HIGH PRESSURE TRANSITION IN CADMIUM SULFIDE

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The wurtzite-rock salt phase boundary of a single crystal of cadmium sulfide was investigated experimentally over a P, T range of about 25 kb and 700°C by observing electrical resistance behavior in a cubic compact anvil device.

In single crystal samples, the room temperature transition pressure was found to be at 22.5 ± 1.4 kb. At the transition the electrical resistivity decreases by several orders of magnitude. The transition pressure is lowered with increasing temperature. The wurtzite-rock salt phase boundary has a slope of -74.7°C/kb.

Introduction

It is known that cadmium sulfide shows, under the normal condition, two modifications, one having the haxagonal—wurtzite structure, the other the cubic—zinc blende structure. The phase transition of cadmium sulfide was first discovered by Drickamer and his co-workers.[1]—[4] The transition, which has been observed in the range 20–30 kb, is accompanied by a large discontinuous red shift in the optical absorption edge and a corresponding increase by several orders of magnitude in the electrical conductivity. To explain the results which they obtained, Drickamer and his co-workers suggested that at high pressures the transition from the wurtzite to the zinc blende structure takes place in CdS. The basis for such an interpretation was the presence of the zinc blende lines along with lines of the wurtzite structure in the x-ray patterns of the samples of CdS which had been subjected to high pressure.

Recently the direct identification of the high pressure phase of CdS has been briefly reported.[5]—[8] In these cases, the identification was achieved by means of high pressure x-ray cameras. It is agreed that the high pressure phase has the cubic—rock salt structure. The volume change accompanying the transition is about 20%.

Only tentative works have been reported concerning the effect of temperature on the transition

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pressure for these phases. Electrical resistance measurements[10] showed a negative slope, while the volume discontinuity measurements to 200°C[10][11] suggested a positive slope.

The present investigation was undertaken in order to determine the wurtzite-rock salt phase boundary of CdS at high temperatures. Observation of discontinuous changes in electrical resistance at various pressures under isothermal conditions was used to define the phase diagram. Furthermore, the theoretical aspects of the wurtzite-rock salt transition are discussed.

Experimentals

These experiments were performed with a 1,200-ton cubic compact anvil apparatus constructed at this laboratory. The principal design and the operation characteristics of the device have been described in detail earlier.[12] The pressure calibration of the apparatus was obtained from the oil pressure (to the hydraulic ram) required to produce phase transitions in the specimens of bismuth, thallium and barium. In accordance with the customary practice, the transitions were revealed by the changes in electrical resistance. The reference pressures employed are Bi (I–II) at 25.4 kb, Tl (II–III) at 37.0 kb, Ba (I–II) at 59 kb, and Bi (V–VI) at 89 kb.[13] A linear dependence of the specimen pressure (above 25.4 kb) on oil pressure was indicated. The calibration for pressures below 25.4 kb was provided by a freezing point of mercury at room temperature.[14] A straight line was drawn through 25.4 kb (Bi$_{I-II}$), 11 kb (freezing of mercury) and zero. No correction was made for the effect of elevated temperature on the pressure calibration. The pressures given are thought to be accurate within ±1.4 kb below 25 kb and ±1.0 kb above 25 kb.

Electrical resistance measurements

A schematic diagram of the cross section of the sample cube used for resistance measurements is shown in Fig. 1. Pyrophyllite was used for the specimen container and served as the pressure trans-mitting medium. The specimens were enclosed in the center of pyrophyllite cube, the edges of which were 13 mm long. The matching square faces of the six anvils were 10 mm on the edge. The pyro-phyllite cube contained a 6 mm-diam. glassy carbon heater with copper current leads, in which was placed a 4 mm cylinder of pyrophyllite which served to transmit pressure to the 2 mm cylindrical sample. Holes were drilled from the mid-points of each of two edges directed toward the center of the cube. The thermocouple was inserted so that the junction was positioned at the outer surface of the heater.

Two anvils afforded electric contact to the heater through copper wires; two anvils afforded electric contact to the sample through platinum foils. The insulation of the electric contacts was pro-vided by teflon sheet. The heater current up to a few hundred amperes was provided by a transformer.

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

11) A. Jayaraman, W. Klement, Jr. and G. C. Kennedy, *Phys. Rev.*, **130**, 2277 (1963)

12) J. Osugi, K. Shimizu, K. Inoue and K. Yasunami, *This Journal*, **34**, 1 (1964)

13) F. P. Bundy, "Modern Very High Pressure Techniques", edited by R. H. Wentorf, Jr. p. 19, Butter-worths, London (1962)

