PHYSICAL REVIEW VOLUME 137, NUMBER 5A 1 MARCH 1965

Properties of the Group VI B Elements under Pressure. II. Semiconductor-to-Metal Transition of Tellurium†

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(Received 5 October 1964)

The electrical resistance of tellurium was measured at pressures to 60 kbar and temperatures to 600°C in a tetrahedral anvil device. A semiquantitative resistance-pressure-temperature phase diagram was determined, showing three solid polymorphs and the liquid phase. The room temperature Te I–II transition pressure was found to be at about 43 kbar. The Te I–II phase boundary has a slope of $-30°\mathrm{C/kbar}$. The triple point for coexistence of Te I, Te II, and liquid Te is at about 29 kbar and 445°C. The semiconductor-to-metal nature of the Te I–II phase change is well established by the isobaric temperature characteristics of the resistance. The magnitude of the resistance change at the Te I–II phase transformation was found to decrease significantly with increasing temperature. At room temperature the resistance of Te I just above the transition is smaller than the atmospheric-pressure resistance of Te by a factor of about 10^3. The locus of points defining the pressure dependence of the electronic energy gap E_g of Te I, determined from the resistance measurements, is convex toward the pressure axis, E_g decreasing monotonically from 0.33 eV at atmospheric pressure to zero at the Te I–II phase boundary. The slope of this curve is about -0.017 eV/kbar at atmospheric pressure. The experimental data are used with theoretical expressions to calculate the electronic contribution to the thermal conductivity and an upper bound on the thermoelectric figure of merit as a function of pressure. The pressure-induced approach to the metallic state of the Group VI B elements is discussed.

I. INTRODUCTION

As part of a continuing effort[1] to understand and correlate the effects of pressure on the properties of the Group VI B elements, a study of the electrical resistance of tellurium at pressures to 60 kbar and temperatures to 600°C is presented here. Discontinuities in the pressure and temperature dependence of the resistance define the boundaries of three solid phases and the liquid state. Typical resistance isobars and isotherms are given yielding both a conventional two-dimensional pressure-temperature phase diagram and a three-dimensional resistance-pressure-temperature phase diagram. Special emphasis is given the interesting phenomenon of the pressure transformation of tellurium from a semiconducting state (Te I) to a state having characteristic metallic conduction (Te II). That this pressure induced approach to a metallic state is a continuous process, is emphasized by the monotonic decrease in the electronic energy gap to zero at the Te I–II phase boundary. Further discussion of the pressure dependence of E_g and its significance with respect to recent theoretical developments is given.

The remainder of this paper is divided into three sections. Section II describes the experimental techniques used and problems encountered. Section III is subdivided into three portions, giving results and specific discussions of the matter at hand on the subjects of the phase diagram, the electrical resistance, and the electronic energy gap of tellurium. As a conclusion, Sec. IV contains a brief general discussion of the results as a whole and the relation of these results to the properties of the other Group VI B elements under pressure.

II. EXPERIMENTAL TECHNIQUES

All high-pressure measurements were made in a tetrahedral anvil device whose use and calibration have been described in detail earlier.[2,3] Pressure is transmitted to a pyrophyllite tetrahedron containing the specimen by four hydraulically driven rams which advance simultaneously. A schematic diagram of a cross section of the sample tetrahedron used for resistance measurements is shown in Fig. 1. The nominal outside diameters of the cylindrical sections of the sample tetrahedron are: (1) sample, 0.06 in.; (2) pressure transmitting cylinder, 0.18 in.; and (3) graphite heating core, 0.20 in. The cylindrical section of the sample tetrahedron is approximately 0.25 in. in length. The Chromel-Alumel thermocouple was placed in the boron nitride, about 0.06 in. from the center of the sample. Thermocouples were used in all elevated temperature runs, in lieu of calibration of the graphite heating elements. The graphite served as a heat source as a result of joule heating due to passage of a high-current ac through it.

Pressure calibration was achieved by correlation of the ram force with the accepted pressures necessary to induce phase transitions in Bi, Tl, and Ba at room temperature.[4] No correction was made for the effect of elevated temperature on the pressure calibration. The pressures given are thought to be accurate to ±2.5% above 20 kbar and to ±0.5 kbar below 20 kbar. Tem-

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† This research was sponsored by the General Dynamics Corporation.

