HIGH PRESSURE TRANSITION IN CADMIUM TELLURIDE

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The zinc blende—rock salt phase boundary of a single crystal of cadmium telluride was investigated experimentally over the P, T range up to about 35 kb and 800°C by observing the electrical resistance behavior in a cubic compact anvil device.

In single crystal samples the room temperature transition pressure is found to be 33.3 ± 1.8 kb. At the transition the electrical resistance decreases by several orders of magnitude. The magnitude of the resistance change at the transition decreases with increasing temperature. In the pressure-temperature phase diagram the zinc blende —rock salt phase boundary has a slope of -0.015 kb/deg. The phase boundary, determined in the range from room temperature to 800°C, is a straight line that may be extrapolated nearly to the triple point between the liquid and two solid phases of CdTe reported by Jayaraman et al. The heat of transition at room temperature calculated from the Clapeyron equation is 6.6×10^2 cal/mole. The change in entropy is found to be 2.3 e. u.

From the measurements of electrical resistance as a function of temperature, it is found that the energy gap of CdTe of the zinc blende phase is about 1.3 eV and it increases with pressure.

Introduction

Cadmium telluride (CdTe) crystallizes under the normal condition in the cubic zinc blende structure represented by the space group $F\bar{4}3m\text{-}T_d{}^2$. The existence of metastable hexagonal wurtzite-type CdTe has been reported by Semiletov[1], Shiojiri and Suito[2], Weinstein et al.[3], and Shalimova et al.[4] in evaporated films.

It has been shown by the optical absorption[5], the volume change[6,7], the x-ray diffraction[8]~[11], and the electrical resistance[12] measurements that CdTe undergoes a phase transition from the zinc blende to the rock salt structure under a pressure of approximately 30 kb. The transition is accom-

(Received December 10, 1969)

1) S. A. Semiletov, Kristallografiya, 1, 306 (1956)
2) M. Shiojiri and E. Suito, Japanese J. Appl. Phys., 3, 314 (1964)
3) M. Weinstein, G. A. Wolff and B. N. Das, Appl. Phys. Letters, 6, 73 (1965)
4) K. V. Shalimova, O. S. Bulatov, É. N. Voronkov and V. A. Dmitriev, Soviet Phys.—Cryst., 11, 431 (1966)
5) A. L. Edwards and H. G. Drickamer, Phys. Rev., 122, 1149 (1961)
6) A. Jayaraman, W. Klement, Jr. and G. C. Kennedy, ibid., 130, 2277 (1963)
7) C. F. Cline and D. G. Stephens, J. Appl. Phys., 36, 2869 (1965)
8) A. N. Mariano and E. P. Warekois, Science, 142, 672 (1963)
9) P. L. Smith and J. E. Martin, Phys. Letters, 6, 42 (1963)
10) N. B. Owen, P. L. Smith, J. E. Martin and A. J. Wright, J. Phys. Chem. Solids, 24, 1519 (1963)
11) I. Y. Borg and D. K. Smith, Jr., ibid., 28, 49 (1967)
12) G. A. Samara and H. G. Drickamer, ibid., 23, 457 (1962)

panied by a large discontinuous red shift in the optical absorption edge and an increase by several orders of magnitude in the electrical conductivity. Jayaraman, Klement and Kennedy[6] have studied the compression of powdered samples using a piston-cylinder apparatus and have reported a volume decrease of about 10 per cent at the transition. Cline and Stephens[7], using single crystal samples in a piston-cylinder apparatus, have reported a volume decrease of about 17 per cent at the transition.

Samara and Drickamer reported[12] a further transition in CdTe at about 100 kb. This polymorph is believed[12][13] to be typically metallic. Using high-pressure x-ray techniques, several investigators [9]~[11] have observed this phase transition and identified the new phase as the white tin (body-centered tetragonal) structure. As for the value of the transition pressure to the conducting state in CdTe, Semerchan et al.[14] have reported that it is 50,000 kg/cm^2, and have observed no further transition between 50,000 and 200,000 kg/cm^2.

Only a tentative work has been reported concerning the effect of temperature on the pressure of the transition from the zinc blende to the rock salt phase of CdTe. The volume discontinuity measurements[6] at about 120°C showed a negative slope.

The present investigation was undertaken in order to determine the zinc blende — rock salt phase boundary of CdTe at high temperatures. Observation of discontinuous changes in electrical resistance at various pressures under isothermal conditions was made to define the phase diagram. Furthermore, the temperature dependence of the conductivity of the zinc blende phase was studied over a wide temperature range and the estimates of the width of the energy gap were obtained. A final discussion will be devoted to some generalizations of the results obtained in cadmium chalcogenides.

Experimentals

The experimental techniques utilized in the present investigation have been described in detail in the previous publications[15]~[17] and only specific items will be presented here. The anvil press[18] was calibrated for each sample geometry in accordance with Kennedy and LaMori's scale[19]. No correction was made for the effect of elevated temperature on the pressure calibration. The pyrophyllite cubes contained a 6 mm diameter graphite heater with copper current leads, inside of which was placed a 4 mm cylinder of pyrophyllite which served to transmit pressure to the 2 mm cylindrical sample. Electrical contacts were made at the two ends of the sample through platinum foils. Temperatures were monitored with the chromel-alumel thermocouples. The readings of the thermocouples were

13) S. Minomura, G. A. Samara and H. G. Drickamer, *J. Appl. Phys.*, 33, 3196 (1962)

14) A. A. Semerchan, L. F. Vereshchagin, N. N. Kuzin and L. N. Drozdova, *Soviet Phys. — Doklady*, 8, 586 (1963)

15) J. Osugi, K. Shimizu, T. Nakamura and A. Onodera, *This Journal*, 36, 59 (1966)

16) J. Osugi, K. Shimizu, T. Nakamura and A. Onodera, *ibid.*, 36, 74 (1966)

17) A. Onodera, *ibid.*, 39, 65 (1969)

18) J. Osugi, K. Shimizu, K. Inoue and K. Yasunami, *ibid.*, 34, 1 (1964)

19) G. C. Kennedy and P. N. LaMori, "Progress in Very High Pressure Research", ed. by F. P. Bundy *et al.*, p. 304~311, John Wiley & Sons, New York (1961)

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corrected for the effect of pressure in accordance with the data of Hanneman and Strong[20].

