PHYSICAL REVIEW VOLUME 157, NUMBER 3 15 MAY 1967

Effect of Pressure on the Elastic Parameters and Structure of CdS†

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(Received 2 December 1966)

The effective elastic constants of CdS have been measured by the ultrasonic pulse-echo method as a function of hydrostatic pressure to 4 kbar. The logarithmic pressure derivatives determined were $d\ln C_{11}/dP=3.56$, $d\ln C_{33}/dP=3.44$, $d\ln C_{13}/dP=10.0$, $d\ln C_{44}/dP=-4.22$, $d\ln C_{66}/dP=-4.97$ (in Mbar^{-1}). A continuous-deformation model of the wurtzite-to-rocksalt pressure-induced transformation in CdS is presented. A combination of elastic constants characteristic of this deformation is derived and the transformation discussed in terms of a microscopic shear mechanism based on these results.

INTRODUCTION

THIS paper proposes a mechanism for the well-known pressure-induced structural transformation in CdS based on the possibility of microscopic instabilities in the wurtzite structure developing under high applied stresses. The ability of a material to resist a given deformation is a direct function of the elastic parameters of the material, and the measurements reported in this paper were undertaken to determine how these parameters (and hence the structural stability) are affected by external pressures.

The mechanism proposed is a continual deformation from the wurtzite structure to the rocksalt structure on a microscopic scale which propagates throughout the crystal when initiated at points of stress concentration. The required deformation of the wurtzite structure into the rocksalt structure is described, and an elastic constant C_t characteristic of this deformation is developed. The data reported in the experimental section show the pressure derivative of this characteristic elastic constant C_t to be negative, indicating that with increasing pressure the wurtzite structure becomes less stable with respect to this type of deformation.

EXPERIMENTS AND RESULTS

The sound velocities used to determine the effective elastic constants of CdS were measured by the ultrasonic pulse-echo method. The techniques of ultrasonic pulse-echo experiments are well known,[1] and the details pertinent to this experiment are as follows. A 10-Mc pulse, approximately 1 μsec in duration from a gated oscillator, was used to activate the quartz transducer. This pulse and the subsequent echos were displayed on one trace of a dual trace oscilloscope. A timing comb and a 10-Mc wave from a time mark generator were displayed on the other trace to calibrate the oscilloscope screen. Photographic records of the traces were made and the transit-time measurements taken from these photographic records with the aid of a telereader. By this method the time positions of the cycles within the pulses were determined to better than $\pm 5\times 10^{-9}$ sec.

It can be shown[2] that for low-resistivity crystals, the piezoelectric coupling may be ignored and the sound velocities directly correlated to the elastic constants. The crystals used in these experiments were purchased from Harshaw Chemical Company and had dark resistivities of less than 1 Ω-cm. The crystals were in the form of right parallelepipeds (1 cm×1 cm×2 cm) with the square faces of the crystals oriented at 0°, 90°, and 45° from the crystallographic *c* axis. The crystals were denoted as crystal *A*, crystal *B*, and crystal *C*, respectively, and the orientations substantiated by x-ray analysis to be within ±0.2°. The three orientations permitted eight separate velocity measurements. Cadmium sulfide, being hexagonal, has five independent elastic constants; therefore, the eight velocity measurements provided several internal crosschecks.

The 10-Mc quartz transducers were bonded to the crystals with polyethylene. The pressure experiments were limited to 4 kbar by failures of the polyethylene bonds at higher pressures. Several other bonding materials, including epoxy, were also tried. In all cases the bond failed at pressures less than 5 kbar, and the crystals were eventually destroyed in attempts to obtain data at higher pressures. The pressure apparatus was a simple piston-cylinder device. Prior pressure experiments in this apparatus involving the change in resistance of a manganin wire coil and the solidification of Hg at room temperature (taken to be 12.30 kbar at 23°C) have shown the friction in the apparatus to be small and quite reproducible. The pressure on the sample was calculated from these prior calibrations and the load applied to the piston. The uncertainty introduced by this method of pressure calculation was less than 1% at 4 kbar. The experiments were performed at room temperature (23°C) and data recorded at pressure intervals of approximately $\frac{1}{2}$ kbar.

