese and O'Keeffe (1991), all the bonds were assumed to have valences greater than 0.04 times the cation valence.

While R_0 can be determined with much greater precision than B (or N), the correlation between the parameters means that making changes in B (or N), even changes that lie well within the range of experimental uncertainty, requires a corresponding, but significant, change in R_0 . One must be careful, therefore, to make sure that the value of R_0 used is the one appropriate to the value of R_0 (or R_0) chosen.

B (or N) can only be determined with a precision of around 10 per cent even if care is taken (Tytko 1999), but the observation that B lies between 32 and 42 pm for many bonds means that it is convenient to fix its value at 37 pm for all bond types (Brown and Altermatt 1985). Any error that this assumption introduces is usually negligible for most bonds to O^{2-} provided that the appropriate value of R_0 is used. Using the same value of B for all bond types makes the determination of R_0 simpler since only one parameter now needs to be fitted. Combining eqn (3.1) with the valence sum rule and rearranging yields eqn (A1.3):

$$R_{0i} = B \ln \left\{ V / \left[\sum_{j} \exp(-R_{ij}/B) \right] \right\}, \tag{A1.3}$$

where the summation is over all the bonds in a single coordination sphere, i. Since all the terms on the right-hand side of this equation are known, it is easy to calculate R_{0i} , the value of R_0 that will give a valence sum exactly equal to V for

 $^{^{1}}$ Recent work suggests that B may be significantly larger than 37 pm for bonds between soft and hard ions (Adams 2001).

228 APPENDIX 1

the *i*th coordination sphere. This procedure gives separate values of R_{0i} for each coordination sphere examined but, if the valence sum rule and the value of B chosen are valid, the values of R_{0i} should all be similar. Some variation is expected as a result of experimental uncertainty and the presence of cation environments that suffer from lattice-induced strain (Chapter 12), but it is easy to check whether R_{0i} varies systematically with coordination number which would be an indicator that the wrong value of B has been assumed. If the variations in the individual values of R_{0i} are acceptable, the best value for R_0 is taken as the average (eqn (A1.4)):

$$R_0 = \langle R_{0i} \rangle. \tag{A1.4}$$

The advantage of this method is that it can be easily used with any number of cation coordination spheres whose bond distances are available. Even one coordination sphere is sufficient to give a trial value though the more that are used the more confidence one can have in the value of R_0 . One needs to exercise a little care if only a few coordination spheres are known, since the oxidation state may be unstable except in the presence of strained bonds which could lead to a false value of R_0 . There are a number of potential pitfalls in determining bond valence parameters. For example, the inclusion of poorly determined structures in the sample tends to increase the value (and uncertainty) of B with a corresponding decrease in R_0 . A critique of these problems has been given by Tytko (1999).

The above procedure was used by Brown and Altermatt (1985) to produce an extensive table of bond valence parameters, mostly of bonds to O^{2-} . They based their refinement on cation environments in ordered structures with crystallographic agreement indices (R) of less than 0.1 reported in the Inorganic Crystal Structure Database (Bergerhoff *et al.* 1983). A routine for calculating R_{0i} is available in the program VALENCE (Brown 1996) which can also be used for calculating bond valences from bond lengths and vice versa. In this book, the bond valence parameters of Brown and Altermatt (1985) are used where available.

Brese and O'Keeffe (1991) extended the table of Brown and Altermatt to many other anions by showing that R_0 for a bond between any cation and an anion X (R_{0X}) is related to the value for the bond between the same cation and $O^{2-}(R_{0O})$ by eqn (A1.5):

$$R_{0X} = a + bR_{0O},$$
 (A1.5)

where a and b are constants which they tabulate for each of the 11 anions (X) they examined. Using eqn (A1.5), they were able to calculate values of R_0 for 969 different bond types. While these values are not as accurate as those found by direct fitting, they are satisfactory for most purposes. In some cases Brese and O'Keeffe ignore the variation of R_0 with oxidation state but for many

cations this does not introduce a large error, though for some of the softer ions like Cu, R_0 is quite sensitive to oxidation state. For the best results, the influence of the oxidation state on R_0 should not be ignored.

In a second paper O'Keeffe and Brese (1991) showed that R_0 could be approximately determined from atomic parameters using eqn (A1.6):

$$R_0 = r_i + r_j - \left\{ r_i r_j (\sqrt{c_i} - \sqrt{c_j})^2 / (c_i r_i + c_j r_j) \right\},$$
 (A1.6)

where r_i and r_j are the atomic radii and c_i and c_j are the electronegativities of the terminal atoms i and j respectively. While eqn (A1.6) extends the range of bond valence parameters to cover virtually all bond types, the parameters it gives are not accurate enough for most of the uses described in this book. These parameters should be used with caution in quantitative work.

More recently Liu and Thorp (1993) and others have addressed the problem of determining the values of R_0 in cases where the ligand is only present in mixed ligand environments, so that it is impossible to determine R_{0i} in the manner described above. Most of these studies have been made on transition-metal complexes extracted from the Cambridge Structural Database (Allen *et al.* 1979). Since these complexes usually have a mixture of ligating atoms (typically O, N, or S), Liu and Thorp refined the values of R_{00} , R_{0N} , and R_{0S} simultaneously against the available bond lengths, the sample varying in size from 13 (for Ni³⁺) to 116 (for Fe²⁺). Because the values for O²⁻ and N³⁻ are very similar, there is a strong correlation between the values of R_{00} and R_{0N} . On the other hand, Liu and Thorp derive different values for cations with different atomic valences and even list different parameters for the vanadyl bond (V⁴⁺=O) and normal V⁴⁺-O bonds. Where comparison is possible the values of R_0 obtained by Liu and Thorp generally differ by less than 3 pm from those of Brown and Altermatt (1985).

In a series of papers Palenik and his coworkers (Palenik 1997a,b,c; Kanowitz and Palenik 1998; Wood and Palenik 1998, 1999a,b; Wood et al. 2000) have determined bond valence parameters for transition metals. Some of these have been chosen to be independent of oxidation state in an attempt to provide values of R_0 that can be used when the oxidation state of the cation is not known. While these parameters are not as accurate as those that take the oxidation state into account, they can be used to make an approximate determination of the oxidation state, after which the correct value of R_0 can be substituted.

In recent studies See *et al.* (1998) and Shields *et al.* (2000) suggest that R_0 sometimes depends on factors other than the oxidation states of the cation and anion. To obtain correct bond valence sums around transition metals with nitrogen ligands, it is necessary to use different values of R_0 depending on the coordination number of N^{3-} as discussed in Section 9.2.

As the temperature of a crystal increases, it expands and the length of its bonds also increases though the bond valences do not change. In order to 230 APPENDIX 1

calculate the correct bond valence for structures determined at high temperatures, one needs to correct the value of R_0 for temperature using eqn (9.21) (Brown *et al.* 1997).

The bonds formed by H⁺ need special treatment as described in Section 7.8. No satisfactory analytical expression has been found that relates bond valence to bond length though some suggested expressions are given in Section A1.3. Using eqn (3.1) Alig *et al.* (1994) fitted H–O bonds with the parameters $R_0 = 91.4 \,\mathrm{pm}$ and $B = 40.4 \,\mathrm{pm}$ determined from the bond valence sums around H⁺. Although these values give good valence sums around the H⁺ ion, the valence sums around O²⁻ were not checked and Alig *et al.*'s parameters do not agree with the curve shown in Fig. 7.1. The table given at http://www.ccp14.ac.uk/ccp/web-mirrors/i_d_brown/bond_valence_parm/ works around the problem by providing three sets of values for R_0 and R_0 , respectively 90.7 and 28 pm for H–O distances less than 105 pm, 56.9, and 94 pm for H–O distances between 105 and 170 pm, and 99 and 59 pm for H–O distances greater than 170 pm. In general, it is best to assign valences to H–O bonds using the graphical methods discussed in Section 7.8.

A1.3 Other bond valence expressions

While eqns (3.1) and (3.2) have proved satisfactory for most purposes, several other expressions have been proposed. Most do not address the failure of eqns (3.1) and (3.2) to give correct valences at extreme distances but are motivated by an attempt to use atom-based parameters or to provide some physical justification for the relationship. As a result they are often more complex, sometimes involving more than two parameters per bond. Some make direct use of ionic radii which, however, come in many flavours. In general, it is not clear that these other formulations provide significantly better fits to the valence sum rule than the eqns (3.1) and (3.2), even though they may give more insight into the underlying physics.

Ziołkowski (1985) derived an equation (A1.7) for the bond valence based on notional free ionic radii, r_a and r_c , extrapolated to zero coordination:

$$S = V(a - bV - cr_{c} - dVr_{c})/R - (r_{c} + r_{a}).$$
 (A1.7)

Here *a*, *b*, *c*, and *d* are universal constants which, however, depend on the way in which the radii are defined. Since the true free ion radii are often negative (which is unphysical), Ziołkowski defines a second set in which hydrogen is assumed to have zero radius.

Ziołkowski's equation can be simplified to the form given in eqn (A1.8),

$$S = e/(R - f), \tag{A1.8}$$

since, for a given bond type, e and f are constants which can be treated as empirical parameters and fitted to observed bond lengths. This curve is steeper

than eqn (3.1) for short bonds, f representing the bond distance at which S becomes infinite. Subtracting a third constant, g, from the left-hand side of eqn (A1.8) gives eqn (A1.9),

$$S = e/(R - f) - g, \tag{A1.9}$$

and ensures that S=0 when R=f+e/c. The length of a bond of 1.00 vu is then R=f+e/(1+g). Brown (1987b) proposed that the H–O bond valence given by the thin line in Fig. 7.1 could be approximated using eqn (A1.9) with e=41 pm, f=60 pm and g=0.16 pm. Bargar et al. (1997c) recommend eqn (A1.8) with e=24.1 pm and f=67.7 pm. Both these sets of parameters are better than eqns (3.1) and (3.2) for O–H bonds, though neither is perfect. Brown's parameters give a marginally better fit, but at the expense of a third fitted parameter.

Naskar *et al.* (1997) were interested in using bond valences to determine oxidation states around transition-metal cations, particularly those with negative or zero formal oxidation states. Since these numbers cannot, in principle, be reached by the standard equations, they proposed to create a fictional positive oxidation state by arbitrarily adding 4.0 to the actual oxidation state. They proposed to write the valence sum rule in the form of eqn (A1.10):

$$V_i + 4 = (1 + a/n_i) \sum_{j=1,n} (R_1/R_{ij}),$$
 (A1.10)

where n_i is the coordination number and a (=20) and R_1 are fitted parameters. One may question the underlying assumptions of this equation, and the bond valences determined in this way are different in kind from those determined by the more traditional methods since different values are obtained depending on whether one uses the cation or the anion as the central atom. However, the expression, being empirical, must be judged on how well it discriminates between the oxidation states and this still needs to be demonstrated.

Valach (1999) has proposed the use of the five-parameter eqn (A1.11) based on a Taylor expansion of the quantum stabilization energy:

$$S = \sum_{\nu=1.5} (\alpha_{\nu}/r^{\nu}). \tag{A1.11}$$

The values of α_{ν} are not determined from the theory but, like other bond valence parameters, are fitted to observed bond lengths in the manner described in Section A1.2. The parameters that Valach reports for Cu–O and Cu–N bonds give zero valence at finite bond lengths, but the valences calculated for very short bonds are probably too low.

Mohri (2000) has proposed eqn (A1.12) based qualitatively on the notion that the electron density in the interatomic region will be roughly uniform.

$$S = S_0 ((R^0 - \lambda)^3 / (R - \lambda)^3),$$
 (A1.12)

232 APPENDIX 1

where R^0 is the bond length observed at a valence of S_0 , and λ is the sum of the core radii (Pauling's cationic radii) of the two atoms. The parameters of eqn (A1.12) can be directly related to the softness parameters of eqns (3.1) and (3.2) by using the value of R^0 for $S_0 = 1$.

$$B = (R^0 - \lambda)/3, (A1.13)$$

$$N = 3R^0/(R^0 - \lambda). (A1.14)$$

Using the parameters of eqn (A1.12) Mohri finds that 75 per cent of the values of B lie within 5 pm of 37 pm and that the values of N lie within about 10 per cent of the values reported by Brown and Shannon (1973).

Appendix 2

Space group spectra

For a definition of space group spectra see Section 10.5. Spectra for all space groups are arranged below (Tables A2.1–A2.10) in order of decreasing symmetry. The multiplicities of the Wyckoff positions, m_w , are given across the top of each table. The symmetries of sites with multiplicity 1 are given at the end of each line followed by structure types that crystallize in that space group (site symmetries in parentheses refer to positions of multiplicity 2).

Table A2.1 Space groups of non-translational order 48

		1	2	3	4	6	8	12	16	24	48	Site symmetry	Example
229	Im3̄m	1	0	1	1	*	*	*	0	*	*	m3̄m	
225	$Fm\bar{3}m$	2	1	0	0	*	*	*	0	*	*	m3̄m	NaCl, CaF ₂
221	Pm3̄m	2	0	2	0	*	*	*	0	*	*	$m\bar{3}m$	CsCl, SrTiO ₃

Table A2.2 Space groups of non-translational order 24

		1	2	3	4	6	8	12	16	24	Site symmetry	Example
227	Fd3m	2	2	0	*	*	0	*	0	*	43m	NaTl, spinel
226	Fm3c	2	0	2	0	*	*	*	0	*	432, $m\bar{3}$	
224	Pn3m	1	2	1	*	*	0	*	0	*	$\bar{4}3m$	
223	Pm3n	1	0	1	1	*	*	*	0	*	$m\bar{3}$	
222	Pn3n	1	0	1	1	*	*	*	0	*	432	
217	$I\bar{4}3m$	1	0	1	*	*	0	*	0	*	$\bar{4}3m$	
216	$F\bar{4}3m$	4	0	0	*	8	0	*	0	*	$\bar{4}3m$	ZnS
215	P43m	2	0	2	*	*	0	*	0	*	$\bar{4}3m$	
211	I432	1	0	1	1	*	*	*	0	*	43	
209	F432	2	1	0	0	*	*	*	0	*	43	
207	P432	2	0	2	0	*	*	*	0	*	43	
204	Im3	1	0	1	1	*	*	*	0	*	$m\bar{3}$	
202	Fm3	2	1	0	0	*	*	*	0	*	$m\bar{3}$	
200	Pm3	2	0	2	0	*	*	*	0	*	$m\bar{3}$	
191	P6/mmm	2	*	2	*	*	0	*	0	*	6/mmm	

Table A2.3 Space groups of non-translational order 16

		1	2	3	4	6	8	12	16	Site symmetry
139 123	I4/mmm P4/mmm	2 4	*	~	*	0	*	0	*	4/mmm 4/mmm
123	F 4/ IIIIIIII	4	*	U	*	U	*	U	*	4/111111111

 Table A2.4
 Space groups of non-translational order 12

		1	2	3	4	6	8	12	Site symmetry	Example
230	Ia3d	0	2	2	*	*	0	*	(3, 32)	Garnet
228	Fd3c	1	2	1	*	*	0	*	23	
219	F43c	2	0	2	*	*	0	*	23	
218	P43n	1	0	3	*	*	0	*	23	
210	$F4_{1}32$	2	2	0	*	*	0	*	23	
208	P4 ₂ 32	1	2	3	*	*	0	*	23	
203	$\overline{Fd3}$	2	2	0	*	*	0	*	23	
201	$Pn\bar{3}$	1	2	1	*	*	0	*	23	
197	I23	1	0	0	*	*	0	*	23	
196	F23	4	0	0	*	*	0	*	23	
195	P23	2	0	2	*	*	0	*	23	
194	P6 ₃ /mmc	4	*	*	0	*	0	*	$\bar{3}$ m, $\bar{6}$ 2m	
193	P6 ₃ /mcm	2	*	*	*	*	0	*	3m, 62m	
192	P6/mcc	2	*	2	*	*	0	*	62, 6/m	
189	Pē2m	2	*	*	*	*	0	*	$\bar{6}2m$	
187	Pēm2	6	*	*	0	*	0	*	<u>6</u> 2m	
183	P6mm	*	*	*	0	*	0	*	6mm	
177	P622	2	*	2	*	*	0	*	622	
175	P6/m	2	*	2	*	*	0	*	6/m	
166	$R\bar{3}m$	2	*	2	0	*	0	*	$\bar{3}$ m	$CdCl_2$
164	$P\bar{3}m1$	2	*	2	0	*	0	*	$\bar{3}$ m	CdI_2
162	P31m	2	*	2	*	*	0	*	$\bar{3}$ m	_

