band and v valence band):

$$E_0: \quad R_1^v \to \text{lower branch of } R_{15}^c,$$
$$E_1 \text{ and } E_1 + \Delta: \quad \Gamma_{15}^v \to \Gamma_{12}^c,$$
$$E_2: \quad M_1^v \to M_{5'}^c,$$
$$E_3: \quad X_1^v \to X_{4'}^c.$$

In addition to these absorption peaks, Hinson and Stevenson (1967) have observed strong features in the ϵ_2 curve (from reflectivity measurements) of TlBr at 10·2 ev, 14·7 ev and 16·4 ev. The last two are likely to be associated with transitions from the Tl(5d) and Br(4s) valence bands, and the first to a transition from Γ_{15}^v to the upper branch of the conduction d states ($\Gamma_{25'}$ not shown). It is possible that E_1 and $E_1 + \Delta$ are associated with the transition $R_{15}^v \to R_{15}^c$, though this assignment seems less probable from a consideration of the selection rules. The assignment for E_2 and E_3 may also be interchanged.

The proposed band structure and the assignment of optical transitions are consistent with the dependence of the band energies with temperature and pressure. It is not accidental that the maximum absorption occurs in the neighbourhood of E_3 (see also Hinson and Stevenson 1967), since the region in k-space near (100) is capable of giving a high density of states for optical transitions. This can also be seen from the virtually parallel bands between M(110) and X(100). The average energy gap $\langle E_g \rangle$ can be calculated using

$$\epsilon_\infty = 1 + \left(\frac{E_p}{\langle E_g \rangle} \right)^2,$$

where ϵ_∞ is the high frequency dielectric constant and E_p the free electron plasma energy. Assuming $\epsilon_\infty = 5\cdot6$ and the plasma energy calculated as 13·5 ev for eight valence electrons per formula unit, $\langle E_g \rangle = 6\cdot3$ ev, which is in agreement with the observation that the maximum absorption occurs in the neighbourhood of this energy. A more detailed discussion on this topic is given by Phillips (1969).

From the similarity between the absorption spectra of TlCl and TlBr (Bachrach and Brown 1970), the band structures of these materials are also expected to be similar. It is however of interest that while the pressure coefficients for the band gaps are negative and the lattice constant for TlBr is 3·97 Å compared with TlCl 3·83 Å, the energies of these gaps are larger in TlCl than in TlBr. The explanation appears to be connected with the difference in ionicity between these two materials. Thus a greater reduction in the screening of the Tl(6s) electrons in TlCl due to more complete charge transfer from Tl(6p) to Cl(3p), will give rise to a bigger Tl(6s) to Tl(6p) energy gap, despite the opposing effect due to the reduction in lattice constants.

4.4. *The Properties of 'Cation' Excitons*

Unlike the alkali halides in which an exciton may be regarded, in crude terms, as the excitation of an anion valence electron, an exciton in Tl

halides is associated with the valence electrons of the Tl cation. The conduction band is made up of cation states in both cases. In other words, the amplitude of the Bloch wave functions representing both the electron and hole in Tl halides are centred on the cations. Such excitons appear to have extremely narrow line widths at low temperatures, yet attempts to find the higher order excitons have not been successful. Two side bands at energies 0·013 and 0·032 ev higher than the E_0 exciton energy have been observed in TlBr at 4·2°K (fig. 7). The shape and position of these side bands suggest, however, that these derive from the bound states of an exciton with one or more phonons (Liang and Yoffe 1968). A distinct exciton absorption at 273°K, on the other hand, suggests that the binding energy is comparable or greater in magnitude than the thermal energy, i.e. ⩾ 0·024 ev.

Fig. 7
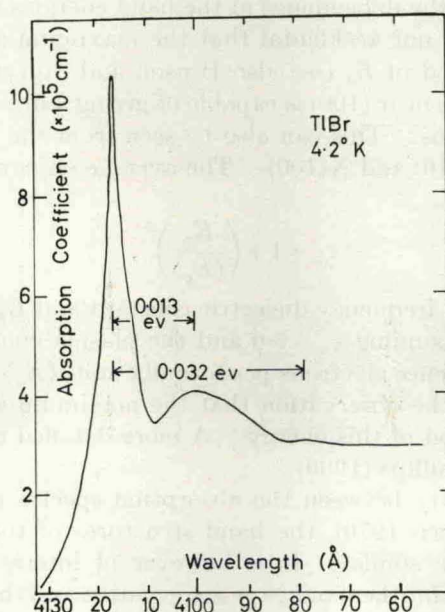
Fine structure near the E_0 exciton in single crystals of TlBr at 4·2°K.

§ 5. CONCLUSION

The transmission spectra of very thin single crystals of TlBr and evaporated films of TlCl and TlI have been measured, and by using thin samples it has been possible to study accurately the change in energy of well-defined features such as exciton peaks with pressure. A strong temperature dependence of the pressure coefficient and deformation potential of the minimum gap has been observed, and there is as yet no convincing explanation to this phenomenon.