Table 1

The pressure coefficient of the first exciton peak in the optical spectra of thallous, lead, and bismuth halides

| | $E_o$ (eV) | $(\partial E_o/\partial p)_T$ ($10^{-6}$ eV/bar) | T (°K) | $(\partial E/\partial T)_{average}$ ($10^{-4}$ eV/deg) |
|---|---|---|---|---|
| TlBr cubic | 3.0 | $-20.1 \pm 1.0$<br>$-9.5 \pm 0.4$ | 274<br>80 | +3.4 |
| $PbI_2$ layer | 2.5 | $-18.5 \pm 1.0$<br>$-16.5 \pm 0.5$ | 294<br>80 | -1.25 |
| $BiI_3$ layer | 2.0 | $-16.6 \pm 1.0$<br>$-11.2 \pm 0.8$ | 274<br>80 | -2.6 |

perimental investigations (8) and energy band calculations (9) for TlBr have established that the $E_o$ exciton peak in TlBr is associated with a valence band maximum in which there is a significant contribution from the Tl ion 6s-states. The appropriate conduction band is formed from Tl p-states. The large negative pressure coefficients which are obtained in the case of $PbI_2$ and $BiI_3$ therefore provide strong evidence of significant contributions from metal 6s-states to the upper valence band in each material, since states of s-like symmetry rise in energy much faster under pressure than do p- or d-like states.

The detailed band structure of $PbI_2$ and $BiI_3$ is not known, and an unequivocal assignation of the transition associated with the peak $E_o$ in each material to a specific critical point in the Brillouin zone cannot be made. However, considerations of band curvature suggest that in common with the thallous halides, the first transition in both $PbI_2$ and $BiI_3$ is likely to occur at the zone boundary.

It was found for thallous bromide (8) that the positive temperature coefficient of the $E_o$ peak energy may be attributed substantially to the effect of lattice dilatation, with a relatively small electron-lattice interaction term $(\partial E/\partial T)_V$. In the case of $PbI_2$ and $BiI_3$ however, the energy of the first peak in optical absorption has both a negative temperature coefficient (10, 7) and a large negative pressure coefficient, so that the electron-lattice interaction term must be negative in both materials, with a magnitude greater than that of the total temperature coefficient.