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Analysis of the Short-range Force Including the r^{-s}-type Functional Force

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In treating the lattice dynamics strictly, it is important to separate the short-range forces into various kinds according to their characters: covalent-bond, characteristic repulsive, and van der Waals. The purpose of this paper is to describe a method of separation and an appropriate treatment which is applicable to any crystal with any properties. For the repulsive and the van der Waals interactions, we apply the Jones-type potential function, varying as an inverse power of the distance. The results indicate that the repulsive force serves to emphasize the ionicity in the crystal-force field and that the covalent-bond force cannot be represented reasonably by the use of the valence force to such a crystal as the wurtzite structure, forming a coordination lattice.

We have studied the lattice dynamics of the wurtzite-type structure on the basis of the polarizable-ion model (PIM). A force-field model including the Coulomb force, where ions are assumed to be point-charge, is termed the rigid-ion model (RIM) regardless of the kind of short-range force. On the other hand, a model including the interaction of the induced electronic polarization is termed PIM. Though this model includes the effect of the electronic extension, we pay no heed to it in this paper, having submitted our ideas in an earlier paper.1) In another earlier paper2) the short-range force constants were estimated so as to reproduce the observed macroscopic quantities, such as, the Γ-point optical-mode frequencies, the elastic constants, and the piezoelectric constants, by the use of the effective ionic charge and the electronic polarizability, evaluated separately.3)

In general, a crystal has two characteristics, ionicity and covalency, at the same time; this is not, however, true of the NaCl-type and the Diamond-type crystals. The atomic interaction in a partial ionic crystal will be treated as consisting of three parts, aside from the polarization part: electric Coulomb (long-range), overlap, and van der Waals.4) By the overlap part, we mean the covalent attractive term and the characteristic repulsive term. Thus, three kinds of forces are contained in the short-range force: covalent-bond, characteristic repulsive, and van der Waals. In spite of this circumstance, they were previously not distinguished, but were treated collectively.2) The purpose of this paper is thus to describe a method of separation and an appropriate treatment which is applicable to any crystal with any properties.

The Born-type functional form5a) is available for use for the repulsive and the van der Waals forces, which are assumed to be expressed by a function varying as an inverse power of the atomic or ionic distance. From a formal point of view, the covalency of crystals differs from the ionicity in the greater complexity of representing explicitly the potential function. The formal theory of lattice vibrations has been described in terms of the interaction of the electrons and the nuclei involved in a solid.6) As a phenomenological model, the shell model has been widely used in valency crystals.7) A fornal justification of the shell model shows a rather large amount of arbitrariness possible in defining the parameters, because the number of parameters to be definde is too great. The valence-force-field model, taken from the theory of molecular vibration, describes the covalent-bond force directly.8) While consisting of merely the nearest neighbor interaction, this is known to reproduce observed macroscopic quantities fairly well. For the covalent-bond force, therefore, we apply the valence-force-field model.

Method

Dynamical Matrix. The dynamical matrix, $\boldsymbol{D}$, for PIM is written as:

$$\boldsymbol{D} = \boldsymbol{D}^{\mathrm{N}} + \boldsymbol{D}^{\mathrm{C}} + \boldsymbol{D}^{\mathrm{P}}, \tag{1}$$

with three constituents:5b) $\boldsymbol{D}^{\mathrm{N}}$, a short-range non-Coulomb contribution; $\boldsymbol{D}^{\mathrm{C}}$, a long-range Coulomb contribution; and $\boldsymbol{D}^{\mathrm{P}}$, a long-range electronic polarization contribution. $\boldsymbol{D}$ is the $(3n \times 3n)$ matrix, where n is the number of atoms per unit cell; it is a continuous function within the limits of the vanishing vector ($\boldsymbol{q}=0$) of the reciprocal space. It can be expanded into a MacLaurin series. The macroscopic quantities can be expressed by the use of coefficients of various orders of this series.2)

For the short-range force, we used the valence-force-field (VFF) method in our preceding paper;2) this method can be represented in terms of a function dependent on several force constants. Though VFF contains coupling terms between forces, we omitted these less important terms in order to simplify the procedure.9) We have distinguished the following force constants: K_1 (parallel to the **c** axis) and K_2 (not parallel to it) for first-neighbor bond stretching, H for bending (without distinction between two sorts: cation-anion-cation and anion-cation-anion), and K_3 for second-neighbor stretching; *cf.* Fig. 1.

