

Thermoelectrics Run Hot and Cold

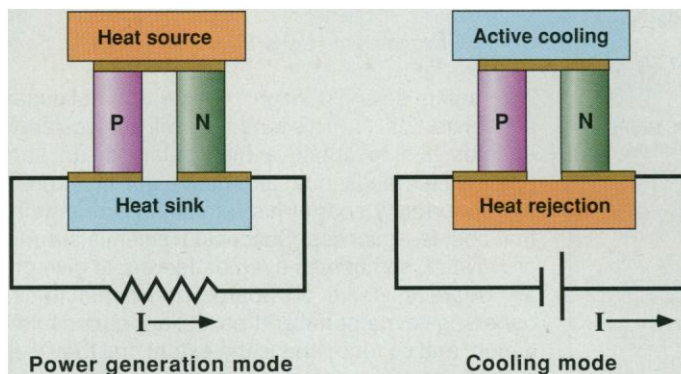
Terry M. Tritt

Thermoelectricity, or the Seebeck effect, is the physical phenomenon used in thermocouples for temperature measurement: a voltage difference is measured for a specific temperature difference. Less common is the use of thermoelectric materials for use in electronic refrigeration or power generation. Over the past 2 to 3 years there has been a renewed interest in the field of thermoelectrics for these applications. This interest has been primarily driven by the need for new and higher performance thermoelectric materials. There have been preliminary reports of new materials and new concepts for materials with some possibility of higher performance than existing materials (1, 2). The report by Sales *et al.* in this issue (3) describes some very promising results on a new class of materials, the skutterudite system, which includes IrSb₃ and CoSb₃ (1, 4-6).

Thermoelectric energy conversion utilizes the heat generated (as a result of the Peltier effect) when an electric current is passed through a thermoelectric material to provide a temperature gradient (see figure). Heat is absorbed on the cold side and rejected at the sink, thus providing a refrigeration capability. Conversely, an imposed temperature difference will result in a voltage or current, that is, power generation on a small scale. This aspect is widely utilized in deep-space applications, for example, on the Voyager I and II satellites, which were launched in 1977 and are still sending back pictures today, almost 20 years later. A radioactive material acts as the heat source in these radioactive thermoelectric generators and thus provides a long-lived energy supply. They will also be used in the upcoming Cassini mission to Saturn.

The advantages of thermoelectric solid-state energy conversion are compactness, quietness (no moving parts), and localized heating or cooling. Some applications include cooling of CCDs (charge-coupled devices), infrared detectors, low-noise amplifiers, and computer chips. Such thermoelectric coolers are also very stable and can be

used for temperature stabilization of laser diodes or electronic components. Given the harmful effect of standard chlorofluorocarbon and greenhouse refrigeration gases on the environment and the need for small-scale localized cooling in computers and electronics, the field of thermoelectrics is in need of higher performance room-temperature materials than those that currently exist. In addition, as the field of cryoelectronics (utilizing high-transition temperature super-



Thermoelectric module illustrating the versatility of such materials for use in solid-state power generation or in thermoelectric refrigeration. The thermoelectric module is composed of an *n*-type and a *p*-type semiconducting material connected by electrical contact pads, depicted in orange. The cooling stage, or cold side, is shown in blue, and the heat source, or heat sink, is shown in red.

conducting electronics) develops, the need for lower temperature (100 to 200 K) and higher performance thermoelectric materials is becoming more prevalent.

Thermoelectric materials are also being considered in the automobile industry for use in the "next-generation vehicle." Possible uses range from power generation using waste engine heat to seat coolers for comfort or electronic component cooling. The most common application of these materials today is the thermoelectric cooler-warmer, which sells for \$80 to \$100 at many local stores. It provides cooling to about 25°C below and warming to about 55°C above ambient temperature with just a flip of a switch. It can be plugged into a car cigarette lighter or operated by a small dc power source, useful at remote locations far from ac outlets or supplies of ice. This could be important, for example, in biological applications for temperature stabilization of specimens, as well as just keeping a favorite beverage cold.

The essence of defining a good thermoelectric material lies in determining the

material's figure of merit

$$Z = \alpha^2 \sigma / \lambda \quad (1)$$

where α is the Seebeck coefficient, defined as $\alpha = \Delta V / \Delta T$, V is voltage, T is temperature, σ is the electrical conductivity, and λ is the total thermal conductivity ($\lambda = \lambda_L + \lambda_e$, the lattice and electronic contributions, respectively).

