THERMOELECTRIC CONVERSION

Thermoelectric effects offer a means of converting heat to electric power using only solid-state components. By supplying electrical power to a thermoelectric material, it may also be used to produce refrigeration. Because a thermoelectric system has no moving parts, it may be reliable and compact. However, currently available power generators and refrigerators based upon thermoelectric effects are too expensive and inefficient for large-scale applications. Today, thermoelectric generators are used to produce electric power in satellites and thermoelectric refrigerators are used to cool small heat loads or in situations requiring portability.

In this article, we review the physics of thermoelectric effects and survey some present and potential applications of thermoelectric technology. Then an explanation of the thermoelectric effects and the operation of thermoelectric generators and refrigerators is given. There is no attempt to be comprehensive here as the detailed theory of thermoelectric effects has been well described elsewhere (1,2).

Following this, we briefly discuss the present status of thermoelectric refrigeration and power generation. These technologies are commercially active, with thermoelectric options dominating several niche markets. We also describe several lines of research that attempt to improve the efficiency of thermoelectric materials.

Finally, a new research field, cryogenic thermoelectric refrigeration, is described. Here, the efficiency can be quite high, so that the temperature may be reduced by a large factor. Also, we describe proposed designs for thermoelectric refrigeration using quantum-scale devices as well as recent experimental verification of these concepts in superconducting tunnel junctions.

THERMOELECTRIC EFFECTS

Thermoelectric effects occur because electrons and holes (which are vacancies in the electron sea) in conductive materials carry energy. Thermal energy at a temperature T (in K or Kelvin, measured from absolute zero) is distributed among all parts of a conductive material—the atoms making up the crystal lattice, the electrons, and the holes. As a result, electrons and holes have a range of energies; the electronic "energy spread" in a metal is a few times $k_B T$, where k_B is Boltzmann's constant. A thermoelectric effect occurs when the most energetic (or "hot") electrons and holes are transported preferentially during current flow in a conductive material. In a sense, the hot electrons and holes "evaporate" from one part of a material to another, cooling the region that they leave in the same way as the evaporation of water has a cooling effect.

There are several distinct but related physical effects that arise from this heat capacity of electrons and holes. When an electric current is driven through a thermoelectric material (for instance, by applying a voltage across the thermoelectric material), a heat flow occurs as well. This is called the Peltier effect, which is the basis of thermoelectric refrigeration. When one end of a piece of thermoelectric material is hotter than the other, a voltage develops across the material. This is called the Seebeck effect, which is used in thermoelectric power generation. Finally, when a temperature gradient exists inside a thermoelectric material, a gradient in the electric potential develops due to the Thomson effect. We will not discuss the Thomson effect here, since it is beyond the scope of this article, but more details may be found in Refs. 1–3.

These effects are known in the science of thermodynamics as reversible processes (1), in the sense that they may operate in the forward or in reverse directions. For instance, by reversing the direction of current flow in a thermoelectric refrigerator, the direction of heat flow is reversed, thereby causing heating instead of cooling. The efficiency of thermoelectric refrigerators and generators is limited by certain irreversible phenomena (1). The two main irreversible effects are thermal conduction and electrical resistance.

When a temperature gradient exists in any material, heat flows through the material to minimize the temperature gradient. This is clearly an irreversible process, otherwise objects would spontaneously develop cold and hot spots until they cracked or evaporated. Thermal conduction in a thermoelectric refrigerator represents a heat leak. In a thermoelectric generator, it is manifest as a power loss.

The passage of electricity through a conducting material is accompanied by the generation of heat, as the electrons and holes lose energy to various mechanisms such as the crystal lattice. Similar to thermal conduction, this resistive process is irreversible. If it were reversible, then a warm object would spontaneously emit electric current and cool itself to absolute zero. Also similar to thermal conduction, resistive losses represent an irreversible heat leak in a thermoelectric refrigerator and a power loss in a thermoelectric generator.

Under some conditions, thermoelectric effects take on an irreversible nature when they are driven past the "small-signal" limit (4–6). In the following, we will discuss situations under which these extreme conditions are of benefit to thermoelectric refrigeration.

A generic thermoelectric circuit is shown in Fig. 1(a). The thermoelements **n** and **p** embody the thermoelectric effects in this generic circuit. In the *positive* thermoelement **p**, electric current I and heat Q flow in the *same* direction. In the *negative* thermoelement **n**, heat is conducted in the direction *opposite* to current flow. In the circuit of Fig. 1(a), the thermoelements **n** and **p** are said to be thermally in parallel, as heat flows through each in parallel, and electrically in series, because electric current must traverse them sequentially. To enhance the thermoelectric performance of this circuit, it can be seen from Fig. 1(b) that many more such elements may be added so that they are electrically in series, and thermally in parallel.

The circuit is completed by metallic elements **R**, $\mathbf{E_n}$ and $\mathbf{E_p}$, which serve as conductors and heat sinks. **R** is a "reservoir" that is attached to a heat source (in the case of a thermoelectric generator) or to a device to be cooled (in a thermoelectric refrigerator). $\mathbf{E_n}$ and $\mathbf{E_p}$ are "electrodes" that are used to electrically connect the thermoelectric circuit to an external electric circuit (a current source to drive thermoelectric refrigeration or an electric load in the case of thermoelectric generation). $\mathbf{E_n}$ and $\mathbf{E_p}$ also are thermally sunk to a heat sink to maintain their temperature at T.

When the thermoelectric circuit of Fig. 1(a) is in operation, electric current flows from $\mathbf{E_n}$, through **n**, through **R**, through **p**, to $\mathbf{E_p}$. Heat Q flows from **R**, through **n** and **p**, to $\mathbf{E_n}$ and $\mathbf{E_p}$. In the case of a thermoelectric refrigerator, a voltage is applied between $\mathbf{E_p}$ and $\mathbf{E_n}$ to drive an electric current which causes the flow of heat Q from the heat load to the heat sink by the thermopower of **n** and **p**. For thermoelectric power generation, a source of heat is applied to **R**, which causes heat Q to flow down. Due to the thermopower of **n** and **p**, electric

