THE EFFECT OF PRESSURE ON ZINC BLENDE AND WURTZITE STRUCTURES*

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Abstract—The effect of pressure has been measured on the absorption edges of GaP, GaAs, GaSb, ZnS, ZnSe, ZnTe, ZnO and CdS. A tentative interpretation can be given consistent with previous work on silicon and germanium. Regularities in the shifts in horizontal and diagonal sequences are discussed.

An absorption peak which appears (irreversibly) on the low-energy side of the edge of the higher-molecular-weight compounds, and grows with pressure, indicates either the formation of a disordered phase or some chemical decomposition. For GaAs and GaSb both events may be present, but for ZnTe the former course seems definitely the more probable.

THE effect of pressure has been measured on the absorption edges of GaP, GaAs, GaSb, ZnS, ZnSe, ZnTe, ZnO and CdS. The first six of these have the zinc blende structure, while the last two have the wurtzite structure at 1 atm, but transform to zinc blende under pressure.

The apparatus and procedure has been previously described,[1-3] and results have been discussed for germanium and silicon[3] which will be compared with the present results.

1. GROUP IIIB–VB COMPOUNDS

(a) Gallium phosphide

Single crystals of GaP were obtained from Dr. A. A. GIARDINI, of the U.S. Army Signal Research and Development Laboratory. The samples used for the pressure runs were very slightly doped with titanium, which was not expected to have any effect on the pressure shift of the absorption edge. Figure 1 presents the data obtained from 1 to 50,000 atm. For the highest absorption coefficient, $\alpha = 100$ cm^{-1}, there is an initial blue shift with pressure. Above 22,000 atm, the shift is red for all values of α below 100 cm^{-1}, with a slope of $-1\cdot7(10^{-6})$ eV/atm.

(b) Gallium arsenide

Single crystals of GaAs were obtained from Dr. J. H. WHELAN, of the Bell Telephone Laboratories

1 $\nu_0 = 19\,600$ cm^{-1}, $\alpha = 100$ cm^{-1}
2 $\nu_0 = 19\,300$ cm^{-1}, $\alpha = 64$ cm^{-1}
3 $\nu_0 = 18\,850$ cm^{-1}, $\alpha = 32$ cm^{-1}
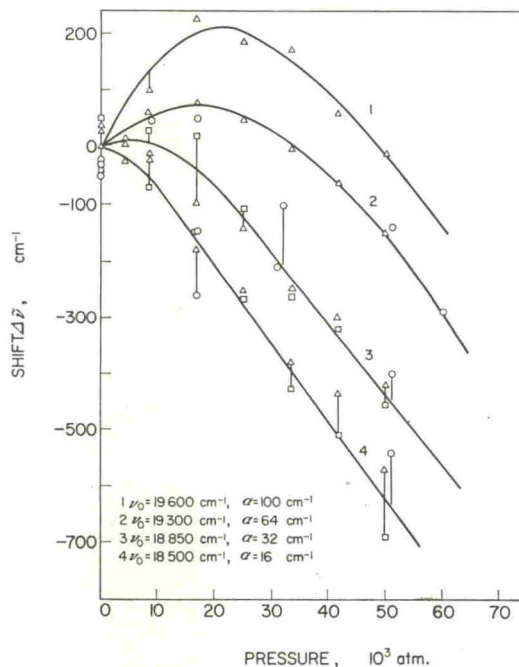4 $\nu_0 = 18\,500$ cm^{-1}, $\alpha = 16$ cm^{-1}

PRESSURE, 10^3 atm.

FIG. 1. Shift of gallium phosphide absorption edge with pressure.

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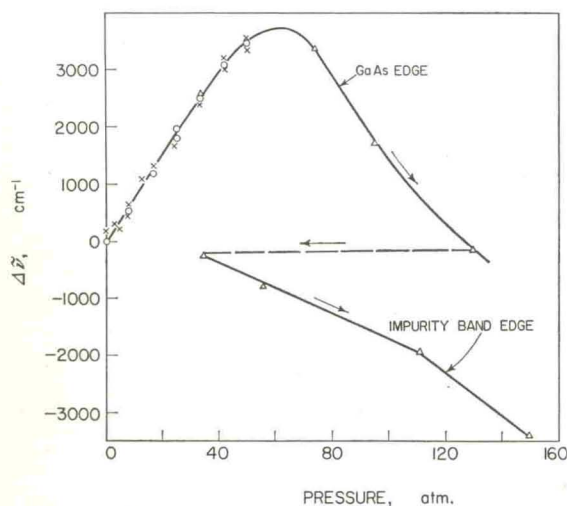

FIG. 2. Shift of gallium arsenide absorption edge with pressure ($\nu_0 = 11,850$ cm^{-1}, $\alpha = 50$ cm^{-1}).