The Seebeck coefficient is related to the Peltier effect by $\Pi = \alpha T = Q_p / I$, where Π is the Peltier coefficient, Q_p is the rate of heating or cooling, and I is the electrical current. In summary, the efficiency η and coefficient of performance (COP) of a device are directly related to the figure of merit of the material. In fact, η and COP are proportional to $(1 + ZT)^{1/2}$ where T is the absolute temperature in kelvin. As Z goes to infinity, the η and COP go to the thermodynamic limit of Carnot efficiency.

Alloys based on the $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-x}\text{Se}_x)_3$ system for room-temperature applications and the $\text{Bi}_{1-x}\text{Sb}_x$ system for lower temperatures are considered state-of-the-art materials for thermoelectric refrigeration. Higher temperature thermoelectric materials that are used for power generation include the $\text{Si}_{1-x}\text{Ge}_x$ system or the PbTe system. For all the current state-of-the-art materials, the dimensionless figure of merit, $ZT \cong 1$. This $ZT = 1$ has been an upper limit for more than 35 years, but there is no theoretical or thermodynamic reason why it cannot be larger if an appropriate material can be found.

One group of materials receiving a great deal of attention as a promising higher performance thermoelectric material is the skutterudite materials, which get their name from a naturally occurring mineral, skutterudite or CoAs₃, found in Skutterud, Norway. The general skutterudite composition is AB₃, where A is a transition metal atom (such as Ir, Co, or Rh) and B is a pnictogen atom (such as P, As, or Sb). These materials have a somewhat complex structure, with 32 atoms per cubic unit cell [see figure 1 in (3)]. A complex unit cell structure with a large number of atoms is typically associated with a low λ ; however, these materials have a rather high room-temperature thermal conductivity for a thermoelectric material, $\lambda \approx 16$ to $20 \text{ W m}^{-1} \text{ K}^{-1}$, with approximately 90% of the thermal conductivity resulting from the lattice or phonon contributions. There are large voids in the structure of these materials that can possibly be filled by an additional atom. The filling atoms allow manipulation of the thermal conductivity by increasing the

The author is in the Materials Physics Branch, Code 6341, Naval Research Laboratory, Washington, DC 20375, USA, and also in the Department of Physics, Clemson University, Clemson, SC 29634, USA. E-mail: tritt@zoltar.nrl.navy.mil

phonon scattering to “rattle in the cages.” The increased scattering should produce a greatly reduced lattice thermal conductivity and thus has the possibility of greatly enhancing the figure of merit for these materials (5). From Slack’s minimum thermal conductivity theory (7), it is estimated that the thermal conductivity in these skutterudite materials could be lowered by as much as a factor of 40 by filling these voids. For example, Nolas *et al.* found large reductions (by a factor of 20) in λ_L by void filling in the IrSb_3 system (6). In general, these skutterudite materials meet many of the basic criteria for a material to exhibit a high

ZT , as pointed out by Slack: large, complex unit cell with heavy constituent atoms, high mobility carriers, and a small band gap. Sales *et al.* (3) present very promising results on the properties of “filled skutterudites” based on CoSb_3 (specifically $\text{LaFe}_3\text{CoSb}_3$ and $\text{CeFe}_3\text{CoSb}_3$), which further indicate that when fully optimized, this family of compounds may lead to much higher performance thermoelectric materials.

References and Notes

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A Molecular Paramagnetic Superconductor

Patrick Cassoux

Superconductors consisting of molecular solids (as opposed to metals) present a variety of technological opportunities, and understanding how they work is essential before applications can follow. It has long been thought that the presence of magnetic ions in the molecular structure should decrease or even suppress superconductivity. Recently, however, Kurmoo *et al.* (1) prepared and characterized the first example of a molecular superconductor containing iron(III) magnetic anions. These results contradict our preconceived notions about the coexistence of magnetism and superconductivity and, more generally, our ideas about systems exhibiting interaction between conduction electrons and localized spins.

Most molecular superconductors are electron-transfer salts of the type $(\text{BEDT-TTF})_2\text{A}$, where BEDT-TTF is bis(ethylene-dithio)tetrathiafulvalene and A is a counteranion. The anion A may be octahedral (such as $[\text{PF}_6]^-$), tetrahedral $[\text{ClO}_4]^-$, linear $[\text{I}_3]^-$, or polymeric $[\text{Cu}(\text{NCS})_2]^-$ (2). The highest superconducting critical temperature T_c observed to date for a molecular superconductor is 12.8 K in the κ -(BEDT-TTF) $_2$ (Cu[N(CN) $_2$ Cl] phase (3). In none of these molecule-based superconducting salts is the counter anion A magnetic; that is, none of these salts contains localized anion spins.