The samples of CdTe were cut from large single crystals produced from the melt, whose purity was 99.999 per cent. Measurements on powder samples of 99.995 per cent purity were also made at room temperature. Optical analysis indicated that the major impurities in CdTe were Cu and Mg, or Al in single crystals, and Cu and Mg in the powder sample. There was no apparent reaction between the CdTe and pyrophyllite or platinum foils in the temperature and pressure range covered.

The powder samples of CdO obtained from commercial source of 99 per cent purity were also used in the electrical resistance measurements at room temperature in order to be compared with cadmium chalcogenides. The crystal structure of CdO is rock salt form.

The experimental points of zinc blende—rock salt phase boundary of a single crystal of CdTe were obtained by fixing the temperature and raising the pressure in small increments. The electrical resistance was continuously recorded. Discontinuity in the pressure dependence of the resistance defined the boundary of two solid phases. The data were obtained at temperatures from room temperature to 800°C on several different samples.

The energy gaps were estimated by the measurements of the temperature dependence on electrical conductivity at constant pressures. The isobars of resistance as a function of temperature were measured at three different pressures in the zinc blende phase. The electrical resistance of CdTe in the rock salt phase was also measured as a function of temperature. With the pressures above about 55 kb, at which a thermocouple could not be inserted into the high-pressure cell without its failing over a long period, it was necessary to use the temperature curve of the sample plotted against power supply, which had been calibrated at lower pressures, in order to determine the temperature.

Results

Pressure-temperature phase diagram

The measurements on room temperature resistance *versus* pressure were performed on single crystals produced from the melt, and compacted powder samples. Fig. 1 shows the results for the single crystal and powder samples. The initial resistivities were $\sim 3 \times 10^6 \, \Omega \cdot cm$, and $\sim 2 \times 10^6 \, \Omega \cdot cm$, respectively. For the pressures up to approximately 30 kb, the electrical resistance decreases slightly with pressure. In the single crystal samples the transition of zinc blende-to-rock salt occurs at 33.3 ± 1.8 kb accompanied by a sharp decrease in resistance of over three orders of magnitude. In powder samples the transition occurs at the same pressure as the single crystal samples within the limit of error. The resistance exhibits further decrease to about 50 kb, which probably corresponds to the end of the transition. Above this point the resistance decreases very slowly with increasing pressure. The resistivity of the high pressure phase was in the order of $10^{-2} \sim 10^{-3} \, \Omega \cdot cm$ at about 70 kb. There is a marked hysteresis effect in these curves on pressure release, as has been observed for the transition in CdS[15] and CdSe[17].

The pressure of the transition of zinc blende-to-rock salt in CdTe at room temperature is compared

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20) R. E. Hanneman and H. M. Strong, *J. Appl. Phys.*, **36**, 523 (1965)

with the previous investigations[5)~7)10)~12)] in Table 1. The single crystal samples were used by Drickamer and his colleagues[5)12)], and by Cline and Stephens[7)], and by the author. Drickamer and his colleagues used the same material in their optical[5)] and electrical[12)] studies.
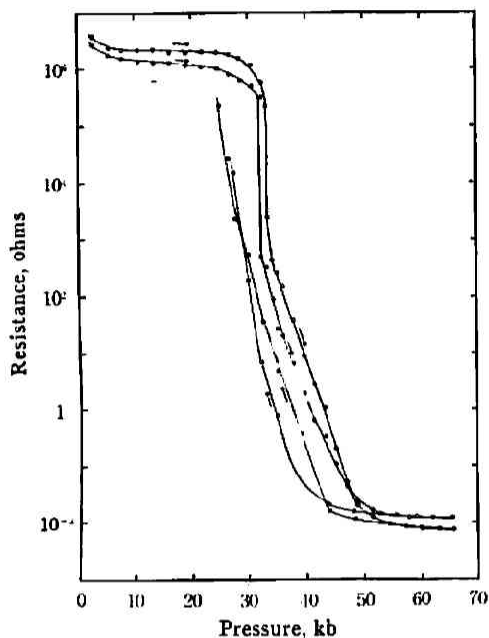

Fig. 1 Resistance *versus* pressure for CdTe
at room temperature
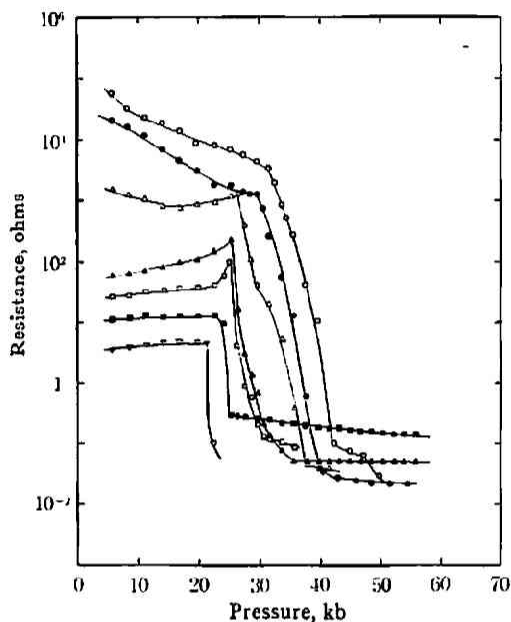○: single crystal   ●: powder

