Thermoelectric Devices: Solid-State Refrigerators and Electrical Generators in the Classroom

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Thermoelectric devices are solid-state devices that convert thermal energy from a temperature gradient into electrical energy (the Seebeck effect) or convert electrical energy into a temperature gradient (the Peltier effect). The first application is used most notably in spacecraft power generation systems (for example, in Voyager I and II) and in thermocouples for temperature measurement, while the second application is largely used in specialized cooling applications. Both applications can be demonstrated in the lecture hall to illustrate thermodynamic principles in a compelling manner. They also provide insight into the workings of a high-tech system that is achieving more widespread consumer use. The most visible consumer use of thermoelectric devices utilizing the Peltier effect is in portable electric food coolers/warmers that plug into an automobile cigarette lighter.

Conventional cooling systems such as those used in refrigerators utilize a compressor and a working fluid to transfer heat. Thermal energy is absorbed and released as the working fluid undergoes expansion and compression and changes phase from liquid to vapor and back, respectively (*1*). Semiconductor thermoelectric coolers (also known as Peltier coolers) offer several advantages over conventional systems. They are entirely solid-state devices, with no moving parts; this makes them rugged, reliable, and quiet. They use no ozone-depleting chlorofluorocarbons, potentially offering a more environmentally responsible alternative to conventional refrigeration. They can be extremely compact, much more so than compressor-based systems. Precise temperature control ($< \pm 0.1$ °C) can be achieved with Peltier coolers. However, their efficiency is low compared to conventional refrigerators. Thus, they are used in niche applications where their unique advantages outweigh their low efficiency. Although some large-scale applications have been considered (on submarines and surface vessels), Peltier coolers are generally used in applications where small size is needed and the cooling demands are not too great, such as for cooling electronic components.

Apparatus

Acquiring and Preparing a Thermoelectric Module

A thermoelectric cooling module can be obtained by purchasing and disassembling a portable food cooler, (e.g., Coleman™ or Igloo™ brands). These are available at many department stores. If several model sizes are available, buy the least expensive: all contain thermoelectric modules that are suitable for demonstration purposes. Portable food coolers can be bought for less than $90. These will probably include the cooler and a power cord, fitted with a cigarette lighter adapter for 12-V automotive use. For classroom demonstrations a power supply will be needed; these can usually be purchased at the same place as the portable food cooler for about $30.

Disassembling an Igloo KoolMate™ series Kool Rider™ 6-quart Thermoelectric Roadster reveals that the cooling system is entirely contained in the cooler lid. A number of screws have to be removed to access the thermoelectric module. The module comes equipped with finned aluminum heat sinks attached to both sides; one of these has to be detached in order to remove the module from the lid. The heat sink is then reattached to the module, as shown in Figure 1. The module itself is approximately 3 cm by 3 cm and a few millimeters thick. Electrical connections for the module are simply a red and a black wire. The lid also contains a small fan used to circulate air over the heat sinks for more efficient heat transfer.

This module runs on 12 volts dc and draws from 3.0 to 4.2 amps. Power can be provided from a car battery or from a suitable ac-to-dc converter, such as the Igloo KoolMate™ ac/dc converter. The converter can generally be purchased separately; other 12-V dc power supplies may be obtained at lower cost, since they are quite common, but if the output current is less than 3 amps, the performance of the module will suffer. A small automotive battery charger providing 3-4 amps at 12-V dc would be adequate. Batteries other than automotive lead-acid batteries will probably not be adequate, because the module current draw is quite high. The Igloo KoolMate™ ac/dc converter was used for the experiments described below.[1]

Experimental Procedure

Demonstrations Using the Thermoelectric Cooling Module

The simplest demonstration of the Peltier effect is simply to power the module, allow it to establish a temperature difference between the heat sinks, and permit students to touch the hot and cold heat sinks. If direct contact by touch is not practical, digital thermometers can

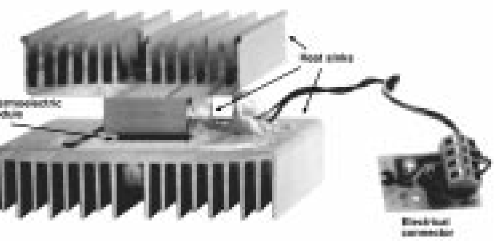

Figure 1. Thermoelectric module with attached heat sinks, from a disassembled portable food cooler. The smaller heat sink provides cooling to the cooler's interior in normal operation. A small fan is used to circulate air over the heat sinks. Note that the module itself is very small compared to the attached hardware.

