

The relative volume deformation potential of the minimum gap for the thallous halides and Pb chalcogenides is shown in table 3. Considering these materials as a whole, it can be seen that the pressure coefficients do agree rather better than the deformation potentials. It is also of interest that, while according to Morse and Lawson (1967) the isothermal compressibility of TlBr decreases by approximately 10% as the pressure is increased from 1 bar to 4 kbars, the pressure coefficient remains a constant in this range. This once again indicates that as far as the thallous halides (and probably Pb chalcogenides) are concerned the pressure coefficient appears to be a more useful parameter than the deformation potential.

The temperature coefficient, the pressure coefficient and the relative volume deformation potential for the absorption peak E_0 have been plotted as functions of temperature in fig. 5. It can be seen that all these quantities have a strong temperature dependence, approaching a threshold behaviour in the region $150 \sim 200^\circ\text{K}$. The upsurge in the magnitude of the pressure coefficient (and deformation potential) at high temperatures has so far not been reported for any other material. It is not possible to say whether this property is peculiar to TlBr and TlCl. Since these materials may have considerable lattice distortion at high temperatures because of the complex nature of the phonon modes (Lowndes and Martin 1970), it is possible that the measured energy gap at a given temperature will be different from the energy gap calculated for the average interatomic distance at that temperature.

4.2. Temperature Dependence of Energy Gaps and the Electron-Phonon Interaction

It is usual (Paul, De Meis and Finegold 1962) to separate the temperature coefficient of an energy gap, E_{ji} , into a part depending only on the change in lattice constant, and a part expressing the explicit change due to electron-phonon interaction. Thus

$$\left(\frac{\partial E_{ji}}{\partial T}\right)_p = \left(\frac{\partial E_{ji}}{\partial T}\right)_v - \frac{\alpha}{\beta} \cdot \left(\frac{\partial E_{ji}}{\partial p}\right)_T,$$

where α is the volume thermal expansion coefficient and β the isothermal volume compressibility.

The first term on the right represents the electron-phonon interaction and may be calculated for a given interband gap if the pressure and temperature coefficients are known. The electron-phonon term is made up of a number of contributions of which only the most important two in a cubic solid will be briefly mentioned. These are:

(a) The virtual transitions of the electron to intermediate states via phonon scattering. Fan (1951) and Radkowsky (1948) were the first to discuss the effect of electron-phonon interactions which result in both broadening and shifting of an energy level through phonon scattering.

We are only concerned with the shift of an energy level. By perturbation theory, the change in the energy of an electron level (l, k) at temperature T (also known as the self-energy) is given by

$$\Delta E_s(l, \mathbf{k}) = \sum_{l'} \sum_{\mathbf{k}'} \frac{|M|^2}{E(l, \mathbf{k}) - E(l', \mathbf{k}')},$$

where $E(l, \mathbf{k})$ is the energy of the one-electron Bloch state of band l and wave vector \mathbf{k} , and M is the matrix element connecting the states (l, \mathbf{k}) and (l', \mathbf{k}') via real or virtual transitions. The temperature dependence of ΔE_s enters through the phonon occupancy term in M , which increases with temperature and becomes appreciable near to and above the Debye temperature. It can be seen that for a simple energy band, ΔE_s is positive (negative) at a band maximum (minimum), so that the effect of phonon scattering for a simple direct minimum gap is always negative. Fan (1951) has treated the effects due to acoustical and optical vibrations separately, and found that acoustical vibrations play an important role in materials with large deformation potential and soft phonon modes, while optical phonons are important in materials of large polarizability. It is known that phonon states of very low energy exist in the thallos halides and also that there is a large difference between the optical and static dielectric constants (Lowndes and Martin 1969). It is therefore expected that both acoustical and optical vibrations will make appreciable contributions. The calculations of ΔE_s for interband edges beyond the minimum gap is complicated by the fact that there are states near $E(l, \mathbf{k})$ with both larger and smaller energies, and the sign of ΔE_s can then be either positive or negative.

(b) Yu (1964) discussed the effect of lattice vibrations on reducing the potential which a Bloch electron sees in a solid at some finite temperature T . This is most conveniently expressed in terms of the pseudopotential form factors $V_i(k, T)$:

$$V_i(k, T) = V_i(k, 0) \exp[-2\pi^2 \langle u_i^2(T) \rangle / d^2(k)],$$

where the subscript i labels ions, $\langle u_i^2 \rangle$ is the mean square thermal displacement of the i th ion, which increases linearly with T , and $d(k)$ is the interplanar spacing associated with k . This theory has been further elucidated by Keffer, Hayes and Bienenstock (1968) and used to explain the positive explicit temperature coefficient $(\partial E_g / \partial T)_v$ in PbTe. It should be pointed out that the reduction in $V_i(k, T)$ with temperature need not always lead to a positive explicit temperature coefficient. However, in the case of the Pb chalcogenides and Tl halides, where the wave functions of states near the valence and conduction band extrema centre mainly on the metal ions, a positive contribution would be expected.

Figure 5 shows that the explicit temperature coefficient $(\partial E_0 / \partial T)_v$ for the minimum gap E_0 in TlBr starts off with a small positive value (close to experimental error) at low temperature, goes through zero and becomes significantly negative as the temperature is raised beyond the Debye