

## § 4. DISCUSSION

The absorption spectra of single crystals of TlBr (fig. 1) are in good agreement with the results of Bachrach and Brown (1970) who used strain-free evaporated films as specimens. Bachrach and Brown (1970) also obtained the absorption spectra of TlCl and found a striking similarity in the spectra of these compounds. The corresponding peaks  $E_0$ ,  $E_1$ ,  $E_2$ , etc. in TlCl were found at an energy approximately 0.5 to 1.0 eV higher than in TlBr. The doublet structure  $E_1$  and  $E_1 + \Delta$  arises from the spin-orbit interaction of the halogen p-states. The energy of this splitting  $\Delta$  at 4.2°K is 0.43 eV and 0.10 eV for TlBr and TlCl respectively. It should also be mentioned that the intensity of absorption of the peaks  $E_1$  and  $E_1 + \Delta$  is considerably weaker than  $E_0$ ,  $E_2$  and  $E_3$  at low temperatures.

The effect of pressure is, in general, to raise the energy of a band. The shift is expected to be large if the electron Bloch states representing the band have a large amplitude in the space outside the atomic core (Paul 1966). This means, as a rule, an s-like band under pressure will shift more than a p-like band, which in turn will shift more than a d-like band. The pressure coefficient of a band gap is then determined by the relative movement of the valence and conduction bands. This would lead normally to a negative (positive) pressure coefficient for a transition associated with an s(p)-like valence band and a p(s)-like conduction band.

4.1. Variation of the  $E_0$  Edge with Temperature and Pressure

The  $E_0$  edge of thallous halides provides an excellent example of Paul's empirical rule (1961) mentioned in § 1. The pressure coefficients at 80°K for the film samples are practically the same for all three halides, with TlBr having a somewhat larger value (table 2). This clearly indicates that the same interband states are responsible for the  $E_0$  edge in these halides. Furthermore, the pressure coefficients of the minimum band gap in the Pb chalcogenides (table 3) also show similar behaviour as well as similar values to those found in the thallous halides. Although the unit cell symmetry of the thallous halides is body-centre cubic, while that of the Pb chalcogenides is face-centre cubic, the close agreement in the pressure coefficients for the minimum gap of these materials suggests that this transition can only occur at the (111) or R point of the Brillouin zone of TlBr and TlCl, in order to be compatible with the case of the Pb chalcogenides where the minimum gap has been well established to be at the (111) or L point of the zone (Lin and Kleinman 1966, Prakash 1967, Overhof and Rössler 1970). The comparison of pressure coefficients between solids of different crystal symmetry can be made strictly only for transitions occurring at the centre of the Brillouin zone. However, it can be shown from the group character table that the centre of the zone is directly linked in each case with the (111) point. A band theoretic argument in the following section also favours the assertion that the minimum gap  $E_0$  is at the (111) or R point of the Brillouin zone of the thallous halides.

Table 3. The hydrostatic pressure coefficients and volume deformation potentials of the minimum gap  $E_0$  in thalious halides ( $80^\circ\text{K}$ ), and Pb chalcogenides (room temperature) (Prakash 1967)

Materials (film samples)	Minimum gap $E_0$ (eV)	Pressure coefficient $dE_0/dp$ ( $\times 10^{-6}$ eV/bar)	Isothermal compressibility $\beta$ ( $\times 10^{-6}$ /bar)	Volume deformation potential $\bar{V}(dE_0/dV)$ (eV)
TlCl	3.40	-8.6	3.6†	2.40
TlBr	3.03	-9.2	3.9	2.34
TlI (orthorhombic)	2.80	-8.6	—	—
PbS	0.42	-9.2	1.85	4.97
PbSe	0.27	-9.1	2.1	4.33
PbTe	0.31	-7.4	2.55	2.90

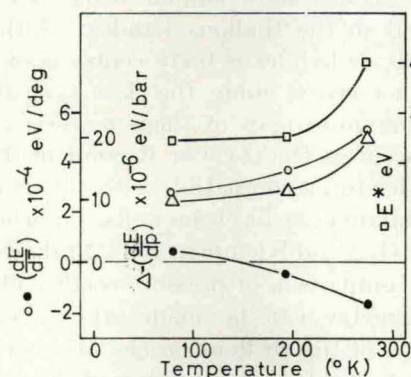
† Estimated.

The interband gap variation as a function of volume change is sometimes quoted, and the deformation potential of an energy level is used in place of the pressure coefficient. The relative volume deformation potential of a gap may be obtained from the pressure coefficient if the compressibility  $\beta$  of the solid is known:

$$V \left( \frac{dE_{ji}}{dv} \right) = V \left( \frac{dp}{dv} \right) \left( \frac{dE_{ij}}{dp} \right) = - \frac{1}{\beta} \left( \frac{dE_{ji}}{dp} \right),$$

where  $E_{ji} = E_j - E_i$  represents the energy of transition from band  $i$  to  $j$ .

Fig. 5



The variation with temperature of the pressure coefficient (triangles), volume deformation potential (squares), experimental (open circles) and explicit (solid circles) temperature coefficients, for the  $E_0$  exciton in TlBr.