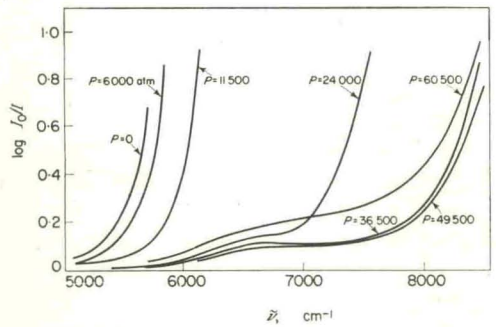

FIG. 7. Shift of absorption edges of zinc sulfide selenide, and telluride with compression ($\alpha = 65$ cm^{-1}).

(b) *Wurtzite type*

The compounds ZnO and CdS are closely related to the other compounds included in this work, not only in structure, but also in many important physical and electronic properties. A transformation under pressure to the zinc blende structure from their original wurtzite form was expected, and did in fact occur in both cases.

(i) *Zinc oxide.* Single crystals of zinc oxide were obtained from Dr. A. R. HUTSON, of the Bell Telephone Laboratories. These crystals were in the form of needles about 0·25 in. long and some 0·004–0·010 in. in dia., making them most suitable for the 250,000-atm bomb. The shift of the absorption edge observed with pressure is shown in Fig. 8. A blue shift with pressure first occurs, at an increasing rate with higher pressure. The slope changes from $0{\cdot}6(10^{-6})$ eV/atm at 1 atm to $1{\cdot}9(10^{-6})$ eV/atm at 100,000 atm. At a pressure of about 100,000 atm, the light transmitted by the sample began to cut off, and reached a minimum at pressures ranging from 130,000 to 150,000 atm in different runs. The sample then cleared up somewhat, and the shift shown by the upper curve in Fig. 9 was measured. The red shift at the transition amounts to about —0·10 eV, and the initial slope of the upper curve is $1{\cdot}9(10^{-6})$ eV/atm at 130,000 atm.

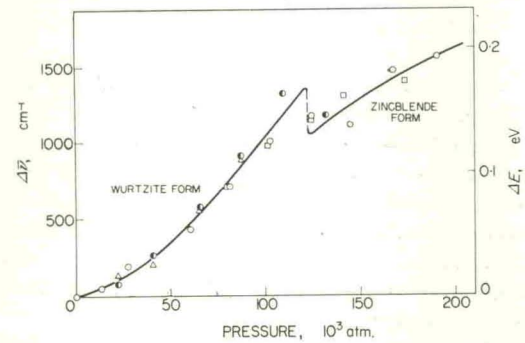

FIG. 8. Shift of zinc oxide absorption edge with pressure ($\alpha = 60$ cm^{-1} measured from $\tilde{\nu}_0 = 25{,}300$ cm^{-1}).

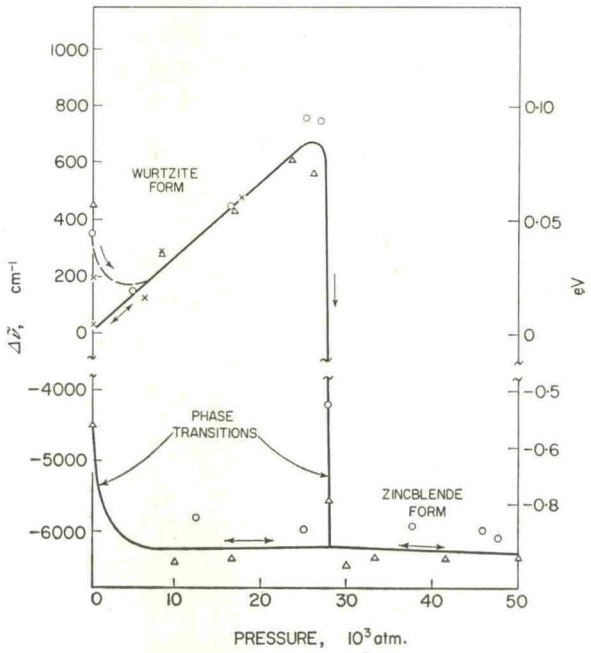

FIG. 9. Shift of cadmium sulfide absorption edge with pressure ($\nu_0 = 20{,}110$ cm^{-1}, $\alpha = 64$ cm^{-1}).