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peratures were measured with Chromel-Alumel thermocouples. Standard thermocouple conversion tables were used. No corrections were made for pressure-induced emf's in the thermocouples,[5] but temperatures are believed to be accurate within approximately ±1.5%. However, due to the rather unpredictable temperature gradients in the sample cell, temperatures given represent actual sample temperatures only within about ±2.5%.

All data reported result from measurements on compacted powders of Te. Two grades of purity were used: (1) Te A, "purified tellurium metal" supplied by the Fisher Scientific Co.; and (2) Te B, 99.999% pure tellurium supplied by the American Smelting and Refining Co. Qualitative spectrographic analysis indicated that the major impurities in Te A are Ag and Cu.

Several different materials were used for resistance leads in the high-pressure cell. Results using platinum wire as leads were not reproducible under identical experimental conditions. Bridgman observed this same difficulty and attributed it to the difference in the compressibilities of Te and Pt, resulting in a variable and unpredictable contact resistance.[6] Tantalum leads were found to be most useful, especially in the higher temperature ranges. Copper and silver were found to undergo diffusion alloying with the tellurium at high pressure and temperature. The alloying process became so rapid as the temperature was increased that electrical contact between the wire and the sample was destroyed at a critical temperature which depended on the pressure. The temperature at which electrical contact was destroyed increased with pressure, as would be expected for a diffusion process. The alloying occurred for all solid phases of tellurium investigated. Metallographic inspection of samples after alloying under pressure indicated a complete intermixing of the two materials in the zone previously occupied by the resistance leads.

For phase transformations determined by the differential thermal conductivity analysis technique (DTCA) reported by the authors recently,[7] the resistance leads in Fig. 1 were replaced by a Chromel-Alumel thermocouple passing through the center of the sample.

All data were recorded automatically on x-y recorders with calibrated scales. Therefore, data presented in the form of curves result from continuous variation of the indicated parameters rather than discrete sampling. A calibrated pressure transducer was used to give a voltage output directly proportional to the hydraulic ram pressure, facilitating data recording. Measurements indicated as resistance are actually determinations of the voltage drop across the sample and its leads. However, since the resistance of the leads was ordinarily quite small compared to the sample resistance and since the sample current was constant to an accuracy of less than 1%, these values are effectively the resistance of the sample, presuming no geometry changes take place. Geometrical distortions of the sample do occur during the time of gasket formation, i.e., below pressures of about 15–20 kbar. Above these pressures the elliptical distortion is generally very small.

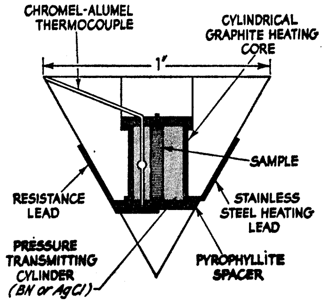

FIG. 1. Cross section of a sample tetrahedron used for high pressure, high-temperature resistance measurements.

A few annoying experimental difficulties were encountered. Most troublesome was the development of electrical shorts between the various probes and leads in the high-pressure cell, often making the sample cell useless. Also, electrical shorting sometimes resulted from movement of the sample while in the liquid state under pressure. Depending on the nature of these electrical shorts, they often introduced mixing of the various ac and dc electrical signals. Somewhat less prevalent was the pinching off of the thermocouples in the gasket area. Although ordinary electrical tape was used to electrically insulate the thermocouples from the anvils and to protect the thermocouple wire, complete elimination of the pinching off of the wires was not possible. Also, the resistance leads were severed, at times, by shear stresses created at the face of the sample tetrahedrons during the gasket formation period of the increasing pressure cycle. Sudden releases in pressure by extrusion of parts of the sample tetrahedron out one of the gaskets (often termed a "blowout") gave some trouble, especially on the decreasing pressure cycle and at high temperatures.

III. DISCUSSION AND RESULTS

A. Phase Diagram

The phase diagram of tellurium as indicated by our measurements is shown in Fig. 2 with an appropriate phase labeling. The inset table in Fig. 2 gives the material used and the nature of the experiment by which the particular phase transformation point was determined. By far, the majority of the transition points in Fig. 2 are indications of discontinuous changes in isobaric or isothermal measurements of electrical resistance. A few points, as indicated, result from investigations by DTCA (discussed previously). Since changes in the measured properties upon passage through a phase transition have a nonzero width, the

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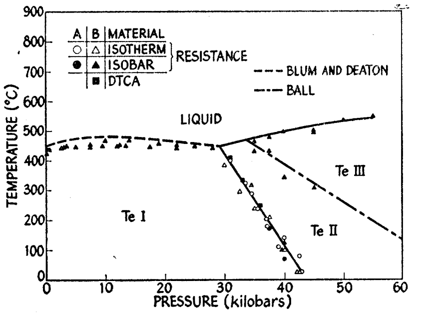

FIG. 2. Phase diagram of tellurium.

midpoint of the transition region was taken as the point of transformation.

