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## KINETICS OF THE POLYMORPHIC TRANSITIONS OF CADMIUM CHALCOGENIDES UNDER HIGH PRESSURE

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The rate of the high pressure transitions of CdS and CdSe from the wurtzite to the rock salt structure and of CdTe from the zinc blende to the rock salt structure was investigated under pressures ranging up to 40kb and temperatures ranging up to 300°C. The rate was followed by measuring the electrical resistance while the sample was under high pressure in a compact cubic anvil device.

The rate of transitions showed both pressure and temperature dependence. The rate curves showed a rapid initial rise, followed by considerable tail-off. The effect of crystalline size on the transition kinetics was appreciable.

### Introduction

The investigation of the kinetics of polymorphic transition processes in solids might elucidate some structural, chemical and physical properties of solids as follows:

- 1) Both the rate of transitions and the shape of rate curves can give information about the type of transition involved. Buerger<sup>1)</sup> has classified transitions into broad categories; dilatational and reconstructive for transitions of first coordination, and displacive and reconstructive for transitions of secondary coordination. In the displacive transitions, the features of the original configuration are retained and the displacement of atoms due to transition is less than an interatomic distance. The dilatational transition is similar to the displacive one in that it is achieved by very small shifts of atoms. Reconstructive transitions may involve a drastic breakage of bonds and their rearrangement results in an essentially new structure. The transitions tend to proceed rapidly when essentially displacive or dilatational processes are involved, and sluggishly when reconstructive processes are involved.
- 2) The kinetics of transition might explain the influence of a lattice transition on the velocity of

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- 1) M. J. Buerger, "Phase Transformations in Solids", pp. 183~211, ed. by R. Smoluchowski *et al.*, John Wiley & Sons, New York (1951)
- 2) A. J. E. Welch, "Chemistry of the Solid State", Chap. 12, ed. by W. E. Garner, Butterworths, London (1955)
- 3) F. A. Kröger, "The Chemistry of Imperfect Crystals", John Wiley & Sons, New York (1964)
- 4) C. N. R. Rao and K. J. Rao, "Progress in Solid-State Chemistry", Vol. 4, pp. 131~185, ed. by H. Reiss, Pergamon, Oxford (1967)

reactions occurring in the solid state: It has been shown<sup>2)-4)</sup> that certain reactions in the solid state exhibit a pronounced increase of reactivity in the vicinity of the transition point of the reactant.

3) The presence of impurities in the substances shows importance in determining the nature of the kinetics of transitions. There is also the possibility that the rate of transition may be altered by physical characteristics of the sample and its environment. For instance, the effect of crystalline size on the kinetics of a transition may be appreciable. Certain transitions proceed faster when the samples are in the state of fine particle, and others when they are single crystals. Similarly, the surface area may play a role in determining the rate of transition.

In spite of the voluminous literature on the phase equilibria studies under high pressure a few investigations have been reported on the kinetics of phase transitions under high pressure. This type of study was first carried out by Bridgman<sup>5)</sup>, in which various solid-solid transition rates were studied by measuring the rate of the fall or rise of pressure toward the equilibrium lines due to the volume change accompanied by the transitions. In his work the rate increased rapidly as pressure was displaced from the pressure of equilibrium between the phases. The rate of phase transition may be measured with another method. The ideal situation is to obtain *in situ* X-ray patterns while the transition proceeds under pressure. Davis and Adams, using the beryllium pressure vessel, have studied the transitions of  $\text{KNO}_3$ <sup>6)</sup>, calcite  $\rightleftharpoons$  aragonite<sup>7)</sup>, and  $\text{NH}_4\text{I}$  and  $\text{AgI}$ <sup>8)</sup> by the X-ray analysis. If the high pressure phases can be quenched by rapid cooling under pressure, the X-ray diffractometry at atmospheric pressure can be used for the study of the phase transition. Roy and his colleagues have studied the transitions of  $\text{PbO}_2$  (I)  $\rightleftharpoons$   $\text{PbO}_2$  (II)<sup>9)10)</sup> and  $\text{GeO}_2$  (quartz)  $\rightarrow$   $\text{GeO}_2$  (rutile)<sup>11)</sup> by quenching techniques. The rate of the  $\gamma \rightarrow \alpha$  phase transition of  $\text{Fe}_2\text{O}_3$  has been found to increase remarkably with increasing pressure<sup>12)</sup>. Tanaka<sup>13)</sup> has studied the transition kinetics amongst three polymorphs of  $\text{ZnP}_2$  up to 50 kb and 600°C. For metals and semiconductors the electrical resistance measurements are utilized. Such works have been performed on the transitions of  $\text{Yb}$ <sup>14)</sup>,  $\text{InSb}$ <sup>15)</sup>,  $\text{HgTe}$ <sup>16)</sup> and red to black phosphorus<sup>17)</sup>, and the order-disorder transformation in  $\text{Cu}_3\text{Au}$ <sup>18)</sup>. The progress of the orthorhombic to cubic transition in TII was followed by monitoring the change in sample capacitance<sup>19)</sup>. The austenite to pearlite

5) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **52**, 57 (1916)

6) B. L. Davis and L. H. Adams, *Z. Krist.*, **117**, 399 (1962); *J. Phys. Chem. Solids*, **24**, 787 (1963)

7) B. L. Davis and L. H. Adams, *J. Geophys. Res.*, **70**, 433 (1965)

8) B. L. Davis and L. H. Adams, *Amer. J. Sci.*, **263**, 359 (1965)

9) F. Datchile and R. Roy, "Reactivity of Solids", pp. 502~511, ed. by J. de Boer, Elsevier, Amsterdam (1961)

10) F. Datchile and R. Roy, *J. Geol.*, **72**, 243 (1964)

11) R. J. Zeto and R. Roy, "Reactivity of Solids", pp. 803~815, ed. by J. W. Mitchell *et al.*, Wiley-Interscience, New York (1969)

12) Y. Goto, *Japanese J. Appl. Phys.*, **3**, 739 (1964)

13) Y. Tanaka, *This Journal*, **38**, 151 (1968)

14) H. T. Hall and L. Merrill, *Inorg. Chem.*, **2**, 618 (1964)

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

16) A. Lacam, B. A. Lombos and B. Vodar, *Phys. Earth Planet. Interiors*, **3**, 511 (1970)

17) I. Sorgato, G. B. Guarise and A. Marani, *High Temperatures — High Pressures*, **2**, 105 (1970)

18) M. C. Franzblau and R. B. Gordon, *J. Appl. Phys.*, **38**, 103 (1967)

19) G. A. Samara, L. C. Walters and D. A. Northrop, *J. Phys. Chem. Solids*, **28**, 1875 (1967)

## Kinetics of the Polymorphic Transitions of Cadmium Chalcogenides under High Pressure 3

transformation was studied by metallographic method and others after the pressure treatment of the specimens<sup>20</sup>). The kinetics of the transformation of graphite to diamond and the graphitization of diamond have been studied extensively<sup>21</sup>).