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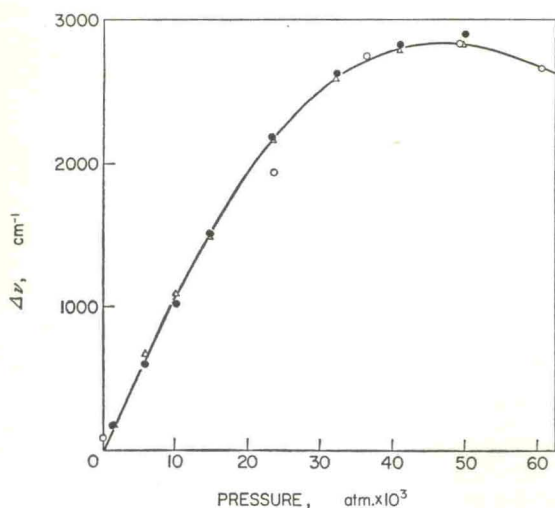

FIG. 3. Shift of gallium antimonide absorption edge with pressure ($\nu_0 = 5620$ cm^{-1}, $\alpha \simeq 20$ cm^{-1}).

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 $\alpha = 20$ 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}) 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 $50,000$ 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,
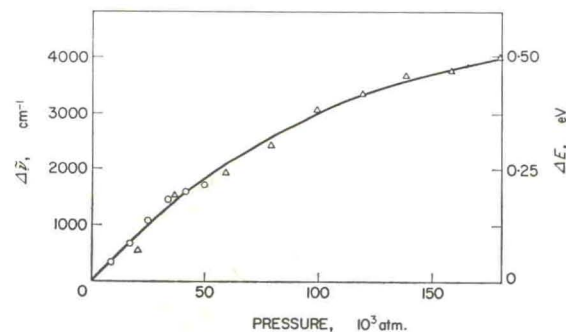

FIG. 4. Shift of zinc sulfide absorption edge with pressure ($\alpha = 60$ cm^{-1} measured from $\bar{\nu}_0 = 28,600$ cm^{-1}).

consists of a monotonic blue shift, appearing to approach a maximum of about 0.50 eV at the highest pressure obtained, $180,000$ atm. The initial slope of 5.7 (10^{-6}) eV/atm compares with $9(10^{-6})$ 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 $6 \cdot 2$ eV/Å, 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 $2 \cdot 58$ eV. The results, shown in Fig. 5, are quite similar to the results for ZnS.
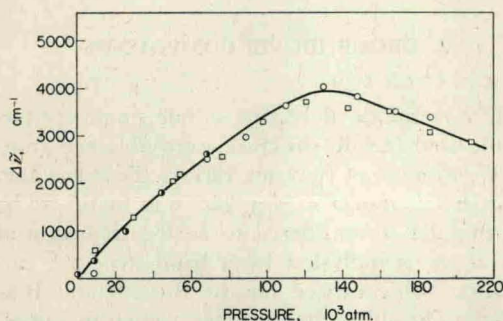
FIG. 5. Shift of zine selenide absorption edge with pressure ($\nu_0 = 20{,}800$ cm⁻¹, $\alpha = 65$ cm⁻¹).

The initial shift is blue, with a slope of $6 \cdot 0(10^{-6})$ eV/atm at 1 atm. The maximum shift is $0 \cdot 49$ eV at 130,000 atm, followed by a red shift with a slope of about $-2 \cdot 0(10^{-6})$ eV/atm.

From BRIDGMAN's compressibility data, the shift has been plotted against relative compression in Fig. 7, which shows a slope of $3 \cdot 3$ eV/Å up to 15,000 atm $(\Delta V/V_0 = 0 \cdot 032)$, a slope of $4 \cdot 6$ eV/Å up to 130,000 atm $(V/V_0 = 0 \cdot 130)$, and a slope of $-4 \cdot 0$ eV/Å above 130,000 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 1Ω-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 cm⁻¹ or $2 \cdot 27$ eV. The shift from 4000 to 45,000 atm is blue, with a slope of $6 \cdot 0(10^{-6})$ eV/atm. The portion of the curve from 5000 to 40,000 atm is completely reversible, and is possibly due to the direct transition at $k = 0$.

