A band structure for TlBr has been deduced, which satisfactorily explains the negative pressure coefficient and the positive temperature coefficient for the thallous halides. The general feature in which the valence band maxima are s-like and the conduction band minima are p-like will probably prevail in compounds other than the isoelectronic PbSe, for example in PbI_2, BiI_3 and TlN_3. A first principle theoretical band structure calculation† for these materials will be difficult, not only because some of the constituent elements are fairly heavy, but also because there are often a number of band extrema lying close together in a small energy range. Such a difficulty has already been experienced in the band structure calculations of the Pb chalcogenides (Conklin, Johnson and Pratt 1965, Lin and Kleinman 1966, Rabii 1968, Overhof and Rössler 1970). The band structure of TlBr also predicts the existence of 'cation' excitons, whose electron and hole wave functions are centred on the Tl ions. It would be useful to make a more detailed study of the properties of this type of exciton. The sensitive electro-modulation technique could be used to reveal any fine structure associated with the exciton, provided that strain can be avoided in the preparation of the specimen.

The explicit temperature coefficient for the minimum gap of TlBr which changes sign in the neighbourhood of the Debye temperature and becomes negative at higher temperatures suggests that the electron–phonon interaction is complex. A qualitative analysis based on Fan's self-energy theory and the Debye–Waller correction has been given.

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† A calculation has now been made by Overhof and Treusch (1970) which places the minimum band gap at X.

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