

Fig. 2. The shortest interionic distances of alkali halides in the NaCl structure as a function of pressure.

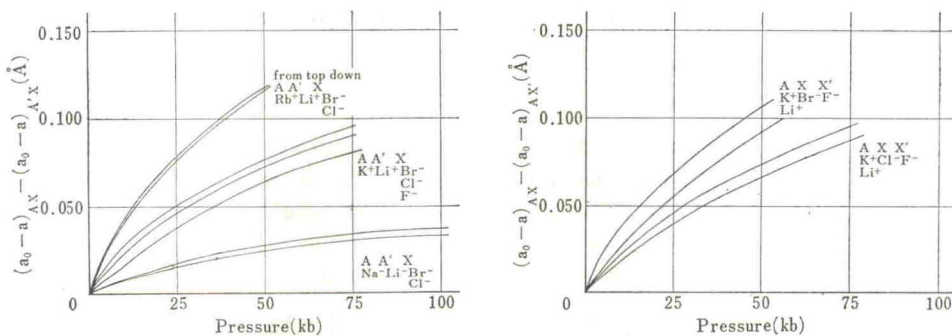


Fig. 3 and Fig. 4. The examinations of the additive character of the ionic radii in the NaCl structure.

becomes better or not increasing pressure. In Fig.'s 3 and 4 the calculated results are given. We can say that the approximation is also fair at high pressure, but not so fair as at atmospheric pressure. The ions in the CsCl structure will be treated in the next part B.

Ions in CsCl structure

The alkali halides except CsCl, CsBr and CsI have the NaCl structure at atmospheric pressure. But, increasing pressure, some alkali halides transform to the CsCl structure⁵⁾. The theoretical treatments of the transitions of these

Table 2. Calculated values of a'_0 's and a'_0/ρ 's

Compound	$\frac{a'_0(\text{\AA})}{T=273^\circ\text{C}, P=0}$	a'_0/ρ
KCl	3.250	10.02
KBr	3.460	10.21
KI	3.642	10.39
RbCl	3.394	9.198
RbBr	3.558	10.19
RbI	3.785	10.75

alkali halides are as follows¹⁾. We assume that the experimental parameters b and p in eq. (1) are independent of pressure and structures. With this assumption a'_0 for the CsCl structure corresponding to a_0 for the NaCl structure can be calculated. Substituting a'_0 instead of a_0 into eq. (2), we can calculate the lattice energies of those alkali halides in the CsCl structure and then, the Gibbs' free energies. The stability of a structure is determined by the magnitude of the Gibbs' free energy for each structure. The Gibbs' free energy of each alkali halides except CsCl, CsBr and CsI has a smaller value in the NaCl structure than that in the CsCl structure below the transition pressure. Therefore a'_0 's of those alkali halides are the imaginary nearest neighbor distances in the CsCl structure. However, these a'_0 's are useful to examine the additive character of ionic radii in the CsCl structure. The imaginary nearest neighbor distance a' is calculated by the equation

$$\frac{1}{a'^2} \exp\left(\frac{a'_0}{\rho}\right) = \frac{8\alpha}{6\alpha'} \cdot \frac{1}{a_0^2} \exp\left(\frac{a_0}{\rho}\right) \quad (9)$$

where α' is the Madelung constant for the CsCl structure and a_0 is the actual nearest neighbor distance in the NaCl structure at room temperature and atmospheric pressure. In Table 2, the imaginary nearest neighbor distances a'_0 's and a'_0/ρ 's of some alkali halides are given.

Using a'_0 and c ($=2/\sqrt{3}a'_0$) in eq. (5), eq. (6) becomes

$$P = \frac{\alpha'}{4.611} \cdot \frac{e^2}{K'^{1/2}a'^4} \left[K'^{2/3} \exp\left\{\frac{a'_0}{\rho}(1 - K'^{1/3})\right\} - 1 \right] \quad (10)$$

where K' is defined as $K'=(a'/a_0)^3$ and a' is the nearest neighbor distance in the CsCl structure at pressure P . The calculated results of P - K' relations are shown in Fig. 5. Here we extended the calculations to the pressure regions in which the NaCl structure is more stable for same alkali halides. Fig. 6 shows P - a' relations which are calculated to examine additive character of ionic radii at high pressure. We compare our results with the observed values by Bridgman⁵⁾ in Fig. 5. The imaginary nearest neighbor distances were obtained by the extrapolations in these cases. Here the solid curves (except the curves for CsCl, CsBr and CsI which were observed by Bridgman⁵⁾ show the calculated results. In this case, the discrepancies between the calculated results and the observed values are rather large. However we must be careful about the observed values and the extrapolated values of V_0 [$= (2/\sqrt{3})^3 a_0^3$]. The later values are determined predominantly from the observed values in the small