

V. THERMOELECTRIC PROCESSES AND MATERIALS*

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A. ANISOTROPIC THERMOELECTRIC EFFECTS

1. THEORY

The thermoelectric power of Bi_2Te_3 has been worked out by Goldsmid (1) with the use of the simple model of spherical constant-energy surfaces. But no calculation of the thermoelectric effects based on the more recent models of band structure has been seen by the writer, although Drabble (2) states that it appears in a Ph. D. thesis by Goldsmid (3). While awaiting receipt of Goldsmid's work we felt that it was worth while to make a calculation of the thermoelectric power, using a "many-valley" model of constant energy surfaces in momentum space. This model has been used successfully by Drabble and Wolf (4) for explaining magnetoresistance data. A summary of the results of this calculation follows.

The energy-band model consists of six ellipsoids centered on the reflection planes in reciprocal space. These are shown in Fig. V-1. Let K'_x , K'_y , K'_z be the principal axes of a valley. The K'_z axis coincides with the c axis of the reciprocal lattice. Let the K'_x axis be perpendicular to the K'_z axis and be in one of the six reflection planes. The K'_y axis is perpendicular, in a right-handed sense, to the K'_z and K'_x axes and makes angles of 30° with the nearest reflection planes. The valley centered at $K'_x, 0, K'_z$ has its K'_y axis parallel to the K'_y axis of the reciprocal lattice. The other valleys are so located in their reflection planes that they satisfy the symmetry of the crystal. In particular, three valleys are centered at the same value of K'_z and 120° apart, say at 0° , 120° , and 240° . The K'_z axes of these valleys make an angle θ (a parameter to be determined by experiment, along with the effective masses) with the K'_z axis. The other three valleys are centered at $-K'_z$, and are at angles of 60° , 180° , and 300° . Their K'_z axes make an angle θ with the $-K'_z$ axis.

The perturbation of the equilibrium distribution function attributable to the applied electrical and thermal gradients is found by solving Boltzmann's equation. This perturbed distribution f is used to find the flux of particles

$$J^e = \int (\nabla_p \epsilon) f d^3 P \quad (1)$$

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and the flux of energy carried by the particle

$$C = \int \epsilon (\nabla_{\mathbf{p}} \epsilon) f d^3 P \quad (2)$$

A tensor transformation is made to transform these equations from K_x, K_y, K_z space to the K'_x, K'_y, K'_z space of a particular valley. The integrations are performed over

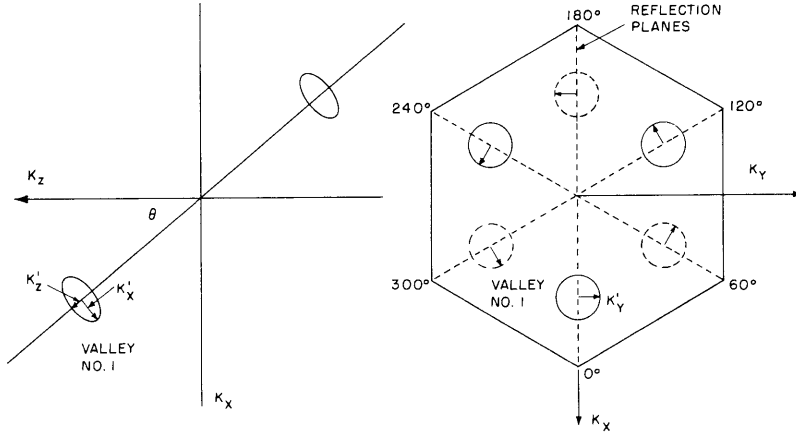


Fig. V-1. Constant-energy surfaces.

the constant-energy surfaces of the particular valley. The force-flux equations for the i^{th} valley then reduce to the following form:

$$J_i = \frac{2^{7/2}}{3} \pi \frac{(m_1 m_2 m_3)^{1/2}}{m_i} \left\{ \left[-e \frac{d\phi}{dx_i} + T \frac{d}{dx_i} \left(\frac{\epsilon'}{T} \right) \right] K_i^{(1)} + K_i^{(2)} \frac{1}{T} \frac{dT}{dx_i} \right\} \quad (3)$$

$$C_i = \frac{2^{7/2}}{3} \pi \frac{(m_1 m_2 m_3)^{1/2}}{m_i} \left\{ \left[-e \frac{d\phi}{dx_i} + T \frac{d}{dx_i} \left(\frac{\epsilon'}{T} \right) \right] K_i^{(2)} - K_i^{(3)} \frac{1}{T} \frac{dT}{dx_i} \right\} \quad (4)$$

where

$$K_i^{(j)} = \int \tau \epsilon^{(j+1/2)} \frac{df}{d\epsilon} d\epsilon$$

We multiply Eq. 3 by ϵ' and subtract it from Eq. 4 to put them in a form that is easier to transform back to the unprimed system:

