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 ± 1.0 -9.5 ± 0.4	274 80	+3.4
PbI_2 layer	2.5	-18.5 ± 1.0 -16.5 ± 0.5	294 80	-1.25
BiI_3 layer	2.0	-16.6 ± 1.0 -11.2 ± 0.8	274 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.