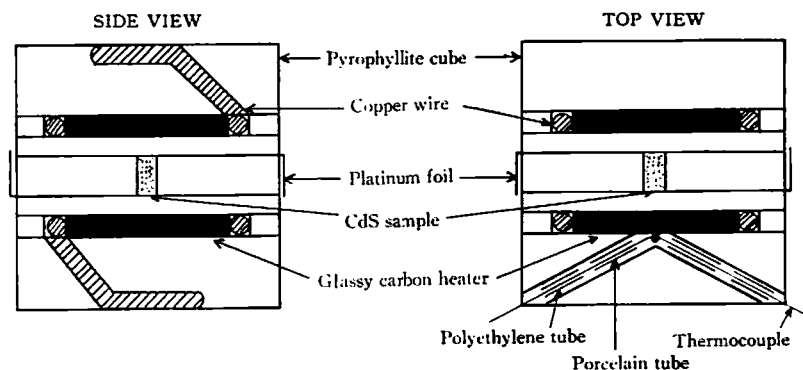14) W. Klement, Jr., A. Jayaraman and G. C. Kennedy, *Phys. Rev.*, **131**, 1 (1963)

Fig. 1 Sample configurations for resistance measurements in cubic anvil apparatus

Temperature was monitored by Chromel-Alumel thermocouples which had been calibrated against the melting points of tin, lead, zinc and aluminum. The readings of the thermocouples were corrected for the effect of pressure in accordance with the results reported by Hanneman and Strong.[15] Temperatures were determined with a precision of $\pm 1°C$.

The CdS samples (wurtzite form) for the electrical resistance measurments were cleft from high purity single crystals produced from the melt or by the sublimation method. The samples used for the pressure measurements were usually 0.4–1.6 mm thick. The platinum foil electrodes were used in contact with the large faces of the sample. There was no apparent reaction between the CdS and platinum foil or pyrophyllite in the temperature and pressure range covered.

The experimental points of wurtzite-rock salt phase boundary of single crystal specimen were obtained by fixing the temperature and raising the pressures in the small increments which, near the transition point, were 1.4 kb. The pressure was held constant (for 10 min to 1 hr) at each value until no changes in resistance could be observed. Discontinuity in the pressure dependence of the resistance defines the boundaries of two solid phases. The high resistance measurements were made using a TOA PM-8 type vacuum tube voltmeter. The low resistance measurements utilized a potentiometer.

The electrical resistance measurements were reduced to absolute resistivity data by measuring the dimensions of the CdS specimens at room conditions after the runs. It was not possible, however, to obtain resistivity values at the end of every experiment. The CdS samples usually shattered, and their final measurement was not possible. For this reason the data are given in terms of relative values only.

Recovery of the high pressure phase

In some instances, quenching has been applied, whereby the temperature of the material is lowered before the pressure is released. In the cubic compact anvil apparatus the quench was sufficient to drop the specimen temperature from 1,100°C to 200°C in about 10 sec; this quench made possible the re-covery of the metastable high pressure phase. As shown in Fig. 2, the specimen was placed inside the pyrophyllite cube by encapsulating it in a sheath of pyrophyllite and placing the sheath inside a

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

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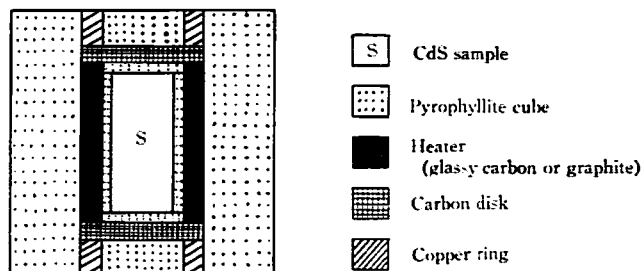|	
S	CdS sample
⬚	Pyrophyllite cube
■	Heater (glassy carbon or graphite)
▤	Carbon disk
▨	Copper ring

Fig. 2 Sample geometry for quenching treatment

graphite or a glassy carbon tube.

The pressure was first raised to a predetermined value with the temperature maintained at room temperature. Next the temperature was gradually raised to the desired value. Once at a certain temperature, the temperature was held for 1~5 hours, and then the heating current was switched off to quench the specimen. After the temperature had dropped to room temperature, the pressure was slowly released and the sample was removed for x-ray diffraction analysis. In the experiments on the recovery of the high pressure phase, a curve of the temperature of the specimen plotted against electric power supply of heating was used in order to determine the temperature. Temperatures are believed to be accurate within ±10°C below 300°C and ±50°C at about 1,000°C.