 Table A2.5
 Space groups of non-translational order 8

		1	2	3	4	6	8	Site symmetry	Examples
141	I4 ₁ /amd	2	*	0	*	0	*		Anatase
140	I4/mcm	4	*	0	*	0	*	$422, \bar{4}2m, 4/m, mmm$	8-CN perovskite
137	P4 ₂ /nmc	2	*	0	*	0	*	$\bar{4}2m$	•
136	P4 ₂ /mnm	2	*	0	*	0	*	mmm	Rutile
134	$P4_2/nnm$	2	*	0	*	0	*	$\bar{4}2\mathrm{m}$	
132	P4 ₂ /mcm	4	*	0	*	0	*	$\bar{4}2\mathrm{m}$	
131	P4 ₂ /mmc	6	*	0	*	0	*	$\bar{4}2m$, mmm	
129	P4/nmm	*	*	0	*	0	*	42m, 4mm	
128	P4/mnc	2	*	0	*	0	*	4/m	
127	P4/mbm	4	*	0	*	0	*	4/m, mmm	8-CN perovskite
126	P4/nnc	2	*	0	*	0	*	42	•
125	P4/nbm	4	*	0	*	0	*	$\bar{4}2\mathrm{m}$	
124	P4/mcc	2	*	0	*	0	*	4/m, 42	
121	I42m	2	*	0	*	0	*	$\bar{4}2m$	
119	$I\bar{4}m2$	4	*	0	*	0	*	$\bar{4}2\mathrm{m}$	
115	$P\bar{4}m2$	4	*	0	*	0	*	$\bar{4}2m$	

Table A2.5 (Continued)

		1	2	3	4	6	8	Site symmetry	Examples
111	P42m	4	*	0	*	0	*	42m	
107	I4mm	*	*	0	*	0	*	4mm	
99	P4mm	*	*	0	*	0	*	4mm	
97	I422	2	*	0	*	0	*	42	
89	P422	4	*	0	*	0	*	42	
87	I4/m	2	*	0	*	0	*	4/m	
83	P4/m	4	8	0	*	0	*	4/m	
71	Immm	4	*	0	*	0	*	mmm	
69	Fmmm	2	*	0	*	0	*	mmm	
65	Cmmm	4	*	0	*	0	*	mmm	
47	Pmmm	8	*	0	*	0	*	mmm	

 Table A2.6
 Space groups of non-translational order 6

		1	2	3	4	6	Site symmetry	Examples
213	P4 ₁ 32	2	*	*	0	*	32	
206	Ia3	2	*	*	0	*	$\bar{3}$	Bixbyite
205	Pa3	2	*	0	0	*	$\bar{3}$	
199	$12_{1}3$	0	*	8	0	*	(3)	
190	Pē2c	4	*	*	0	*	32, $\bar{6}$	
188	Pēc2	6	*	*	0	*	32, $\bar{6}$	
186	P6 ₃ mc	*	0	*	0	*	3m	Wurtzite
185	P6 ₃ cm	*	*	*	0	*	3m	
184	P6cc	*	*	*	0	*	6	
182	$P6_{3}22$	4	*	*	0	*	32	
176	$P6_3/m$	2	*	*	0	*	$\bar{3}, \bar{6}$	
174	$P\bar{6}$	6	*	*	0	*	$\bar{6}$	
168	P6	*	*	*	0	*	6	
167	$R\bar{3}c$	2	*	*	0	*	32	Corundum, 9-CN perovskite
165	Pc31	2	*	*	0	*	32	
163	P31c	4	*	*	0	*	$\bar{3}$, 32	
160	R3m	*	0	*	0	*	3m	
157	P31m	*	*	*	0	*	3m	
156	P3m1	*	0	*	0	*	3m	
155	R32	2	*	*	0	*	32	
150	P321	2	*	*	0	*	32	
149	P312	6	*	*	0	*	32	
148	$R\bar{3}$	2	*	2	0	*	$\frac{\bar{3}}{\bar{3}}$	
147	$P\bar{3}$	2	*	2	0	*	$\bar{3}$	

236 APPENDIX 2

 Table A2.7
 Space groups of non-translational order 4

		1	2	3	4	Site symmetry
181	P6 ₄ 22	4	*	0	*	222
180	$P6_{2}22$	4	*	0	*	222
142	I4 ₁ /acd	2	*	0	*	$\bar{4}$, 222
138	P4 ₂ /ncm	*	*	0	*	4, 2/m, 222, mm2
135	P4 ₂ /mbc	4	*	0	*	4, 2/m, 222
133	P4 ₂ /nbc	4	*	0	*	$\bar{4}$, 222
130	P4/ncc	*	*	0	*	$\bar{4}$, 222
122	I42d	2	*	0	*	$\bar{4}$
120	$I\bar{4}c2$	4	*	0	*	$\bar{4}$, 222
118	$P\bar{4}n2$	4	*	0	*	$\bar{4}$, 222
117	$P\bar{4}b2$	4	*	0	*	$\bar{4}$, 222
116	P4c2	4	*	0	*	$\bar{4}$, 222
114	$P\bar{4}2_1c$	2	*	0	*	$\bar{4}$
113	$P\bar{4}2_1m$	*	*	0	*	4, mm2
112	P42c	6	*	0	*	$\bar{4}$, 222
109	$I4_1$ md	*	*	0	*	mm2
108	I4cm	*	*	0	*	4, mm2
105	P4 ₂ mc	*	*	0	*	mm2
104	P4nc	*	*	0	*	4
103	P4cc	*	*	0	*	4
102	P4 ₂ nm	*	*	0	*	mm2
101	P4 ₂ cm	*	*	0	*	mm2
100	P4bm	*	*	0	*	4, mm2
98	$I4_{1}22$	2	*	0	*	222
94	$P4_22_12$	2	*	0	*	222
93	$P4_{2}22$	6	*	0	*	222
90	P42 ₁ 2	*	*	0	*	4, 222
88	$I4_1/a$	2	*	0	*	$\bar{4}$
86	$P4_2/n$	2	*	0	*	$\bar{4}$
85	P4/n	*	*	0	*	$\bar{4}$, 4
84	$P4_2/m$	6	*	0	*	2/m
82	$I\bar{4}$	4	*	0	*	$\bar{4}$
81	$P\bar{4}$	4	*	0	*	$\bar{4}$
79	I4	*	*	0	*	4
75	P4	*	*	0	*	4
74	Imma	*	*	0	*	2/m
72	Ibam	4	*	0	*	222
70	Fddd	2	*	0	*	222
68	Ccca	2	*	0	*	222
67	Cmma	*	*	0	*	2/m
66	Cccm	6	*	0	*	222
64	Cmca	2	*	0	*	2/m
63	Cmcm	*	*	0	*	2/m

Table A2.7 (Continued)

		1	2	3	4	Site symmetry	
59	Pmmn	*	*	0	*	mm2	
58	Pnnm	4	*	0	*	2/m	CaCl ₂
55	Pbam	4	*	0	*	2/m	
53	Pmna	4	*	0	*	2/m	
51	Pmma	*	*	0	*	2/m, mm2	
50	Pban	4	*	0	*	222	
49	Pccm	8	*	0	*	2/m	
48	Pnnn	4	*	0	*	222	
44	Imm2	*	*	0	*	mm2	
42	Fmm2	*	*	0	*	mm2	
38	Amm2	*	*	0	*	mm2	
35	Cmm2	*	*	0	*	mm2	
25	Pmm2	*	*	0	*	mm2	
23	I222	4	*	0	*	222	
22	F222	4	*	0	*	222	
21	C222	4	*	0	*	222	
16	P222	8	*	0	*	222	
12	C2/m	4	*	0	*	2/m	
10	P2/m	4	*	0	*	2/m	

 Table A2.8
 Space groups of non-translational order 3

		1	2	3	Site symmetry
198	P2 ₁ 3	*	0	*	3
173	P6 ₃	*	0	*	3
161	R3c	*	0	*	3
159	P31c	*	0	*	3
158	P3c1	*	0	*	3
146	R3	*	0	*	3
143	P3	*	0	*	3

 Table A2.9
 Space groups of non-translational order 2

		1	2	Site symmetry	Example
179	P6 ₅ 22	*	*	2	_
178	$P6_{1}22$	*	*	2	
172	$P6_4$	*	*	2	
171	$P6_1$	*	*	2	
154	P3 ₂ 21	*	*	2	
153	P3 ₂ 12	*	*	2	
152	P3 ₁ 21	*	*	2	

Table A2.9 (Continued)

		1	2	Site symmetry	Example
151	P3 ₁ 12	*	*	2	
110	$I4_1cd$	*	*	2	
106	P4 ₂ bc	*	*	2	
96	$P4_{3}2_{1}2$	*	*	2	
95	P4 ₃ 22	*	*	2	
92	$P4_{1}2_{1}2$	*	*	2	
91	P4 ₁ 22	*	*	2	
80	$I4_1$	*	*	2	
77	$P4_2$	*	*	2	
73	Ibca	*	*	$2, \bar{1}$	
62	Pnma	*	*	m, Ī	
61	Pbca	2	*	Ī., 1	Brookite
60	Pben	*	*	2, 1	Brookite
57	Pbcm	*	*	$\frac{2}{1}$, $\frac{1}{1}$	
56	Pccn	*	*	$\frac{2}{2}, \frac{1}{1}$	
54		*	*	$\frac{2}{2}, \frac{1}{1}$	
	Pcca				
52	Pnna	*	*	$2, \bar{1}$	
46	Ima2	*	*	m, 2	
45	Iba2	*	*	2	
43	Fdd2	*	*	2	
41	Aba2	*	*	2	
40	Ama2	*	*	m, 2	
39	Abm2	*	*	m, 2	
37	Ccc2	*	*	2	
36	$Cmc2_1$	*	*	m	
34	Pnn2	*	*	2	
32	Pba2	*	*	2	
31	$Pmn2_1$	*	*	m	
30	Pnc2	*	*	2	
28	Pma2	*	*	m, 2	
27	Pcc2	*	*	2	
26	$Pmc2_1$	*	*	m	
24	$12_{1}2_{1}2_{1}$	*	*	2	
20	C222	*	*	2	
18	$P2_{1}2_{1}2$	*	*	2	
17	P222 ₁	*	*	2	
15	C2/c	*	*	$\overline{2}$, $\overline{1}$	
14	$P2_1/c$	4	*	<u>1</u>	
13	P2/c	*	*	$\frac{1}{2}, \bar{1}$	
11	P2/C $P2_1/m$	*	*	$m, \overline{1}$	
8	Cm	*	*	m	
6	Pm	*	*	m 2	
5	C2	*	*	2	
3	P2	*	*	$\frac{2}{1}$	
2	$P\bar{1}$	8	*	1	

 Table A2.10
 Space groups of non-translational order 1

		1	Site symmetry
170	P6 ₅	*	1
169	$P6_1$	*	1
145	P3 ₂	*	1
144	$P3_1$	*	1
78	P4 ₃	*	1
76	$P4_1$	*	1
33	$Pna2_1$	*	1
29	Pca2 ₁	*	1
19	$P2_12_12_1$	*	1
9	Cc	*	1
7	Pc	*	1
4	$P2_1$	*	1
1	P1	*	1

Appendix 3

Solution of the network equations

The network equations constitute a set of N_a-1 valence sum rule equations (eqn (3.3)) and N_b-N_a+1 loop equations (eqn (3.4)) where the network contains N_a atoms and N_b bonds. Alternatively one can use the equivalent Kirchhoff equations (2.7) and (2.11). One can readily write down N_a equations of type 3.3 but one of these is redundant since the sum of all atomic valences in the crystal must be zero. There are many more than N_b-N_a+1 possible loops in most bond graphs, but only N_b-N_a+1 are independent. Equations (3.3) and (3.4) thus constitute a set of N_b equations which is exactly the number needed to solve for the N_b unknown bond valences, s.

These equations can be written using the connectivity matrix M:

$$\mathbf{M} \cdot \mathbf{s} = \mathbf{V},\tag{A3.1}$$

where s is the vector containing the N_b bond valences and V is the vector containing $N_a - 1$ atomic valences and $N_b - N_a + 1$ zeros representing the sum of the bond valences around the loops. The solution to this equation is

$$s = M^{-1} \cdot V, \tag{A3.2}$$

which can be evaluated using standard matrix inversion methods, providing M is known.

The $N_{\rm a}-1$ equations of the type 3.3 can be easily written down, but selecting the correct set of loop equations is more difficult since the inclusion of even one loop that can be derived from other loops in the matrix makes the matrix singular. The best procedure for selecting the correct loops is to construct a spanning tree, i.e. a graph which contains no loops but in which all the atoms are connected to the tree (Figs. 2.4, 2.5). This leaves $N_{\rm b}-N_{\rm a}+1$ bonds from the bond graph unselected. Each time one of these unselected bonds is added to the tree, a loop is closed. An independent set of $N_{\rm b}-N_{\rm a}+1$ loops can be chosen by ensuring that each loop contains a different loop-closing bond.

A program to solve these equations has been described by Orlov et al. (1998). O'Keeffe (1989) has described an alternative method that is suitable for performing the calculation by hand. Rutherford (1990) has presented a way of inverting the matrix that retains the symmetry of the equations by including all N_a of the equations of type 3.3. Brown (1977) has described a robust iterative technique for solving the equations based on recognizing that eqn (3.4) is an expression of the principle of maximum symmetry (Rule 3.1). In this procedure

an initial set of bond valences is chosen by taking the average of V/ν for the two terminal atoms, where V is the atomic valence and ν the coordination number. These initial values do not obey the valence sum rule, so the valences of the bonds around each atom are, in turn, either increased or decreased by equal amounts until the valence sum rule around that atom is satisfied. After carrying out this procedure around each atom in the bond graph, each bond has been adjusted twice, once to give the correct valence sum around the cation and once to give the correct valence sum around the anion. The procedure is iterated to convergence which usually requires a number of cycles equal to the number of bond valences to be determined.

Alternatively the network equations can be solved by the method of simultaneous equations which is illustrated here for the case of CaCrF₅ whose bond graph is shown in Fig. A3.1.

The symmetry of the bond graph shown in Fig. A3.1 can be used to simplify the calculation by recognizing that two bonds joining the same pair of atoms, and symmetry equivalent bonds, must have the same valences. This reduces the number of independent bonds to six, whose valences are given symbolic values a, b, c, d, e, and f. The valence sum equations (eqn (3.3)) around Ca, Cr, F1, and F2 are then respectively:

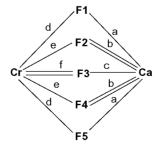
$$2a + 4b + c = 2, (A3.3)$$

$$2d + 2e + 2f = 3, (A3.4)$$

$$a+d=1, (A3.5)$$

$$2b + e = 1.$$
 (A3.6)

The sum equation around F3 is redundant since it is determined by the condition of charge neutrality.



A3.1. The bond graph of CaCrF₅ showing the assignment of symbolic valences (see Fig. 2.5).

Two loop equations (eqn (3.4)) are needed to solve for six unknowns. One possible choice is

$$a - b + e - d = 0,$$
 (A3.7)

$$a - c + f - d = 0.$$
 (A3.8)

One then proceeds to eliminate the variables one at a time. From (A3.5) and (A3.6) one gets

$$d = 1 - a,$$

$$e = 1 - 2h$$

Substituting these into the remaining four equations gives

$$2a + 4b + c = 2 \quad \text{(unchanged)}, \tag{A3.3'}$$

$$2a + 4b - 2f = 1, (A3.4')$$

$$2a - 3b = 0, (A3.7')$$

$$2a - c + f = 1.$$
 (A3.8')

From (A3.7') one gets

$$2a = 3b$$
.