Fig. 2 Resistance *versus* pressure isotherms
of single crystals of CdTe
○: 100°C   ●: 200°C   △: 300°C
▲: 400°C   □: 500°C   ■: 600°C
▽: 700°C

Table 1   Pressures of the zinc blende-to-rock salt transition in CdTe

Investigator	P_T (kb)	Method	Reference
Present work	33.3±1.8	electrical resistance	
Samara and Drickamer	30	electrical resistance	12
Jayaraman *et al.*	33	volume change	6
Cline and Stephens	31.8±0.5	volume change	7
Edwards and Drickamer	35	optical absorption	5
Owen *et al.*	30	x-ray diffraction	10
Borg and Smith	32	x-ray diffraction	11

The boundary between the zinc blende and rock salt structures of CdTe was determined by compressing the single crystal at constant temperature. Typical isotherms are shown in Fig. 2. The beginning of the resistance change was selected for the P, T points of the transition. The magnitude of the resistance change at the transition decreases with increasing temperature.

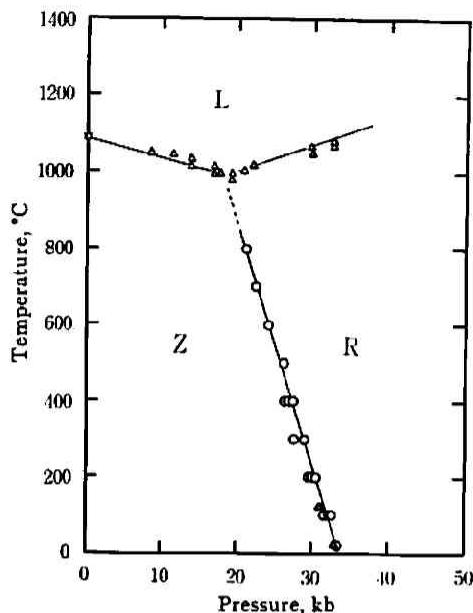The results on the phase diagram are summarized in Fig. 3. The transition pressure is lowered

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Fig. 3 Phase diagram of CdTe
(Z: Zinc blende, R: Rock salt, L: Liquid)
○: present work
△: Jayaraman et al.

by increasing temperature, dP/dT being -0.015 kb/deg. Using the above slope and the value of -6.3 cm^3/mole for the relative volume change at the transition, determined by the x-ray diffraction analysis[11], the enthalpy change $\varDelta H$, and the entropy change $\varDelta S$, can be calculated from the Clapeyron equation

$$\frac{dP}{dT} = \frac{\varDelta S}{\varDelta V} = \frac{\varDelta H}{T \varDelta V}. \tag{1}$$

The change in enthalpy is found to be 6.6×10^2 cal/mole, and in entropy to be 2.3 e. u.

In Fig. 3 are plotted the melting data obtained from the differential thermal analysis studies and the solid-solid transition points obtained from the volume discontinuity measurements of Jayaraman et al.[6] It has been reported that the triple point among liquid, zinc blende and rock salt phases is located near 19.2 kb and 996°C[6]. It seems most probable that the zinc blende—rock salt phase boundary determined in this experiment will terminate in the triple point reported by Jayaraman et al.[6]

Attempts were made to retain the rock salt phase of CdTe. The techniques were described earlier[15)17]. In all cases the CdTe returned to the zinc blende form on the release of pressure to 1 atm. There was found no trace of the rock salt form from powder x-ray data. Rooymans[21] obtained the NbO-type structure of CdTe on release of pressure.

In the previous papers[15)17], the effects of particle size and pressure cycling on the transition pressure of CdS and CdSe were reported. In the present work the same procedure was undertaken. The single crystal of CdTe was crushed to particles in an agate mortar. The average diameters of the classified samples were determined by an optical microscope. No difference in the transition pressures of the classified samples of CdTe (40~60μ, 120~180μ and 560~640μ) was observed within the

21) C. J. M. Rooymans, "5th International Symposium on the Reactivity of Solids", ed. by G.-M. Schwab, p. 100~109, Elsevier, Amsterdam (1965)

limit of error. In support of this, the pressure cycling experiment indicated that the transition pres-
sures in the recompression were located at the same pressure as in the initial compression. This was
undertaken by starting with a single crystal of CdTe, compressing it into the rock salt phase, decom-
pressing to the zinc blende phase, then recompressing to the rock salt phase, and so on. In Fig. 4, the
electrical resistance as a function of pressure at room temperature is shown. The transition pressures
are the same on initial compression ①, and recompressions ② and ③. Starting with a single crystal
specimen of CdTe, the polycrystallinity of the specimen might become higher and the grain size
smaller during the pressure cycling to introduce the phase transition zinc blende ⇌ rock salt. This
experiment may also explain that in CdTe the grain size gives no appreciable effect on the pressure
of the transition of zinc blende to rock salt.