Results

Pressure-temperature phase diagram

The measurements on room temperature resistance *versus* pressure were performed on single
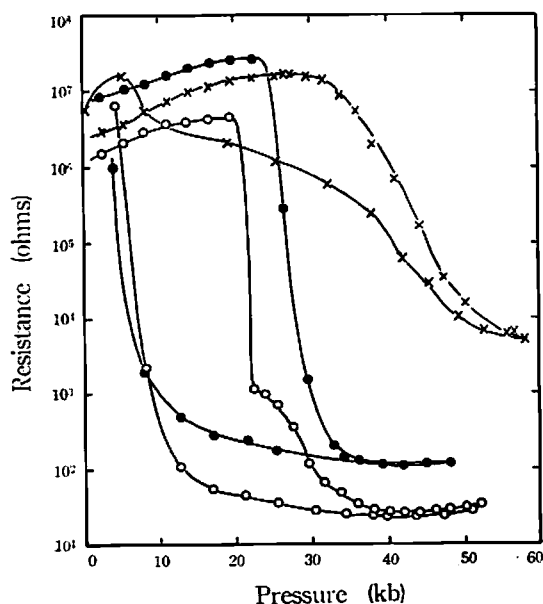
Fig. 3 Resistance *versus* pressure (at room temperature) for CdS sample initially in wurtzite form
  O: single crystal
  ●: coarse grained particles
  ×: powder

crystals produced from the melt and by the sublimation method, coarse grained crystals, and com-
pacted powder samples precipitated from the $Cd(NO_3)_2$ solution, all initially in the wurtzite form.
Fig. 3 shows the results for the single crystal produced from the melt and its coarse grained sample,
and the powder sample. For pressures up to approximately 20 kb, the electrical resistance increases
slightly with pressure. In the single crystal samples the wurtzite-to-rock salt transition occurs
at 22.5 ± 1.4 kb accompanied by a sharp decrease in resistance of over four orders of magnitude. The
resistance exhibits a minimum at about 42 kb, whose pressure probably corresponds to the end of the
transition. Above this point the resistance increases with pressure. This behavior is reversible with
a hysteresis of about 12 kb (corrected for the hysteresis of the apparatus). Single crystals produced
by the sublimation method showed almost the same feature as those from the melt. From Fig. 3 it
can be seen that the transition pressure of coarse grained specimen and powder specimen differ
markedly from those of single crystal specimen. The transition pressure of single crystal CdS at
room temperature is compared with the other data[1)-4)10)16)] in Table 1.

Table 1 Transition pressure of CdS

Investigator	P_T (kb)	Method	References
Osugi *et al.*	22.5 ± 1.4	electrical resistance	Present work
Samara and Giardini	23	electrical resistance	10
Samara and Giardini	$23\ \pm1$	volume change	10
Drickamer *et al.*	27	electrical resistance	3, 4
Drickamer *et al.*	27.5	optical absorption	1, 2
Cline and Stephens	17.5 ± 0.8	volume change	16

The boundary between the wurtzite and rock salt structures of CdS was determined by holding
the single crystal samples at constant temperature and increasing the pressure. Typical isotherms are
shown in Fig. 4. Because of the unstableness of temperature no data can be reported with release of
pressure. The transition pressures were read at the beginning of the discontinuous resistance drop.
The transition pressure is lowered with increasing temperature. The results are summarized in Fig.
5. The slope of the line in Fig. 5 defining the CdS phase boundary is $-74.7°C/kb$.

A question was raised[17] as to the applicability of the Clausius-Clapeyron equation

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

to the solid-solid transition. In the first order phase transition with large values of $\varDelta V$ and dP/dT,
however, it was indicated[18] that the thermodynamic parameters of transitions can be obtained
by the application of the Clausius-Clapeyron relationship. The volume change[5)-7)9)10)10)19)] at the
transition is thought large enough to adopt the Clausius-Clapeyron equation. Using a value of 21%

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17) A. R. Ubbelohde, *Quart. Rev.*, **11**, 246 (1957)
18) A. J. Majumdar and R. Roy, *J. Inorg. Nucl. Chem.*, **27**, 1961 (1965)
19) J. D. Kennedy and W. B. Benedick, *J. Phys. Chem. Solids*, **27**, 125 (1966)
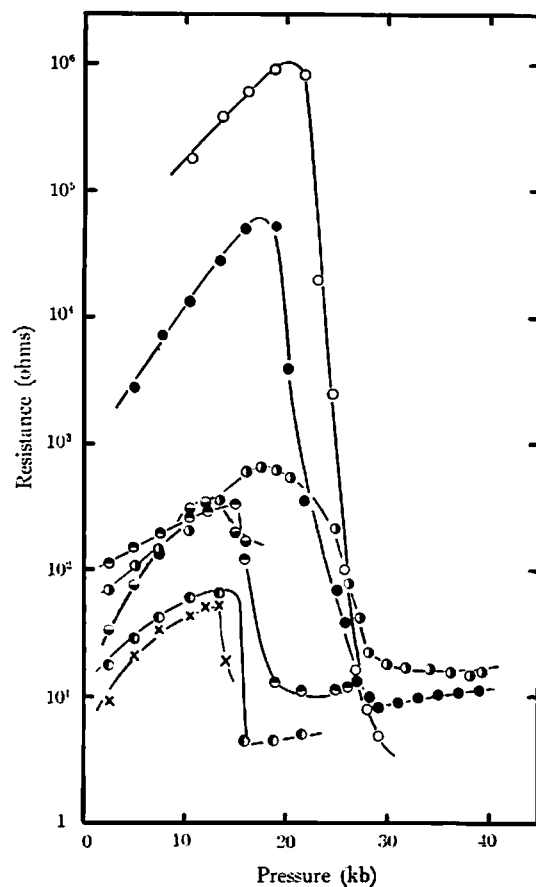
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Fig. 4 Resistance *versus* pressure isotherms of single crystals of CdS
The isotherms are from different experiments.