It has been pointed out in some studies cited above that the inhomogeneity of pressure inherent in the pressure chamber gives the results that are difficult to be treated analytically. The effect of shearing stresses upon transition rates has also been reported<sup>9,10</sup>). Increase in the rates of transitions of two or three orders of magnitude can be attained with the displacive shear.

The present investigation was undertaken in order to elucidate the kinetics of the high pressure transitions of cadmium chalcogenides whose phase equilibria studies have been reported earlier by the author<sup>22)~24</sup>). No quantitative investigations on the kinetics of the phase transitions of cadmium chalcogenides have been reported. The progress of transitions was followed by electrical resistance in a compact cubic anvil device, in which quasi-hydrostatic pressure was obtained. The transitions in cadmium chalcogenides are accompanied by a large resistance drop. In the present work, attention was directed to the following items in order to obtain any reproducible data; (a) samples of high purity were used, (b) high pressure devices and sample assembly were carefully set up in the identical, and precisely controlled conditions at the initial stage of every experiment.

## Experimentals

## Materials

The experiments were carried out with pure single crystal and powder samples. Table 1 summarizes materials, purities and sources. The single crystals used were the same as those used in the phase equilibria<sup>22)~24</sup>) and electrical<sup>25</sup>) studies. The particle sizes of the powder samples were  $\sim 2 \mu$ ,

Table 1 Description of samples

Sample	Purity (%)	Source	
CdS	S	99.999	Matsushita Elec. Co.
	P	99	Yamada Chem. Co.
CdSe	S	99.999	Eagle-Picher Co.
	P	99.99	Yokozawa Chem. Co.
CdTe	S	99.999	Matsushita Elec. Co.
	P	99.995	Sakai Chem. Co.

S: single crystal, P: powder

- 20) J. E. Hilliard and J. W. Cahn, "Progress in Very High Pressure Research", pp. 104~125, ed. by F. P. Bundy *et al.*, John Wiley & Sons, New York (1960)
- 21) For example, F. P. Bundy, "Reactivity of Solids", pp. 817~826, ed. by J. W. Mitchell *et al.*, Wiley-Interscience, New York (1969)
- 22) J. Osugi, K. Shimizu, T. Nakamura and A. Onodera, *This Journal*, **36**, 59 (1966)
- 23) A. Onodera, *ibid.*, **39**, 65 (1969)
- 24) A. Onodera, *ibid.*, **39**, 78 (1969)
- 25) J. Osugi, K. Shimizu, T. Nakamura and A. Onodera, *ibid.*, **36**, 74 (1966)

$\sim 10 \mu$  and  $\sim 20 \mu$  for CdS, CdSe and CdTe, respectively.

#### Apparatus

All the high-pressure and high-temperature measurements were performed in a compact cubic anvil apparatus whose use and calibration were described in detail earlier<sup>26)</sup>. The anvils made of tungsten carbide in 10 mm square face were driven together simultaneously on a pyrophyllite cube having an edge length of 13 mm. Teflon sheets were in place between the bases of the anvils and the guide blocks to improve lubrication and to provide electrical insulation. The anvils were insulated from each other by the extruded pyrophyllite gasket. The pressure values in the cubic press were calibrated at room temperature by measuring sharp resistance change in the strip samples of Bi, Tl and Ba on the pressure increase scale. The values of transition pressure, 25.4 kb for Bi<sub>I-II</sub>, 36.7 kb for Tl<sub>I-II</sub>, 55 kb for Ba<sub>I-II</sub>, and 77 kb for Bi<sub>III-V</sub> were adopted as the fixed calibration points following the recommendation of Lloyed *et al.*<sup>27)</sup>.

The pyrophyllite cube contained a 6 mm-diameter graphite heater with copper electric leads, inside of which was placed a 4 mm cylinder of pyrophyllite which served to transmit pressure to the 2 mm cylindrical sample. Platinum foil leads were in contact with the faces of two of the six anvils. Electric power was supplied to the graphite heater through copper leads which were made in contact with the faces of two of the remaining four anvils. The regulation of the increase and decrease of temperature of the heater was done manually.

Temperatures were measured with the chromel-alumel thermocouple. Before their use, the thermocouples were calibrated against the melting points of tin, lead and zinc. Thermocouple leads from the hot junction were brought out between the anvils through extruded pyrophyllite gaskets. The corrections of the measured temperatures for the effect of pressure on the thermocouple were made in accordance with the results reported by Hanneman and Strong<sup>28)</sup>. Temperature control was within  $\pm 2^\circ\text{C}$ .

In order to obtain good reproducibility of the pressure generation, the following manipulations were conducted. 1) The stucked pyrophyllite after experiments was scraped off from the anvil faces before each experiment, 2) the pressure at the initial attachment of the anvils to the pyrophyllite cube was carefully controlled and applied slightly at the fixed value, 3) the fabricated components of the sample assembly were used from the same pyrophyllite block and 4) Teflon sheets were newly replaced in each experiment.

#### Procedure

Electrical resistance change at the transitions was used to follow the rate. The electrical resistance was either recorded automatically with the strip-chart recorder, operating at a definite rate, or directly observed. The kinetic time was started with the beginning of the resistance drop.

The experiments were of three types:

- 1) The single crystal samples were kept at constant temperatures of 100, 200 and 300°C. The pressure

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

27) "Accurate Characterization of the High-Pressure Environment", ed. by E. C. Lloyed *et al.*, NBS Spec. Pub. 326 (1971)

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

was raised to the desired values in the stable region of the higher pressure phases and the rates were recorded.

- 2) Pressure on the single crystal samples was increased at room temperature and then the samples were kept under pressures considerably below the room temperature transition pressures. Then temperature was abruptly raised across the phase boundaries and the rates were recorded at a fixed temperature.
- 3) The experiments at room temperature were performed on the single crystal and the powder samples.

Each rate curve was the result of an individual run.