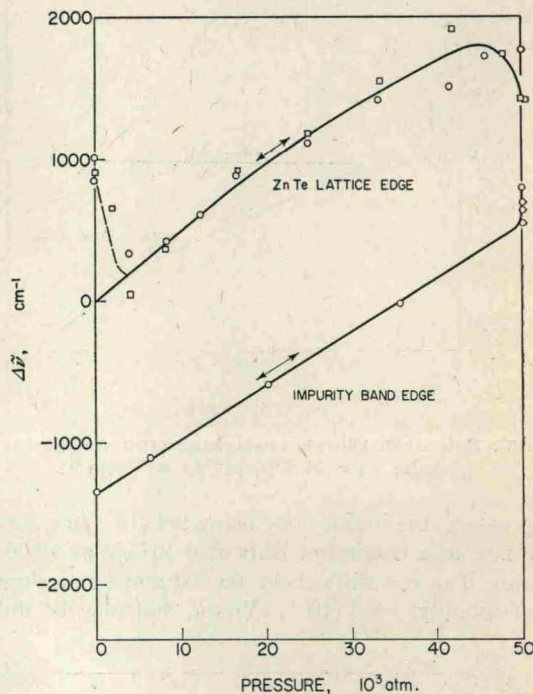FIG. 6. Shift of zinc telluride absorption edge with pressure ($\nu_0 = 18{,}300$ cm⁻¹, $\alpha = 64$ cm⁻¹).

Above 45,000 atm, a time-dependent irreversible red shift takes place, reaching an equilibrium value about $0 \cdot 18$ 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 $4 \cdot 7$ (10^{-6}) eV/atm, the energy gap reaching a final value of $2 \cdot 10$ eV at 1 atm. This last shift is reversible over the range 1–50,000 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 $3 \cdot 18$ eV/Å up to the beginning of the phase change at $7 \cdot 5$ per cent volume compression.
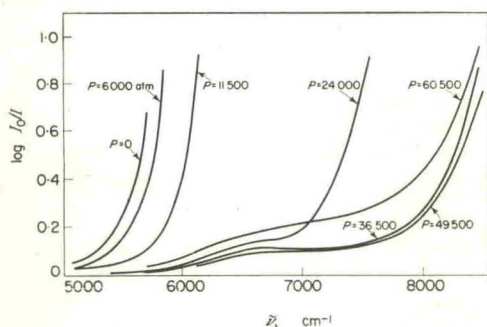
FIG. 7. Shift of absorption edges of zinc sulfide selenide, and telluride with compression ($\alpha = 65$ cm^{-1}).

(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 $0\cdot6(10^{-6})$ eV/atm at 1 atm to $1\cdot9(10^{-6})$ 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
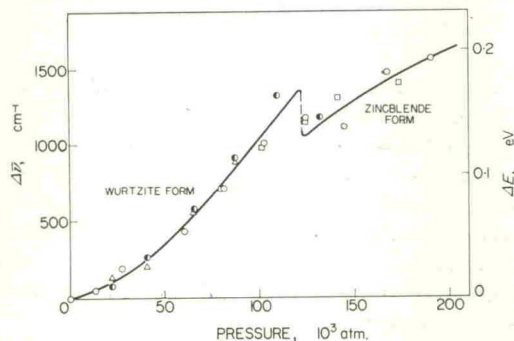

FIG. 8. Shift of zinc oxide absorption edge with pressure ($\alpha = 60$ cm^{-1} measured from $\bar{\nu}_0 = 25{,}300$ cm^{-1}).

