

The spectrum of the thallos ion in alkali halides consists of a low-frequency and a high-frequency peak ('A' and 'C') corresponding to the $^1S_0 \rightarrow ^3P_1$ and $^1S_0 \rightarrow ^1P_1$ transitions.⁽²⁾ A third peak (the 'B' peak) occurs between 'A' and 'C' in CsI : Tl and in some other alkali chlorides.⁽³⁾

Fig. 1 shows the shifts of the 'A' peak with pressure to 50,000 atm in three potassium halides. All three potassium salts have the face-centered NaCl structure below about 19,000 atm, at which pressure they transform to the simple cubic CsCl lattice.⁽⁴⁾ In the region below the transition, all three show a red shift with increasing pressure and the magnitude is the same for all three salts. This is consistent with other evidence^(2,5) that the phenomenon is confined to the impurity ion and does not involve an electron-transfer process. At the transition there is a discontinuous blue shift for KCl : Tl a smaller blue shift for KBr : Tl, and a red shift for KI : Tl. It seems probable that the direction

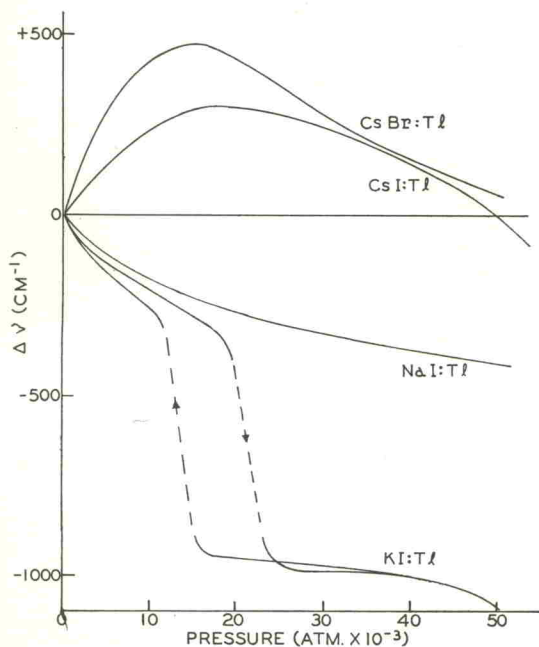


FIG. 2. 'A' peak frequency shift versus pressure to 50,000 atm MX : Tl.

and magnitude of the shift are associated with the increasing polarizability of the halide ions ($I^- > Br^- > Cl^-$), but a really satisfactory explanation is not yet available. The difference between

the location of the transition on raising and lowering the pressure is due to the 'region of indifference' (region of metastability) discussed by BRIDGMAN.⁽⁴⁾ The effect of friction amounts to about 5 per cent.

Fig. 2 compares the 'A' peaks in KI : Tl, NaI : Tl, CsI : Tl, and CsBr : Tl to 50,000 atm. NaI has the face-centered cubic NaCl lattice. CsBr and CsI have the simple cubic CsCl lattice. The NaI : Tl closely resembles the potassium salts, except that it has no transition. The cesium salts show a blue shift in the low-pressure region followed by a red shift at higher pressures. The two salts give qualitatively similar results, although the blue shift on CsI : Tl is less than that of CsBr : Tl by an amount distinctly exceeding the experimental error. This again may be associated with the higher polarizability of the iodide ion.

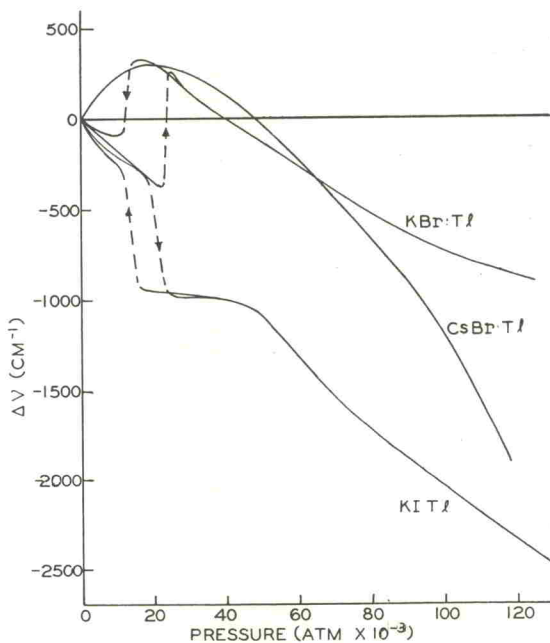


FIG. 3. 'A' peak frequency shift versus pressure to 130,000 atm.

