V. THERMOELECTRIC PROCESSES AND MATERIALS*

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RESEARCH OBJECTIVES

We are trying to understand the relationships between the structure of a solid and its relevant properties as a thermoelectric converter. Now, and for some time to come, we expect to remain interested primarily in compound semiconductors, and in mixed crystals of them.

Besides the very considerable matters of actually making and handling the materials involved, the obvious properties of thermoelements which command immediate attention are: the thermoelectric power (Seebeck coefficient) or Peltier heat (Peltier coefficient), the electrical conductivity, and the thermal conductivity. The first two properties are dependent upon the electronic energy-band structure of the solid and the electronic scattering mechanisms in it. Underlying the third property are the dynamics and mechanical perfection of the crystal lattice.

Collateral features of interest in thermoelectric applications are such device-oriented topics as the diffusion (or other transport) of contact materials in the semiconductor and the performance of completed coolers or generators.

A little progress has been made during the past year on selected parts of each topic mentioned above. We have learned how to grow good single crystals of the well-understood material Bi_2Te_3, and the group in France has struggled with new compounds of Mo and W, and they have made successfully polycrystalline solid solutions in the Se-Te system.

We have also helped Professor David C. White's Energy Conversion Group, of the Electronic Systems Laboratory, M.I.T., with their preparation of polycrystalline HgTe and mixed polycrystals in the HgTe-CdTe system. A great deal of effort has been expended in developing our ability to cut, etch, make contact to, and conduct the necessary thermal and electrical measurements on the various materials.

As for the thermoelectric parameters, we have made some theoretical speculations on the connection of the anisotropic thermoelectric power in iodine-doped Bi_2Te_3 with multiple electronic scattering mechanisms in nondegenerate (probably compensated) material, and experiments to pursue these ideas have been carried out at the same time.

The band-structure investigation of HgTe has just been started by conducting measurements of Hall effect and resistivity over a moderately broad temperature range.

Professor Aigrain's group, in Paris, has perfected its thermal-diffusivity equipment and used it to measure the thermal conductivity of germanium, silicon, and compounds in the Se-Te system. They have gone quite far in pursuing Tavernier's theory of the thermal conductivity produced by random mass fluctuations in the lattice, and they have checked it successfully in many cases against their own experimental data and the results of others.

The diffusion of copper in Bi_2Te_3 at room temperature has been observed in a preliminary way, it having been previously determined that the copper seizes tellurium

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by chemical reaction at temperatures higher than approximately 300°C. Several contributions to the general theory of diffusion have been made, and papers have been accepted for journal publication. As by-products of this work, we hope to have soon an interesting check of the effective mass in bismuth telluride from measurements on samples into which copper has diffused.

Finally, some amusing work on devices has been carried out by using bismuth telluride as a heat pump to cool a power transistor. Such efforts are worth while to keep us abreast of both the more practical fabrication problems and the theory of the performance of devices.

In the coming year, most of the current programs are expected to continue, but it is clear that the group at Research Laboratory of Electronics needs to learn much more about thermal conductivity, so that we can help to carry forward the very effective work being done on this key problem by Prof. Aigrain and his associates.

R. B. Adler

A. MERCURY TELLURIDE EVALUATION

Ingots of mercury telluride have been prepared by the Bridgman method from a stoichiometric ratio of mercury and tellurium. Single crystals, approximately 1 cm^3 in volume, have been obtained. Hall data on three wafers cut from the ingots indicate that the mercury telluride measured thus far is p-type. Because of a high electron-to-hole mobility ratio ($b \approx 50\text{-}70$), room-temperature electronic Hall mobilities of 20,000 cm^2/volt sec have been measured. Room-temperature thermoelectric powers, are n-type, and approximately 120 $\mu v/°C$ in magnitude. From the Hall data at 4.2°K, acceptor densities of the order of 10^{18} per cm^3, and hole mobilities ranging from 50 to 250 cm^2/volt sec, have been computed. Hole mobilities appear to be affected by the acceptor density, since the higher hole mobility was measured in the more lightly doped sample.