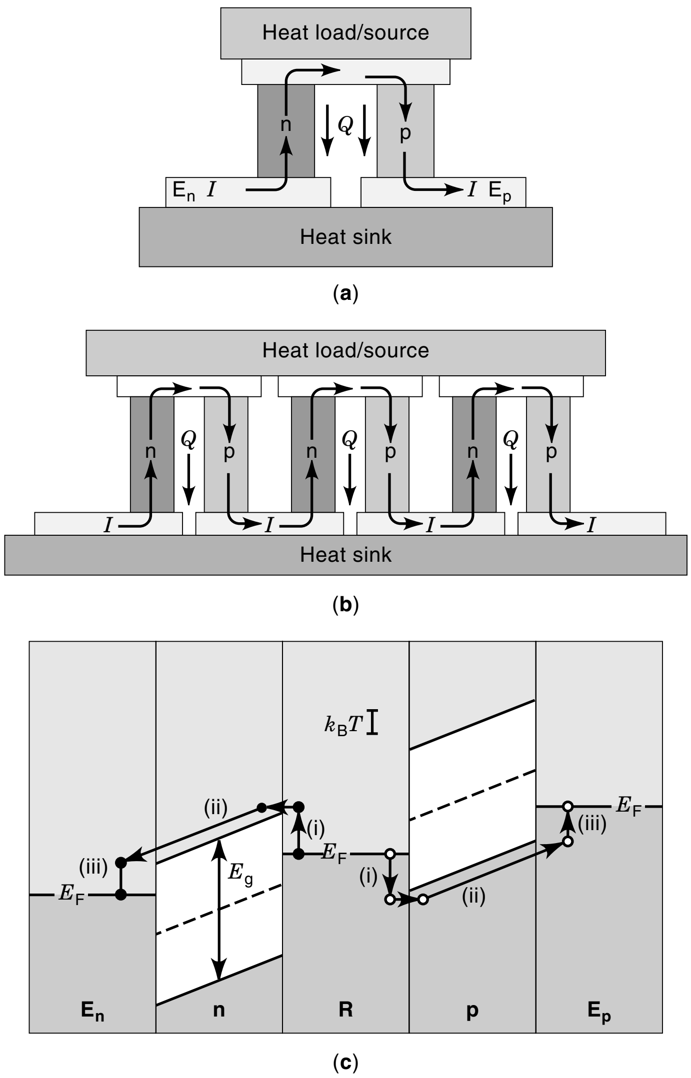

Figure 1. Diagram of a thermoelectric device. (a) Heat flows vertically and electric current flows from left to right. (b) Placing multiple thermoelements electrically in series and thermally in parallel increases the cooling power. (c) Representation of the microscopic mechanism of thermoelectric effects in terms of electron energy states in each material. Vertical scale is electron energy.

current I flows up through **n** and down through **p**, the net result of which is to drive electric current from $\mathbf{E_n}$ to $\mathbf{E_p}$, which may be used to drive an electric load.

Any thermoelectric effect is caused by differences in the energy levels electrons occupy in a material, and hence may be visualized by tracing the path of electrons through these different energy levels. Such a diagram is shown in Fig. 1(c), which represents the energy levels (vertical scale) that electrons occupy when they are traveling through the circuit components of Fig. 1(a).

Several aspects of solid-state physics must be understood to interpret Fig. 1(c). First, electrons are thermally excited so that they are continually absorbing and emitting energy from other electrons and the crystal lattice. The typical amount of energy exchanged is about k_BT, as mentioned earlier. The magnitude of k_BT is shown in Fig. 1(c) for reference. If we could employ "Maxwell's demon" (3) to capture the electrons when they were excited to a high energy and use their excess energy to perform work, then heat would be extracted from the metal, resulting in a cooling effect. This is how a thermoelectric refrigerator works.

Consider an electron in **R**, at an energy called the "Fermi level" $\mathbf{E_F}$, which is essentially the average energy for the electrons that participate in electrical transport (3). Because electrons belong to the particle class called Fermions, they fill energy states one at a time until $\mathbf{E_F}$ is reached. Thermal excitations occur for energies around $\mathbf{E_F}$, with a range of k_BT. Some states below $\mathbf{E_F}$ are vacated by an electron, which has absorbed energy to be excited to an empty state. These vacant states are called holes, and can move about in the same way as electrons. One can imagine this as a percolation process, although in terms of quantum mechanics electrons and holes are described similarly (3). The excitation energy of a hole is opposite to that of an electron; thermally excited holes lie below $\mathbf{E_F}$.

To understand the microscopic operation of a thermoelectric circuit, we can trace the path of an electron through Fig. 1(c). (i) First, the electron in **R** is thermally excited to above $\mathbf{E_F}$. Then the electron may move to the conduction band of the semiconductor **n**. This band is shown with a slope because the electrical resistance of **n** causes a voltage drop with distance (ii). Finally, the electron is deposited in the electrode $\mathbf{E_n}$, where it gives up its "extra" energy relative to $\mathbf{E_F}$. An analogous path for a hole is shown in Fig. 1(c) as well.

One thing to note is that the direction of current flow for both the electron and hole paths in Fig. 1(c) is to the right because the charge of the electron is negative and the charge of a hole is positive. An analogy between electrostatic potential energy (as is shown in this diagram) and gravity might be drawn here; it is as though electrons slide down slopes in the energy bands and holes percolate up like bubbles. Thus, no "extra" current source must be connected to **R** for a current to traverse the circuit. It is also important to note where the different energy-exchange mechanisms are taking place. In Step (i), the electron and hole absorb thermal energy from the other electrons or the crystal lattice of **R**, which in turn absorbs heat from the heat source in the case of thermoelectric generation or the heat load in the case of thermoelectric refrigeration. In Step (ii), the electron and hole give up heat by Ohmic heating due to the electrical resistance of **n** and **p**. Finally, in Step (iii), the electron and hole release their excitation energy to the electrodes $\mathbf{E_n}$ and $\mathbf{E_p}$, which then release the heat to the heat sink. The heat leak due to the thermal conductivity of **n** and **p** is not shown here, since it is mostly due to the crystal lattice rather than the electrons.

THERMOELECTRIC REFRIGERATION

By applying electric current to the thermoelectric circuit of Fig. 1(a), heat is extracted from **R**. This refrigerator is driven by the Peltier effect. Specifically, if a current I is driven through a thermoelectric material, a flow of heat

$$Q = \Pi I \tag{1}$$

accompanies the flow of current; Π is known as the Peltier coefficient of the thermoelectric material.

For a negative thermoelement such as **n** in Fig. 1(a), Π is negative. Thus, the electric current and heat current flow in opposite directions in **n**, so that while the current flows up, heat flows down. For a positive thermoelement such as **p** in Fig. 1(a), Π is positive. In this case, the electric and heat currents flow in the same direction; in Fig. 1 (a), both heat and electric current flow downward through **p**. Thus, heat flows downward through both **n** and **p** so that both contribute to cooling **R**.

In a real thermoelectric refrigerator, there are other sources and flows of heat that must be considered when trying to understand the refrigerating behavior. If the thermoelectric refrigerator is cooling a heat load (e.g., a semiconductor diode laser or a solid-state infrared detector), which is producing a heat flow Q_L, then this heat flows into **R** and adds to the heat load that the thermoelements must carry away to accomplish a given amount of refrigeration.

In an ideal thermoelectric material, there would be no electrical resistance, and hence no Ohmic heating. However, this is not the case for real materials. If the electrical resistance of **n** is R_n and that of **p** is R_p, then Ohm's law (3) dictates that the amount of heat I^2R_n is generated in **n** and $I^2R_p$is generated in **p**. Since this heat is generated uniformly throughout the thermoelectric materials, it is generally assumed that half the heat is transmitted up to **R**, and half goes down to $\mathbf{E_n}$ and $\mathbf{E_p}$.