Substituting this into the remaining three equations gives

$$7b + c = 2,$$
 (A3.3")

$$7b - 2f = 1,$$
 (A3.4")

$$3b - c + f = 1.$$
 (A3.8")

From (A3.3'') and (A3.4'') one gets

$$c = 2 - 7b,$$

 $f = (7b - 1)/2.$

Substituting this into (A3.8") gives

$$b = 7/27 = 0.26 \,\mathrm{vu},$$

hence substituting back one finds

$$c = 5/27 = 0.18 \text{ vu},$$

 $f = 11/27 = 0.41 \text{ vu},$
 $a = 21/54 = 0.39 \text{ vu},$
 $a = 13/27 = 0.48 \text{ vu},$
 $a = 33/54 = 0.61 \text{ vu}.$

These values can be compared with the observed bond fluxes and valences given in Table 3.1.

One problem with the network equations is that they can, on occasion, give rise to negative bond valences which have no physical significance (expect to indicate that, from a chemical point of view, the bond should not exist). Rutherford (1998) has explored the resonance bond model as an alternative to the use of the loop equation (Section 14.4) while Rao and Brown (1998) have suggested using the method of maximum entropy (Section 11.2.2.1).

Appendix 4

Cation and anion bonding strengths

Table A4.1 Bonding strengths for cations

Element	Atomic valence	Bonding strength (vu)	Ideal coordination number
H	1+	0.82, 0.18	
Li	1+	0.205	4.9
Na	1+	0.156	6.4
K	1+	0.126	7.9
Rb	1+	0.124	8.0
Cs	1 +	0.109	9.2
Be	2+	0.501	3.99
Mg	2+	0.334	5.98
Ca	2+	0.274	7.31
Sr	2+	0.233	8.57
Ba	2+	0.195	10.24
Sc	3+	0.49	6.2
Y	3+	0.43	7.0
La	3+	0.35	8.5
Ti	4+	0.67	6.0
Zr	4+	0.60	6.7
V	5+	1.08 (average)	4.6
V	4+	0.71	5.6
V	3+	0.50	6.0
Nb	5+	0.82	6.1
Ta	5+	0.82	6.1
Cr	6+	1.50	4.0
Cr	3+	0.50	6.0
Mo	6+	1.23	4.9
W	6+	1.07	5.6
Mn	4+	0.67	6.0
Mn	3+	0.52	5.8
Mn	2+	0.34	5.9
Re	7+	1.51	4.6
Re	5+	0.83	6.0
Fe	3+	0.53	5.7
Fe	2+	0.34	5.9
Ru	5+	0.83	6.0
Co	3+	0.51	5.9
Co	2+	0.35	5.7
Rh	3+	0.50	6.0
Ni	2+	0.34	5.9
Pd	2+	0.46	4.4

Table A4.1 (Continued)

Table A4.1	(Continuea)		
Element	Atomic valence	Bonding strength (vu)	Ideal coordination number
Pt	4+	0.67	6.0
Cu	2+	0.45, 0.20	5.1
Cu	1 +	0.45	2.2
Ag	1 +	0.12 - 0.50	5.1
Zn	2+	0.33 - 0.50	5.0
Cd	2+	0.25 - 0.40	6.1
Hg	2+	0.25 - 0.50	5.5
В	3+	0.87	3.46
Al	3+	0.57	5.27
Ga	3+	0.65	4.62
In	3+	0.50	5.98
T1	3+	0.49	6.1
T1	1+	0.11 - 0.33	6.9
C	4+	1.35	2.96
Si	4+	1.00	4.02
Ge	4+	0.89	4.51
Sn	4+	0.68	5.86
Sn	2+	0.4 - 0.7	4.4
Pb	4+	0.70	5.73
Pb	2+	0.2 - 0.5	6.9
N	5+	1.67	3.00
P	5+	1.25	4.01
As	5+	1.13	4.41
As	3+	0.98	3.07
Sb	5+	0.83	6.05
Sb	3+	0.43 - 0.75	4.8
Bi	3+	0.37 - 0.75	6.2
S	6+	1.5	4.0
S	4+	1.0 - 1.3	3.4
Se	6+	1.5	4.0
Se	4+	1.2	3.3
Te	6+	1.0	6.0
Te	4+	0.8 - 1.3	4.1
Cl	7+	1.75	4.0
I	7+	1.2	5.6
I	5+	1.3	3.8
NH_4	1 +	0.12 - 0.25	
$N(CH_3)_4$	1 +	0.083	

The bonding strengths and ideal coordination numbers (average coordination numbers observed for O ligands) are mostly taken from Brown (1988a). For soft cations a range of bonding strengths is given. The cations are ordered by group, then by period, and then by oxidation state. Complex cations are given at the end. A range of bonding strengths is given for soft cations.

(CH₃)₂SO (dmso)

Table 11.12 Bonding strengths for innited unions and carrons			
Complex	Cation bonding strength (vu)	Anion bonding strength (vu)	
H ₂ O (liquid)	0.17	0.17	
H ₂ O (solid)	0.20	0.20	
HF	0.17	0.06	
NH_3	0.17	0.50	

0.25

Table A4.2 Bonding strengths for mixed anions and cations

Table A4.3 Bonding strengths for anions

0.07

Anion	Formal charge	Bonding strength
I	1 –	0.083*
ClO ₄	1 —	0.083
Br	1 —	0.100*
NO_3	1 —	0.111
Cl	1 —	0.142*
H_2PO_4	1-	0.167
HCO_3	1 —	0.167
SO_4	2-	0.167
HPO_4	2-	0.22
CO_3	2-	0.22
F	1 —	0.25
PO_4	3-	0.25
BO_3	3-	0.33
SiO ₄	4-	0.33
OH	1 —	0.39
O	2 –	0.50

The anions are arranged in order of increasing bonding strength. These values are calculated by assuming that O is four coordinate. The method of calculating bonding strengths of protonated anions is described in Section 5.4. Anions marked with an asterisk (*) are soft and can adopt a range of bonding strengths. Only the lower limit is shown.

Appendix 5

References to the ICSD and the CSD

Table A5.1 References to the Inorganic Crystal Structure Database (ICSD, Bergerhoff *et al.* (1983).

Collection code	Formula	Reference
1312	B_2H_6	Mullen, D. J. E. and Hellner, E. (1977). Acta Cryst. B33 , 3816–22.
1914	Li(H ₂ O) ₃ ClO ₄	Sequiera, A., Bernal, I., Brown, I. D., and Faggiani, R. (1975). <i>Acta Cryst.</i> B31 , 1735–9.
2156	$[Na_2F(H_2O)_{15}]$ $Na(PO_4)_2 \cdot H_2O$	Baur, W. H. and Tillmans, E. (1974). <i>Acta Cryst</i> . B30 , 2216–24.
2625	Ba ₂ TiO ₄	Wu, K. K. and Brown, I. D. (1973). <i>Acta Cryst.</i> B29 , 2009–12.
6029	$Hg_{2.86}AsF_6$	Brown, I. D., Cutforth, B. D., Davies, D. G., Gillespie, R. J., and Ireland, P. R. (1974). <i>Can. J. Chem.</i> 52 , 791–3.
6148	LaMnO ₃	Tofield, B. C. and Scott, W. R. (1974). J. Solid State Chem. 10, 183–94.
9852	TiO ₂ (anatase)	Horn, M., Schwerdtfeger, C. F., and Meager, E. P. (1972). <i>Zeit. Kristallogr</i> . 136 , 273–81.
9863	MgO	Sasaki, S., Fujino, K., and Takeuchi, Y. (1979). <i>Proc. Japan. Acad.</i> 55, 43–8.
9872	NH ₄ F	Adrian, H. W. W. and Feil, D. (1969). <i>Acta Cryst.</i> 25 , 438–44.
10196	Tl_3BO_3	Marchand, R., Piffard, Y., and Tournoux, M. (1973). C. R. Acad. Sci. c276 , 177–9.
10253	$BaRuO_3$	Donahue, P. C., Katz, L., and Ward, R. (1965). <i>Inorg. Chem.</i> 4 , 306–10.
10286	CaCrF ₅	Wu, K. K. and Brown, I. D. (1973). Mater. Res. Bull. 8, 593–8.
15198	CaCO ₃ (aragonite)	dal Negro, A. and Ungaretti, L. (1971). <i>Amer. Miner.</i> 56 , 768–72.
15962	NH ₄ HgCl ₃	Harmsen, E. J. (1938). Zeit. Kristallogr. 100 , 208–11.
16031	CrO_3	Stephens, J. S. and Cruickshank, D. W. J. (1970). <i>Acta Cryst</i> . B26 , 222–6.
16382	CaSO ₄	Kirfel, A. and Will, G. (1980). Acta Cryst. B36 , 2881–90.
16488	$Bi_4Ti_3O_{12}$	Dorran, J. F., Newnham, R. E., and Smith, D. K. (1971) Ferroelectrics 3, 17–27.

Table A5.1 (Continued)

Collection code	Formula	Reference
16759	MgSO ₄	Rentzerperis, P. J. and Soldatas, D. T. (1958). Acta Cryst. 11, 686–8.
18183	NaHCO ₃	Sharma, B. D. (1965). Acta Cryst. 18, 818-9.
18189	NaCl	Abrahams, S. C. and Bernstein, J. L. (1965). <i>Acta Cryst.</i> 18 , 926–32.
20201	Sc(NO ₃) ₃ urea ₄	Kuskov, V. I., Treushnikov, E. N., Sobolov, L. E., Ilyukhin, V. V., and Belov, N. V. (1978). <i>Dokl. Akad. Nauk</i> SSSR 239, 1097–1100.
22030	$Cs_2Cr_3O_{10}$	Mattes, R. and Meschade, W. (1973). Zeit. Anorg. Allgem. Chem. 395, 216–22.
22173	CsCl	Ahtee, M. (1969). <i>Ann. Acad. Sci. Fenn. Ser.</i> <i>A6 Physica</i> 313 , 1–11.
23598	$Ca_3(PO_4)_2$	Gopal, R. and Calvo, C. (1972). <i>Nature</i> 237 , 30–2.
23759	BaTiO ₃	Harada, J., Petersen, T., and Barnea, Z. (1970). <i>Acta Cryst.</i> 26 , 336–44.
24392	$Cs_2Sn_2O_3$	Braun, R. M. and Hoppe, R. (1981). Zeit. Anorg. Allgem. Chem. 480, 81–9.
24418	$Mo(Mo,V)_{1.4}O_6$	Koslowski, R. and Stadnicka, K. (1981). J. Solid State Chem. 39, 271–6.
24916	NH ₄ Br (CsCl)	Seymour, R. S. and Pryor, A. W. (1970). <i>Acta Cryst.</i> B26 , 1487–91.
24944	$Ca_3Al_2Si_3O_{12}$	Meagher, E. P. (1975). Amer. Miner. 60 , 218–28.
26127	K₂TeCl ₆	Engel, G. (1935). Zeit. Kristallogr. 90, 341–73.
26332	$Sn_4Sb_6S_{13}$	Jumas, J. C., Olivier-Fourcade, J., Philippot, E., and Maurin, M. (1980). Acta Cryst. B36 , 2940–5.
26368	$(Mg(H_2O)_6)_2CdCl_6$	Ledesert, M. and Monier, J. C. (1981). Acta Cryst. B37 , 652–4.
26374	Mg ₂ SiO ₄	Fujino, K., Sasaki, S., Takeuchi, Y., and Sadanaga, R. (1981). <i>Acta Cryst</i> . B37 , 513–8.
26579	NH ₄ Br (III)	Levy, H. A. and Peterson, S. W. (1953). <i>J. Amer. Chem. Soc.</i> 75 , 1536–42.
27139	CoSi ₂	Bertaut, F. and Blum, P. (1950). C. R. Acad. Sci. 231, 626–8.
28247	FeOOH	Szytula, A., Busewicz, A., Dimitrijewic, Z., Krasnicki, S., Rzany, H., Dodorovic, T., et al. (1968). Physica Statu Solidi 226, 429–34.

 Table A5.1 (Continued)

Collection code	Formula	Reference
29008	CaF ₂	Willis, B. T. M. (1965). <i>Acta Cryst</i> . 18 , 75–6.
29107	TICI	Möller, K. (1933). Naturwissenschaften 21 , 223.
29384	$MgSO_4(H_2O)_7$	Calleri, M., Gavetti, A., Ivaldi, G., and Rubbo, M. (1984). <i>Acta Cryst.</i> B40 , 218–22.
30409	$ZnSb_2O_6$	Byström, A., Hök, B., and Mason, B. (1942). <i>Ark. Kemi.</i> 15 , 1–8.
30880	ZnV_2O_6	Andreetti, G. D., Calestani, G., Montenero, A., and Bettinelli, M. (1984). <i>Zeit. Kristallogr.</i> 168 , 53–8.
31840	ZnTe	Zachariesen, W. H. (1926). Norsk Geol. Tijdskr. 8 , 302–6.
34243	β -Ga ₂ O ₃	Geller, S. (1960). J. Chem. Phys. 33 , 676–84.
35076	MoO_3	Kihlborg, L. (1963). Ark. Kemi. 21, 357-64.
36406	$NH_4Co(NH_3)_4$ $(SO_3)_2 \cdot 3H_2O$	Raston, C. L., White, A. H., and Yandell, J. K. (1978). <i>Australian J. Chem.</i> 31 , 999–1004.
38293	PbS	Noda, Y., Ohba, S., Sato, S., and Saito, Y. (1983). <i>Acta Cryst.</i> B39 , 312–7.
39159	Sr ₂ ZnGe ₂ O ₇	Ochi, Y., Tanaka, K., Morikawa, H., and Marumo, F. (1982). <i>Kobutsugaku Zasshi</i> 15, 331–41.
49915	$(Mg(H_2O)_6)_2CdBr_6$	Duhlev, R., Faggiani, R., and Brown, I. D. (1987). <i>Acta Cryst</i> . C43 , 2044–6.
60311	Na ₂ CO ₃	van Aalst, W., den Hollander, J., Peterse, W. J. A. M., and de Wolff, P. M. (1976). Acta Cryst. B32 , 47–58.
60378	ZnS (sphalerite)	Jumpertz, E. A. (1955). <i>Zeit.</i> <i>Electrochem.</i> 59 , 419–25.
60435	Na ₂ O	Zintl, E., Harder, A., and Douth, B. (1934). <i>Zeit. Electrochem.</i> 40 , 588–93.
60679	NH ₄ Br (NaCl)	Callanan, J. E. and Smith, N. O. (1966). <i>Adv. X-ray Anal.</i> 9 , 159–69.
62089	Li ₂ SO ₄ · H ₂ O	Karppinen, M., Liminga, R. M., and Lundgren, JO. (1986). <i>J. Chem. Phys.</i> 85 , 5221–7.
62149	CaTiO ₃	Sasaki, S., Prewitt, C. T., and Bass, J. D. (1987). <i>Acta Cryst</i> . C43 , 1668–74.
63363	RbClO ₄	Granzin, J. (1988). Zeit. Kristallogr. 184, 157–9.