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be connected to the heat sinks and the displays situated so the audience can view them. In a room that is equipped to display a computer's output, another option is to acquire the temperature data through a computer and display the results. Relatively inexpensive data acquisition hardware and software for Macintosh or IBM-compatible platforms are available from Vernier Software (503-297-5317, or e-mail at dvernier@vernier.com on Internet). A Serial Box Interface for Macintosh ($99), Data Logger software ($30, includes site license), and two Direct-Connect Temperature Probes ($25 each) were purchased.[2]

Setting up the equipment is straightforward, requiring about 15 minutes. Temperature probes were fastened against the base of the hot- and cold-side heat sinks, data acquisition was initiated, and power applied to the module from the ac adapter. After some experimentation, the cold side was found to reach its minimum temperature in about ten minutes, after which the temperature increased with time. A representative plot of temperature versus time is shown in Figure 2. The cold side would presumably maintain its temperature if heat were being actively dissipated from the hot side with forced air, as in the original design. The same experiment can be repeated with the power supply's polarity switched to reverse the hot and cold sides of the device.

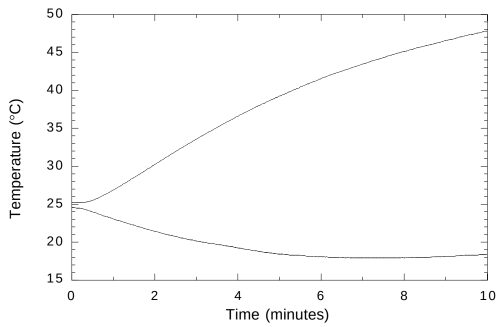

Figure 2. Temperature at the two heat sinks of the thermoelectric module as a function of time. The module was turned on at time zero with a polarity corresponding to cooling the food chamber. A similar temperature profile was obtained when the polarity was reversed, corresponding to heating the food chamber.

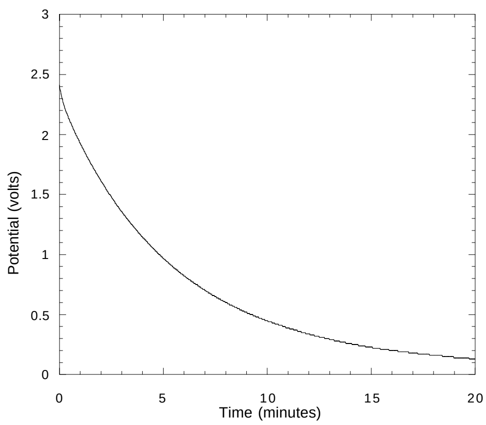

Figure 3. Voltage produced by the thermoelectric module after the temperature gradient shown in Fig. 2 was established (t = 0 in this figure corresponds to t = 10 min in Fig. 2). A similar profile was obtained if the module was powered with the polarity reversed.

To demonstrate the Seebeck effect (in which a temperature gradient produces a potential), a small electrical device can be connected to the module in place of the power supply after the module has reached its maximum temperature gradient; power can be extracted from the module until the temperature gradient becomes too small. A small motor or light bulb or buzzer could be used—some experimentation will be necessary to determine the size of the device that can be powered. We used a small motor from Radio Shack (about $1), rated to run on from 1.5 to 4.5 V, which turned a small propeller. This motor could be run for about 6 minutes after the device had received power for ten to twenty minutes. This is an excellent demonstration of the reversibility of the processes involved: an electric potential gradient (voltage) is used to create a temperature gradient; and the temperature gradient is used to create a voltage that powers a device. The computer data acquisition system was used to measure the voltage produced by the device. After the device had received power for 10 minutes, the Seebeck voltage produced was measured as a function of time. The initial voltage was about 2.5 V, decaying to nearly zero over about 20 minutes. The Serial Box Interface is able to handle a voltage of up to 5 V. A plot of voltage versus time is shown in Figure 3.

Other variations on this demonstration involve simply connecting a small motor or light bulb to the electrical leads and creating a temperature gradient by heating up or cooling down one side of the device. For example, immersing the smaller of the heat sinks in an ice-water bath started the aforementioned motor in less than a minute; it ran for about four minutes, at which point the large heat sink had cooled down due to thermal conduction (dry ice also works well to cool the heat sink but is quite loud). Heating the large heat sink with hot air from a heat gun for about a minute started the motor again and allowed it to run for eight minutes. The motor can also be powered by heating the heat sink without first immersing the other side in ice water. Once the motor has started running, it can be made to run in the opposite direction by heating the other heat sink and establishing a temperature gradient in the opposite direction.

Theory

When a temperature gradient is imposed on a conductor under open circuit conditions (i.e., no current is allowed to flow), the creation of a steady-state potential difference between the high- and low-temperature regions of the conductor is called the Seebeck effect. Consider a metal bar where one side is kept at a higher temperature than the other. If the free electrons in the metal are considered to behave as a gas, the kinetic theory of gases predicts that the free electrons in the hot side of the bar will on average have higher kinetic energy and will be moving at greater speeds than those in the cold side of the bar. As the faster moving electrons spread out, there will be a net flow of electrons from the hot side to the cold side of the bar, resulting in an accumulation of negative charge at the cold side and preventing further charge buildup (Fig. 4a). In a closed circuit, as shown in Figure 4b, current will flow to reduce the charge buildup and will continue to flow as long as the temperature gradient is maintained. The net result is that an imposed temperature gradient drives an electric current.

