CONF-970824--3

LA-UR-97- 951

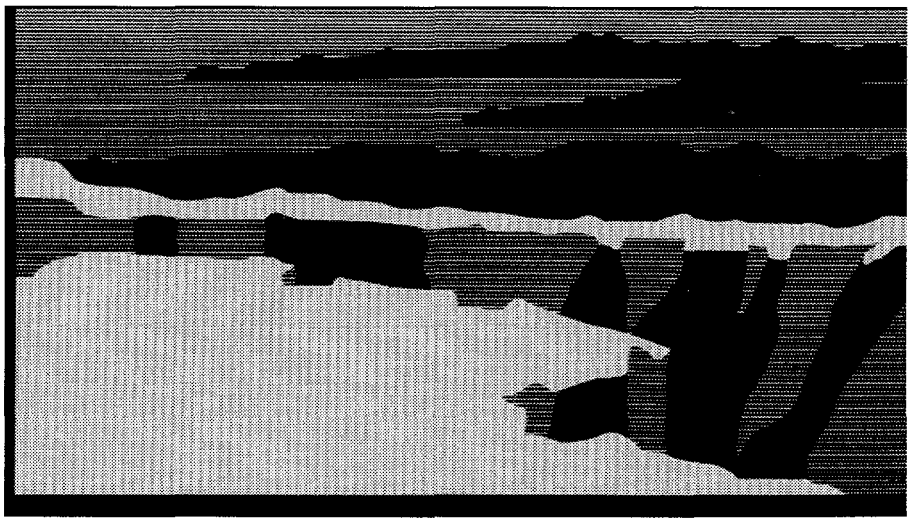
Title: New Approaches to Thermoelectric Cooling Effects in Magnetic Fields

Author(s):
A. Migliori
T. Darling
F. Freibert
S. Trugman
E. Moshopoulou
J. Sarrao

RECEIVED
MAY 05 1997
OSTI

Submitted to: 1997 National Heat Transfer Conference
August 10-12, 1997
Baltimore, Maryland

MASTER
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED



Los Alamos
NATIONAL LABORATORY

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

Form No. 836 R5
ST 2629 10/91

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

New Approaches to Thermoelectric Cooling Effects in Magnetic Fields

A. Migliori, T.W. Darling, F. Freibert, Stuart A. Trugman, E. Moshopoulou[1], J.L.Sarrao[2]

ABSTRACT

We review thermoelectric effects in a magnetic field at a phenomenological level. Discussions of the limiting performance and problems with its computation for both Peltier and Ettingshausen coolers are presented. New principles to guide the materials scientist are discussed for magnetic effects, and an brief review of the subtle measurement problems is presented.

Our intent in this paper is to provide a basic review of thermoelectric cooling in materials in which a strong magnetic field is present, and to indicate new directions in this old and extensively studied area of electronic transport in solids. The basic physical effects are the Peltier effect, the process in zero magnetic field which governs all modern thermoelectric coolers, and the Ettingshausen effect, a somewhat obscure but powerful refrigeration process that, combined with the Peltier effect, completes the description of heat transport by charge carriers in solids. Because of the extensive literature on these processes and because of the detailed complexity of the new approaches developed at our laboratory, we will attempt only to present an accurate but simple view. We begin with an historical perspective outlining briefly why there is some motivation to revisit this old problem.

For some period of time, there has been an established interest in $Bi_{1-x}Sb_x$ alloys for use in electronic refrigerators. This appreciation was initiated by the experimental work of Jain[1] on the electrical properties of single crystalline $Bi_{(1-x)}Sb_x$ and inspired by the large magneto-thermoelectric figure of merit data [2] of Smith and the equally impressive thermomagnetic figure of merit data [3] of Cuff, et. al These data have shown that the orientation of the applied magnetic field with respect to crystal axes plays an important role in optimizing figure of merit values in $Bi_{(1-x)}Sb_x$ alloys. In fact the behavior of the thermopower in a transverse magnetic field for Bi [4] and $Bi_{(1-x)}Sb_x$ [5] is very different dependent on the magnetic field-crystallographic axes orientation and is closely related to the crystal symmetry and band structure of these materials. However, little has been published to rationalize physically this fact in terms of a microscopic picture. Goldsmid [6] has attempted to justify a preferred magnetic field orientation based on theoretical predictions for the infinite field thermomagnetic figure of merit as derived from experimentally determined physical parameters given for single crystal Bi. Supported by this argument, the preferred orientation requires the electric current to flow along the trigonal direction, with the magnetic field along a bisectrix direction and the generated Ettingshausen heat flow along a binary direction. This experimental orientation has become the conventional orientation used in most experiments when determining the optimum operating efficiency of $Bi_{(1-x)}Sb_x$ alloys for use in an electronic refrigerator. However the apparent lack of understanding of the

[1]Los Alamos National Laboratory, Los Alamos, NM
[2]NHMFL, Florida State University, Tallahassee, FL

relationship between the band structure of Bi and its alloys with Sb, and the physics of thermoelectric and thermomagnetic effects leaves an interesting approach open, to be described below, that may provide substantially improved materials for Ettingshausen cooling.