As the thermoelectric refrigerator operates, the flow of heat Q causes a temperature difference ΔT to develop between **R** and $\mathbf{E_n}$ and $\mathbf{E_p}$. In an ideal thermoelectric material, the thermal conductivity would be zero, so that no heat leaked back across to the cold side. However, thermoelectric materials always have a significant thermal conductivity. Assume that the values of thermal conductance for **n** and **p** are K_n and K_p, respectively. Then a heat leak of $K_n\Delta T$ flows upward through **n** and $K_p\Delta T$ flows through **p**.

Without a heat load, the net heat that flows from **R** to $\mathbf{E_n}$ is

$$Q_n = -\Pi_n I - K_n \Delta T - \tfrac{1}{2} I^2 R_n \tag{2}$$

and that flowing from **R** to $\mathbf{E_p}$ is

$$Q_p = \Pi_p I - K_p \Delta T - \tfrac{1}{2} I^2 R_p \tag{3}$$

The *cooling power* of the thermoelectric refrigerator is the sum of Q_n, Q_p, and the heat load $-Q_L$

$$\begin{aligned} Q_{\text{cooling}} = Q_n + Q_p - Q_L &= (\Pi_p - \Pi_n)I - (K_n + K_p)\Delta T \\ &\quad - \tfrac{1}{2} I^2 (R_n + R_p) - Q_L \end{aligned} \tag{4}$$

Q_{cooling} represents the heat flow that the thermoelectric refrigerator draws from **R** and the heat load. If Q_{cooling} is positive at any temperature, then **R** will drop in temperature due to the net cooling action. If Q_{cooling} is positive in the absence of a temperature difference ΔT, then **R** will cool until it sits at a temperature below the "ambient" temperature T.

The coefficient of performance φ of a thermoelectric refrigerator is defined to be the ratio of the cooling power to the electrical power P required to drive the current I through the refrigerator

$$\varphi = \frac{Q_{\text{cooling}}}{P} \tag{5}$$

P is computed by the relationship $P = IV$, where V is the voltage drop across the device. To compute V, we need to describe the other major thermoelectric effect—the Seebeck effect.

A contact potential V_{contact} generally exists at a junction of dissimilar materials. In thermoelectric devices, this contact potential and its temperature dependence are utilized. In particular, the contact potential between a thermoelectric material (e.g., **n** or **p**) and an ordinary metal (e.g., **R**, $\mathbf{E_n}$, or $\mathbf{E_p}$) is given by

$$V_{\text{contact}}\{\textbf{thermoelectric}, \textbf{metal}\} = \alpha T + V_0 \tag{6}$$

where V_0 depends upon the particular materials chosen and the text in curly brackets indicates the direction of positive contact potential, in this case from thermoelectric material to metal. The linear temperature coefficient α in the contact potential is called the Seebeck coefficient. Because the junctions at **R** and those at $\mathbf{E_n}$ and $\mathbf{E_p}$ sit at different temperatures, a net potential drop occurs across each thermoelement

$$\begin{aligned}
V_n &= V_{\text{contact}}\{\mathbf{E_n}, \mathbf{n}\} + V_{\text{contact}}\{\mathbf{n}, \mathbf{R}\} \\
&= -V_{\text{contact}}\{\mathbf{n}, \mathbf{E_n}\} + V_{\text{contact}}\{\mathbf{n}, \mathbf{R}\} \\
&= -(\alpha_n T + V_0) + (\alpha_n (T - \Delta T) + V_0) \\
&= -\alpha_n \Delta T; \\
V_p &= V_{\text{contact}}\{\mathbf{R}, \mathbf{p}\} + V_{\text{contact}}\{\mathbf{p}, \mathbf{E_p}\} \\
&= -V_{\text{contact}}\{\mathbf{p}, \mathbf{R}\} + V_{\text{contact}}\{\mathbf{p}, \mathbf{E_p}\} \\
&= -(\alpha_p (T - \Delta T) + V_0) + (\alpha_p T + V_0) \\
&= \alpha_p \Delta T
\end{aligned} \tag{7}$$

Due to the electrical resistance of the thermoelements, there is also an Ohmic voltage drop $I(R_n + R_p)$ in the circuit; thus the total power supplied to the thermoelectric refrigerator is

$$\begin{aligned}
P &= IV \\
&= I(\alpha_p - \alpha_n)\Delta T + I^2(R_n + R_p)
\end{aligned} \tag{8}$$

The coefficient of performance becomes

$$\begin{aligned}
\varphi &= \frac{Q_{\text{cooling}}}{P} \\
&= \frac{(\Pi_p - \Pi_n)I - (K_n + K_p)\Delta T - \frac{1}{2}I^2(R_n + R_p) - Q_L}{I(\alpha_p - \alpha_n)\Delta T + I^2(R_n + R_p)}
\end{aligned} \tag{5$'$}$$

Generally, one would like to know the best coefficient of performance that a given material system can supply. For this case, we consider the limit with no load ($Q_L = 0$). Also, we consider the case when the thermoelements have similar properties, namely

$$\begin{aligned}
&R_n = R_p \equiv R; \quad K_n = K_p \equiv K; \quad -\alpha_n = \alpha_p \equiv \alpha; \\
&-\Pi_n = \Pi_p \equiv \Pi
\end{aligned} \tag{9}$$

so that the coefficient of performance simplifies to

$$\varphi = \frac{\Pi I - K\Delta T - \frac{1}{2}I^2 R}{I\alpha\Delta T + I^2 R} \tag{5$''$}$$

We can further simplify Eq. (5″) using the Kelvin relationship

$$\Pi = T\alpha \tag{10}$$

which may be derived from the Onsager relation in the theory of irreversible thermodynamics. Equation (10) is only valid for small V and ΔT. This topic is beyond the scope of this article; more details may be found in Refs. 2–4.

We can find the value of I at which Eq. (5″) reaches its maximum value by taking the derivative of ϕ with respect to I and setting it equal to zero. After performing this operation and substituting this current value into Eq. (5″), we arrive at the optimal value of the coefficient of performance

$$\begin{aligned}
\varphi_{\max} &= \frac{T - \Delta T}{\Delta T}\left(\frac{\sqrt{1 + Z\overline{T}} - \dfrac{T}{T - \Delta T}}{\sqrt{1 + Z\overline{T}} + 1}\right) \\
&= \varphi_{\text{Carnot}}\left(\frac{\sqrt{1 + Z\overline{T}} - \varphi_{\text{Carnot}}^{-1}}{\sqrt{1 + Z\overline{T}} + 1}\right)
\end{aligned} \tag{5$'''$}$$

where $\overline{T} \equiv 1/2(T + (T - \Delta T))$ is the mean temperature in the thermoelements and $\varphi_{\text{Carnot}} = (T - \Delta T)/\Delta T$ is the Carnot thermodynamic maximum efficiency of a refrigerator (1–3). The quantity

$$Z = \frac{\alpha^2}{RK} \tag{11}$$

is known as the thermoelectric figure of merit, and has the dimensions of inverse temperature. Thus, the quantity

$$ZT = \frac{\alpha^2}{RK}T \tag{12}$$

is known as the dimensionless figure of merit, which summarizes the thermoelectric performance of a material at temperature T. More analytical details of the efficiency of a thermoelectric refrigerator may be obtained from Refs. 1 and 2. Here, we will restrict ourselves to general comments regarding the status of thermoelectric technology.