Electrical resistance change

The isobars of resistance as a function of temperature were measured in the zinc blende phase of
single crystals of CdTe. The electrical resistance R, in the intrinsic region of conduction, is given by

$$R = R_0 \exp (E_g/2kT), \qquad (2)$$

where E_g is the energy gap, k is the Boltzmann constant, T is the absolute temperature, and R_0 is
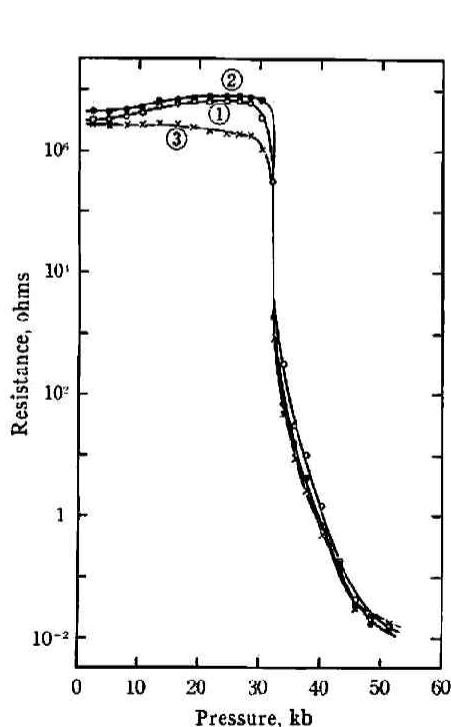an essentially temperature-independent constant. Then

Fig. 4   Resistance *versus* pressure behavior
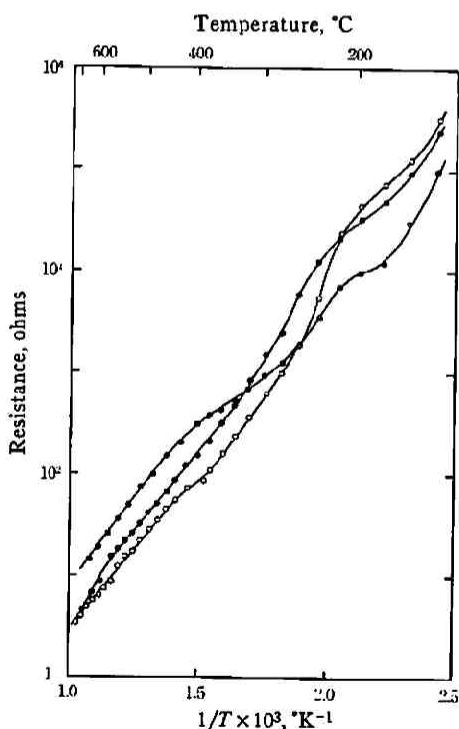of CdTe during three cycles of com-
pression (① → ② → ③)

Fig. 5   Resistance *versus* $1/T$ isobars of CdTe
of the zinc blende phase
○: 5.7 kb   ●: 11.2 kb   ◉: 16.7 kb

$$E_g = 2k \frac{\partial \ln R}{\partial (1/T)}. \tag{3}$$

The plots of log R versus $1/T$ shown in Fig. 5 yield the energy gap. The three isobars are obtained from different samples. For the energy gap of the zinc blende structure the data in Fig. 5 yield the value $E_g=1.2$ eV at 5.7 kb, $E_g=1.3$ eV at 11.2 kb, and $E_g=1.3$ eV at 16.7 kb, respectively. These values compare favorably with the atmospheric value of about $1.4 \sim 1.5$ eV obtained from the optical data[22]~[24] and electrical resistance measurements[25]~[27]. The observed increase in E_g with pressure,

$$\frac{dE_g}{dP} = 8.9 \times 10^{-6} \, eV/bar,$$

is in qualitative agreement with the optical measurements which give $dE_g/dP=4.4 \times 10^{-6}$ eV/bar[5] or $dE_g/dP=8.2 \times 10^{-6}$ eV/bar[28]. The extrinsic region of conductivity of the CdTe sample lies in the temperature between room temperature and about 300°C. The resistance decreases with pressure at 100°C and 200°C in the zinc blende phase as seen in Fig. 2. Above about 400°C the conduction is intrinsic and the resistance increases with increasing pressure.

As shown above, the present results indicate that the resistivity of CdTe of the rock salt phase is in the order of $10^{-3} \sim 10^{-2} \, \Omega \cdot cm$ at room temperature. In Fig. 6, the electrical resistance of CdTe of the rock salt phase is shown as a function of temperature from room temperature to about 800°C. At 50.0 and 55.0 kb the electrical resistance at first decreases near room temperature, and then develops a positive temperature coefficient at higher temperature. The initial negative temperature coefficient becomes more and more smeared as the pressure becomes higher. The initial negative temperature dependence of the resistance may be due to the semiconducting behavior of the untransformed zinc blende phase. At 60.0 kb the resistance shows a metal-like behavior with temperature. The temperature coefficient of resistance S, of the rock salt phase of CdTe was measured at 60.0 kb. Here S is defined by

$$\frac{R_{T_1}}{R_{T_2}} = 1 + S(T_1 - T_2). \tag{4}$$

In equation (4) R_{T_1} and R_{T_2} are the resistance at temperatures T_1 and T_2, respectively. The values obtained are $2.9 \times 10^{-3} \, deg^{-1}$ below about 300°C and $1.1 \times 10^{-3} \, deg^{-1}$ above about 300°C, which are compared with those of high-pressure metallic phase of other materials, for instance, about 2×10^{-3} deg^{-1} in the white tin phase of InSb[29], $4.2 \times 10^{-3} \, deg^{-1}$ in the white tin phase of Ge[30], and 1.8×10^{-3} deg^{-1} in the metallic phase of Te[31].