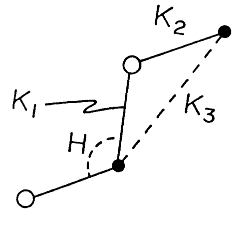

Fig. 1. The explanation of force constants used in this paper.

In this paper, the repulsive force (RF), whose role is known, together with the Coulomb force, for ionic crystals, and the van der Waals force are given separately in addition to the valence force (VF). After this separation is accomplished, the force analogous to RF and the van der Waals force are separated from VF. Accordingly, VF will denote the covalent-bond force more strictly than before. After the short-range force is separated into forces, the dynamical matrix is written as:

$$\boldsymbol{D} = \boldsymbol{D}^{\mathrm{V}} + \boldsymbol{D}^{\mathrm{R}} + \boldsymbol{D}^{\mathrm{W}} + \boldsymbol{D}^{\mathrm{C}} + \boldsymbol{D}^{\mathrm{P}}. \tag{2}$$

The van der Waals force, $\boldsymbol{D}^{\mathrm{W}}$, will not be treated separately because of its small contribution. Our new attempt is applied to the well-examined wurtzite-type structure in this paper. Though only one example, that of BeO, is treated, any other material may be treated similarly.

The repulsive force is assumed to be written as the sum of the two-body repulsive interaction. This is only approximately true. As the covalency is increased, the interactions of atoms with their different neighbors become more interdependent. Thus, the many-body interaction begins to take on an important role. As many authors have noted,[10] indeed, the many-body interaction is not negligibly small; in spite of this evidence, the interaction of the two bodies is large in comparison with it. The force, represented as a function of a force constant, H, denoting an angular rigidity, is, in a sense, the three-body force. Thus, the many-body interaction is considered to be included collectively in VF as a function of H. For the repulsive interaction, we apply the Jones-type potential function following Born's first assumption,[5a] where atoms or ions were pictured as rigid spheres mutually attracted by a force varying as an inverse power of the distance, r:

$$\beta \times r^{-s}, \tag{3}$$

where β is a strength parameter and s is a hardness parameter. s is independent of the species of ions in a given crystal. Another function of the repulsive interaction is assumed to have a form exponential with the distance; this is suited to the quantum-mechanical results more than the inverse power form. Since the exponential form is virtually equal to the inverse power form, we will employ the latter form, whose function is simple and which has been well examined mathematically.

Pauling[11] has studied the effect of relative ionic sizes on the properties of the alkali halides and has given an approximate formula providing a quantitative theory of the anion-contact and double-repulsive effect:

$$\beta_{\mathrm{AB}} B_0 e^2 (r_{\mathrm{A}}+r_{\mathrm{B}})^{s-1} r_{\mathrm{AB}}{}^{-s}, \tag{4}$$

where r_{AB} is the distance between the A and B ions, where r_{A} and r_{B} are constants representing their radii (which Pauling calls standard radii), where B_0 is a characteristic repulsive coefficient (whose value can be determined conveniently), and where β_{AB} is a constant obtained from a quantum-mechanical treatment.[11]

Characteristic Repulsive Force. The method for the calculation of RF will now be shown briefly. An expansion of the potential energy with respect to the nuclear displacement gives various orders of coefficients, which are denoted by various orders of derivatives with respect to the displacement. Among them, the second-order coefficient approximately gives the force field described by matrix elements.[5a] The definite expressions for evaluating these coefficients have scarcely been given. Now those will be given: the formula for the second-order coefficient of Eq. 4, those for the first- and second-order coefficients, given by the expansion of the second-order coefficient with repsect to the wave vector, and the method for checking the resulting values evaluated with the use of these formulas. The potential, ϕ, at a point $\boldsymbol{r}$ in a lattice space is given by summing up the influence from all lattice sites, $\boldsymbol{r}_l$:

$$\phi = \textstyle\sum_l' |\boldsymbol{r}-\boldsymbol{r}_l|^{-s}. \tag{5}$$

In order to gain a rapid convergence of the summation, various methods of treatments have been given.[12] We have employed Tosi's method,[13] which is applicable to any value of s except for $s \leqq m$ (=dimension of lattice space).

