PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON THE PHYSICS OF SEMICONDUCTORS, KYOTO, 1966
JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 21, SUPPLEMENT, 1966

XVII-1. Analysis of dc Transport Phenomena in Bismuth

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The origins of the magneto-thermoelectric effects in the semimetal bismuth are investigated by calculating the effects of various changes in the band structure and the current contributions from individual groups of carriers. It is shown that the "Umkehr" effect (the change in the thermoelectric power upon reversal of the magnetic field) would still occur for certain orientations even in a material with only electrons or holes and even if the energy ellipsoids are not tilted with respect to the crystal axes. In bismuth it is found that, under certain conditions, while the total current flows in one direction, the current contribution from a given group of carriers can be in the opposite direction. This effect is related to the observed change in sign of the thermoelectric power in a transverse magnetic field.

§ 1. Introduction

In previous studies of the magneto-thermoelectric and galvanomagnetic effects in single crystal bismuth[1] several unusual phenomena were observed. These included that thermoelectric "Umkehr" effect (the change in magnitude when the transverse applied magnetic field is reversed), the change in sign of the Seebeck coefficient from negative to positive with reversal of the magnetic field for certain orientations,[2] and the complicated anisotropy of all the transport properties in moderate transverse fields. A theory was developed[1] which accounted for all of these phenomena. In this extended transport theory, all of the well established features of the band structure of bismuth were included: electrons in three tilted k-space ellipsoids with a non-parabolic energy-momentum relationship and an equivalent number of holes in one ellipsoid of revolution.[3] Also, an energy dependent relaxation time tensor was assumed. Expressions for the transport tensors were obtained by summing the contributions to the total electrical and thermal currents from each of the separate groups of carriers. These contributions were expressed in terms of tensorial transport integrals. The theory was written in a very concise form and curves for comparison with experiment had to be calculated with a digital computer. This had the advantage that it was not necessary to introduce simplifying assumptions into the model to make the algebraic expressions tractable, but the disadvantage of obscuring the physical origins of the various phenomena.

In the present investigation, further insight into the transport properties was obtained by two types of computer calculations. First, in order to identify which features of the bismuth band model give rise to the observed phenomena, several changes were introduced into the model:

a. the relative numbers of electrons and holes were varied.

b. the tilt of the electron ellipsoids was eliminated and the orientation dependence for this case was investigated.

c. the energy dependence of the relaxation time and effective mass was eliminated.

Second, using the complete model, the separate contributions to the total current of the various groups of electrons and holes were calculated and the origin of the thermoelectric sign reversal was revealed.

§ 2. Outline of Transport Theory

In order to compare the theory to experiment, it is convenient to make use of the well known phenomenological equations[4] for current and heat flow. The contribution to the fluxes from a single ellipsoid designated by subscript i are

$$\vec{J}_i=\overleftrightarrow{\sigma}_i\cdot\left(\frac{\vec{\nabla}\bar{\mu}}{e}-\overleftrightarrow{S}_i\cdot\vec{\nabla}T\right) \qquad (1)$$

and

$$\vec{Q}_i=\left(\overleftrightarrow{\pi}_i-\frac{\bar{\mu}}{e}\right)\cdot\vec{J}_i-\overleftrightarrow{\kappa}_i\cdot\vec{\nabla}T \qquad (2)$$

where $\overleftrightarrow{\sigma}_i$ is the conductivity tensor, $\overleftrightarrow{S}_i$ the thermoelectric power (Seebeck) tensor, $\overleftrightarrow{\pi}_i$ the Peltier tensor, and $\overleftrightarrow{\kappa}_i$ the thermal conductivity tensor.

The electrochemical potential is $\bar{\mu}=e\Phi+E_F$ where Φ is the electrostatic potential and E_F is the Fermi energy. The electric field is $\vec{\mathscr{E}}=\vec{\nabla}\bar{\mu}/e$.