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 $-0\cdot10$ eV, and the initial slope of the upper curve is $1\cdot9(10^{-6})$ eV/atm at 130,000 atm.
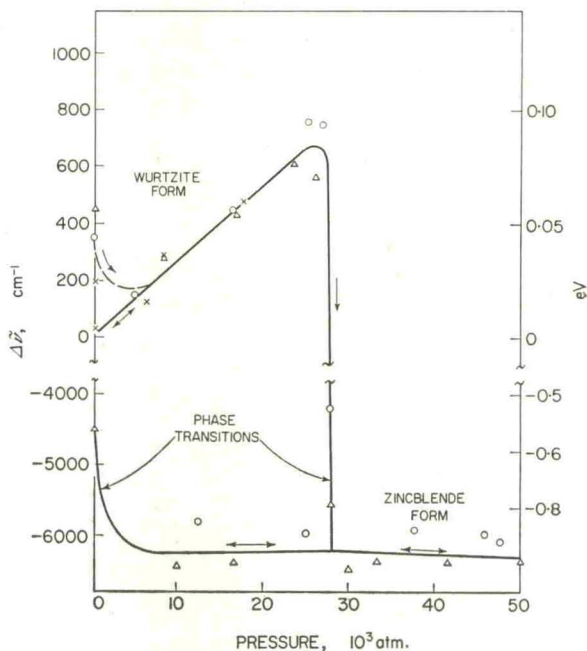

FIG. 9. Shift of cadmium sulfide absorption edge with pressure ($\nu_0 = 20{,}110$ cm^{-1}, $\alpha = 64$ cm^{-1}).

(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 $3\cdot3(10^{-6})$

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]
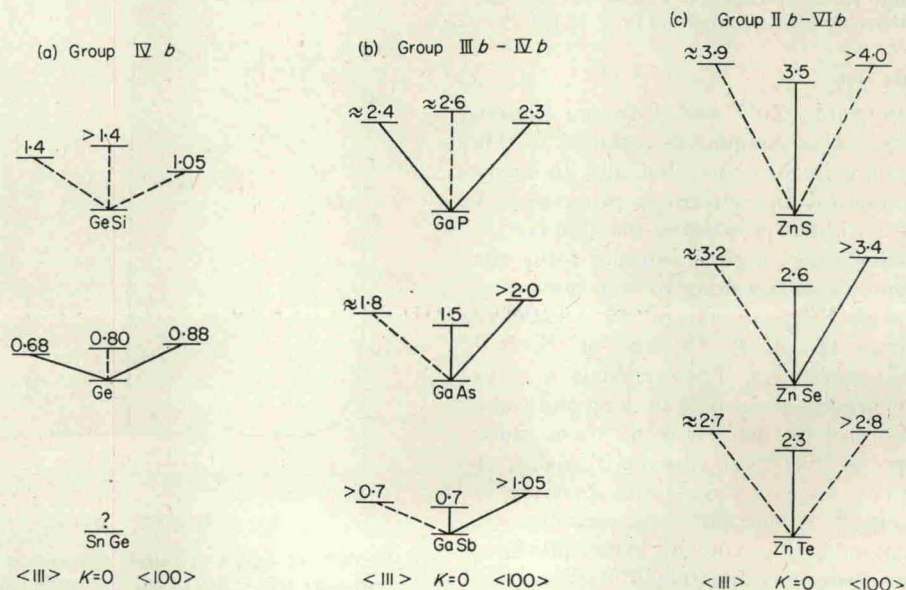

FIG. 10. Estimated conduction-band levels of semiconductors (above valence-band maximum 300°K).

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.

Table 1. *Effect of pressure on band structure of semiconductors*

Compound	ΔE_g(eV)* (1 atm)	$P(10^3$ atm)	Speculated transition direction†	$d\Delta E_g/dP$‡ (10^{-6}eV/atm)	$d\Delta E_g/dr$§ (eV/Å)	Max. blue shift (eV)
Si	1·08	0–140	(100)[10,11]	−2·0	−1·12	
Ge	0·70	0–50 50–129	(111)[11] (100)[3]	+8·0 −1·2	3·8 −0·6	0·15
GaP	2·34	0–20 20–50	(111) or (000) (100)	1·8 −1·7		0·02
GaAs	1·47	0–60 60–130	(000) or (111)[12,13] (100)	+9·4 −8·7		0·47
GaSb	0·70	0–50 50	(000) or (111) (100)	+12·3 ?		0·35
ZnS	3·54	0–180	(000) or (111)[4]	+5·7	6·2	0·50
ZnSe	2·57	0–130 130–210	(000) or (111) (100)	+6·0 −2·0	4·6	0·50
ZnTe	2·26	0–45	(000) or (111)	+6·0	3·2	0·22
ZnO	3·14 (wtz) (Znbl)	0–130 130–220	(111) or (000) (111) or (000)	0·6–1·9 1·9		0·15 0·20
CdS	2·50 (wtz) 1·7 (Znbl)	0–27·5 27·5–50 50–10	(000) or (111) ? ?	+3·3 ≈0 ≈0		0·08 ≈0 ≈0

*Zero point from which shift was measured.