The electric field produced, **E**, (volts/distance) is proportional to the thermal gradient[3] ($\Delta T/\Delta x$, kelvins/distance, for a one-dimensional case) with a proportionality constant called the thermopower or Seebeck coefficient, Q (volts/kelvin)

$$\mathbf{E} = Q(\Delta T/\Delta x)\mathbf{i} \quad (1)$$

The boldface type indicates vector quantities (note that **i** is the unit vector in the *x*-direction). For a given temperature gradient, a larger thermopower means a larger electric field (and therefore potential) is generated.

In the example described above, Q is negative: The electric current, defined as the direction of the flow of positive charge (negatively charged electrons move in the direction opposite the electric current), is from the cold side of the bar to the hot side, opposite to the direction of the thermal current. If Q is positive, the thermal and electric currents flow in the same direction. In fact, metals exhibit both positive and negative thermopowers, and, for a given metal, Q can actually be positive at one temperature and negative at another. The large observed variation in thermopower sign and magnitude in metals can be explained in large part by electron scattering: The efficiency with which electrons are scattered is a function of temperature. If, for example, the hot high-energy electrons are scattered more efficiently by the lattice than are cooler low-energy electrons, the low-energy electrons can more easily flow to the hot side of the sample than high-energy electrons can flow to the cold side. This effect then opposes the gas-law-based argument described above, and the effect can be large enough to cause a material to exhibit a positive thermopower.[4]

It should also be noted that when current flows in a conductor, heat is generated by a process known as joule heating or resistive heating. When electrons in a conductor are made to move under an applied potential, they are moving from a state of higher potential energy to lower potential energy. The electrons are of course in constant random motion, but this produces no net motion of electrons. The applied potential imposes a small net velocity on the electrons. The electrons may be regarded as being accelerated by the electric field; they accelerate until they have a collision with another electron or a positively charged metal ion, which reduces their velocity. These collisions liberate energy in the form of heat. Unlike the thermoelectric effects, this process is not thermodynamically reversible. Joule heating is described by eq 2

$$P = I^2R \quad (2)$$

where P is the rate at which heat is produced (watts = joules/second), I is the current flowing in the conductor (amperes), and R is the conductor's resistance (ohms). Because the current term is squared, the direction of current flow is unimportant—heat is always generated when a current is flowing through a conductor. This is the familiar resistive heating that we see in space heaters, hair dryers, and light bulbs. Note that in these cases some of the energy is also given off as light.

Until now, the only charge carriers considered have been electrons. In semiconductors, however, there is also the possibility that positively charged "holes" will be important in conduction (*2*). Holes are simply vacant electron states in the valence band of a semiconductor; they have the same magnitude of charge as an electron, but they are positive instead of negative. Semiconductors in which holes are the majority carrier are termed p-type. The Seebeck effect for p-type semiconductors will cause holes to move from a hot region to a cold region, like electrons. But because they are positively charged, the potential created will be opposite to that created by electrons.

The Peltier effect may be thought of as the opposite of the Seebeck effect. Figure 5a shows an n-type semiconductor (one in which conduction band electrons are the predominant charge carriers, "majority carriers") connected to a voltage source by metallic conductors. An electric current flows through the semiconductor from left to right (electrons flow from right to left). For the electrons to enter the semiconductor from the metal, they must overcome the energy barrier, which is the difference in energy between the conduction band edge E_C and the Fermi level, E_F, to enter the conduction band; the highest-energy or "hottest" electrons from the metal are most likely to surmount this barrier and cross to the other metal–semicon-

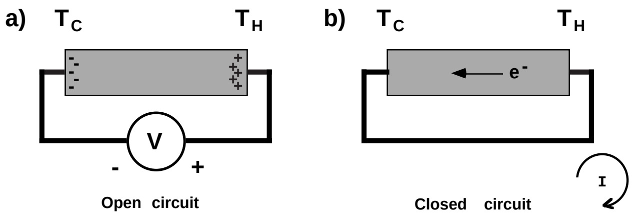

Figure 4. Illustration of the Seebeck effect. A temperature difference in a conductor causes a net flow of electrons from the hot side (T_H) to the cold side (T_C). If the circuit is not complete, charge build up occurs. (a) If the circuit is complete, an electric current *I* flows in the circuit. (b) Note that the direction of current *I* is opposite the direction of electron flow.

