IV. THERMOELECTRIC PROCESSES AND MATERIALS*

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A. MERCURY TELLURIDE EVALUATION

The preparation of ingots of mercury telluride has continued. Additions of from 10^{18} to 10^{19} atoms of cadmium per cm^3 to a number of melts have, thus far, failed to produce an n-type semiconductor. Acceptor concentrations, however, have been reduced from the 10^{18}-10^{19} per cm^3 level to an estimated density of from 10^{16} to 10^{17} per cm^3.

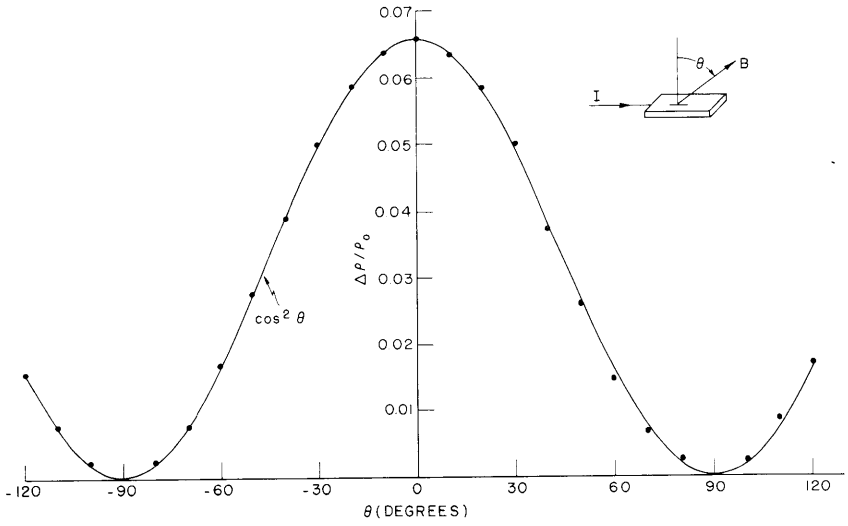

Fig. IV-1. Angular dependence of magnetoresistance. (Sample No. 19Aa-6: B = 7200 gauss, T = 313°K.)

Magnetoresistance measurements were performed on unoriented samples of mercury telluride. The angular dependence of the magnetoresistance for one specimen is shown in Fig. IV-1. Although this is a p-type sample, the density of thermally

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generated electrons with high mobility (20,000 cm^2/volt-sec) is sufficient to provide a predominantly electronic contribution to the magnetoresistance. The conclusion based on the data of Fig. IV-1, therefore, is that the conduction band in mercury telluride is spherically symmetrical and the energy minimum occurs at k = 0. The usual experimental precaution of making potential contacts of small area to the sample had to be observed in order to obtain the results indicated in Fig. IV-1.

The transverse magnetoresistance was found to obey the expected square-law variation with magnetic field. The temperature variation of the magnetoresistance was similar to the variation of the Hall constant; this is typical behavior for mixed-conduction systems.

Hall-coefficient variations with magnetic field were measured. At room temperature, when the electrons are believed to be degenerate, the Hall coefficient was found to be independent of magnetic field (up to 7500 gauss). At lower temperatures (at 77°K, for example), both hole and electron statistics are expected to be nondegenerate, and the Hall constant was found to decrease with increasing magnetic field. Consequently, galvanomagnetic measurements of mercury telluride have yielded readily interpretable data.

R. E. Nelson

B. TRANSPORT OF CONTACT MATERIALS IN BISMUTH TELLURIDE

Measurements of thermoelectric power and resistivity in single crystals of p-type bismuth telluride, which have been exposed to copper for various lengths of time and at several temperatures, indicate that the compensation process cannot be interpreted on the basis of simple nondegenerate semiconductor theory.

The value of the activation energy for diffusion of copper in the direction parallel to the cleavage planes of bismuth telluride was found to be $0.21 \pm .01$ ev for concentrations up to approximately 10^{19} copper atoms/cm^3. This value is in close agreement with that reported by Carlson (1). There is some evidence that when the concentration of copper in bismuth telluride exceeds approximately 2×10^{19} atoms/cm^3, a chemical reaction occurs, even at 0°C.