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$$J_i = \frac{2^{7/2}}{3} \pi \frac{(m_1 m_2 m_3)}{m_i} \left[K_i' \frac{d}{dx_i} (\epsilon' - e\phi) + \left(K_i^2 - \epsilon' K_i' \right) \frac{1}{T} \frac{dT}{dx_i} \right]$$

$$h_i = \frac{2^{7/2}}{3} \pi \frac{(m_1 m_2 m_3)}{m_i} \left[\left(K_i^2 - \epsilon' K_i' \right) \frac{d}{dx_i} (\epsilon' - e\phi) + \left[K_i^3 - \epsilon' K_i' - \epsilon' \left(K_i^2 - \epsilon' K_i' \right) \right] \frac{1}{T} \frac{dT}{dx_i} \right]$$

(5)

These equations are of the form obtained by Nye (5) from phenomenological considerations

$$J_i = a_i \frac{d\bar{\mu}}{dx_i} + \beta_i \frac{1}{T} \frac{dT}{dx_i}$$

$$h_i = \beta_i \frac{d\bar{\mu}}{dx_i} + \gamma_i \frac{1}{T} \frac{dT}{dx_i}$$

when $\bar{\mu} = (\epsilon' - e\phi)$ is the chemical potential, and h_i is the flow of entropy carried by the particles. In vector notation, we have

$$\vec{J} = \vec{a} \nabla \bar{\mu} + \vec{\beta} \frac{\nabla T}{T}$$

$$\vec{h} = \vec{\beta}^t \nabla \bar{\mu} + \vec{\gamma} \frac{\nabla T}{T}$$

when \vec{a} , $\vec{\beta}$, and $\vec{\gamma}$ are diagonal tensors in the valley system, and the superscript t indicates the transpose of the corresponding tensor.

We transform the preceding equations from the valley system back into the reciprocal lattice system. This gives the contribution of a particular valley to the particle or entropy flow. The resulting tensors will not be diagonal.

The sum of the results from all six valleys, however, will yield diagonal tensors that conform to crystal symmetry. For the hexagonal close-packed structure ($\bar{3}m$), \vec{a} and $\vec{\beta}$ will have the form

$$\vec{a} = \begin{bmatrix} a_{11} & & \\ & a_{11} & \\ & & a_{33} \end{bmatrix} \quad \vec{\beta} = \begin{bmatrix} \beta_{11} & & \\ & \beta_{11} & \\ & & \beta_{33} \end{bmatrix}$$

The thermoelectric tensor $\vec{\Sigma} = \vec{a}^{-1} \vec{\beta}$ will have the same form:

$$\vec{\Sigma} = \begin{bmatrix} \Sigma_{11} & & \\ & \Sigma_{11} & \\ & & \Sigma_{33} \end{bmatrix}$$

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Going back to the detailed calculation, we find that the condition $\Sigma_{11} \neq \Sigma_{33}$ for anisotropy of the thermoelectric tensor is

$$\int \frac{\tau'_{x'}}{m_{x'}} \epsilon^{3/2} \frac{df}{d\epsilon} d\epsilon \int \frac{\tau'_{y'}}{m_{y'}} \epsilon^{5/2} \frac{df}{d\epsilon} d\epsilon - \int \frac{\tau'_{y'}}{m_{y'}} \epsilon^{3/2} \frac{df}{d\epsilon} d\epsilon \int \frac{\tau'_{x'}}{m_{x'}} \epsilon^{5/2} \frac{df}{d\epsilon} d\epsilon \neq 0 \quad (6)$$

In order for expression 6 to be nonzero, $\tau_{x'}$ and $\tau_{y'}$ must be different functions of energy.

Hence an experimentally anisotropic thermoelectric power could provide interesting information about the scattering mechanism. Further theoretical work on this mechanism would, however, involve a complete solution of the phonon-electron interaction problem. This problem is only tractable when rather drastic simplifying assumptions are made. Since it is not clear without experimental data just what assumptions it would be reasonable to make, it seems inadvisable to continue with ad hoc theory concerning an anisotropy which has never really been observed with confidence until a reliable experimental determination of the magnitude of the effect is available. We are attempting to produce more suitable materials for this purpose.

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References

1. H. J. Goldsmid, Proc. Phys. Soc. (London) 71, 633 (1957).
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3. H. J. Goldsmid, Ph. D. Thesis, University of London, 1957.
4. J. R. Drabble and R. Wolf, Proc. Phys. Soc. (London) 69, 1101 (1955).
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2. EXPERIMENTS WITH BISMUTH TELLURIDE

For the purpose of determining whether or not there are any significant anisotropies, some preliminary measurements were made of the Seebeck coefficient of bismuth telluride at room temperature. The approximately cubical samples, about 0.5 cm on an edge, were cut from ingots grown by the Bridgman process. The samples were placed between two planar nickel-plated copper electrodes in different orientations so that the thermoelectric voltage could be measured in three orthogonal directions. In Table V-1, the Seebeck coefficient in a direction perpendicular to the cleavage planes is indicated as a_{\perp} , the Seebeck coefficient parallel to the cleavage planes and parallel to the direction of crystal growth is indicated as a'_{\parallel} , and a''_{\parallel} is the thermoelectric power parallel to the cleavage planes and transverse to the direction of growth.

