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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 PbI_2 and bismuth iodide BiI_3, has been measured and the values are compared with those for the first exciton in thallous bromide TlBr.

Thallium, lead, and bismuth occupy successive positions in the periodic table, and have the outer electronic configurations: Tl $6s^2 6p^1$: Pb $6s^2 6p^2$: 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 PbI_2 and 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 PbI_2 (3 to 6) and 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 PbI_2 and BiI_3 grown by vacuum sublimation were cleaved by means of transparent adhesive tape to about 1000 Å, at which thickness optical transmission measurements could be made in the vicinity of the exciton peak energy at 2.5 eV in PbI_2 and 2.0 eV in BiI_3. The pressure apparatus used has already been described (8).

The exciton peak in both PbI_2 and 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 thallous bromide TlBr (8). Ex-