The room temperature Te I–II transition pressure was found to be at about 43 kbar. The triple point defined by the intersection of the phase boundaries of Te I, Te II, and liquid tellurium is at about 29 kbar and 445°C. The data definining the Te I–II phase boundary agree well with Bridgman's[8] three points at about 150°C, as well as his room temperature values.[9] The slope of the line in Fig. 2 defining the Te I–II phase boundary is −30°C/kbar. Using Bridgman's[9] value of 5.5% for the relative volume change $\Delta V/V_0$ at the Te I–II transition at 25°C and the above slope, the resulting heat of transformation, as calculated from Clapeyron's equation, is 270 cal/g-atom.

Upon completion of this work the authors were informed of Ball's[10] results on the phase diagram of tellurium. All the data of Fig. 2 agree reasonably well with Ball's data. The dashed line of Fig. 2 represents Ball's results on the Te II–III transition corresponding to Bridgman's[9] reported transition at 70 kbar and room temperature. Only four data points indicative of this phase boundary are given. The changes in resistance associated with this phase line were found to be very small, at times only inflections. In fact, no evidence of the transition could be detected below 300°C. We do not feel our data to be conclusive enough to well establish the position of the Te II–III phase boundary and merely rely on the apparent agreement with Ball.

The data presented for the melting points of Te II and Te III agree well with those determined by differential thermal analysis (Kennedy and Newton[11]) and resistance measurements (Ball[10]). However, as was pointed out in I, greater deviation among the various investigators[10–12] occurs for the fusion curve of Te I. Also, the resistance data for Te I melting are seen to have greater internal scatter. This scatter seems attributable to the rather unpredictable temperature gradients of the sample cell, as is indicated by the low-pressure extrapolation of the data to unreasonably low atmospheric pressure melting points. The maximum in the melting curve of Te I is best illustrated by the DTCA data which are considered much more accurate than the resistance data. This maximum was fully discussed in I.

No evidence was found for the existence of a low pressure (about 36 kbar at room temperature) polymorphic transition which Bridgman[8] reported. Bridgman himself cast considerable doubt on the existence of this phase.

Kabalkina *et al.*[13] have reported a structure change for tellurium from $A8$ to $A7$ at 15 kbar and room temperature with zero volume change. No indication of this transition was found by either resistance or DTCA measurements. McWhan and Jamieson[14] have also failed to find evidence for this transition in their x-ray diffraction studies of tellurium.

B. Electrical Resistance

At atmospheric pressure the electrical resistance of tellurium exhibits the properties of a typical semiconductor. The nature of its properties as a semiconductor depend strongly on the amount and nature of its impurities. With notably few exceptions, impurities make tellurium a *p*-type semiconductor.[15] Only high-purity tellurium conducts intrinsically at room temperature.

Bridgman[6] first studied the effect of pressure on the electrical resistance of tellurium at pressures to 12 kbar and at four temperatures from −182.8 to 95°C. He found the resistance of single crystals to decrease by two orders of magnitude at 12 kbar and noted a striking similarity of logarithmic plots of the data for two orientations with respect to the crystal symmetry. He later[16,17] extended the pressure range of these measurements to 30 kbar and found a decrease in resistance by a factor of 400 to 600 at these pressures. More recently, Bridgman[18] measured the resistance of polycrystalline tellurium samples to 100 kbar, observing the Te I–II transition. The pressure-induced reduction in resistance found was much smaller than that he previously reported for single crystals, being a factor of about a thousand above 50 kbar. He made no mention of a

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[9] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **74**, 21 (1939); Phys. Rev. **60**, 351 (1941); and Proc. Am. Acad. Arts Sci. **74**, 425 (1942).

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discontinuity in resistance corresponding to the Te II–III transition.