ZERO MAGNETIC FIELD

The root of all thermoelectric effects is the small variation of the energy and momentum distribution of charge carriers caused by temperature gradients. Such variations produce, among other things, a non-zero electric field inside electric conductors-the Seebeck effect-and it is the coupling between this electric field and electric current that provides thermoelectric power generation or refrigeration (the Peltier effect). The size of the effect is dependent on the energy scales and temperature of the solid. In a degenerate metal, where only a few charge carriers near the Fermi energy ε_f (ε_f/k_b is of order 30,000K)are out of their ground state, the effects are small. In semi-conductors and semi-metals where only a few charge carriers are present (Bi has 10^6 fewer charge carriers than Cu, and ε_f/k_b is ~1000K) and very few in the ground state, the effects are large.

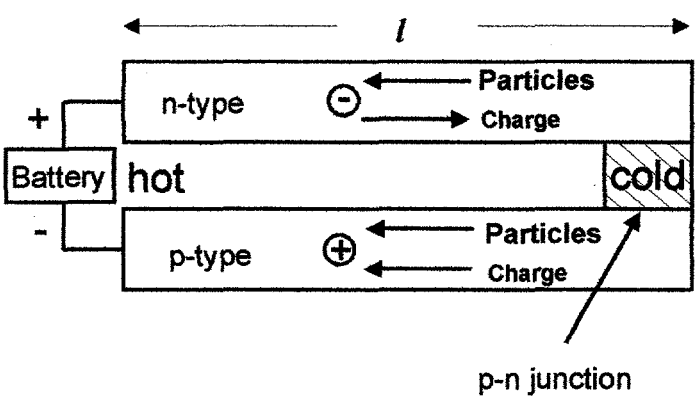


Figure 1. Shown is a simple schematic of a Peltier refrigerator consisting of a p-type and an n-type semiconductors joined at the cold end.

However all large thermoelectric effects, meaning those of sufficient strength to be of practical importance, arise only in solids that carry electric current via carriers (quasiparticles) of both negative (e or electron-like) and positive (h or hole-like) charge. Of course, there are really only electrons, but holes in the electronic distribution act just like real particles with positive charge-that is they move in a direction opposite to electrons in an electric field. Because of this "reverse" motion, systems can be constructed where, although electric current circulates, "particle" current is unidirectional, and it is the particle current that carries heat. This is shown schematically in figure 1 for a Peltier cooler that consists of two legs, one of a p-type semiconductor (holes are the majority carrier) and one of an n-type semiconductor (electrons are the majority carrier). The details of the operation of this device have been reviewed extensively by Harman and Honig [7], but several key points, relevant to what follows, will be discussed. Of particular importance is that any holes in the n-type bar or electrons in the p-type bar will carry heat toward the cold end, degrading performance. It should also be noted that ordinary thermal conduction is doing its best to carry heat from hot to cold. A pair of simple definitions [8] serve to quantify this as follows:

$$\bar{j} = \sigma\left(\bar{E} - S\bar{\nabla}T\right) \quad (1$$

$$\bar{j}_q = \sigma ST\bar{E} + \left(\sigma S^2 T - K\right)\bar{\nabla}T \quad (2$$

where $\bar{j}_q$ is the heat flux, $\bar{j}$ is the electrical current, σ is the electrical conductivity tensor, K the thermal conductivity tensor, $\bar{E}$ the electric field, S the thermopower tensor and T temperature. The thermal conductivity has two important components, K_p the phonon thermal conductivity and K_e the electronic thermal conductivity. The third equation of importance to a phenomenological understanding is

$$\nabla \bullet \bar{j}_q - \bar{E} \bullet \bar{j} = 0 \quad (3$$

which is a continuity equation for a time-independent temperature distribution inside the Peltier device, expressing the necessity for a balance between the difference between energy(heat) flowing into and out of a small volume (first term) and the electrical energy consumed in that volume (second term). Substituting (1) into (2) we obtain

