

They were *n*-type with a specific resistivity of $0.08 \Omega\text{-cm}$. The results are shown in Fig. 2. The initial energy gap is about 1.4 eV at $\alpha = 30 \text{ cm}^{-1}$. The absorption edge shifts blue with

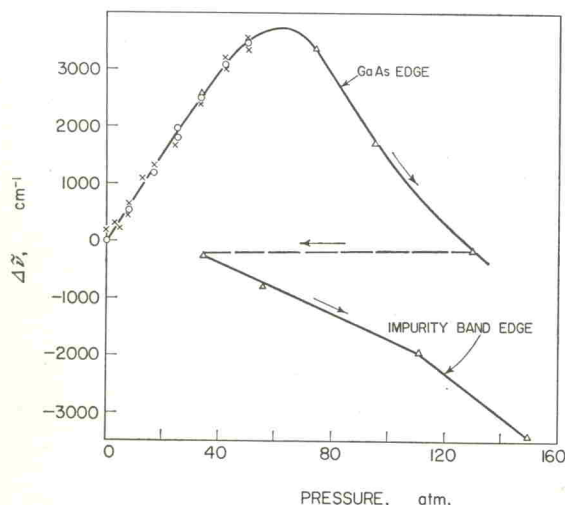


FIG. 2. Shift of gallium arsenide absorption edge with pressure ($\nu_0 = 11,850 \text{ cm}^{-1}$, $\alpha = 50 \text{ cm}^{-1}$).

pressure, the initial slope being $9.4 (10^{-6}) \text{ eV/atm}$, rising to a maximum shift of 0.465 eV at $60,000 \text{ atm}$. The red shift above $60,000 \text{ atm}$ has a slope of roughly $-8.7 (10^{-6}) \text{ eV/atm}$, and may be due

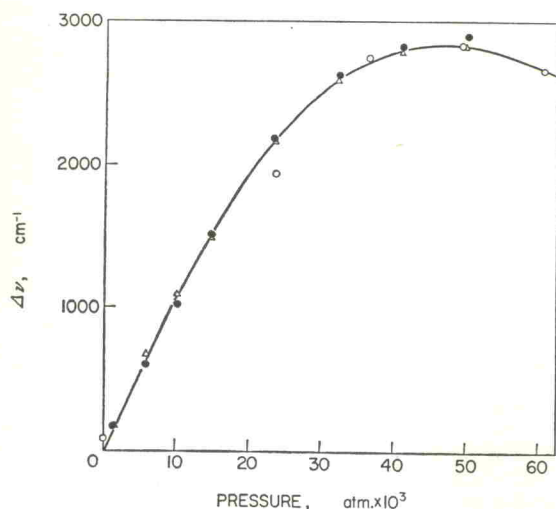


FIG. 3. Shift of gallium antimonide absorption edge with pressure ($\nu_0 = 5620 \text{ cm}^{-1}$, $\alpha \approx 20 \text{ cm}^{-1}$).

in part to the indirect (100) transition, and in part be due to the irreversible effects discussed below.

(c) Gallium antimonide

The GaSb was obtained from Dr. J. H. WHELAN, of the Bell Telephone Laboratories. It was of unknown but high purity. The results are shown in Fig. 3. The initial transition has an energy gap of 0.7 eV at $\alpha = 20 \text{ cm}^{-1}$, compared to 1.5 eV for GaAs and 2.4 eV for GaP. The initial blue shift of GaSb has a slope of $12.3 (10^{-6}) \text{ eV/atm}$, indicating a more rapid rise of the conduction-band minimum than in GaAs. The maximum apparent shift of 0.35 eV occurs at about $50,000 \text{ atm}$, after which the red shift, probably corresponding to the indirect (100) transition, begins.

2. GROUP IIB-VIB COMPOUNDS

(a) Zinc blende type

(i) *Zinc sulfide*. Pure zinc sulfide single crystals in the zinc blende structure were obtained from L. W. STROCK, of Sylvania Electric Products Inc. The initial optical energy gap was found to be 3.5 eV , and is considered to be the transition at $k = 0$, as is indicated by a band-structure calculation being carried out by SHAKIN and BIRMAN⁽⁴⁾. The shift with pressure, shown in Fig. 4,

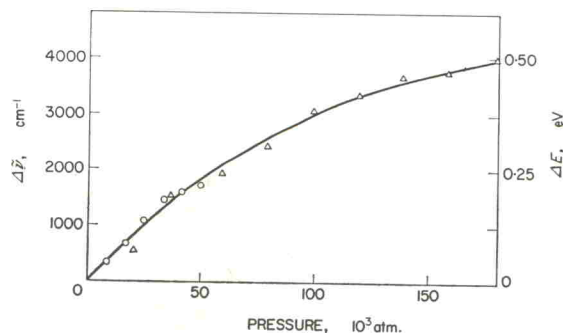


FIG. 4. Shift of zinc sulfide absorption edge with pressure ($\alpha = 60 \text{ cm}^{-1}$ measured from $\bar{\nu}_0 = 28,600 \text{ cm}^{-1}$).

consists of a monotonic blue shift, appearing to approach a maximum of about 0.50 eV at the highest pressure obtained, $180,000 \text{ atm}$. The initial slope of $5.7 (10^{-6}) \text{ eV/atm}$ compares with $9 (10^{-6}) \text{ eV/atm}$ obtained by PIPER *et al.*⁽⁵⁾ for hexagonal ZnS (wurtzite) up to 1700 atm . One

would expect comparable results for the wurtzite form, as the band structure is probably very similar to that of the zinc blende.