Other investigators have studied the resistance of tellurium under pressure. Alekseevskiĭ *et al.*[19] measured some galvanomagnetic properties of tellurium at low temperatures and pressures to 1.7 kbar. Vereshchagin *et al.*[20] determined the room temperature resistance of Te between 30 and 250 kbar, finding the resistance at 250 kbar lower by a factor of 10^6 than the resistance at atmospheric pressure.

The effect of pressure and temperature on the resistance of tellurium found in the present work is indicated by the resistance isotherms of Fig. 3 and the resistance isobars of Fig. 4.

The isotherms of Fig. 3 show the Te I–II transition and the effect of temperature on its position on the pressure scale. At room temperature the resistance of Te I just above the transition is smaller than the atmospheric pressure resistance of tellurium by a factor of about 10^3, in good agreement with Bridgman's[18] measurements on polycrystalline samples. The resistance of Te II drops slowly with pressure, the rate, however, being negligible compared to that for Te I at these pressures. The magnitude of the room temperature resistance changes at the Te I–II transition varied from sample to sample from about 0.8 to 1.2 orders of magnitude. Thus, the isotherms of Fig. 3 should be viewed only in a semiquantitative manner. However, the qualitative trend with increasing temperature toward smaller changes in resistance upon transformation from Te I to Te II appears well established.

The resistance isobars of Fig. 4 illustrate transitions to all four phases of tellurium. The isobars of Fig. 4(a) show the characteristic semiconducting exponential decrease in resistance with increasing temperature followed by the transition from Te I to the liquid state.

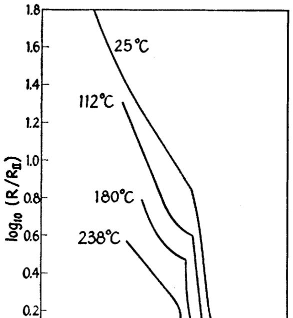

FIG. 3. Resistance isotherms for Te A showing the Te I–II phase change. R_{II} is the resistance of Te II at the temperature in question just above the transition region.

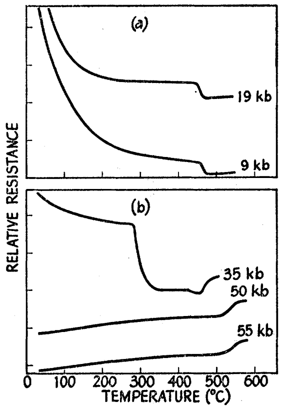

FIG. 4. The temperature variation of the resistance of Te B relative to the liquid state (R/R_L) for several pressures (in kilobars). Each division of the ordinate represents a change in R/R_L of (a) 76% and (b) 17%.

These isobars at high pressure deviate from their exponential character as the melting point is approached, as opposed to the continuous exponential character of the temperature dependence of the resistance at amospheric pressure.[21] In fact, some curves possessed a positive temperature coefficient of resistance just below the melting point, indicating that the predominant process limiting the electrical conductivity is electron-phonon scattering. The magnitude of the change in resistance upon melting of Te I was approximately independent of pressure. The isobars of Fig. 4(b) give the typical nature of the temperature dependence of the resistance of Te II, Te III, and Te liquid at these pressures. The curve at 35 kbar shows sharp changes in resistance at 300 and 465°C, and a slight change at 430°C, indicative of the Te I–II, Te III-liquid phase, and Te II–III transformations, respectively. The curves at 50 and 55 kbar give no indication of the Te II–III transition, but do show melting and the characteristic positive temperature coefficient of resistance of Te II. In the temperature range 25 to 200°C, the resistance of Te II behaves as that of a normal metal and may be written in the form

$$R=R_0(1+\beta T), \qquad (1)$$

where β is independent of the temperature T (°C) and R_0 is the resistance at 25°C and the pressure in question. Measurements at various pressures between 43 and 60 kbar indicate that β is essentially independent of pressure having a mean value of 1.8×10^{-3} $(^\circ\mathrm{C})^{-1}$.

Resistance isobars crossing the Te I–II phase boundary possess a large temperature hysteresis, the Te II–I transition occurring at a temperature 25 to 75°C lower than the Te I–II transition. In fact, samples transformed from Te I to Te II at pressures above about 40 kbar failed to return to the Te I phase upon decreasing the temperature.

The nature of the electrical conduction of tellurium under pressure is clear from the data of Figs. 3 and 4.