An outline of the calculation of these fluxes from the Boltzmann equation, expressions for the partial transport tensors in terms of transport integrals and the details of the assumed model of the band structure have been presented previously.[1]

The total current density $\vec{J}$ and heat flux $\vec{Q}$ are

$$\vec{J}=\sum_{i=1}^{4}\vec{J}_i \tag{3}$$

and

$$\vec{Q}=\sum_{i=1}^{4}\vec{Q}_i\,. \tag{4}$$

Phenomenological coefficients for total fluxes are written by dropping the subscripts i from eqs. (1) and (2). By matching coefficients one obtains

$$\overleftrightarrow{\sigma}=\sum_{i=1}^{4}\overleftrightarrow{\sigma}_i \tag{5}$$

$$\overleftrightarrow{\pi}=\left(\sum_{i=1}^{4}\overleftrightarrow{\pi}_i\cdot\overleftrightarrow{\sigma}_i\right)\cdot\overleftrightarrow{\sigma}^{-1} \tag{6}$$

$$\overleftrightarrow{S}=\overleftrightarrow{\sigma}^{-1}\cdot\left(\sum_{i=1}^{4}\overleftrightarrow{\sigma}_i\cdot\overleftrightarrow{S}_i\right) \tag{7}$$

and

$$\overleftrightarrow{\kappa}=\sum_{i=1}^{4}\overleftrightarrow{\kappa}_i+\sum_{i=1}^{4}\overleftrightarrow{\pi}_i\cdot\overleftrightarrow{\sigma}_i\cdot\overleftrightarrow{S}_i-\overleftrightarrow{\pi}\cdot\overleftrightarrow{\sigma}\cdot\overleftrightarrow{S}+\overleftrightarrow{\kappa}_{ph}\,. \tag{8}$$

The last term in the thermal conductivity $\overleftrightarrow{\kappa}_{ph}$ is the phonon contribution and is taken from experiment.

In the present investigation the flux directions, the measured voltage V, and the measured temperature difference ΔT are all along the same direction $\vec{r}$ ($|\vec{r}|$ is the distance between the voltage and temperature probes) so that in an isothermal resistivity measurement, $\vec{\nabla}T=0$, $\vec{J}\neq 0$, and

$$V=\vec{r}\cdot\vec{\mathscr{E}}=\vec{r}\cdot\overleftrightarrow{\sigma}^{-1}\cdot\vec{J}. \tag{9}$$

For a thermoelectric power measurement, $\vec{\nabla}T\neq 0$, $\vec{J}=0$, so that the measured voltage is

$$\begin{aligned}V&=\vec{r}\cdot\vec{\mathscr{E}}=\vec{r}\cdot\overleftrightarrow{S}\cdot\vec{\nabla}T\\&=\vec{r}\cdot\overleftrightarrow{S}\cdot\overleftrightarrow{\kappa}^{-1}\cdot\vec{Q}\end{aligned} \tag{10}$$

and the temperature difference is

$$\Delta T=\vec{r}\cdot\vec{\nabla}T=\vec{r}\cdot\overleftrightarrow{\kappa}^{-1}\cdot\vec{Q}. \tag{11}$$

What we plot as thermoelectric power is (since $\vec{Q}=(\vec{r}/|\vec{r}|)Q$)

$$S=\frac{V}{\Delta T}=\frac{\vec{r}\cdot\overleftrightarrow{S}\cdot\overleftrightarrow{\kappa}^{-1}\cdot\vec{r}}{\vec{r}\cdot\overleftrightarrow{\kappa}^{-1}\cdot\vec{r}}\,. \tag{12}$$

It should be noted that this expression involves *all* of the partial transport tensors S_i, σ_i, π_i and κ_i, and that each of these involves very complicated transport integrals. The algebraic expressions for S would be formidable even for principal orientations.