An ingot of mercury telluride has been prepared with gold as principal impurity. But the gold segregated to the top of the ingot, where the material was distinctly polycrystalline. No measurements were made on this portion except for those on the thermoelectric power at room temperature, which was found to be p-type and 160 $\mu v/°C$ in magnitude.

R. E. Nelson

B. THERMOELECTRIC TEMPERATURE CONTROL OF ELECTRONIC COMPONENTS

A joint report with P. E. Gray and J. Blair, of the Energy Conversion Group, M.I.T., on the static and dynamic performance of a bismuth telluride Peltier cooler was presented at the Northeast Electronics Research and Engineering Meeting, held in Boston, November 19, 1959.

This device had a heat-pumping capacity of 10 watts and a maximum unloaded

temperature drop of 53°C below heat-sink temperatures, in the range 0°C-100°C. The complete description of, and experimental results obtained with, the thermoelectric cooler will be published in the proceedings of the meeting.

R. E. Nelson

C. TRANSPORT OF CONTACT MATERIALS IN BISMUTH TELLURIDE

When copper enters p-type Bi_2Te_3, the semiconductor changes into n-type if the concentration of copper is high enough. In a homogeneous starting material the location of the p-n junction will correspond to a fixed concentration of copper. Thus, by following the motion of the p-n junction, the transport parameters for Cu in Bi_2Te_3 may be determined.

Preliminary measurements indicate that the width of the p-n junction region is several millimeters. Since, furthermore, the Debye radius for Bi_2Te_3 is generally a few lattice parameters, it is permissible to perform meaningful 4-point probe measurements in the junction region. It can be demonstrated that, because of compensation in that region, the conductivity goes through a fairly sharp minimum. If it is assumed that the charge-carrier mobility is relatively independent of charge-carrier concentration – an assumption justified by the absence of ionized-impurity scattering at or near room temperature – then it can be shown that the difference between acceptor and donor concentrations is given by

$$N_d + n_d - N_A - p_A = -\frac{\sigma}{2e\mu_n}\left[(b-1) \pm (b+1)\left(1 - \left(\frac{\sigma_{min}}{\sigma}\right)^2\right)^{1/2}\right]$$

where

N_d = concentration of ionized donors
n_d = concentration of un-ionized donors
N_A = concentration of ionized acceptors
n_A = concentration of un-ionized acceptors
μ_n = electron mobility
b = ratio of electron to hole mobilities
σ = conductivity at the point of interest
σ_{min} = minimum conductivity

The plus sign is to be used when

$$N_d + n_d - N_A - P_A < -\frac{\sigma_{min}}{2e\mu_n}(b-1)$$

Since $N_A + p_A$ is presumed to be known and constant throughout a homogeneous

starting sample, $N_d + n_d$, the donor concentration, and hence the Cu concentration, can be determined from conductivity data. Moreover, it can be shown that, subject to the stated assumptions, at the point where the conductivity has its minimum value, σ_{min}, the thermoelectric power, α, is given by

$$\alpha = \frac{k}{e}\left[\frac{3}{4}\ln\frac{m_p^*}{m_n^*} - \frac{1}{2}\ln b\right]$$

where m_p^* and m_n^* are the density-of-states effective masses of holes and electrons, respectively, and k is Boltzmann's constant. Thus, there exists a good possibility of determining the ratios of the pertinent effective masses in Bi_2Te_3.

Inspection of the equations given above reveals that in order to exploit fully the conductivity and thermoelectric-power data, it is necessary to locate, as well as measure accurately, the minimum in the electric conductivity. It is also necessary to measure accurately the thermoelectric power in the region where it has a very small value. To fulfill these objectives, a four-point probe system with approximately 0.3 mm probe separation was constructed for conductivity measurements; and a new thermoelectric probe is now being completed. This probe is designed around a Keithley microvoltmeter which will permit accurate determination of small values of the thermoelectric power α.