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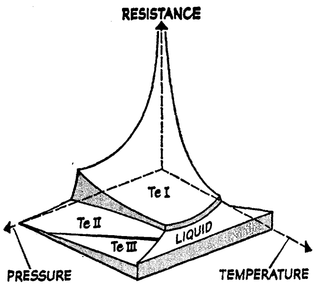

FIG. 5. Semiquantitative representation of the resistance phase diagram of tellurium.

The semiconducting nature of Te I is demonstrated by: (1) its rather high resistance, and (2) the fact that its resistance at constant pressure decreases exponentially with increasing temperature. The metallic nature of Te II is indicated by: (1) its very low resistance (approximately 0.005 Ω for the sample size used), and (2) its positive thermal coefficient of resistance at any given pressure. Thus, the Te I–II transition is from a semiconducting to a metallic phase.

Figure 5 is a qualitative representation of the resistance data presented, showing the very interesting and striking effect of pressure and temperature on the resistance of tellurium.

C. Electronic Energy Gap

Since Te I is a semiconductor, the electrical resistance R, in the intrinsic region of conduction, is given by

$$R=R_\infty \exp(E_g/2kT)\,, \qquad (2)$$

where E_g is the electronic energy gap, k is the Boltzmann constant, T is the absolute temperature, and R_∞ is an essentially temperature-independent constant. Thus, the slope of $\log R$ versus $(1/T)$ curves yields the energy gap. Such determinations were made at various pressures up to the room temperature transition pressure of 43 kbar. The results of these measurements are shown in Fig. 6. The atmospheric-pressure value of 0.33 eV for E_g was determined in equipment independent of the high-pressure apparatus and is in good agreement with that determined by other investigators for polycrystalline samples.[22]

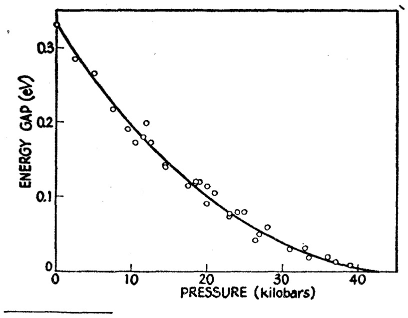

FIG. 6. Pressure dependence of the electronic energy gap for polycrystalline tellurium at room temperature.

Bardeen[23] made similar calculations on the basis of Bridgman's[16] measurement of the pressure dependence of the resistance of single crystals of tellurium at two temperatures to 30 kbar. The unreasonably low values that he calculated for E_g below 8 kbar indicate that Bridgman's sample was not in the intrinsic range of conduction at the temperatures of measurement. The agreement between the data presented and Bardeen's calculations is reasonable considering the fact that the sample in one case was a polycrystal, while in the other a single crystal. However, Bardeen's curve extrapolates to zero at about 32 kbar whereas the curve in Fig. 6 approaches zero at 43 kbar.

Harris *et al.*[24] also reported the pressure dependence of E_g for tellurium. As with Bridgman's measurements, their unreasonably low values for E_g at low pressures indicate that the conduction was not intrinsic at these pressures and temperatures. Their unusually high values for E_g at pressures above 15 kbar probably result from the large pressure gradients[25] existing over the sample volume at a given applied force for an opposed anvil device such as theirs.

Of further interest are some studies of E_g for tellurium made at pressures to 2 kbar. Long[26] determined the variation of E_g with pressure in this range by measuring electrical conductivity and Hall coefficient. He found a decrease in E_g of 0.032 eV at 2 kbar from an atmospheric pressure magnitude of 0.336 eV. Neuringer[27] measured the infrared absorption of single crystals of tellurium under pressure, finding a pressure coefficient of E_g of about -2×10^{-2} eV/kbar. The results of both investigators are in good agreement with the data of Fig. 6.

Since the resistance measurements were made on compacted powders (Te B), it was found necessary to cycle the temperature up and down several times to achieve an equilibrium situation. Each cycle lowered the relative resistance. Harris *et al.*[24] observed this same difficulty in making measurements on other semiconductors.

Several investigators[28–32] have discussed the electronic band structure of tellurium and the qualitative nature of the initial effect of pressure on it. All predict a decrease in E_g with increasing pressure. However,

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TABLE I. Pressure dependence of the temperature coefficient of the energy gap.