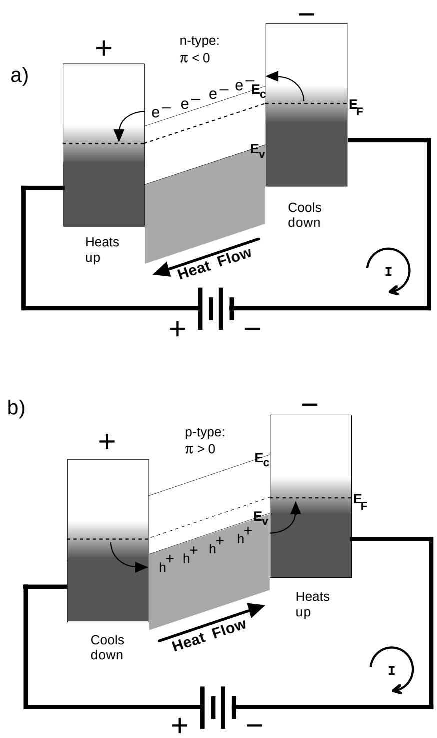

Figure 5. Illustration of the Peltier effect for a semiconductor between two pieces of metal. (a) n-Type semiconductor. Electrons flow from right to left in the semiconductor, carrying heat from the right to the left side of the semiconductor, opposite to the electric current direction; Π is negative. (b) p-Type semiconductor. Holes flow from left to right in the semiconductor, carrying heat from the left to the right side of the semiconductor, in the same direction as the electric current; Π is positive. E_C, E_V, and E_F refer to the energies of the conduction band edge, the valence band edge, and the Fermi energy (or electrochemical potential), respectively. Figure adapted from Hannay, N. B. *Semiconductors;* Reinhold: New York, 1959; p 41.

ductor interface. The result is that the right side is depleted of high-energy electrons. These electrons travel through the semiconductor and face no energy barrier as they enter the metal on the left side, which therefore has a net gain of high-energy electrons. The result is that heat is transported from right to left; an electrical current is accompanied by a thermal current. One side heats up above the ambient temperature, the other side cools down below the ambient temperature.

A p-type semiconductor connected to a voltage source is shown in Figure 5b. The electric current is carried by positive holes traveling from left to right in the semiconductor valence band. They must overcome the energy barrier between the Fermi level and the valence band edge, E_v. (It is important to note that the formalism associated with holes is such that their energy increases downward on the figure as shown.) The highest energy holes will be depleted from the left side, resulting in a thermal current from left to right.

The magnitude of the Peltier effect is quantified with the Peltier coefficient, Π, as follows:

$$\mathbf{j}^q = \Pi \mathbf{j} \tag{3}$$

where $\mathbf{j}^q$ is the thermal current density (in units of watts/area) and $\mathbf{j}$ is the electrical current density (in units of amperes/area). The units of Π are volts. For a given electrical current density, a material with a larger Peltier coefficient will have a larger accompanying thermal current density. Note that the Peltier coefficient, like the thermopower, can be positive or negative. In Figure 5a, the thermal current and electric current were in opposite directions; Π is negative. In Figure 5b, the two currents are in the same direction; Π is positive.

The Peltier coefficient and the thermopower are related by the expression

$$\Pi = TQ \tag{4}$$

where T is the absolute temperature (kelvins).

Relation to Thermodynamics

The laws of thermodynamics, particularly the second law, provide us with a powerful perspective for evaluating the performance we can expect from thermoelectric devices (*3*). The second law defines the state function of entropy, S, which is a measure of the disorder of a system. For an ideal, reversible process, the entropy of an isolated system may remain constant; however, in all real processes the entropy or disorder of the system increases. This increase in the disorder of a system may also be viewed as a measure of the degradation of the quality of energy in a system from a more useful form such as chemical or mechanical energy to a less useful form, heat energy. By referring to energy as "useful" or of "higher quality," we mean that a higher percentage of work can be extracted from it. The second law leads to the inequality of Clausius

$$\Delta S \geq q/T \tag{5}$$

where ΔS is the change in entropy of the system, q is the heat input into the system, and T is the system's absolute temperature. The equation is an equality for an ideal, reversible process but an inequality for an irreversible (spontaneous) process.

Heat Engines

To evaluate the performance of thermoelectrics, we consider their efficiency. The efficiency, η, is defined as the ratio of work output to work input. We can imagine a device for converting electrical work to mechanical work (e.g., an electric motor) that could theoretically be 100% efficient—that is, have an efficiency of one; similarly, the reverse process of converting mechanical work to electrical work could theoretically have an efficiency of one. An efficiency greater than one violates the first law of thermodynamics, in that energy would not be conserved. For a heat engine (a device that extracts work from the flow of heat from a hot reservoir to a cold reservoir), the efficiency is similarly defined: $\eta = w/q_h$ where w is the work extracted and q_h is the heat leaving the hot reservoir. Conservation of energy (the first law) allows us to state that (neglecting parasitic losses) the energy leaving the hot reservoir must equal the energy entering the cold reservoir plus the work extracted from the system, $q_h = q_c + w$. In the case of a heat engine, the second law imposes a further restriction on the efficiency. The great strength of the second law is that it allows us to equate heat with absolute temperature through the state function of entropy. By using eq 5 for a reversible entropy change, we obtain the expression for the maximum efficiency of a heat engine, the Carnot efficiency, η_{max}, given by

$$\eta_{max} = (T_h - T_c)/T_h = 1 - T_c/T_h \tag{6}$$

where T_h and T_c are the absolute temperatures of the hot and cold reservoirs, respectively. It can be seen that as T_c approaches absolute zero, or T_h approaches infinity, the efficiency approaches unity. The concept of energy quality again becomes useful: higher temperatures correspond to higher energy quality. Useful work (representing the highest energy quality) can be extracted more efficiently with a large T_h and small T_c. The efficiency becomes zero when $T_h = T_c$ (cf. the principle of Thomson); no work can be extracted if there is no temperature gradient, as we saw in the demonstration (the motor didn't run until a temperature gradient was established).