$$\bar{j}_q = ST\bar{j} - K\nabla T \quad (4$$

which has the curious property that the total heat flow is the simple sum of the heat flow from ordinary thermal conduction and the heat pumped by the Peltier effect. For a one-dimensional system, (j is independent of position) and using (1), (3) and (4) we obtain

$$Tj\frac{dS}{dT}\frac{dT}{dx} - K\frac{d^2T}{dx^2} - \frac{j^2}{\sigma} = 0 \tag{5}$$

from which all the important stuff can be calculated. Note first that the second derivative of temperature with position is a critical piece, meaning that no matter how short the Peltier device is, if it is operating in a useful region, we cannot neglect the variation of the temperature gradient. Second, in the usual treatments [6] the first term is neglected. This term is basically the Thomson heat, and for the cryogenic refrigerators our work is focused on where T varies substantially, it can be of comparable size to the other terms and should not be neglected. However, to get a feel for what goes on, let's neglect it anyway, as well as the temperature dependencies of all the other material properties and solve (5) using (1) and (4) with the hot end anchored at T_h, and the cold end at T_c. We also assume that the n-type and p-type semiconductors have the same material properties (true for Bi_2Te_3, the most popular material, but difficult in general to achieve) except for the sign of S and that the total area of both materials is unity (it can be shown that nothing clever can be done by shaping the bars of semiconductor to improve things)[9].

Keeping in mind that Peltier refrigerators, though capable of coefficients of performance (COP) greater than unity, are never competitive on an energy usage basis with conventional refrigerators, we shall emphasize maximum heat pumped from the cold end, NOT maximum efficiency or COP. We find from (5) that

$$T_h - T_{c0} = \frac{\sigma S^2}{K}T_c^2 \tag{6}$$

$$j_0 = \frac{\sigma S T_c}{l} \tag{7}$$

$$j_{q0} = ST_c j_0 - K\frac{T_h - T_c}{l} - \frac{1}{2}\frac{j_0^2 l}{\sigma} = \frac{K}{l}(T_c - T_{c0}) \tag{8}$$

$$W_0 = \frac{j_0^2 l}{\sigma} + Sj_0(T_h - T_c) = \frac{\sigma S^2 T_c T_h}{l} \tag{9}$$

and, finally

$$COP_0 = \frac{W_0}{j_{q0}} = \frac{1}{2}\frac{T_c - T_{c0}}{T_h - T_{c0}}\frac{T_c}{T_h} \tag{10}$$

where T_{c0} is the minimum possible temperature, j_0 is the current for maximum heat pumped j_{q0}(which, of course, is valid when T_c=T_{c0} as well), W_0 is the electrical power required when maximum heat is pumped and COP_0 is the COP for maximum heat pumped. Note that if T_c is close to T_h, the best COP_0 is less than 1/2. Note also that in (8) under this approximation, the maximum heat pumped is degrade by exactly the heat that would flow by normal thermal conduction, and half the heat that would be generated if the device were a simple resistor. It is very interesting to observe also that from (8) and (9), the shorter the device, the more heat it pumps, but that the COP_0 and minimum temperature T_{c0} are independent of length.

It is seen that everything depends more or less on T_{c0} which is a function of the dimensionless quantity, $\sigma S^2 T/K$, historically called ZT, a particularly unhelpful appellation. Much more revealing is to note that $K/\sigma T$ has units of thermopower squared $(\mu V/K)^2$ so that a critical thermopower S_0 can be defined such that

$$S_0 = \sqrt{\frac{K}{\sigma T_c}} \tag{11}$$

which expresses a value for the thermopower that must be achieved for any reasonable thermoelectric material. If the material were such that the phonon thermal conductivity could be neglected, the quantity inside the square root is the Lorenz number L=$(155\mu V/K)^2$, a constant that comes from the Wiedemann-Franz law, a very general relationship between the electronic thermal conductivity and the electrical conductivity that is valid for complicated metals and fairly rigorous theories[8]. Thus any material with a thermopower less than about 155μV/K is not going to be a good candidate for a Peltier refrigerator, especially if K_p is not negligible. S_0, computed from measured properties, is then a very intuitive and simple-to-measure break point for material searches because

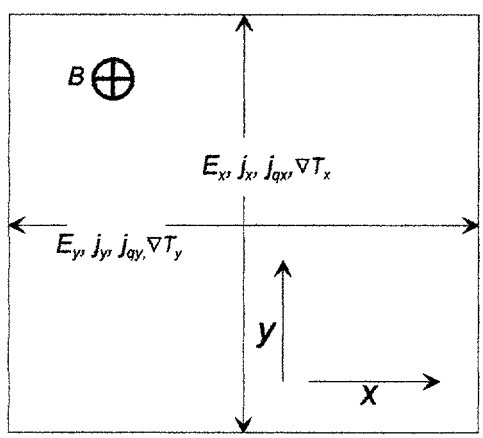
$$\frac{T_h}{T_{c0}} = 1 + \frac{1}{2}\left(\frac{S}{S_0}\right)^2 . \tag{12}$$

