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

JAMES A. CORLL

Sandia Laboratory, Albuquerque, New Mexico

(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 $\times$ 1 cm $\times$ 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 $\pm 0.2°$. 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

[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).

JAMES A. CORLL

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
				Jaffe[a]	Bolef[b]	McSkimin[c]	Present study	$d \ln C_{ij}/dp$ in Mbar^{-1}
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 (ρv^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]

$$(\beta = 11.02 \times 10^{-6}/°C, \ \beta_a = 4.25 \times 10^{-6}/°C,$$
$$\beta_b = 2.50 \times 10^{-6}/°C)$$

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.

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

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 $(C_{ij} \to 0)$ 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

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

[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.