

Table 2. Spectral location of the "A" band adsorption due to impurities in alkali halide crystals

Crystal	Impurity	Peak (Å)	Ref. No.	Max. pressure (atm.)
NaCl	Thallium	2540	8	50000
NaBr	Thallium	2670	8	127000
NaI	Thallium	2930	8	50000
KCl	Thallium	2475	8	50000
KBr	Thallium	2610	8	130000
KI	Thallium	2870	8	129500
RbBr	Thallium	2590	8	94000
RbI	Thallium	2860	8	110000
CsBr	Thallium	2630	8	158000
CsI	Thallium	2990	8	118000
0.8KI/0.2KBr	Thallium	2858	—	124000
0.6KI/0.4KBr	Thallium	2836	—	50000
0.4KI/0.6KBr	Thallium	2810	—	50000
0.2KI/0.8KBr	Thallium	2708	—	50000
KCl	Indium	2815	9	120500
KBr	Indium	2930	10	131000
KBr	Bismuth	3712	—	114000
NaCl	Lead	2740	11	131000
NaBr	Lead	3040	11	111500
NaI	Lead	3578	—	50000
KCl	Lead	2730	11	140000
KBr	Lead	3020	11	170000
KI	Lead	3542	—	130500
RbCl	Lead	2720	11	50000
RbBr	Lead	3004	—	120000
RbI	Lead	3541	—	5000
CsCl	Lead	2849	—	89000
CsI	Lead	3705	—	50000
NH ₄ Br	Lead	3077	—	143000
NH ₄ I	Lead	3580	—	1
KCl	Copper (ic)	2650	12	50000
KBr	Copper (ic)	2650	12	117000

ions next to the impurity produce at most a perturbation on the system, but not a first-order effect. This is consistent with the Seitz model, but inconsistent with the complex ion model.

At phase transitions, such as occur in the potassium halides at around 20,000 atm, a discontinuous shift in the A-band frequency is observed. These shifts are to lower energies for the alkali iodides and to higher energies for the alkali bromides or chlorides. This is possibly related to the much stronger spin-orbital interaction

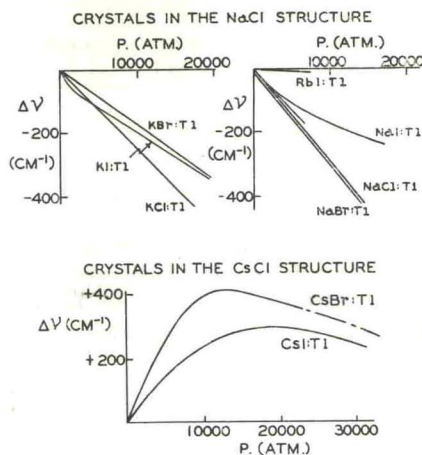


FIG. 2. Initial frequency shift vs. pressure—ten alkali halides activated by Tl⁺.

of the iodide ion, compared to the chloride or bromide.

A study was made to determine if varying the impurity concentration affected the pressure shift of the impurity spectra. Thallium activated potassium iodide, in concentrations from 2×10^{-1} per cent to 4×10^{-3} per cent was used for the study. No dependence on concentration was observed.

Measurements have been made of the spectra of several mixed crystals of potassium bromide and potassium iodide, activated by thallium, and of the effect of pressure on this spectra. The spectral

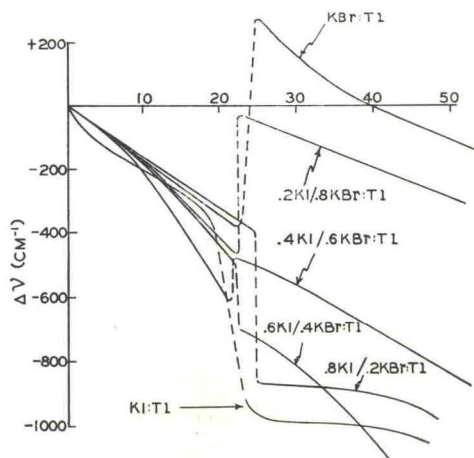


FIG. 3. The effect of pressure on A-band spectra in mixed crystals of KI:Tl and KBr:Tl.

position of the *A* band at 1 atm. in these mixed crystals is tabulated in Table 2. It can be seen that in the mixed crystals, the iodide ion is a much stronger perturbing force than the bromide ion, since the mixed crystal spectra are displaced towards KI:Tl. This is to be expected, since the iodide ion is both larger and more polarizable than the bromide ion.