The material parameters of the thermoelements enter Eq. (5‴) only through Z. In this sense, the figure of merit summarizes the thermoelectric performance of a thermoelectric material. Although Eq. (11) includes the electrical parameters R and K, we can see that it may also be defined in terms of intensive material parameters. For instance, suppose that the thermoelements are of uniform cross-sectional area A and length L. Then the thermal conductance and electrical resistance may be written as

$$K = \kappa \frac{A}{L}; \quad R = \rho \frac{L}{A} \tag{13}$$

where κ is the thermal conductivity and ρ is the electrical resistivity of the thermoelements. The figure of merit then becomes

$$Z = \frac{\alpha^2}{\rho\kappa} \tag{11$'$}$$

which contains only intensive quantities, and thus the thermoelectric figure of merit is itself an intensive material parameter. The dimensionless figure of merit becomes

$$ZT = \frac{\alpha^2}{\rho\kappa}T \tag{12$'$}$$

Maximizing ZT is thus seen as the central goal of thermoelectric materials research. In practice, it has been difficult to exceed $ZT = 1$ (at room temperature). There has even been speculation that $ZT = 1$ represents a fundamental physical limit (1,2). In any case, ZT must be in the range of 3 to 5 for thermoelectric refrigeration to compete with conventional vapor-compression refrigeration (1). Efficiency is important in a refrigerator, both in terms of the economic and environmental costs of power consumption and in terms of the amount of heat rejected for a given amount of cooling. Thus, thermoelectric materials have not yet offered a strong competitor in the area of large-scale refrigeration or air conditioning.

The practical difficulties in maximizing ZT are in a compromise between the material parameters that comprise ZT. For instance, metals have a low electrical resistivity but also a low thermopower and a high thermal conductivity. The least thermally conductive materials are often electrically insulating.

As it turns out, the best thermoelectric materials have been heavily doped semiconductors. Figure 2 shows a summary of the thermal and electrical properties of conductive materials as a function of electron concentration. It can be seen that electrical and thermal conductivity tend to increase with the electron concentration, whereas the thermopower tends to decrease. These factors lead to a peak in thermoelectric figure of merit in the semiconductor range.

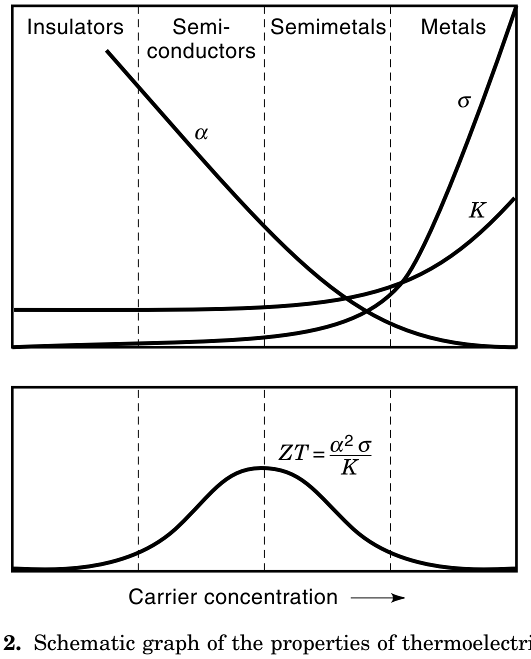

Figure 2. Schematic graph of the properties of thermoelectric materials as a function of electron concentration (1).

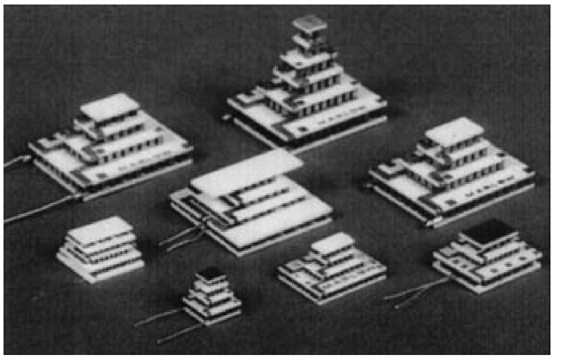

Figure 3. Photograph of a commercially available thermoelectric refrigerator using Bi_2Te_3 semiconductors as thermoelements. Product literature from Marlow Industries, Inc.

The best materials for thermoelectric refrigeration are compound semiconductors. The most common material is bismuth telluride (Bi_2Te_3). This material is used in commercially available thermoelectric refrigerators (such as the one shown in Fig. 3), and may attain ZT values approaching 1. In fact, thermoelectric refrigerators (such as the one depicted) have a growing market in cooling solid-state electronic devices such as diode lasers and infrared radiation detectors. They are also dominant in areas where compactness or portability are required, such as in portable refrigerated food containers or biological-specimen transport vessels. Also, thermoelectric refrigerators can be operated in reverse to heat a sample; thus active temperature control is possible, as utilized in biological applications.

Another practical aspect of thermoelectric technology is the use of multiple stages in commercial devices. These can offer improved efficiency because the design and materials properties can be optimized for the operating temperature of each stage. Lower temperatures can be achieved this way in thermoelectric refrigerators.

THERMOELECTRIC POWER GENERATION

The circuit of Fig. 1(a) may be used as a thermoelectric generator by heating **R**. Heat Q_S is supplied from a heat source to the hot electrode, which causes a flow of thermoelectric current I. The thermal conductance K of the thermoelements allows heat to leak from the hot electrode to the ambient-temperature heat sink, and Ohmic heating of the thermoelements dissipates some of the generated power. The efficiency η of a thermoelectric generator is defined to be

$$\eta = \frac{P}{Q_s} = \frac{IV}{Q_s} \tag{14}$$

where P is the electrical power supplied to a load through the ambient-temperature electrodes and V is the total voltage drop across the generator. By following a line of reasoning analogous to the forementioned one for thermoelectric refrigeration, the efficiency of a thermoelectric generator may be expressed in terms of the dimensionless figure of merit of the thermoelement materials

$$\begin{aligned}\eta &= \frac{\Delta T}{T+\Delta T}\left(\frac{\sqrt{1+Z\overline{T}}-1}{\sqrt{1+Z\overline{T}}+\left(\dfrac{T}{T+\Delta T}\right)}\right)\\ &= \eta_{\text{Carnot}}\left(\frac{\sqrt{1+Z\overline{T}}-1}{\sqrt{1+Z\overline{T}}+(1-\eta_{\text{Carnot}})}\right)\end{aligned} \tag{14'}$$