Table A5.1 (Continued)

Collection code	Formula	Reference
63324	Ba ₂ YCu ₃ O _{6+x}	Greedan, J. E., O'Reilly, A. H., and Stager, C. V. (1987). <i>Phys Rev. B</i> 35 , 8770–3.
65340	Fe ₃ O ₄	Fleet, M. E. (1986). <i>J. Solid State Chem.</i> 62 , 75–82.
65441	Hg ₂ Cl ₂	Calos, N. J., Kennard, C. H. L., and Davis, R. L. (1989). <i>Zeit. Kristallogr</i> . 187 , 305–7.
65917	La ₂ NiO ₄	Jorgensen, J. D., Dabrowski, B., Pei, S., Richards, D. K., and Hinks, D. G. (1989). <i>Phys. Rev. B</i> 40 , 2187–99.
67046	FeTiO ₃	Ohgaki, K., Ohgaki, M., Tanaka, K., Marumo, F., and Takei, H. (1989). <i>Miner. J. (Japan)</i> 14 , 179–90.
67453	ZnS (wurtzite)	• • •
67454	ZnO	Kisi, E. H. and Elcombe, M. M. (1989). <i>Acta Cryst.</i> C45 , 1867–70.
68696	KH_2PO_4	Fukiami, T. (1990). <i>Phys. Stat. Solidi</i> A117 , K93–6. (see also 201373).
69127	Ni(H ₂ O) ₆ SO ₄	McIntyre, G. J., Płasiewicz-Bak, H., and Olovsson, I. (1990). <i>Acta</i> <i>Cryst.</i> B46 , 26–39.
69328	Yb ₂ Cu ₂ O ₅	Murasik, A., Fischer, P., Troc, R., and Bukowski, Z. (1990). <i>Solid State Comm.</i> 75 , 785–8.
69387	Ca ₂ ZnGe ₂ O ₇	Armbruster, T., Röthlisberger, F., and Seifert, F. (1990). <i>Amer. Miner.</i> 75 , 847–58.
71892	$MgAl_2Si_3O_{12}$	Armbruster, T., Geiger, C. A., and Leger, G. A. (1992). <i>Amer.Miner</i> . 77, 512–21.
72165	Er ₂ BaCuO ₅	Salines-Sanchez, A., Garcia-Muñoz, J. L., Rodriguez-Carvajal, J., Saez-Puche, R. and Martinez, J. L. (1992). <i>J. Solid State Chem.</i> 100 , 201–11.
72810	$Tl_4V_2O_7$	Jouauneaux, A., Joubert, O., Evain, M., and Ganne, M. (1992). <i>Powder Diffraction</i> 7, 206–11.
75253	TlNO ₃	Sastry, P. U. M., Rajagopal, H., and Sesquiera, A. (1994). <i>Acta Cryst</i> . C50 , 1854–7.
75559	Al_2O_3	Sawada, H. (1994). <i>Mat. Res. Bull.</i> 29 , 127–33.

 Table A5.1 (Continued)

Collection code	Formula	Reference
75892	La ₂ CuO ₄	Izumi, F., Kim, Y-I., Takayama-Muramichi, E., and Kamiyama, T. (1994). <i>Physica C</i> 234 , 841–2.
75896	HgBa ₂ Ca ₂ Cu ₃ O ₈	Bertinotti, A., Colson, D., Hamman, J., Marucco, JF., and Pinatel, A. (1994). <i>Physica C</i> 235 , 891–2.
78387	I_2O_5	Fjellvag, H. and Kjekshus, A. (1994). <i>Acta Chem. Scand.</i> 148 , 815–22.
100218	$Zn(ClO_4)_2(H_2O)_6$	Gosh, M. and Ray, S. (1977). Zeit. Kristallogr. 145 , 146–54.
100676	CaCO ₃ (calcite)	Effenberger, H., Mereiter, K., and Zemann, J. (1981). Zeit. Kristallogr. 156 , 233–43.
200108	lpha-AgI	Cava, R. J., Reidinger, F., and Wuensch, B. J. (1977). <i>Solid State Comm.</i> 24 , 411–6.
200139	MgSiO ₃	Yagi, T., Mao, H. K., and Bell, P. M. (1977). Carnegie Inst. (Washington) Yearbook 76, 516–9.
200405	NaClO ₄	Wartchow, R. and Berthold, H. J. (1978). Zeit. Kristallogr. 147, 307–17.
201256	SrTiO ₃	Hutton, J. and Nelmes, R. J. (1981). J. Phys. C 14, 1713–36.
201373	KH ₂ PO ₄	Nelmes, R. J., Meyer, G. M., and Tibballs, J. E. (1982). <i>J. Phys</i> . <i>C</i> 15 , 59–75 (see also 68696).
201773	AlPO ₄	Goiffron, A., Jumas, JC., Maurin, M., and Philippot, E. (1986). <i>J. Solid</i> State Chem. 61 , 384–96.
202240	TiO ₂ (rutile)	
202242	TiO ₂ (anatase)	Burdett, J. K., Hughbanks, J., Miller, G. J., Richardson, J. W., and Smith, J. V. (1987). <i>J. Amer. Chem. Soc.</i> 109 , 3639–46.

252 APPENDIX 5

 Table A5.2
 References to the Cambridge Structural Database (CSD, Allen et al. 1979)

Ref code	Formula	Reference
ADENDP	Adenosine P ₂ O ₇	Hosur, M. V. and Viswamitra, M. A. (1979). <i>Curr. Sci.</i> 48 , 627–8.
ADENTP	Na Adenosine P ₃ O ₁₀	Kennard, O., Isaacs, N. W., Motherwell, W. D. S., Coppola, J. C., Wampler, D. L., Larson, A. C., and Watson, D. G. (1971). <i>Proc. Roy. Soc.</i> <i>Lond.</i> A325 , 401–36.
DMSARU	$Ru(NH_3)_5DMSO(PF_6)_2$	March, F. C. and Ferguson, G. (1977). <i>Can. J. Chem.</i> 49 , 3590–5.
OXACDH04	$(COOH)_2(H_2O)_2$	Sabine, T. M., Cox, G. W., and Craven, B. M. (1969). <i>Acta Cryst.</i> B25 , 2437–41.
PDDMSX	PdCl ₂ (DMSO) ₂	Bennett, M. J., Cotton, F. A., Weaver, D. L., Williams, R. S., and Watson, W. H. (1967). <i>Acta</i> <i>Cryst.</i> 23, 788–96.
SIACET	(CH ₃ CO ₂) ₄ Si	Kamenar, B. and Bruvo, M. (1975). <i>Zeit. Kristallogr.</i> 141 , 97–103.

References

- Abramov, Yu., Zavodnik, V. E., Ivanov, S. A., Brown, I. D., and Tsirelson, V. G. (1995). The chemical bond and atomic displacements in SrTiO₃ from X-ray diffraction analysis. *Acta Cryst.* **B51**, 942–51.
- Adams, St. (1996). Crystal structure and Ag⁺ conductivity in the solid electrolyte Ag₈I₄V₂O₇. Zeit. Kristallogr. **211**, 770–6.
- Adams, St. (2001). Relationship between bond valence and bond softness of alkali halides and chalcogenides. *Acta Cryst.* **B57**, 278–87.
- Adams, St. and Maier, J. (1998). Ag migration pathways in crystalline and glassey solid electrolytes AgI, AgM_xO_y. Solid State Ionics **105**, 67–74.
- Adams, St. and Swenson, J. (2000a). Determining ion conductivity from structural models. *Phys. Rev. Lett.* **84**, 4144–7.
- Adams, St. and Swenson, J. (2000b). Migration pathways in Ag-based superionic glasses and crystals investigated by the bond valence method. *Phys. Rev. B* **63**, 054201.
- Adams, St., Ehses, K.-H., and Spilker, J. (1993). Proton ordering in Peierls-distorted hydrogen molybdenum bronze H_{0.33}MoO₃: Structure and physical properties. *Acta Cryst.* **B49**, 958–67.
- Alcock, N. W. (1972). Secondary bonding to nonmetallic elements. *Adv. Inorg. Rad. Chem.* **15**, 1–57.
- Alig, H., Lösel, J., and Trömel, M. (1994). Zur Kristallchemie der Wasserstoff-Sauerstoff-Bindungen. *Zeit. Kristallogr.* **209**, 18–21.
- Alkorta, I., Barrios, L., Rozes, I., and Elguero, J. (2000). Comparison of models to correlate electron density at the bond critical point and bond distance. *J. Mol. Struct. (Theochem)* **496**, 131–7.
- Allen, L. C. (1989). Electronegativity is the average one-electron energy of the valence-shell electrons in ground-state atoms. *J. Amer. Chem. Soc.* **111**, 9003–14.
- Allen, F. H., Bellwood, S., Brice, M. D., Cartwright, B. A., Doubleday, A., Hicks, H., *et al.* (1979). The Cambridge Crystallographic Data Centre: Computer-based search, retrieval, analysis and display of information. *Acta Cryst.* **B35**, 2331–9.
- Allmann, R. (1975). Beziehungen zwischen Bindungslängen und Bindungstärken in Oxidstrukturen. *Monatshefte Chem.* **106**, 779–93.
- Alonso, J. A., Martínez-Lope, M. J., Casais, M. T., García-Muñoz, J. L., and Fernandez-Díaz, M. T. (2000). Room-temperature monoclinic distortion due to charge disproportionation in *R*NiO₃ perovskites with small rare-earth

- cations (R = Ho, Y, Er, Tm, Yb and Lu): A neutron diffraction study. *Phys. Rev. B* **61**, 1756–63.
- Altermatt, D. and Brown, I. D. (1985). The automatic searching for chemical bonds in inorganic structures. *Acta Cryst.* **B41**, 240–4.
- Andersson, A. (1982). An oxidized surface state model of vanadium oxides and its application to catalysis. *J. Solid State Chem.* **42**, 263–75.
- Armbruster, T., Röthlisberger, F., and Seifert, F. (1990). Layer topology, stacking variation, and site distortion in melilite-related compounds in the system CaO-ZnO-GeO₂-SiO₂. *Amer. Miner.* **75**, 847–58.
- Åsbrink, S. (1980). The crystal structure of and valency distribution in the low-temperature modification of V₃O₅. The decisive importance of a few very weak reflections in a crystal structure determination. *Acta Cryst.* **B36**, 1332–9.
- Bader, R. W. F. (1990). Atoms in Molecules, A Quantum Theory. Oxford: Clarendon Press.
- Bagautdinov, B., Hagiya, K., Kusaka, K., Ohmasa, M., and Iishi, K. (2000). Two dimensional incommensurately modulated structure of (Sr_{0.13}Ca_{0.87})₂-CoSi₂O₇ crystals. *Acta Cryst.* **B56**, 811–21.
- Bargar, J. R., Brown, G. E. Jr, and Parks, G. A. (1997a). Surface complexation of Pb(II) at oxide water interfaces I. XAFS and bond valence determination of mononuclear and polynuclear Pb(II) sorption products on aluminum oxides. *Geochim. Cosmochim. Acta* **61**, 2617–37.
- Bargar, J. R., Brown, G. E. Jr, and Parks, G. A. (1997b). Surface complexation of Pb(II) at oxide water interfaces II. XAFS and bond valence determination of mononuclear Pb(II) sorption products and surface functional groups on iron oxides. *Geochim. Cosmochim. Acta* **61**, 2639–52.
- Bargar, J. R., Towle, S. N., Brown, G. E. Jr, and Parks, G. A. (1997c). XAFS and bond valence determination of the structures and compositions of surface functional groups and Pb(II) and Co(II) sorption products on single-crystal α -Al₂O₃. *J. Colloid. Interface. Sci.* **185**, 473–92.
- Baur, W. H. (1970). Bond length variation and distorted coordination polyhedra in inorganic crystals. *Trans. Amer. Cryst. Ass.* **6**, 129–55.
- Baur, W. H. (1972). Prediction of hydrogen bonds and hydrogen atom positions in crystalline solids. *Acta Cryst.* **B28**, 1457–65.
- Beevers, C. A. and Schwarz, C. M. (1935). The crystal structure of nickel sulphate heptahydrate NiSO₄· 7H₂O. *Zeit. Kristallogr.* **91**, 157–69.
- Bell, J., Ash, D. E., Snyder, W. M., Kulathila, R., Blackburn, N. J., and Merkler, D. J. (1997). Structural and functional investigations on the role of zinc in bifunctional rat peptidylglycine α -amidating enzyme. *Biochem.* **36**, 16239–44.
- Bergerhoff, G., Hundt, R., Sievers, R., and Brown, I. D. (1983). The Inorganic Crystal Structure Database. *J. Chem. Inf. Comp. Sci.* **23**, 66–9.
- Bergerhoff, G., Berndt, M., Brandenburg, K., and Degen, T. (1999). Concerning inorganic structure types. *Acta Cryst.* **B55**, 147–56.

- Bertaut, F. (1952). L'energie electrostatique des resaux ioniques. *J. Phys. Rad.* 13, 459–505.
- Bleam, W. F. (1993). Atomic theories of phyllosilicates: Quantum chemistry, statistical mechanics, electrostatic theory and crystal chemistry. *Rev. Geo-phys.* **31**, 51–73.
- Blenzen, A., Foglia, F., Furet, E., Helm, L., Merbach, A. E., and Weber, J. (1997). Second coordination shell water exchange rate mechanism: Experiments and modelling on hexaaquochromium(III). *J. Amer. Chem. Soc.* **118**, 12777–87.
- Boison, M. B., Gibbs, G. V., and Zhang, Z. G. (1988). Resonant bond numbers: A graph theoretic study of bond length variations in silicate crystals. *Phys. Chem. Miner.* **15**, 409–15.
- Born, M. and Landé, A. (1918). [The absolute calculation of crystal properties with the aid of the Bohr atom model]. *Sitsungsber. Preuss. Akad. Wissen. Berlin* **45**, 1048–68 (in German).
- Born, M. and Mayer, J. E. (1932). Zur Gittertheorie der Ionenkristalle. Zeit. *Phys.* **75**, 1–18.
- Bouhmaida, N., Ghermani, N. E., Lecompte, C., and Thalai, A. (1997). Modelling electrostatic potential from experimentally determined charge density. II. Total potential. *Acta Cryst.* **A53**, 556–63.
- Bragg, W. L. (1930). The structure of silicates. Zeit. Kristallogr. 74, 237–305.
- Brammer, L., Zhao, D., Lapido, F. T., and Bradock-Wilking, J. (1995). Hydrogen bonds involving transition metal centres—a brief review. *Acta Cryst.* **B51**, 632–40.
- Brese, N. E. and O'Keeffe, M. (1991). Bond valence parameters for solids. *Acta Cryst.* **B47**, 192–7.
- Brese, N. E., Rohrer, C. L., and Rohrer, G. S. (1999). Brightness degradation in electroluminescent ZnS:Cu. *Solid State Ionics* **123**, 19–24.
- Brink, G. and Falk, M. (1970). Infrared spectrum of HDO in aqueous solutions of perchlorates and tetrafluoroborates. *Can. J. Chem.* **48**, 3019–25.
- Brock, C. P. and Dunitz, J. D. (1994). Towards a grammar of crystal packing. *Chem. Mater.* **6**, 1118–27.
- Brown, I. D. (1974). Bond valence as an aid to understanding the stereochemistry of O and F complexes of Sn(II), Sb(III), Te(IV), I(V) and Xe(IV). *J. Solid State Chem.* **11**, 214–33.
- Brown, I. D. (1976a). On the geometry of O-H...O bonds. *Acta Cryst.* A32, 24-31.
- Brown, I. D. (1976b). Hydrogen bonding in perchloric acid hydrates. *Acta Cryst.* **A32**, 786–92.
- Brown, I. D. (1977). Predicting bond lengths in inorganic crystals. *Acta Cryst.* **B33**, 1304–10.
- Brown, I. D. (1978). Bond valences, a simple structural model for inorganic chemistry. *Chem. Soc. Rev.* 359–76.

