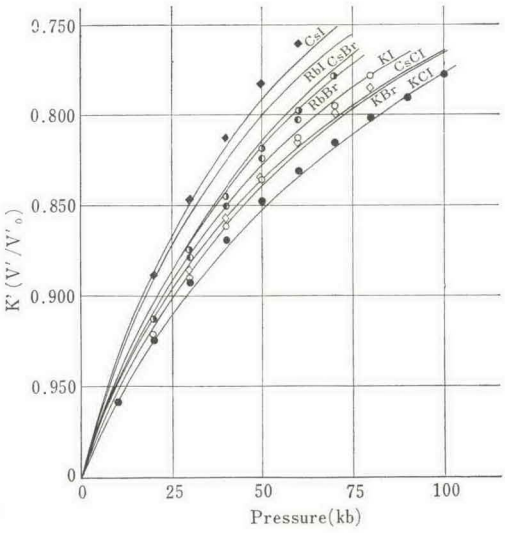


Fig. 5. The volume decreases of alkali halides in the CsCl structure as a function of pressure. Solid curves (except the curves for CsCl, CsBr and CsI, which were observed by Bridgman), the calculated results (extended to the pressure range in which the NaCl structure is more stable for some alkali halides). The observed values (5), ● KCl, ○ RbCl, ◇ KBr, ◐ RbBr, ◑ KI, ◆ RbI.

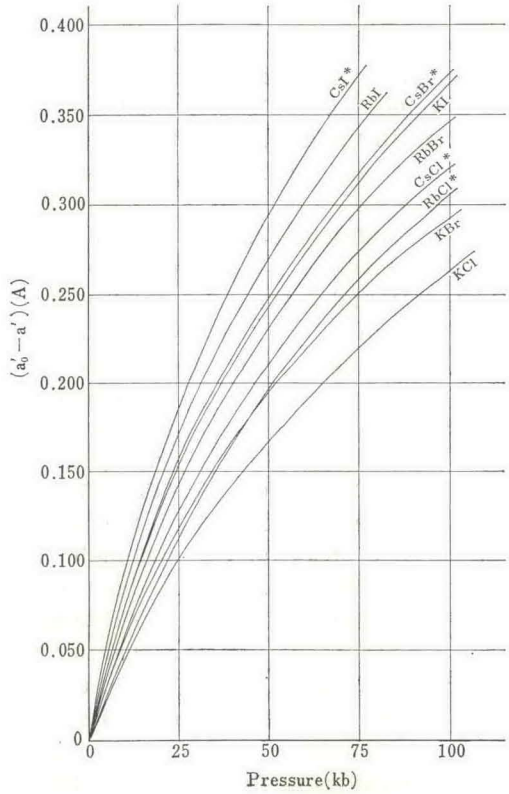
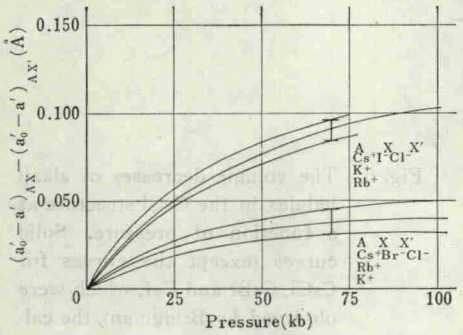


Fig. 6. The shortest interionic distances of the alkali halides in the CsCl structure as a function of pressure.



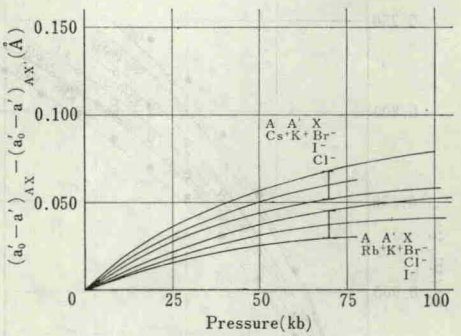


Fig. 7 and Fig. 8. The examination of the additive character of the ionic radii in the CsCl structure.

pressure ranges after the transitions and the slopes at the transition pressures. If a transition is not terminated completely at the transition pressure, the slope at the pressure must be larger than that at the pressure at which the transition is terminated completely. This yields the larger value of V'_0 and the smaller value of K'. We see in Fig. 5 that, for example, RbI is observed more compressible than CsI. But this may not be true and must be due to the fact that the transition of RbI is not terminated completely at the transition pressure. Therefore we shall use the calculated values for KCl, KBr, KI, RbBr, RbI and the observed values for CsCl, CsBr, CsI, in examining the additive character of the ionic radii in the CsCl structure.

The additive character of ionic radii at high pressure are examined by the similar manner in the last Part A., and this is made in Fig.'s 7 and 8. We may say that the ionic radii are additive quantities at high pressure, but the additive character becomes slightly worse as increasing pressure.

We can see in Fig.'s 1 and 5 that the eq. (1) gives good results. The approximation that the ionic radii are additive quantities may be also fair at high pressure, but not so fair as at atmospheric pressure. An ion surrounded by small ions may be more compressible than the ion surrounded by large ions. This character grows evident with increasing pressure for the ions in the CsCl structure (See Fig.'s 7 and 8), but this character is nearly independent of pressure for the ions in the NaCl structure (See Fig.'s 3 and 4). These tendencies may be due to the repulsive interactions between the second nearest neighbors.

Even though the additive character of ionic radii has these tendencies, it may be useful to determine the ionic radii at high pressure. The repulsive term in the expression (1) of the lattice energy was determined rather ambiguously, because this form was estimated from the quantum mechanical expression of the energy of the hydrogen like molecule[6) 7)]. But, in fact, the interaction between the outermost closed shells of an ion and its nearest neighbors predominantly yields the repulsive energy, because of the Pauli's principle[8)]. Therefore, if we use the wave functions of the outermost electrons expressed by the effective changes of the nuclei screened by the inner electrons, the repulsive term may be expressed by the linear combination of the three different terms