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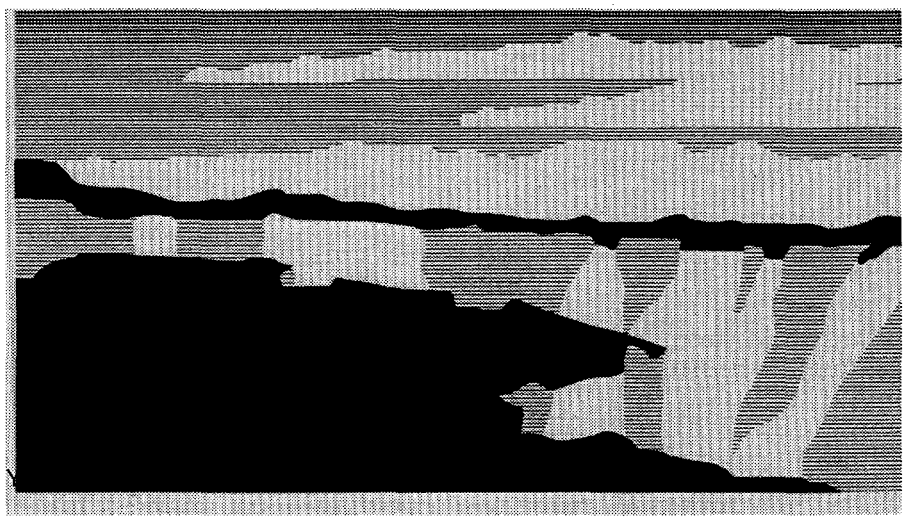

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NEW DIRECTIONS IN MATERIALS FOR THERMOMAGNETIC COOLING

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Abstract

We review thermoelectric effects in a magnetic field at a phenomenological level. Discussions of the difficulties in computing the limiting performance for both Peltier and Ettingshausen coolers are presented. New principles are discussed to guide the materials scientist in the search for better Ettingshausen materials. These principles are based on the tensor transport and solid state electronic properties of $Bi_{1-x}Sb_x$ alloys. A brief review of the subtle measurement problems is presented.

INTRODUCTION

Our intent in this paper is to indicate new directions in the extensively studied area of solid state electronic transport in high magnetic fields. The basic physical effects which describe electric field induced heat transport by charge carriers in solids are the Peltier and the Ettingshausen effects. The Peltier effect is a thermal transport process requiring no magnetic field in which a thermal gradient is created parallel with an applied electric current. The Ettingshausen effect, a somewhat obscure but powerful refrigeration process, is a thermal transport process in which a thermal gradient is created perpendicular to an applied electric current and both these are perpendicular to an applied magnetic field.

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 experimental work (Jain 1959) on the electrical properties of single crystalline $Bi_{(1-x)}Sb_x$ and inspired by large magneto-thermoelectric figure-of-merit (FOM) data (Smith 1962) and equally impressive thermomagnetic FOM data (Cuff 1963). These data have shown that the orientation of the applied magnetic field with respect to its rhombohedral crystal axes plays an important role in optimizing FOM values in $Bi_{(1-x)}Sb_x$ alloys. In fact the behavior of the thermopower in a transverse magnetic field for Bi (Gruneisen 1936) and $Bi_{(1-x)}Sb_x$ (Wolfe 1963) is very different, dependent on the relative orientation of magnetic field and crystallographic axes 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 has attempted to justify a preferred magnetic field orientation based on measurements and infinite-magnetic-field thermomagnetic FOM as derived from experimentally determined physical parameters for single crystal Bi (Goldsmid 1986). 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 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 coolers (EC).

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 (Peltier effect). The size of the effect is dependent on the energy scales and temperature of the solid.

A Peltier cooler (PC) consists of two legs, one of a p-type semiconductor and one of an n-type semiconductor. The details of the operation of these devices have been reviewed extensively (Harman 1967). The following set of simple phenomenological definitions serve to describe the electrical and thermal currents, j and j_q within conductors:

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

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

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

where σ and K are the electrical and thermal conductivity tensors, E is the electric field, S the thermopower tensor and T temperature. The thermal conductivity has two important components, K_p the phonon and K_e electronic thermal conductivities.