P (kbar)	$10^5\times\delta$ (eV/°C)
30.0	9.0
32.5	8.3
35.0	7.3
37.5	6.0
40.0	4.4

Reitz,[29] and Dresselhaus[30] have questioned the validity of Callen's[31] simplified tetragonal model. Also, Nussbaum and Hager's[32] results differ from both those of Callen and those of Reitz.

The explicit dependence of E_g on temperature (due to electron-lattice interactions), i.e., that excluding the volume dependence, is given by

$$\left(\frac{\partial E_g}{\partial T}\right)_V=\left(\frac{\partial E_g}{\partial T}\right)_P+\frac{\alpha}{K_T}\left(\frac{\partial E_g}{\partial P}\right)_T, \tag{3}$$

where α is the isobaric volume coefficient of thermal expansion, P is the pressure, and K_T is the isothermal compressibility. The slope $(\partial E_g/\partial P)_T$ of the curve in Fig. 6 at $P=0$ is -0.017 eV/kbar. Using Bridgman's[33] values for α (5.28×10^{-5} °K^{-1}) and K_T (5.08×10^{-6} bar^{-1}), -4×10^{-5} eV/°K for $(\partial E_g/\partial T)_P$,[34] and the above value for $(\partial E_g/\partial P)_T$ in Eq. (3) yields $(\partial E_g/\partial T)_V=-21\times10^{-5}$ eV/°K. This value for the electron-lattice interaction term is in good agreement with the results of Loferski,[35] Neuringer,[27] and Moss.[36] Caldwell and Fan[37] have discussed these experimental values in relation to those calculated using the theory of electron-lattice interactions and pointed out that a calculation such as that above does not take into account the anisotropy of the tellurium lattice.

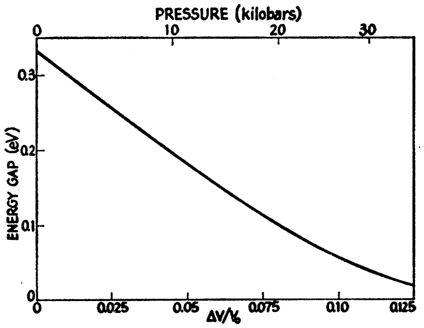

FIG. 7. Dependence of the electronic energy gap on volume for tellurium. The volume measurements are P. W. Bridgman's results (see Ref. 23).

Careful measurement of the temperature dependence of the resistance of Te I at pressures just below the 43 kbar, 25°C transition point indicate that, within experimental error, E_g approaches zero at the Te I–II phase boundary. Since 25°C occupies no apparent point of symmetry with respect to the Te I–II phase boundary, E_g must be zero at all points on the boundary. Thus, the variation of R with T at pressures above 30 kbar should become a curve with zero slope at temperatures approaching the phase boundary. Unfortunately, as a result of broadening of the resistance transition due to sample temperature gradients, conclusive verification of this fact was not possible. However, assumption of a linear decrease with temperature in the energy gap to zero at the Te I–II phase boundary permits calculation of an approximate temperature coefficient for E_g. This assumption is expressed in a relationship of the form

$$E_g[T(°\text{C})]=E_g[25°\text{C}]-\delta[T(°\text{C})-25°\text{C}], \tag{4}$$

where δ is the temperature coefficient. The values of δ at different pressures are given in Table I.

Since the energy gap measurements extrapolate to zero at the Te I–II phase boundary, it appears that the overlapping of the valence and conduction bands occur at the onset of the discontinuous change in crystal structure as opposed to occurring in a discontinuous manner simultaneous with the discontinuous change to metallic bonding. In the latter case, the energy gap would extrapolate to a value greater than zero at the Te I–II boundary.

Figure 7 shows E_g as a function of volume using Bridgman's[38] volume measurements and the data of Fig. 6. Within experimental error, the relationship between E_g and $(\Delta V/V)$ is linear for pressures below about 15 kbar. As a result of the marked anisotropy of the tellurium crystal structure, no direct relationship between E_g and the lattice spacing can be deduced from the data in this form. The linearity at low pressures of the curve in Fig. 7 illustrates the utility of the assumption of such a linear dependence in the deformation potential theory of Bardeen and Shockley.[39]

Recent theoretical developments relating thermoelectric properties of substances to their energy gaps are of interest in light of the data given in Fig. 6.