The lattice summation of Eq. 5 is rewritten by Tosi[13] for the m-dimensional space as:

$$\begin{aligned} \boldsymbol{S}^{(m,s)}(\boldsymbol{q}, kk') &= \textstyle\sum_l' |\boldsymbol{r}-\boldsymbol{r}_l|^{-s} \\ &= \frac{1}{\Gamma(\sigma)} \left\{ \frac{2\pi^{\tau}\omega^{\sigma-\tau}}{v(s-m)} + \frac{\pi^{\tau}}{v} \textstyle\sum_h' \exp\left[2\pi \mathrm{i}(\boldsymbol{k}_h+\boldsymbol{q})\cdot\boldsymbol{r}\right] \right. \\ &\quad \times \frac{\Gamma[\tau-\sigma, \pi^2(\boldsymbol{k}_h+\boldsymbol{q})^2/\omega]}{(\pi|\boldsymbol{k}_h-\boldsymbol{q}|)^{m-s}} - \frac{2}{s}\omega^{\sigma} \\ &\quad \left. + \textstyle\sum_l' \exp(2\pi\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_l) \frac{\Gamma[\sigma, (\boldsymbol{r}-\boldsymbol{r}_l)^2\omega]}{|\boldsymbol{r}-\boldsymbol{r}_l|^{s}} \right\}, \end{aligned} \tag{6}$$

where $\boldsymbol{r}=\boldsymbol{x}\binom{0}{k'}-\boldsymbol{x}\binom{0}{k}$ and $\boldsymbol{r}_l=\boldsymbol{x}\binom{l}{k}-\boldsymbol{x}\binom{0}{k}$, where $\sigma=s/2$ and $\tau=m/2$, where the subindices l and h indicate, respectively, the direct-space and the reciprocal-space lattice points, where $\boldsymbol{q}$ is the wave vector, and where v is the unit-cell volume. $\Gamma(\mathrm{x})$ is the complete gamma function, and $\Gamma(\nu,\mathrm{x})$ is the incomplete gamma function. The second-order derivative of Eq. 6 with respect to the displacement comes out to:

$$\begin{aligned} \boldsymbol{S}_{\alpha\beta}^{\mathrm{m,s}}(\boldsymbol{q}, kk') &= \frac{1}{\Gamma(\sigma)} \left\{ \frac{\pi^{\tau}}{v}(-4\pi^2) \textstyle\sum_h' (k_{h_\alpha}+q_\alpha)(k_{h_\beta}+q_\beta) \right. \\ &\quad \times \exp\left[2\pi\mathrm{i}(\boldsymbol{k}_h+\boldsymbol{q})\cdot\boldsymbol{r}\right] \frac{\Gamma[\tau-\sigma, \pi^2(\boldsymbol{k}_h+\boldsymbol{q})^2/\omega]}{(\pi|\boldsymbol{k}_h+\boldsymbol{q}|)^{m-s}} \\ &\quad + \textstyle\sum_l' \exp(2\pi\mathrm{i}\, \boldsymbol{q}\cdot\boldsymbol{r}_l) 4(r_\alpha - r_{l_\alpha})(r_\beta - r_{l_\beta}) \\ &\quad \times \frac{\Gamma[\sigma+2, \omega(\boldsymbol{r}-\boldsymbol{r}_l)^2]}{|\boldsymbol{r}-\boldsymbol{r}_l|^{s+4}} - 2\delta_{\alpha\beta} \textstyle\sum_l' \exp(2\pi\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_l) \\ &\quad \left. \times \frac{\Gamma[\sigma+1, \omega(\boldsymbol{r}-\boldsymbol{r}_l)^2]}{|\boldsymbol{r}-\boldsymbol{r}_l|^{s}} + \delta_{\alpha\beta}\delta_{kk'} \frac{4}{s+2}\omega^{\sigma+1} \right\}. \end{aligned} \tag{7}$$