Heat Pumps

The influence of thermodynamics can be seen in the experimental data of Figure 2. Note the temperature difference from ambient temperature that the two heat sinks reach: the hot side is over 20 °C hotter than ambient temperature, while the cold side is only about 6 °C colder than ambient temperature. Although resistive heating and transport effects are affecting the temperatures at both heat sinks, ideal thermodynamic effects are also apparent. If one were to consider the reversed operation of the device as a heat engine, some work is extracted from the flow of heat from a hot to a cold reservoir. In other words, not all of the heat leaving the hot reservoir reaches the cold reservoir because some is converted to useful work. An analogous argument can therefore be made for a heat pump, where work is put into a system to move heat from a cold reservoir to a hot reservoir, as in the experiment of Figure 2. The heat entering the hot reservoir is the amount of heat leaving the cold reservoir plus the work put into the system to move the heat. If we assume similar heat capacities for the hot and cold sides of the device, we expect to see, as is observed, a greater temperature change at the hot side than at the cold side because $|q_h| > |q_c|$.

Heat pumps are generally quantified using the coefficient of performance ε, the ratio of heat transferred or pumped to the work input. Again, the thermodynamic limit is represented by the Carnot coefficient of performance, $\varepsilon_{max} = T_c/(T_h - T_c)$. Note that when $T_h = T_c$, ε_{max} is infinite; it is very easy to pump heat when the reservoirs are at equal temperatures. Also, ε_{max} approaches zero as T_c approaches zero; the application of an infinite amount of work is required to bring T_c to absolute zero. The ratio of a heat pump's coefficient of performance to ε_{max} can be used to compare heat pumps (the larger the ratio, the more efficient the heat pump). Thermoelectric heat pumps have ratios of up to 10%, conventional residential refrigeration systems have ratios of 30 to 40%, and large refrigeration units can have ratios up to 80%.

Materials

Metals typically have thermopowers on the order of μV/K, which are too small for most practical applications with the exception of thermocouples. Many semiconductors, however, have much larger values of Q, on the order of hundreds of μV/K.[5] Although metals produce a smaller potential for a given temperature difference, they are good thermocouple materials because they are inexpensive and can easily operate in high temperature environments.

Although large thermopower values are important to good thermoelectric materials, other factors are also important. Since charge carriers must move through the material to transport heat, the material should conduct electricity well; otherwise, the deleterious effect of resistive heating (see eq 2) will be enhanced. In addition, the material should act as a thermal insulator; the purpose of the device (when operated as a heat pump) is to produce a hot and cold region, so a good thermal conductor will rapidly dissipate the temperature difference established. The best thermoelectric materials involve a trade-off among the three factors, combining a high thermopower and electrical conductivity with low thermal conductivity.[6] All three parameters are affected by the carrier concentration, n, of a solid (*2*). Carrier concentrations range from about 10^{14} to 10^{21} carriers/cm^3 in a semiconductor, and are about 10^{22} cm^{-3} in a metal. Electrical conductivity, σ, increases with n. The thermal conductivity, κ, has two components, a lattice thermal conductivity κ_l and an electronic thermal conductivity κ_{el}, such that $\kappa = \kappa_l + \kappa_{el}$. The lattice component does not vary significantly with n; the electronic component increases with n.[7] The thermopower, Q, generally decreases with increasing carrier concentration.[8] These relationships are displayed in Figure 6, along with the figure of merit Z. The greatest Z value is obtained with a carrier concentration between 10^{18} and 10^{21} cm^{-3}. This implies that the best thermoelectric materials will be semiconductors with a relatively high carrier concentration.

The choice of carrier type is also important. As mentioned above, the direction of both the Seebeck and Peltier effects is reversed depending on whether the carriers are electrons or holes. If both carrier types are present in a material, their effects will work against each other. Semiconductors always contain both carrier types, but often the semiconductor is intentionally laced with impurities ("doped") so that one carrier type is greatly predominant (*2*). In this case, the semiconductor is said to be extrinsic. Intrinsic semiconductors, on the other hand, have roughly equal numbers of each type of carrier, causing their performance as thermoelectric materials to suffer. Extrinsic semiconductors, then, are the better choice for thermoelectric devices.

Researchers are continually trying to increase the efficiency of thermoelectric materials, through the processing of existing materials or the creation of new ones. Strategies to further improve the figure of merit of semiconductors generally involve decreasing the lattice thermal conductivity through a number of techniques that affect the microstructure of the material (*4*). These include solid-solution alloying of different semiconductors and dispersing inert particles in the semiconductor. Both treatments disrupt the regular ordering of the crystalline grains and decrease the ability of the material to carry heat through lattice vibrations. Put another way, the mean free path of phonons (quantized lattice vibrations) in the material decreases.