The effective adiabatic elastic constants C_{ij} and their logarithmic pressure derivatives, $d\ln C_{ij}/dP$, calculated from the velocity measurements of these experiments are listed in Table I. The reduction of the pressure data required the knowledge of several physical parameters. The isothermal compressibility ($k_t=1.625$ Mbar^{-1}) was

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† This work was supported by the U. S. Atomic Energy Commission.

[1] W. B. Daniels and C. S. Smith, in *The Physics and Chemistry of High Pressures* (Society of the Chemical Industry, London, 1963), p. 50.

[2] A. R. Hutson and D. L. White, J. Appl. Phys. 33, 40 (1962).

TABLE I. The adiabatic elastic constants of CdS, and their logarithmic pressure derivatives at 23°C. The acoustic waves were propagated parallel to, perpendicular to, and at 45° from the crystallographic c axis for the crystals A, B, and C, respectively.

Crystal	Type of wave	Wave velocity in m/sec	Related constant	Value of elastic constant calculated C_{ij} in Mbar				Pressure Derivative $d\ \ln C_{ij}/dp$ in Mbar^{-1}
				Jaffe[a]	Bolef[b]	McSkimin[c]	Present study	
A	Longitudinal	4408	C_{33}	0.938	0.9397	0.9370	0.9361	$+3.44$
B	Longitudinal	4216	C_{11}	0.907	0.8432	0.8581	0.8565	$+3.56$
C	Longitudinal	4146	C_{13}	0.510	0.4638	0.4615	0.4616	$+9.92$
A	Transverse	1756	C_{44}	0.1504	0.1489	0.1487	0.1487	-4.28
B	Transverse	1756	C_{44}	0.1504	0.1489	0.1487	0.1486	-4.16
B	Transverse	1835	C_{66}	0.1630	0.1610	0.1623	0.1622	-4.97
C	Transverse	2122	C_{13}	0.510	0.4638	0.4615	0.4612	$+10.10$
C	Transverse	1794	$\frac{1}{2}(C_{66}+C_{44})$	···	···	···	···	$-4.65(\rho v^2)$

[a] H. Jaffe, D. Berlincourt, H. Krueger, and L. Shiozawa, in Proceedings of the Fourteenth Annual Symposium on Frequency Control, 1960 (unpublished).
[b] D. I. Bolef, N. T. Melamed, and M. Menes, Westinghouse Research Labs. Scientific Paper No. 6-40301-1-P5 (unpublished). Also, Bull. Am. Phys. Soc. **5**, 169 (1960).
[c] H. J. McSkimin, T. B. Bateman, and A. R. Hutson, J. Acoust. Soc. Am. **33**, 856 (1961).

calculated from the room-pressure measurements using the thermal expansivity data of Jost and Shiozawa[3]

$$(\beta=11.02\times10^{-6}/°\mathrm{C},\ \beta_a=4.25\times10^{-6}/°\mathrm{C},\ \beta_b=2.50\times10^{-6}/°\mathrm{C})$$

and assuming[4] c_p to be 4 cal/mole-g°C. The isothermal changes in length $(1/L)(dL/dP)$ and in orientation $d\theta/dP$ of the crystals as a function of pressure were calculated in a similar manner.

$$(1/L)(dL/dP)=-(0.5441\sin^2\theta+0.5335\cos^2\theta)\ \mathrm{Mbar}^{-1},$$
$$d\theta/dP=0.0106\sin\theta\cos\theta\ \mathrm{Mbar}^{-1}.$$

The effective elastic constants and their pressure derivatives listed in Table I are defined by the acoustic wave equation $C=\rho v^2$. These effective elastic constants may be converted to the elastic constants defined as the derivatives of the internal energy in the manner discussed by Wallace.[5]

DISCUSSION

The above elastic-constant pressure data open the possibility of a pressure-induced shear instability of the wurtzite structure as the mechanism of the transformation in CdS. A rough extrapolation of the data (assuming that $d^2C_{ij}/dP^2=0$) suggests that a macroscopic shear instability ($C_{ij}\rightarrow 0$) would occur at pressures greater than 200 kbar. A shear instability mechanism is consistent with the rapid nature[6] of the transformation, but is inconsistent with the experimental observations of the occurrence of the transformation at pressures (20–25 kbar) an order of magnitude lower than the predicted macroscopic shear instability. The object of the following discussion is to correlate these aspects and suggest a mechanism for the transformation.