Figure 7 shows the absorption-edge shift plotted against relative volume compression, obtained from the data of BRIDGMAN⁽⁶⁾. The rate of change of energy gap with bond length, assuming isotropic compression, is $6.2 \text{ eV/\AA}$, at 1 atm.

(ii) *Zinc selenide*. Pure single crystals of ZnSe were obtained from Dr. R. H. BUBE, of RCA Laboratories. The shift of the absorption edge was measured at 65 cm^{-1} , for which the initial energy gap was 2.58 eV . The results, shown in Fig. 5, are quite similar to the results for ZnS.

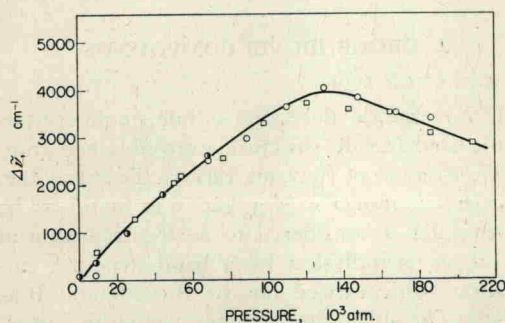


FIG. 5. Shift of zinc selenide absorption edge with pressure ($\nu_0 = 20,800 \text{ cm}^{-1}$, $\alpha = 65 \text{ cm}^{-1}$).

The initial shift is blue, with a slope of $6.0(10^{-6}) \text{ eV/atm}$ at 1 atm. The maximum shift is 0.49 eV at $130,000 \text{ atm}$, followed by a red shift with a slope of about $-2.0(10^{-6}) \text{ eV/atm}$.

From BRIDGMAN's compressibility data, the shift has been plotted against relative compression in Fig. 7, which shows a slope of $3.3 \text{ eV/\AA}$ up to $15,000 \text{ atm}$ ($\Delta V/V_0 = 0.032$), a slope of $4.6 \text{ eV/\AA}$ up to $130,000 \text{ atm}$ ($V/V_0 = 0.130$), and a slope of $-4.0 \text{ eV/\AA}$ above $130,000 \text{ atm}$.

(iii) *Zinc telluride*. The source of the zinc telluride single crystals used here was Dr. R. N. HALL, of the General Electric Company. The particular samples used were made from a stoichiometric mixture of zinc and tellurium, which contained a few parts per million of copper, resulting in a resistivity of about $1\Omega\text{-cm}$. The shift of the absorption edge with pressure is shown in Fig. 6. The initial sharp red shift of the edge is thought to be due to surface effects during the

fusing of the salt around the sample, so the shift was measured from an extrapolated zero point of $18,300 \text{ cm}^{-1}$ or 2.27 eV . The shift from 4000 to $45,000 \text{ atm}$ is blue, with a slope of $6.0(10^{-6}) \text{ eV/atm}$. The portion of the curve from 5000 to $40,000 \text{ atm}$ is completely reversible, and is possibly due to the direct transition at $k = 0$.

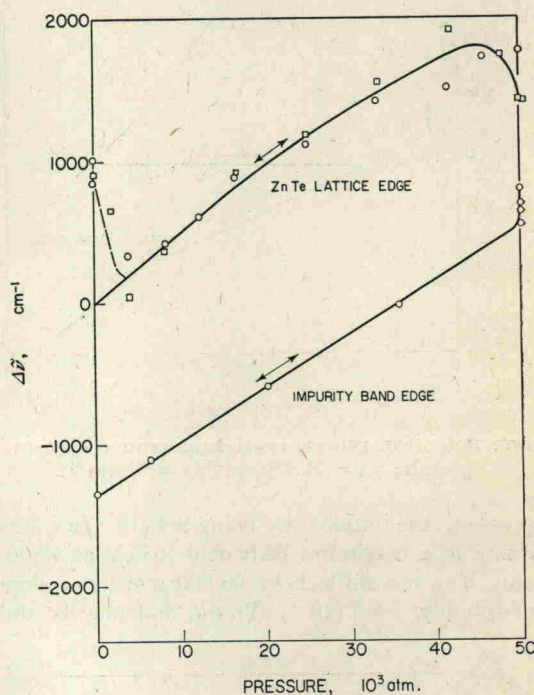


FIG. 6. Shift of zinc telluride absorption edge with pressure ($\nu_0 = 18,300 \text{ cm}^{-1}$, $\alpha = 64 \text{ cm}^{-1}$).

Above $45,000 \text{ atm}$, a time-dependent irreversible red shift takes place, reaching an equilibrium value about 0.18 eV below the original energy gap. In several runs, equilibrium was reached in about 20 min . On reduction of pressure, the shift parallels the original shift, with a slope of $4.7(10^{-6}) \text{ eV/atm}$, the energy gap reaching a final value of 2.10 eV at 1 atm . This last shift is reversible over the range $1\text{--}50,000 \text{ atm}$ and is interpreted tentatively below.

From the plot of shift against compression (Fig. 7), the shift of energy gap with bond length is found to be $3.18 \text{ eV/\AA}$ up to the beginning of the phase change at 7.5 per cent volume compression.