A detailed report dealing with these matters is now in preparation.

O. P. Manley

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1. R. O. Carlson, Anisotropic diffusion of copper in bismuth telluride, J. Phys. Chem. Solids (to be published).

C. THERMAL CONDUCTIVITY STUDIES*

1. Theory

In a semiconductor, the heat is mostly carried by the thermal vibrations of the lattice. If these vibrations were harmonic, they would propagate freely in the crystal, and no thermal resistivity could exist. The anharmonic terms in the potential of the lattice, acting as perturbations, give rise to phonon scattering. This can occur in two ways. If the wave vector of the new phonon lies within the first Brillouin zone (this is always the case with low-energy phonons), the momentum is conserved in the collision; we have a "normal" process that does not give rise to thermal resistance but tends to rearrange the phonon distribution. However, if the sum of the wave vectors of the interacting phonons lies outside the Brillouin zone, the wave vector of the new phonon, which must lie within the Brillouin zone, differs from the vector sum by a basis vector of the reciprocal space. This "Umklapp" process does not conserve momentum, and hence gives rise to thermal resistance.

Mass fluctuations in the lattice (for example, those resulting from the presence of isotopes) also scatter the phonons, and can give rise to thermal resistivity if the phonon distribution is rearranged by the normal processes. More precisely, the thermal resistivity caused by mass fluctuations becomes important if the probability of scattering by normal processes, which varies as the square of the wave vector for longitudinal phonons, prevails over the probability of scattering by mass fluctuations, which varies as the fourth power of the wave vector. In other words, the thermal resistivity caused by mass fluctuations is important for $k < k'_m$ (k'_m being the value of the wave vector below which the scattering probability resulting from the normal processes prevails). In this region of the reciprocal space, the thermal conductivity from mass fluctuations can (as reported previously) be written

$$K \propto T_f^{5/4} M^{-5/4} \rho^{1/2} \epsilon^{-1/2} T^{-1/2} \tag{1}$$

where T_f is the melting point of the compound; M is its molecular weight; ρ is the density; ϵ is the mass fluctuation parameter, defined as

$$\epsilon = \left\langle \left(\frac{1}{M} - \left\langle \frac{1}{M} \right\rangle \right)^2 \right\rangle \frac{1}{\left\langle \frac{1}{M} \right\rangle^2}$$

and T is the absolute temperature.

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

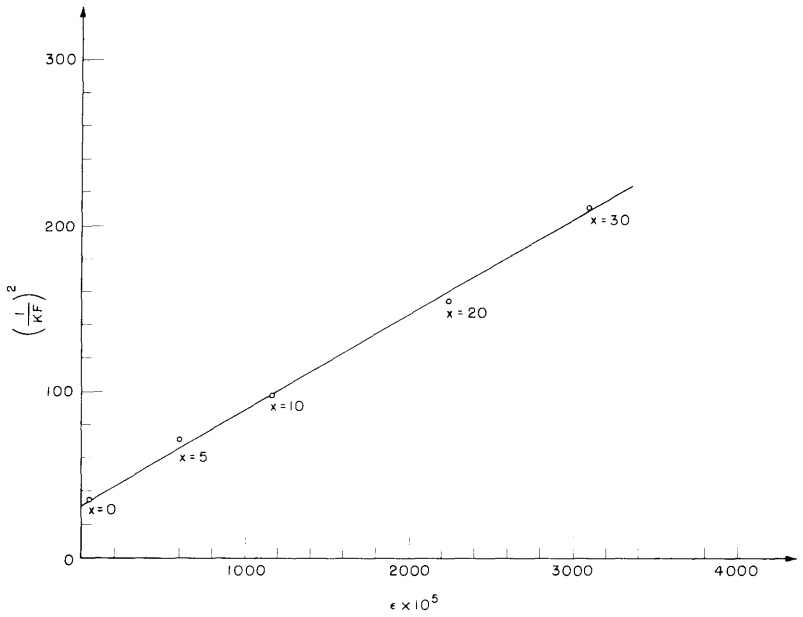

Fig. IV-2. Normalized square of the thermal resistivity of $Mg_2Pb_xSn_{1-x}$ as a function of the mass-fluctuation parameter ϵ.

