THE EFFECT OF PRESSURE ON THE SPECTRA OF THE Tl+ ION IN ALKALI HALIDE LATTICES*

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Abstract—The effect of pressure on the spectra of the Tl+ ion in several alkali halide lattices has been measured to 130,000 atm (in some cases to 50,000 atm). The results can be summarized as follows:

(1) In the face-centered cubic lattice, the 'A' peak shows a red shift with increasing pressure. The magnitude of the shift is independent of the alkali halide involved.

(2) In the simple cubic lattice, the 'A' peak shifts blue at low pressures (up to 15,000 atm) and red at high pressures (above about 25,000 atm).

(3) At the phase transition in the potassium halides, KCl : Tl and KBr : Tl show a discontinuous blue shift; KI : Tl shows a red shift.

(4) The 'B' peak appears in CsI : Tl and also appears discontinuously at the transition to the simple cubic lattice in KI : Tl. It shifts blue with pressure.

The results are, in most ways, consistent with available theory.

THE absorption spectra of Tl+ ions in alkali halide lattices have been measured as a function of pressure to about 130,000 atm (in some cases to 50,000 atm). The systems studied and the pressure range for each are shown in Table 1. The crystals used

Table 1. *Systems studied and pressure range*

System	Maximum pressure (atm)
KCl : Tl	50,000
KBr : Tl	130,000
KI : Tl	129,500
NaI : Tl	50,000
CsBr : Tl	50,000
CsI : Tl	118,000

were obtained from Harshaw Chemical Company and contained 0·1–0·2 per cent Tl+. The pressure apparatus has been described elsewhere.[1] Each pressure run was repeated with at least two separate loadings, and several were run four or five times.
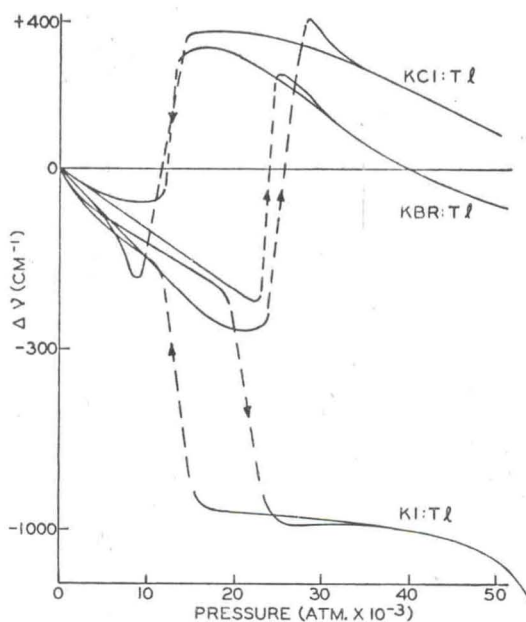
FIG. 1. 'A' peak frequency shift versus pressure to 50,000 atm—3 KX : Tl crystals.

The maximum scatter from the smoothed curves was ± 100 cm^{-1}, and the average scatter was not over one-half this value.

180

The spectrum of the thallous ion in alkali halides consists of a low-frequency and a high-frequency peak ('A' and 'C') corresponding to the $^1S_0 \to {}^3P_1$ and $^1S_0 > {}^1P_1$ 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
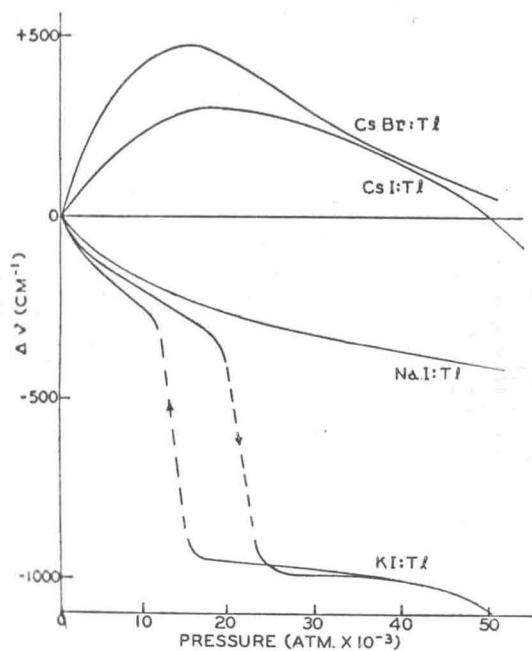
the location of the transition on raising and lowering the pressure is due to the 'region of indifference' (region of metastability) discussed by BRIDGMAN.[4] The effect of friction amounts to about 5 per cent.

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.
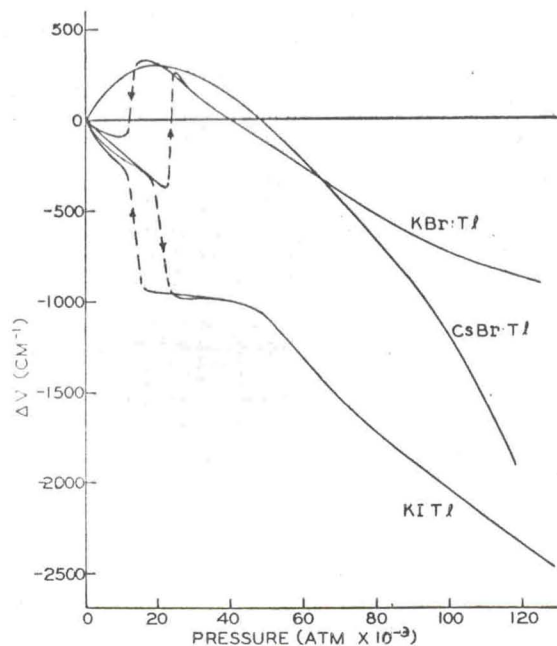

FIG. 2. 'A' peak frequency shift versus pressure to 50,000 atm MX : Tl.

