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Thermal and Electrical Resistivity of Tellurium at Low Temperatures

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Measurements are reported of the electrical and thermal resistivity between 2°K and room temperature of high-purity tellurium rods prepared by zone refining. The maximum thermal conductivity in the case of a single crystal of 3-mm diameter is about 10 watts/cm deg at 4°K; analysis of the measurements suggests that in the specimens used the thermal conductivity—due predominantly to lattice waves—is limited by scattering at grain boundaries or dislocations for temperatures below 4°K and at higher temperatures (~100°K) by phonon-phonon interaction. The absence of an exponential "Umklapp" region may be explained by the presence of many isotopes in tellurium.

INTRODUCTION

THE Group VI A element, tellurium, like selenium, has a highly anisotropic crystal structure, consisting of long spiral chains of atoms arranged in such a way that, in addition to the two nearest neighbors lying in the same chain, each atom has four next-nearest neighbors in adjacent chains.[1] Its semiconducting electrical properties have been known for many years, and recently considerable attention[2–5] has been paid to the electrical resistivity and Hall effect at both high and low temperatures. From this work it appears that at room temperature and above, high-purity tellurium behaves as an intrinsic semiconductor with a band gap of about 0.34 ev. However, Mooser and Pearson[6] have suggested that in both Se and Te, the energy gap is bridged by a band with a low state density which overlaps the valence band and gives rise to a small and temperature-independent density (10^{14} to 10^{16} cm^{-3}) of free charge carriers.

This paper deals principally with the results of thermal conductivity measurements on tellurium as there appeared to be little available data with the exception of isolated values at 90 and 300°K due to Cartwright.[7] Some years ago one of us (G.K.W.) at the suggestion of Dr. P. G. Klemens made some thermal conductivity measurements (unpublished) on glassy selenium and more recently the authors measured the conductivity of a fine-grained polycrystalline rod but were unable at that time to obtain single crystals or large-grained samples of high-purity selenium. As a result, when one of us (G.F.) recently succeeded in producing very pure crystalline rods of tellurium by zone refining, we turned our attention to this element. We still hope to complete the selenium studies in the near future when we can obtain or produce single crystals, and also to study further the effect of "doping" tellurium in order to obtain data on the scattering of lattice waves by added chemical impurities acting as point defects.

EXPERIMENTAL METHOD AND SPECIMENS

The thermal and electrical resistivity were determined by mounting samples in the form of rods in a cryostat described previously,[8] the temperatures being determined by gas thermometers and the electrical resistance with the aid of a potentiometer.

The first specimen (denoted by Te 1) was a rod of 5 mm diameter, about 1.5 cm long, broken from a longer

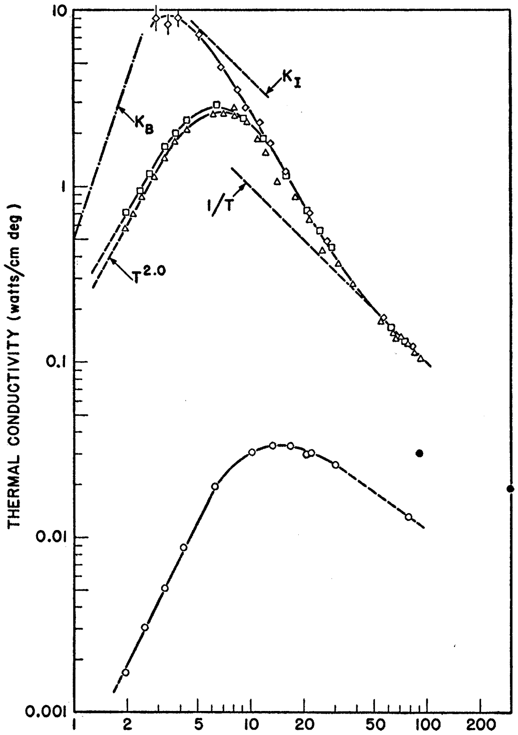

FIG. 1. Thermal conductivity of tellurium. ○ Te 1; △ Te 2; □ Te 3; ◇ Te 5; ● Cartwright (1933); —·— $K_B=0.52T^3$; - - - $K_I=40/T$.

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[1] A. von Hippel, J. Chem. Phys. **16**, 372 (1948).

[2] Virgil E. Bottom, Science **115**, 570 (1952).