It can be seen that the search for good thermoelectric cooling materials is a battle to make S greater than S_0 (S/S_0=1 for very good materials)and minimize K_p (not much can be done about K_e because one is not going to

beat the Wiedemann-Franz law substantially in a system with enough carriers to pump heat). Note that (12) neglects the variation of thermopower with temperature, as stated earlier. Some numerical studies have shown discrepancies greater than 10% for (12) an error comparable to the target of entire thermoelectric funding agencies.

EFFECTS IN A MAGNETIC FIELD

We are, however, not working on Peltier coolers, but on the more complex Ettingshausen cooler. The complexities come in because all the material properties are now tensors and the analysis is more difficult. Figure 2 exemplifies this. In figure 3 we show a schematic of what the charge carriers must do. Referring to figure 3 it can be seen that the idea is to use a single material in which both electrons and holes are present. An electric field in the y-direction makes the holes travel roughly upward and the electrons roughly downward. The magnetic field B, however, deflects both carriers to the positive x-direction, and it is this effect that, exactly analogous to Peltier cooler, pumps heat. Notice that just as in a Peltier cooler, the electric current carried by holes is opposite in direction to the current carried by electrons but there is a net flow of particles toward the hot end.



Ettingshausen Effect:
input a voltage V_x
set $\Delta T_x=0$
find ΔT_y

Nernst Effect:
input a ΔT_x
set $j_x, j_y=0$
find E_y

Figure 2. Shown is a bar of material in a magnetic field, and the various transport quantities that contribute to thermoelectric cooling (the Ettingshausen effect) and thermoelectric power generation (the Nernst effect).

Our goal here is to provide guidance in the selectio of optimum Ettingshausen materials. It is clear that or quality of importance is to maximize the total number of particles moving toward the hot end. If the number and x-component velocity of electrons did not equal the same quantity for holes, then very quickly, charge would pile up at the hot end, creating a voltage (the Hall voltage) that would reduce (or stop if only one carrier were present) the flow of the majority carriers, degrading refrigeration. Therefore, the ideal Ettingshausen material must have equal numbers of electrons and holes with equal mobility. This is called particle-hole symmetry or e-h symmetry. Such a syste has ZERO thermopower and would produce no temperature drop if used in a Peltier cooler. The key guide for materials searches is, then, the electronic band structure. In what follows, we shall consider systems with parabolic bands in which the energy ε of the electron or hole is $p^2/(2m_i)$ where p is the momentum and m_i is the effective mass of the ith carrier. This is the same dispersion curve as a stone in vacuum. However, the electron band, a parabola facin up (it would hold water) and the hole band (parabola facing down, unable to hold water) can overlap (the tc of the hole parabola, or hole band edge, is above the bottom of the electron parabola or electron band edge or not. If the bands overlap in a material with an even number of electrons per unit cell, we have a semi-metal. If they do not overlap, the material is a semiconductor. In both cases, the Fermi energy, ε_f, lie between the band edges, its exact location dependent on the band masses m_i and temperature. The number c electrons available for conduction is the total number below ε_f, and for holes it is the number above ε_f. In a semi-metal like Bi, ε_f crosses the two bands at a point such that there are exactly the same number of holes a electrons, but because the curvature of the parabolas(which determines the effective mass) is not the same, the masses are different, and so are the mobilities.

To get a feel for Ettingshausen cooling, let's proceed under the assumption that we have two bands e and h, with the same masses and with the same mea free path-that is, perfect e-h symmetry. Equations (1)-(3) are still valid except that there is no ordinary thermopower and no Hall effect. This is expressed as

follows

$$\sigma = \begin{pmatrix} \sigma_{11} & 0 \\ 0 & \sigma_{11} \end{pmatrix} \text{ and } S = \begin{pmatrix} 0 & S_{12} \\ -S_{12} & 0 \end{pmatrix} \tag{13}$$

where σ_{12}, S_{12} are the non-zero components of the resistivity and thermopower tensors. We shall assume K to be a scalar. Noting that $j_x = E_x = dT/dy = 0$, we can obtain two more equations

$$j_y = \sigma_{11}\left(E_y + S_{12}\frac{dT}{dx}\right)$$

and (14)

$$j_{qx} = \sigma_{11} S_{12} T E_y - \left(K - \sigma_{11} S_{12}^2 T\right)\frac{dT}{dx}$$

except that the current j is not independent of position, while E_y is. Thus (14) is very definitely not of the same form as (5), as is occasionally stated [6]. Another key point is that now $\sigma_{11} S_{12}^2 T/K$ cannot exceed unity because if it did, useless circulating currents would exist. Thus the very curious boundary of unity on a set of parameters not obviously constrained by physics is another key difference between the two refrigeration processes. The resulting differential equation for a refrigerator, and its solution for temperature-independent parameters are