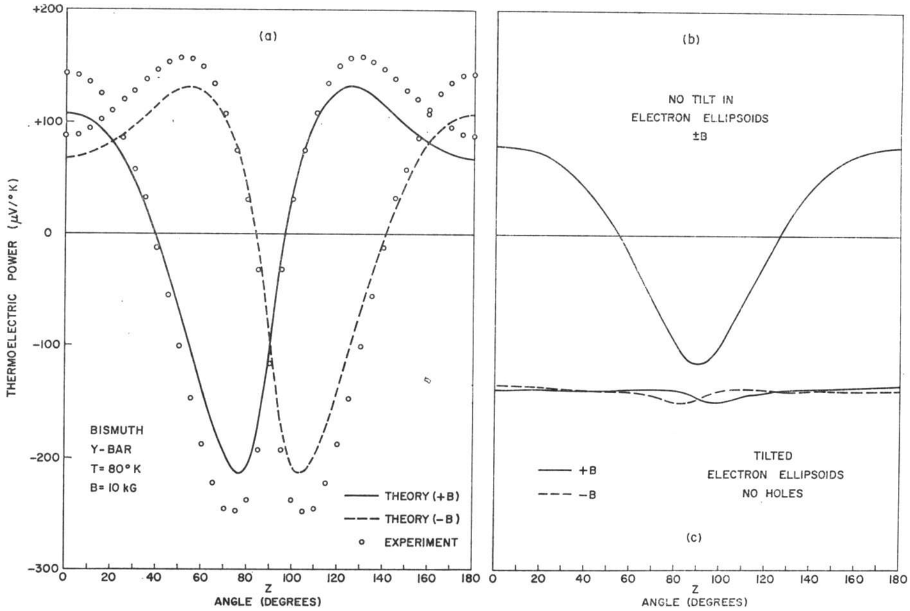


Fig. 1. Thermoelectric power in the y-direction vs. orientation of a 10 kG magnetic field in the $x-y$ plane. x is at 0°, z at 90°, and $-x$ at 180°.

The computer calculation of S for a bismuth bar oriented in the y (bisectrix) direction as a function of transverse magnetic field orientation is shown in Fig. 1 a. The temperature is 80°K and the magnitude of the field is 10 kG. The band parameters used in this calculation (see ref. 1)) are in reasonable agreement with those determined by other types of experiment, and they lead to fair agreement with the experimental data. In order to determine which features of the band model give rise to the observed anisotropy and Umkehr effects, the calculations were repeated with various band modifications introduced into the computer program.

§ 3. Modifications of the Band Model

For a simple two band model in which both electrons and holes have the same densities, effective mass tensors and scattering times the Seebeck coefficient is identically zero. The observed effects obviously depend entirely on the differences between the electrons and holes.

To investigate the importance of equal numbers of electrons and holes, the relative numbers of electrons and holes were varied in the calculation while retaining the parameters of ref. 1). As the density of holes was reduced, the Seebeck coefficient versus field orientation changed continuously from the curve shown in Fig. 1 a to that in Fig. 1 c in which the hole density was set equal to zero. The anisotropy is greatly reduced but a small Umkehr effect still exists as long as the tilt in the electron ellipsoids is retained in the model. In zero magnetic field, of course, the thermoelectric power tensor is isotropic for a single carrier.

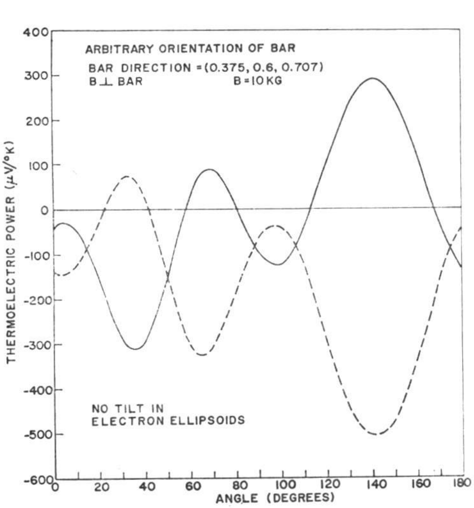


Fig. 2. Calculated thermoelectric power vs. orientation of a 10 kG transverse magnetic field.

In Fig. 1 b, the tilt of the electron ellipsoids was eliminated ($m_4=0$) while the other parameters were those in ref. 1). Note that the Umkehr effect no longer exists but S does change from n-type to p-type as the magnetic field is rotated. The vanishing of the Umkehr effect with tilt for this orientation has previously been calculated by Harman, Honig, and Jones.[5] For this case of a bar along a principal direction (the y axis), the magnetic field lies in a principal plane (the $x-z$ plane). In Fig. 2, a bar direction in a non-principal direction was arbitrarily chosen while the magnetic field was rotated in the plane perpendicular to the bar direction. The model again uses the parameters of ref. 1) but with the tilt of the electron ellipsoids removed, as in Fig. 1 b. In this calculation, the Umkehr effect returns and is very large.

In a further calculation, the electrons were eliminated leaving only holes in one ellipsoid of revolution. For principal directions, in a 10 kG field, the Umkehr effect vanishes but for the arbitrary off-axis direction defined in Fig. 2, a small (~2%) Umkehr effect does appear.

