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.

The vibrations associated with an ultrasonic experiment, however, are at the low-frequency end of the acoustic lattice vibration dispersion curve and are not

[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.
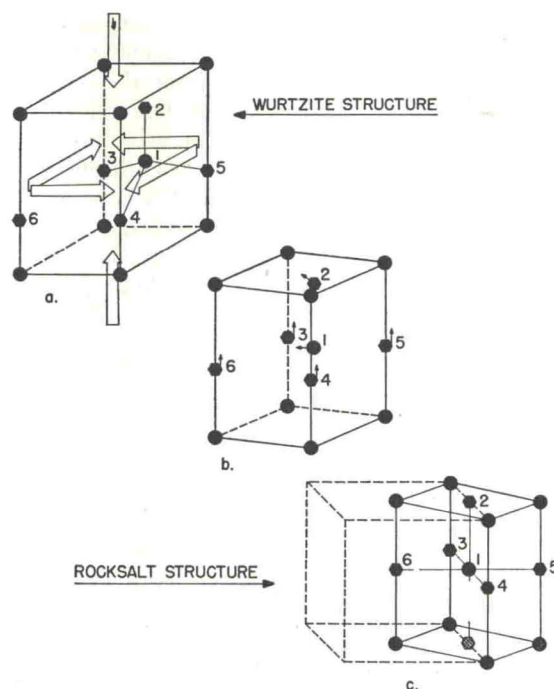
FIG. 1. The wurtzite-to-rocksalt structural transformation by continuous deformation. (a) The normal hexagonal representation of the CdS wurtzite structure, with the broad arrows representing the stresses associated with the deformation. (b) The cell is shown slightly distorted with the logical (spring 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.

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

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.,

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

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

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

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

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 $i$th direction, $\epsilon_i$ is the strain in the $i$th 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 $\epsilon_i$, 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 $\epsilon$, we obtain

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

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

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