Fig. 1 shows the solid-solid phase boundaries of cadmium chalcogenides reported in the previous papers<sup>22)~24)</sup>. The low-pressure phases are of the wurtzite structure for CdS and CdSe, and the zinc blende structure for CdTe. The high-pressure phases are of the rock salt structure.

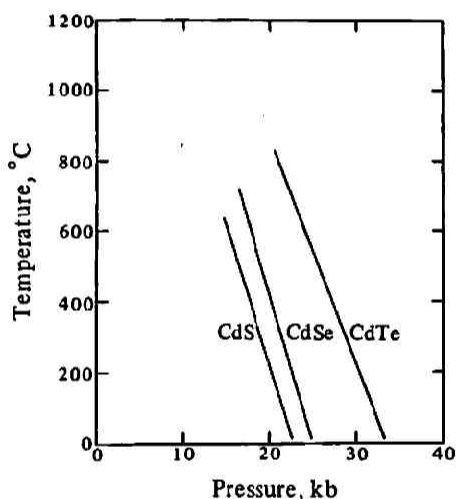


Fig. 1 Solid-solid phase boundaries of cadmium chalcogenides

## Results

### Kinetic data

Preliminary measurements were made at room temperature. The single crystal samples were held for 48 hr at 50 kb for CdS and CdSe, or at 60 kb for CdTe, which were enough above the transition pressures. Fig. 2 (a) shows the electrical resistance changes with pressure increase. At the transitions the electrical resistance dropped by several orders of magnitude. In Fig. 2 (b) the electrical resistance behavior after the transitions were recorded for 48 hr. The points A, B and C correspond with A', B' and C'. The electrical resistance remained unchanged or decreased slightly while the pressure was kept constant for 48 hr. It shows that the drops in the electrical resistance of several orders of magnitude at the transition of these materials are due to the changes of electronic configurations accompanied by the crystallographical changes, and not due to the grain boundary conduction.

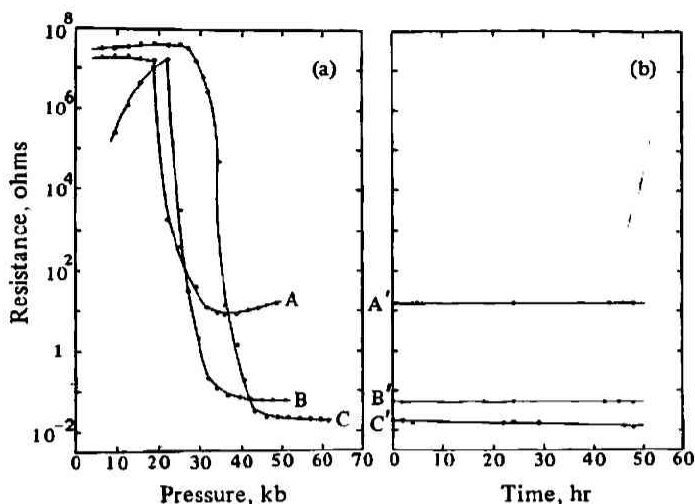


Fig. 2 Resistance change with pressure (a) and with time while the pressure was kept constant for 48 hr (b)

○: CdS, ●: CdSe, ◐: CdTe

Figs. 3 and 4 show typical experimental data on the pressure and temperature induced transitions, respectively. As can be seen from Figs. 3 and 4, the low-pressure/temperature to high-pressure/temperature phase transitions in cadmium chalcogenides are indicated by considerable decreases in electrical resistance. If the pressure or the temperature at which the transition was observed to start was kept constant, a decrease in resistance was initiated, which did not indicate a full transition. This could be achieved if the pressure or temperature was increased further.

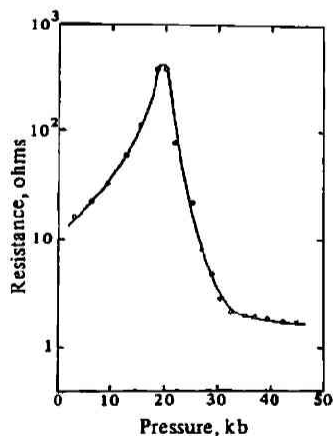


Fig. 3 Typical experimental data showing the pressure induced transition

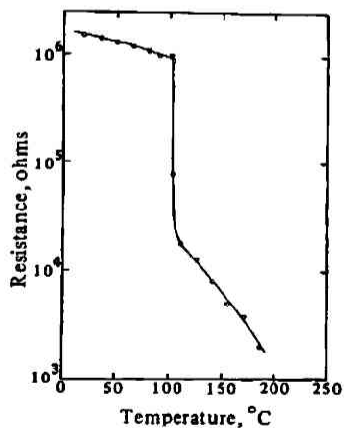


Fig. 4 Typical experimental data showing the temperature induced transition

Making the assumption that the fraction of the materials transformed to the high pressure form,  $\alpha$ , is proportional to the change in resistance, the untransformed fraction,  $(1-\alpha)$ , is represented in equation (1).

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$$1 - \alpha = \frac{R - R_H}{R_L - R_H} \quad (1)$$

where  $R_L$  and  $R_H$  are the resistances of low- and high-pressure phases, respectively, and  $R$  is the resistance at finite time during the transition. Since  $R_L \gg R_H$ ,

$$1 - \alpha \approx \frac{R}{R_L} \quad (2)$$

The results of the various experiments on single crystals are shown in Figs. 5 to 10. The ordinate gives the fraction of the transition. Figs. 5 to 7 show the influence of pressure on the transition kinetics

