pounds have the wurtzite structure, while CdTe has the zincblende structure. This difference must be considered in comparing the results for CdS and CdSe with those for CdTe and those for the group III–V compounds considered above.

The results for CdS and CdSe indicate that the band structures are similar. This would also follow from the results of Khanseverov, Ryvkin, and Ageeva,[17] who found that the energy gap varies in a smooth curve with composition for solid solutions of CdS and CdSe. Thomas, Hopfield, and Power[18] measured the absorption coefficient of CdS from 10 to 300 cm^{-1} in polarized light, from 20° to 300°K, in the region of the absorption edge, and concluded that the transition was direct at the zone center. However, Boer and Gutjahr,[19] from measurements of the absorption constant at 90° and 300°K, concluded that an indirect transition involving phonons was responsible. The shift of the absorption edge of CdS with pressure up to 4 kilobars was measured by Gutsche[20] who found a slope of 0.0044 ev/kilobar, compared with the value 0,0033 ev/kilobar obtained in this work. He also obtained a compressibility $(-dV/VdP)$ of 0.00166 per kilobar up to 4 kilobars. Preliminary calculations on the band structure of CdS have been started by Cohen and Reitz.[21] The shifts with pressure of the absorption edges of the high pressure forms resemble the shifts of the corresponding group I–VII compounds much more than those of the corresponding group III–V compounds.

The blue shift of the absorption edge of CdTe indicates that the initial transition is probably to a conduction band minimum either in the [111] direction or at the zone center. An analysis of the shape of the absorption edge according to the theory of Bardeen, Blatt and Hall,[22] was carried out for CdTe by Davis and Shilliday[23] at various temperatures. The results indicate that the lowest conduction band minima are in [111] directions, and 1.440 ev above the valence band maximum at room temperature, and that the [000] conduction band minimum is at 1.505 ev, or 0.065 ev higher.

The irreversible red shifts which occur in CdS, CdSe, and CdTe on being pressed in, may conceivably be due to strain and shear, although the experiments with CdSe failed to produce this effect outside the bomb, or prevent it from occurring in the bomb. The samples are very brittle, and many cracks probably develop when they are pressed into the sample chamber of the bomb.

The phase transitions occurring in CdS and CdSe under pressure are quite similar, both in the pressure at which they take place and in their effect on the location of the absorption edge. The actual thermodynamic transition points are probably about 19 kilobars in each case, with a region of indifference of about 8–12 kilobars on either side of the thermodynamic point. This can be seen in Fig. 8, for a typical CdSe run. With either increasing or decreasing pressure, the transitions require about 10 kilobars to become essentially complete, once they have begun. The transitions do not progress at constant pressure, but only for a few seconds after each pressure increase. This might indicate that the transitions are of the diffusional type, requiring a shear or strain mechanism to progress rapidly.

Although no direct identification of the high-pressure phases has been made, the x-ray patterns for CdS which has been subjected to high pressure do show some evidence of a small amount of the zincblende form being present. The shifts of the absorption edges after the transitions look considerably like the pressure shifts of the zincblende phases of CuCl, CuBr, and CuI, which will be presented and discussed below.

The phase transition in CdTe results in a form with an energy gap no larger than about 0.35 ev, which could be wurtzite, a distorted zincblende structure, or even the liquid form. On using approximate values of the heat of fusion and volume decrease on melting for CdTe of 10±5 kcal/mole and 10±4%, respectively, the pressure required to bring the melting point from 1041° to 27°C is 120±90 kilobars, so that melting is possible. The large volume decrease is reasonable, since the average coordination number in the melt would probably be 6 or 8 compared to 4 in the solid.

C. I–VII COMPOUNDS

The effects of pressure on the optical properties and lattice stability of the group I–VII compounds CuCl, CuBr, and CuI have been measured, up to pressures of 160 kilobars. Each compound underwent at least two phase transitions under pressure, and the shifts of the absorption edges were measured in each phase. The phase transitions in CuCl and CuBr were studied in the

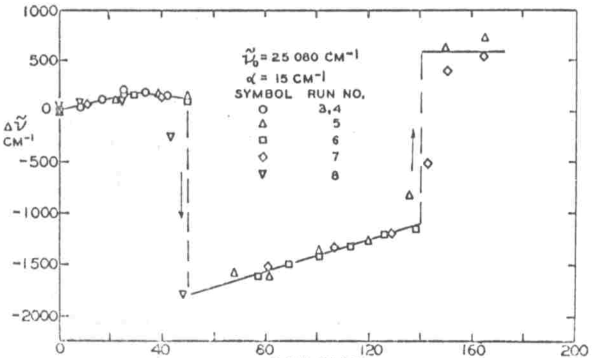

FIG. 10. Shift of CuCl absorption edge with pressure.

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