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[5] Donald Long, Phys. Rev. **101**, 1256 (1956).

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[8] G. K. White and S. B. Woods, Can. J. Phys. **33**, 58 (1955).

polycrystalline rod (purity about 99.5%) supplied by Messrs. A. D. MacKay, Inc. The ends of the rod were coated with "Silver-Print" (General Cement Manufacturing Company) and copper leads were then soldered with Wood's metal to the silvered surface.

The other specimens (Te 2, 3, 5) were about 4 to 6 cm long and 3 mm in diameter; the ends of these were plated first with nickel, then with copper, and copper leads were soldered to the plated surface. The original tellurium from which these were prepared by zone refining was a 99.99% pure crystalline lump supplied by Messrs. A. D. MacKay, Inc.

Te 2 was polycrystalline, individual crystals being 1 or 2 mm wide and up to 1 cm in length inclined along the axis of the rod.

Te 3 was expected to be a single crystal, but subsequent x-ray examination across a section of the rod indicated that about 5 or 6 different crystals were present. Both Te 2 and Te 3 were prepared from tellurium which had been zone-refined in a vacuum-sealed silica tube. The purified material was then etched and put in Pyrex tubes. These tubes were vacuum-sealed again and the tellurium was melted and allowed to recrystallize from the bottom by slowly cooling in a furnace with a temperature gradient.

Te 3 was later annealed for about 5 days at a temperature just below its melting point then cooled slowly over a period of 24 hours and after mounting was denoted by Te 5. It appeared to be a single crystal, the crystallographic axis of which makes an angle of about 80° with the axis of the cylindrical specimen. This means that our measurements were made almost perpendicular to the *c* axis.

RESULTS

The results of the thermal conductivity measurements are shown in Fig. 1, together with two values obtained by Cartwright[7] for a single crystal of 99.999% tellurium, measured parallel to the main crystal axis.

In Te 1, 2, and 3 the thermal conductivity, K, appears to be proportional to T^2 at very low temperatures and after passing through a maximum falls, becoming approximately proportional to $1/T$ at liquid oxygen temperatures. For Te 5, the maximum conductivity was substantially larger and we were unable to measure K with any accuracy below 3°K as the heat input required to produce a measurable temperature gradient raised the temperature of the specimen more than one degree above the temperature of the bath of pumped liquid helium.

Figure 2 shows the electrical resistivity of these four specimens as a function of temperature; by plotting the logarithm of the electrical resistivity, ρ, in the vicinity of room temperature against $1/T$, a value of about 0.34 ev was deduced for the band gap.

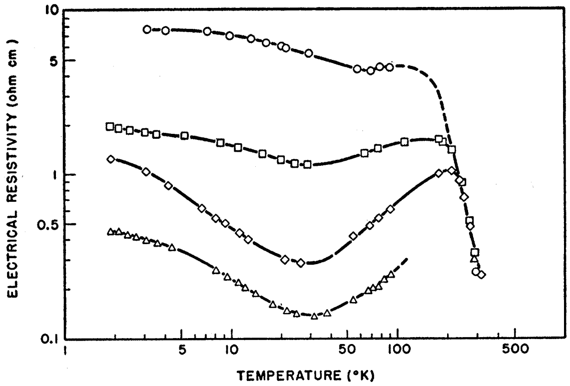

FIG. 2. Electrical resistivity of tellurium. ○ Te 1; △ Te 2; □ Te 3; ◇ Te 5.

DISCUSSION OF THERMAL CONDUCTIVITY

As in the case of germanium and silicon which we discussed recently,[9] it is expected that for these elements having few conduction electrons and a relatively high electrical resistance, the heat is carried almost wholly by lattice waves; hence the thermal conductivity should exhibit the type of temperature dependence shown by crystalline dielectric solids (see, e.g., comprehensive reviews by Berman[10] and Klemens[11]). In such solids, the thermal conductivity is limited at very low temperatures, where the dominant phonon wavelengths are long, by large-scale imperfections such as grain boundaries or dislocations, rather than by point defects or mutual interaction between the phonons.