O: 100°C   ◑: 500°C
●: 200°C   ◒: 600°C
◑: 300°C   ×: 700°C
◐: 400°C

for the relative volume change $\Delta V/V_0$ at the transition at 25°C[10] and the above slope, the resulting heat of transition, as calculated from equation (1), is 5.6×10^2 cal/mole. The change in entropy is found to be 1.9 e.u.

It is realized that there are both pressure and temperature gradients within the sample container. An additional uncertainty is introduced by employing a room temperature calibration for the pressure values at elevated temperatures. The actual pressure values at elevated temperatures are probably higher than those based on the room temperature calibration.

The electrical resistance of both the wurtzite and the rock salt phases increases with pressure at any temperature. The semiconducting properties of both phases will be presented in the following paper.

After the runs the single crystal specimens were found to be brown-colored, with no identification of contamination. When ground to powder in an agate mortar they changed their color to orange-red. The structure of the recovered materials was wurtzite.
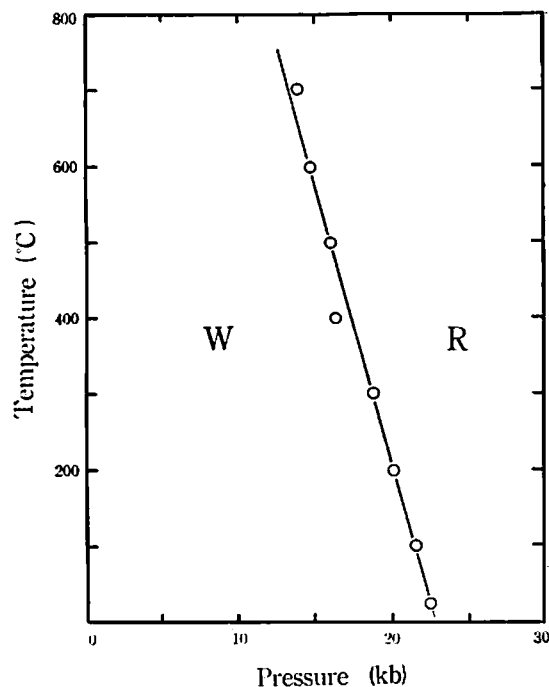
Fig. 5   Phase diagram of wurtzite (W)-rock salt (R) structures of CdS

Recovery of the high pressure phase

For single crystal samples the experiments were run between 19 and 44 kb and between 100 and 1,000°C for 1~5 hours in the stability region of the rock salt phase in the P, T phase diagram of CdS given in Fig. 5. The samples were thermally quenched to room temperature before the pressure release. Upon releasing the pressure, the structure of the recovered material was wurtzite.

For the powder samples the experiments were run between 27 and 37 kb and between 300 and 1,000°C for 1~2 hours (Table 2). The rock salt phase of CdS was recovered for the samples held at

Table 2   Pressure-temperature data for quenching treatment

Pressure kb ±1 kb	Temperature °C ±10~50°C	Time hr	Results W = Wurtzite R = Rock salt
27	300	1	W
27	600	1	W
27	1,000	1	W
27	1,000	2	W
29	300	1	R
29	300	2	R
29	600	1	W
30	600	2	W
32	1,000	1	W
37	300	2	R
37	600	2	W

300°C and 29 or 37 kb, for 1 or 2 hours. The rock salt pellets were almost black and had a submetallic luster. When ground to powder, the rock salt phase lost its luster but was still much darker than the powders of the normal phases and had stimulant smell.

Table 3 lists the d-spacings and approximate relative intensities of the x-ray lines obtained from the retained rock salt phase. The lattice parameter value from the present results is 5.45Å. It is in good agreement with the reported value of Corll[20] (5.464±0.012Å) within experimental error. Rooymans[5] gives the lattice parameter of the rock salt phase a value of 5.30Å and Mariano and Warekois[6] a value of 5.30Å and Owen et al.[9] a value of 5.42Å, all presumably measured just above the transition using high pressure cameras.

Table 3   X-ray data of the retained high pressure phase of CdS

hkl	d (Å)	a (Å)	$(I/I_0)_{obs}$
111	3.16	5.48	100
200	2.73	5.46	70
220	1.93	5.47	57
311	1.64	5.44	19
222	1.57	5.44	18
400	1.36	5.43	11
420	1.22	5.44	14
422	1.11	5.44	10
		$a_{av.} = 5.45$Å	

The rock salt samples became brown-colored and lost its smell after one day and changed to a zinc blende structure. After a week, it came to have a wurtzite structure. This is consistent with the reverse structural sequence[10]: rock salt→zinc blende→wurtzite.