22) D. A. Jenny and R. H. Bube, *Phys. Rev.*, **96**, 1190 (1954)

23) R. H. Bube, *ibid.*, **98**, 431 (1955)

24) C. Z. Van Dovrn and D. De Nobel, *Physica*, **22**, 338 (1956)

25) J. Appel, *Z. Naturforsch.*, **9a**, 265 (1953)

26) J. Appel and G. Lautz, *Physica*, **20**, 1110 (1954)

27) P. Höschl, *Phys. Stat. Sol.*, **13**, K101 (1966)

28) G. A. Babonus, V. L. Girchené, A. B. Zakarka, Ya. F. Kabalyauskas and A. Ya. Shileika, *Litov. Fiz. Sbornik* (USSR), **4**, 529 (1964) [*Phys. Abs.*, **68**, Abs. No. 15543 (1965)]

29) R. E. Hanneman, M. D. Banus and H. C. Gatos, *J. Phys. Chem. Solids*, **25**, 293 (1964)

30) F. P. Bundy, *J. Chem. Phys.*, **41**, 3809 (1964)

31) F. A. Blum, Jr. and B. C. Deaton, *Phys. Rev.*, **137**, A1410 (1965)

The electrical resistance of CdO

In order to be compared with cadmium chalcogenides the electrical resistance of the powder samples of CdO was measured at room temperature, and the results are shown in Fig. 7. The initial resistivity was $\sim 10^0 \, \Omega \cdot cm$, and that at about $20 \sim 60$ kb was $\sim 10^{-1} \, \Omega \cdot cm$. As seen in Fig. 7, no abrupt resistance change was observed in CdO at pressures up to about 60 kb. Drickamer et al.[32] observed no phase transition in the study of the lattice parameter of CdO by means of the x-ray diffraction under high pressure up to 300 kb.
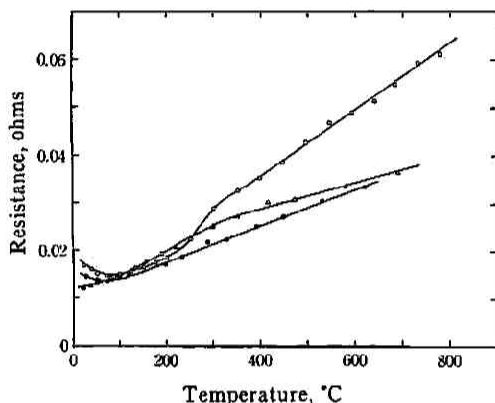

Fig. 6   Resistance *versus* temperature isobars of CdTe of the rock salt phase
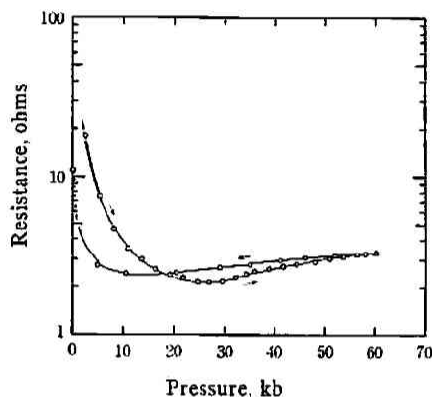○: 50.0 kb   ●: 55.0 kb   △: 60.0 kb

Fig. 7   Resistance *versus* pressure for CdO at room temperature

Considerations

CdTe and its isoelectric compounds

Tin and its iso-row compounds, InSb, CdTe and AgI may be expected to show a systematic variation in their behavior, in view of the fact that their physical and electrical properties at atmospheric pressure show systematic variations. The atmospheric and high pressure structures of these substances[10)11)33)~38)] are given in Table 2. The ionicity calculated by Suchet[39] is also shown. As seen in Table 2, the rock salt structure is formed under pressure by the more ionic compounds and the white tin type structure is formed by the less ionic compounds.

32)   G. K. Lewis, E. A. Perez-Albuerne and H. G. Drickamer, *J. Chem. Phys.*, **45**, 598 (1966)
33)   P. L. Smith and J. E. Martin, *Nature*, **196**, 762 (1962)
34)   M. D. Banus, R. E. Hanneman, A. N. Mariano, E. P. Warekois, H. C. Gatos and J. A. Kafalas, *Appl. Phys. Letters*, **2**, 35 (1963)
35)   J. C. Jamieson, *Science*, **139**, 845 (1963)
36)   L. H. Adams and B. L. Davis, *ibid.*, **146**, 519 (1964)
37)   A. Van Valkenburg, *J. Res. Natl. Bur. Std.*, **68A**, 97 (1964)
38)   M. J. Moore and J. S. Kasper, *J. Chem. Phys.*, **48**, 2446 (1968)
39)   J. P. Suchet, *J. Phys. Chem. Solids*, **21**, 156 (1961)

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Table 2   Sequence of the polymorphic transition at high pressure

Substance	Ionicity	Atmospheric phase	High pressure phase	Transition pressure (kb)
Sn		White tin		
InSb	0.24	Zinc blende → White tin		23
CdTe	0.54	Zinc blende → Rock salt → White tin		33, 100
AgI	0.81	Wurtzite Zinc blende } → Tetragonal → Rock salt → Cesium chloride		3, 4, 100

Structural considerations

The spacial arrangement of the atoms in the zinc blende and rock salt structures of CdTe are shown in Fig. 8. In the zinc blende structure each atom is tetrahedrally surrounded by four nearest neighbors. In the rock salt structure each atom has six nearest neighbors. Both structures can be described as consisting of two interpenetrating face-centered cubic lattices. If there is no difference in dimensions, one structure can be transformed to the other by shifting only one kind of ion as is the case of AgI[40]. In CdTe the cadmium ions, because of their smaller size, shift much more easily than the tellure ions. The lattice parameters of CdTe are 6.48 Å at atmospheric pressure[41] and 6.33 Å near the transition pressure[11] in the zinc blende structure, and 5.96 Å in the rock salt structure just above the transition[11], respectively. The difference between these is probably not too great to prevent a shift of the structure, zinc blende → rock salt.