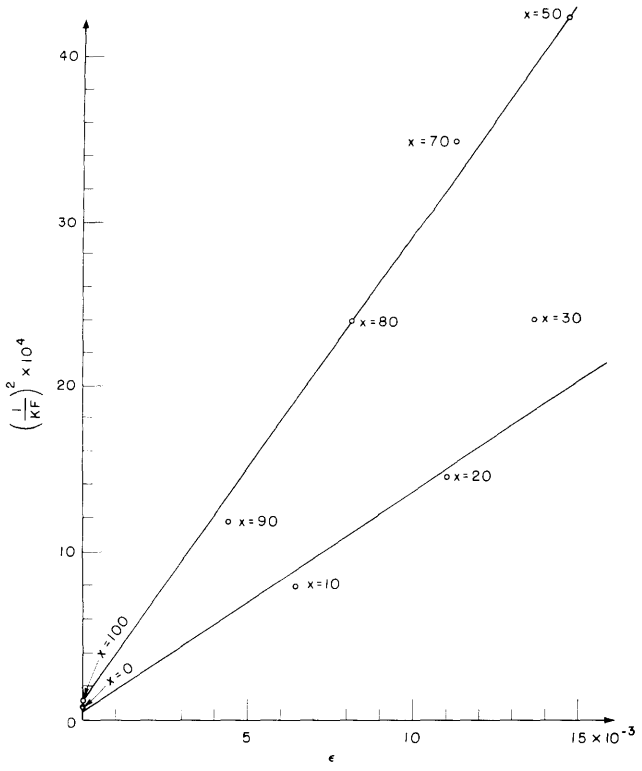

Fig. IV-3. Normalized square of the thermal resistivity of $Ga_xIn_{1-x}As$ as a function of the mass-fluctuation parameter ϵ.

A formula for the thermal resistivity resulting from the Umklapp processes has been derived, and has the form

$$K^{-1} \propto T_f^{-3/2} M^{+7/6} \rho^{-2/3} T \tag{2}$$

If the mass fluctuations and Umklapp processes are considered simultaneously, the resulting thermal resistivity is obtained by adding the transition probabilities. The result can be put into the form

$$K^{-1} \propto F(\epsilon + AT)^{1/2} \tag{3}$$

with $F \equiv T_f^{-5/4} M^{5/4} \rho^{-1/2}$. In this formula, ϵ comes from the mass fluctuations, and A is a parameter characterizing the Umklapp processes. To test this theory, experimental values of $(KF)^{-2}$ have been plotted against ϵ for several compounds of the form $Mg_2Pb_xSn_{1-x}$.

It can be seen that the points for $x < 40$ per cent actually lie on a straight line (Fig. IV-2). It would also be interesting to check the linearity with respect to the temperature.

Analysis of Rosi's (1) data on $Ga_xIn_{1-x}As$ shows that the points representing $(KF)^{-2}$ versus ϵ lie mainly on two straight lines: one for $0 < x < 20$ per cent, and the other for 50 per cent $< x <$ 100 per cent (Fig. IV-3). This is not surprising, for the following reason. Our theory assumes that the anharmonic terms are independent of x. This assumption is certainly not justified for the whole range $0 \leq x \leq 100$ per cent, although the data indicate that it is a good approximation for $x < 25$ per cent and $x > 50$ per cent. Similar comments can be made concerning Joffe's results on $PbSe_xTe_{1-x}$.

Rosi's results show that our theory should be made to account for the variation of the anharmonic terms of the potential with x, that is, with ϵ. A detailed account of the conductivity theory presented here will be available in Tavernier's thesis.

2. Preparation of Samples

(a) Preparation of Mg_2Pb and Mg_2Sn

The magnesium compounds must be prepared with special care because magnesium, which has a high vapor pressure at the melting point of the compounds, reduces SiO_2 when cofusion is attempted in a sealed silica tube.

Accordingly, the cofusion is performed in a special oven (2) under a pressure (up to 50 kg/cm^2) of purified argon, which considerably lowers the rate of evaporation of the magnesium. The crystals are grown by controlled cooling of the melt and then purified by "zone melting," under approximately 5 kg/cm^2 pressure, since the magnesium vapor pressure is considerably reduced, once the compound is formed.