Casimir[12] has shown that when boundary scattering is the limiting process the conductivity is given by

$$K_B \simeq 3.2\times 10^3 R B^{\frac{2}{3}} T^3 \text{ watts/cm deg,}$$

where R is the effective crystal radius and B is defined by the expression for the lattice specific heat, $C_v = BT^3$ joules/cm^3 deg. Although De Sorbo[13] has shown that the specific heat of tellurium can be adequately represented down to about 50°K by a function based on a one-dimensional continuum model (recalling the "linear" chain structure), recent experimental work by Smith[14] indicates that $C_v \propto T^3$ below 3°K, with an effective Debye characteristic temperature, $\theta \simeq 150$°K. Using Smith's data and assuming $R \simeq 1.5$ mm, we find (see Fig. 1):

$$K_B = 0.52T^3 \text{ watts/cm deg,}$$

which should be the conductivity of a crystal of this size at helium temperatures if no other scattering process limits it at a lower value. If as in the case of

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[9] G. K. White and S. B. Woods, Phys. Rev. **103**, 569 (1956).

[10] R. Berman, Phil. Mag. Suppl. **2**, 103 (1953).

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[12] H. B. G. Casimir, Physica **5**, 495 (1938).

[13] W. De Sorbo, J. Chem. Phys. **21**, 764 (1953).

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Te 2 and Te 3, R has a value of 0.5 to 1 mm, we should expect rather $K \sim 0.3T^3$, whereas Fig. 1 shows that $K \propto T^2$ and also is rather smaller in magnitude. This may of course be due to the presence of dislocations, which are not unlikely in view of the fact that these samples were solidified in a Pyrex tube and rather severe strains may have been produced while cooling to room temperature.

Klemens[11] has deduced a formula for the scattering due to dislocations in isotropic materials which reduces to

$$K_{\text{dis}}/T^2 \simeq \frac{17\times10^{-23}}{v\gamma^2}\left(\frac{A}{b^2}\right) \text{ watts/cm deg,}$$

where v, γ, and b are, respectively, the velocity of sound, Grüneisen parameter, and Burgers vector appropriate to the material and A^{-1} is the number of dislocations per cm^2. Although the application of this expression to a highly anisotropic material like tellurium is rather dubious, we may assume probable values of $v \sim 2.5\times10^5$ cm/sec, $\gamma \sim 2$, and $b \sim 5\times10^{-8}$ cm, and thus obtain $A^{-1} = 7\times10^{-9}T^2/K$. For Te 2 and Te 3, $K/T^2 \sim 0.15$ below 4°K and substituting this value in the above expression gives $A^{-1} \simeq 5\times10^9$ dislocations/cm^2.

Whether the actual density of dislocations is of this order of magnitude it seems at present impossible to say. However the results on Te 5 show that annealing —which of course increased the crystal size as well as reducing the density of dislocations—certainly increased the conductivity so that it then approaches the limit imposed by boundary scattering.

Turning our attention to the region of liquid oxygen temperatures, we observe that all the zone-refined specimens exhibit a conductivity, $K \simeq 10/T$ watts/cm deg. Here, where the temperature is comparable with θ, we should expect phonon-phonon interaction to be the dominant resistive mechanism in a relatively pure sample but again, only for isotropic solids do we have theories, e.g., those of Leibfried and Schlömann[15] and Dugdale and MacDonald[16] which might be applicable. On the basis of central-force models these theories predict that anharmonic coupling between lattice waves will produce a thermal resistance proportional to T, i.e., $K \propto 1/T$. If we apply their formulas to tellurium and assume $\gamma \sim 2$, we obtain $K \simeq 30/T$ to be compared with the experimental value of $K \simeq 10/T$ (see discussion by White and Woods[8] for Ge and Si).

Possibly the most interesting part of the temperature dependence of the thermal conductivity is that between 4° and 20°K, i.e., from a temperature $\theta/10$ down to the region where scattering by boundaries or dislocations becomes important. Peierls' theory of Umklapp[17,18] processes suggests that phonon-phonon interaction becomes much less probable in this region so that for temperatures below about $\theta/20$, we might expect K to increase exponentially as T decreases. Such a temperature dependence, $K \propto e^{\theta/bT}$ ($b \simeq 1$), has been observed over a narrow range of temperature in solid helium, sapphire, diamond, quartz crystals, and bismuth (see review by Klemens[11]) but in specimens of very-high-purity Ge and Si[8] and also in some alkali halides[19] such behavior appears to be masked by some other scattering process; the rather high sharp maximum observed in the conductivity of sapphire, for example, is reduced to a much more flat maximum. Berman, Foster, and Ziman[19] have recently suggested that this may be explained by scattering at lattice sites occupied by atoms of minority isotopes if they are present in appreciable quantities. Klemens[20] has shown that in an assembly of atoms of mass M containing a few atoms of mass $M+\Delta M$, the presence of the "impurity" species results in a scattering of the lattice waves proportional to $(\Delta M/M)^2$. For an isotropic material Klemens deduced that the conductivity, K_I, i.e., the reciprocal of the thermal resistance produced by such scattering, is approximately given by

