

III. THERMOELECTRIC PROCESSES AND MATERIALS*

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A. ANISOTROPIC THERMOELECTRIC EFFECTS

1. THEORY

It was shown in Quarterly Progress Report No. 53, page 34, that the analysis of a nondegenerate semiconductor would yield an anisotropic thermoelectric power, provided that the relaxation times $\tau_{\parallel}(\epsilon)$ and $\tau_{\perp}(\epsilon)$ differ as functions of energy by more than a multiplicative constant.

According to the deformation-potential theory of lattice scattering, as generalized to anisotropic media by Herring and Vogt (1), the relaxation time that results from lattice scattering alone will be different in different directions but the difference involves only a multiplicative constant. That is, $\tau_{\parallel} = c_{\parallel} f^{\ell}(\epsilon)$ and $\tau_{\perp} = c_{\perp} f^{\ell}(\epsilon)$ when the c 's are constants. With this scattering mechanism operating alone, the thermoelectric power remains isotropic.

Suppose, however, that there are two scattering mechanisms operating simultaneously. Let the additional scattering be isotropic, $\tau_i(\epsilon) = f^i(\epsilon)$. Then, if the relaxation times add as reciprocals,

$$\frac{1}{\tau_{\text{resultant}}} = \frac{1}{\tau_{\ell}} + \frac{1}{\tau_i}$$

we have

$$\frac{1}{\tau_{r_{\parallel}}} = \frac{1}{c_{\parallel} f^{\ell}(\epsilon)} + \frac{1}{f^i(\epsilon)} = \frac{f^i(\epsilon) + c_{\parallel} f^{\ell}(\epsilon)}{c_{\parallel} f^{\ell}(\epsilon) f^i(\epsilon)}$$

$$\frac{1}{\tau_{r_{\perp}}} = \frac{1}{c_{\perp} f^{\ell}(\epsilon)} + \frac{1}{f^i(\epsilon)} = \frac{f^i(\epsilon) + c_{\perp} f^{\ell}(\epsilon)}{c_{\perp} f^{\ell}(\epsilon) f^i(\epsilon)}$$

from which the energy dependence is no longer factorable.

In order for the preceding analysis to be valid, the material must be nondegenerate,

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(III. THERMOELECTRIC PROCESSES AND MATERIALS)

and the doping must be high enough for impurity scattering to be comparable with lattice scattering. Ordinarily, this much doping would make the material degenerate. We want to obtain many impurities, but few free carriers. One way to obtain such a condition is by compensation. A bismuth-telluride crystal grown from a bismuth-rich melt with iodine doping, or a tellurium-rich melt with lead doping, would therefore be likely to exhibit an anisotropic thermoelectric power. This conclusion is being pursued.

Jane H. Dennis

References

1. C. Herring and E. Vogt, Transport and deformation-potential theory for many-valley semiconductors with anisotropic scattering, Phys. Rev. 101, 944-961 (1956).

2. EXPERIMENT

We have succeeded in pulling good single crystals of bismuth telluride, with dimensions 12 cm \times 1 cm \times 2 mm, from a stoichiometric melt. Crystals made in this way were carefully potted in de Khotinsky cement and cut at a very slow rate on a high-speed saw. Etching revealed cracks extending 1/4 inch from the edge of the cut. Cutting with a hot wire was tried, but such a large wire was required to carry the necessary heating power that the precision of the cut was not very high. Further attempts to solve the cutting problem are being made.

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B. TRANSPORT OF CONTACT MATERIALS IN BISMUTH TELLURIDE

1. EXPERIMENT

Construction of a furnace for reacting bismuth and tellurium in an inert atmosphere has been completed, and it is in use in conjunction with the crystal puller. The furnace consists of a hermetically sealed vycor tube into which a crucible containing up to 100 g of bismuth and tellurium can be inserted. The inert atmosphere is maintained inside the furnace by a continuous flow of helium at the rate of approximately 4 ft³/hr.

2. THEORY

Two papers dealing with the theory of diffusion have been submitted for publication. A paper co-authored with S. A. Rice, entitled "Comments on 'Dynamical Theory of Diffusion in Crystals'," was submitted to the Physical Review. This paper corrects the errors in Rice's original publication (1); it also includes a calculation that greatly

(III. THERMOELECTRIC PROCESSES AND MATERIALS)

simplifies the ultimate appearance of the pair correlation functions introduced by Rice. A second paper, entitled "A Method of Evaluating Diffusion Coefficients in Crystals," was submitted to the Journal of the Physics and Chemistry of Solids. This paper reconsiders Rice's model for diffusion with the aid of an extension of Kac's theorem (2). The analysis yields an activation energy which, as predicted by Zener (3), is simply related to the minimal local deformation energy. It is also found that, in contrast with Rice's treatment, the activation energy may, in the first approximation, be calculated directly from the atomic force constants without resorting to normal-mode analysis.

