

## V. THERMOELECTRIC PROCESSES AND MATERIALS\*

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### A. ANISOTROPIC THERMOELECTRIC EFFECTS

#### 1. Experiments with Bismuth Telluride

The major part of the anisotropy of the thermoelectric power of the bismuth telluride samples that were described (1) in Quarterly Progress Report No. 53, has been attributed to precipitated tellurium between cleavage planes. Tellurium, particularly tellurium with oxide impurities, can have a high p-type thermoelectric power (2). Consequently, an increase in the thermoelectric power of p-type bismuth telluride and a decrease in n-type material will be detected when the temperature gradient is perpendicular to the cleavage planes. Thermoelectric voltages generated in the tellurium by temperature gradients parallel to the cleavage planes, however, will be short-circuited by the higher electric conductivity of the bismuth telluride. Therefore, the presence of tellurium affects the thermoelectric power of bismuth telluride in directions perpendicular to the cleavage planes and, to a much lesser degree, in directions parallel to the cleavage planes.

The aforementioned conclusion was based on hot-point probing measurements on the surfaces of the samples. A hot point placed on the surface of a thermoelectric material will indicate the thermoelectric power of the material in a volume, the magnitude of which is governed by the size of the point. Since the small volume that is being measured is near the surface, this technique can be used to make a somewhat quantitative estimate of the effect of surface treatments. The surface of a p-type bismuth telluride sample was probed after a sequence of surface treatments. A surface that had been sandblasted exhibited large variations in thermoelectric power. The ratio of maximum-to-minimum value was as large as a factor of four. Etching the sample with aqua regia decreased the variation of measured values of thermoelectric power to approximately 10 per cent. The magnitude of the surface thermoelectric power, however, was found to be approximately 20 per cent higher than that measured previously for the same sample by means of planar electrodes. It is expected that reaction products formed during the etching process remain on the surface and cause the higher thermoelectric powers. Buffering

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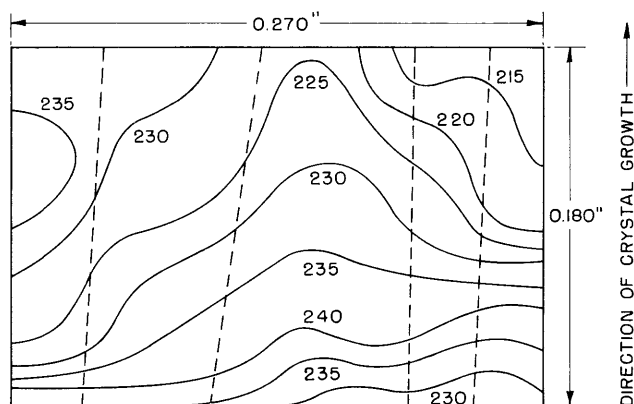


Fig. V-1. Lines of constant thermoelectric power. Numbers indicate values of p-type thermoelectric power (in  $\mu\text{v}/^\circ\text{C}$ ). Dashed lines indicate twin lines.

with acetic acid after etching with aqua regia lowered the variation of the surface thermoelectric power to approximately 3 per cent, and also lowered the magnitude of the thermoelectric power to a value 10 per cent higher than that previously measured for the bulk ( $244 \mu\text{v}/^\circ\text{C}$ ). In addition, sandblasting the surface after any of the etching processes destroyed the uniformity. Finally, a freshly cleaved surface was probed. Figure V-1 illustrates the results in terms of lines of constant thermoelectric power.

In an attempt to develop an explanation for the varying values of thermoelectric power obtained after the surface treatments – especially for the variations after sandblasting – the presence of a surface barrier or inversion layer has been considered. If a considerable fraction of the total temperature drop occurs in a potential barrier region at the surface, the measured value of thermoelectric power will not necessarily be indicative of the thermoelectric power of the bulk. The requirement that a significant temperature drop occur in a barrier region will be satisfied if the radius of the hot point is of the order of magnitude of the Debye length of the material that is being measured, or if the hot point makes a "patchy" contact with the surface. A "patchy" contact can be considered realistic for a sandblasted surface.

The theory of the calculation of thermoelectric power in a potential barrier has not been carried out, but a simplified case has been considered. If a high barrier to the flow of majority carriers exists at the surface of the semiconductor, the condition of zero current in the presence of a temperature gradient requires approximately a zero current of minority carriers. This leads to a calculation of the thermoelectric power that takes into account only the minority carriers. Consequently, the thermoelectric power measured near the surface in a barrier region can be significantly different from that of the bulk and, in extreme cases, can have the opposite sign.

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### References

1. R. E. Nelson, Experiments with bismuth telluride, Quarterly Progress Report No. 53, Research Laboratory of Electronics, M.I.T., pp. 37-38.
2. R. A. Horne, Effect of oxide impurities on the thermoelectric powers and electrical resistivities of bismuth, antimony, tellurium, and bismuth-tellurium alloys, J. Appl. Phys. 30, 393-397 (1959).