where $\overline{T}$ and Z are defined in the foregoing and $\eta_{\text{Carnot}} = \Delta T/(T + \Delta T)$ is the Carnot thermodynamic limit on the efficiency of a generator (1–3). As discussed in the foregoing, ZT is around 1 at best. For this value, η ranges from $0.2\eta_{\text{Carnot}}$ to $0.3\eta_{\text{Carnot}}$. For a temperature difference of 100°C with $T = 300$ K, $\eta_{\text{Carnot}} = 0.25$ and the thermoelectric efficiency with $ZT = 1$ would be under 5%. Thus, thermoelectric power generation is not competitive with more conventional means. For comparison, a solar cell may have a generating efficiency of 8%, an automobile engine may have 15% efficiency, and a steam-generating plant may achieve 20 to 40% efficiency (1).

What would it take for thermoelectrics to compete in power generation? Suppose for a moment that ZT for a given material was optimized over the temperature range 300 to 600 K, and that $T = 300$ K and the heat-source temperature is 600 K. Then $\eta_{\text{Carnot}} = 0.5$ and, for $ZT = 1$, the generator becomes 11% efficient. For $ZT = 3$, the generator becomes 20% efficient, the point at which it begins to compete. Thus, if thermoelectric materials are to be competitive with more conventional systems for mainstream power-generation applications, ZT must be improved by at least a factor of three. Furthermore, the materials must be inexpensive, whereas semiconductors tend to be fairly expensive. Thus, the prospects for large-scale power generation using thermoelectrics are not great at present.

As in refrigeration, the present applications of thermoelectric power generation take advantage of the compactness and reliability of solid-state components. The most prominent application is in power generation for satellites, in which a radiation source such as a radioactive isotope is used to supply heat to the generator. The material system of choice is the alloy of silicon and germanium, which has a lower thermal conductivity than the crystalline forms due to enhanced phonon scattering, and is thermally stable enough to operate at a high hot-electrode temperature. These generators have been found to be extremely reliable, and nuclear power provides sufficient heat to overcome the relatively low generating efficiency (1).

EFFORTS TO IMPROVE THERMOELECTRIC EFFICIENCY

The traditional approach to optimizing the efficiency of thermoelectric conversion has been incremental. For instance, commercial devices today are still based upon Bi_2Te_3 and related compounds, developed in the 1950s and 1960s, with advances mostly coming in the form of material purity or means of attaching thermoelements.

Recently, a number of workers have become interested in revisiting the basic assumptions of thermoelectric conversion (4–10). Later, we will discuss the new field of cryogenic thermoelectric refrigeration (4,5,7,8). Here, we briefly summarize recent work in thermoelectric conversion at higher temperatures, which could impact the broadest range of applications.

A notable improvement in materials synthesis over the last few decades has been thin-film deposition with high crystalline quality and purity by using methods such as molecular-beam epitaxy (11). With this capability, traditional semiconducting materials may be formed into structures not available to the original designers of thermoelectric devices in the 1950s and 1960s.

Accordingly, several groups have begun exploring the thermoelectric properties of multilayer structures composed of layers of the Bi_2Te_3 and related compounds traditionally used as thermoelectric elements (9). This activity was initially of a theoretical nature, and it was observed that the thermoelectric figure of merit of these materials in a properly designed multilayer may be increased from its bulk value. This was confirmed experimentally, but the figure of merit of the entire structure, including nonthermoelectric layers, has not been demonstrated yet to exceed the bulk value of the thermoelectric materials.

It has recently been proposed (6) that thermionic effects might be used to overcome limitations imposed by the “linear-response” regime implicitly assumed in the traditional theoretical understanding of thermoelectric effects as described in earlier. In a thermionic effect, electrons or holes are thermally excited across a large potential barrier and then transported away. In terms of the microscopic picture of Fig. 1(c), the conduction would become thermionic if the barrier between **R** and **n** or **p** were much higher than k_BT. To overcome the potential barrier, each electron or hole must absorb a large amount of energy from the crystal lattice; thus a large amount of heat is extracted for a relatively smaller amount of electric current than is the case for a traditional thermoelement. With thermionic effects, there is also the possibility of introducing a vacuum barrier or insulating material between electrodes to reduce heat leaks.

Another exciting area of materials research is along the traditional lines of bulk thermoelectric devices, but in new material systems. The skutterudites are a new thermoelectric system proposed recently (10). These materials have a complex crystal structure which frustrates heat flow, and can be doped to provide electrical conductivity. Initial measurements of the dimensionless figure of merit in this system have exceeded 1, with values of 1.4 to 1.5 being reported by several groups. Because the skutterudites family is unexplored and fairly extensive, there may exist a skutterudites thermoelectric material with a sufficiently high figure of merit and adequate thermal and mechanical stability to compete in more large-scale applications.

CRYOGENIC THERMOELECTRIC REFRIGERATION

At temperatures near absolute zero, the reduction in ambient thermal energy allows quantum-mechanical effects to dominate the properties of some types of matter, giving rise to extraordinary phenomena. Some metals lose all electrical resistance and fall into the superconducting state (3). The viscosity of liquid helium vanishes, causing it to flow over the sides of a container (3). This superfluidity of liquid helium gives rise

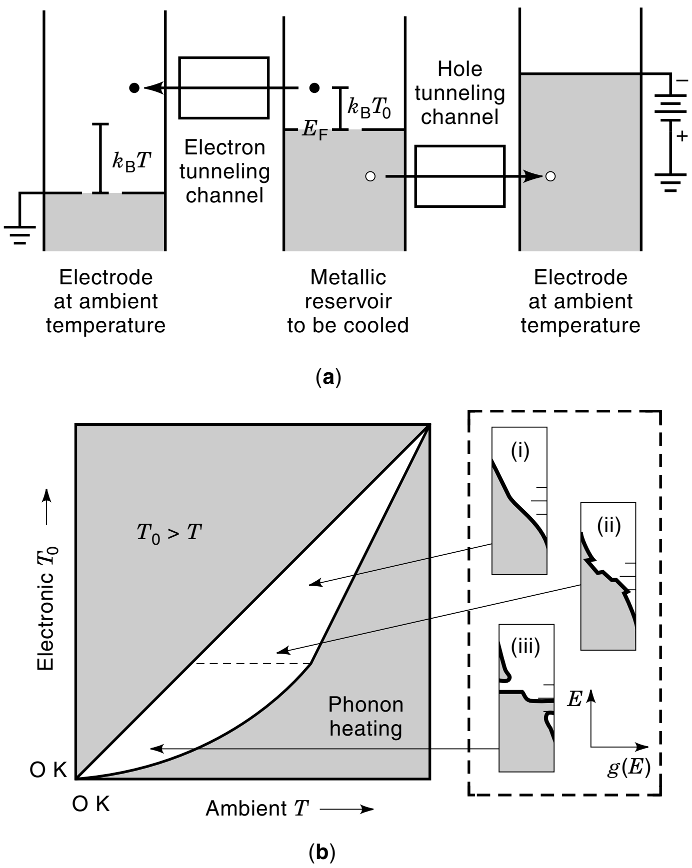

Figure 4. (a) Energy-level diagram and (b) temperature regime of operation of a cryogenic thermoelectric refrigerator. Reproduced from Ref. 5.

to thermodynamic properties, which are exploited in the dilution refrigerator, the most common means of performing experimental work at temperatures between 0.01 and 1 K.