The application of a magnetic field suppresses superconductivity (the Meissner effect), as do internal magnetic fields gener-

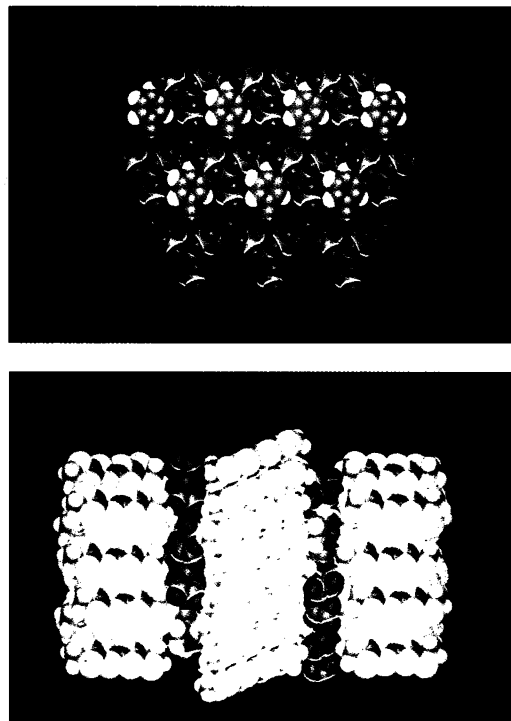
ated in ferromagnetic materials. This effect may be understood within the framework of the Bardeen-Cooper-Schrieffer theory (BCS) for three-dimensional systems exhibiting a spherical Fermi surface (4). According to BCS theory, the occurrence of singlet-state superconductivity results from the pairing of electrons having opposite spins (Cooper pairs). This pairing is mediated by lattice vibrations and can be disrupted by the close

vicinity of magnetic impurities. These impurities must only be sufficiently diluted, that is, paramagnetic and thus without either short- or long-distance magnetic order. For example, a few parts per million of iron prevent molybdenum from becoming superconducting; this observation has been also made for the commonly used superconducting alloys of transition metals.

Several attempts have been made to couple interesting conducting and magnetic behaviors in a molecular compound. A first example was given by the [TTF] $[\text{MX}_4\text{C}_4(\text{CF}_3)_4]$ compounds ($\text{M} = \text{Cu}, \text{Au}$; $\text{X} = \text{S}, \text{Se}$), which exhibit low conductivities but undergo a unique, so-called spin-Peierls, second-order transition at low temperatures to a nonmagnetic state (5). The $[\text{2,5-X-Y-DCNQI}]_2\text{Cu}$ compounds ($\text{DCNQI} = \text{N}, \text{N}'$ -dicyanoquinone diimine; $\text{X}, \text{Y} = \text{Me}, \text{Cl}, \text{Br}$)

were shown to exhibit metallic properties down to low temperatures and a ferromagnetic ordering of the copper spins (6). In the $(\text{perylene})_2[\text{M}(\text{mnt})_2]$ compounds ($\text{M} = \text{transition metal}$; $\text{mnt} = \text{maleonitriledithiolate}$, $[\text{C}_4\text{N}_2\text{S}_2]^{2-}$), instabilities typical of one-dimensional conducting (Peierls instability, for the perylene chains) and magnetic [spin-Peierls instability, for the $\text{M}(\text{mnt})_2$ chains] systems were observed (7).

The first examples of BEDT-TTF-based metals incorporating magnetic anions—such as FeX_4^- and CuX_4^- , with $\text{X} = \text{Cl}, \text{Br}$ —have been reported by Day *et al.* (8). Although these materials did exhibit interesting conducting and magnetic properties, none of them showed superconducting behavior. Further work along this line by Kurmoo *et al.* (1) showed that the β -(BEDT-TTF) $_4[(\text{H}_2\text{O})\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot \text{C}_6\text{H}_5\text{CN}$ phase does more than its forerunners. This salt exhibits a sharp (width about 0.2 K) superconducting transition with a T_c of 7.0 K, which is rather high for a molecule-based system. The magnetic susceptibility above T_c is a sum of a Pauli component typical of a metal and



The anionic (**top**) and cationic (**bottom**) layers in the paramagnetic molecular superconductor β' -(BEDT-TTF) $_4(\text{H}_2\text{O})[\text{FeCC}_2\text{O}_4)_3] \cdot \text{C}_6\text{H}_5\text{CN}$. [Courtesy: P. Day]

The author is in the Laboratoire de Chimie de Coordination de Toulouse, CNRS, 205 Route de Narbonne, 31077 Toulouse Cedex, France. E-mail: cassoux@lcc.toul.lcc-toulouse.fr