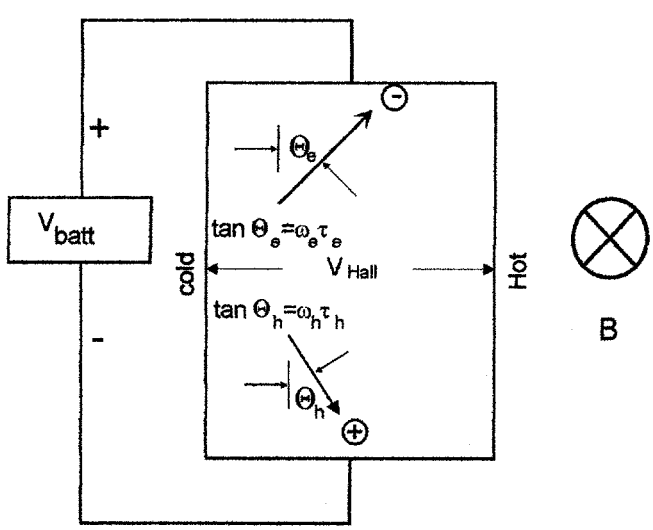


Figure 3. Shown is an Ettingshausen refrigerator. The angles will be discussed below.

$$-E_y^2\sigma_{11} = E_y T\frac{d(\sigma_{11}S_{12})}{dx} + \frac{d}{dx}\left[\left(\left[K - \sigma_{11}S_{12}^2 T\right]\right)\frac{dT}{dX}\right] \quad (15$$

$$\int\left(\left[K - \sigma_{11}S_{12}^2 T\right]\right)dT = \int\left(-xE_y^2\sigma_{11} + const.\right)dx$$

where we dropped all terms arising from errors in e-h symmetry. The integral solution to the differential equation is of particular note because on the left is an integral with respect to T, not x, over materials properties, mitigating the huge problem of position integrals over material properties when T is not known Even though the conductivity appears on the right under the integral, this is only one material property tc be dealt with. Unlike the Peltier case, the use of a temperature-independent thermal conductivity is bette justified because the magnetic field greatly reduces th electronic thermal conductivity which is usually proportional to temperature, leaving only the phonon term which is not constrained by the Wiedemann-Frar law.

Because the electric field and j are perpendicular to the heat flows, two or more Ettingshausen coolers (EC) in series can make electrical contact between the hot end of the smaller stage and the cold end of the larger stage, making it possible to produce a sequence of staged coolers simply by machining the correct shape from the bar of single material. Therefore, in a properly engineered EC, there is no obvious minimum temperature, T varies strongly, and a set of formulae like those for the Peltier cooler is not very useful. Nevertheless, it is interesting to note that (15) can be solved for the minimum temperature if materials properties are independent of temperature- the equation is

$$\frac{T_{c0}}{T_H} = 1 - \frac{T_H}{2T_0} \text{ where} \quad (16$$

$$T_0 = \frac{K}{\sigma_{11}S_{12}^2} > T_H \text{ and } E_{y0} = \frac{S_{12}T_c}{l}.$$

Because of the form of (16) one must be very cautious about defining a figure of merit, but using T_0 as a parameter is at least simple. However, for the Ettingshausen cooler, the minimum value of T_{c0}/T_H =1/2 when $T_0 = T_H$ [10].

As is obvious, no really simple direct comparison can be made because the Peltier figure of merit can be unbounded while the Ettingshausen figur of merit is computed for an unrealistically (unstaged)

simple geometry. Furthermore, the physics and the equations are fundamentally different, even though some authors attempt to map the EC problem onto the Peltier problem by using different definitions for K and σ [6]. Such attempts are no help to the materials scientist who is interested only in how well the refrigerator can be made to work. The best approach to an EC is to use measured values of the conductivity tensor, the thermopower tensor and the thermal conductivity, and the complete version of (15) to optimize the shape and driving electric and magnetic fields. It is our belief that this has never been done as well as it is possible to do and that the real potential of EC's has not yet been realized as the approximations [11] used in the past are based on models that leave out essential physics.