†More probable direction is given first in uncertain cases. Where no reference is given, the estimate is based on the direction and magnitude of the pressure shift found in this paper.

‡Slope of shift at 1 atm, or average slope after a reversal of shift direction. These are, in general, estimated for $\alpha = 20$–65 cm^{-1}, since in only a few cases are values available for $\alpha = 0$. E.g., at $\alpha = 0$ for germanium the slope is $5\cdot0 \times 10^{-6}$ eV/atm.[10]

§Based on bond length.

the rise of the (111) minimum in the conduction band and the lowering of the (100) minimum, relative to the maximum of the valence band. The 50:50 germanium–silicon alloy has an energy gap of 1·05 eV, due to the transition to the (100) minimum, and the (111) minimum is about 0·35 eV higher, or 1·4 eV above the valence band, according to the data of JOHNSON and CHRISTIAN[7].

The effect of increasing asymmetry in this sequence seems to be a general rise in the conduction band relative to the valence band, the rate of rise being greatest for the minimum in the (100) direction. In ZnS, the (apparent) (100)

minimum is at least 0·5 eV above the lowest conduction band level, thus explaining the fact that ZnS has an initial blue shift while GaP shifts red. Following this trend, one would expect the next member of this sequence, CuCl, to have a large blue shift with pressure before the red shift which should eventually follow.

(b) Ge, GaAs *and* ZnSe

In this sequence, the bond length is between 2·43 and 2·45 Å, with a total of 32 electrons per atom. The conduction-band minimum rises relative to the valence band, with the (100)

K

minimum rising the most rapidly, as the asymmetry of the compound increases. There is evidence in this sequence that the (111) minimum rises faster than the minimum at $k = 0$, since the (111) minimum is lower in germanium and the $k = 0$ transition is considered to be lower in energy for GaAs.[12,13] If this is generally true, then the transition in ZnSe should be direct, and the blue-shifting transitions of GaP and ZnS in the last sequence might also be direct at atmospheric pressure. Considering the Kronig one-dimensional model from the viewpoint of SERAPHIN[14] and of WELKER and WEISS[15], the planes perpendicular to the (111) direction may be represented by potential troughs having different depths, as there are alternate planes containing like atoms. It is found that the energy gap for this model increases with an increase in the difference between the two potential troughs, other parameters being constant. In the real crystal then, an electron state with a propagation vector k in the (111) direction should have a greater energy gap between its ground state and its excited state, as the potential difference of the two planes increases. This corresponds to a rise of the Λ_1 state in the conduction band above the similar state in the valence band, which are both in the (111) direction. An electron propagating in the (100) direction encounters alternate layers containing like atoms also, so that the energy gap in the (100) direction should also increase with increasing asymmetry or electronegativity of the bonds. In the immediate vicinity of $k = 0$, one would expect smaller effects, as the charge distribution in space of the atomic s-functions from which the $^1\Gamma_2$ state is made up is not directional, and the atomic p-functions making up the $^3\Gamma_{22}$ state in the valence band are directed only toward like atoms, and are thus less affected by a charge difference between unlike atoms.

The next member of the sequence, CuBr, has a greater energy gap than ZnSe, and if the tendency described above continues, the transition at atmospheric pressure should be direct, and should shift blue with pressure before eventually shifting red with the (100) transition.