Though Eq. 6 is valid for $s>m$, it can be generalized for any real value of s.[12] Equation 7 is, hence, valid for any real value of s. Values evaluated according to Eq. 7 may be checked with the use of this relation:

$$\textstyle\sum_{\alpha=1}^{m} \boldsymbol{S}_{\alpha\alpha}^{(m,s)}(\boldsymbol{q}, kk') = s(s-1)\boldsymbol{S}^{(m,s+2)}(\boldsymbol{q}, kk'). \tag{8}$$

If $s=1$ and $m=3$, there holds the well-known equation given by Born:

$$\textstyle\sum_\alpha \boldsymbol{S}_{\alpha\alpha}^{(3,1)}(\boldsymbol{q}, kk') = \frac{4\pi}{v}. \tag{9}$$

Moreover, the first- and the second-order derivatives with respect to the wave vector are given as:

$$S^{(m.s)}_{\alpha\beta.\gamma}(\boldsymbol{q}, kk') = \frac{2\pi \mathrm{i}}{\Gamma(\sigma)}(A+B),$$

$$A = \frac{\pi^{\tau}}{v}\,(-2\pi\mathrm{i})\textstyle\sum'_h\Big\{[\delta_{\alpha\gamma}(k_{h_\beta}+q_\beta)+\delta_{\beta\gamma}(k_{h_\alpha}+q_\alpha)]$$
$$\times\frac{\Gamma[\tau-\sigma, \pi^2(\boldsymbol{k}_h+\boldsymbol{q})^2/\omega]}{(\pi|\boldsymbol{k}_h+\boldsymbol{q}|)^{m-s}} - 2\pi^2(k_{h_\alpha}+q_\alpha)(k_{h_\beta}+q_\beta)(k_{h_\gamma}+q_\gamma)$$
$$\times\frac{\Gamma[\tau-\sigma+1, \pi^2(\boldsymbol{k}_h+\boldsymbol{q})^2/\omega]}{(\pi|\boldsymbol{k}_h+\boldsymbol{q}|)^{m-s+2}}\Big\}\ \exp\,[2\pi\mathrm{i}(\boldsymbol{k}_h+\boldsymbol{q})\cdot\boldsymbol{r}],$$

$$B = \textstyle\sum'_l r_{l_\gamma}\ \Big\{4(r_\alpha-r_{l_\alpha})(r_\beta-r_{l_\beta})\frac{\Gamma[\sigma+2, \omega(\boldsymbol{r}-\boldsymbol{r}_l)^2]}{|\boldsymbol{r}-\boldsymbol{r}_l|^{s+4}}$$
$$-2\delta_{\alpha\beta}\frac{\Gamma[\sigma+1, \omega(\boldsymbol{r}-\boldsymbol{r}_l)^2]}{|\boldsymbol{r}-\boldsymbol{r}_l|^{s+2}}\Big\}\exp\,(2\pi\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_l), \tag{10}$$

$$S^{(m.s)}_{\alpha\beta.\gamma\nu}(\boldsymbol{q}, kk') = \frac{-4\pi^2}{\Gamma(\sigma)}(C+D),$$

$$C = \frac{\pi^{\tau}}{v}\Big\{(\delta_{\alpha\gamma}\delta_{\beta\nu}+\delta_{\beta\gamma}\delta_{\alpha\nu})\frac{\Gamma[\tau-\sigma, \pi^2(\boldsymbol{k}_h+\boldsymbol{q})^2/\omega]}{(\pi|\boldsymbol{k}_h+\boldsymbol{q}|)^{m-s}}$$
$$-2\pi^2[\delta_{\alpha\nu}(k_{h_\beta}+q_\beta)(k_{h_\gamma}+q_\gamma)+\delta_{\beta\nu}(k_{h_\alpha}+q_\alpha)(k_{h_\gamma}+q_\gamma)$$
$$+\delta_{\gamma\nu}(k_{h_\alpha}+q_\alpha)(k_{h_\beta}+q_\beta)+\delta_{\alpha\gamma}(k_{h_\beta}+q_\beta)(k_{h_\nu}+q_\nu)$$
$$+\delta_{\beta\gamma}(k_{h_\alpha}+q_\alpha)(k_{h_\nu}+q_\nu)]\frac{\Gamma[\tau-\sigma+1, \pi^2(k_h+q)^2/\omega]}{(\pi|\boldsymbol{k}_h+\boldsymbol{q}|)^{m-s+2}}$$
$$+4\pi^4(k_{h_\alpha}+q_\alpha)(k_{h_\beta}+q_\beta)(k_{h_\gamma}+q_\gamma)(k_{h_\nu}+q_\nu)$$
$$\times\frac{\Gamma[\tau-\sigma+2, \pi^2(\boldsymbol{k}_h+\boldsymbol{q})^2/\omega]}{(\pi|\boldsymbol{k}_h+\boldsymbol{q}|)^{m-s+4}}\Big\}\ \exp\,[2\pi\mathrm{i}(\boldsymbol{k}_h+\boldsymbol{q})\cdot\boldsymbol{r}],$$