A systematic study has shown that the type (n or p) of the semiconductor obtained

depends upon the cooling rate. A very slow cooling rate yields n-type material, whereas a relatively fast cooling yields p-type. This circumstance results from the influence of the cooling rate on the segregation constant. We also noticed that magnesium that is in excess with respect to the stoichiometric composition behaves like a donor, and vice versa.

(b) Preparation of $Mg_2Pb_xSn_{1-x}$

The cofusion of the elements is performed in the pressure oven, but zone melting cannot be carried out.

After preparation, the samples are tested. The sign of the Hall effect and of the thermoelectric power give the conductivity type of the sample. The thermoelectric power at the ambient temperature is checked by the hot-point method. The impurity concentration is deduced from the Hall constant at low temperature. The resistivity, measured by a four-probe method, and combined with the Hall data, yields the carrier mobility.

(c) The Se_xTe_{1-x} system doped with antimony

This system is being studied for practical, as well as theoretical, reasons. From the practical standpoint, tellurium has a relatively low thermal conductivity that can even be reduced by the addition of selenium, which mixes with tellurium in all proportions and increases the scattering of phonons by mass fluctuations. The electric conductivity of the mixture can be increased by proper doping, for instance, with antimony. In other words, we hope to be able to produce a compound having a high figure of merit.

From a theoretical standpoint, this system could be used to test our theory of thermal resistivity produced by mass fluctuations. The raw materials, purified by zone melting and crushed into powder, are introduced into a Pyrex tube that is evacuated and placed in a zone-leveling apparatus. The bottom end of the tube is made cone-shaped to favor the growth of crystals. The heating coil, made of Kanthal wire, moves up and down at the rate of 10 cm/hr, and can raise the temperature of the hot zone to approximately 1000°C.

Samples containing from 4 per cent to 30 per cent Se have been prepared. The measurements of thermoelectric power and resistivity have been almost completed, but must be supplemented with the measurements of thermal conductivity that are now in progress.

(d) Investigation of Cd_3As_2

A new investigation is being started on the compound Cd_3As_2. According to Rosenberg and Harman (3), the electronic mobility in this compound is high ($\mu_e \approx 10^4$ cm^2/volt-sec even in very impure samples ($n_{imp} = 4 \times 10^{18}$ cm^{-3}). These data

indicate a high value of the ratio μ/K, which seems very promising for thermoelectric applications.

3. Measurements of Thermal Conductivity

(a) Dynamic measurement (Ångström method)

The principle of the method will be indicated. If the temperature, T_A, of one end of a sample is forced to vary, for example, as $\Delta T_A = a \cos \omega t$, a heat wave propagates along the rod, toward the other end. Under the assumption that the heat wave is practically damped before reaching the other end, so that no reflection occurs, the temperature T_B at point B of the sample varies as $\Delta T_B = b \cos (\omega t - \phi)$.

If the radiation losses are neglected, it can be shown that

$$\frac{b}{a} = e^{-\phi} \tag{4}$$

with

$$\phi = \left(\frac{\omega c \rho}{2K}\right)^{1/2} \ell \tag{5}$$

In these formulas, ρ is the density of the material; c, its specific heat; K, its thermal conductivity; and ℓ, the distance AB. When ρ, c, and ℓ are known, relations 4 and 5 provide two independent means of obtaining K: by measurement of ϕ, and by measurement of b/a. Since both measurements should yield the same result if radiation losses are negligible, the double measurement provides for the detection of these losses. When losses are not negligible, the simultaneous measurement of b/a and ϕ, by means of a proper correction, permits the exact determination of K.

In the experiment, the material, cut in the form of a rod (2-4 cm long), is placed in a sample holder inserted in a copper tube that keeps the temperature uniform. The tube, with the sample holder in it, can be heated to approximately 500°C by a coaxial electric oven. The whole assembly can be placed in a vacuum jar.