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

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

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.

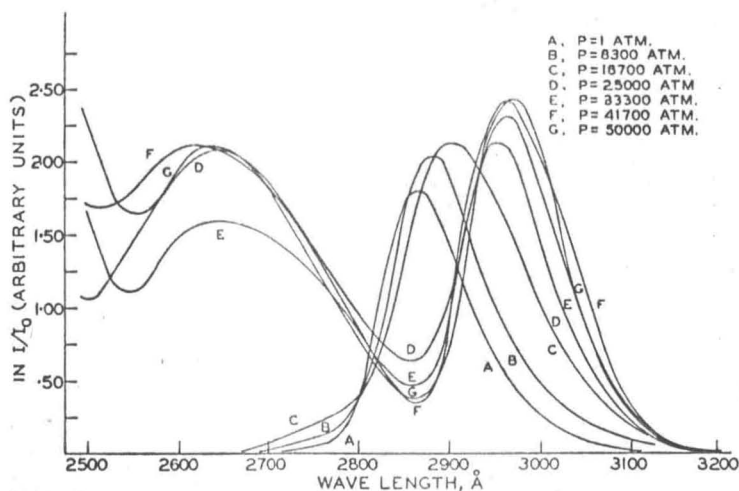The 'B' peak does not appear in the KI : Tl
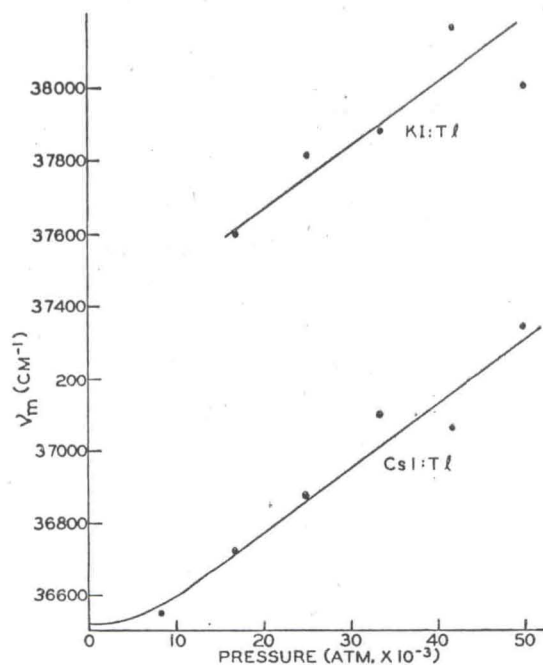
FIG. 4. Spectra of KI : Tl to 50,000 atm.

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

FIG. 6. Variation of peak intensity with pressure.

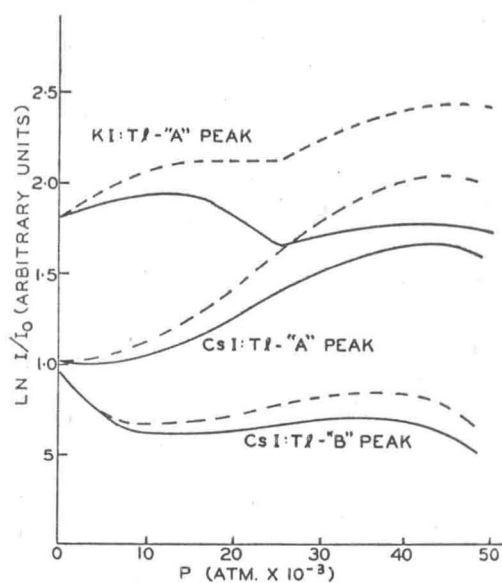were much harder to determine accurately than in the case of the 'A' peaks, and there was more scatter.

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

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.

The results obtained are generally consistent with the configurational co-ordinate model proposed by SEITZ[2] and amplified by WILLIAMS.[6] However, since the 'B' band appears so sharply at the transition and disappears equally sharply below
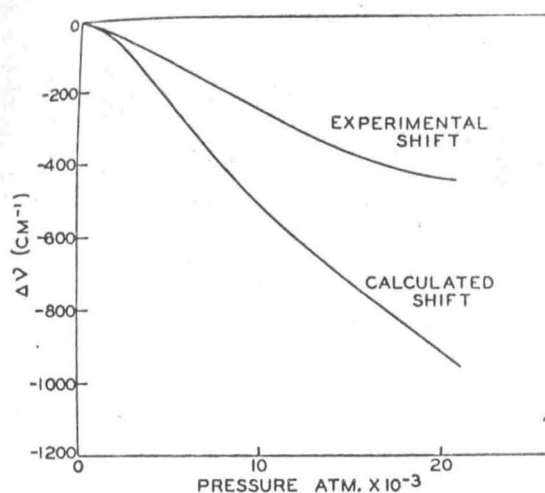

FIG. 7. Comparison of WILLIAMS' theory with experiment.

the transition, it is doubtful that it is associated with lack of cubic symmetry due to imperfections, as has been suggested.[2]

JOHNSON and WILLIAMS[7] have proposed a model for calculation of the effect of pressure on the 'A' peak for KCl : Tl. Using this model, calculations have been made to 20,000 atm. These are compared with experiment in Fig. 7. The calculation predicts the correct direction for the shift, but about twice the magnitude obtained experimentally. The discrepancy is probably associated with the assumption that pressure contributes equally to the ground and first excited states of the thallous ion.

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