O. P. Manley

D. THERMAL CONDUCTIVITY STUDIES*

1. Theory and Measurements

Thermal conductivity measurements have been carried out on solid solutions $Mg_2Pb_xSn_{1-x}$ at room temperature, in order to test our theoretical predictions. Preliminary results cover the range $0 \leq x \leq 30$ per cent.

If the coefficient A in the formula

$$K = A\,T_f^{5/4}\,M^{-5/4}\,\rho^{1/2}\,\epsilon^{-1/2}\,T^{-1/2} \qquad (1)$$

giving the thermal conductivity caused by mass fluctuations (1), is chosen to fit the experimental data for x = 10 per cent, then the results obey the theory fairly well, except for $x < 5$ per cent (Fig. V-1). The discrepancy can be explained if we assume that for low Pb concentrations, Umklapp processes may also contribute to the thermal

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

resistivity. Then the total thermal resistivity is of the form

$$K^{-1} = A^{-1} T_f^{-5/4} M^{5/4} \rho^{-1/2} \epsilon^{1/2} T^{1/2} + B^{-1} T_f^{-3/2} M^{7/6} \rho^{-2/3} T \qquad (2)$$

where B is the coefficient giving the thermal conductivity caused by Umklapp processes alone.

It turns out that the factors $T_f^{-5/4} M^{5/4} \rho^{-1/2}$ and $T_f^{-3/2} M^{7/6} \rho^{-2/3}$ have very similar variations, and so we can write Eq. 2 in the form

$$K^{-1} = (A^{-1} T^{1/2} \epsilon^{1/2} + B^{-1} T) F \qquad (3)$$

where

$$F \equiv T_f^{-5/4} M^{5/4} \rho^{-1/2}$$

If $(KF)^{-1}$ is plotted against $\epsilon^{1/2}$, the points actually fall roughly on a straight line (Fig. V-2), which supports the theory.

The thermal conductivity, K, of a sample is compared with that of Constantan (K_o), as shown in Fig. V-3. The sample and the reference rod are placed end to end between a heating element and a thermostat. The system is evacuated. 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 position of the junctions on the rods is accurately measured. The temperature differences ΔT and

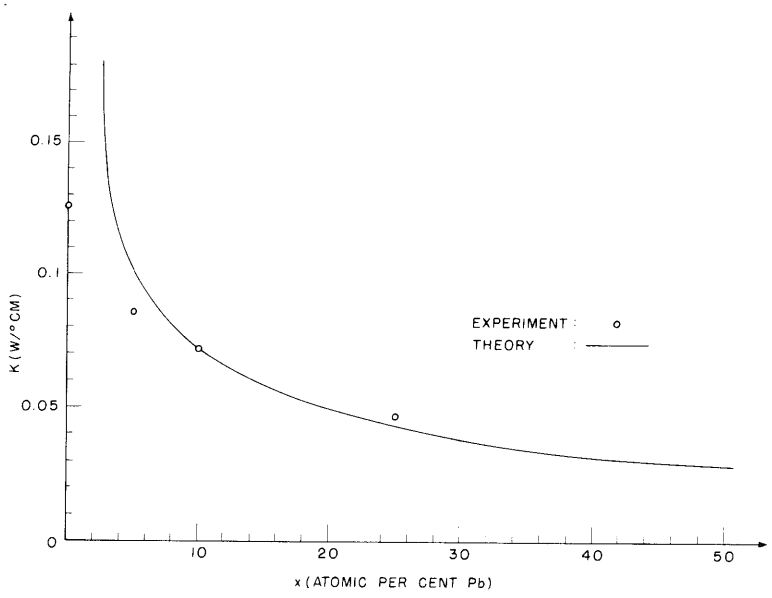

Fig. V-1. Thermal conductivity, K, as a function of composition, x, in the material $Mg_2Pb_xSn_{1-x}$.