$$D = \textstyle\sum'_l r_{l_\gamma} r_{l_\nu}\Big\{4(r_\alpha-r_{l_\alpha})(r_\beta-r_{l_\beta})\frac{\Gamma[\sigma+2, \omega(\boldsymbol{r}-\boldsymbol{r}_l)^2]}{|\boldsymbol{r}-\boldsymbol{r}_l|^{s+4}}$$
$$-2\delta_{\alpha\beta}\frac{\Gamma[\sigma+1, \omega(\boldsymbol{r}-\boldsymbol{r}_l)^2]}{|\boldsymbol{r}-\boldsymbol{r}_l|^{s+2}}\Big\}\ \exp\,(2\pi\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_l). \tag{11}$$

Values evaluated according to Eq. 11 may be checked by the use of this relation:

$$\textstyle\sum_{kk'}z(k)z(k')\boldsymbol{S}^{(m,s)}(\boldsymbol{q}, kk') =$$
$$\{s(s+1)\}^{-1}\textstyle\sum_{\alpha\beta}\sum_{kk'}z(k)z(k')\boldsymbol{S}^{(m.s)}_{\alpha\beta.\alpha\beta}(\boldsymbol{q}, kk'), \tag{12}$$

which is a generalization of the equation given by Keffer *et al.*[14)] for $s=1$ and $m=3$. The symbol $z(k)$ is the effective ionic charge of the kth ion. The left-hand side of Eq. 12 corresponds to the well-known Madelung constant, A, if $s=1$:

$$A = (2n)^{-1}\textstyle\sum_{kk'}z(k)z(k')\boldsymbol{S}^{(m,s)}(\boldsymbol{q}, kk'). \tag{13}$$

Result

Before the evaluation of the repulsive interaction by means of Eq. 4 is made, the definite values of the repulsive parameters, B_0, β and s, and the ionic radii have to be given. Except for β, these parameters in a family of salts were determined by a simultaneous fit of the assumed expression of the lattice energy to the equation of the state and its volume derivative for the alkali halides with the NaCl structure, where the number of salts sizably exceeds the number of component ion species. β is independently determined by the use of the valence charge and the number of outer electrons of the pth ion following Pauling's equation:

$$\beta_{pp'} = 1 + (z_p/n_p) + (z_{p'}/n_{p'}). \tag{14}$$

By means of the fact that the attractive forces and the repulsive forces are balanced in ionic crystals, Pauling determined B_0. The repulsive parameters for a wurtzite structure, however, can not be determined by a simultaneous fit because, in this case, the number of salts scarcely exceeds the number of component ion species. Therefore, the results for the NaCl structure are approximately applied here after converting them into the wurtzite structure.

The ionic radii for Be and O in the wurtzite-type structure are 0.293 and 1.32 Å respectively, after the values derived by Pauling in the NaCl-type structure had been modified as:[14)]

$$r_{\mathrm{Wurztie}} = r_{\mathrm{NaCl}} \times c,$$
$$c = [(B_{\mathrm{W}}/B_{\mathrm{N}})(A_{\mathrm{N}}/A_{\mathrm{W}})]^{1/(s-1)} = 0.944, \tag{15}$$

where A is the Madelung constant and B is the coordination number. BeO is of the same ionic type as LiF. However, the value of the observed compressibility of BeO is not similar to that of LiF; rather, it is similar to that of MgO.[15)] In spite of this evidence, $s=6$, which is the value for LiF on the average, is used so as to keep consistency with other parameters.