The wurtzite structure may be deformed into the rocksalt structure by a combination of a compression along the crystallographic c axis and a shear about this axis. The wurtzite-to-rocksalt phase transformation is depicted in Fig. 1 as it would occur by this type of deformation. The stresses corresponding to this type of deformation are shown as broad arrows acting on the faces of the hexagonal unit cell in Fig. 1(a). In Fig. 1(b) the cell is shown slightly distorted and the logical (spring-model) motions of the atoms with respect to the cell are indicated by the small arrows. In Fig. 1(c), the distortion is completed, and the atoms have become the body-centered tetragonal arrangement of the rocksalt structure. The normal representation of the rocksalt structure, a face-centered cubic arrangement, is indicated by the dashed lines for clarity. The lightly shaded atom in the base of the rocksalt arrangement in Fig. 1(c) would be the atom from the cell directly below corresponding to the atom labeled 2.

By considering the distortion to take place at constant volume, we may calculate the strain energy (per unit volume) associated with small distortions from the wurtzite structure. This calculation follows the procedure suggested by Huntington[7] for c/a variation of hexagonal crystals at constant volume. The second derivative of this strain energy with respect to strain yields a combination of the effective elastic constants characteristic of the distortion. The calculation (see Appendix) of the characteristic elastic constant C_t for the distortion shown in Fig. 1 yields

$$C_t=(C_{11}+C_{33}+3C_{66}-2C_{13})=+1.3564\ \mathrm{Mbar}.$$

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[3] J. M. Jost and L. R. Shiozawa, Clevite Corporation Engineering Memorandum No. 64-28, 1964 (unpublished).

[4] The specific heat of CdS is reported to be in a paper by A. N. Krestovnikov, M. S. Vendrikh, and E. I. Feigina [Sb. Nauchn. Tr., Mosk. Inst. Tsvetn. Metal i Zolota **26**, 233 (1957)]. This paper was not available to the author. The uncertainty in the calculation introduced by a rather large error in c_p is unimportant, therefore the value used was estimated from known values of similar compounds.

[5] D. C. Wallace, Rev. Mod. Phys. **37**, 57 (1965).

[6] During static pressure experiments in which the wurtzite-to-rocksalt structural change in a single-crystal CdS sample is observed by monitoring the resistance of the sample, at the onset of the transition, the resistance will drop several orders of magnitude in less than the reaction time of most recorders.

[7] H. B. Huntington, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 237.

The change in C_t with increasing pressure is

$$\frac{dC_t}{dP}=\frac{dC_{11}}{dP}+\frac{dC_{33}}{dP}+3\frac{dC_{66}}{dP}-2\frac{dC_{13}}{dP}=-5.388,$$

and

$$d\ln C_t/dP=-3.97\ \text{Mbar}^{-1}.$$

A linear extrapolation of this result indicates that the wurtzite phase of CdS would become macroscopically unstable with respect to this type of deformation at approximately 250 kbar. The experimental data do not display any noticeable curvature (i.e., $d^2C_{ij}/dP^2\simeq 0$) that would suggest C_t would approach zero in the 20–25 kbar region. However, the strain-energy calculation of the characteristic elastic constant of the deformation was made assuming the volume remained constant during the deformation. This artificial restriction was imposed to facilitate the calculation. The calculation should include the decrease in volume which undoubtedly occurs concurrently with the deformation. The inclusion of the concurrent decrease in volume should account for part of the discrepancy between the observed and estimated transformation pressure. The decreasing volume would correspond to an increasing pressure and decrease the structure's effective resistance to the deformation.