Fig. 3 shows the shifts of the 'A' peak with pressure to 130,000 atm for KBr : Tl, KI : Tl, and CsI : Tl. In the high-pressure region these all have the simple cubic CsCl structure and they all show large red shifts.

The 'B' peak does not appear in the KI : Tl

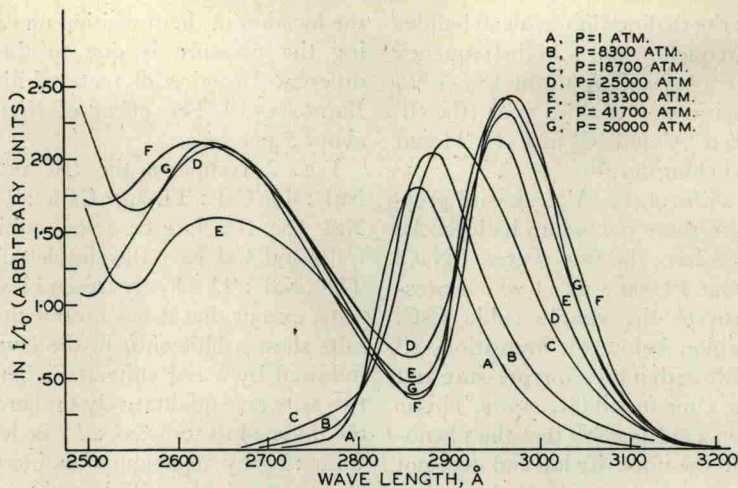


FIG. 4. Spectra of KI : Tl to 50,000 atm.

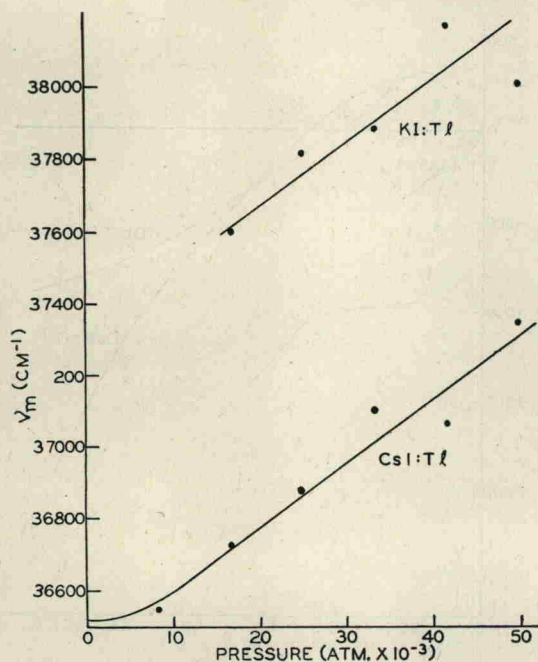


FIG. 5. 'B' peak frequency shift versus pressure.

at atmospheric pressure. It appears sharply in KI : Tl at the transition and disappears immediately upon lowering the pressure through the transition. The spectra are illustrated in Fig. 4. The 'B' peak shifts blue with increasing pressure, as is shown in Fig. 5. The two curves appear to have the same slope with pressure, but the data

were much harder to determine accurately than in the case of the 'A' peaks, and there was more scatter.

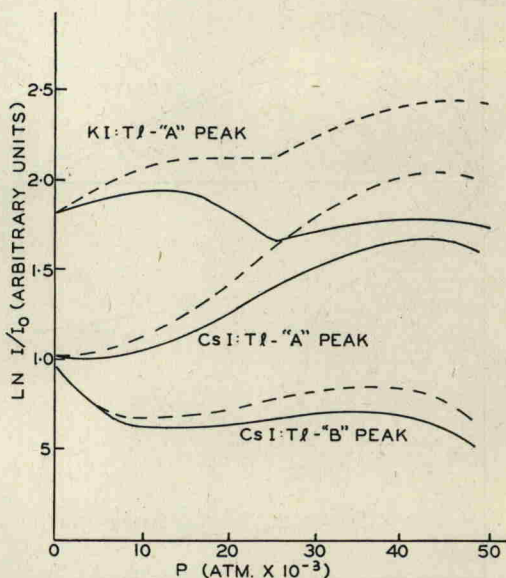


FIG. 6. Variation of peak intensity with pressure.

Fig. 6 shows the estimated change in peak intensity with pressure, both uncorrected and corrected for the increase of material in the light path. The slight drop in intensity near 50,000 atm is probably not real, but is due to the piston cutting across the window.