Narrow band-gap semiconductors are generally used for cooling and for power-generation applications.[9] Most Peltier coolers are made with alloys of bismuth telluride

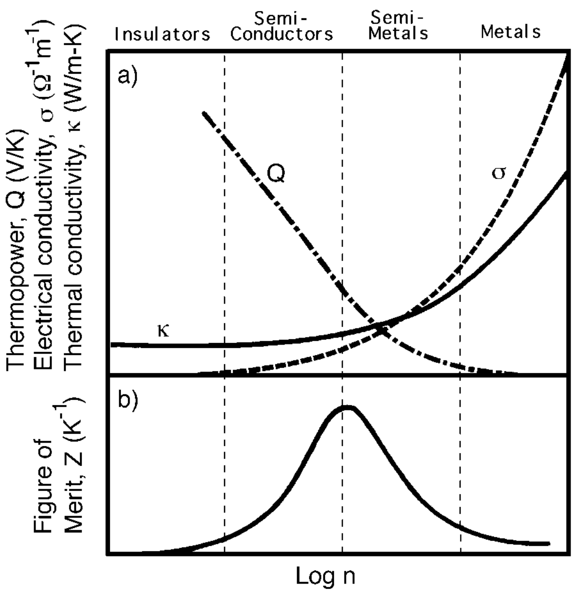

Figure 6. (a) Generalized dependence of electrical and thermal conductivity and thermopower on the carrier concentration. (b) The resultant dependence of the figure-of-merit, Z, on the carrier concentration. Adapted from Heikes, R. R., and Ure, R. W., Jr. *Thermoelectricity: Science and Engineering*; Interscience: New York, 1961; p 20.

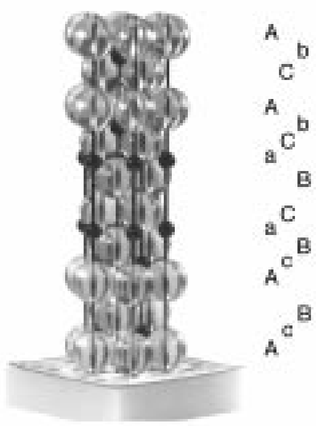

Figure 7. Perspective view of the bismuth telluride unit cell. Small dark spheres represent Bi; large clear spheres represent Te. The upper- and lower-case letters to the right indicate the relative orientation of the Te and Bi layers, respectively. Corresponding upper- and lower-case letters (e.g., A and a) represent layers that are aligned vertically (along the *c*-axis) with one another; see Fig. 8. The model was constructed using the Institute for Chemical Education Solid-State Model Kit, with some modifications: a second base (not shown) was used at the top to provide more stability, and longer rods than those supplied with the model kit had to be used to make the complete unit cell. The rods used were 10 in. long, cut from 3/32-in. stainless steel welding rods. Sb_2Te_3 and Bi_2Se_3 have the same structure.

(Bi_2Te_3), antimony telluride (Sb_2Te_3), and/or bismuth selenide (Bi_2Se_3), the best materials to date for near-room-temperature operation. At higher temperatures, lead telluride (PbTe) is used. For power generation systems, which typically operate at still higher temperatures, silicon–germanium (Si-Ge) alloys are often used.

Bismuth telluride (also known as tellurobismuthite), antimony telluride, and bismuth selenide have a nine-layer structure. They are composed of close-packed anions (Te or Se) with cations (Bi or Sb) occupying two-thirds of the octahedral holes (*5*). Let *A, B,* and *C* represent different relative orientations of the anion close-packed layers; and *a, b,* and *c* represent different relative orientations of the cations in the octahedral holes that lie midway between the close-packed layers. The structure can then be written as

$$A_cBA_cB_aCB_aC_bAC_bA\ldots$$

A perspective view of the unit cell of this structure is shown in Figure 7; a top view (looking down the crystal's *c*-axis) is shown in Figure 8. The dominant defect in Sb_2Te_3 is an antimony atom on a tellurium site. Since an antimony atom has one less valence electron to donate to the crystal, it can be thought of as an acceptor site, trapping a valence band electron and producing a hole. Sb_2Te_3 is therefore normally p-type. Bi_2Te_3 contains both bismuth on tellurium site defects and tellurium on bismuth site defects; these are acceptors and donors, respectively, so Bi_2Te_3 can be either p- or n-type. A good positive thermoelectric material (i.e., $Q > 0$) is a solid solution of composition 75:25 at. % Bi_2Te_3:Sb_2Te_3. A good negative thermoelectric material (i.e., $Q < 0$) is 75:25 at. % Bi_2Te_3:Bi_2Se_3, also a solid solution.