In order to retain the rock salt phase under atmospheric pressure it is necessary to heat it at high pressures prior to cooling. This heating process presumably destroys the wurtzite nuclei present after the room temperature wurtzite→rock salt transition. The results in Table 2 show that there may exist optimum temperature for annealing.

The effect of particle size on the transition pressure

During the experiments one test was conducted to find whether the particle size would effect the transition pressure of CdS. Single crystals were crushed to particles in an agate mortar. It was confirmed by the x-ray diffraction that the wurtzite structure did change neither to the zinc blende nor to the rock salt phase during grinding. The average diameters of the classified samples were determined by an electron microscope and/or an optical microscope. The wurtzite-to-rock salt transition pressures observed by electrical resistance measurements are listed in Fig. 6. The transition pressure increases with the decreases in particle size.

A single crystal sample transformed from the wurtzite to the rock salt structure is considered to be a polycrystalline one. Pressure cycling to introduce the wurtzite-to-rock salt and rock salt-to-

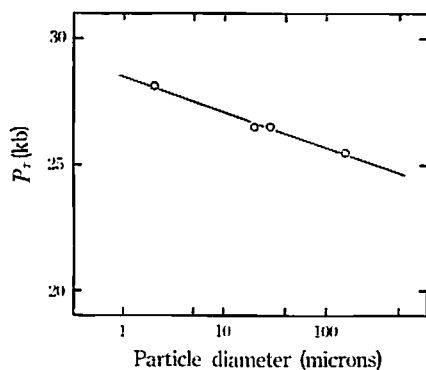20)   J. A. Corll, *J. Appl. Phys.*, **35**, 3032 (1964)

Fig. 6 Transition pressure of coarse-grained particles as a function of particle diameter

wurtzite transition would make the polycrystallinity of the specimens higher and the grain size smaller. The experiment was done by starting with a single crystal specimen of CdS, compressing into the rock salt phase, decompressing, and so on. The electrical resistance as a function of pressure is shown in Fig. 7. During the initial compression, ①, the resistance dropped by nearly five orders of
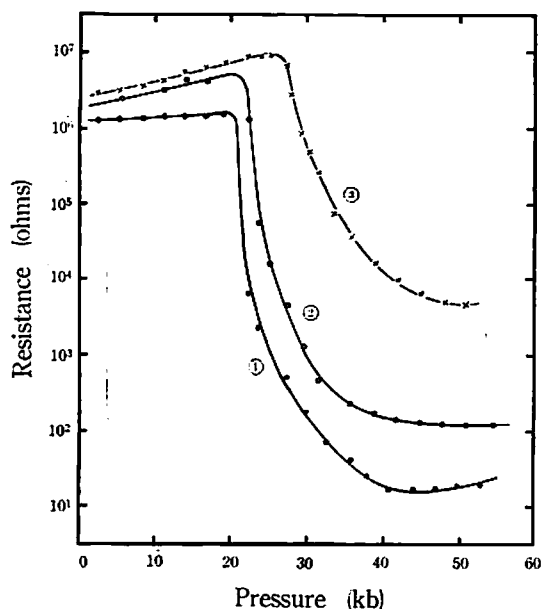

Fig. 7 Resistance *versus* pressure behavior of CdS during three cycles of compression (①→②→③)

magnitude to the level of the rock salt phase. Upon recompressions ② and ③, the transition to the rock salt phase were much more sluggish than first it was. This experiment gives the evidence that the grain size gives effect on the transition pressure.

Considerations

The spacial arrangements of the atoms in the wurtzite, zinc blende, and rock salt structures are

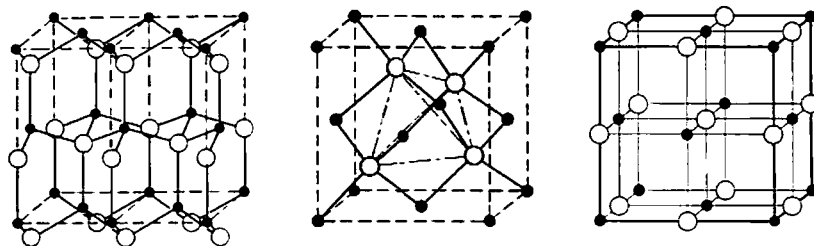J. Osugi, K. Shimizu, T. Nakamura and A. Onodera

Fig. 8   The arrangement of Cd atoms and S atoms in the wurtzite, zinc blende
and rock salt forms of CdS (left to right)   ●: Cd   ○: S

shown in Fig. 8. In the wurtzite and zinc blende forms each cadmium atom is tetrahedrally surrounded by four sulfur atoms and *vice versa*. In the rock salt form each cadmium atom is octahedrally surrounded by six sulfur atoms and *vice versa*. The wurtzite structure consists of two interpenetrating hexagonal close-packed lattices, one of cadmium and the other of sulfur, while the rock salt structure consists similarly of two interpenetrating cubic close-packed lattices. The two structures differ in their layer stacking arrangements; -ABABAB- in the hexagonal close-packed structure parallel to (0001), and -ABCABC- in the cubic structure parallel to (111). The transition mechanism then must introduce one-dimensional stacking disorder. The mechanism is similar to that of the diffusionless martensite-type transition, with shear on (0001) hexagonal planes initiating the transition to the cubic lattice by a succession of identical glides on alternate parallel planes in the $[1\bar{1}00]$ hexagonal directions. This is supported by the fact that shock wave experiments[19] have shown that the transition is virtually completed in less than 1 μsec, a time scale too short for bulk diffusion to take place.