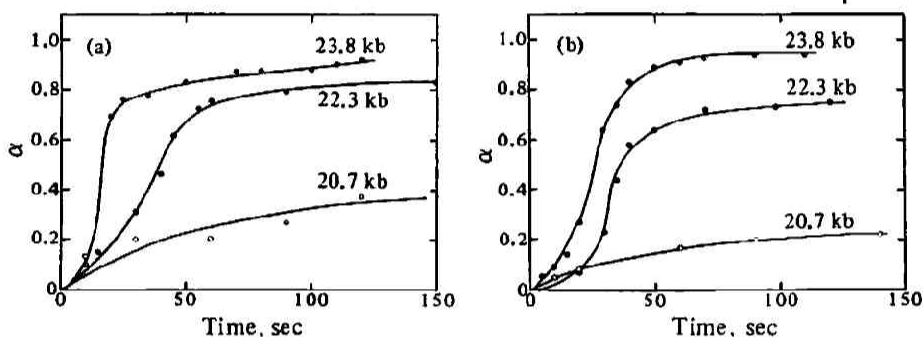


Fig. 5 Observed rates of transition for CdS single crystal (a) 100°C, (b) 200°C

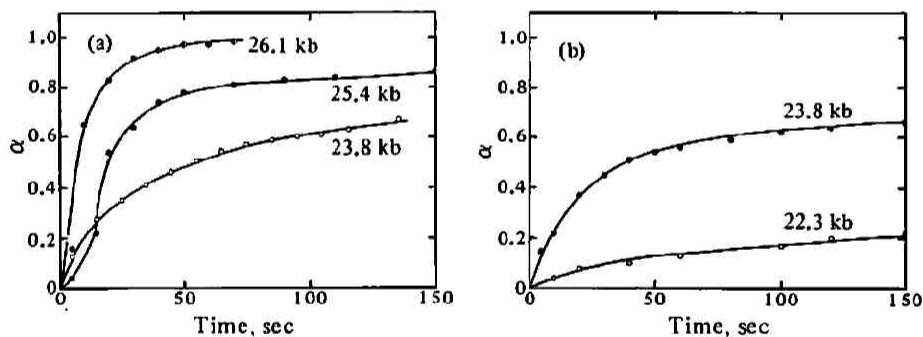


Fig. 6 Observed rates of transition for CdSe single crystal (a) 200°C, (b) 300°C

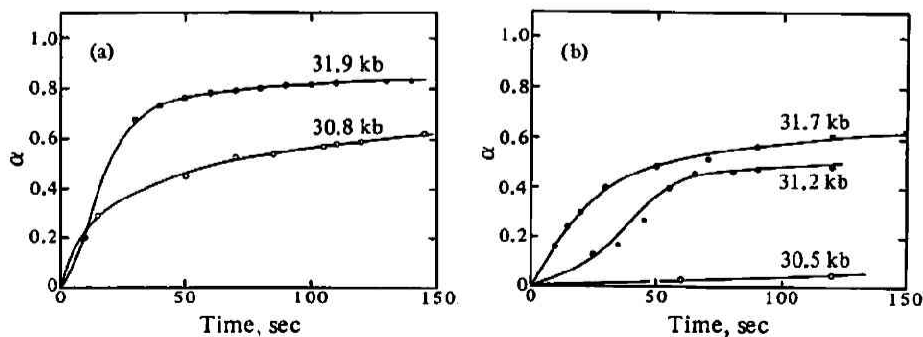


Fig. 7 Observed rates of transition for CdTe single crystal (a) 200°C, (b) 300°C

at constant temperature. All of the rate curves are non-linear. The noticeable feature of these isothermal rate curves is the steep rise in the early stages of the transition, followed by a marked tail-off before the completion of the process. The amount of transformed fraction remains constant over the tail-off. To increase the amount of fraction transformed, the pressure must be increased. It is apparent that the amount of the material transformed depends upon the amount of the excess of the pressure. For the latter part of the transitions, the transition rate appears to be either invariant or slightly decreased with pressure. In these rate curves the induction period ranges from zero to noticeable time. With the solid-media cell, it is conceivable that the pressure would be transmitted to the sample with appreciable time lag. The induction period observed may be attributed to the transition mechanism involved and/or the time delay for pressure transmission.

The influence of temperature on the transition kinetics is represented in Figs. 8 to 10. In several cases of experiments, it was difficult to determine the commencement of the transition because of the conversion that occurred during the heat-up time. The isobaric rate curves for CdS resemble to those of isothermal runs (Figs. 5 to 7). On the other hand, the isobaric rate curves for CdSe and CdTe are somewhat different. It may partly be due to the small increment of the temperature adopted. A larger increment of temperature might introduce the rate behavior similar to that in the case of CdS.

The results on the powder samples at room temperature, together with those on single crystals,

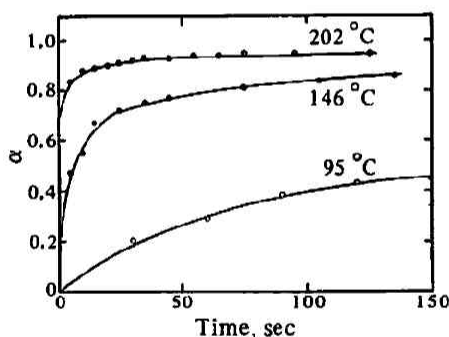


Fig. 8 Observed rates of transition for CdS single crystal at 22.3 kb

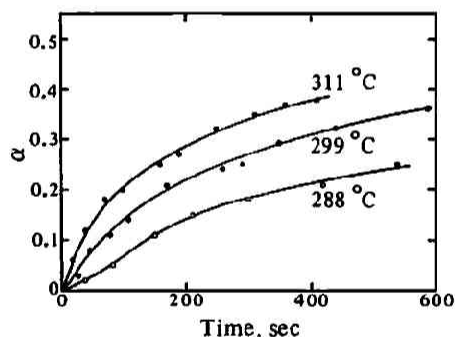


Fig. 9 Observed rates of transition for CdSe single crystal at 20.7 kb

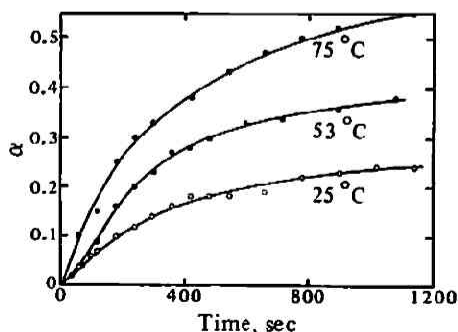


Fig. 10 Observed rates of transition for CdTe single crystal at 31.9 kb



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are shown in Figs. 11 to 13. The transitions of single crystals of CdS and CdSe are very rapid with almost complete conversion within 1 min. In Fig. 13, the difference in the rate of transition between the single crystal and the powder samples of CdTe is also appreciable. In CdTe, however, the powder sample can give the rate curve which is higher than the single crystal.