(c) GeSn, GaSb and ZnTe

The first member of this series is not known to exist. However, an extrapolation by HERMAN[9]

indicates that its conduction and valence band would overlap by about 0·5 eV, in which case it would be a metal and be of little interest here. The remaining members exhibit the same dependence on degree of asymmetry as the two preceding sequences. The bond lengths vary from 2·63 to 2·65 Å and there are 41 electrons per atom. The initial transition is probably direct in both compounds, with slopes of 12·3 for GaSb and 6·0 for ZnTe, in 10^{-6} eV/atm. The apparent maximum shift obtained for GaSb indicates that the least possible distance of the (100) minimum above the $k = 0$ minimum at atmospheric pressure is 0·35 eV. The next compound of the sequence is CuI, which has a higher energy gap than ZnTe, and, like CuCl and CuBr, probably has a direct transition at 1 atm, and a large blue shift of the energy gap with pressure, shifting red again at some pressure above 100,000 atm, or at about 10–12 per cent volume compression. It must be borne in mind, of course, that these three 1B–VIIB compounds may not be stable in the zinc blende form at high pressures, and could transform to the NaCl or CsCl structure.
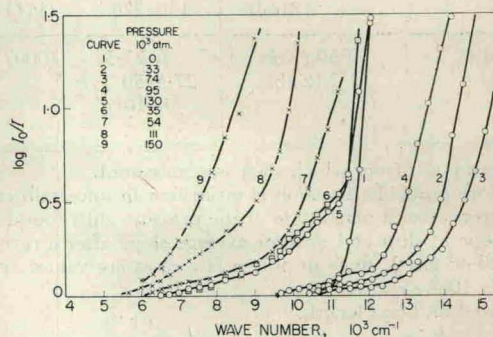

FIG. 11. Log I_0/I versus wave number for gallium arsenide.

4. COMPOUNDS WITH DISORDERING TRANSFORMATIONS

The three compounds of highest molecular weight included in this work were GaAs, GaSb and ZnTe, and these three exhibited similar effects under pressure. Figs. 11–13 show the shape of the absorption curves at different pressures for typical runs with these compounds. In each case, an absorption band appears in the long-wavelength tail of the absorption band at a sufficiently high
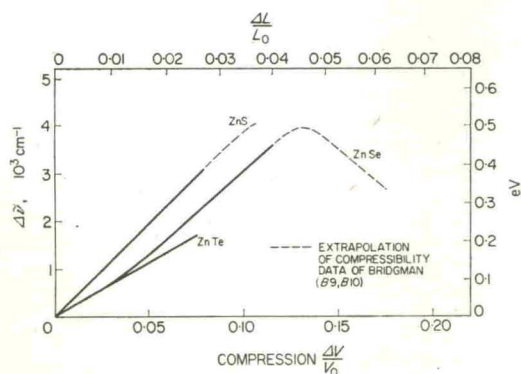
FIG. 12. Log I_0/I versus wave number for gallium antimonide.

pressure, which may in part account for the rapid shift in GaAs at high pressure. The minimum pressure at which the band first occurs depends
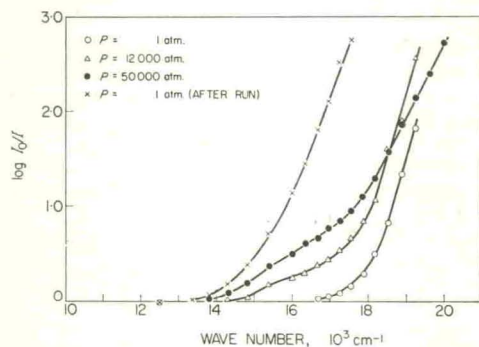

FIG. 13. Log I_0/I versus wave number for zinc telluride.

slightly on the size and preparation of the sample and on the method of loading the sample in the bomb. In general, a higher transition pressure was obtained the smaller and more perfect the sample, and the greater the difference between the height of the sample and the height of the salt pellet between the pistons. Thus, the mechanism of the process is most likely accelerated by imperfections and shear in the sample. GONSER and OKKERSE[16] have obtained a phase change of GaSb at temperatures below the melting point

Table 2. *Effect of pressure on the disorder transition of semiconductors*

Compound	$P(10^3$ atm) for $T_t = 27°C$*	$P(10^3$ atm) at which band appeared†
ZnS	184 ± 119	Not <180
ZnSe	153 ± 100	Small at 90
ZnTe	121 ± 79	12–45
GaP	218 ± 119	Not < 50
GaAs	188 ± 100	90–120
GaSb	130 ± 70	60

*Calculated using $\Delta E = 9 \pm 3$ kcal/mole for ZnS, ZnSe, and ZnTe, $\Delta E = 12 \pm 2$ kcal/mole for GaP, GaAs, and GaSb, and using $\Delta V = 6$–14 per cent of V_m in all cases.