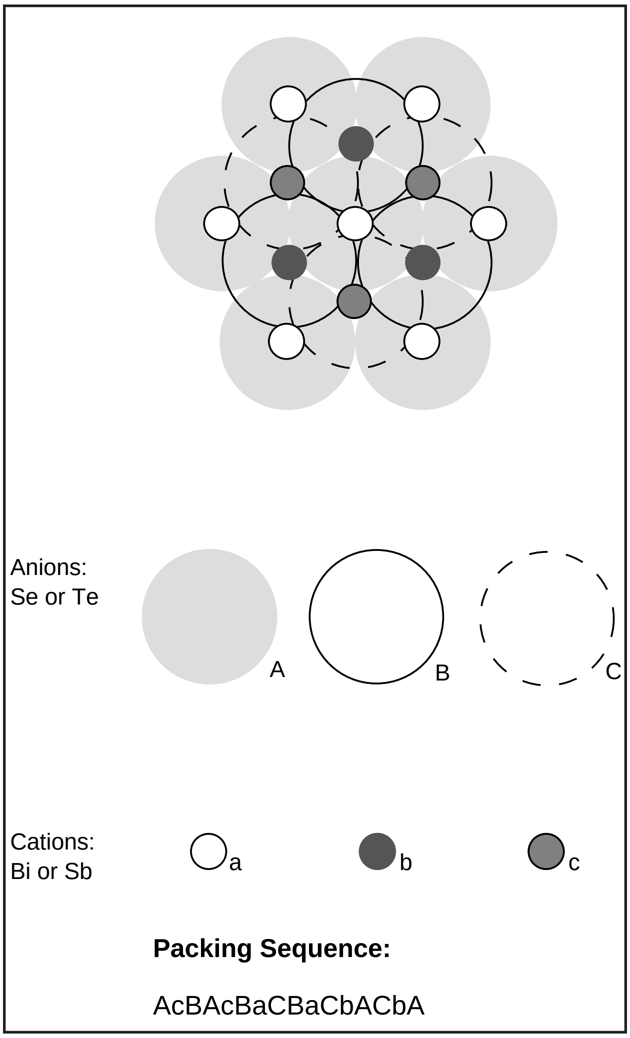

Figure 8. Top view (looking down the crystal's *c*-axis) of the bismuth telluride unit cell. Large circles represent anions, small circles represent cations. Letters denote the different relative arrangements of atomic planes; an upper-case letter indicates a close-packed plane of anions, a lower-case letter indicates a plane of cations in octahedral holes midway between anion planes.

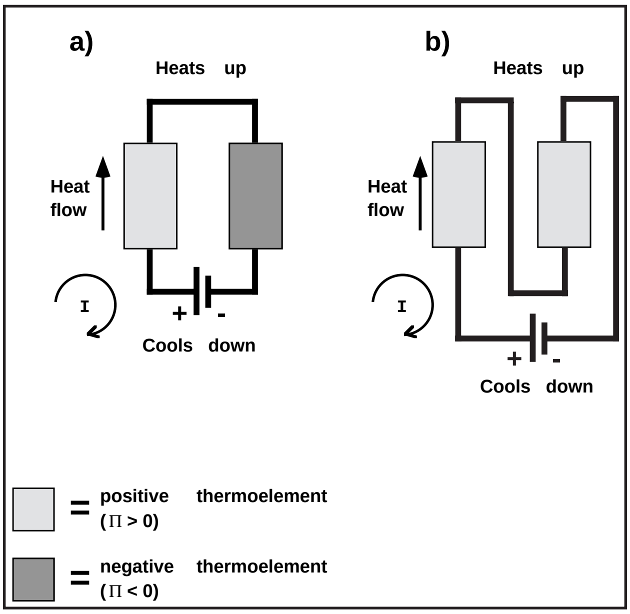

Figure 9. Schematic of a Peltier cooler. Positive thermoelements (where $\Pi > 0$) transfer heat in the same direction as current flow; the opposite is true for negative thermoelements. (a) Using both types of thermoelements simplifies device construction. (b) More complicated electrical connections are required if only one type of thermoelement is used.

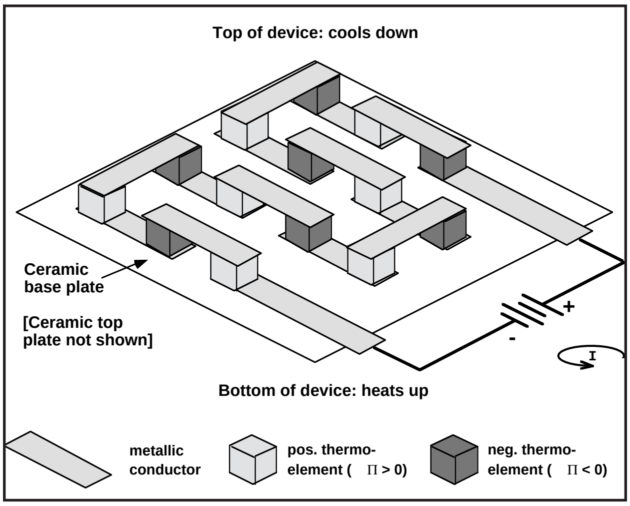

Figure 10. Thermoelectric cooling module. An array of positive and negative thermoelements are arranged between two ceramic plates so that they are electrically in series but thermally in parallel. All of the elements move heat from the top to the bottom of the module. Note that all of the metallic conductors are entirely in the plane of the top plate or the bottom plate.