(ii) *Cadmium sulfide.* This material was obtained in the form of large crystals and polycrystalline masses in the wurtzite structure from Dr. E. C. STEWART, of the Harshaw Chemical Company. The shift of the absorption edge with pressure is shown in Fig. 9. The initial red shift up to 5000 atm is thought to be due to a partial phase change to the zinc blende form induced by shear during the fusing of the salt pellet around the sample. The shift was therefore measured from an extrapolated zero value of 2·50 eV, which is not the true energy gap at atmospheric pressure. Once the pressure exceeded 5000 atm, a reduction in pressure did give a shift down to the extrapolated zero, and the shift was reversible from 0 to 25,000 atm. The initial slope of the shift is $3{\cdot}3(10^{-6})$

eV/atm, and remains fairly constant up to 27,500 atm, at which point a large red shift of about 0·8 eV occurs, presumably due to the transition to the zinc blende structure. This transition resulted in a loss of most of the light available, and in only two runs could the edge be measured beyond the transition. There was no measurable tendency for the new absorption edge to shift with pressure, either increasing or decreasing, until the pressure was reduced below 10,000 atm. The sample then cleared up gradually and the absorption edge slope of the shift with pressure. The following discussion is intended to emphasize the effect of asymmetry in the crystal potential for compounds in isoelectronic sequences, for which the total number of electrons are equal, and for which the bond lengths are almost equal.

The interpretations are based on the (perhaps rash) assumption that the red shifts are due to a transition to a minimum in the (100) direction in the conduction band, as has been reasonably well established for germanium.[9]

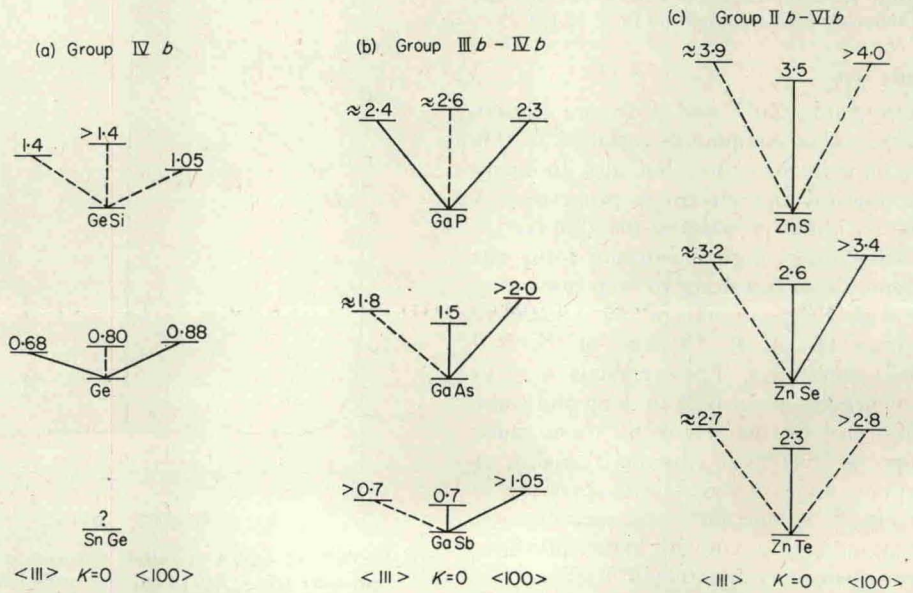

FIG. 10. Estimated conduction-band levels of semiconductors (above valence-band maximum 300°K).

shifted blue again, reaching a final value of 0·56 eV less than the original zero point. No further change was observed after the sample had remained in the bomb for several days at atmospheric pressure.

3. COMPOUNDS IN VARIOUS SEQUENCES

A speculative outline of the results of the previous sections is presented in Fig. 10, which illustrates the energy gaps that are known or can be estimated for the direct and indirect transitions at atmospheric pressure. Table 1 summarizes the effect of pressure in these transitions, with the pressure range in which each occurs and the

(a) SiGe, GaP *and* ZnS

The bond length in this sequence varies from 2·36 to 2·39 Å, and the total number of electrons is 23 per atom. The system silicon–germanium has been investigated by JOHNSON and CHRISTIAN[7] who found a sharp break in the plot of energy gap versus composition at about 15 mole per cent silicon, indicating a difference in the band structure of these two elements. Pressure measurements by PAUL and WARSCHAUER[8] in the range 1–8000 atm on germanium–silicon alloys were consistent with HERMAN'S[9] picture of the band structure, and the behavior of the band minima of these two elements under pressure, i.e.