- Brown, I. D. (1980*a*). On the prediction of angles in tetrahedral complexes and pseudo-tetrahedral complexes with stereoactive lone pairs. *J. Amer. Chem. Soc.* **102**, 2112–3.
- Brown, I. D. (1980b). A structural model for Lewis acids and bases. An analysis of the structural chemistry of the acetate and trifluoracetate ions. *J. Chem. Soc. Dalton Trans.* 1118–23.
- Brown, I. D. (1981). The bond valence method. An empirical approach to chemical structure and bonding. In M. O'Keeffe and A. Navrotsky (eds), *Structure and Bonding in Crystals*, Vol. 2. New York: Academic Press, pp. 1–52.
- Brown, I. D. (1987*a*). Structural chemistry and solvent properties of dimethylsulfoxide. *J. Solution Chem.* **16**, 205–24.
- Brown, I. D. (1987b). Recent developments in the bond valence model of inorganic bonding. *Phys. Chem. Miner.* **15**, 30–4.
- Brown, I. D. (1988*a*). What factors determine coordination numbers? *Acta Cryst.* **B44**, 545–53.
- Brown, I. D. (1988b). A chemical model of Frankel defects in fluorite. *Solid State Ionics* **31**, 203–8.
- Brown, I. D. (1991a). Internal strain in perovskite related materials. In P. K. Davies and R. S. Roth (eds), *Chemistry of Electronic Materials*. Washington: US Department of Commerce, pp. 471–83.
- Brown, I. D. (1991b). The influence of internal strain on the charge distribution and superconducting transition temperature in Ba₂YCu₃O_x. J. Solid State Chem. **90**, 155–67.
- Brown, I. D. (1992a). Modelling the structures of La₂NiO₄. *Zeit. Kristallogr*. **199**, 255–72.
- Brown, I. D. (1992b). Chemical and steric constraints in inorganic solids. *Acta Cryst.* **B48**, 553–72.
- Brown, I. D. (1995). Anion–anion repulsion, coordination numbers and the asymmetry of the hydrogen bond. *Can. J. Phys.* **73**, 676–82.
- Brown, I. D. (1996). A program for calculating bond valences. *J. Appl. Cryst.* **29**, 479–80 (available at http://www.ccp14.ac.uk/ccp/web-mirrors/valence).
- Brown, I. D. (1997). The influence of chemical and steric constraints on the structures of inorganic compounds. *Acta Cryst.* **B53**, 381–93.
- Brown, I. D. (2000). The bond valence model as a tool in teaching inorganic chemistry: The ionic model revisited. *J. Chem. Edu.* 77, 1070–5.
- Brown, I. D. and Altermatt, D. (1985). Bond-valence parameters obtained from a systematic analysis of the Inorganic Crystal Structure Database. *Acta Cryst.* **B41**, 244–7.
- Brown, I. D. and Duhlev, R. (1991). Divalent metal halide double salts in equilibrium with their aqueous solutions II. Factors determining their crystal structures. *J. Solid State Chem.* **95**, 51–63.
- Brown, I. D. and Faggiani, R. (1980). The structure of thallium(I) tetra-acetatothallate(III): When is the lone pair of electrons on Tl^I stereoactive? *Acta Cryst.* **B36**, 1802–6.

- Brown, I. D. and Shannon, R. D. (1973). Empirical bond-strength—bond-length curves for oxides. *Acta Cryst.* **A29**, 266–82.
- Brown, I. D. and Skowron, A. (1990). Electronegativity and Lewis acid strength. *J. Amer. Chem. Soc.* **112**, 3401–3.
- Brown, I. D., Gillespie, R. J., Morgan, K. R., Tun, Z., and Ummat, P. K. (1984). Preparation and crystal structure of Hg₃NbF₆ and Hg₃TaF₆: Mercury layer compounds. *Inorg. Chem.* **23**, 4506–8.
- Brown, G. E. Jr, Farges, F., and Calas, G. (1995). X-ray scattering and X-ray spectroscopy studies of mineral melts. *Rev. Miner.* **32**, 317–409.
- Brown, I. D., Dabkowski, A., and McCleary, A. (1997). Thermal expansion of chemical bonds. *Acta Cryst.* **B53**, 750–61.
- Browning, N. D. and Pennycook, S. J. (1996). Direct experimental determination of the atomic structure at internal interfaces. *J. Phys. D* **29**, 1779–88.
- Browning, N. D., Buban, J. P., Nellist, P. D., Norton, D. P., Chisholm, M. F., and Pennycook, S. J. (1998*a*). The atomic origins of reduced critical currents at [001] tilt grain boundaries in YBa₂Cu₃O_{7- δ} thin films. *Physica C* **294**, 183–93.
- Browning, N. D., Moltaji, H. O., and Buban, J. P. (1998b). Investigation of three-dimensional grain-boundary structure in oxides through multiple-scattering analysis of spatially resolved electron-energy-loss spectra. *Phys. Rev. B* **58**, 8289–300.
- Browning, N. D., Buban, J. P., Moltaji, H. O., and Duscher, G. (1999). Investigating the structure-property relations at grain boundaries in MgO using bond valence pair potentials and multiple scattering analysis. *J. Amer. Ceram. Soc.* **82**, 366–72.
- Brunner, G. O. and Laves, F. (1970). Zur Problem der Koordinationzahl. *Wiss. Zeit. Tech. Univ. Dresden* **20**, 387–90.
- Burdett, J. K. (1980). Molecular Shapes. New York: Wiley-Interscience.
- Burdett, J. K. and Hawthorne, F. C. (1993). An orbital approach to the theory of bond valence. *Amer. Miner.* **78**, 884–92.
- Burnahm, C. W. (1990). The ionic model. Perceptions and realities in mineralogy. *Amer. Miner.* **75**, 443–63.
- Burzlaff, H. and Malinovsky, Y. (1997). A procedure for the classification of non-organic crystal structures I. Theoretical background. *Acta Cryst.* **A53**, 217–24.
- Busing, W. and Levy, H. A. (1964). The effect of thermal motion on the estimation of bond lengths from diffraction measurements. *Acta Cryst.* **17**, 142–6.
- Byström, A. and Wilhelmi, K.-A. (1951). The crystal structure of (NH₄)₂Cr₂O₇ with a discussion of the relation between bond number and interatomic distance. *Acta Chem. Scand.* **5**, 1003–10.
- Caminiti, R., Licheri, G., Piccaluga, G., and Pinna, G. (1978). Hydration water—external water interactions around Cr³⁺ ions. *J. Chem. Phys.* **69**, 1–4.
- Canadell, E. and Whangbo, M.-H. (1991). Conceptual aspects of structure-property correlations and electronic instabilities with application to low dimensional transition-metal oxides. *Chem. Rev.* **91**, 965–1034.

- Cario, L., Lefond, A., Palvadeau, A., Deudon, P., and Meerschault, C. (1999). Evidence of a mixed valence state for europium in the misfit layer compound [(EuS)_{1.5}]_{1.15}NbS₂ by means of a superspace structural determination, Mössbauer spectroscopy and magnetic measurements. *J. Solid State Chem.* **147**, 58–67.
- Catlow, C. R. A. (ed.) (1997). *Computer Modelling in Inorganic Crystallography*. San Diego and London: Academic Press.
- Clark, J. R., Appleman, D. E., and Papike, J. J. (1969). Crystal chemical characterisation of clinopyroxene based on eight new structure refinements. *Miner. Soc. Amer. Sp. Papers* **2**, 31–50.
- Clark-Baldwin, K., Tierney, D. L., Govindaswamy, N., Gruff, E. S., Kim, C., Berg, J., *et al.* (1998). The limitations of X-ray absorption spectroscopy for determining the structure of zinc sites in proteins. When is a tetrathiolate not a teterathiolate?. *J. Amer. Chem. Soc.* **120**, 8401–9.
- Coulson, C. A. (1961). Valence, 2nd edn, Oxford: Oxford University Press.
- Datars, W. R., Razavi, F. S., Gillespie, R. J., and Ummat, P. K. (1985). Electrical properties of chain and sheet mercury compounds. In R. J. Gillespie and P. Day (eds), *Electrical and Magnetic Properties of Low-Dimensional Solids*. The Royal Society of London, pp. 105–14.
- Deng, H., Ray, W. J. Jr, Burgner, J. W. II, and Callender, R. (1993). Comparison of vibrational frequencies of critical bonds in ground-state complexes and in a vanadate-based transition-state analog complex of muscle phosphoglucomutase. Mechanistic implications. *Biochem.* 32, 12984–92.
- Deng, H., Burgner, J. W. II, and Callender, R. H. (1998). Structure of the ribonuclease-uridine-vanadate transformation state analogue complex by Raman difference spectroscopy. Mechanistic implications. *J. Amer. Chem. Soc.* **130**, 4717–22.
- Dent-Glasser, L. (1979). Non-existent silicates. *Zeit. Kristallogr.* **149**, 291–325. Depero, L. E. (1993). Coordination geometry and catalytic activity of vanadium on TiO₂. *J. Solid State Chem.* **103**, 528–32.
- Desiraju, G. R. and Steiner, Th. (1999). *The Weak Hydrogen Bond in Structural Chemistry and Biology*. Oxford: Oxford University Press/International Union of Crystallography.
- Donnay, G. and Allmann, R. (1970). How to recognise O²⁻, OH⁻ and H₂O in crystal structures determined by X-rays. *Amer. Miner.* **55**, 1003–15.
- Dooley, D. M., Scott, R. A., Knowles, P. K., Colangelo, C. M., McGuirl, M. A., and Brown, D. E. (1998). Structures of the Cu(I) and Cu(II) forms of amine oxidases from X-ray absorption spectroscopy. *J. Amer. Chem. Soc.* **120**, 2599–605.
- Duhlev, R., Brown, I. D., and Balarew, Chr. (1991). Divalent metal halide double salts in equilibrium with their aqueous solutions I. Factors determining their compositions. *J. Solid State Chem.* **95**, 39–50.
- Dunitz, J. D. and Orgel, L. E. (1960). Stereochemistry of inorganic solids. *Adv. Inorg. Chem. Radiochem.* **2**, 1–60.

- Eby, R. K. and Hawthorne, F. C. (1993). Structural relations in copper oxysalt minerals I. Structural hierarchy. *Acta Cryst.* **B49**, 28–56.
- Efremov, V. A. (1990). Characteristic features of the crystal chemistry of lanthanide molybdates and tungstates. *Russ. Chem. Rev.* **59**, 627–42.
- Evans, J. S. O. (1999). Negative thermal expansions in materials. *J. Chem. Soc. Dalton Trans.* 3317–26.
- Ewald, P. P. (1921). Die Berechnung optischer und elektrostatische Gitterpotentiale. *Ann. Physik* **64**, 253–87.
- Ferraris, G., Khomyakov, A. P., Belluso, E., and Soboleva, S. V. (1997). Polysomatic relationships in some titanosilicates occurring in the hyperagpaitic alkaline rocks of the Kola Peninsula, Russia. *Proc. 30th Internat. Geol. Congress* **16**, 17–27.
- Galiulin, R. V. and Khurchaturov, V. R. (1994). An algorithm for determining crystal structures having a given chemical formula. In V. R. Khatchalurov (ed.) (Russian), *Mathematical Modelling of Composite Objects*. Moscow: Academy of Science Computer Centre.
- Galy, J., Meunier, G., Andersson, S., and Aström, A. (1975). Stéreochemie des elément comportant des pair non-liées: Ge(II), As(III), Se(IV), Br(V), Te(IV),I(V), Xe(VI), Tl(I), Pb(II), et Bi(III) (oxides, fluorures et oxyfluorures). *J. Solid State Chem.* **13**, 142–59.
- Gao, D. and Williams, D. E. (1999). Molecular packing groups and *ab initio* crystal structure prediction. *Acta Cryst.* **A55**, 621–7.
- Garcia-Muñoz, J. L. and Rodríguez-Carvájal, J. (1995). Structural characterisation of R₂Cu₂O₅ (R = Yb, Tm, Er, Y and Ho) oxides by neutron diffraction. *J. Solid State Chem.* **115**, 324–31.
- García-Rodríguez, L., Rute-Pérez, A., Ramón-Piñero, J., and González-Silgo, C. (2000). Bond valence parameters for ammonium—anion interactions. *Acta Cryst.* **B56**, 565–9.
- Garner, C. D., Collinson, D., and Pidcock, E. (1996). The nature of coordination sites of transition metals in proteins. *Phil. Trans. R. Soc. Lond. A* **354**, 325–57.
- Garrett, J. D., Greedan, J. E., Faggiani, R., Carbotte, S., and Brown, I. D. (1982). Single crystal growth and structure determination of Ag₁₆I₁₂P₂O₇. *J. Solid State Chem.* **42**, 183–90.
- Gibbs, G. V., Hill, F. C., Boisen, M. B., and Downs, R. T. (1998). Power law relationship between bond length, bond strength and electron density distributions. *Phys. Chem. Miner.* **25**, 585–90.
- Gillespie, R. J. and Hargittai, I. (1991). *The VSEPR Model of Molecular Geometry*. New York: Prentice-Hall.
- Gillespie, R. J. and Robinson, E. A. (1996). Electron domains and the VSEPR model of molecular geometry. *Angew. Chem. Int. Ed.* **35**, 495–514.
- Gillespie, R. J., Brown, I. D., Datars, W. R., Morgan, K. R., Tun, Z., and Ummat, P. K. (1985). The preparation and structure of chain and sheet mercury compounds. In R. J. Gillespie and P. Day (eds), *Electrical and*

- Magnetic Properties of Low-Dimensional Solids. The Royal Society of London, pp. 115–24.
- Glusker, J. P. (1991). Structural aspects of metal liganding to functional groups in proteins. *Adv. Protein Chem.* **42**, 1–76.
- Gonzáles-Platas, J., Gonzáles-Silgo, C., and Ruis-Pérez, C. (1999). VALMAP2-0: Contour maps using the bond-valence-sum method. *J. Appl. Cryst.* **32**, 341–4.
- Gründermann, S., Limbach, H.-H., Buntkowsky, G., Sabo-Etienne, S., and Chaudret, B. (1999). Distance and scalar HH-coupling correlations in transition metal dihydrides and dihydrogen complexes. *J. Phys. Chem. A* **103**, 4752–4.
- Hati, S. and Datta, D. (1995). Nature of the active sites in haemocyanin and iron-rich hydgrogenases: The bond valence sum approach. *J. Chem. Soc. Dalton Trans.* 1177–82.
- Hawthorne, F. C. (1985). Towards a structural classification of minerals: The ${}^{VI}M^{IV}T_2\Phi_n$ minerals. *Amer. Miner.* **70**, 455–73.
- Hawthorne, F. C. (1992a). The role of OH and H₂O in oxides and oxysalt minerals. *Zeit. Kristallogr.* **201**, 183–206.
- Hawthorne, F. C. (1992b). Bond topology, bond valence and structural stability. In G. D. Price and N. L. Ross (eds), *The Stability of Minerals*. London: Chapman and Hall, pp. 25–87.
- Hawthorne, F. C. (1994). Structural aspects of oxide and oxysalt crystals. *Acta Cryst.* **B50**, 481–510.
- Hawthorne, F. C. (1997). Short range order in amphiboles. A bond valence approach. *Can. Miner.* **35**, 201–16.
- Hawthorne, F. C. (1998). Structure and chemistry of phosphate minerals. *Miner. Mag.* **62**, 141–64.
- Hazen, R. M. and Finger, L. W. (1982). Comparative Crystal Chemistry. Temperature Pressure Composition and the Variation of Crystal Structure. New York: Wiley.
- Hiemstra, T., Venema, P., and Riemsdijk, W. H. (1996). Intrinsic proton affinity of reactive surface groups of metal (hydr)oxides: The bond valence principle. *J. Colloid Interface Sci.* **184**, 680–92.
- Hoppe, R. and Köhler, J. (1988). Schlegel projections and Schlegel diagrams—new ways to describe and discuss solid state compounds. *Zeit. Kristallogr.* **183**, 77–111.
- Hughes, J. M., Bloodaxe, E. S., Hanchar, J. M., and Foord, E. E. (1997). Incorporation of rare earth elements in titanate: Stabilization of the A2/a dimorph by creation of antiphase boundaries. *Amer. Miner.* **82**, 512–6.
- Hunter, B. A., Howard, C. J., and Kim, D. J. (1999). Bond valence analysis of tetragonal zirconias. *J. Solid State Chem.* **146**, 363–8.
- Hyde, B. G. and Andersson, S. (1989). *Inorganic Crystal Structures*. New York: John Wiley.