The existence of both positive and negative thermoelements is of great utility in terms of device construction. A compact device can be made because individual thermoelements can be easily connected in series electrically, but in parallel thermally. Consider the model Peltier cooler depicted in Figure 9a, which consists of a power source, metallic conductors (wires), and positive and negative thermoelectrics. Current flows clockwise in the circuit as shown. In the positive thermoelement, heat flows in the direction of electric current flow; it is transported "up" in the diagram. In the negative thermoelement, heat is also transported "up" because now the electric current is flowing "down". If only positive thermoelements, for example, were available, it would be more difficult to arrange thermoelements in an array to move heat, as shown in Figure 9b.

Commercial Peltier coolers are typically an array of positive and negative thermoelements arranged as shown in Figure 10. All of the elements are connected in series electrically, but they all shunt heat from the top to the bottom of the device. The thermoelectric module shown in Figure 1 has several hundred thermoelements.

Conclusion

Thermoelectric devices provide an engaging high-tech demonstration suitable for illustrating thermodynamic principles in the classroom. They also showcase an elegant solid-state method of refrigeration, heating, and power generation. Thermoelectric effects can be understood at a qualitative level through the familiar chemical concept of the kinetic molecular theory of gases. The materials used in thermoelectric devices and described herein can be used to introduce a variety of solid-state structures. Insight is also gained into some of the engineering issues that must be considered when bringing a promising technology to the marketplace.

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Notes

1. Thermoelectric modules can be obtained from several other sources: Arbor Scientific (800 367-6695) sells a 1 cm × 1 cm module attached to a heat sink for about \$60. It draws 2.5 A of current at 2 V dc. Melcor (609 393-4178), a large manufacturer of thermoelectrics, sells models ranging in size from 1.8 mm × 3.4 mm (~\$13) up to 6.2 cm × 6.2 cm (~\$70). MacConnection (800 800-1111) sells a 1 in. × 1 in. module designed to cool the CPUs of IBM-compatible PCs for \$50 (stock number 19080).

2. Vernier also sells Texas Instruments' Calculator-Based Laboratory (CBL), a convenient data collection system useful where portability is desired and/or a computer is not available. It costs \$185 and utilizes the same probes as the Serial Box Interface (adapter required, \$5), and transfers the data to a TI-82 (\$90) or TI-85/CBL (\$105) calculator. These data can be graphed on the calculator or transferred to a computer (special hardware/software required, \$55). A special version of the TI-82 can be purchased with an overhead display panel (\$310 for both) suitable for use with an overhead projector.

3. Most generally, the gradient is a vector that points in the direction of greatest rate of change of a quantity, in this case temperature, and whose magnitude indicates the rate of change of the quantity. In the one-dimensional case above, the temperature gradient is simply given by $\nabla T = (dT/dx)\mathbf{i}$ where $\mathbf{i}$ is the unit vector in the x-direction. The general form of eq 1 is written $\mathbf{E} = Q\nabla T$, where ∇T is read as "gradient T", "grad T", or "del T".

4. Another effect, known as "phonon drag", makes an important contribution to the thermopower at low temperatures. Some of the phonons (quantized lattice vibrations) carrying heat from the hot region to the cold region collide with carriers and sweep them along.

5. This is largely because in these semiconductors the kinetic energy of the charge carriers is strongly temperature-dependent, whereas in metals it is not strongly temperature-dependent. The electrons in metals are said to be degenerate, and the familiar Maxwell–Boltzmann statistics of the kinetic molecular theory of gases are not as applicable in this case as they are for the case of nondegenerate semiconductors.

6. Materials used for thermoelectric devices are rated based upon their materials figure-of-merit, Z, or by the quantity ZT. The figure-of-merit Z is defined as $Z = Q^2\sigma/\kappa$, where Q is the thermopower, σ is the electrical conductivity (units of ohm^{-1}m^{-1}), and κ is the thermal conductivity (units of W/m-kelvin). Z has units of K^{-1}; the quantity ZT is therefore unitless and is called the dimensionless figure-of-merit.

7. The lattice component, κ_l, is largely accounted for by phonon–phonon interactions, the frequency of which is strongly determined by the phonons' mean free paths; these are largely unaffected by changes in carrier concentration. The electronic component, κ_{el}, is largely accounted for by electron–atom collisions; the rate of these collisions does depend on the electron concentration, n, and on their mean free path, which is relatively independent of n.

8. This can be explained with reference to Figure 5a. The energy carried by each electron is dependent on the difference in energy between the semiconductor's conduction band edge and the Fermi energy, E_F; as carrier concentration increases, the Fermi energy is closer to the conduction band edge (*2*), reducing the energy difference and the amount of thermal energy each electron carries. An analogous argument can be made for holes in p-type semiconductors.

9. Although wider band-gap semiconductors can be doped to high levels, they do not provide optimum electrical or thermal conductivity. A general rule is that the optimum band gap of a thermoelectric material is approximately 10 kT; kT represents the thermal energy available at a given absolute temperature T. At room temperature, kT is about 0.026 eV.

Literature Cited

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