The thermal conductivity K of semiconductors can be qualitatively accounted for by the consideration of several methods of heat conduction. The theory of phonon scattering yields the lattice thermal conductivity, at temperatures T higher than the Debye temperature, $K_{\text{lat}}=a/T$, where a is a constant. A further contribution to the thermal conductivity is the "free motion" and ambipolar diffusion[40] of the charge

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carriers:

$$K_{\mathrm{el}}=L(\sigma_{+}+\sigma_{-})+L\frac{\sigma_{+}\sigma_{-}}{\sigma_{+}+\sigma_{-}}T\left[\frac{E_g}{2kT}+2+r\right]^2, \qquad (5)$$

where $L=(k/e)^2(2+r)$, σ_{-} and σ_{+} are the electron and hole contributions to the electrical conductivity σ ($\sigma=\sigma_{+}+\sigma_{-}$), e is the electronic charge, and r is the power in the dependence of the mean free path on carrier kinetic energy. The first term in Eq. (5) is equivalent to the Wiedmann-Franz contribution to the thermal conductivity of metals. Still another contribution to the thermal conductivity, important in certain temperature ranges, results from a consideration of heat transfer by photons. Obtaining a of the expression $K_{\mathrm{lat}}=a/T$ by a low-temperature fit of experimental data, assuming $\sigma_{+}=\sigma_{-}$, and setting r equal to zero, Smirnov and Shadrichev[41] quantitatively accounted for the thermal conductivity of tellurium at atmospheric pressure above 580°K. With the utility of Eq. (5) thus demonstrated in the case of tellurium, it seems that calculation of K_{el} as a function of pressure using the data of Fig. 6 should have at least qualitative significance. Figure 8 shows the ratio of $(K_{\mathrm{el}})_0$ to K_{el} as a function of pressure, where $(K_{\mathrm{el}})_0$ is the electronic contribution to K at atmospheric pressure. These values were determined for $T=300$°K using a resistance isotherm given in Sec. III.B, the data of Fig. 6, and assuming $\sigma_{+}=\sigma_{-}$ and $r=0$. The resulting dashed curve of Fig. 8 illustrates the marked increase in K_{el} with pressure, which is expected on the basis of the above presented resistance measurements.

The figure of merit Z of a thermoelectric is given by $Z=(S^2\sigma/K)$ where S is the thermoelectric power (Seebeck coefficient) and σ is the electrical conductivity. Using a single-band energy model with a spherical Fermi surface, assuming the mean free path varies as the rth power of the kinetic energy, and neglecting the phonon scattering thermal conductivity component, Rittner[42] arrived at a theoretical upper bound on Z:

$$Z_m=[r+2+(E_g/2kT)]^2/[r+2]\bar{T}, \qquad (6)$$

where $\bar{T}$ is the arithmetic average of the hot and cold junction temperatures. This upper bound Z_m, normalized with respect to the atmospheric pressure upper bound $(Z_m)_0$, is shown as a function of pressure by the solid line in Fig. 8. The values of Z_m were calculated on the basis of the data of Fig. 6, assuming $r=0$ and $\bar{T}=300$°K. As is expected, these calculations indicate a decrease in the figure of merit with increasing pressure. It should be noted that Donahoe[43] and Rittner and Neumark[44] have made further calculations of Z_m arriving at slightly different values.

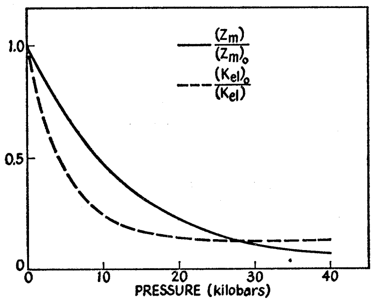

FIG. 8. Normalized (with respect to atmospheric pressure values) theoretical variation with pressure of an upper bound on the thermoelectric power Z_m and the electronic contribution to the thermal conductivity K_{el}, based on the electronic energy gap measurements given in Fig. 6.

IV. CONCLUSION

The results of this investigation demonstrate that applying pressure to tellurium induces a continuous approach to a metallic state followed by an abrupt shift in its properties (excluding E_g). Thus tellurium is transformed from a semiconducting state with an open chain-like hexagonal crystal structure[45] whose cohesion is characterized by covalent bonding and van der Waals forces, to a metallic state with a closely packed, distorted rhombohedral structure[14] having metallic bonding. In this respect experiments on tellurium under pressure create an excellent opportunity to study the relation between the various types of bonding and macroscopic physical properties. A. von Hippel[45] has pictured the crystal structure and conductivity of the Group VIB elements as a resonance between an insulating chain structure with van der Waals cohesion on the one hand, and a metallic form with a simple cubic lattice on the other hand. From this point of view, considering the results of McWhan and Jamieson[14] for tellurium, pressure moves the state of resonance closer to the metallic form, diminishing the contribution of the insulating form.