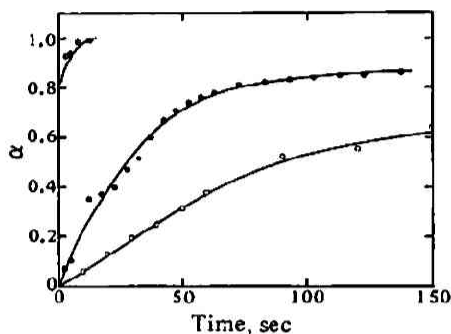


Fig. 11 Observed rates of transition for CdS at room temperature  
 ○: Powder at 38.8 kb,  
 ●: Powder at 40.7 kb,  
 ▲: Single crystal at 22.5 kb

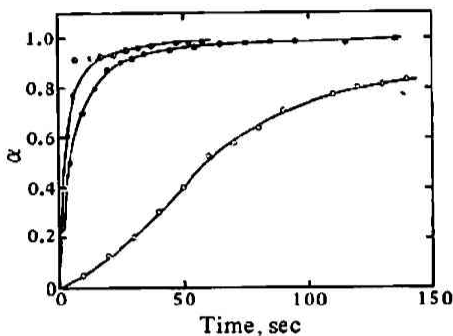


Fig. 12 Observed rates of transition for CdSe at room temperature  
 ○: Powder at 29.5 kb,  
 ●: Powder at 30.9 kb,  
 ▲: Single crystal at 24.7 kb

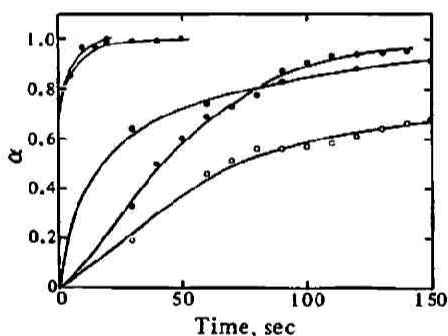


Fig. 13 Observed rates of transition for CdTe at room temperature  
 ○: Powder at 32.3 kb,  
 ⊙: Powder at 34.2 kb,  
 ●: Powder at 35.2 kb,  
 ▲: Single crystal at 32.3 kb,  
 ▴: Single crystal at 33.3 kb

#### Effect of crystalline size

Experiments were also made in order to investigate the influence of the size of crystallites on the transition velocity. For CdS, the measurements on the single crystal, the pressurized and the powder samples were performed. The measurement on the pressurized sample was made in the course of repeated pressurizing to the single crystal sample. The results are shown in Fig. 14. It is apparent that the rate of the transition is low in the small crystalline samples. For CdSe, the rate of the coarse-grained particles were measured. The average diameters of the classified particles were measured by means of an electron microscope. Fig. 15 clearly indicates that larger particle size favors the transition in CdSe. In Fig. 16 are shown the results on the coarse-grained particles of CdTe. The noticeable features of the results are that the smaller particle size favors the transition in CdTe.

#### Reverse transition

The CdS sample starting from the wurtzite form was kept under pressure high enough to keep

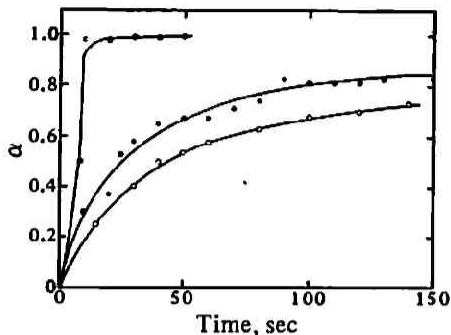


Fig. 14 Effect of crystalline size on the rates of transition of CdS

- : Powder at 37.8 kb,
- : Once-pressurized at 29.5 kb,
- : Single crystal at 22.5 kb

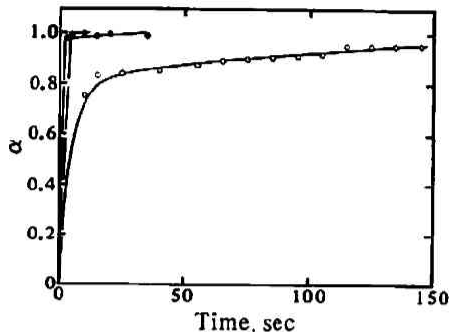


Fig. 15 Observed rates of transition for coarse-grained crystals of CdSe

- :  $\sim 100 \mu$  (27.7 kb),
- :  $\sim 300 \mu$  (25.8 kb),
- :  $\sim 500 \mu$  (24.7 kb)

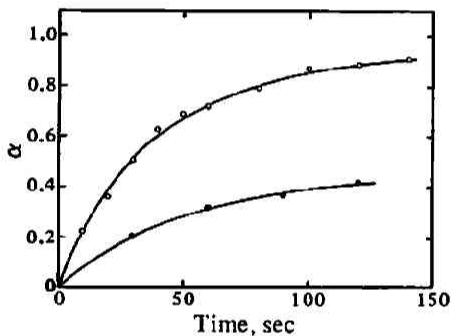


Fig. 16 Observed rates of transition for coarse-grained crystals of CdTe

- :  $\sim 150 \mu$  (33.3 kb),
- :  $\sim 600 \mu$  (33.3 kb)

in the stable region of the rock salt structure while the temperature was raised to the desired value. The pressure was then dropped to the desired value. Fig. 17 shows the results of the transition of CdS from the rock salt to the wurtzite phase observed at 13.7 kb and 25°C and 100°C. The shape of the rate curves is essentially the same as that of forward transitions.

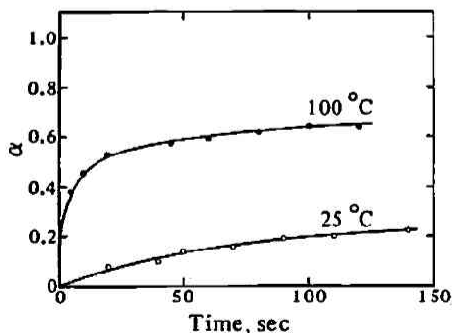


Fig. 17 Observed rates of reverse transition of CdS at 13.7 kb

**Kinetic analysis**

A larger number of rate curves in the present study are reminiscent of the rate curves of thermal

decomposition of solids in which the initial induction period is either very small or virtually absent<sup>29)</sup>. Such a situation suggests a high nucleation rate at least in the early stages of conversion.

Attempts were made to fit the results to a large number of kinetic laws as discussed below. The rate of transition has been theoretically treated by Avrami<sup>30)</sup> and developed by several authors, and his equation has been applied to explain the phenomena in the transition of several substances. The Avrami equation represented in equation (3)

$$1 - \alpha = \exp(-at^b), \quad (3)$$

where  $a$  and  $b$  are the constants, did not hold after the tail-off of the rate curves in the present work.