EFFECTS IN A MAGNETIC FIELD

Working in a magnetic field, the material transport properties must be treated as tensors resulting in a more difficult analysis of the EC. Figure 2(a) exemplifies this schematically. In figure 2 (b) we show a schematic of charge carrier transport in a single material in which both electrons and holes are present. An electric field applied in the y-direction

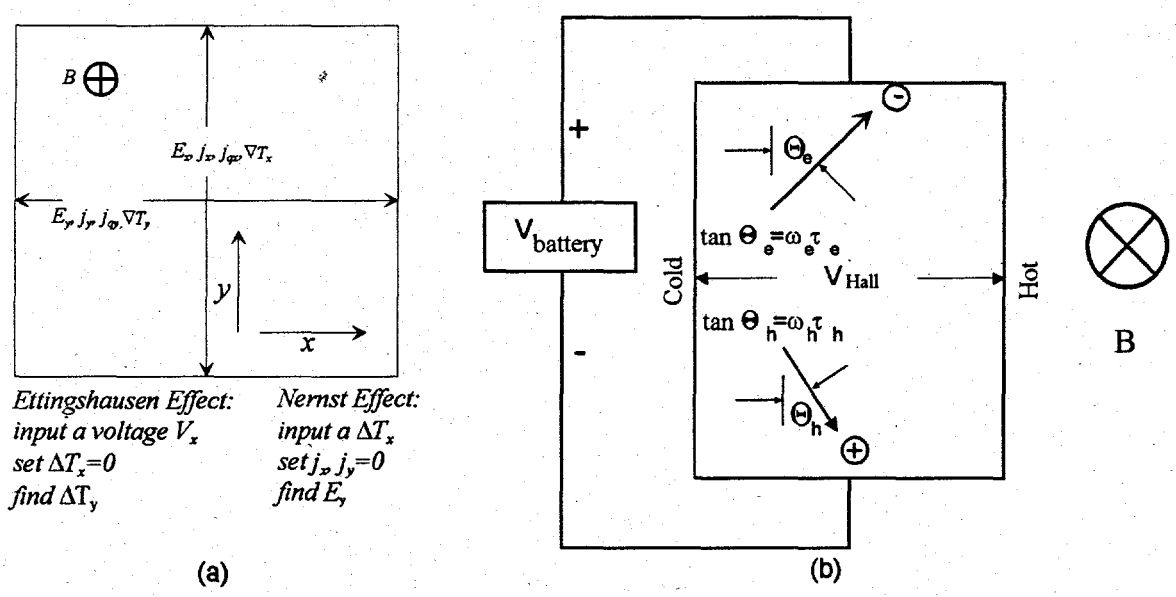

Figure 2. (a) The various transport quantities that contribute to thermoelectric cooling (Ettingshausen effect) and thermoelectric power generation (Nernst effect). (b) An Ettingshausen refrigerator (the angles are dicussed in the text).

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 PC, pumps heat.

Our goal here is to provide guidance in the selection of optimum EC materials. It is clear that one point of importance is to maximize the total number of particles moving toward the hot side. If the number and x-component velocity for electrons did not equal the same quantities as for holes, then very quickly, charge would pile up at the hot side, creating a Hall voltage that would reduce (or stop) the flow of the majority carriers, degrading refrigeration. Therefore, the ideal

EC material must have equal numbers of electrons and holes with equal mobilities. This is called 'electron-hole symmetry'. Such a system has ZERO longitudinal thermopower and would produce no temperature drop if used in a PC. Key to the materials search is 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. The electron and hole bands may (semi-metal) or may not (semiconductor) overlap. In both cases, ε_f, lies between the band edges, its exact location dependent on the band masses and temperature. The number of 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 level such that there are exactly the same number of holes as 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.

We proceed under the assumption that we have perfect e-h symmetry. Equations (1)-(3) are still valid except that there is no ordinary thermopower and no Hall effect. This is expressed for the induced conduction plane as follows:

$$\sigma = \begin{pmatrix} \sigma_{11} & 0 \\ 0 & \sigma_{11} \end{pmatrix}; \quad S = \begin{pmatrix} 0 & S_{12} \\ -S_{12} & 0 \end{pmatrix} \tag{4}$$

where σ_{11}, 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

$$j_y = \sigma_{11}(E_y + S_{12}\, dT/dx); \quad j_{qx} = \sigma_{11} S_{12} T E_y - (K - \sigma_{11} S_{12}{}^2 T)\, dT/dx \tag{5}$$

except that the current j is not independent of position, while E_y is. Another key point is that now $\sigma_{11}S_{12}^2T/K$ cannot exceed unity because if it did, heat would flow from cold to hot with no energy input to the system. The resulting differential equation desribing electronic and thermal transport in an EC is,

$$-E_y{}^2\sigma_{11} = E_y T(d(\sigma_{11}S_{12})/dx)[(K - \sigma_{11}S_{12}{}^2T)\, dT/dx] \tag{6}$$

where we dropped all terms arising from departures from e-h symmetry.

Because E and j are perpendicular to the heat flows, two or more ECs 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 with length, and one must be very cautious about defining a FOM. The best approach to developing an EC material is to use measured values of the elctrical and thermal conductivity tensors, the thermopower tensor, and (5) 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 (Kooi 1968).