The p-type sample No. 9 demonstrates an isotropic Seebeck coefficient, which is

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Table V-1. Seebeck Coefficients.

Sample Number	Conductivity Type	Mean Temperature (°C)	a_{\perp} ($\mu v/^{\circ}C$)	a_{\parallel}' ($\mu v/^{\circ}C$)	a_{\parallel}'' ($\mu v/^{\circ}C$)
8	p-type	30.8	280	243	245
9	p-type	30.5	237	239	239
3	n-type	37.0	41.3	79.0	84.5
5	n-type	33.9	169	168	223
6	n-type	12.0	182	232	263
7	n-type	33.0	136	135	153

in agreement with Goldsmid's experimental observation (1) that the thermoelectric power in p-type bismuth telluride is isotropic with an accuracy of 1 per cent. Sample No. 8, however, exhibits an unusually high a_{\perp} but is isotropic in directions parallel to the cleavage planes. All of the n-type samples are anisotropic, but the only other generalization that can be made about them is that the magnitude of a_{\perp} is usually less than that of the a_{\parallel} . The large spread in experimental values is believed to be caused by inhomogeneities in the n-type material. The presence of inhomogeneities was particularly evident in the ingot from which sample No. 3 was cut, in which precipitated tellurium was found among the cleavage planes. Since doping gradients appear to be responsible for the major anisotropies in the experimental thermoelectric powers, the effect of inhomogeneities on the thermoelectric properties is being studied.

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References

1. H. J. Goldsmid, Ph. D. Thesis, University of London, 1957; cited by J. R. Drabble, Galvanomagnetic effects in p-type bismuth telluride, Proc. Phys. Soc. (London) 72, 380-390 (1958).

B. THERMAL CONDUCTIVITY STUDIES*

Our work has proceeded along both theoretical and experimental lines. Most emphasis, however, has been placed on theory, as the work of Tavernier gave promise of achieving reasonably good predictions on the thermal conductivity of semiconductor alloys. Such predictions could be of much help in planning experiments for producing better thermoelements.

*This work is being performed at Laboratoire Central des Industries Électriques, Fontenay-aux-Roses, France.

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1. Theory

Tavernier has carried out a better analysis of thermal conductivity in crystals in which phonon scattering is caused mostly by: (a) isotope (or mass fluctuation) effects at short wavelengths, measured by the parameter

$$\epsilon = \sum p_i \left[\frac{1}{M_i} - \left\langle \frac{1}{M} \right\rangle \right]^2$$

where P_i is the proportion of the i^{th} isotopic or atomic species, M_i is the mass of the i^{th} species, and $\langle \rangle$ indicates "mean value"; and (b) three phonon processes at long wavelengths.

The details of the theory will be published as a note in "Comptes rendus," but we can summarize the main results as follows. The heat conductivity K is related to the melting point T_f , the mean mass M , the density ρ , and the parameter ϵ by the formulas

$$K = \alpha T_f^{7/6} M^{-3/2} \rho^{2/3} \epsilon^{-2/3} T^{-1/3} \quad (\text{if transverse phonons predominate}) \quad (1)$$

$$K = \beta T_f^{5/4} M^{-5/4} \rho^{1/2} \epsilon^{-1/2} T^{-1/2} \quad (\text{if longitudinal phonons predominate}) \quad (2)$$

where α and β are parameters that cannot now be computed.

But if α , for example, is computed from known experimental data and Eq. 1, the results are remarkably alike for those materials with large ϵ and for which the theory

Table V-2.

	<u>α</u>	<u>$\epsilon \times 10^5$</u>
PbTe	6	4.5
PbSe	5.2	7.9
SbCd	3.6	24.7
SbZn	3.6	10.2
KBr	4.9	9.8
KCl	5.5	18
NaCl	5	21
LiF	2.3	30
Ge	155	63
Si	40	25
C	10	8
Te	11	30

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should apply. Exceptions are germanium and silicon (K , too large), and lithium fluoride (K , too low). Outside of these materials, α is found to vary only from 3.6 to 6. The main correlation is with crystal structure: materials of similar crystal structure have similar values of α within ± 15 per cent, as Table V-2 shows.

2. Experiment

As the theory develops, it becomes obvious that better methods of measurement of heat conductivity are necessary. For this reason, apparatus for measurement of heat conductivity by ac heat flow is being built.

Tavernier has analyzed the Danielsen method without making the assumption of planar isotherms. This analysis is contained in the note to "Comptes rendus."

A very low frequency oscillator, with the circular motion of a probe in an electrolyte across which dc is applied, has been built, and it is expected that the apparatus will soon be operational.

Furthermore, from Tavernier's work, it seems more and more likely that the alloys of the formula $(\text{Mo}_x \text{W}_{1-x})(\text{Se}_y \text{Te}_{1-y})_2$ will be most promising materials.

MoTe_2 has been prepared by co-melting the constituents in a sealed quartz tube. For MoSe_2 it appears that an excess of selenium is necessary for obtaining MoSe_2 .

The aforementioned materials are being measured for heat conductivity, thermoelectric power, and electron mobility.

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