Attempts to interpret the results in terms of models based on boundary-controlled, diffusion-controlled, or nucleation-controlled processes, and also in terms of the formal first-order kinetics were unsuccessful. Prout-Tompkins' equation, which represents well thermal decomposition of solids did not comply with the present data. Other rate laws, such as based on recrystallization or precipitation, were not applicable to the kinetic data.

The second-order rate law was found to be compatible with the data virtually over the entire range of pressure and temperature. Figs. 18 and 19 show the second-order plots of  $1/(1-\alpha)$  against time.

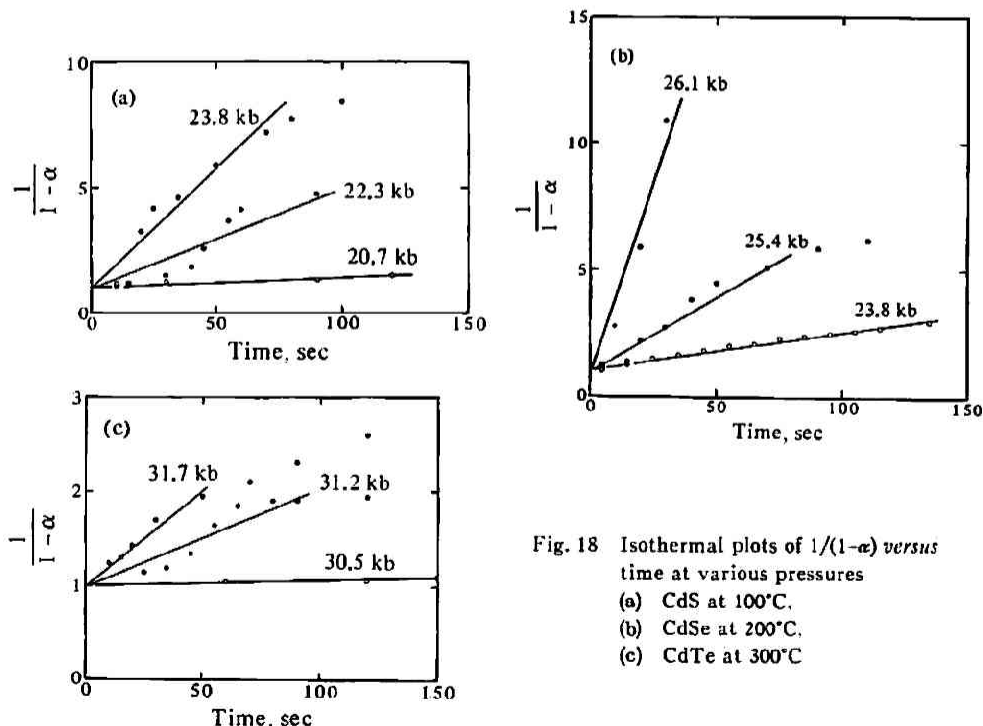


Fig. 18 Isothermal plots of  $1/(1-\alpha)$  versus time at various pressures  
 (a) CdS at 100°C.  
 (b) CdSe at 200°C.  
 (c) CdTe at 300°C

29) P. W. M. Jacobs and F. C. Tompkins, in Ref. 2, Chap. 7

30) M. Avrami. *J. Chem. Phys.*, **7**, 1103 (1939); **8**, 212 (1940); **9**, 177 (1941)

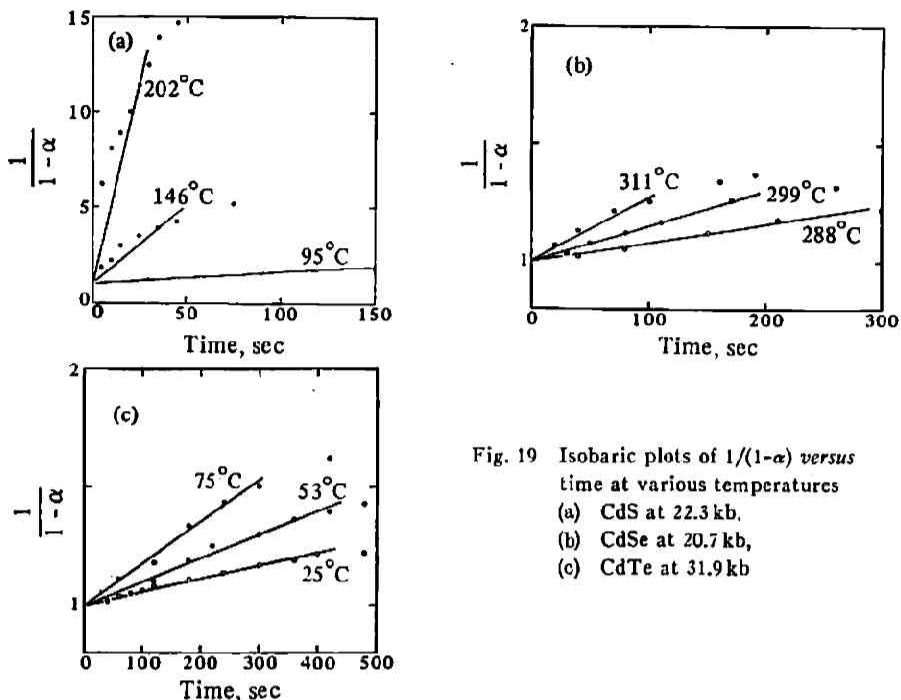


Fig. 19 Isobaric plots of  $1/(1-\alpha)$  versus time at various temperatures  
 (a) CdS at 22.3 kb,  
 (b) CdSe at 20.7 kb,  
 (c) CdTe at 31.9 kb

From the slopes the rate constants  $k$  in the following expression are obtained,

$$\frac{1}{1-\alpha} = 1 + kt. \quad (4)$$

The apparent activation volumes  $\Delta V^*$  are estimated from the following relation on the basis of the transition state theory of reaction rates<sup>31)</sup>

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^*}{RT}. \quad (5)$$

Fig. 20 gives a typical example showing the dependence of  $\log k$  on pressure. Table 2 summarizes the values of the apparent activation volume.

Since

$$\left(\frac{\partial \ln k}{\partial T}\right)_P = \frac{E_a}{RT^2}, \quad (6)$$

the apparent activation energies  $E_a$  are estimated from the Arrhenius plots of  $\log k$  against  $1/T$ . Fig. 21 shows typical examples of the plots of  $\log k$  against  $1/T$ . In Table 3, the results are listed together with the values from the literature.