For a BeO compound with an ionic structure, β_{++}, β_{+-}, and β_{--} are taken as 3.0, 1.75, and 0.5 respectively by means of Eq. 14. If BeO has such a structure as wurtzite, the ionicity is weakened and the valence charge is deprived of its meaning. At this stage, the effective ionic charge seems to take the place of the valence charge in Eq. 14. The results are 3.0, 1.71, and 0.43—the effective ionic charge is nearly 1.0.[3)] The values of the B_{AB} [$=\beta_{\mathrm{AB}}(r_{\mathrm{A}}+r_{\mathrm{B}})^{s-1}$] coefficient between like or unlike ions, then, are in this ratio:

$$B_{++}:B_{+-}:B_{--} = 1:94:276. \tag{15}$$

The wurtzite-type structure has two "molecules," with two cations and two anions, in a unit cell (see Fig. 2).

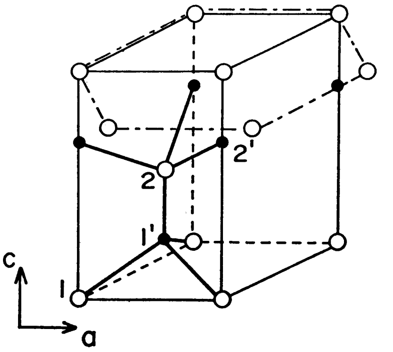

Fig. 2. Crystal structure of wurtzite type.

Since these four ions, displacing in one one and the same direction and amount, do not cause any relative displacement, that is, since the acoustic mode of frequency at the Γ point is kept at zero, the three coefficients, B_{AB}'s, should satisfy this relation:

$$B_{++}\times B_{--}/B_{+-}^{\ 2} = c_{\mathrm{B}} = 1.^{\dagger\dagger} \tag{17}$$

[††] Fowler[16)] has obtained the value of $B_{\mathrm{AB}}{}^0$ $(=B_{\mathrm{AB}}\times B_0)$ for alkali halides with the use of thermodynamical data. The approximate relation (Ref. 19, Eq. 922) suggested upon examination of the results of the study of an inert-gas mixture

$$(B_{+-}{}^0)^{1/s} = \{(B_{++}{}^0)^{1/s} + (B_{--}{}^0)^{1/s}\}/2,$$

has been used in order to estimate the ratio. Here, $(B_{+-}{}^0)^{1/s}$ is the arithmetic mean of $(B_{++}{}^0)^{1/s}$ and $(B_{--}{}^0)^{1/s}$.

That is, B_{+-} is the geometrical mean of B_{++} and B_{--}. As the ratio given in Eq. 16 does not satisfy Eq. 17 ($c_B=0.031\neq 1.$), the values of B_{AB} given in Eq. 16 seem to be unreliable; the $\beta_{++}\times\beta_{--}>\beta_{+-}{}^2$ relation has to be maintained, at least in order to satisfy Eq. 17. On the other hand, the ionic radii estimated by Born[13)] reproduce the experimental ones quite well. It is known that the difference in ionic radius between a cation and an anion given by Pauling is too large in comparison with that derived from experiments.[13,17)] The ionic radii for CsCl-type crystals derived by Hollinger *et al.*[18)] with the use of observed elastic constants also show this tendency. Consequently, it is reasonable at present to treat B_{AB} as an adjustable parameter to be fitted empirically, keeping the relation in Eq. 17, just as the force constant is. After B_{AB} is estimated for compounds of salts, it can be divided into parameters, B_{AB} and β_{AB}, in a family of salts. This treatment is as follows: first, an arbitrary ratio of B_{AB} between like or unlike ions is chosen, and then the force constants of the covalent-bond force are estimated so as to reproduce the observed marcoscopic quantities. The results will be shown for four kinds of ratio:

$$B_{++}\quad B_{+-}\quad B_{--} \tag{18.N}$$

$$=0.25\ :0.5\ :1.0, \tag{18.1}$$

$$=0.01\ :0.1\ :1.0, \tag{18.2}$$

$$=0.0025:0.05:1.0, \tag{18.3}$$

$$=0.0001:0.01:1.0. \tag{18.4}$$

If the short-range force is represented only by the use of RF, one of the calculated e_2-mode frequencies becomes a imaginary number. As the most characteristic feature of the covalent bonds is their directional nature, the force constant, H, in VF, representing an angular rigidity, is taken into account as a temporary expedient so that the imaginary number can be done away with. The effect of the ratio (B_{++}: B_{+-}: B_{--}) on the calculated macroscopic quantities is then examined. Table 1 shows the value of H, which is the limiting value to make the calculated results real, and the other parameters used here. The set of $B_0\times B_{+-}=1.6$ and $H=0.04$ ($B_0\times B_{+-}$ and H take constant values, regardless of the variable B_{+-}) are the limiting values when the imaginary number is done away with. $B_0\times B_{+-}$ being a constant value independent of the value of B_{+-} means that only the proportion of the two kinds of repulsive forces between like ions is varied, while the repulsive force between unlike ions is kept intact. The calculated results are shown in Table 2 for frequencies and elastic constants. (Since the short-range non-Coulomb contribution is not important with regard to piezoelectric constants, the results for them are omitted.) The results in the fourth column show the case where the characteristic repulsive force is not taken into account.

TABLE 1. THE PHYSICAL QUANTITIES USED IN THIS PAPER

Polarizability	$\alpha_+(1/\text{Å}^3)$	0.04
	$\alpha_-^{//}(1/\text{Å}^3)$	1.269
	$\alpha_-^{\perp}(1/\text{Å}^3)$	1.259
Effective ionic charge	z(esu)	1.105
Force constant	H (mdyn/Å)	0.04
Structural parameter[a)]	a(Å)	2.6979
	c(Å)	4.3772
	u	0.3786

a) Ref. 19.

The variation in the ratio of B_{AB} is remarkable in macroscopic quantities, as can be seen in Table 2. Let us first examine the frequencies. At the Γ point, the lattice vibration can be classified, by factor-group analysis, into the $2a_1+2b_1+2e_1+2e_2$ modes. Among these, though the a_1 and e_1 modes are independent of the ratio, the two frequencies belonging to b_1 and e_2

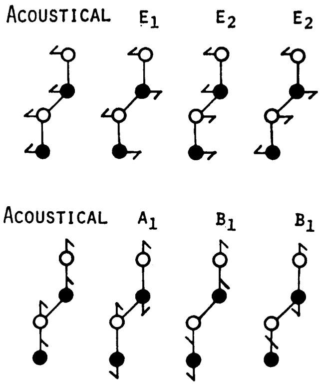

Fig. 3. The vibrational modes of wurtzite-type structure.

TABLE 2. THE CALCULATED MACROSCOPIC QUANTITIES AGAINST THE VARIETY OF B_{+-}

		Obsd	Calcd				
B_{+-}			0.0	0.5	0.1	0.05	0.01
Wavenumber[a)] (cm^{-1})	a_1	678	680.3	690.7	690.7	690.6	690.7
	b_1	—	894.9	769.8	950.5	1165.4	2255.5
		—	784.7	597.2	621.7	628.7	634.8
	e_1	722	725.4	738.3	738.3	738.3	738.3
	e_2	684	642.8	638.9	655.7	679.3	886.7
		338	378.0	47.6	131.8	189.1	337.4
Elast. const.[b)] (10^{11} dyn/cm^2)	c_{11}	47.0	48.9	−48.0	33.3	66.0	289.3
	c_{12}	16.8	21.4	105.5	59.2	72.5	218.1
	c_{13}	11.9	20.9	29.6	40.8	55.4	172.6
	c_{33}	49.3	44.7	25.2	49.4	81.0	335.2
	c_{44}	15.3	15.9	1.9	5.1	9.2	42.0

a) Ref. 20. b) Ref. 21.

modes are particularly interesting. Each vibrational mode is shown in Fig. 3. In the a_1 and e_1 modes, the interatomic distance remains unchanged between like ions, but is changed between unlike ions. As the repulsive force between unlike ions is kept intact, the calculated results do not vary in spite of the variety of the ratio. The variety of the ratio denotes the relation between cation-cation and anion-anion repulsive forces: as the ratio decreases, the cation-cation repulsive force is decreased and the anion-anion repulsive force is increased. As the interatomic distance between like ions is changed, on the contrary, the calculated results vary remarkably with the ratio. The case where RF makes the main contribution as the short-range force causes a large splitting of the e_2- and b_1-mode frequencies. This splitting becomes rather too large in comparison with the observed values.