The low-temperature properties of matter of interest here are related to phonons, the quantum-mechanical manifestation of vibrations in the crystalline lattice. Phonons are the predominant repository of heat in solids at temperatures more than a few kelvins above absolute zero. Near absolute zero, however, electrons in a metallic solid hold most of the heat, and hence thermal energy. Thus, cooling the electrons in a metal at these low temperatures should provide an effective means of refrigerating the entire metal.

Because it is a vibration or deformation wave in the crystalline lattice, a phonon has a wavelength. At higher temperatures, the predominant wavelength—that of phonons that carry the thermal energy k_BT—is shorter. Near absolute zero, this phonon wavelength becomes so long that it barely interacts with electrons in the solid, analogous to the way that broad swells on the sea do not overturn a small boat as do abrupt breakers.

This "decoupling" of the electrons and the phonons in a solid enables the operation of certain devices based upon "ballistic" electron transport (12). It also allows the temperature of the electrons in small devices to be controlled independently of the phonon temperature. This is the basis of the first experimental demonstrations of cryogenic thermoelectric refrigeration, to be discussed in the following.

The structure and operation regime of a cryogenic thermoelectric refrigerator are depicted in Fig. 4 (5). In Fig. 4(a), the metallic reservoir at the center is cooled by the removal of hot electrons and holes and their deposition in electrodes that reside at the "ambient" temperature, which here may refer to the phonon temperature or the true ambient temperature of the medium surrounding the refrigerator structure. Physically, such a refrigerator would probably be comprised of thin metal films or semiconductor layers on a substrate; the diagram of Fig. 4(a) shows electron energies, rather than physical structure.

In this light, the vertical position of an electron in Fig. 4(a) corresponds to its energy. The "sea" of electrons in the various structures corresponds to the Fermi sea of electrons in a metal. It is at the surface E_F of this Fermi sea that thermal excitations—in the form of thermally excited electrons and holes—are contained. Thus, it can be seen that a hole below the "sea level" of E_F carries the same amount of thermal energy as an electron excited an equal amount above E_F. If this Fermi sea of electrons is at temperature T, the average excitation energy of its electrons and holes from E_F is roughly k_BT (3). In addition, we use the term "hole" hereafter to refer to a vacant electronic state in a metal, which is more general than the definition used for p-type semiconductor material (3). This nomenclature simplifies the understanding of a thermoelectric device.

The voltage differences between different pieces of metal, such as the electrodes and the reservoir of Fig. 4(a), are reflected in differences between their Fermi levels. By applying a voltage to this structure, an electric current flows. The structures marked "electron tunneling channel" and "hole tunneling channel" will be explained in more detail in what follows, but the basic idea is the following. Because the temperature of an electron sea is defined by the energies to which electrons and holes are excited from the Fermi levels, removing the excited electrons and holes should cool the remaining electrons. The alternative to this selective process is to allow both electrons and holes to move arbitrarily through both interfaces, resulting in a loss of control over the direction of heat flow. The preferential control over the direction of heat flow during electrical transport is the basis of thermoelectric refrigeration.

Thus, for thermoelectric refrigeration to be possible, it is required to preferentially remove excited charge carriers from near the Fermi level. The conventional way of doing this is to use a negative thermoelement, which carries thermally excited electrons away from the reservoir, and a positive thermoelement that removes thermally excited holes. The terms "negative" and "positive" arise from the sign of the charge carriers. Another interpretation of these terms is that, for a positive thermoelement, heat and electric current flow in the same direction, whereas the opposite is true for a negative thermoelement.

As was mentioned in the foregoing, an important difference between the thermal properties of matter at room temperature and cryogenic temperatures is the fact that the electrons hold most of the heat within 1 K of absolute zero. Combined with the fact that electrons and phonons and other degrees of freedom of a metal tend to decouple at cryogenic temperatures, this gives rise to some exotic possibilities for thermoelectric refrigeration. Figure 4(b) shows a diagram of the ambient temperature T versus the electronic temperature T_0 for a "generic" thermoelectric refrigerator as shown in Fig. 4(a), in which we assume that the electrons are cooled independently of the phonons. There are several temperature regimes of interest.

In the upper left-half of the $\{T, T_o\}$ diagram of Fig. 4(b), the electronic temperature exceeds the ambient; thus this region is not of interest in a discussion of refrigeration. In the lower right-half, the electrons are cooler than the ambient, and there are situations one can image. First, if the ambient temperature T is too high, the electrons will absorb more energy from phonons than can be removed by the electron and hole tunneling channels, and hence the electrons will be heated. This situation is depicted for the hashed region in the lower right corner of the diagram.

The unhashed area to the center of the $\{T, T_o\}$ diagram of Fig. 4(b) is thus the region in which the refrigerator is operational. In this region, there are several additional types of behavior, which come into play according to the rate at which the electrons can "thermalize," in other words, refill states emptied by the electron and hole tunneling channels. In regime (i), the electron distribution $g(E)$ [shown as a function of electron energy E on the right-hand side of Fig. 4(b)], is continuous, and has a form expected for the thermally excited electron distribution near the Fermi level (3). However, as the temperature decreases [regime (ii)], the hot electrons and holes are removed at a rate approaching that at which the electrons scatter among themselves to smooth their energy distribution. Finally, at the lowest temperatures [regime (iii)], the bands of energy that are aligned with the electron and hole tunneling channels will be fully saturated by the cooling process. In essence, the electrons are not only decoupled from the phonons, but from each other, as far as the refrigeration process is concerned; and individual sets of energy states may be selectively cooled even when "hot" electrons and holes exist at other energies.

Figure 4(b) describes the case when the electrons and phonons are decoupled. To apply such a refrigerator, the "metallic reservoir to be cooled" would have to be able to exchange electrons with any heat load, which requires integral design and fabrication. Cryogenic thermoelectric cooling would be most useful when the electrons and phonons are coupled and the cooling power is strong enough to achieve bulk cooling. In the following, we will show two examples of cryogenic thermoelectric refrigerators and illustrate the temperature regime over which these limits apply.