Thus, the Umkehr effect can occur even when only one type of carrier contributes to conduction and even when the carrier energy surfaces are not tilted with respect to the crystal axes. It appears that the Umkehr effect must vanish only when the magnetic field lies in a mirror plane with respect to the symmetry of the Fermi surface. For the rhombohedral crystal symmetry considered here, the $y-z$ plane is always a mirror plane of the crystal and of the Fermi surface. The $x-z$ plane is equivalent to a Fermi surface mirror plane (neglecting displacements of the ellipsoids in k-space) only if the ellipsoids are not tilted, as in Fig. 1 b.

The energy dependence of the electron effective mass (resulting from the non-parabolic model) and of the relaxation time was eliminated and found to change the magnitudes but not the general features of the curves. Also when the relaxation time is reduced so that $\omega_c\tau \ll 1$ (ω_c is the cyclotron frequency), the anisotropies and Umkehr effect are greatly reduced.

§ 4. Partial Currents

To investigate the current contributions from the individual groups of electrons and holes, the experimental situation of Fig. 1a was chosen with the magnetic field orientated at $\theta=70°$

($-B$ corresponds to $+B$ at $\theta=250°$). For this case, the measured and calculated Umkehr effect is very large and S is negative for $+B$ and positive for $-B$.

It can be seen from eqs. (7), (8) and (12) that the expression for S is very complex so we have

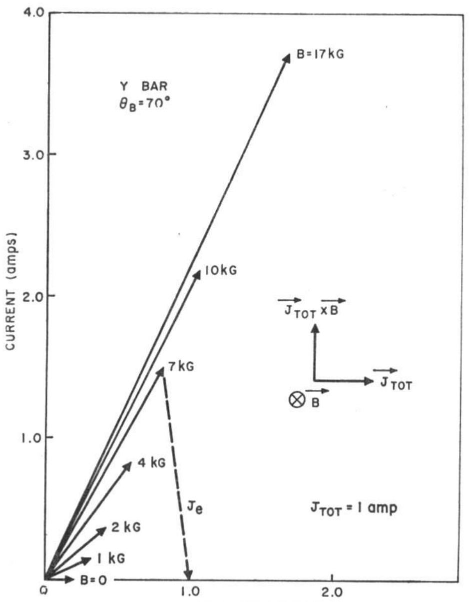


Fig. 3. Hole current vs. magnetic field in a plane perpendicular to the field direction ($+B$).

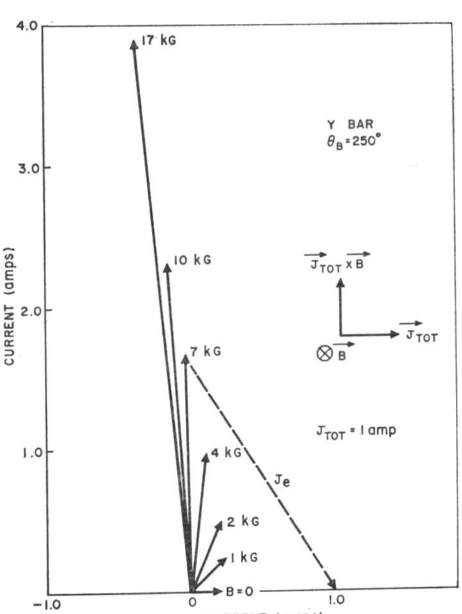


Fig. 4. Hole current vs. magnetic field in a plane perpendicular to the field direction ($-B$).

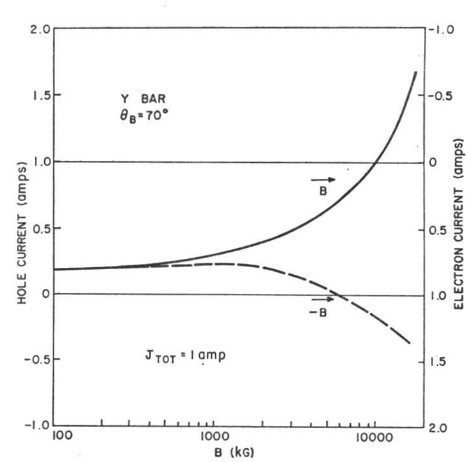
chosen to look at the partial currents $\vec{J}_i$ under the conditions of an applied current $\vec{J}$ and no temperature gradient. In this case,

$$\vec{J}_i = \overleftrightarrow{\sigma}_i \cdot \vec{\mathscr{E}} = \overleftrightarrow{\sigma}_i \cdot \overleftrightarrow{\sigma}^{-1} \cdot \vec{J}. \tag{13}$$

The cause of the sign reversal was sought by calculating these partial currents.