It has been pointed out that the transition between the wurtzite and zinc blende structures in CdS,[21][22] and also in ZnS[21][22] and AgI,[23] takes place through the martensite-type mechanism. One modification changes to the other, if the ionic planes connected, makes a glide parallel to themselves.[24] On the other hand, the zinc blende structure goes to the rock salt structure by shifting only one kind of ion.[25] Under high pressures the wurtzite structure would transform to the rock salt structure, rather than to the zinc blende structure, because the density difference between the wurtzite and zinc-blende structure is little as discussed below.

The initial variation of the axial ratio (c/a) with pressure may be estimated from the elastic moduli.

$$\xi = \frac{c}{a} \times \frac{C_{33} - C_{13}}{C_{11} + C_{12} - 2C_{13}} \tag{2}$$

In equation (2), $\xi > 1$ means an increase and $\xi < 1$ a decrease in the axial ratio under hydrostatic pressure. From the room temperature elastic moduli[26] one obtains $\xi = 1.8$, so it may be expected that the

21)   H. Blank, P. Delavignette, R. Grevers and S. Amelinckx, *Phys. Status Solidi*, **7**, 747 (1964)

22)   F. S. D'Aragona, P. Delavignette and S. Amelinckx, *ibid*, **14**, K115 (1966)

23)   G. Burley, *J. Phys. Chem.*, **68**, 1111 (1964)

24)   K. Sasvári, *Acta Phys. Hungr.*, **8**, 245 (1958)

25)   M. L. Huggins, "Phase Transformations in Solids" edited by R. Smoluchowski *et al.* pp. 239–256, John Wiley & Sons, New York (1951)

26)   D. I. Bolef, N. T. Melamed and M. Menes, *J. Phys. Chem. Solids*, **17**, 143 (1960)

axial ratio of CdS increases with pressure slightly from $c/a = 1.624$, whose value corresponds to the atmospheric pressure. Under pressure the CdS single crystal would be nearly isotropically compressed keeping the value of axial ratio close to that of ideal haxagonal, 1.633.

It is seen that the wurtzite-to-rock salt transition pressure of coarse-grained CdS is a function of particle size, those specimens composed of small particles having a higher transition pressure than those of larger size particles. Some possibilities to introduce this phenomenon are enumerated below :

1. The role of the individual crystal grain

2. The role of the impurities introduced during grinding

3. The role of an interstitial impurity.

The effect of increasing pressure is analogous to the effect of decreasing temperature. It has been reported[27]–[29] that the transition temperature decreases in the martensite transition as the particle size becomes smaller, or in other words, small particles are less likely to transform than large ones. Thermodynamic consideration are described below by the modification of the equations of Knapp and Dehlinger.[30][31]

Each wurtzite and rock salt phase has a chemical free energy that varies with pressure, and there may be a pressure (P_0) at which the two free energies are equal ($F^W = F^R$). At any other pressure, the difference in free energy may be expressed as

$$F^R - F^W = \Delta F^{W \to R} \qquad\qquad (3)$$
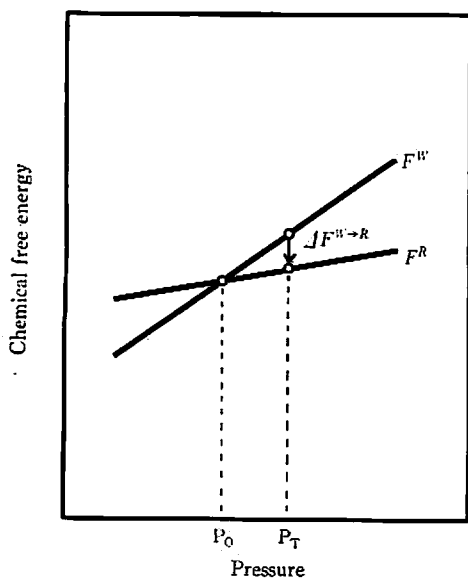

Fig. 9 Schematic representation of F^W and F^R versus pressure

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28) R. E. Cech and D. Turnbull, J. Metals, 8, 124 (1956)

29) S. Kachi, Funtai Oyobi Funmatsuyakin (J. Japan Soc. Powder Met.), 8, 4 (1961)