THERMOELECTRIC REFRIGERATION USING QUANTUM-SCALE DEVICES

The promising nature of cryogenic thermoelectric refrigeration was suggested in 1993 (4), when it was proposed that quantum dots be used as thermoelements. Although this quantum-dot refrigerator has not yet been realized in practice, it is a good example because its efficiency can be shown to approach the Carnot limit (5). Figure 5(a) shows the physical structure and Fig. 5(b) shows the energy-level diagram of one such quantum-dot thermoelectric refrigerator. The individual electronic states of the quantum dots are separated by Δ, and each is lifetime-broadened by δ. These are the only important properties of quantum dots for this device—the quantum dots may actually be larger or smaller than the reservoir R to be cooled, depending upon the material system and the temperature range of interest (6).

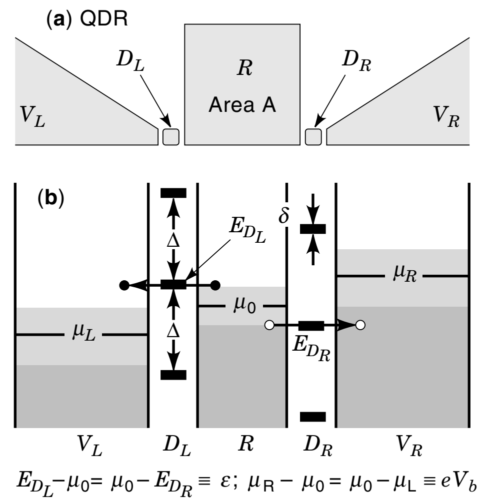

Figure 5. (a) Schematic of the physical structure and (b) energy-level diagram of a quantum-dot thermoelectric refrigerator. The quantum dots act as thermoelements removing hot electrons and holes from the reservoir R by resonant tunneling. This cools the remaining electrons in R. Reproduced from Ref. 5.

A quantum dot is a piece of metal so small that the individual quantum states, which electrons occupy, are separated by an energy comparable to or in excess of the thermal energy k_BT. In Fig. 5(b), the individual quantum states in the quantum dots are denoted by horizontal lines. One property of such states is that electrons and holes may travel through them from states aligned in energy with them, in a process called resonant tunneling. Thus, if a quantum state of a quantum dot is aligned in energy with the thermally excited electrons above the Fermi sea in R, the electron may undergo resonant tunneling to be removed from R and deposited in the electrode, where its excess energy is dissipated as heat. A similar process occurs for holes resonantly tunneling through the other electrode.

The net effect of these processes is the cooling of R as thermally excited electrons and holes are removed. In addition, it can be seen that electric current passes from left to right. Thus, this structure is a Peltier refrigerator with the left-hand quantum dot serving as the negative thermoelement and the right-hand quantum dot serving as the positive thermoelement. Now, of course, one might wonder under what circumstances such a device produces a significant cooling effect.

Most quantum-dot studies have taken place at or below 1 K, although quantum-dot devices have been demonstrated to work at room temperature as well (13). At 1 K, k_BT is 8.6×10^{-5} eV or 1.6×10^{-23} J. This is the amount of heat one could expect to remove from a piece of metal at 1 K by removing a typical electron that is thermally excited above the Fermi level. Resonant-tunneling through quantum dots typically produces electric currents in the range of 10^{-6} A, which is equivalent to the passage of 5×10^{12} electrons/s. Thus, a cooling power of 8×10^{-11} W could be extracted by such a device. Compared to a 100 W light bulb, this seems minuscule. However, the heats exchanged at 1 K are in the picowatt range, and electrons hold most of the heat at 1 K and below—there simply is not much heat to be spread around so near absolute zero.

The models of Ref. 5 indicate that a quantum-dot thermoelectric refrigerator could cool a micrometer-sized metallic reservoir of electrons in the 1 K regime; here, such a small collection of electrons is not strongly coupled to the crystal lattice and hence is not heated by the absorption of phonons. Thus, quantum-effect thermoelectric refrigeration might be a viable means of cooling microelectronic components that rely upon sub-1 K material properties (e.g., superconductivity or ballistic transport) in which a temperature difference between electrons and phonons is acceptable.

As it turns out, a thermoelectric refrigerator with quantum dots as thermoelements may be capable of bulk cooling at temperatures a thousand times lower (1 mK) or below (5). Due to the fine scale of the energy levels of quantum dots, this might be an effective means of microkelvin or nanokelvin cooling of metals. Such refrigerators have not been tested, however, thus their true performance is an open question. However, the thermoelectric transport properties of various quantum structures have been measured and found to be consistent with the assumptions of the theoretical simulations of Ref. 5. The greatest experimental challenge in the realization of a quantum-dot thermoelectric refrigerator remains the accurate measurement of the temperature of the electrons in R.

THERMOELECTRIC REFRIGERATION USING A SUPERCONDUCTING TUNNEL JUNCTION

Although resonant tunneling through a single quantum state is simple to model and may be capable of refrigeration near the Carnot limit, there are other low-temperature phenomena which may be exploited in the lab to perform refrigeration. One such system is a tunneling junction between a superconducting metal and one in the "normal" state. A normal-insulating-superconductor (NIS) refrigerator was demonstrated (7) shortly after cryogenic thermoelectric refrigeration was originally proposed (4).

The NIS refrigerator is depicted in Fig. 6. In a superconducting metal, electrons form into pairs, which in turn coalesce into the superconducting condensate, a macroscopic quantum state of matter from which an energy of 2Δ is required to excite them (3). When the required energy has been applied to an electron or hole, a subtle excitation called a quasi-particle is formed. This is represented in an energy-band diagram in Fig. 6(b) as a "forbidden gap" of 2Δ about the Fermi energy. Because paired electrons in the superconducting condensate have a lower energy than quasi-particles, one can say that quasi-particles carry heat.

In the NIS structure, refrigeration is accomplished by transport of thermally excited electrons above the Fermi level in R into quasi-particle states in the superconductor [in Fig. 6(b), the aluminum electrode serves this purpose]. Quasi-particles are transported through the Al electrode to be deposited (along with the heat they carry) in a heatsink (not shown in the figure). Thus, heat is removed from R to the "external" world through the quasi-particle states and R is cooled by the "negative thermoelement" Al electrode. In this experiment (7), a lead counterelectrode with a thin, high-conductance tunneling barrier (to maintain Fermi-level alignment) was used to inject electrons at the Fermi level. However, a second aluminum electrode identical to the one shown could be used in its place to extract thermally excited holes into hole-quasi-particle states, in a configuration analogous to the other thermoelectric refrigerators discussed in this article. In this case, the second aluminum electrode would be the positive thermoelement.