OPTIMIZATION OF MATERIALS

Even without a complete solution to (5), 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 alloys to suggest improvements. In figure 3 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 (figure 4). Even though there are several electron surfaces, the total number of electrons 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 another because the masses (inverse of the curvature) would all 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 type of carriers,

$$\begin{pmatrix} E_x \\ E_y \end{pmatrix} = \begin{pmatrix} m_1/ne^2\tau & B/nec \\ -B/nec & m_1/ne^2\tau \end{pmatrix} \begin{pmatrix} j_x \\ j_y \end{pmatrix} \tag{7}$$

where n is the number of electrons (or holes) and c is the speed of light, e the charge on an electron, B is the magnetic field, τ is the mean time between scattering events, m_1 the carrier mass in the x-direction, m_2 in the y-direction. The low mass would occur for particles traveling across a narrow direction of the Fermi surface. A second version of (7) for the other carrier type would look the same except that the signs 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(a) gives the geometry) and so would the total j_x. However, what we are after is a very 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 (7) 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. We know that E_x will be zero when both carrier contributions are summed, so we set it to zero in (7) to obtain

$$\frac{j_x}{j_y} = \frac{eB\tau}{m_1 c} = (\omega\tau)_1 \tag{8}$$

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 2(b)), and that the angle that the current makes with the electric field is the Hall angle $\Theta=\tan(\omega\tau)$, the angle that the x- and y- components of the electric field would make with each other if only one carrier were present and $j_x=0$ (figure 2(b)).

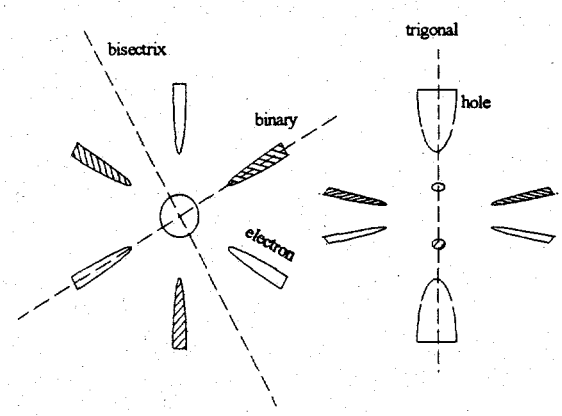

FIGURE 3. Shown is the Fermi surface of Bi. Under some doping conditions, it may be possible to eliminate the hole in the middle, so that at temperatures of order 100K, both electrons and holes would be where only the electron pockets are now.

Maximizing (8) is a very important priority (if $\omega\tau$ is of order unity the magnetic field is considered strong), but one cannot simply increase the magnetic field because if B exceeds 1T or so, permanent magnets can't be used. 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, 'rule 1'. In Bi, the electron masses are much less than the hole masses so the hole pocket forces the temperature gradient to be 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 $\hbar\omega$ ($\hbar$ is Planck's constant) 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 electrons, which are very light must not have the long axis of their pockets along B, the 'rule 2'. Thus B must be along the binary axis, leaving j along the bisectrix, as shown in figure 3.

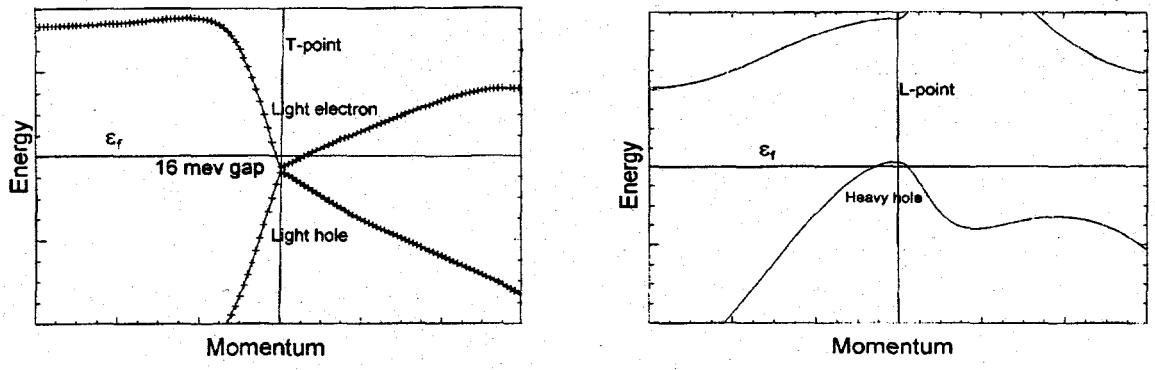

FIGURE 4. Expanded views of the band structure of Bi near the heavy hole at the L-point and the light electron/light hole at the T-point. These calculations were provided by R.E.Allen and are the same values used in a recent publication (Lui 1995).