### B. THERMAL CONDUCTIVITY STUDIES\*

#### 1. Theory

The final form of Tavernier's theory of thermal conductivity has been written for "Comptes rendus" and is now in press.

Comparison of this theory with experiments indicates that in most substances longitudinal acoustic phonons carry most of the heat, although transverse phonons do enter the theory as final states for three-phonon scattering of longitudinal phonons. The heat conductivity at high temperatures then takes the form

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

where  $T_f$  is the melting point;  $M$ , the mean atomic mass;  $\rho$ , the specific weight;  $\epsilon$ , the mass fluctuation parameter;  $T$ , the temperature; and  $\beta$  depends on crystal structure, having values of  $8 \times 10^{-6}$  ( $\pm 20$  per cent) for cubic face-centered and related structures (Sb, Zn, etc.), and  $25 \times 10^{-6}$  ( $\pm 20$  per cent) for diamond and related structures (Mg<sub>2</sub>, Sn, etc.). Exceptions are Ge and Si, presumably because of the anomalous dispersion of these materials (diamond, however, fits into Tavernier's theory), and a few materials with  $\epsilon < 10^{-5}$  (Tl, Cl), in which the Tavernier cutoff,  $k'_m$ , is outside the first Brillouin zone. In these cases Ziman's theory applies.

We feel that this theory of heat conductivity is a significant advance in the thermoelectric field, because a priori computation of  $K$  now seems possible. Efforts are being made to check these formulas experimentally.

The equipment for the heat-wave method of measuring heat conductivity is now almost complete. It will be used on various alloys to check the  $\epsilon$  and  $T$  dependence of  $K$ .

#### 2. Experiment

As a result of the foregoing theory, we have decided to engage in a program for the measurement of  $K$  in simple solid solutions of two elementary semiconductors. Since

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the Ge-Si system is anomalous, the Te-Se system has been chosen. Mixed crystals have been prepared, and it has been confirmed that crystallization troubles usually encountered with pure Se are not bothersome with alloys containing enough Te (> 25 per cent Te). A further advantage of this system is that the segregation coefficient is almost unity, which makes it easy to prepare uniform samples. The low K of these alloys may make them quite useful for Peltier cooling if low-resistance electric contacts can be realized, although only p-type conductivity has been observed in our preparations.

We have encountered many difficulties in the preparation of the materials  $\text{MoSe}_2$ ,  $\text{MoTe}_2$ ,  $\text{WSe}_2$ , and  $\text{WTe}_2$ . New methods, involving chemical double decomposition (such as sodium selenide reduction of  $\text{MoO}_2$ ), are being tried.

P. Aigrain

### C. TRANSPORT OF CONTACT MATERIALS IN BISMUTH TELLURIDE

#### 1. Experiment

The topic of concern in this section, reported here for the first time, relates to the movement of copper in bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ). The behavior of copper and bismuth telluride together, which was expected to result in a diffusion process, has shown reaction products at temperatures higher than  $300^\circ\text{C}$ . We hope that diffusion can be observed at lower temperatures, and this objective is now being pursued. The earlier work that was done on the Cu- $\text{Bi}_2\text{Te}_3$  system is summarized in a technical report (1).

Recently, a thermostat for the temperature range  $0^\circ\text{C}$ - $150^\circ\text{C}$  was constructed and tested. With reasonable care it is possible to control the temperature of the bath within  $\pm 0.1^\circ\text{C}$ . At first, ethylene glycol (boiling point, approximately  $200^\circ\text{C}$ ) was used as the thermostat liquid; but it was found that at temperatures above approximately  $90^\circ\text{C}$  the rate of evaporation is sufficiently high to make this fluid inapplicable to the present experiment. At the present time, Dow Corning 200 fluid (50 cs) is being used with some success.

A considerable part of the time was spent on enlarging and improving the crystal-pulling apparatus with a view to providing a sufficient quantity of high-quality single crystals of  $\text{Bi}_2\text{Te}_3$ . These are needed for quantitative experiments on transport phenomena. A few apparently good crystals have been pulled and their evaluation is in progress.

A reaction furnace for rapid preparation of  $\text{Bi}_2\text{Te}_3$  from purified bismuth and tellurium is being constructed and further details will be reported later.

#### 2. Theory

A dynamic theory of diffusion has been proposed by S. A. Rice (2). This theory is of great interest, in that it formally introduces the dynamics of lattice vibrations into

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the calculation of diffusion coefficients. However, diffusion coefficients calculated on the basis of this theory seem to decrease exponentially with the size of the crystal. Some of Rice's assumptions are being critically investigated, and a paper on this subject is being written.

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References

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2. S. A. Rice, Dynamic theory of diffusion in crystals, Phys. Rev. 112, 804 (1958).