- International Tables for Crystallography. (1996). Vol. A, 4th edn. Dordrecht: D. Reidel.
- Jansen, L. and Block, R. (1991). On the concept of 'bond valence sums' and its applicability in the analysis of high-T_c superconductors. *Physica C* **181**, 149–59.
- Jansen, L., Chandra, L., and Block, R. (1992). On the concept of 'bond valence sums' and its applicability in solid state chemistry and physics. *J. Mol. Struct.* (*Theochem*) **260**, 81–96.
- Johnson, D. A. (1968). Some Thermodynamic Aspects of Inorganic Chemistry. Cambridge: Cambridge University Press.
- Kanowitz, S. M. and Palenik, G. (1998). Bond valences in coordination chemistry. A simple method for calculating the oxidation state of iron in Fe-O complexes. *Inorg. Chem.* 37, 2086-8.
- Karpppinen, M. and Yamauchi, H. (1999). The doping routes and distribution of holes in layered cuprates: A novel bond valence approach. *Phil. Mag.* **79**, 343–66.
- Klein, O., Bonvehi, M. M., Aguilar-Parrilla, F., Jagerovic, N., Elguero, J., and Limbach, H.-H. (1999). Hydrogen bond compression during triple proton transfer in crystalline pyrazoles. A dynamic ¹⁵N NMR study. *Israel J. Chem.* **39**, 291–9.
- Koller, H., Englehardt, G., Kentgens, A. P. M., and Saur, J. (1994). ²³Na NMR spectroscopy of solids: Interpretation of quadrupole interaction parameters and chemical shifts. *J. Phys. Chem.* **98**, 1544–51.
- Koretsky, E. M., Sverjensky, D. A., and Sahai, N. (1998). A model of surface site types on oxide and silicate minerals based on crystal chemistry—implications for site types and densities, multisite adsorption, surface infrared-spectroscopy, and dissolution kinetics. *Amer. J. Sci.* **298**, 349–438.
- Krivovichev, S. V. and Filatov, S. K. (1999). Structural principles for minerals and inorganic compounds containing anion-centred tetrahedra. *Amer. Miner.* **84**, 1099–106.
- Kroll, H., Maurer, H., Stöckelmann, D., Becker, W., Fulst, J., Krüsemann, R., *et al.* (1992). Simulation of crystal structures by a combined distance-least-squares valence-rule method. *Zeit. Kristallogr.* **199**, 49–66.
- Kroon, J., Kanters, J. A., Van Duijneveldt-Van de Rijdt, J. G. C. M., Van Duijneveldt, F. S., and Vliegenthart, J. A. (1975). O–H... O hydrogen bonds in molecular crystals. A statistical and quantum-chemical analysis. *J. Mol. Structure* **24**, 109–29.
- Kubayashi, K., Kawata, H., and Mori, K. (1998). Site specification on normal and magnetic XANES of ferrimagnetic Fe₃O₄ by means of resonant magnetic Bragg scattering. *J. Synch. Rad.* **5**, 972–4.
- Kunz, M. and Brown, I. D. (1995). Out-of-center distortions around octahed-rally coordinated d⁰-transition metals. *J. Solid State Chem.* **115**, 395–406.
- Labouriau, A., Higley, T. J., and Earl, W. L. (1998). Chemical shift prediction in the Si–29 MAS NMR of titanosilicates. *J. Phys. Chem.* **B102**, 2897–904.

- Leonyuk, L., Babonas, G.-J., Maltsev, V., and Ribakov, V. (1999). Polysomatic series in the structures of complex cuprates. *Acta Cryst.* **A55**, 628–34.
- Lewis, G. N. (1923). Valence and the Structure of Atoms and Molecules. New York: The Chemical Catalogue Company Inc.
- Liebau, F. (1985). Structural Chemistry of Silicates. Structure, Bonding and Classification. Berlin: Springer.
- Lima de Faria, J. and Figueiredo, M. O. (1975). Classification, notation and ordering on a table of inorganic structure types. *J. Solid State Chem.* **16**, 7–28.
- Liu, W. and Thorp, H. H. (1993). Bond valence sum analysis of metal-ligand bond lengths in metalloenzymes and model complexes. 2. Refined distances and other enzymes. *Inorg. Chem.* 32, 4102–5.
- Lock, C. J. L. (1980). Structural studies of the hydrolysis products of platinum anticancer drugs, and their complexes with DNA base. In A. E. Martell (ed.), *ACS Symposium Series*, Vol. 140: *Inorganic Chemistry in Biology and Medicine*, pp. 209–24.
- Lu, H., Isralewitz, B., Kramer, A., Vogel, V., and Schulten, K. (1998). Unfolding of titin immunoglobulin domains by steered molecular dynamics simulation. *Biophys. J.* **75**, 662–71.
- Luaña, V., Costales, A., and Pendás, A. M. (1997). Ions in crystals: The topology of the electron density in ionic materials II. The cubic halide perovskites. *Phys. Rev. B* **55**, 4285–97.
- McGibbon, M. M., Browning, N. D., Chisholm, M. F., McGibbon, A. J., Pennycook, S. J., Ravikumar, V., et al. (1994). Direct determination of the grain boundary atomic structure in SrTiO₃. Science **266**, 102–4.
- McGibbon, M. M., Browning, N. D., McGibbon, A. J., and Pennycook, S. J. (1996). The atomic structure of asymmetric [001] tilt boundaries in SrTiO₃. *Phil. Mag.* A73, 625–41.
- McGreevy, R. L. (1997). Reverse Monte Carlo methods for structure modelling. In C. R. A. Catlow (ed.), *Computer Modelling in Inorganic Crystallography*. San Diego and New York: Academic Press, pp. 151–84.
- Madelung, E. (1918). Physik. Zeit. 19, 524.
- Mahapatra, S., Halten, J. A., Wilkinson, E. C., Pan, G., Wang, X., Young, V. G. Jr, *et al.* (1996). Structural, spectroscopic and theoretical characterization of bis(μ -oxo)dicopper complexes, novel intermediates in copper mediated dioxygen activation. *J. Amer. Chem. Soc.* **118**, 11555–74.
- Manceau, A. and Gates, W. P. (1997). Surface structural model for ferrihydrite. *Clay and Clay Miner.* **45**, 448–60.
- Manceau, A., Chateigner, D., and Gates, W. P. (1998). Polarised EXAFS distance least squares valence modelling (DVLS) and quantitative texture analysis approaches to the structural refinement of Garfield nontronite. *Phys. Chem. Miner.* **25**, 347–65.
- Megaw, H. D. (1939). The thermal expansion of crystals in relation to their structure. *Zeit. Kristallogr.* **100**, 58–76.

- Meier, W. M. and Olson, D. H. (1992). *Atlas of Zeolite Structure Types*, 3rd edn. London: Butterworths.
- Mitchell, K. A. R., Schlatter, S. A., and Sodhi, R. N. S. (1986). Further analysis of surface bond lengths measured for chemisorption on metal surfaces. *Can. J. Chem.* **64**, 1435–9.
- Mohri, F. (2000). A new relation between bond valence and bond distance. *Acta Cryst.* **B56**, 626–38.
- Murray-Rust, P., Bürgi, H.-B., and Dunitz, J. D. (1975). Chemical reaction paths. V. The SN1 reaction of tetrahedral molecules. *J. Amer. Chem. Soc.* **97**, 921–3.
- Naskar, J. P., Hati, S., and Datta, D. (1997). New bond valence model. *Acta Cryst.* **B53**, 885–94.
- Nayal, M. and Di Cera, E. (1994). Predicting Ca²⁺-binding sites in proteins. *Proc. Natl. Acad. Sci. USA* **91**, 817–21.
- Nayal, M. and Di Cera, E. (1996). Valence screening of water in protein crystals reveals potential Na⁺ binding sites. *J. Mol. Biol.* **256**, 228–34.
- Niggli, P. (1918). Geometrische Kristallographie des Diskontinuums. Leipzig: Gebr. Bornträger.
- O'Keeffe, M. (1989). The prediction and interpretation of bond lengths in crystals. *Structure and Bonding* **71**, 161–90.
- O'Keeffe, M. (1991a). Empirical methods in oxide crystal chemistry. In P. K. Davies and R. S. Roth (eds), *Chemistry of Electronic Ceramic Materials*. US Department of Commerce, pp. 485–98.
- O'Keeffe, M. (1991b). Application of the bond valence method to Si/NiSi₂ interfaces. *J. Mater. Res.* **6**, 2371–4.
- O'Keeffe, M. and Brese, N. E. (1991). Atom sizes and bond lengths in molecules and crystals. *J. Amer. Chem. Soc.* **113**, 3226–9.
- O'Keeffe, M. and Hyde, B. G. (1982). Anion coordination and cation packing in oxides. *J. Solid State Chem.* 44, 24–31.
- O'Keeffe, M. and Hyde, B. G. (1984). Stoichiometry and the structure and stability of inorganic solids. *Nature* **309**, 411–4.
- O'Keeffe, M. and Hyde, B. G. (1985). An alternative approach to non-mole-cular crystal structures with emphasis on the arrangement of cations. *Structure and Bonding* **61**, 77–144.
- O'Keeffe, M., Eddaoudi, M., Li, H., Reinecke, T., and Yaghi, O. M. (2000). Frameworks for extended solids: Geometric design prinicples. *J. Solid State Chem.* **152**, 3–20.
- Orlov, I. P., Popov, K. A., and Urusov, V. S. (1998). A program for predicting interatomic distances in crystals by the bond valence method. *J. Struct. Chem.* **39**, 575–9.
- Otero-Diaz, L. C., Landa, A. R., Fernandez, F., Saez-Puche, R., Withers, R. and Hyde, B. G. (1992). A TEM study of the ordering of excess interstitial oxygen atoms in $\text{Ln}_2\text{NiO}_{4+\delta}$ (Ln = La, Nd). J. Solid State Chem. 97, 443–51.

- Palenik, G. J. (1997a). Bond valence sums in coordination chemistry using oxidation state independent R_0 values. *Inorg. Chem.* **36**, 122.
- Palenik, G. J. (1997b). Bond valence sums in coordination chemistry using oxidation state independent R_0 values. A simple calculation of the oxidation states of titanium in compounds containing Ti-N, Ti-O, and Ti-Cl bonds. *Inorg. Chem.* **36**, 3394-7.
- Palenik, G. J. (1997c). Bond valence sums in coordination chemistry using oxidation state independent R_0 values. A simple method for calculating the oxidation state of manganese in complexes containing only Mn–O bonds. *Inorg. Chem.* **36**, 4888–90.
- Pannetier, J., Bassas-Alsina, J., Rodrigues-Carvajal, J., and Caignaert, V. (1990). Prediction of crystal structures from crystal chemistry rules by simulated annealing. *Nature* **346**, 343–5.
- Parthé, E. (1996). Elements of Inorganic Structural Chemistry. Selected Efforts to Predict Structural Features. Switzerland: K. Sutter-Parthé, Petit-Lancy.
- Partington, J. R. (1964). A History of Chemistry, Vol. 4. London: McMillan.
- Pauling, L. (1929). The principles determining the structure of complex ionic crystals. *J. Amer. Chem. Soc.* **51**, 1010–26.
- Pauling, L. (1947). Atomic radii and interatomic distances in metals. *J. Amer. Chem. Soc.* **69**, 542–54.
- Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd edn. Ithaca: Cornell University Press.
- Payne, M. C., Teter, M. P., Allen, D. C., Arias, T. A., and Joanopolus, J. D. (1992). Iterative minimization techniques for *ab initio* total energy calculations: Molecular dynamics and conjugate gradients. *Rev. Mod. Phys.* **64**, 1045–97.
- Pearson, R. G. (1973). *Hard and Soft Acids and Bases*. PA, USA: Dowden, Hutchinson and Ross, Stroudberg.
- Pendás, A. M., Costales, A., and Luaña, V. (1997). Ions in crystals: The topology of electron density in ionic materials. I. Fundamentals. *Phys. Rev. B* **55**, 4275–84.
- Pendás, A. M., Costales, A., and Luaña, V. (1998). Ions in crystals: The topology of electron density in ionic materials. III. Geometry and ionic radii. *J. Phys. Chem. B* **102**, 6937–48.
- Perloff, A. (1970). The crystal structure of sodium hexamolybdatochromate(III) octahydrate, $Na_3(CrMo_6O_{24}H_6) \cdot 8H_2O$. *Inorg. Chem.* **9**, 2228–39.
- Plenio, H. (1998). The coordination chemistry of CF units in fluorocarbons. *Chem. Rev.* **97**, 3363–84.
- Plenio, H. and Hermann, J. (1998). Synthesis and X-ray crystal structures of 48-membered fluoromacorcycles and an investigation of their coordination chemistry. *Zeit. Anorg. Allgem. Chem.* **624**, 792–6.
- Preiser, C. Lösel, J., Brown, I. D., Kunz, M., and Skowron, A. (1999). Long range Coulomb forces and localised bonds. *Acta Cryst.* **B55**, 698–711.
- Pyatenko, Yu. A. (1973). Unified approach to analysis of the local balance of valence in inorganic structures. *Sov. Phys. Cryst.* 17, 677–82.

- Rao, G. H. and Brown, I. D. (1998). Determination of bonding and valence distrtibution in inorganic solids by the maximum entropy method. *Acta Cryst.* **B54**, 221–30.
- Rao, G. H., Bärner, E., and Brown, I. D. (1998). Bond valence analysis on the structural effects in magnetoresistive manganese perovskites. *J. Phys.: Con*dens. Matter 10, L757–63.
- Rao, G. H., Brown, I. D., and Bärner, E. (1999). Structural effects in $R_{0.5}Sr_{0.5}MnO_3$ perovskites (R = rare earth). *J. Phys.: Condens. Matter* 11, 8103-9.
- Ray, W. J. Jr, Burgner, J. W. II, Deng, H., and Callender, R (1993). Internal chemical bonding in solutions of simple phosphates and vanadates. *Biochem.* **32**, 12977–83.
- Rohrer, C. L. and Rohrer, G. S. (1994). Monte Carlo simulations of Mg(Al)O solid solutions based on crystal chemical rules. *Chem. Mater.* **6**, 501–7.
- Rosenfield, R. E., Trueblood, K. N., and Dunitz, J. D. (1978). A test for rigid-body vibrations based on a generalization of Hirschfeld's 'rigid-bond' postulate. *Acta Cryst.* **A34**, 828–9.
- Rutherford, J. S. (1990). Theoretical prediction of bond-valence networks. *Acta Cryst.* **B46**, 289–92.
- Rutherford, J. S. (1998). Theoretical prediction of bond valence networks II. Comparison of the graph matrix and resonant bond approach. *Acta Cryst.* **B54**, 204–10.
- Salinas-Sanchez, A., Garcia-Muñoz, J. L., Rodriguez-Carvajal, J., Saez-Puche, R., and Martinez, J. L. (1992). Structural characterization of R₂BaCuO₅ (R=Y, Lu, Yb, Tm, Er, Ho, Dy, Gd, Eu and Sm) oxides by X-ray and neutron diffraction. *J. Solid State Chem.* **100**, 201–11.
- Santoro, A., Sora, I. N., and Huang, G. (1999). Bond valence analysis of the structure of (Ba₀₈₇₅Sr_{0.125})Ru O₃. *J. Solid State Chem.* **143**, 69–73.
- Santoro, A., Sora, I. N., and Huang, G. (2000). Bond valence analysis of BaRuO₃. *J. Solid State Chem.* **151**, 245–52.
- Sato, M. (1982). [Computer simulation of crystal structures]. *Rikagi Denki J.* **13**, 48–52 (in Japanese).
- Sato, M. and Uehara, H. (1997). *Ab initio* computer modelling of zeolite fameworks I. Modelling the basic clusters. *Prog. Zeolite Microporous Mater.* **105**, 2299–306.
- Scarrow, R. C., Brennan, B. A., Cummings, J. G., Jia, H., Duong, D. J., Kindt, J. T., *et al.* (1996). X-ray spectroscopy of nitrile hydratase at pH7 and pH9. *Biochem.* 55, 10078–88.
- Schindler, M., Hawthorne, F. C., and Baur, W. H. (2000). Crystal chemical aspects of vanadium polyhedral geometries, characteristic bond valences, and polymerization of (VO_n) polyhedra. *Chem. Mater.* **12**, 1248–59.
- See, R. F., Kruse, R. A., and Strub, W. M. (1998). Metal-ligand bond distances in first-row transition metal coordination compounds: Coordination number oxidation state and specific ligand effects. *Inorg. Chem.* 37, 5369–75.