First, consider hole current flow in a plane perpendicular to the magnetic field. The total current down the length of the bar is fixed at 1 ampere in this calculation and the total transverse current must, of course, vanish. In Fig. 3, the hole current is shown for various values of the field at $\theta=70°$. For zero field, the holes carry 0.2 amps along the bar and the electrons carry the remaining 0.8 amps. As the field increases, the Hall angle of the holes increases and also the magnitude of the current increases and becomes larger than the forward current. The electron current required to make the total current 1 ampere along the bar is shown for the case of $B=7$ kG. In Fig. 4, the same plot is shown for the magnetic field reversed. Again, large currents flow in the Hall direction and in this case the Hall angle for holes becomes greater than 90° for large fields and hence the current component along the bar is reversed.

Consider now these partial current components parallel to the bar as a function of magnetic field. The calculation was made for the orientations described above and the results are shown in Fig. 5. Again, at zero field, 20% of the total



ELECTRON AND HOLE CURRENTS
// TOTAL CURRENT

Fig. 5. Partial currents along the bar as a function of magnetic field. Note that the ordinate for holes increases upward and that the ordinate for electrons increases downward.

1 ampere current is carried by holes and 80% by the higher mobility electrons. As the field in the positive direction is increased, the hole contribution increases until near 10 kG the holes carry the total current and the electrons none. At higher fields, the hole contribution exceeds the total current of 1 ampere and the electron contribution is *negative*.

The opposite effect occurs when the magnetic field is reversed. In this case, as the field is increased, the hole current drops to zero near 6 kG and in larger fields the holes travel in the negative direction while the electrons carry more than 1 ampere down the bar.

If we consider the Peltier effect under these unusual conditions, in a large positive field (the solid curve in Fig. 5) the holes must make an unusually large contribution to the heat flux. Above 10 kG the electrons, which travel in the same direction as the holes (from positive to negative), will also carry heat in this direction. The resultant Peltier coefficient is therefore the sum of two positive components rather than the resultant of a positive hole component and a negative electron component. Similarly, in a large reversed magnetic field, the electron contribution to the Peltier coefficient is large and negative and the contribution from the reverse current of holes is also negative.

Thus the Peltier coefficient is positive in a field $+B$ and negative in the reverse field $-B$ for this orientation. The Seebeck coefficient is related to the Peltier coefficient by the Kelvin relation, which in a magnetic field is

$$\overleftrightarrow{S}(\vec{B})T = \overleftrightarrow{\pi}(-\vec{B}). \tag{14}$$

The Seebeck coefficient in $+B$ therefore has the same sign as the Peltier coefficient in $-B$. Using this argument then, $S(+B)$ is negative and $S(-B)$ is positive, in agreement with Fig. 1 a.

The reason behind this unusual current behavior lies in the fact that the velocity of the carriers (which determines the current) can be at a different angle than the momentum (because of anisotropy in the Fermi surface) and it is the momentum which is changed by the application of external forces. The magnitudes which this anisotropy can assume is exemplified in Fig. 6. Here the components of current perpendicular to the bar are plotted on a polar diagram. The designations e_1, e_2 and e_3 refer to the contributions from the three electron ellipsoids. For an isotropic material, the current directions would be perpendicular to the magnetic field directions but here it is seen that the anisotropy causes some of the electrons to have larger components parallel to the field than perpendicular to it. In the figure it appears that the currents reverse magnitude and direction with magnetic field but actually there are small deviations from this exact relationship.

§ 5. Energy Dependence of Current

The experimental conditions at $T=80°\mathrm{K}$ are such that kT is comparable with the Fermi energy (E_F). Exact statistics were therefore used in the calculation and the total current obtained from an expression of the form $J=\int j(E)dE$ where the integration is over all energies E and $j(E)$ is found from the Boltzmann equation. A

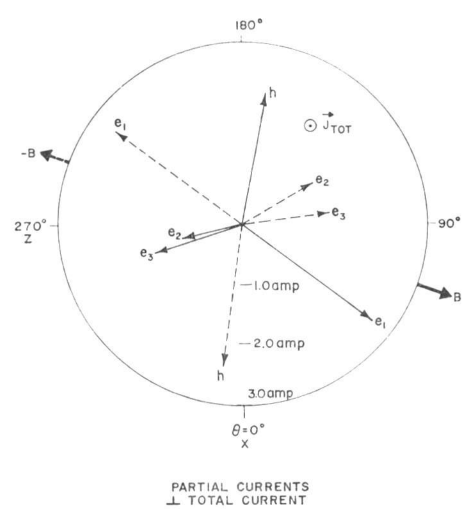


Fig. 6. Partial currents in a plane perpendicular to the total current.