The power needed to propagate the sinusoidal heat wave along the sample is monitored by a probe rotating slowly (from 1/4 to 1/2 rpm) between the plates of a water-filled condenser, in a plane perpendicular to that of the plates. The potential at the probe is the 600-cps signal applied to the plates, modulated by the motion of the probe. It is amplified by a one-stage push-pull amplifier, the output of which drives the heating coil, raising the temperature T_A by a few tenths of a degree (4).

The temperatures T_A and T_B are plotted on the same graph by means of a spot follower, so that the evaluation of the intensity ratio and phase shift is very easy to perform.

The equipment was tested by using a rod of silicon, with the result that the thermal

conductivity was found to be in good agreement with published values.

(b) Static measurement

This is a relative measurement, in which the thermal conductivity, K, of a sample is compared with that of constantan (K_o). This method is particularly adaptable to the investigation of the role of mass fluctuation in a series of compounds like $Mg_2Sn_xPb_{1-x}$.

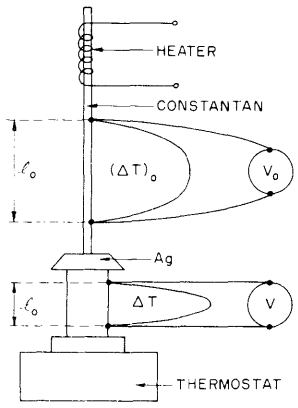

Fig. IV 4. Schematic diagram of apparatus for static measurement of thermal conductivity.

The sample and the reference rod are placed end to end between a heating element and a thermostat. The system is evacuated, to avoid losses by convection (Fig. IV-4). A silver pad keeps the heat flux uniform at the boundary between the sample and the reference rods. The temperature gradients are measured with two thermocouple circuits, the positions of whose junctions are accurately measured. The temperature differences ΔT and $(\Delta T)_o$ are deduced from the thermal voltages V and V_o that are measured with 2-μv accuracy by a zero-current method.

If the radiation losses are disregarded, the heat flux Φ in the system is conserved:

$$\Phi = \frac{\Delta T}{\frac{I}{K}\frac{\ell}{S}} = \frac{(\Delta T)_o}{\frac{I}{K_o}\frac{\ell_o}{S_o}} \tag{6}$$

where S and S_o represent the measured cross sections of the rods. From Eq. 6 we obtain

$$K = K_o \frac{(\Delta T)_o}{\Delta T}\frac{\ell}{\ell_o}\frac{S_o}{S} \tag{7}$$

We have investigated the influence of radiation losses under the pessimistic hypothesis that the thermal resistance representing radiation losses is in parallel with that of the sample. If we assume that sample and container behave as black bodies, the resistance representing radiation losses is found to be

$$r = \frac{\Delta T}{\sigma A\left[(T_o+\Delta T)^4 - T_o^4\right]}$$

where A is the side area of the sample. Under these assumptions, it can be shown that the true thermal conductivity K_{true} is related to the measured conductivity K_m by

$$K_{true} = K_m \left(1 - 4 \frac{\sigma A \ell}{K_m S} T_o^3 - \frac{6\sigma}{K_m} \frac{A\ell}{S} T_o^2 \Delta T \ldots\right) \tag{8}$$

The first corrective term in Eq. 8 yields a systematic error of approximately 10 per cent for typical sample dimensions at room temperature; the second yields another error that varies linearly with ΔT, as verified by the measurements. In any event, the radiation losses are unimportant when the thermal conductivity of the sample is in excess of approximately 0.1 watt deg^{-1} cm^{-1}.

Our method was tested with a lead sample. In metals, the heat is carried mostly by electrons, and, consequently, the thermal conductivity is proportional to the electric conductivity, both conductivities being related by the law of Wiedeman-Franz. The measured thermal conductivity of lead was in good agreement with that calculated by the Wiedeman-Franz relation from the known electric conductivity of lead. Once the validity of the method had been established, measurements on several compounds of the form $Mg_2Pb_xSn_{1-x}$ were carried out. The data of Fig. IV-2 were, in fact, obtained in this way.

P. Aigrain, J. Tavernier

References

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4. J. Tavernier, Thermal conductivity studies, Quarterly Progress Report No. 55, Research Laboratory of Electronics, M.I.T., Oct. 15, 1959, pp. 50-51.