As pointed out in I, the results of McWhan and Jamieson and von Hippel's interpretation strongly suggest that pressure will force S, Se, and Te into the metallic polonium structure. This possibility and the marked similarity between the structure of Se and Te leads to the expectation that the electrical properties of selenium under pressure will be almost identical to those of tellurium. Electrical and optical studies of selenium under pressure already indicate a strong similarity with tellurium.[46,47] On this basis, it is also

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expected that the initial effect of pressure on sulfur will be a decrease in its energy gap to such an extent that thermal excitation of large numbers of electrons into the conduction band will occur at room temperature, making it a semiconductor. Then, at pressures above that necessary to produce this semiconducting state, a discontinuous increase in conductivity indicative of a phase change to a metallic state would be expected. Such an effect of pressure on sulfur has not been observed. However, Slykhouse and Drickamer[46] have shown by optical studies that the energy gap of sulfur decreases with increasing pressure as expected.

The calculations using the theoretical expressions for Z_m and K_{el}, and the measured values of E_g point to the desirability of measurements of the thermal conductivity of tellurium as a function of pressure and temperature. These measurements would permit a direct comparison of the theory and experiment for K_{el}, testing the general validity of the theoretical model.

ACKNOWLEDGMENTS

Our thanks go to J. W. Hagemeyer for interesting and informative discussions and D. N. Peden for help in making the measurements. We are indebted to D. L. Ball, D. B. McWhan, and J. C. Jamieson for communication of their results prior to publication.

PHYSICAL REVIEW VOLUME 137, NUMBER 5A 1 MARCH 1965

Absolute Intensities of X-Rays Anomalously Diffracted through Nearly Perfect Copper Crystals*

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(Received 7 October 1964)

Absolute integrated intensities of the x-ray beams "anomalously transmitted" through nearly perfect copper crystals have been measured for the (111) planes for values of μt ranging from 10 to 90. Results obtained for both the symmetric and asymmetric Laue geometries are compared with theory. These comparisons yield a value of 0.965 ± 0.003 for the ratio $f''(111)/f''(000)$ and indicate that the crystals investigated have a high degree of perfection. The measurements were made with Mo $K\alpha$ radiation using a double-crystal spectrometer arranged in the parallel condition and with the first crystal diffracting in the Bragg geometry. Measured profiles of the Bragg-Laue double-crystal rocking curves for $\mu t=10$ and 90 are in semiquantitative agreement with the theory.

INTRODUCTION

It has been demonstrated recently[1] that large copper crystals having low dislocation densities ($\lesssim 10^4/\mathrm{cm}^2$ as determined by etch-pit count) appear to be nearly perfect with respect to their x-ray diffraction properties. Such crystals exhibit anomalous transmission of x rays when set to diffract in the Laue geometry and give diffraction peaks when examined in the Bragg geometry which have half-widths in agreement with the prediction of Darwin's[2] theory for perfect crystals.

In the present investigation further examination has been made of the x-ray diffraction properties of nearly perfect copper crystals. In particular, absolute integrated intensities and peak profiles of the anomalously transmitted x-ray beams obtained by diffraction from the (111) planes have been measured and compared with theory.

THEORY

The theory of the diffraction of x rays through thick, absorbing, perfect crystals (Laue geometry) has been thoroughly investigated by Zachariasen,[3,4] Von Laue,[5] Hirsch,[6] Kato,[7] and others. The geometry under consideration is shown in Fig. 1 and the situation may be described as follows. When the direction of an incident parallel beam makes the appropriate angle θ_B for diffraction from the planes (hkl), two plane waves of x rays, one in the incident beam direction and one in the diffracted beam direction, are coupled inside the crystal. Their interaction produces a standing wave electromagnetic field with nodes at the planes of the atoms. Thus, there is a reduction in photoelectric absorption which results in an increase in the intensity of transmitted x rays. At the exit surface of the crystal, the wave field then splits into two uncoupled beams, the transmitted and the diffracted beams. This effect is very

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* Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corporation.

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