Zinc blende structure   Rock salt structure
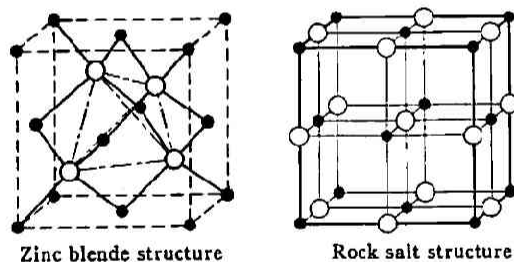
Fig. 8   The arrangement of Cd atoms and Te atoms in the zinc blende and rock salt structures of CdTe
●: Cd,   ○: Te

High pressure phase of CdTe

Several relationships have been suggested to obtain some insight into the cause of high pressure transition to the metallic state, particularly for the group IV and III–V compounds. Jamieson[35] has pointed out the empirical relation

$$P_T \Delta V = \frac{1}{2} E_g , \qquad (5)$$

where P_T and ΔV are the pressure and volume change at the transition, respectively, and E_g is the energy gap at atmospheric pressure. Owen et al.[10] have shown that equation (5) yields for CdTe a

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40)   M. L. Huggins, "Phase Transformations in Solids", ed. by R. Smoluchowski et al., p. 238~256, John Wiley & Sons, New York (1951)

41)   P. W. Davis and T. S. Shilliday, Phys. Rev., 118, 1020 (1960)

transition pressure of 118 kb to the metallic state, using $\Delta V = 12.3\ cm^3/mole$, and a energy gap E_g of 1.50 eV.

Musgrave[42] has suggested that the transition to the metallic state is brought about by the destabilizing electronic configuration which can occur when the conduction band becomes critically populated, and thereupon derived two relationships between the transition pressure and the energy gap. In one of them, the hydrostatic strain energy of compression is considered to be equal to the energy required by a critical number of electrons per atom to jump the energy gap and initiate the instability. The equation is given by

$$\frac{P_T^2}{2K^*} = nE_0{}^T, \qquad (6)$$

where P_T is the transition pressure, K^* is the bulk modulus, n is the critical number of electrons per atom to jump the energy gap, and $E_0{}^T$ is the energy gap at the transition. In the case of CdTe the value n was calculated to satisfy equation (6) by using the value of $P_T = 90\ kb$. The value obtained was stated to be approximately the same as the values of the other substances of group IV and III-V.

On the other hand, as noted above, Semerchan et al.[14] have measured the electrical resistance of CdTe at room temperature and reported that the transition to the conducting phase occurs at 50,000 kg/cm² using Bridgman's pressure scale (the pressure of the transition $Bi_{V \to VI}$ is located at about 125,000 kg/cm²). The pressure corresponds to about 41 kb in Kennedy-LaMori's scale which is used in this work. Taking into account that Semerchan et al. have observed no further transition in CdTe between 50,000 and 200,000 kg/cm², the transition observed at about 41 kb may be considered to correspond to the one which was observed near 33 kb in this work, and also to the one which was observed at 30 kb by Samara and Drickamer[12], in spite of rather large discrepancy in the pressure value. The discrepancy is not well understood. Although the resistivity of the rock salt phase of CdTe ($10^{-3} \sim 10^{-2}\ \Omega \cdot cm$ at room temperature and at about 60 kb) is higher than that of typical metals by a factor of $10^1 \sim 10^2$, the positive temperature coefficient of the resistance in the wide range of temperature suggests that the rock salt phase of CdTe may be in the metallic state. It is felt that further work should be undertaken before more definite statements can be made.

Some generalizations in cadmium chalcogenides

Phase diagram

Various authors[43]~[46] have discussed the systematic variation of the energy gap, the carrier mobility and the melting point, with the lattice constant, the average atomic number and the degree of ionicity of semiconducting compounds. The sequence CdS, CdSe and CdTe shows obvious regu-

42) M. J. P. Musgrave, *Proc. Phys. Soc.*, **84**, 585 (1964)

43) O. Mikami, *Oyo Butsuri (J. Appl. Phys. Japan)*, **25**, 3, 47 (1956)

44) H. Welker and H. Weiss, "Solid State Physics", ed. by F. Seitz and D. Turnbull, p. 1~78, Academic Press, New York (1956)

45) O. Folberth and H. Welker, *J. Phys. Chem. Solids*, **8**, 14 (1959)

46) D. A. Wright, *Electronic Eng.*, 659 (1959)

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larities both in the thermodynamic properties, as well as in other physical, chemical and structural properties. In Table 3 are listed several properties at atmospheric pressure.

Table 3   Properties of cadmium chalcogenides

Property	CdS	CdSe	CdTe
Melting point (°C)	1,475	1,258	1,090
Energy gap (eV)	W : 2.5	1.6	1.4
	Z : 1.7		
Mean atomic number	72.0	95.2	120.5
Lattice parameters (Å)	W : 4.14, 6.71	W : 4.31, 7.02	6.48
	Z : 5.82	Z : 6.04	
Density (g/cc)	W : 4.82	W : 5.73	5.85
	Z : 4.87	Z : 5.78	
Compressibility (10^{-6} bar^{-1})	2.62	3.56	3.96

W: Wurtzite structure   Z: Zinc blende structure

In the previous papers[15)17)] and in this work, the wurtzite-to-rock salt transition in CdS and CdSe, and the zinc blende-to-rock salt transition in CdTe have been presented. The structures of Cd–VI compounds are given in Table 4. As shown in Table 4 the high pressure phase is the rock salt structure. However, the atmospheric phases of Cd-chalcogenides are the wurtzite and/or zinc blende structure. The similarity between the wurtzite and the zinc blende structure has been noted in several works concerned with the macroscopic properties of the wurtzite[47)] and its band structure[48)49)].

