

Table 1. Effect of pressure on band structure of semiconductors

Compound	$\Delta E_g(\text{eV})^*$ (1 atm)	$P(10^3 \text{ atm})$	Speculated transition direction†	$d\Delta E_g/dP‡$ ( $10^{-6}\text{eV/atm}$ )	$d\Delta E_g/dr§$ ( $\text{eV}/\text{\AA}$ )	Max. blue shift (eV)
Si	1.08	0-140	(100) <sup>(10,11)</sup>	-2.0	-1.12	
Ge	0.70	0-50 50-129	(111) <sup>(11)</sup> (100) <sup>(3)</sup>	+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) <sup>(12,13)</sup> (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) <sup>(4)</sup>	+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  $\alpha = 20-65 \text{ cm}^{-1}$ , since in only a few cases are values available for  $\alpha = 0$ . E.g., at  $\alpha = 0$  for germanium the slope is  $5.0 \times 10^{-6} \text{ eV/atm}$ .<sup>(10)</sup>

§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<sup>(7)</sup>.

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)

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.<sup>(12,13)</sup> 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<sup>(14)</sup> and of WELKER and WEISS<sup>(15)</sup>, 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  $\Delta_1$  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<sup>(9)</sup>

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.

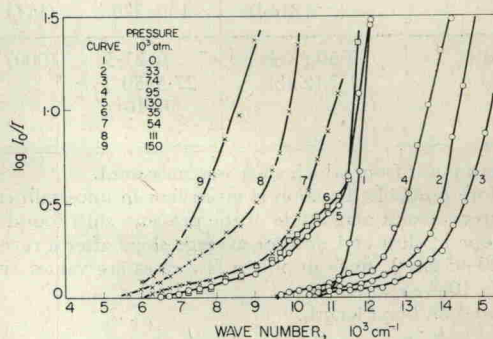


FIG. 11. Log  $I_0/I$  versus wave number for gallium arsenide.

#### 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