30) H. Knapp and U. Dehlinger, Acta Met., 4, 288 (1956)

31) L. Kaufman and M. Cohen, "Progress in Metal Physics", edited by B. Chalmers and R. King. pp. 165–246, Pergamon Press, London (1958)

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This quantity is negative when the rock salt phase is more stable than the wurtzite phase and is positive for the opposite. Fig. 9 is a schematic representation of F^W and F^R as a function of pressure. A wurtzite-to-rock salt transition cannot take place spontaneously at a given pressure and temperature unless the pressure is above P_0. On the other hand, such transition does not occur immediately above P_0. The reason for the necessity of over-pressure (P_T-P_0) is that the non-chemical factors, such as internal energy and strain energy, act as opposing the transition. The condition for transition to occur is

$$\Delta W^{W \to R} \equiv \Delta F^{W \to R} + \Delta G^{W \to R} < 0 \qquad (4)$$

where $\Delta G^{W \to R}$ is the non-chemical free energy and $\Delta W^{W \to R}$ is the net driving force.

An interface grows when the transition occurs. For a thin oblate spheroid of rock salt embryo with the radius r and semithickness c

$$\Delta G_s = 2\pi r^2 \sigma, \qquad (5)$$

where σ is an interfacial energy coefficient. Another non-chemical term is the elastic strain energy

$$\Delta G_\varepsilon = \frac{4}{3}\pi r^2 c \times \frac{Ac}{r}, \qquad (6)$$

where A is an elastic constant.
Thus,

$$\Delta G^{W \to R} = \Delta G_s + \Delta G_\varepsilon = 2\pi r^2 \sigma + \frac{4}{3}\pi r^2 c \times \frac{Ac}{r}. \qquad (7)$$

Referring to a unit volume of rock salt, equation (4) becomes

$$\Delta w = \Delta f + \Delta g, \qquad (8)$$

where Δf is the change in chemical free energy attending the formation of $1\,cm^3$ of rock salt, Δg being the corresponding non-chemical free energy change, and Δw is the net change in free energy per unit volume of rock salt formed. Dividing from equation (7) by the volume of rock salt embryo, $\frac{4}{3}\pi r^2 c$, one obtains

$$\Delta g = \frac{3\sigma}{2c} + \frac{Ac}{r}. \qquad (9)$$

For a given volume of the rock salt embryo, Δg can be minimized.

$$\Delta g_{min} = \frac{5}{2}\left(\frac{\sigma A}{r}\right)^{1/2}. \qquad (10)$$

From equation (10) one can see that Δg_{min} decreases monotonously with increasing size of the embryo. This means that the larger the embryo, the smaller is the restraining force which opposes the transition. For a given embryo, Δf becomes more negative as the pressure increases until Δf exceeds Δg_{min} for the size in question, then the chemical driving force overbalances the non-chemical driving force, and net driving force arises.

At pressure below P_0, the rock salt embryos in the wurtzite cannot grow because both the chemical driving force and the net driving force favor the formation of wurtzite. Above P_0 but below P_T, the chemical driving force becomes favorable for the rock salt formation, but the net driving force is unfavorable; that is, even for the largest embryo, the non-chemical driving force Δg_{min} exceeds the chemical driving force. Above P_T, the chemical driving force exceeds Δg_{min} for the larger embryos, and the net driving force favors the formation of rock salt. The size of embryo may be determined by the wurtzite grain size. In view of the foregoing thermodynamic considerations it could be said that a large wurtzite particle is more likely to transform into the rock salt phase than a small one. The observed increase in the transition pressure in Fig. 6 may be partly due to the particle size effect.

The possibilities also arises with regards to the role of impurities or an interstitial impurity which may be introduced during the crushing of the crystal to small particles in an agate mortar. It is possible that their role might be such as to prevent the coherent action from one wurtzite grain to the next.

If we now compare the crystallographic parameters for the wurtzite, zinc blende, and rock salt structures, we get the results shown in Table 4.

Table 4   Structures of CdS

| | Atmospheric phase | | High pressure phase |
	wurtzite	zinc blende	rock salt
lattice constant	4.14[*)] 6.71	5.82[*)]	5.45[**)]
density	4.82	4.87	5.93

[*)]   Data from ASTM card   [**)]   Data from the present work

The Cd-S interatomic distance is equal to 2.53Å in the wurtzite lattice $\left(=\dfrac{\sqrt{6}}{4}\times4.14\text{Å}\right)$. The distance in the rock salt lattice is about 2.73A $\left(=\dfrac{1}{2}\times5.45\text{Å}\right)$, and so an increase 8%. Therefore, the increase in coordination number from four to six is in agreement with this greater distance. This can be most readily interpreted by simple consideration as described below.