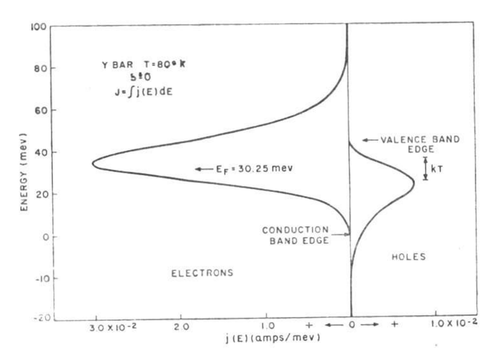


Fig. 7. Electron and hole currents as a function of energy in zero magnetic field. The electron current is the sum over the three electron ellipsoids.

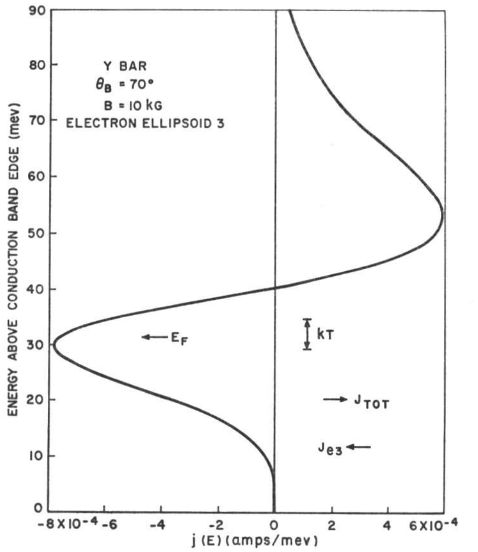


Fig. 8. Electron current vs. energy in a magnetic field for a single electron ellipsoid.

plot of the integrand $j(E)$ as a function of energy is shown in Fig. 7 for the case of $B=0$ in order to visualize this energy distribution of current. What is plotted here is the component of current along the bar; the perpendicular components resulting from anisotropy are only about 5% of the total current. The valence band which lies 15 meV directly below the electron band contributes essentially zero current, since it lies about $7\,kT$ below the Fermi energy. This distribution shifts as a function of magnetic field. An extreme example is shown in Fig. 8. This shows the current contribution along the bar for electron ellipsoid 3. The low energy electrons make a negative contribution while the high energy ones contribute positive current, resulting in a total contribution close to zero. This effect results from the increase in effective mass and decrease in relaxation time as a function of energy. The lower mobility (high energy) carriers have a Hall angle less than 90° and the high mobility carriers have a Hall angle exceeding 90°.

§ 6. Conclusions

These computer calculations of the contributions of the electrons and holes to the total current in bismuth in a transverse magnetic field have illustrated some unexpected behavior. Electrons or holes can make negative contributions to the total current and this gives rise to the observed thermoelectric sign reversal. Also, low energy electrons may drift "up hill" while high energy electrons in the same group drift "down hill". The partial currents in the "Hall effect" direction or in the magnetic field direction may be much larger than those down the length of a bar. A further analysis of these currents would lead to detailed information about the Hall effect and the transverse thermomagnetic effects.

The calculations of the magneto thermoelectric anisotropy for hypothetical materials with modified bismuth bands have shown that the Umkehr effect can exist even for a single carrier with non-tilted ellipsoidal energy surfaces. In fact, any material with even the slightest departure from spherical energy surfaces should exhibit an Umkehr effect as long as the magnetic field is not parallel to a mirror plane of the Fermi surface. In bismuth and related semimetals, the effects are very large because the equal numbers of anisotropic, high-mobility electrons and holes allow large transverse currents to flow.

Acknowledgement

The assistance of S. E. Haszko in the experimental portion of this investigation is gratefully acknowledged.

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DISCUSSION

Polder, D.: How sensitive are your results to a slight unbalance of the hole and electron concentration ?

Smith, G. E.: Not very sensitive. For example, a 10% decrease in hole concentration will change the thermoelectric power about 10%.