Table 4   Structures of the Cd-VI compounds

	Atmospheric phase	High pressure phase
CdO	Rock salt	——
CdS	Wurtzite, Zinc blende	Rock salt
CdSe	Wurtzite, Zinc blende	Rock salt
CdTe	Zinc blende	Rock salt

Recent investigations at high pressure have suggested many kinds of correlation among the structural and phase relations of chemically similar compounds. It has been suggested[50)] that the P, T phase diagrams of the elements of the same group of the periodic table are very similar. Similarities among the phase diagrams of inorganic solids have been demonstrated in the ammonium halides[51)], and in the pair SbCl$_3$ and SbBr$_3$[52)], and in the pair Na$_2$SO$_4$ and Na$_2$CrO$_4$[53)], and also in the pair CuBr

47)   D. Berlincourt, H. Jaffe and L. R. Shiozawa, *Phys. Rev.*, 129, 1009 (1963)
48)   J. L. Birman. *ibid.*, 115, 1493 (1959)
49)   M. Cardona. *ibid.*, 129, 1068 (1963); *J. Phys. Chem. Solids*, 24, 1543 (1963)
50)   V. V. Evdokimova, *Soviet Phys.—Uspekhi*, 9, 54 (1966)
51)   R. Stevenson, *J. Chem. Phys.*. 34, 1757 (1961)
52)   B. F. Bowles, G. J. Scott and S. E. Babb, Jr., *ibid.*, 39, 831 (1963)
53)   C. W. F. T. Pistorius, *ibid.*, 43, 2895 (1965)

and CuCl[54]. A common P, T pattern has been noted[30)55] in the group IV elements and the III–V compounds.

In the previous paper[15] it has been predicted that the phase diagrams among cadmium chalco-genides might be similar, and might be common to those of the group IV elements and the III–V compounds. In Fig. 9, the phase diagrams of cadmium chalcogenides are shown. The solid-solid
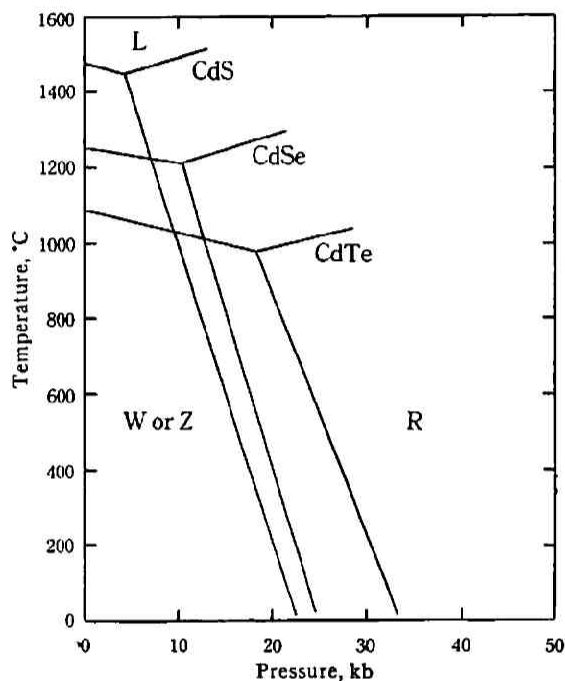

Fig. 9 Phase diagrams of cadmium chalcogenides

boundaries are obtained from the present work and previous publications[15)17]. The melting lines of CdTe are from the data of Jayaraman *et al.*[5] In the cases of CdS and CdSe, the melting lines are drawn on the assumption that the slopes of the melting curves may be similar to those of CdTe ac-cording to the suggestion that, for crystals of similar structure, the entropy change and the volume change upon melting should be constant[56], and thereupon to the requirement of the Clapeyron equation. The common features in Fig. 9 are that the boundaries between the low pressure and high pressure phases intersect the liquidus with the resulting triple points above the atmospheric pressure, and the solid-solid boundaries have negative slopes. The slopes are compared with those of the group IV element, Ge[30], and III–V compound, InSb[29] in Table 5.

The sign of the slope of the solid-solid phase boundary of CdS deserves some comment. After the publication of the previous paper[15] on the wurtzite—rock salt phase boundary of CdS, the author

54) E. Rapoport and C. W. F. T. Pistorius, *Phys. Rev.*, **172**, 838 (1968)

55) A. Jayaraman, W. Klement, Jr. and G. C. Kennedy, *ibid.*, **130**, 540 (1963)

56) A. R. J. P. Ubbelohde, "Advances in Chemical Physics", ed. by I. Prigogine, Vol. 6, p. 459~480, Interscience, London (1964)

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Table 5   Thermodynamic parameters at the transitions

Substance	Low pressure phase	High pressure phase	$10^2 \times dP/dT$ (kb/deg)	ΔV (cm^3/mole)	ΔS (e.u.)	$10^{-2} \times \Delta H$ (cal/mole)
CdS	Wurtzite	Rock salt	-1.3	-6.1	1.9	5.6
CdSe	Wurtzite	Rock salt	-1.2	-6.2	1.7	5.0
CdTe	Zinc blende	Rock salt	-1.5	-6.3	2.3	6.6
Ge[a]	Diamond	White tin	-3.0	—	—	—
InSb[b]	Zinc blende	White tin	-1.7	-3.9	1.7	5.0

a: Ref. 30   b: Ref. 29

was informed of the report[57] of Miller, Dachille and Roy on the P–T diagram of CdS. They found a new polymorph and located a triple point at 16.5 ± 0.5 kb and $425°\pm5°C$ between the wurtzite (and zinc blende), rock salt and a new polymorph by electrical resistance experiments and using visual, x-ray diffraction and petrographic techniques. According to Miller et al.[57], the boundary between the wurtzite and the rock salt phase has a positive slope. The trend agrees with the volumetric measurements of Jayaraman et al.[6], and of Samara and Giardini[58], but is against the results of the electrical resistance measurements of the author[15], and of Samara and Giardini[58]. In the previous paper[15], the electrical resistance measurements were performed at constant temperatures. During the course of the investigation into the kinetics of the transition[59], the resistance measurements were also performed at constant pressures. The transition was observed when the temperature on the CdS of the wurtzite phase was raised from room temperature at constant pressures which were below the room temperature transition pressure, indicating again the negative slope of the phase boundary. In the case of CdSe and CdTe, it was also observed that the solid-solid boundaries have negative slopes in these studies.