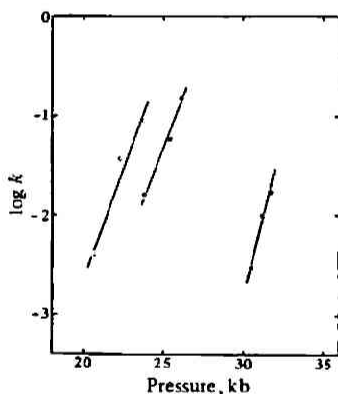
The activation entropy can be calculated from the following equation,

31) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 31, 875 (1935)

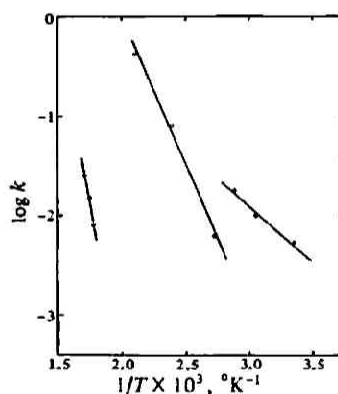
Table 2 Apparent activation volumes

Substance	Temperature (°C)	$\Delta V^*$ (cc/mole)	Reference
CdS	100	-26	Present work
	200	-36	
CdSe	200	-24	Present work
	300	-31	
CdTe	200	-35	Present work
	300	-38	
GeO <sub>2</sub>		-15~-25	11
HgTe		-126	16
Yb		-17~-31	14
P (red→black)	179	-13.8	17
	433	-15.2	

$$\left\{ \frac{\partial T \ln(k/T)}{\partial T} \right\}_P = \frac{\Delta S^*}{R} + \ln \frac{k}{h}, \quad (7)$$

Fig. 20 Plots of  $\log k$  versus pressure

- : CdS at 100°C,
- : CdSe at 200°C,
- ◐: CdTe at 300°C

Fig. 21 Plots of  $\log k$  versus  $1/T$ 

- : CdS at 22.3 kb,
- : CdSe at 20.7 kb,
- ◐: CdTe at 31.9 kb

where  $k$  and  $h$  are the Boltzmann and the Planck constants, respectively,  $R$  is the gas constant and  $\Delta S^*$  is the activation entropy. The values of  $\Delta S^*$  are shown in Table 4.

### Considerations

#### Mechanisms of transitions

Solid-state transitions generally proceed by a process of the formation of new domains of the

Table 3 Apparent activation energies

Substance	Pressure (kb)	$E_a$ (kcal/mole)	Reference
CdS	19.0	42	Present work
	22.3	14	
	13.7†	11†	
CdSe	20.7	32	Present work
	23.8	12	
CdTe	28.3	9	Present work
	31.9	5	
PbO <sub>2</sub>		3.5	10
GeO <sub>2</sub>	15.7~25.5	29±9	11
InSb	I→II	100	15
	II→I	50	
P (red→black)	20	40.1	17
	60	23.4	

† Reverse transition

Table 4 Apparent activation entropies

Substance	Pressure (kb)	$\Delta S^*$ (e. u.)	Reference
CdS	19.0	-11	Present work
	22.3	-34	
CdSe	20.7	-15	Present work
	23.8	-38	
CdTe	28.3	-64	Present work
	31.9	-54	
P (red→black)	20	-16.0	17
	60	-20.1	

product referred to as nucleation and the advancement of the new phase boundaries termed growth. The growth of the new phase may occur according to a diffusion-like mechanism or a distortion mechanism<sup>32)</sup>. In the latter, the growth occurs by the motion of a coherent or semicoherent interface between the two phases, and thus the process is characterized to be diffusionless. In this case the transition is called martensitic. Avrami<sup>30)</sup> derived the expression for the rates of transition in terms of the rates of nucleation and growth (eq. (3)). Later, Johnson and Mehl<sup>33)</sup>, Erofeev<sup>34)</sup>, and Allnatt

32) M. E. Fine, "Introduction to Phase Transformations in Condensed Systems", MacMillan, New York (1965)

33) W. A. Johnson and R. T. Mehl, *Trans. A. I. M. E.*, **135**, 416 (1939)

34) B. V. Erofeev, *Dokl. Akad. Nauk SSSR*, **52**, 515 (1940)

and Jacobs<sup>35)</sup> have derived the modified equations. These authors were successful in theoretically reproducing the sigmoid curves which were found experimentally for many solid-state reactions.

There are three general possibilities for the rate controlling step in the transitions of these cadmium chalcogenides: (1) nucleation, (2) diffusionless-growth and (3) diffusional growth. Edwards and Drickamer<sup>36)</sup> have proposed that the high pressure transitions of CdS and CdSe are of diffusional type. Jayaraman, Klement and Kennedy<sup>37)</sup> also concluded that the high pressure transitions in cadmium chalcogenides are clearly diffusion controlled. For CdS, Samara and Giardini<sup>38)</sup> proposed the kinetic process, the controlling step being either the formation of nucleation sites or the crystal growth. They excluded the bulk diffusion since the transition of CdS was completed under shock wave conditions within  $10^{-6}$  sec<sup>39)</sup>, the time scale being too short for the bulk diffusion to take place. Their remarks were consistent with the observation of the progress of the transition by an optical microscopy. All the works described above are only qualitative. Rooymans<sup>40)</sup> has noticed that the possibility of martensite processes based on some kind of nucleation, and not controlled by diffusion, must also be taken into consideration as other II-VI, III-V compounds and IV elements.

In the present work the following obvious features of rate curves and kinetic data are obtained.

1) A greater number of rate curves are not sigmoidal. Only in a few examples an induction period of noticeable amount was observed. As noted above, this is indicative of a high nucleation rate, at least in the early stages of transition.

2) As shown in Table 3, the apparent activation energies for the transitions in cadmium chalcogenides decrease with pressure. Since the activation energies for diffusion processes are, generally, either increased (for vacancy diffusion) or are relatively unaltered (for interstitial diffusion) with pressure, it is conceivable that the diffusional type mechanism would be ruled out. In addition, the activation energies for diffusion of cadmium or chalcogens in cadmium chalcogenides at or near atmospheric pressure are as follows: 46 kcal/mole for Cd in CdS<sup>41)</sup>, 36~51 kcal/mole for Se in CdSe<sup>42)</sup>, and 32~62 kcal/mole for Cd and Te in CdTe<sup>43)</sup>. These values are already larger than those in Table 3, respectively. Since the values of activation energy for diffusion increase or remain unchanged with pressure, as noted above, the activation energies for diffusion of cadmium or chalcogens in cadmium chalcogenides under pressure may become well larger than those in Table 3, respectively. The activation energies for the rate controlling step in the transitions of cadmium chalcogenides are, therefore, below the activation energies for diffusion, again indicative of the preclusion of the diffusional mechanism.