$$K_I \simeq \frac{hv^2}{\pi^2 a^3 T} G \left\{ \sum f \frac{(\Delta M)^2}{\bar{M}^2} \right\}^{-1},$$

where G^{-1} is the number of imperfections per unit cell, a^3 is the volume of the unit cell, v is the mean velocity of sound in the material, and f is the proportion of each isotope of mass $M = \bar{M} + \Delta M$. The calculations of Berman *et al.*[19] showed that for several substances including Ge, Si, and KCl this does seem to provide an adequate explanation.

In tellurium (Fig. 1), K does increase more rapidly than $1/T$ with decreasing temperature but certainly not as rapidly in the region of 10°K as the Peierls theory would predict if only phonon-phonon interaction were limiting the conductivity. However in tellurium there are present almost equal quantities (33%) of Te^{130} and Te^{128} and progressively smaller but appreciable amounts of isotopes 126, 125, 124, 122, and 123. Thus $f(\Delta M)^2/\bar{M}^2$ has a value of about 3×10^{-4} and, assuming again that $v \sim 2.5\times10^5$ cm/sec, we obtain $K_I \simeq 40/T$. As is obvious from Fig. 1, such a value represents quite well the upper limit for the conductivity although the close agreement must be considered fortuitous. Further measurements with doped tellurium samples may provide a more conclusive test of the theory.

The first rather impure rod (Te 1), measured as received from Messrs. A. D. MacKay, Inc., has a very small thermal conductivity which appears to be only partly explained by its small grain size and high

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[19] Berman, Foster, and Ziman, Proc. Roy. Soc. (London) **A237**, 344 (1956).

[20] P. G. Klemens, Proc. Phys. Soc. (London) **A68**, 1113 (1955).

impurity content. The measurements also showed hysteresis effects after warming to room temperature and cooling again. This is even more marked in the electrical measurements (discussed below) and suggests that internal "fissures" are developed, so that it cannot be considered a representative specimen.

In view of the stated purity of 99.999% the conductivity at 90°K for Cartwright's single-crystal specimen is surprisingly small.

DISCUSSION OF ELECTRICAL RESISTIVITY

The increased electrical conductivity at low temperatures of the annealed specimen, Te 5, over that of the same unannealed specimen (Te 3), may be attributed to the increase of crystal perfection. Annealing not only produced a single crystal but also removed many dislocations, and therefore improved the structure of the atomic chains within the lattice.[6] The room temperature resistivity of these samples is nearly 0.5 ohm cm which is in agreement with the value perpendicular to the *c* axis found by Kronmüller *et al.*[4] Their data also indicate that our Te 3 and Te 5 have a concentration of electrically active impurities of not more than 10^{16} atoms per cm^3. The over-all impurity content, as shown by spectrographic analysis, does not exceed 10^{17} atoms per cm^3.

The higher conductivity of Te 2 is due to the presence of a larger number of impurities. This sample was prepared from a slightly less pure section of the zone-purified rod and the surface was not etched prior to recrystallization.

Sample Te 1 exhibits a very odd behavior. For this sample, room temperature is very near the transition between the intrinsic and impurity ranges. The maximum resistivity observed while cooling the sample was at about −20°C. This is to be expected considering the relatively low purity of the sample (99.5%, the main impurities being Pb, Sn, and Si). As the specimen was now warmed, the resistivity increased very rapidly and the maximum, now much increased, was shifted toward room temperature. Cooling and warming several times increases the resistivity by a factor of ten or more. This is very probably due to the particular texture of Te 1. The cylindrical specimen consists of small, needle-shaped crystallites of about 0.01 mm^2 cross section and 1 mm length, all pointing toward the axis of the cylinder and leaving a hole in the center. The highly anisotropic thermal expansion of tellurium produces fissures between the crystallites as the temperature is changed, thus increasing the resistivity of the sample.

As mentioned above, this hysteresis is also reflected in the thermal conductivity of Te 1 but to a lesser extent.

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