

temperature ( $\sim 130^\circ\text{K}$ ). In the absence of a detailed analysis of the individual contributions above, we suggest that both acoustical and optical phonon scattering are important and are probably responsible for the negative explicit temperature coefficient at high temperature ( $\sim 130^\circ\text{K}$ ), while the Debye–Waller correction to the pseudopotential gives the more important contribution at lower temperatures ( $\sim 80^\circ\text{K}$ ). The explicit temperature coefficient for the Pb chalcogenides, on the other hand, has a much greater positive value (Prakash 1967). This is probably due to the significant reduction in the contribution from optical phonon scattering compared to the Tl halides.

#### 4.3. Band Structure of TlBr and the Interpretation of High Energy Transitions

The following discussion on the band structure of TlBr is based largely on plausible arguments derived from the overlap of atomic orbitals whose energies are given by Herman and Skillman (1963). The comparison is made with the band structures of the isoelectronic Pb chalcogenides (Overhof and Rössler 1970), and isomorphous CsI (Onodera 1968). The band gaps have been chosen to agree with the pronounced features in the absorption spectra.

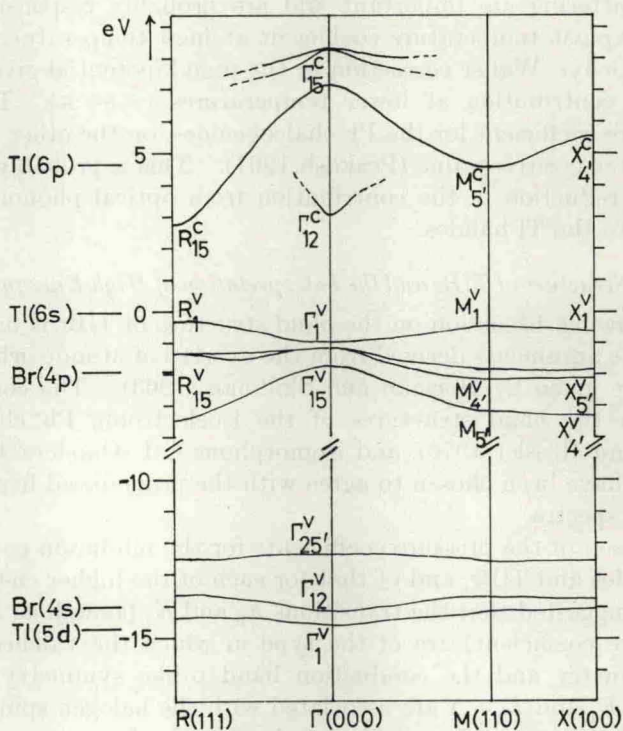
Comparison of the pressure coefficients for the minimum gap in the Pb chalcogenides and TlBr, and of that for each of the higher energy gaps in TlBr, has suggested that the transitions  $E_0$  and  $E_2$  (as well as  $E_3$  from the temperature coefficient) are of the type in which the valence band has s-like symmetry and the conduction band p-like symmetry, while the transitions  $E_1$  and  $E_1 + \Delta$  are associated with the halogen spin-orbit split p-like bands and possibly a d-like conduction band.

We consider the outer electron orbital states in TlBr,  $\text{Tl}^+ : 5d^{10} 6s^2 (6p\ 5f)$  and  $\text{Br}^- : 4s^2 4p^6(4d)$ , where empty states are shown in brackets. The relative energies of these states (Herman and Skillman 1963) are indicated in fig. 6. From a knowledge of the band structure of the Pb chalcogenides obtained using muffin-tin potentials (Overhof and Rössler 1970), it is reasonable to expect that these levels represent a fair estimate of the actual energy bands at the  $\Gamma(000)$  point of the Brillouin zone. The approximation is better for those states whose wave functions are centred on the Br ions. However, corrections due to relativistic effects, and the reduction in the screening on the s electrons after the removal of the p electrons in the heavy Tl ions, have to be taken into account when considering those levels associated with the Tl orbitals.

The relativistic corrections and the normalization of the Bloch wave functions, as in the case of the Pb chalcogenides, lead to spin-orbit splitting and to an increase in the energy of the Tl levels. The reduction in the screening will, however, shift the Tl(6s) level in the opposite direction. The net result is an increase in the gap between Tl(6s) and (6p) and a decrease between Tl(6s) and Br(4p) at  $\Gamma$ .

We may now speculate on a possible band structure for TlBr and this is shown in fig. 6. The conduction band is made up predominantly of Tl(6p)

Fig. 6



Possible band structure of TlBr; the atomic energy levels for the outer electronic shells are indicated.

states. It has a number of minima all situated near the edges of the Brillouin zone. The lowest of these minima will be found at R(111). The spin-orbit splitting at  $\Gamma(000)$  of the conduction band is of the order of 1.2 eV. The Tl(6s) states will dominate throughout the upper valence band, with the maximum at R(111) and a number of subsidiary maxima at M(110) and X(100). Approximately 0.5 eV below the Tl(6s) band at  $\Gamma$ , lies a second valence band made up of predominantly Br(4p) states. The maximum is at  $\Gamma$  with a spin-orbit splitting  $\Delta$  of approximately 0.43 eV.

The gross features of the band structure of TlBr are so far not unlike those of PbSe. An important deviation, however, is introduced as a consequence of the CsCl crystal structure of TlBr. This is the presence of a fluted conduction band minimum at  $\Gamma$  which is mainly made up of Br(4d) and Tl(5f, 6d) states (Onodera 1968).

The prominent absorption peaks are assigned to the following transitions (single group representations are given; superscript c denotes conduction