It is clear from figure 3 that it is very difficult to get e-h symmetry in Bi as it is. However, Bi is a low symmetry metal so that in certain symmetry directions the bands can cross or nearly cross at ε_f. This is illustrated in the most recent band structure calculations of Bi (Lui 1995), where we show in figure 4 the very unusual, non-parabolic near-intersection of the light electron band with a normally unoccupied, perfectly symmetric light hole band. If this light hole could be occupied equally with the light electron and the heavy hole pushed down, 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) down and out of the way, forming a semiconductor above 4%-7% Sb, and the Sb atoms scatters phonons well (its mass is very different from Bi), reducing the phonon thermal conductivity. Also, Sb has a minimum effect on τ (it does little to the electron density and scattering), thus keeping the Hall angle large. In fact, as the hole moves down and out of the way, the electron pockets shrink to zero. This might seem to be a problem, and it would be if the cooler were operated at a few K, however, at 100K or so, thermal excitations produce a good supply of e-h pairs, comparable in number to the number present in pure Bi at 0K, and, of course, the pairs are symmetric. A little doping will insure electron-hole symmetry. Under these circumstances, rule 1 tells us to put the temperature gradient along the trigonal axis, now picking up all three e-h pockets equally, instead of only part of one, as in pure Bi. Rule 2 says B must not form widely spaced Landau levels, so B goes along the binary axis, leaving j along the bisectrix. It is this that our work is aiming toward, with doping and Sb concentrations being investigated now. There is almost no systematic study of this region of the direction/concentration space (Brandt 1970) so much new data must be taken.

MEASUREMENTS

In order to explore transport properties in Bi-Sb alloys, a very tedious collection of non-trivial measurements must be made. These must include the resistivity tensor, thermopower tensor and the thermal conductivity for many alloys over a broad temperature range in varying magnetic field. Difficulties arise because a good thermoelectric material (Peltier or Ettingshausen) generates huge thermoelectric voltages and substantial temperature gradients when current is passed through it, mixing up thermopower and resistivity signals in a very complicated 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 change measured voltages. The measured voltage may be a strong function of time, with time constants less than 1 s. The constant voltage measured after a long time, when the gradients are stable, is the adiabatic value and instantaneous

measurements give isothermal values.

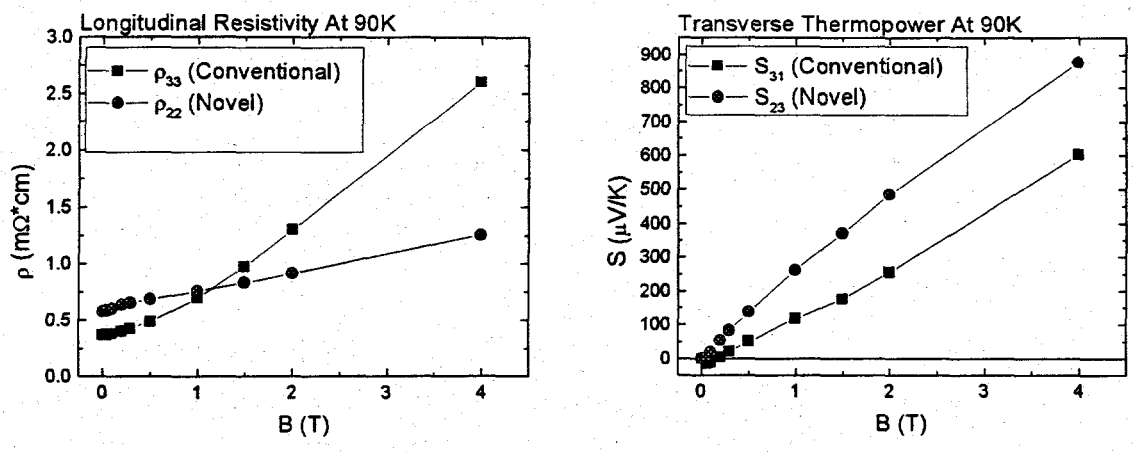

FIGURE 5. Magnetic field dependence of the longitudinal resistivity and transverse thermopower of oriented $Bi_{0.97}Sb_{0.03}$ single crystals at 90K.

As discussed above, the FOM of an EC material depends on σ_{11} and S_{12}. In figure 5 are data for the magnetic field dependence of the longitudinal resistivity and transverse thermopower of oriented $Bi_{0.97}Sb_{0.03}$ single crystals at 90K. Note that above 1T the conventional orientation has a larger magnetoresistivity and lower transverse thermopower than does the novel orientation, supporting the above analysis.

SUMMARY

We have reviewed the Peltier and Ettingshausen effects, discussed phenomenological equations to describe the EC and indicate how the EC can provide better performance for the same effective material properties than a PC via geometry optimization. New rules are described for determining the best directions to use in Ettingshausen materials, and key difficulties with transport measurements are reviewed.

Acknowledgements

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