There is considerable similarity between the wurtzite-rocksalt structural transformation in CdS and the sodium chloride (rocksalt)-cesium chloride structural transformations in the alkali halides. The sodium chloride structure may be deformed into the cesium chloride structure by a compression along the cube diagonal[8] of the structure. A constant-volume strain-energy calculation for this deformation discloses the elastic constant characteristic of this deformation to be C_{44}. Ultrasonic pressure measurements by Reddy and Ruoff[9] have shown that dC_{44}/dP is negative for the compounds which undergo this transformation. Similar to the transformation in CdS, the transformations in the alkali halides are experimentally observed to occur quite rapidly at pressures an order of magnitude lower than the pressures necessary for the macroscopic shear instabilities predicted by extrapolation of the ultrasonic data. Reddy and Ruoff[9] have performed ultrasonic measurements on RbBr at pressures sufficient to produce the transformation and have observed the elastic constant matrix for the sodium chloride structure to be positive definite at the transformation. Clearly the transformation does not occur via a macroscopic shear instability in this case.

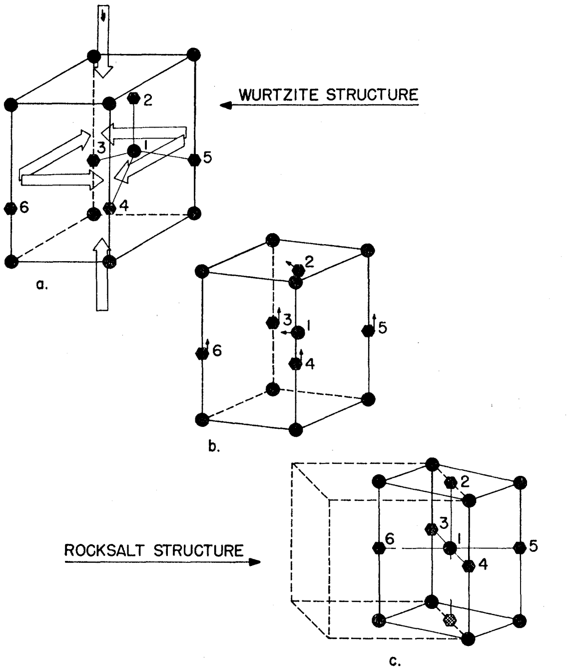

FIG. 1. The wurtzite-to-rocksalt structural transformation by continuous deformation. (a) The normal hexagonal representation of the CdS wurtzite structure, with the broad arrows representing the stresses associated with the deformation. (b) The cell is shown slightly distorted with the logical (spring model) motion of the atoms with respect to the cell indicated by the small arrows. (c) The distortion is completed, and the atoms have become the body-centered tetragonal arrangement of the rocksalt structure. The normal representation of the rocksalt structure, a face-centered cubic arrangement, is indicated by the dashed lines for clarity.

The vibrations associated with an ultrasonic experiment, however, are at the low-frequency end of the acoustic lattice vibration dispersion curve and are not necessarily representative of the entire spectrum. Daniels and Smith have hypothesized that the rubidium halide rocksalt structures became unstable by the vanishing of one of the short-wavelength lattice frequencies in a mode of the C_{44} type. The feasibility of this hypothesis is supported by their interpretation of the anomalous temperature dependence of Grüneisen's gamma (see Ref. 1 and references therein) for Ge, Si, and InSb. These materials have tetrahedrally bonded structures similar to the tetrahedrally bonded wurtzite structure of CdS and also exhibit similar pressure-induced structural transformations. The hypothesis of a vanishing mode must certainly be considered as a possibility in CdS.

If we consider the transformation in microscopic terms rather than macroscopic terms, the shear instability argument becomes more plausible, and it is unnecessary to invoke a gross distortion of the acoustic lattice vibration dispersion curve by hydrostatic pressure as low as the transition pressure. The theme of this argument is that in all real crystals there are a large number of imperfections, which act as points of extreme stress concentration. When high external pressures are applied to the crystal, it can become microscopically shear unstable at points of stress concentration such as

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[8] P. M. Buerger, in *Phase Transformations in Solids* (John Wiley & Sons, Inc., New York, 1958) p. 183.