The effect of pressure on these mixed crystals is shown in Fig. 3. A gradual change in the magnitude of the transition discontinuity occurs, proceeding from KI:Tl to KBr:Tl in a regular manner.

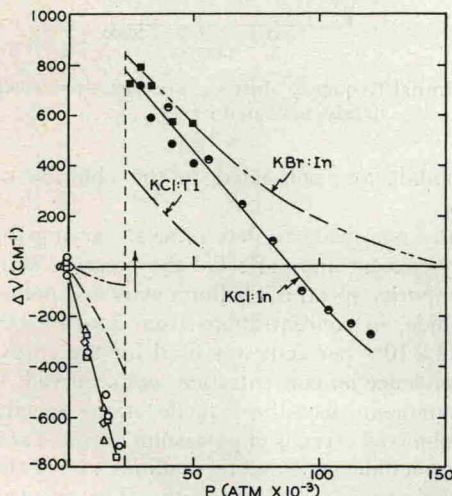


FIG. 4. "A" peak frequency vs. pressure—KCl:In; KBr:In (KCl:Tl shown for comparison); data points are for KCl:In.

The effect of pressure on the In⁺ ion in alkali halide lattices

Studies have also been made of the effect of pressure on the spectra of the *A* band in potassium chloride and potassium bromide activated by indium (see Fig. 4). The shifts are similar to those for thallium, but greater in magnitude. This difference can possibly be attributed to the difference in ground state force constant of the two impurity ions.

The effect of pressure on the lead ion in alkali halide lattices

The effect of pressure on the spectra of the *A* band in twelve alkali halides activated with lead

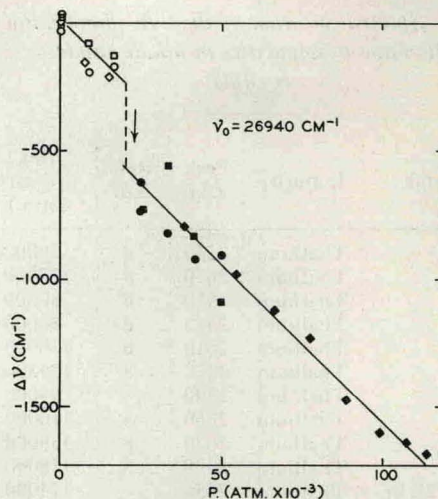


FIG. 5. "A" peak frequency vs. pressure—KBr:Bi.

has been measured to as high as 170,000 atm. The systems studied and the pressure range for each are given in Table 2. The data are shown in Figs. 6-8. In general, the frequency of the band initially shifts to higher energy, except at phase transitions. Then, at very high pressures the shift reverses and moves to lower energy. It is believed that the tendency to shift to higher energy may be connected

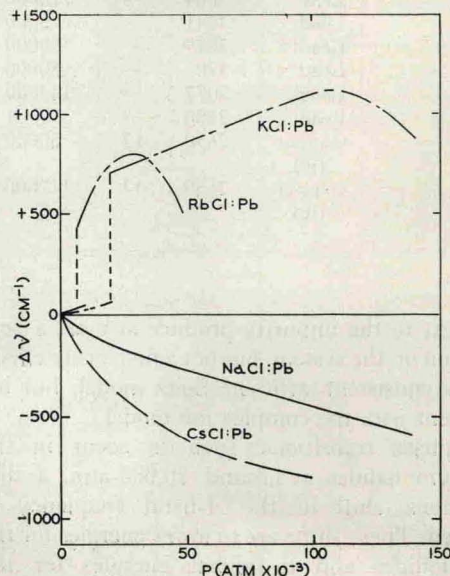


FIG. 6. "A" peak frequency vs. pressure—four alkali chlorides activated by Pb²⁺.