- Shannon, R. D. (1976). Revised effective radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.* **A32**, 751–67.
- Shannon, R. D. and Prewitt, C. T. (1969). Effective ionic radii in oxides and fluorides. *Acta Cryst.* **B25**, 925–46.
- Shannon, R. D., Chenavas, J., and Joubert, J. C. (1975). Bond strength considerations applied to cation coordination in normal and high pressure oxides. *J. Solid State Chem.* **12**, 16–30.
- Sherriff, B. L. and Grundy, H. D. (1988). Calculation of ²⁹Si MAS NMR chemical shift from silicate mineral structure. *Nature* **332**, 819–22.
- Shields, G. P., Raithby, P. R., Allen, F. H., and Motherwell, W. D. S. (2000). The assignment and validation of metal oxidation states in the Cambridge Structural Database. *Acta Cryst.* **B56**, 455–65.
- Shubnikov, A. V. (1922). [Fundamental law of crystal chemistry]. *Izv. Ross. Akad. Nauk* **16**, 515–27 (in Russian). A more accessible account of Shubnikov's law is given by N. V. Smirnova and V. S. Urusov (1988).
- Shui, X. Q., Sines, C. C., McFailisom, L., VanderVeer, D., and Williams, L. D. (1998). Structure of the potassium form of CGCGAATTCGCG-DNA deformation by electrostatic collapse around inorganic cations. *Biochem.* 37, 16877–87.
- Skibsted, J., Vosegaard, T., Bildsøe, H., and Jakobsen, H. J. (1996). ¹³³Cs chemical shielding anisotropies and quadrupole coupling constants from magic angle spinning NMR of cesium salts. *J. Phys. Chem.* **100**, 14872–81.
- Skibsted, J., Jacobsen, C. J. H., and Jakobsen, H. J. (1998). ⁵¹V chemical shielding and quadrupolar coupling in ortho- and metavanadates from ⁵¹V MAS NMR spectroscopy. *Inorg. Chem.* **37**, 3083–92.
- Skowron, A. and Brown, I. D. (1990). Refinement of the structure of robinsonite, Pb₄Sb₆S₁₃. *Acta Cryst.* C46, 527–31.
- Skowron, A. and Brown, I. D. (1994). Crystal chemistry and structures of lead antimony sulfides. *Acta Cryst.* **B50**, 524–38.
- Smirnova, N. V. and Urusov, V. S. (1988). Fundamental law of crystal chemistry by Shubnikov, its applications and restrictions. *Comput. Math. Applic.* **16.** 563–7.
- Smith, J. V. (1988). Topochemistry of zeolites and related materials. *Chem. Rev.* **88**, 149–82.
- Steiner, Th. (1995a). Lengthening of the N-H bond in N-H...N hydrogen bonds. Preliminary structural data and implications of the bond valence concept. *Chem. Comm.* 1331-2.
- Steiner, Th. (1995b). Weak hydrogen bonding Part I. Neutron diffraction data of amino acid C-H suggests lengthening of the covalent C-H bond in C-H...O interactions. *J. Chem. Soc. Perkins Trans. II* 1315-9.
- Steiner, Th. (1997). Unrolling the hydrogen bond properties of C-H...O interactions. *Chem. Comm.* 727–34.
- Steiner, Th. (1998a). Structural evidence for resonance-assisted O-H...S hydrogen bonding. *Chem. Comm.* 411–2.

- Steiner, Th. (1998b). Lengthening of the covalent X–H bond in heteronuclear hydrogen bonds quantified from organic and organometallic neutron crystal structures. *J. Phys. Chem. A* **102**, 7041–52.
- Steiner, Th. and Saenger, W. (1992). Covalent bond lengthening in hydroxyl groups involved in three-center and in cooperative hydrogen bonds. Analysis of low-temperature neutron diffraction data. *J. Amer. Chem. Soc.* 114, 7123–6.
- Steiner, Th. and Saenger, W. (1994). Lengthening of the covalent O-H bond in the O-H...O hydrogen bonds re-examined from low-temperature neutron diffraction data of organic compounds. *Acta Cryst.* **B50**, 348-57.
- Swenson, J. and Adams, St. (2001). The application of the bond valence method to reverse Monte Carlo produced structural models of superionic glasses. *Phys. Rev.* **B64**, 024204.
- Tallon, J. L. (1990). The relationship between bond valence sums and Tc in cuprate superconductors. *Physica C* **168**, 85–90.
- Tanaka, S., Fukushima, N., Niu, H., and Ando, K. (1990). Bond-valence-sum study on possible candidates for High-Tc oxide superconductors. *Jap. J. Appl. Phys.* **29**, L1987–90.
- Taylor, R. and Kennard, O. (1984). Hydrogen bond geometry in organic crystals. *Acc. Chem. Res.* 17, 320–6.
- Thomas, N. W. (1989). A bond-valence approach to one-dimensional ferroelectrics. *Ferroelectrics* **100**, 77–100.
- Thompson, T. (1807). A System of Chemistry, Vol. 3, 3rd edn. Edinburgh, pp. 424–9.
- Thompson, J. G., Rae, A. D., Bliznyuk, N., and Withers, R. L. (1999). Ordering of Ce^{III}/Ce^{IV} and interstitial oxygens in $CeTaO_{4+x}$ (x=0.17) superstructures. *J. Solid State Chem.* **144**, 240–6.
- Thorp, H. H. (1992). Bond valence sum analysis of metal-ligand bond lengths in metalloenzymes and model complexes. *Inorg. Chem.* **31**, 1585–8.
- Thorp, H. H. (1998). Bond valence sum analysis of metalloenzymes. 3. Predicting bond lengths in adjacent redox states using inner-sphere reorganizational energies. *Inorg. Chem.* **37**, 5690–2.
- Trömel, M. (1992). Zu einer Bindungslänger Kristallchemie. *Zeit. Kristallogr.* **200**, 177–87.
- Turrell, G. (1972). *Infrared and Raman Spectra of Crystals*. London and New York: Academic Press.
- Tytko, K. H. (1999). A bond model for polyoxometalate ions composed of MO_6 octahedra (MO_x polyhedra with x > 4). Structure and Bonding 93, 67–127.
- Urusov, V. S. (1995). Semiempirical groundwork of the bond valence model. *Acta Cryst.* **B51**, 641–9.
- Urusov, V. S. and Orlov, I. P. (1999). State-of-art and perspectives of the bond-valence model in inorganic chemistry. *Crystallogr. Rep.* 44, 686–709.
- Valach, F. (1999). A bond valence approach to the semicoordination of copper–oxygen and copper–nitrogen complexes. *Polyhedron* **116**, 699–706.

- van Smaalen, S. and Lüdecke, J. (2000). The valence states of vanadium in the low-temperature superstructure of NaV₂O₅. *Europhys. Lett.* **49**, 250–4.
- Venema, P., Hiemstra, T., Weidler, P. G., and Van Riemsdijk, W. H. (1998). Intrinsic proton affinity of reactive surface groups of metal (hydr)oxides: Application to iron (hydr)oxides. *J. Colloid. Interface Sci.* **198**, 282–95.
- Villiger, H. (1969). DLS Manual. Inst Kristallogr. Petrolog. ETH, Zürich.
- Wakiya, N., Shinozaki, K., Mizutani, N., and Ishizawa, N. (1997). Estimation of phase stability in Pb(Mg_{1/3}Nb_{2/3})O₃ and Pb(Zn_{1/3}Nb_{2/3})O₃ using the bond valence approach. *J. Amer. Ceram. Soc.* **80**, 3217–20.
- Waltersson, K. (1978). A method based upon 'bond strength' calculations for finding probable lithium sites in crystal structures. *Acta Cryst.* **A34**, 901–5.
- Wang, Y. M., Li, Y. S., and Mitchell, K. A. R. (1997). LEED crystallographic analysis for the structure formed by 2 ML of O at the Zr (0001) surface. *Surface Sci.* **380**, 540–7.
- Wegner, T. R. and O'Keeffe, M. (1988). Bond lengths and valences in aluminates with the magnetoplumbite and β -alumina structures. *J. Solid State Chem.* **73**, 211–6.
- Wells, A. F. (1975). *Structural Inorganic Chemistry*, 4th edn. Oxford: Clarendon Press, pp. 119–55.
- Williams, D. E. (1996). *Ab initio* molecular packing analysis. *Acta Cryst.* **A52**, 326–8.
- Withers, R. L., Thompson, J. G., and Rae, A. D. (1991). The crystal chemistry underlying ferroelectricity ini Bi₄Ti₃O₁₂ and related Aurivillius phases. *J. Solid State Chem.* **93**, 404–17.
- Withers, R. L., Schmid, S., and Thompson, J. G. (1998). Compositionally and/or displacively flexible systems and their underlying crystal chemistry. *Prog. in Solid State Chem.* **26**, 1–96.
- Wood, R. M. and Palenik, G. J. (1998). Bond valences in coordination chemistry. A simple method for calculating the oxidation state of cobalt in Co-O complexes containing only Co-O bonds. *Inorg. Chem.* 37, 4149–51.
- Wood, R. M. and Palenik, G. J. (1999a). Bond valence sums in coordination chemistry using new R_0 values. Potassium—oxygen complexes. *Inorg. Chem.* **38**, 1031–4.
- Wood, R. M. and Palenik, G. J. (1999b). Bond valence sums in coordination chemistry. Sodium—oxygen complexes. *Inorg. Chem.* **38**, 3926–30.
- Wood, R. M., Aboud, K. A., Palenik, R. C., and Palenik, G. J. (2000). Bond valence sums in coordination chemistry. Calculation of the oxidation state of chromium complexes containing only Cr–O bonds and a redetermination of the crystal structure of potassium tetra(peroxo)chromate(V). *Inorg. Chem.* 39, 2065–8.
- Woodley, S. M., Battle, P. D., Gale, J. D., and Catlow, C. R. A. (1999). The prediction of inorganic crystal structures using a genetic algorithm and energy minimisation. *Phys. Chem. Phys.* 1, 2535–42.

- Woodward, P. (1997a). Octahedral tilting in perovskites I. Geometrical considerations. *Acta Cryst.* **B53**, 32–43.
- Woodward, P. (1997*b*). Octahedral tilting in perovskites II. Structure stabilizing forces. *Acta Cryst.* **B53**, 44–66.
- Woodward, P. M., Cox, D.E., Mashopoulou, E., Sleight, A. W., and Morimoto, S. (2000). Structural studies of charge disproportionation and magnetic order in CaFeO₃. *Phys. Rev. B* **62**, 844–55.
- Wright, S. E., Foley, F. A., and Hughes, J. M. (2000). Optimization of site occupancies in minerals using quadratic programming. *Amer. Miner.* **85**, 524–31.
- Wu, Z. and Farges, F. (1999). Anharmonicity around Th in crystalline oxide-type compounds: An in-situ high temperature XAFS spectroscopy study to 1500°C. *Physica B*, **266**, 282–9.
- Xia, K., Bleam, W., and Helmke, P. A. (1997a). Studies of the nature of Cu²⁺ and Pb²⁺ binding sites in soil humic substances using X-ray absorption spectroscopy. *Geochim. Cosmochim. Acta* **61**, 2211–21.
- Xia, K., Bleam, W., and Helmke, P. A. (1997b). Studies of the nature of binding sites of first row transition elements bound to aquatic and soil humic substances using X-ray absorption spectroscopy. *Geochim. Cosmochim. Acta* **61**, 2223–35.
- Xiang, S., Short, S. A., Wolfenden, R., and Carter, C. W. (1996). Cytidene deaminase complexed to 3-deazacytidine: A 'valence buffer' in zinc enzyme catalysis. *Biochem.* **35**, 1335–41.
- Yan, Y., Chisholm, M. F., Duscher, G., and Pennycook, S. J. (1998). Atomic structure of a Ca-doped [001] tilt grain boundary in MgO. *J. Electron Microscopy* 47, 115–20.
- Zachariesen, W. H. (1954). Crystal chemical studies of the 5f series elements. XXIII. On the crystal chemistry of uranyl compounds and of related compounds of transuranic elements. *Acta Cryst.* 7, 795–9.
- Zachariesen, W. H. and Pletinger, H. A. (1959). Crystal chemical studies of the 5f-series elements. XXV. The crystal structure of sodium uranyl acetate. *Acta Cryst.* **12**, 526–30.
- Ziółkowski, J. (1983*a*). Catalytic properties of defective brannerite-type vanadates. II. A model of sites active in oxidation of propylene on the (201) and $(20\bar{2})$ planes of $Mn_{1-x}\Phi_xV_{2-2x}Mn_{2x}O_6$. J. Catal. **81**, 311–27.
- Ziółkowski, J. (1983*b*). Advanced bond strength model of active sites on oxide catalysts. *J. Catal.* **84**, 317–32.
- Ziółkowski, J. (1985). New relation between ionic radii, bond length, and bond strength. *J. Solid State Chem.* **57**, 269–90.
- Ziółkowski, J. (1986). Crystallochemical model of active sites on oxide catalysts. *J. Catal.* **100**, 45–58.
- Ziółkowski, J. (1988). New method of calculation of surface enthalpy of solids. *Surface Sci.* **209**, 536–61.

- Ziółkowski, J. and Dzienbaj, L. (1985). Empirical relationships between individual cation oxygen bond length and bond-energy in crystals and molecules. *J. Solid State Chem.* **57,** 291–9.
- Ziółkowski, J. and Wiltowski, T. (1984). Interaction of acetone with MoO₃. *J. Catal.* **90**, 329–36.
- Zuo, J. M., Kim, M., O'Keeffe, M., and Spence, J. C. H. (1999). Direct observation of d-orbital holes and Cu-Cu bonding in Cu_2O . *Nature* **401**, 49-52.

List of symbols

- B bond valence parameter (pm) in eqn (3.1)
- N bond valence exponent in eqn (3.2)
- N_a number of atoms
- $N_{\rm b}$ number of bonds
- R bond length (pm)
- R_0 bond valence parameter (pm) in eqns (3.1) and (3.2) (length of a bond of unit valence)
- r ionic radius (pm)
- s theoretical bond valence (vu^1) defined by eqns (3.3) and (3.4)
- s_a anion bonding strength (vu) defined by eqn (4.1)
- s_b cation bonding strength (vu) defined by eqn (4.2)
- s' effective valence (vu) defined by eqn (6.1)
- S experimental bond valence (vu) defined by eqn (3.1) or (3.2)
- S_h valence of the weak side of a hydrogen bond (vu)
- V atomic valence (formal ionic charge) (vu)
- Φ bond flux (vu) (Section 2.4)
- ν ideal coordination number (Rule 4.1)

¹vu valence unit corresponding to one electron unit of charge.