Entropy of transition

The entropy, volume and enthalpy relations of the transitions together with the structures are also given in Table 5. In general, for a given substance, the phase of lower density and lower co-ordination is the one of higher entropy and would be expected to be stable at lower pressures. Conversely, the phase of higher density and higher coordination is the one of lower entropy and would be expected to be stable at higher pressures. In cadmium chalcogenides, however, the phase of higher coordination is the one of higher entropy, the low pressure phases having the wurtzite or zinc blende structures with the coordination number 4 and the high pressure phases having the rock salt structure with the coordination number 6.

The entropy change of a crystal can be divided into vibrational entropy change ΔS_{vib} and entropy change of configurational disorder ΔS_{con}. Then

$$\Delta S = \Delta S_{vib} + \Delta S_{con}. \qquad (7)$$

It could be estimated that $\Delta S_{con} < 0$ because the increase in the coordination number from four to six results in the decrease in configurational disorder. Therefore, ΔS_{vib} should be positive in order that

57) R. O. Miller, F. Dachille and R. Roy, J. Appl. Phys., 37, 4913 (1966)

58) G. A. Samara and A. A. Giardini, Phys. Rev., 140, A388 (1965)

59) A. Onodera, to be published.

$\Delta S > 0$ as shown in Table 5. This may be ascribed to the effect of the increased number of the nearest neighbor interactions, and also to the alteration in the nature of the interactions accompanying the change from somewhat covalent to more ionic lattices.

Sequence of the transition pressure

In the series CdS, CdSe and CdTe, the pressure of the transition to the rock salt structure increases with increasing mean atomic number. This is opposite to the behavior of the zinc chalcogenides. As seen in Table 6, the pressure of the transition[12][13] in ZnS, ZnSe and ZnTe from the zinc blende to the rock salt structure[60] decreases in this sequence. Also in Table 6 are listed the transition pressures[13] [29][61] of the group IV elements and the III–V compounds, from the diamond or zinc blende structure to the white tin structure. The sequence of the transition pressure in these substances is consistent with the behavior of zinc chalcogenides. In other chalcogenides, such as HgSe and HgTe[6], the sequence of the transition pressure behaves like cadmium chalcogenides. Phase transitions in the compounds PbS, PbSe and PbTe are accompanied by abrupt increase in electrical resistivity by several orders of magnitude[14][62][63]. The transition pressure in PbTe differs according to the experimental method. The electrical resistance measurements[14][52] have reported that it is located near 70 kb, while the x-ray diffraction[64][65] and the volume change[66] measurements have reported that the transition occurs at about 40~45 kb. The data of Minomura et al.[65] are the latest ones and will, therefore, be used for the present discussions. In the series PbS, PbSe and PbTe the sequence of the pressure of the transition from the rock salt to the orthorhombic (distorted NaCl) structure is also the same as that in cadmium chalcogenides.

Table 6   Transition pressures in some IV, III-V, II-VI and IV-VI compounds

Substance	P_T (kb)	Reference	Substance	P_T (kb)	Reference
CdS	23	15	GaP	>550	61
CdSe	25	17	GaAs	245	13, 61
CdTe	33	present work	GaSb	80	13, 61
ZnS	245	12, 13	InP	128	13, 61
ZnSe	165	12	InAs	100	13, 61
ZnTe	140	12, 13	InSb	23	29
HgSe	7	6	PbS	25	64, 65
HgTe	14	6	PbSe	43	64
Si	195	13, 61	PbTe	45	65
Ge	120	13, 61			

60) P. L. Smith and J. E. Martin, *Phys. Letters*, **19**, 541 (1965)
61) S. Minomura and H. G. Drickamer, *J. Phys. Chem.* Solids, **23**, 451 (1962)
62) G. A. Samara and H. G. Drickamer, *J. Chem. Phys.*, **37**, 1159 (1962)
63) A. A. Semerchan, N. N. Kuzin, L. N. Drozdova and L. F. Vereshchagin, *Soviet Phys. — Doklady*, **8**, 982 (1963)
64) A. N. Mariano and K. L. Chopra, *Appl. Phys. Letters*, **10**, 282 (1966)
65) I. Wakabayashi, H. Kobayashi, H. Nagasaki and S. Minomura, *J. Phys. Soc. Japan*, **25**, 227 (1968)
66) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **76**, 55 (1948)

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It is difficult to see any close relationship between the transition pressures for chalcogenides. The trend of the increasing transition pressure as one proceeds down in the series CdS, CdSe and CdTe may be attributed to the increased energy required for the electronic rearrangement to exist in the rock salt structure.

Increase in coordination number

As noted earlier, there are four nearest neighbors in the wurtzite and zinc blende structures. In the rock salt (NaCl) structure the coordination number is 6. In the white tin structure of CdTe there are four nearest neighbors and two additional neighbors at a slightly greater distance. The effective coordination in CdTe, therefore, slightly decreases during the transition from the rock salt to the white tin structure near 100 kb. It is, however, expected that pressure brings about the increase in coordination number.

It is reasonable to expect that at higher pressures CdS and CdSe would transform into the cesium chloride structure with a coordination number of 8, or other structures of higher coordination than the rock salt structure. The cusp in the pressure dependence of the electrical resistance of CdS[12] at about 465 kb might be attributed to further transition. The metallic behavior will appear in the cesium chloride structure, or in any other structure. Although the transition in CdO has not yet been observed in the pressure range up to 300 kb, the compound is also expected to transform into the cesium chloride or any other structure.

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