

## VI. THERMOELECTRIC PROCESSES AND MATERIALS\*

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### RESEARCH OBJECTIVES

Our interest is in gaining a better understanding of some of the physical properties of solids that may be important in thermoelectric energy conversion. We include in our objectives the actual preparation and evaluation of appropriate materials so that we may reach a clearer appreciation of relations between the structure of a solid and its relevant properties for thermoelectric applications. In this work, three separate groups are cooperating very closely, as described in our first report (Quarterly Progress Report No. 51, p. 40). For the present, the two groups at M.I.T. are working primarily with bismuth telluride, which is well enough understood to furnish us with a good base line for our techniques. It is our intention, of course, to move on to other materials, but we expect to be interested, for some time, in the general area of mixed crystals of semiconductor compounds.

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### A. ANISOTROPIC THERMOELECTRIC EFFECTS

The existence of anisotropic thermoelectric effects has been known since 1851 when Thomson (1) derived the relation for expressing the thermoelectric power in a crystalline material,

$$\alpha_{\phi} = \alpha_{\parallel} \cos^2 \phi + \alpha_{\perp} \sin^2 \phi \quad (1)$$

where  $\alpha_{\parallel}$  is the Seebeck coefficient in a direction parallel to the crystalline principal axis,  $\alpha_{\perp}$  is the corresponding coefficient perpendicular to the principal axis, and  $\phi$  is the angle between the measured direction and the principal axis. A similar formula has been derived by Voigt (2). Equation 1 has been tested and substantiated for a number of common metals (Zn, Cd, Sb, and Mg), but Bridgman (3) obtained anomalous results for Sn and Bi. Kohler (4) pointed out that Eq. 1 is true only for vanishingly small temperature gradients, and has removed this restriction by deriving an analogous expression that is applicable to the case of adiabatic heating.

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## (VI. THERMOELECTRIC PROCESSES AND MATERIALS)

$$a_{\phi} = a_{\parallel} \cos^2 \phi + a_{\perp} \sin^2 \phi + \frac{\left(\frac{k_{\perp}}{k_{\parallel}} - 1\right)(a_{\parallel} - a_{\perp})}{\sin^2 \phi + \frac{k_{\perp}}{k_{\parallel}} \cos^2 \phi} \sin^2 \phi \cos^2 \phi \quad (2)$$

where  $k_{\parallel}$  and  $k_{\perp}$  are the thermal conductivities parallel to and perpendicular to the crystalline main axis, respectively. On the basis of Eq. 2, Kohler was able to explain the anomalies detected by Bridgman for Sn and Bi. Consequently, the published theory and experiments concerning anisotropic metals appear to be substantial and nonconflicting. For semiconductors, much less information has been found thus far.

We are therefore examining the theoretical situation with respect to anisotropic thermoelectric effects in materials like bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ), with a view toward performing preliminary experimental work. At the present time, we have two particularly significant pieces of information, both of which were mentioned by Drabble (5):

(a) Experimentally, Goldsmid is reported to have found approximately 10 per cent anisotropy in the Seebeck coefficient for  $\text{Bi}_2\text{Te}_3$  at room temperature (unpublished work).

(b) Herring has shown that the assumption of a free time which depends upon a power of the energy leads theoretically to isotropic thermoelectric parameters. Such a free-time assumption has, however, been suitable for explaining galvano-magnetic effects in several semiconductors, including  $\text{Bi}_2\text{Te}_3$ .

On the basis of these findings, it seems possible that further experiments would be worth while. We have been trying to consider and compare theoretically the Bridgman heat, thermoelectric power, and Peltier heat as possible bases for measurements.

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### References

1. W. Thomson, First Baron Kelvin, Mathematical and Physical Papers Collected from Different Scientific Periodicals from May 1841 to the Present Time (Cambridge University Press, London, 1882-1911), Vol. 1, p. 286.
2. W. Voigt, Lehrbuch der Kristallphysik (Verlag B. G. Teubner, Leipzig, 1910), p. 551.
3. P. W. Bridgman, Proc. Am. Acad. Arts Sci. 63, 351 (1929).
4. M. Kohler, Dependence of thermoelectric phenomena in metallic crystals on the crystallographic orientation, Ann. Physik, Ser. 5, 40, 196-206 (1941).
5. J. R. Drabble and R. Wolfe, Proc. Phys. Soc. (London) IIB, 69, 1101 (Nov. 1, 1956).

### B. THERMAL CONDUCTIVITY STUDIES

The first three months of this research have been almost entirely spent in getting the group into normal operation in its new quarters at Laboratoire Central des Industries

## (VI. THERMOELECTRIC PROCESSES AND MATERIALS)

Électriques. This has involved building or putting equipment needed for future work into operation.

By way of special measuring equipment, the static thermal conductivity apparatus designed by Tavernier is already available. In addition, a transient method, analogous to that of Danielsen, is being set up.

As regards sample preparation, some attempts have been made to prepare molybdenum and tungsten selenides and tellurides from a solution of these products in excess selenium and tellurium, as described in published work. Indeed, the few properties of these materials that are known suggest that they might have great thermoelectric potentialities. However, we found that starting from powdered molybdenum and tungsten led to poor results, presumably because the oxidized surface of the grains kept the reaction from taking place. Coarser samples of the same high-purity tungsten and molybdenum are being obtained for future work.

On the theoretical side, the theory of heat conductivity of disordered solid-state solutions, on which Tavernier and Aigrain are working, has been the subject of a short paper (1). Present efforts are directed toward deriving the numerical values of the undetermined constants of the theory.

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### References

1. J. Tavernier, Sur la conductivité thermique des alliages des ordonnés et isolantes (On the thermal conductivity of disordered, insulating alloys) *Compt. rend.* 247, 1179-1181 (Oct. 20, 1958).