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References

1. S. A. Rice, Dynamical theory of diffusion in crystals, *Phys. Rev.* 112, 804 (1958).
2. M. Kac, On the distribution of values of trigonometric sums with linearly independent frequencies, *Am. J. Math.* 65, 609 (1943).
3. C. Zener, Imperfections in Nearly Perfect Crystals (John Wiley and Sons, Inc., New York, 1952), p. 289.

C. THERMAL CONDUCTIVITY STUDIES*

1. THEORY

The Tavernier theory of thermal conductivity (1) predicts a proportionality relation between thermal conductivity and powers of the parameters T_f , M , ρ , ϵ , T . For a given crystal structure, the proportionality constant in the theory has previously been obtainable only from experimental data. Now the theoretical interpretation of the constant is being considered. Knowledge of the anharmonic terms in the crystal potential energy is necessary for the development of this theory. An expression for the constant is being sought in terms of macroscopic parameters, such as Gruneisen's constant, compressibility, and so forth, but results are not yet available.

2. EXPERIMENT

Equipment for the thermal-diffusivity method of measuring heat conductivity is now available (see Fig. III-1). The first measurements were made at room temperature in high vacuum on germanium and silicon samples. Values of 1 watt/°C cm and 0.6 watt/°C cm for silicon and germanium, respectively, have been observed, but the precision of the measurements on these high-conductivity materials is very poor.

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

(III. THERMOELECTRIC PROCESSES AND MATERIALS)

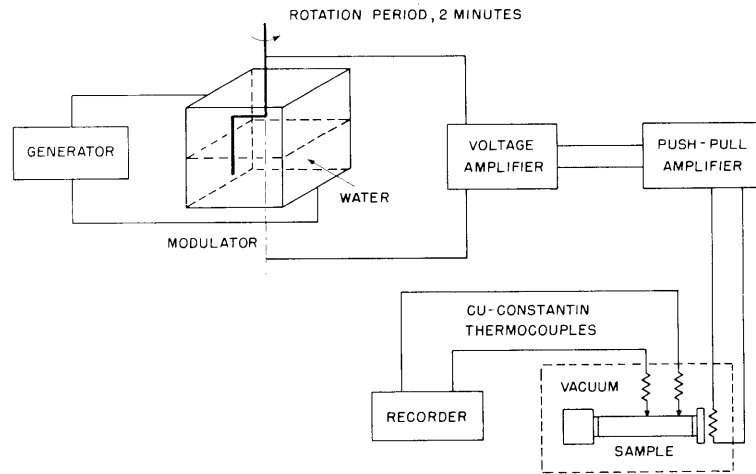


Fig. III-1. Thermal diffusivity method of measuring heat conductivity.

The apparatus is now being used for thermal-conductivity measurements on mixed crystals in the selenium-tellurium system. The crystals are prepared by melting the desired quantities of the elements in vacuum-sealed tubes. The first samples purified by zone melting in sealed tubes are now available. Measurements of the resistivity ρ and thermoelectric power Q of these mixed crystals at room temperature have yielded the results given in Table III-1.

Table III-1.

Composition (atomic percentage)	ρ (ohm cm)	Q ($\mu\text{V}/^\circ\text{C}$)	Type
20% Se	0.8	500	p
30% Se	5	600	p
40% Se	50	800	p

With $0.02 \text{ watt}/^\circ\text{C cm}$ for the thermal conductivity of tellurium, Tavernier's theory shows that thermal conductivities of approximately $10^{-3} \text{ watt}/^\circ\text{C cm}$ can be obtained for such mixed crystals.

The reason for interest in solid solutions in the selenium-tellurium system for thermoelectric applications is apparent from these initial results.

Other mixed crystals with low percentages of selenium (less than 20 per cent) are being prepared.

J. Tavernier

References

1. P. Aigrain, Thermal conductivity studies, Quarterly Progress Report No. 54, Research Laboratory of Electronics, M.I.T., July 15, 1959, p. 49.