

is in contrast to the situation for mixed crystals of the form $\text{Ga}(\text{As}_y\text{P}_{1-y})^{11}$ and for Ge-Si alloys,^{12,13} for which the relationship between composition and the size of the energy gap is not linear. In those cases the shift with pressure was also quite different, comparing GaP with GaAs, or Si with Ge. In the case of InP and InAs, the shifts are quite similar, both having slopes of about 0.0047 eV/kilobar obtained for InAs by Taylor⁷ from 0-2 kilobars. Work done by Lax¹⁴ indicates that the conduction band minimum is probably at the zone center in InAs. Calculations by Kane¹⁵ of the absorption constant associated with direct transitions in the vicinity of the zone center agree fairly well with the experiments of Fan and Gobel.¹⁶ The change in slope of the shift of the absorption edge of InAs with pressure is additional evidence that the initial transition is direct, since the same effect was observed in the case of GaSb.

B. II-VI COMPOUNDS

The effects of pressure on the optical spectra of CdS, CdSe, and CdTe have been measured, and the results are presented and discussed below. In each case, the shift of the optical absorption edge with pressure was measured, and a phase change observed.

1. Experimental Results

CdS was obtained from E. C. Stewart of the Harshaw Chemical Company, in the form of large single crystals and polycrystalline masses, having the wurtzite structure. Spectra were obtained on the DUR Spectrophotometer, using a tungsten lamp source and an RCA 7102 photomultiplier detector. The results of a $\frac{1}{8}$ -in. bomb run, and two $\frac{1}{2}$ -in. bomb runs are shown in Fig. 6. The shift with pressure was measured from an initial value of 19 140 wave numbers at an absorption coefficient of 30 cm^{-1} . The edge shifts red irreversibly when the sample is initially pressed in, to a point about 230 wave numbers red from the location of the absorption edge measured at one atmosphere. The slope of the shift from this point is 0.0033 eV/kilobar. A phase transition occurs, starting at about 27.5 kilobars, and is essentially complete at about 40 kilobars. The absorption edge shifts red about 6000 wave numbers over the transition. In the high-pressure form, the absorption edge shifts very little up to 50 kilobars, then begins to shift red. Between 60 and 160 kilobars, the average slope is about $-0.0007 \text{ eV/kilobar}$. On reduction of pressure, the reverse phase transition begins at 10 kilobars, and does not appear to be complete at 1 atm even after letting the bomb stand for several days. The

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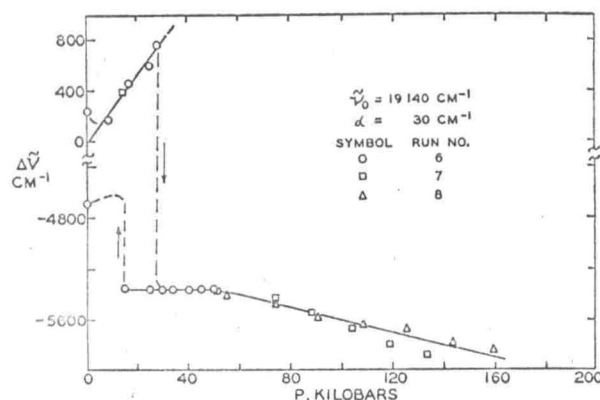


FIG. 6. Shift of CdS absorption edge with pressure.

absorption edge moved back part way, but is still about 4150 wave numbers red from the initial value. The progress of the phase transition was followed by measuring the change in intensity with pressure of the light transmitted by the sample at 10 000 wave numbers. Figure 8 is a plot of such data for a typical run involving a phase change in CdSe, which behaves very much like CdS.

X-ray powder diffraction patterns for 3 CdS samples which had been under 50 kilobars pressure for several minutes showed a faint line corresponding to a planar spacing of 2.915 Å, which could be due to the 200 plane of the zincblende structure. Other strong lines in zincblende pattern correspond too closely to strong lines in the wurtzite pattern to be definitely identified. The lines in the diffraction patterns are much more diffuse than in a pattern for a crushed CdS sample which had

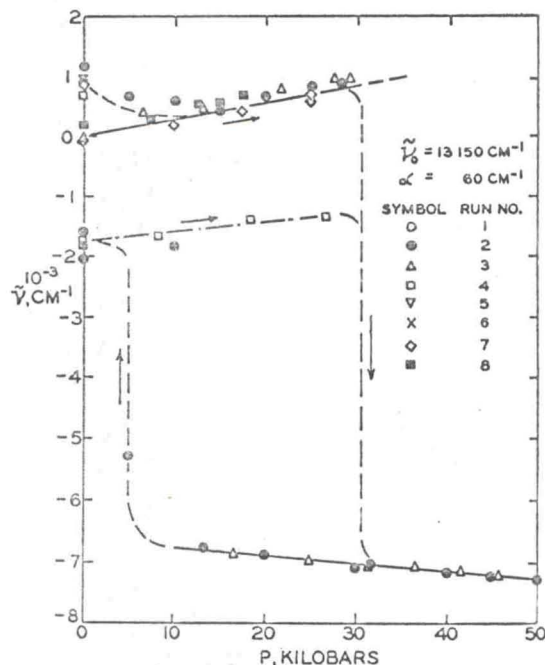


FIG. 7. Shift of CdSe absorption edge with pressure.