OPTIMIZATION OF MATERIALS

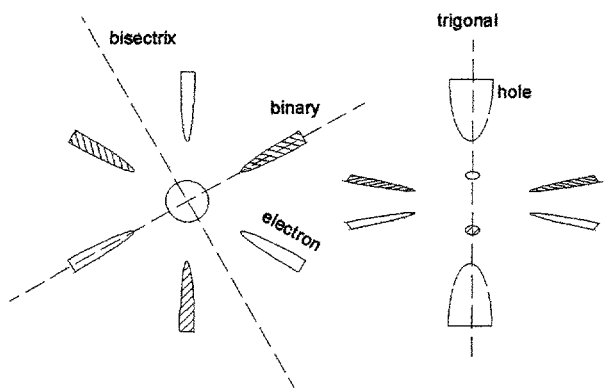


Figure 4. Shown is the Fermi surface of Bi. Under some doping conditions, it may be possible to eliminate the hole in the middle, leaving both electrons and holes at temperatures of order 100K where the electron pockets are now.

Even without a complete solution to (15), there are very good ways to attack the material development problem based on a) the search for e-h symmetry, and b) the need to minimize the effective mass. We can quantify this second point, and at the same time provide a proper basis for the historical choices of B, E, and j in a Bi-based EC cooler. Then, we will use this and the band structure of Bi-Sb to suggest improvements. In figure 4 we show the Fermi surfaces of Bi. This set of surfaces is the intersection of ε_f with the dispersion curves of the electrons and holes. Even though there are several electron surfaces, the total number of electron: equals the number of holes Where the surfaces are narrow, the dispersion curves have a lot of curvature, yielding low effective masses. Remembering that one goal is to maximize the total flux of heat-carrying particles, can we find a rule that will tell us what directions B, E, and j must be in? If all the surfaces were spherical, then any direction is as good as anothe because the masses (inverse of the curvature) would a be the same. However, in a low-symmetry metal like the rhombohedral Bi, the electron masses vary with direction by a factor of 30, and the hole masses somewhat less. If we consider what happens when simple resistive transport occurs we find that for one c the carriers,

$$\begin{pmatrix} \frac{m_1}{ne^2\tau} & \frac{B}{nec} \\ -\frac{B}{nec} & \frac{m_2}{ne^2\tau} \end{pmatrix} \begin{pmatrix} j_x \\ j_y \end{pmatrix} = \begin{pmatrix} E_x \\ E_y \end{pmatrix} \qquad (17$$

where n is the number of electrons or holes and c is th speed of light, e the charge on an electron, B is the magnetic field, τ is the mean time between scattering events, n is the number of carriers, m_1 their mass in th x-direction, m_2 in the y-direction. The light mass woul occur for particles traveling across a narrow dircectio of the Fermi surface. A second version of (17) for the other carrier would look the same except that the sign: of off-diagonal matrix elements are reversed. We can find the overall response by adding current densities linearly for the electrons and holes. If we have a system in which e-h symmetry is present, i.e. a good EC material, then when the full problem is solved, E_x would be zero (figure 2 gives the geometry) and so would the total j_x. However, what we are after is a ver large positive value of j_x for one carrier and a large negative value for the other, summing the electric current to zero but maintaining a large particle flux toward the hot end. We can, therefore, solve each of the two version of (17) separately to maximize j_x/j_y - that is we want the maximum possible transverse component of current for each carrier separately for a given current drawn from the battery. However, we know that E_x will be zero when both carrier contributions are summed, so we set it to zero in (17) to obtain

$$\frac{j_x}{j_y} = \frac{eB\tau}{m_1 c} = (\omega\tau)_1 \qquad (18$$

where ω is the cyclotron frequency. This remarkable result shows that the particle current in the heat-carrying direction depends on the effective mass in that direction alone (figure 3), and that the angle that the current makes with the electric field is the same as the Hall angle, the angle that the x- and y- components of the electric field would make with each other if only one carrier were present and j_x=0.

Maximizing (18) is a very important (if $\omega\tau$ is of order unity the magnetic field is considered strong) priority but one cannot simply increase the magnetic field because if B exceeds 1T or so, permanent magnets can't be used and the system becomes a laboratory curiosity. Thus it is important for the effective mass to be very small, typically 0.01 or less than that of a bare electron. We can, however, keep electronic scattering down (and hence τ up)by minimizing alloy elements that change the electron count, and we can make sure that the temperature gradient points in the direction of lowest mass. This is the first rule. In Bi, the electron masses are much less than the hole masses so the hole pocket forces the temperature gradient perpendicular to the trigonal axis. The next rule is to note that in a magnetic field, electron orbits shift and re-quantize with an energy spacing $\hbar\omega$, so it is important that the magnetic field not align with the low-mass direction or else large gaps will form in the energy spectrum (Landau levels), affecting the ability to get e-h symmetry because usually only one carrier will align. Thus the electron, which are very light must not have the long axis of their pockets along B. This is the second rule. Thus B must be along the binary axis, leaving j along the bisectrix, as shown in figure 4.

