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The Effect of Hydrostatic Pressure on the Energy of the Bandgap  
Exciton Peak in the Layer Crystals Lead Iodide and Bismuth Iodide

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The pressure coefficient of the energy for the first sharp exciton peak in the optical absorption spectra of lead iodide  $\text{PbI}_2$  and bismuth iodide  $\text{BiI}_3$ , has been measured and the values are compared with those for the first exciton in thallos bromide  $\text{TlBr}$ .

Thallium, lead, and bismuth occupy successive positions in the periodic table, and have the outer electronic configurations:  $\text{Tl } 6s^2 6p^1$ ;  $\text{Pb } 6s^2 6p^2$ ;  $\text{Bi } 6s^2 6p^3$ . The metals are respectively mono-, di- and tri-valent in the stable form, and when the halides are formed, it is primarily the 6p-electrons in each metal which are involved in the bonding, leaving the 6s-levels occupied in each case. It has therefore been suggested (1, 2) that the upper valence band in the layer crystals  $\text{PbI}_2$  and  $\text{BiI}_3$  will be formed from iodide  $5p_z$ -states, with contributions from the metal ion 6s-states. The lowest conduction band is expected to be formed from the metal ion 6p-states in each case. The strong exciton peak which is observed in the optical absorption spectrum of  $\text{PbI}_2$  (3 to 6) and  $\text{BiI}_3$  (5, 7) is likely to be associated with the minimum bandgap in each material, and the variation of the exciton peak energy with pressure has been measured in order to obtain information concerning the associated band extrema.

Single crystals of  $\text{PbI}_2$  and  $\text{BiI}_3$  grown by vacuum sublimation were cleaved by means of transparent adhesive tape to about  $1000 \text{ \AA}$ , at which thickness optical transmission measurements could be made in the vicinity of the exciton peak energy at 2.5 eV in  $\text{PbI}_2$  and 2.0 eV in  $\text{BiI}_3$ . The pressure apparatus used has already been described (8).

The exciton peak in both  $\text{PbI}_2$  and  $\text{BiI}_3$  was found to move rapidly, linearly and reversibly to lower energy under pressure. The pressure coefficients are given in Table 1, together with the corresponding data for thallos bromide  $\text{TlBr}$  (8). Ex-

Table 1

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

	$E_0$ (eV)	$(\partial E_0 / \partial p)_T$ ( $10^{-6}$ eV/bar)	T ( $^{\circ}$ K)	$(\partial E / \partial T)$ average ( $10^{-4}$ eV/deg)
TlBr cubic	3.0	$-20.1 \pm 1.0$	274	+3.4
		$-9.5 \pm 0.4$	80	
PbI <sub>2</sub> layer	2.5	$-18.5 \pm 1.0$	294	-1.25
		$-16.5 \pm 0.5$	80	
BiI <sub>3</sub> layer	2.0	$-16.6 \pm 1.0$	274	-2.6
		$-11.2 \pm 0.8$	80	

perimental investigations (8) and energy band calculations (9) for TlBr have established that the  $E_0$  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<sub>2</sub> and BiI<sub>3</sub> 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<sub>2</sub> and BiI<sub>3</sub> is not known, and an unequivocal assignation of the transition associated with the peak  $E_0$  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 thallos halides, the first transition in both PbI<sub>2</sub> and BiI<sub>3</sub> is likely to occur at the zone boundary.

It was found for thallos bromide (8) that the positive temperature coefficient of the  $E_0$  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<sub>2</sub> and BiI<sub>3</sub> 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.

the optical spectra of thalloses

$(\partial E/\partial T)$ average ( $10^{-4}$ eV/deg)
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-1.25
-2.6

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