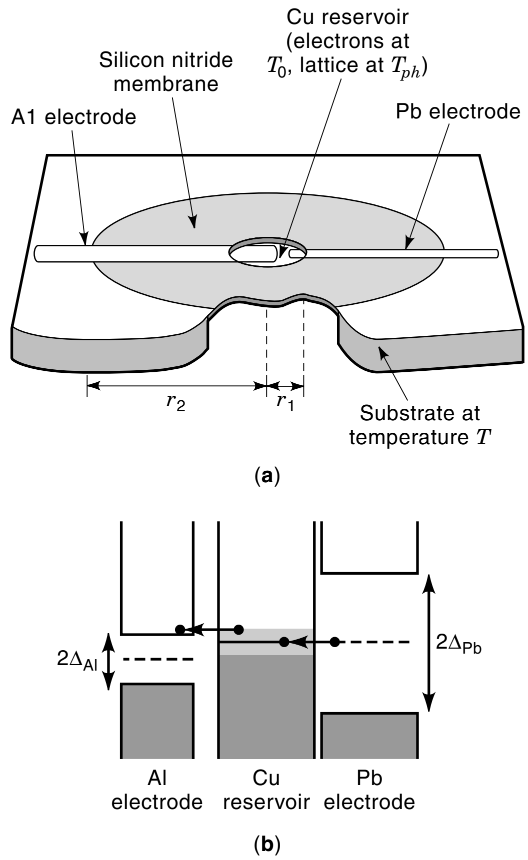

Figure 6. (a) Schematic and (b) energy-level diagram of the normal-insulator-superconductor (NIS) thermoelectric refrigerator. Hot electrons and holes in the Cu reservoir R tunnel into quasi-particle states in the Al superconducting thermoelement, cooling R. The Pb contact electrode is used to inject charge into R, but has no net heating or cooling effect. The structure is shown fabricated on a silicon nitride membrane to minimize the heat leak due to substrate thermal conduction. Reproduced from Ref. 5.

Because tunneling junctions between metal thin films may have a macroscopic surface area, the current and hence the cooling power of such a device may be scaled to larger values than the quantum-dot thermoelectric refrigerator discussed in the foregoing. A measurable temperature reduction of 10 mK below 100 mK was demonstrated in an initial experiment (7). An extra NIS tunneling junction (not shown) was used as a thermocouple to measure electron temperature. In this experiment, the metal thin films comprising the refrigerator were deposited on a bulk substrate, and were patterned on the micron scale; thus it was assumed that the electrons were cooled but the phonons remained at 100 mK, due to the decoupling of electron and phonon degrees of freedom in small, cold metals.

More recently, cooling from 300 to 100 mK was achieved by an improved NIS refrigerator (8). This device was fabricated on a membrane [as depicted in Fig. 6(a)]. Thus, there was not a strong thermal coupling to the ambient-temperature substrate, and the crystal lattice in the metal films comprising the refrigerator could be cooled along with the electrons, thereby reducing the heat leak due to phonon absorption. The feasibility of this experiment was theoretically predicted in Ref. (5). These devices are being developed to cool advanced radiation detectors for use in astronomy, but any electronic device that must operate at temperatures below 1 K could benefit from this type of refrigerator.

The significance of this result is that thermoelectric cooling has been achieved in which the kelvin temperature was reduced by a factor of 3. To accomplish this with a bulk material, the figure of merit would have to be in the range of $ZT = 2$ to 4 (1,2). Thus, previous speculations (1,2) that $ZT = 1$ represents a fundamental limit of physics may now be laid to rest.

PROSPECTS AND APPLICATIONS FOR CRYOGENIC THERMOELECTRIC REFRIGERATION

The success of the NIS refrigerator indicates the promise that thermoelectric refrigeration holds for the sub-1 K regime. Any material interface or device structure, which conducts electric current but has a significant energy dependence, should be capable of thermoelectric refrigeration at some temperature scale (5). One particularly interesting material system is the III/V semiconductors, which may be formed into heterostructures with custom-tailored energy band structures and high carrier mobilities. These structures have been used for power devices, and thus can carry large electric currents, and various structures could be envisioned that would produce a significant cooling effect.

CONCLUDING REMARKS

Widespread application of thermoelectric energy conversion remains a goal of materials science. While certain niche applications support a healthy, small Peltier-cooler industry, thermoelectric energy conversion will not compete economically with conventional methods until inexpensive, robust materials with a higher figure of merit are available. However, a good thermoelectric material would be very useful. For instance, as high-performance microelectronics continues to pack more transistors on a chip, heat loads are expected to exceed 100 W in several generations (14). This will require some form of direct cooling, and an efficient, low-cost thermoelectric alternative is attractive compared to water cooling, which may be hard to maintain reliably in a consumer end product.

One observation that leads to cautious optimism is that the present commercially available thermoelectric systems are based upon decades-old materials science developments. Many advances in computational materials modeling, materials synthesis (such as molecular-beam epitaxy), and materials characterization (such as high-resolution transmission electron microscopy and scanning-probe microscopy) have occurred in the meantime, enabling the exploration of complex material systems such as the high-temperature superconductors and colossal magnetoresistive materials. The skutterudites discussed in this article are an example of the fruits of modern materials science. As further complex material systems are explored, the right combination of low thermal conductivity, high electrical conductivity, and large thermopower may yet be found in an inexpensive, robust material.

New device concepts in thermoelectric conversion may overcome some traditional barriers as well. For instance, by using thermionic effects instead of reversible thermoelectric effects (6), enhanced efficiency might be achieved by high energy barriers and a departure from the traditional linear-response regime of thermoelectric behavior. Therefore, the cooling or power generation process would be far more efficient than would be expected from examination of the material figure of merit.

Cryogenic thermoelectric refrigeration represents a research frontier and, accordingly, applications are still in the research phase. However, although commercial applications remain distant, cryogenic thermoelectric refrigeration may provide an enabling technology for scientific work such as the mK-range radiation detector used in astronomy as discussed in this article. And, of course, if sufficient advantages are realized by cryogenic thermoelectric refrigeration, it may give rise to new commercial applications. For instance, liquid nitrogen is used to cool components in cellular-telephone base stations. If a thermoelectric refrigerator could be used to cool from 77 K to lower temperatures, new classes of electrical components could be utilized in widespread applications such as this.

With even greater extrapolation, one could imagine a cascaded series of thermoelectric refrigerators, for which the "hot side" is at room temperature and the "cold side" is at a cryogenic temperature. An example of an application where such a device might receive widespread commercial application in the future is in quantum computers, which should be capable of massively parallel computations but may have to be kept cold to preserve quantum phase coherence.

Cryogenic thermoelectric refrigeration may also lead to unexpected scientific discoveries; for instance, it is not known whether there exists a class of metals incapable of supporting a superconducting state or if all metals will go superconducting at a low enough temperature. At present, experiments have only been conducted to the range of 10^{-5} K (15). Direct thermoelectric cooling may be able to cool metals further, perhaps answering this fundamental question in our understanding of the electronic structure of matter. Perhaps the most fundamental contribution of this field so far is that $ZT = 1$ is not a universal physical limit, and that there may still be a highly efficient thermoelectric material system waiting to be discovered.

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