It is clear from figure 4 that it is very difficult to get e-h symmetry in Bi as it is. However, Bi is a very low symmetry metal so that in certain symmetry directions the bands can cross or nearly cross at ε_f. This is illustrated in one of the best band structure calculations for Bi done by Liu and Allen [12] where we show in figure 5 the very unusual, non-parabolic near intersection of the light electron band with a normally unoccupied, perfectly symmetric light hole. If this light hole could be occupied equally with the light electron, perfect e-h symmetry would result. This has never been exploited, even though it is well known that the addition of Sb to Bi moves the heavy hole (the hole discussed above, which is normally the only hole present) up and out of the way, forming a semiconductor above 4%-7% Sb. If Sb is added, then the heavy hole moves up, the Sb scatters phonons wel its mass is very different from Bi), reducing the phonc thermal conductivity, and has minimum effect on τ (it does nothing to the electron density), keeping the Hall angle large. In fact, as the hole moves up and out of th way, the electron pockets shrink to zero. This might seem to be a problem, and it would be it the cooler were operated at a few K, however, at 100K or so, thermal excitation produce a good supply of e-h pairs, comparable in number to the number present in Bi at 0K, and, of course, the pairs are symmetric. A little doping will produce a system in which only the very light electron and it s symmetric hole are present. Under these circumstances, rule 1 tells us to put the temperature gradient along the trigonal axis, now

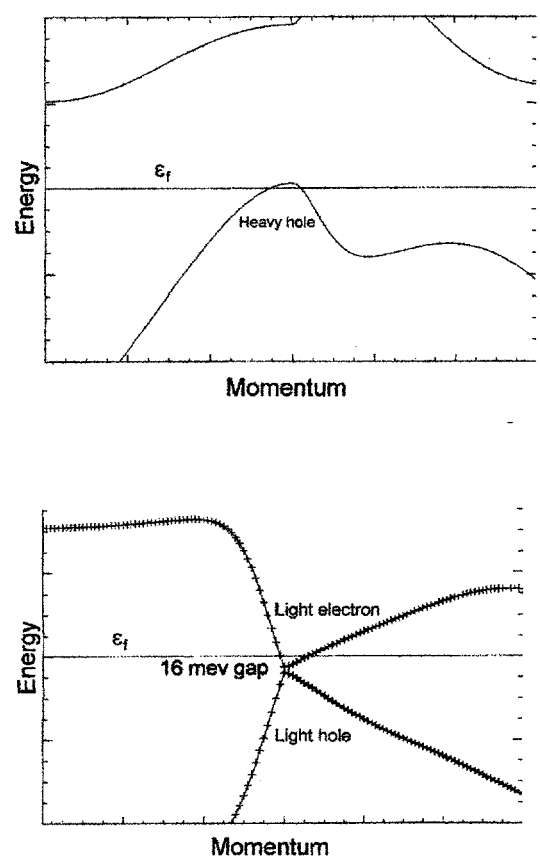


Figure 5. Shown are expanded views of the band structure of Bi near the heavy hole at the L-point and the light electron/light hole at the T-point. These calculations were provided by R.E.Allen and are the same values used in a recent publication [12].

picking up all three e-h pockets equally, instead of only 1+ as in pure Bi. *B* must not form Landau levels, so Rule 2 says it goes along the binary axis, leaving *j* along the bisectrix. It is this that our work is aiming toward,

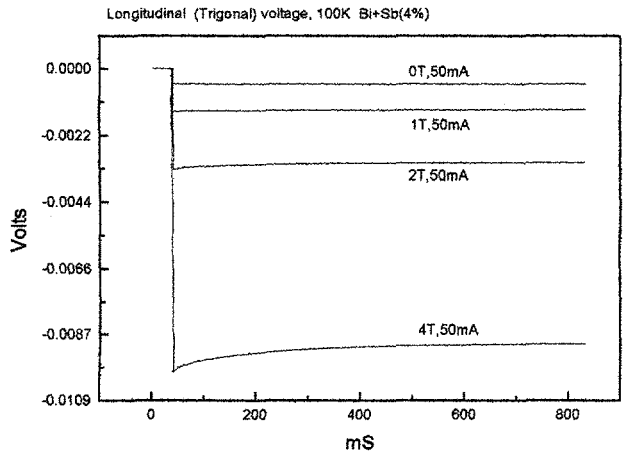


Figure 6. Shown is the response of a sample of $BiSb_{.04}$ alloy to the application of a constant current. The current turns on at the beginning of the trace, about 40ms after the start of recording.

with doping and Sb concentrations being investigated now. There is almost no systematic study of this region of the direction/concentration space [13] so much new data must be taken.