[9] P. J. Reddy and A. L. Ruoff, in *Physics of Solids at High Pressures* (Academic Press Inc., New York, 1965), p. 510.

dislocations, vacancies, interstitials, or impurities. When the microscopic regions become unstable, the transformation would spread rapidly from these regions, similar to the motion of dislocations. Once the mechanism was initiated, the change in structure would spread throughout the crystal if the rocksalt phase were the thermodynamically stable phase. The large pressure hysteresis[10] ($\sim$12 kbar) of the structural transformation in CdS indicates that the rocksalt structure becomes the thermodynamically stable phase below 20 kbar at room temperature.

In conclusion, the effective elastic-constant data reported in this paper provide the basis for a plausible mechanism for the pressure-induced phase transformation in CdS.

APPENDIX

In this Appendix we give the derivation of the characteristic elastic constant for the deformation of the wurtzite structure to the rocksalt structure at constant volume.

For simplicity of calculation the coordinate system is chosen such that the 1 axis is parallel to the longer diagonal of the rhombic base of the hexagonal unit cell, the 2 axis is parallel to the shorter diagonal of the rhombic base of the hexagonal unit cell, and the 3 axis is parallel to the c axis of the hexagonal unit cell. This choice is equivalent to rotating the usual hexagonal coordinate system 30° about the c axis. The symmetry of the structure requires the elastic-constant matrix to be unvaried by this rotation. The required distortion can now be described as a compression along the 1 and 3 axes combined with an extension along the 2 axis. Since we consider the distortion to take place at constant volume, the sum of the strains must be zero, i.e.,

$$\epsilon_1+\epsilon_2+\epsilon_3=0. \tag{1}$$

The constant-volume stipulation also requires that the edge lengths of the base remain constant $[\frac{1}{2}\sqrt{3}\times(\sqrt{8}/\sqrt{3})X^3=\sqrt{2}X^3=\frac{1}{2}(\sqrt{2}X)^3]$ which in turn requires that

$$\epsilon_2=-\tan^2 60^\circ\,\epsilon_1=-3\epsilon_1. \tag{2}$$

Combining Eqs. (1) and (2), we may write

$$\epsilon_1=-\epsilon,\quad \epsilon_2=3\epsilon,\quad \epsilon_3=-2\epsilon. \tag{3}$$

Now, the strain energy W_d of the distortion is merely the sum of the work associated with the various strains W_i. The work associated with a given dilation strain may be written as

$$W_i=T_i\epsilon_i V_0, \tag{4}$$

where T_i is the stress in the ith direction, ϵ_i is the strain in the ith direction, and V_0 is the volume of the structure. Thus

$$W_d=\sum_i W_i=\sum_i T_i\epsilon_i V_0=V_0\sum_i T_i\epsilon_i. \tag{5}$$

The T_i may be calculated from the effective elastic constant matrix and the ϵ_i, to yield the strain energy per unit volume

$$(1/V_0)W_d=(10C_{11}+4C_{33}-6C_{12}-8C_{13})\epsilon^2. \tag{6}$$

In hexagonal crystals, $C_{66}=\frac{1}{2}(C_{11}-C_{12})$. Thus, substituting for C_{12} and differentiating twice with respect to ϵ, we obtain

$$(1/V_0)(d^2W_d/d\epsilon^2)=8(C_{11}+C_{33}+3C_{66}-2C_{13}). \tag{7}$$

The constant in front of the right side relates only to the arbitrary definition of the magnitude of ϵ in Eq. (3), and may be ignored in defining the characteristic elastic constant of the deformation

$$C_t=(C_{11}+C_{33}+3C_{66}-2C_{13}). \tag{8}$$

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[10] J. A. Corll, J. Appl. Phys. **35**, 3032 (1964).