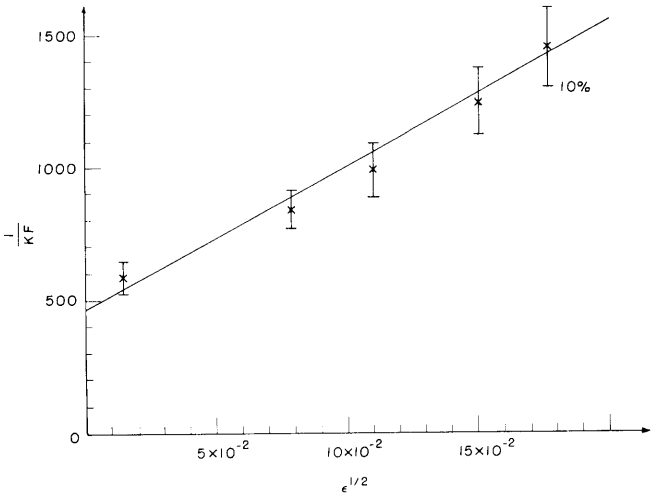

Fig. V-2. Effect of mass fluctuation on thermal conductivity of the material $Mg_2Pb_xSn_{1-x}$.

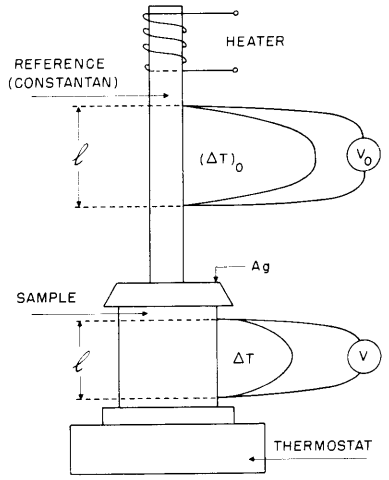

Fig. V-3. Experimental arrangement for measurement of thermal conductivity.

$(\Delta T)_o$ are deduced from the thermal emf's V and V_o, which 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, and thus

$$\Phi = \frac{\Delta T}{\frac{I}{K}\frac{\ell}{S}} = \frac{(\Delta T)_o}{\frac{I}{K_o}\frac{\ell_o}{S_o}} \tag{4}$$

where S and S_o are the cross sections of the rods, measured beforehand. From Eq. 4 we obtain

$$K = K_o \frac{(\Delta T)_o}{\Delta T}\frac{\ell S_o}{\ell_o S} \tag{5}$$

We have investigated the influence of radiation losses under the pessimistic hypothesis that the thermal resistance contributed by radiation losses is in parallel with that of the sample $\left(\rho=\frac{\ell}{SK}\right.$, where K, ℓ, S are the thermal conductivity, the length and cross section of the sample, respectively$\left.\right)$. The resistance associated with radiation losses, if we assume that sample and container behave as black bodies, is

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

where Σ is the side area of the sample.

Under our assumptions, it is easy to show that the true thermal conductivity K_{true} is related to the measured conductivity K_m by

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

The first corrective term in Eq. 6 yields a systematic error of approximately 10 per cent for usual sample dimensions and room temperature; the second yields an additional error that varies linearly with ΔT, which was verified by our measurements.

In any event, the radiation losses are unimportant when the thermal conductivity of the sample is approximately 0.1 w/°cm.

2. Preparation of Samples

The solid solutions of Se-Te, which were previously prepared, proved heterogeneous. To improve this situation, a zone-leveling apparatus has been built and is in operation. Efforts are also continuing to prepare new compounds such as WTe_2, WSe_2, $MoTe_2$, $MoSe_2$, and so on.

P. Aigrain

References

1. P. Aigrain, Thermal conductivity studies, Quarterly Progress Report No. 53, Research Laboratory of Electronics, M.I.T., April 15, 1959, p. 39; see Eq. 2.