MEASUREMENTS

In order to explore carefully new alloys of doped Bi-Sb, a very tedious collection of somewhat difficult measurements must be made. These must include the resistivity tensor, the thermopower tensor and the thermal conductivity for many alloys over a broad temperature range in varying magnetic field. In addition, the measurement techniques are non-trivial. The difficulty arises because a good thermoelectric material (Peltier or Ettingshusen) generates huge thermoelectric voltages and substantial temperature gradients when current is passed through it, mixing up thermopower and resistivity signals in a nearly impossible-to-unscramble way.

If we start with a uniform temperature and magnetic field in a sample to be measured, and drive a constant current through it, electric potentials are set up almost immediately, and then, with some time constant, thermal gradients develop which may chang measured voltages. The measured voltage may be a strong function of time, with time constants less than second. The constant voltage measured after a long time, when the gradients are stable, is the adiabatic value. Measurements made quickly (within milliseconds!) give the isothermal values. Figure 6 shows a typical measurement of the time dependence of the longitudinal voltage on a Bi-Sb alloy. The curved region arises from a compounding of the Ettingshausen effect and the Nernst effect. The isothermal value of the voltage, and the drive current, yields the resistance while the difference between isothermal and adiabatic voltages, with the thermal conductivity, yields the Nernst (or Ettingshausen) coefficient. This also provides a direct measure of the critical thermopower in the material [14].

Two fast, ultra low noise amplifiers in a differential instrumentation amplifier configuration ar used in the voltage measurements. The output of the amplifiers is digitized at rates near 1 kHz to measure a time scale of approximately 800mS, by which time th voltage approaches a steady value. The timing of the current switch is controlled by a PC over a GPIB bus and the timing of the digitization cycle is adjusted to catch the voltage level before the current is switched on.

Fitting a simple exponential growth to the curve gives a time constant of $\tau \sim 150$ mS, although the time dependence is not expected to be exactly exponential [13].

Summary

We have reviewed the Peltier and Ettingshausen effects, developed a new and more accurate phenomenological equation to describe the Ettingshausen cooler and find that the EC provides better performance for the same effective material properties than a Peltier cooler. Rules are described fc determining the best deirection to use in Ettingshause materials, and the key difficulties with measurements are reviewed.

Acknowledgements

This work was supported by the U.S. Department of Energy, Advanced Energy Projects. The authors wish

to thank R.E.Allen for providing us with the data files used to produce figure 5 which is certainly the best band structure calculation on Bi to date.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

1) A. L. Jain, Phys. Rev. **114**, 1518 (1959).
2) G. E. Smith, Phys. Rev. Lett. **9**, 489 (1962).
3) K. F. Cuff, R. B. Horst, J. L. Weaver, S. R. Hawkins, C. F. Kooi, and G. M. Enslow, Appl. Phys. Lett. **2**, 145 (1963).
4) E. Gruneisen and J. Gielessen, Ann. Physik. **27**, 243 (1936).
5) R. Wolfe and G. E. Smith, Phys. Rev. **129**, 1086 (1963).
6) H. J. Goldsmid, *Electronic Refrigeration* (Pion Limited, London, 1986).
7) T. C. Harman and H. J. Honig, *Thermoelectric and Thermomagnetic Effects and Aplications* (McGraw-Hill, Inc., New York, 1967).
8) N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (W. B. Saunders Co., Philadelphia, 1976).
9) A. H. Boerdijk, J. Appl. Phys. **30**, 1080 (1959)
11) C. F. Kooi, R. B. Horst, K. F. Cuff, and S. R. Hawkins, J. Appl. Phys. **34**, 1735 (1963).
11) C. F. Kooi, R. B. Horst, and K. F. Cuff, J. Appl. Phys. **39**, 4257 (1968).
12) Y. Liu and R. E. Allen, Phys. Rev. B **52**, 1566 (1995).
13) N. B. Brandt and E. A. Svistova, J. Low Temp. Phys. **2**, 1 (1970).
14) G. L. Guthrie and R. L. Palmer, J. Appl. Phys. **37**, 90 (1966).