The potential energies of a crystal are expressed in terms of Coulomb-potential and repulsive potential:

$$E=-\frac{Me^2Z^2}{R}+\frac{Be^2}{R^n} \tag{11}$$

where R is interatomic distance, M Madelung constant, Ze the charge of ion, B the repulsion constant, and exponent n varies between 6 and 11. Although the exponential expression for repulsive potential is more ready to explain the experimental data than the inverse power expression,[32] in this case the inverse power expression is adopted. At equilibrium distance

$$\frac{dE}{dR}=\frac{Me^2Z^2}{R^2}-\frac{n\,Be^2}{R^{n+1}}=0, \tag{12}$$

32)   See for example, M. Tosi and T. Arai, "Advances in High Pressure Research" Vol. 1., edited by R. S. Bradley. pp. 265–325, Academic Press, London and New York (1966)

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$$R_0 = \left(\frac{nB}{MZ^2}\right)^{1/(n-1)} . \tag{13}$$

Thus,

$$\frac{R_{rock\,salt}}{R_{wurtzite}} = \left\{\frac{B_{rock\,salt}}{B_{wurtzite}} \cdot \frac{M_{wurtzite}}{M_{rock\,salt}}\right\}^{1/(n-1)} . \tag{14}$$

The ratio of repulsion coefficient $B_{rock\,salt}/B_{wurtzite}$ could be put $6/4$, which is the ratio of the co-ordination number. From equation (14) and the Madelung constant[33], one obtains

$$\frac{R_{rock\,salt}}{R_{wurtzite}} = \left\{\frac{6}{4} \cdot \frac{1.6413}{1.4776}\right\}^{1/(n-1)} .$$

Assuming $n = 9$

$$\frac{R_{rock\,salt}}{R_{wurtzite}} = 1.042 .$$

From the above discussion it should be said that the interatomic distance is greater in the rock salt lattice than in the wurtzite lattice.

The density of wurtzite structure is not so different from that of the zinc blende structure. The large density of rock salt structure is consistent with the reported large volume change accompanied with the transition.

The Cd-VI compounds, CdS, CdSe, and CdTe, exhibit remarkable monotonic decreases in the normal melting points and energy gap. This systematic variation may be said to show the systematic variation of the strength of bonding. The ionic character of the bonding is thought to decrease in the sequence, CdS, CdSe, CdTe. Similarities among the phase diagram and of the sequence of polymorphic structures might be expected in these compounds. The room temperature transition pressure of CdSe and CdTe is 25 and 34 kb, respectively.[34] Although the temperature dependence of the solid-solid boundaries of CdSe and CdTe has not yet been determined, it should be similar to that of CdS.

Table 5   The slope of the solid-solid boundary

Substance	$(dP/dT) \times 10^3$ (kb/deg)
CdS	-13*
InSb	-12**
Ge	-30***

*)   Present work
**)   See ref. 35)
***)   See ref. 36)

In Table 5 the slope of the solid-solid boundary of CdS is compared with those of Group IV element Ge and Group III–V compound InSb. They all have negative slopes. Kennedy et al.[35] and Bundy[36] have noted a common P, T pattern among Group IV elements and Group III–V compounds. It has also been suggested[37] that the P, T phase diagrams of the elements of the same group of the periodic table are very similar and as the atomic number increases they gradually change. Such

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

37) V. V. Evdokimova, *Usp. Fiz. Nauk*, 88, 93 (1966) [*English transl.: Soviet Phys.—Uspekhi*, 9, 54 (1966)]

common behavior is to be expected because each pair of atoms averages the same number of valence electrons, and these compounds would be expected to assume the quantum-mechanical arrangements characteristic of such a group of electrons.

For Cd-VI compounds, it is expected that the P, T phase diagrams might be common to those of Group IV elements and Group III–V compounds. In general the melts are denser than the solids so that their melting temperature decreases with increase in pressure. Their solid-solid boundaries have negative slopes as described above (Table 5). As CdSe and CdTe have a fusion curve with negative slope,[11] it could be expected that CdS might have a fusion curve with negative slope. On the other hand, the fact that CdS has a solid-solid boundary with negative slope leads to the expectation that CdSe and CdTe might have the same features. The melting line of CdS and the solid-solid boundaries of CdSe and CdTe are to be investigated and the results will be reported in the near future.

The sequence of pressure-induced polymorphic transitions in CdS, CdSe, and CdTe may be, initially, wurtzite or zinc blende; next, the rock salt structure and, at still higher pressures, the cesium chloride structure. The coordination number increases from 4 to 6, and to 8. The metallic behavior will appear either in the rock salt structure or in the cesium chloride structure, or in any other structures. Drickamer and his co-workers have reported the matallic transition in CdTe near 100 kb.[3][4] It has been established[38]–[45] that the I–VII compound AgI transforms near 3 kb at room temperature from the wurtzite or zinc blende structure to the rock salt structure. At about 100 kb AgI transforms from the rock salt structure to the cesium chloride structure.[43]–[45] It is, therefore, reasonable to expect that at higher pressures CdS might transform to the cesium chloride structure with a coordination number of 8.

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