Index

acetate ion 36, 87, 108-9	hard 50
acceptor	soft 50
electron, see acid; cation	strength 47
hydrogen bond 184	weak 52
acid	BaTiO ₃ 102, 124, 154, 187, 188-9
hard 50	B_2H_6 21
soft 50, 62, 71, 104	biology, applications in 203-6
strength 48	bond
adenosine diphosphate 201–3	angle 108
adjacency matrix, see connectivity	capacitance 19-20, 26, 30, 93, 103-4
adsorption 201	covalent 31, 207-9, 219
AgI 159-60, 191	critical point (B critical point) 218
alkali halides 44, 61, 70	definition
alkaline earth halides 61	in the ionic model 17
Al ₂ O ₃ 48, 71	operational 43
$AlPO_4$ 47	flux 9, 17–19, 23, 29, 93; see also bond
ammonia (NH ₃) 54n, 62, 246	valence
ammonium ion (NH_4^+) 87, 245	force constant 110–12, 114
amorphous materials, see glasses	fragment, space filling 220
anatase, see TiO ₂	history of 3–5
angle, see bond, angle	ionic 31, 207–9, 219
anion	length 27, 33, 39, 77, 93, 106–10; see also
bonding strength 45–6, 72–4	bond valence, bond length, correlation
difference from cations 213	with
fragments centred on 147, 220	network 20
hard 50	path (B paths) 218
minimum distance between 68	primary 23
reaction with water 57	properties 105–118
repulsion between 64–9, 76–80	secondary 23n, 94–5
soft 50	strain in 78–80, 92, 104, 164–78
strong 47	tertiary 23, 30n
weak 47, 52	thermal expansion 113–16
asymmetric unit, see symmetry, asymmetric	thermal vibration 112–13
unit	Van der Waals 219
atom	see also bond valence model; hydrogen
charge	bonds; ionic model; Lewis electron-pair
actual 16–17, 106–7	model; orbital overlap model;
dipole 91, 95–7, 101	electrostatic valence model;
formal 16–17, 19, 45n	quantum mechanics; topology
multipole 15, 90–1, 93	bond graph 20–23, 102, 168, 210–11, 219
quadrupole 100	creation of 142–5
definition 15–17	spectrum of 155n
fragment, space filling 16–17, 217–18	see also circuit, equivalent
thermal vibration of 112, 209	bond strain index (BSI) 104, 166, 172, 177, 185
valence 3, 210	bond valence
determination of 182–3	bond length, correlation with 27–8, 33, 39,
non-integral 170–1, 174	92–3, 225–6
11011 111000101 110 1, 1/1	expressions 27, 230–2
Ba ²⁺ 68, 72-3, 244	hydrogen bonds 77–80, 87–9
base	energy, correlation with 105–6, 200
ouse	

bond valence (cont.):	chemistry
effective 67–8, 77–80	applications to 197–203
experimental 27, 92-3, 185	crystal
force constant, correlation with 111	the fundamental law of 129, 136
sums 185, 189; see also valence sum rule	of hydrogen 84–6
theoretical 29, 92	circuit, equivalent 22, 104
see also bond flux	cisplatine 205
bond valence model 9, 26–34, 207–10	cleavage 194
physical justification 220	ClO ₄ ⁻ 45, 59, 83–4, 246
bond valence parameters 27, 106–7, 209,	close packing 136
224–30	complexes
determination of 226–30	anion centred 147, 220
for hydrogen bonds 230	cation centred 147, 220
list of 225–6	composite structures 165, 174–6
relations between 228–9	compounds
thermal correction 118, 229	inorganic, being different from organic 4,
of transition metals 229	121
bonding strength	computer programs
anion 45–6, 72–4	bond valence (VALENCE) 228
cation 46, 47, 57	bond valence maps 159
maximum 46	distance least squares (DLS) 161
minimum 46 tables of 244–6	distance valence least squares (DVLS) 161
of water 53–4	occupation numbers (OccQP) 184
brannerite 102, 200	conductivity ionic 190–1
BSI, see bond strain index	superconductivity 189–90
building blocks, fundamental 145–7	connectivity 20–22
bunding blocks, fundamental 143	constraints
Ca^{2+} 49, 60–1, 68, 244	electronic 90–104
CaCrF ₅ 22, 29–30, 32, 172–174, 241–3	spatial 72, 76–80, 123–5, 164–178
CaF ₂ 61, 157–8, 162, 214	coordination number 211
Cambridge Structural Database, see	definition 23, 43
databases	distribution of 65
$Ca_3(PO_4)_2$ 49	ideal (average observed) 44, 67, 244–5
catalysis	prediction of 64–74
heterogeneous 200–1	rule 69, 135
CaTiO ₃ 154, 187	symmetry, relation to 71, 131–2
cations	Coulomb, see electrostatic field, Coulomb
bonding strength 46, 47–9, 57	covalency 198, 207
difference from anions 213	covalent bond 207, 211
entropy of solution 57	Cr ⁶⁺ 68, 103, 245
fragments centred on 220	$Cr(H_2O)_6^{3+}$ 55-6
hard 50	crystal
hydrated 55–6	lattice 122–5
reaction with water 55–7	thermal expansion 116–17
soft 50, 62, 71, 90, 104	crystal chemistry, see chemistry, crystal
strong 48	crystal structure
weak 48	analysis of 184–5
Cd^{2+} 62, 68	composite 165, 174–6
CH ₄ 54n	modulated 165, 174-7
charge	non-stoichiometric 169–70, 174–6
formal 45n	similar 206
formal ionic 16, 19, 45n	solution of 181–4
ordering of 183	strained 29, 90–104, 164–78
surface 195	superstructure, determination of 184
see also atom, charge	unstrained 29
chelation 52	validation of 185
chemical shift 198	see also modelling; space group; symmetry

crystallization 141-2	conservation, law of 19
Cs ⁺ 52, 56, 64–5, 72, 244	electrostatic 14
CsCl 7, 44, 70, 143, 214	free, of solution 61
$Cs_2Cr_3O_{10}$ 69–70	in ionic model 210
CSD, see database	of thermal vibration 111
Cs ₂ Sn ₂ O ₃ 69–70	
Cu^{2+} 99, 245	entropy, see solution, entropy of; symmetry,
Cu 99, 243	entropy as a measure of
database	enzyme 203–6
	epsomite (MgSO ₄ (H ₂ O) ₇) 60
Cambridge Structural (CSD) 199–200, 206	equal valence rule 29, 33, 104
references from 252	esterification 201
Inorganic Crystal Structure (ICSD) 206	(EuS) _{1.725} (NbS ₂) 165, 174–5
references from 247–51	EXAFS 196, 197, 203
defects	expansion, thermal, see bond, thermal
caused by lattice induced strain 169	expansion; crystal, thermal expansion
modelling 161	EGG 1: 120 40
see also grain boundaries	FCC packing 139–40
dimethylsulphoxide (dmso) 38, 62–3, 246	ferroelectricity 188–9
diffraction	FeTiO ₃ 154
electron 201	fluorite (CaF ₂) 61, 157–8, 162, 214
neutron 77, 88, 181, 191	force constant, see bond, force constant
powder 4, 76, 88, 181–2	forsterite (Mg ₂ SiO ₄) 49, 59, 63, 159
x-ray 181	
diffusion 159, 178	garnet $(A_3B_2(XO_4)_3)$ 69, 115–6, 141
disorder, occupational, determination of	Gauss' law 17–18, 26
183–4	genetic algorithm 138, 182
disproportionation 183	GII, see global instability index
distortion	glasses 162, 191, 197
electronic 90–104, 191, 215	global instability index (GII) 104, 166–7, 168,
theorem 33–34, 189	172, 177, 184, 185
see also strain	goethite 195
donor	grain boundaries 192–3
electron, see base; anion	graph
hydrogen bond 184	bipartite 33, 34
	non-bipartite 34–9
EELS 192	theory 7, 20–23
electrolyte, ionic 190	see also bond graphs
electron	
core 221	H^+ 75, 68, 75–80, 244
density 6, 16, 216–19	hydrated 59, 83, 85–6
Laplacian of 219	hard sphere model 64-66
topological description 216–19	HCP 139-40
diffraction, see diffraction, electron	HF 54n, 246
lone pair 93–8	Hg_2^{2+} 35, 39
electronegativity 211	$Hg_{2.82}AsF_6$ 175–6, 190
Allen 48–9	$Hg_2Cl_2 35-6$
Pauling 48	hierarchical principle 141, 193
electroneutrality principle 16, 33, 135	hydrazinium ion $(N_2H_5^+)$ 35
electronic distortion, see distortion, electronic	hydrofluoric acid (HF) 54n
electrostatic valence model 8-9	hydrogen bond 75–89
electrostatic field	anion-anion repulsion in 76-80
Coulomb 14-15, 90-1, 95-6	bond valence, assignment of 87–9, 184, 230
Madelung 15, 17–19, 90–3, 220	bonding scheme 184
electrostatic flux, see bond flux	chemistry, structural 84–6
electrostatic force 207	correlation between length and valence 77–8
electrostatic potential 7, 9, 13, 14	non-oxygen donor or acceptor 86–7
energy	normal 80-1
bond valence, correlation with 105–6, 200	strong 81–3

hydrogen bond (cont.): in water 53–4 weak 83–4 hydrogen ion, see H ⁺ hydrolysis 201	MgSiO ₃ 69 Mg ₂ SiO ₄ 49, 59, 63, 159 MgSO ₄ 60 MgSO ₄ (H ₂ O) ₇ 60 minerals 7, 51–2, 149, 193–7 Mn ³⁺ 99, 191–2, 244
I ⁵⁺ 68, 92–3, 245 ICSD, see database ilmenite (FeTiO ₃) 154 incommensurate structures 165, 174–7 Inorganic Crystal Structure Database, see database interatomic repulsion 64–9, 209–10 interfaces 192–3 I ₂ O ₅ 92–3 ionic bond 207, 212 ionic charge, formal 16, 19, 45n ionic conductivity 190–1 ionic model 5, 13–20, 160, 210 assumptions 13, 15–17, 25 ionicity 207 Jahn-Teller distortion 34, 99–100, 191	modelling a priori 134 of amorphous structures 162 bond graph, creation of 141–5 chemistry-based methods 140–57 of defect structures 161–2 of glasses 162 of inorganic structures 134–163 lattice models 138–40 random structure methods 137–8 refinement of structure 160–1 space based methods 136–40 space group method 6, 151–7 topology 135–57 of weakly bonded structures 156–7 see also genetic algorithm; Monte Carlo methods; simulated annealing modulated structure 165, 174–7
KH ₂ PO ₄ 108 Kirchhoff equations 22, 30, 93, 100, 103	Monte Carlo method 138, 182, 191 multiplicity, see symmetry, multiplicity
La ₂ CuO ₄ 170–1, 190 La ₂ NiO ₄ 164, 168–72, 186–7 lattice, <i>see</i> crystal lattice lattice induced strain, <i>see</i> strain, lattice induced lattice models 138–40 LEED 201 Lewis acid and base strength, <i>see</i> acid strength; base strength Lewis electron-pair model 3, 6, 211–13 liquids 53–63 Li(H ₂ O) ₃ ClO ₄ 84 Li ₂ SO ₄ .H ₂ O 185 Ln ₂ BaCuO ₅ 166–7 lone pair electrons 93–8 loop rule, <i>see</i> equal valence rule	N ⁵⁺ 64-5, 68, 73 Na ⁺ 63, 68, 244 NaCl 4, 21-2, 32, 44, 60-1, 70, 142, 143, 152-3, 214 Na ₂ CO ₃ 60 Na ₂ HCO ₃ 60 Na ₂ O 44, 214 N(CH ₃) ⁺ 61 network equations 28-29, 93 solution of 240-3 see also valence sum rule, equal valence rule, Kirchhoff equations network bond 20 in electron density (B network) 218-19 four-connected three-dimensional 148-9 neutron, see diffraction, neutron
Madelung, see electrostatic field, Madelung magnetoresistance 191–2 maximum symmetry, see symmetry, maximum, principle of melilite ($A_2MN_2O_7$) 177 melts 62–3 mercurous ion (Hg_2^{2+}) 35, 39 metals (metallic compounds) 13, 25, 214 methane (CH ₄) 54n Mg ²⁺ 46, 51, 53, 68, 74, 244 MgBr ₂ , 62	NH ₃ 54n, 62, 246 NH ₄ 67, 245 NH ₄ Br 87 NH ₄ HgCl ₃ 156 Ni(H ₂ O) ₆ SO ₄ 84–5 NMR 197–8 NO ₂ 37, 96 NO ₃ 66, 216 non-bonding repulsion 209 non-stoichiometry 169–70, 174–6
Mg(H ₂ O) ₆ ²⁺ 55–7, 60, 146 Mg(H ₂ O) ₆ CdCd ₆ 146–7 MgO 73–4, 192	orbital 71n, 215–6 orbital overlap model 3, 6 oxalic acid dihydrate 83

packing groups 156-7	magmas 52, 63
Pauling	non-existent 51–2
principles of crystal chemistry 8, 26	thermal contraction in 116–7
see also electronegativity; electrostatic	simulated annealing 137–8, 182
valence model, radii	SiO_2 148-9
Pb ²⁺ 94, 147, 189, 245	Sn^{2+} 94, 245
PbS 94, 97	SO_4^{2-} $45-6$, 57
Pearson hard-soft acid-base, see acid; base	soils 194–6
perchlorate ion (ClO ₄ -) 45, 59, 83–4	solubility
perovskites 124–5,	aqueous 59–62
bond graph, creation of 144–143	of soft cations 62
crystal chemistry 186–8	solution
properties, physical 188–92, 193	aqueous 59–62
space group, selection of 153–6	entropy of, cations 57
pH 58-9	non-aqueous 62–3
phase transformation	space 121–2
displacive 171–2	constraints imposed by 32, 72, 164–78
reconstructive 172–4	space group 121–33
phosphate, see PO ₄ ³⁻	used in modelling 151–7
physics, applications in 186–93	space group spectrum
pi-bonding 199, 209	defined 130
pKa 47, 87, 109	tables of 233–9
PO ₄ ³⁻ 45, 47, 58, 107-8, 216, 246	spanning tree 22
protonated 58–9, 82, 202	spectroscopy
polyhedra	infra-red 110, 203
coordination 64–74	Raman 110
linking of 147–51	see also EELS; EXAFS; XAFS; XANES;
probability density function 158–9	XAS
protein	sphalerite (ZnS) 24, 153, 162, 214
Ca-binding 159, 205	SrTiO ₃ 144–5, 153–4, 193
Na-binding 204	stability 49n
see also enzyme	steric effects, see strain, lattice induced;
proton affinity 195	hydrogen bond, anion-anion repulsion in
	stoichiometry
quadrupole coupling constant 198	lack of in inorganic crystals 169, 174–6
quantum mechanics 6, 160, 216-19	strain
	electronic 90–104, 185, 189
radii	lattice induced 124, 164–8, 185, 187
ionic 65–6	effect on thermal expansion 115
Pauling 66–7	relaxation of 168–74
radius ratio rule 65–6	see also bond, strain; crystal structure,
RbBr 87	strained stress, see strain
RbClO ₄ 214	
refinement of model structure 160-1	structure making and breaking 57
relaxation 168–172	structure, see crystal structure
relaxors 189	sulphate ion (SO_4^{2-}) 45-6 protonated 58-9
repulsion	
interatomic 28, 64–9, 209–10	superconductivity 171, 189–90 surface 195–6, 200–1
O-O 67-9, 71, 76-80	adsorption on 201
resonance 212	charge 195
rutile, see TiO ₂	proton affinity of 195
	- · · · · · · · · · · · · · · · · · · ·
ShO= 04 06	symmetry asymmetric unit 125
SbO ₃ 94, 96 Sabland dia mana 150 1	of bonded neighbours 130–2, 151
Schlegel diagrams 150–1	crystallographic point groups 129
silicates	entropy as a measure of 145, 155–6
enumeration of 148	glide plane 126
formation 52	O-100 President

symmetry (cont.):	determination of 182-3
Hermann-Mauguin symbols 127n	non-integral 170–1
inversion 126	see also bond valence
maximum, principle of 29n, 31-3, 71, 133,	valence map 157-60, 190-1, 205
136, 213	valence matching principle 49, 70
mirror plane 126	applications 51–52, 194
non-translational unit 127–9	in aqueous solutions 60–61
packing group 156–7	in melts $62-3$
rotation 126	in modelling 142–4
screw axis 126	valence sum rule 28, 32, 213
site multiplicity 128–9, 151	valence unit, defined 23n
site symmetry 127–9, 151	VSEPR (valence shell electron pair repulsion)
special positions 126–9	model 93-4, 97, 215
in structure modelling 6	1110401 72 1,77,210
translational 122	
Wyckoff positions 127–32, 151–2	water 85
thermal expansion 113–7, 194	bonding strength 53–4, 246
Ti ⁴⁺ 101-4, 244	reaction with anions 57–9
TiO ₂ 17–18, 23, 29, 150–1, 200–1	reaction with cations 55–7
T1+ 50, 92, 94, 97-8, 245	see also hydrogen bonds; solubility, aqueous
Tl ₃ BO ₃ 97	whitlockite (Ca ₃ (PO ₄) ₂) 49
TINO ₃ 97	wurtzite (ZnO) 24–5, 29, 73–4, 143, 153,
topology 7, 20–3	214
of the electron density 216–19	
of the Madelung field 220	XAEG 104 106 107
modelling 135–57	XAFS 194, 196, 197
transition metal 38, 198–104	XANES 183, 197
bond valence parameters for 199, 225–6,	XAS 196
229–30	Xe ⁶⁺ 94
bonding strength 244–5	x-ray, see diffraction, x-ray
complexes 198–200	
electronic distortions in 98–104	YBCO (YBa ₂ Cu ₃ O _{6+x}) 171, 189, 193
pi-bonding in 199	TBCO (TBa ₂ Cu ₃ O _{6+x}) 171, 169, 193
trifluoroacetate ion 36, 87, 109–10, 208–9	
two-body potential model, see ionic model	zeolites 149, 196-7
	Zn^{2+} 24, 51, 62, 64–5, 68, 73–4, 245
Urey-Bradley force field 110-12	ZnBr ₂ 62
	ZnO see sphalerite, wurtzite
V^{5+} 102-4, 200, 244	ZnSb ₂ O ₆ 102
valence, atomic 3, 33, 210	ZnV_2O_6 102
,	