3) Equation (4) can be interpreted as a special case of the treatment given by Avrami<sup>30)</sup> and

35) A. R. Allnatt and P. W. M. Jacobs, *Canad. J. Chem.*, **46**, 111 (1968)

36) A. L. Edwards and H. G. Drickamer, *Phys. Rev.*, **122**, 1149 (1961)

37) A. Jayaraman, W. Klement, Jr. and G. C. Kennedy, *ibid.*, **130**, 2277 (1963)

38) G. A. Samara and A. A. Giardini, *ibid.*, **140**, A388 (1965)

39) J. D. Kennedy and W. B. Benedick, *J. Phys. Chem. Solids*, **27**, 125 (1966)

40) C. J. M. Rooymans, *Philips Res. Repts, Suppl.*, 1968, No. 5

41) H. H. Woodbury, *Phys. Rev.*, **143**, A492 (1964)

42) P. M. Borsenberger and D. A. Stevenson, *J. Phys. Chem. Solids*, **29**, 1277 (1968)

43) H. H. Woodbury and R. B. Hall, *Phys. Rev.*, **157**, 641 (1967)

formulated by Honig *et al.*<sup>44)</sup>. In the treatment allowance is made for the ingestion of potential growth nuclei into an advancing phase which originated from other growth nuclei. The new phase is nucleated by germ nuclei. The following assumption must be introduced: (a) the rate of the growth of the new phase is constant, (b) the rate of generation of active growth nuclei is constant, (c) there exists a random distribution of the active centers, (d) the exhaustion of the germ nuclei does not occur prior to complete conversion, (e) the growth of the new phase is linear. These conditions may be considered to be satisfied in the transition under pressure. Then, Honig *et al.* obtained the expression,

$$\frac{1}{1-\alpha} = 1 + \sigma GN_0 t, \quad (8)$$

where  $(1-\alpha)$  represents the fraction untransformed,  $\sigma$  is a shape factor,  $G$  is the linear growth rate of the new phase,  $N_0$  is the initial density of germ nuclei, and  $t$  is the time. Since the plots of  $1/(1-\alpha)$  versus time yield an intercept of unity (Figs. 18 and 19), equation (8) is recognized as the integrated form (eq. (4)) of the second-order rate law

$$\frac{d\alpha}{dt} = k(1-\alpha)^2. \quad (9)$$

The rate constant is here given by the composite quantity  $\sigma GN_0$ . With  $\sigma$  and  $N_0$  effectively constant, then the dependence of the rate constant on temperature originates with the term  $G$  in the composite rate constant  $\sigma GN_0$ . The observed activation energy, therefore, represents the activation energy for the rate of the growth of the new phase, or, in this case, the progressive movement of the interface.

4) The effect of crystalline size on the rate of transitions in the present study is remarkable. In the coarse-grained or powdered samples a large number of defects may exist. Further, the application of pressure to the sample may cause intergranular abrasion and fracture of grains. The transition initiates at the nucleation sites which are distributed over the surface of, or embedded in the bulk of, the sample. If the nucleation sites were at the surface, these changes of surfaces would facilitate the transition. On the contrary, if the nucleation center must arise in each grain, the transition may be retarded in coarse-grained or powdered samples. The results in the present work are compatible with the latter case in CdS and CdSe.

5) From the data in Table 3 the values of the activation energy extrapolated back to the atmospheric pressure could be roughly obtained:  $\sim 200$  kcal/mole for CdS,  $\sim 170$  kcal/mole for CdSe and  $\sim 50$  kcal/mole for CdTe. The bond energies of these compounds calculated by Manca<sup>45)</sup> are as follows: 85 kcal/mole for Cd-S, 74 kcal/mole for Cd-Se and 68 kcal/mole for Cd-Te. The activation energy for CdTe extrapolated to ambient pressure falls in the neighborhood of the bond energy of Cd-Te, while the values of CdS and CdSe differ widely from their bond energies.

6) The value of the apparent activation energy of CdTe is considerably small compared with those of CdS and CdSe. On the other hand, the absolute value of the apparent activation entropy of CdTe is larger, compared with those of CdS and CdSe.

44) A. W. Czanderna, C. N. R. Rao and J. M. Honig, *Trans. Faraday Soc.*, **54**, 1069 (1958)

45) P. Manca, *J. Phys. Chem. Solids*, **20**, 268 (1961)



From the discussions mentioned above, it would appear that the rate-controlling step in the transitions of the present study may be the diffusionless growth. The activated state of the transition of CdTe may be somewhat different from those of CdS and CdSe. The difference may be attributed to the difference in the structural sequence of the transitions; wurtzite to rock salt structure in CdS and CdSe, and zinc blende to rock salt in CdTe.

#### Activation volume

In Table 5 are shown the molecular volumes of the atmospheric phases and high pressure phases immediately after the transitions of cadmium chalcogenides at room temperature. From the data in Table 2 the values of the activation volume extrapolated to room temperature could be obtained:  $-18$  cc/mole for CdS,  $-12$  cc/mole for CdSe and  $-30$  cc/mole for CdTe. There seems to exist no close correlation between the activation volume and the molecular volume. Since the activation volumes are, in absolute, larger than the difference in molecular volumes of the atmospheric and the high pressure phases, the value of activation volume may have no real meaning.

Table 5 Molecular volumes of cadmium chalcogenides

Substance	Molecular volume (cc)	
	Atmospheric phase	High pressure phase
CdS	30	24
CdSe	33	25
CdTe	41	32

Because of the reasons described below, high precision cannot be attached to the kinetic values of the present study. In eq. (1) it is assumed that a linear relationship exists between the electrical resistance and the fraction transformed from the one phase. This assumption is seriously in error because, first, the resistivity of a mixture of two phases cannot be taken as just the weighted average of the resistivities of two phases, and second, resistivity is sensitive to such factors as particle size, lattice coherency, *etc.* Therefore, the transition rate cannot be precisely related to the actual change of the resistance. Any good approximation, which is not clear at present, is needed.

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