†Very small peaks were present at lower pressures in the case of ZnTe, GaAs, and GaSb, probably due to impurities included during crystal growth. Microscopic dark specks were originally present in ZnTe, which could act as nucleating centers for phase change.

Table 3. *Effect of pressure on the decomposition of semiconductors*

Compound	ΔE_{dec}* (kcal/mole)	P for 70·7% decomp. (10^3 atm)	P for 0·71% decomp. (10^3 atm)†	$P_{absorb.}$ Peak obs. (10^3 atm)
Zns	48 ± 5	1150 ± 512	968 ± 568	Not <180
ZnSe	34 ± 3	641 ± 313	482 ± 378	Small at 90
ZnTe	29 ± 3	445 ± 217	342 ± 259	12–45‡
GaP	16 ± 2	350 ± 181	204 ± 242	Not <50
GaAs	11 ± 1	209 ± 102	80 ± 154	90–120
GaSb	$10 \pm$	152 ± 75	49 ± 117	60

*Ref. (17, 18); GaP and GaAs values assumed proportional to ZnS and ZnSe values, resp. $\Delta V = 614$ per cent of V_m.

†Where lower limit is negative, equilibrium decomposition would exceed 0·71 per cent at zero pressure.

‡Peaks did not increase greatly in size until a pressure of 45,000 atm. was reached.

by neutron irradiation, and report that the new form is a glassy solid with the liquid structure and has a volume about 8 per cent less than the normal form. The energy accompanying this process is within several per cent of the heat of fusion.

The absorption at the front of the edge could be due to the formation of this disordered state by pressure or to chemical decomposition. Table 2 shows the calculated range of pressures for melting at room temperature, using reasonable ranges of values for ΔH and ΔV. Table 3 shows similar results for 70·7 and 0·71 per cent decomposition. GaAs, GaSb and ZnTe all approach the melting pressure in the range where the band appears. Decomposition could also occur in significant amounts in GaAs and GaSb, but this is less likely for ZnTe.

It might be possible to prepare semiconductors or phosphors with controlled and uniform impurity levels by a combined application of pressure and temperature.

REFERENCES

1. FITCH R. A., SLYKHOUSE T. E. and DRICKAMER H. G., *J. Opt. Soc. Amer.* **47,** 1015 (1957).
2. SLYKHOUSE T. E. and DRICKAMER H. G., *J. Phys. Chem Solids* **7,** 207 (1958).
3. SLYKHOUSE T. E. and DRICKAMER H. G., *J. Phys. Chem. Solids* **7,** 210 (1958).
4. SHAKIN C. and BIRMAN J., *Phys. Rev.* **109,** 810, 818 (1958).
5. PIPER W. W., MARPLE D. T. F. and JOHNSON P. D., *Phys. Rev.* **110,** 223 (1958).
6. BRIDGMAN P. W., *Proc. Amer. Acad. Arts Sci.* **74,** 425 (1942); **76,** 1 (1945).
7. JOHNSON E. R. and CHRISTIAN S. M., *Phys. Rev.* **95,** 560 (1954).
8. PAUL W. and WARSCHAUER D. M., *J. Phys. Chem. Solids* **6,** 6 (1958).
9. HERMAN F., *J. Electronics* **1,** 103 (1955).
10. PAUL W. and WARSCHAUER D. M., *J. Phys. Chem. Solids* **5,** 89, 102 (1958).
11. PAUL W. and PEARSON G. L., *Phys. Rev.* **98,** 1755 (1955).
12. CALLAWAY J., *J. Electronics* **2,** 330 (1957).
13. GRAY P. V. and EHRENREICH H., *Bull. Amer. Phys. Soc.* **3,** 255 (1958).
14. SERAPHIN B., *Z. Naturforsch.* **9a,** 450 (1954).
15. WELKER H. and WEISS H., *Solid State Physics* (Ed. F. SEITZ and D. TURNBULL) Vol. 3, p. 1. Academic Press, New York (1956).
16. GONSER V. and OKKERSE B., *J. Phys. Chem. Solids* **7,** 55 (1958).
17. KIR'IASHKINA E. I., POPOV F. M., BILENKO D. I. and KIR'IASHKIN V. I., *Sov. Phys.* **2,** 69 (1955).
18. SCHOTTKY W. F. and BEVER M. B., *Acta Met.* **6,** 320 (1958).