Let us next discuss the elastic constants. In this case, the variation in the ratio is more remarkable. Comparing the calculated c_{11} and c_{12} species with each other, c_{12} is larger than c_{11}, in contrast with the observed values. This difference varies remarkably depending on the value of the ratio; c_{11} becomes equal to c_{12} at nearly $B_{+-}=0.04$. In Fig. 4 the contribution of RF is shown for several species of elastic constants against the ratio. As the ratio becomes smaller, RF makes a large contribution and causes a large repulsion. This tendency can also be observed in the induced internal strain of the c_{11} and c_{12} species; the contribution of the internal strain of other species is small enough to be negligible. Reflecting the variation in the calculated frequencies, the contribution of the induced internal strain of the c_{11} and c_{12} species does not approach zero, but increases as the ratio increases. It is worthy of notice that the sign of the contribution is different between these two species. The fact that the calculated c_{12} species is larger than that of c_{11} is a result of this.

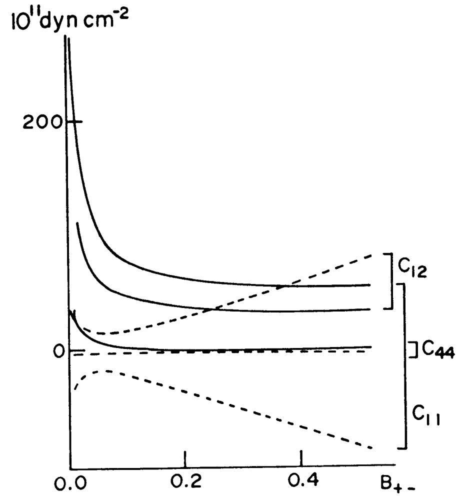

Fig. 4. The contribution of the repulsive force to elastic constants as a function of B_{+-}.

Thus far the characteristic effect of RF on calculated macroscopic quantities has been examined and only the covalent-bond force has been considered, so that the imaginary number has been done away with. Let us now take the covalency strictly into account. Before we do so, however, we must fix the value of B_{+-} by reference to the preceding results. Fortunately, the features appearing in the reproduction of e_2-mode frequencies and the relation between c_{11} and c_{12} are very specific; hence, the ratio can be roughly fixed. If we dare to estimate the approximate value for Be compounds by the use of Fowler's data,[16] in spite of the difference in the relation of B_{AB} (see footnote), the values are reduced to nearly zero except for B_{--}. This suggests that our conclusion derived from the reproduction of the macroscopic quantities is reasonable. Hence, we fix the ratio at:

$$B_{++}:B_{+-}:B_{--} = 0.01:0.1:1.0. \tag{19}$$

This result can be explained as follows: since the radius ratio is quite different from unity, the repulsion between anions is much larger than that between cations. The $B_{+-}=1.0$ ratio corresponds to the case when the ionic radii of cation and anion are nearly equal to each other. The way of treating the consideration of RF separately

Table 3. The calculated macroscopic quantities against B_0

B_0			0.0	3.53	5.0	10.0
K_1			2.22	1.79	1.61	1.00
K_2			2.39	1.92	1.72	1.07
H			0.0	0.0	0.0	0.0
K_3			0.269	0.200	0.177	0.110
		Obsd	Calcd			
Wave number (cm^{-1})	a_1	678	680.3	679.3	678.4	678.0
	b_1	—	894.9	837.6	847.8	912.2
		—	784.4	819.1	801.5	721.0
	e_1	722	725.4	724.7	723.2	726.4
	e_2	684	642.8	649.4	651.8	671.3
		338	378.0	327.4	305.0	219.5
Elast. const. (10^{11} dyn/cm^2)	c_{11}	47.0	48.9	48.8	48.7	48.6
	c_{12}	16.8	21.4	27.1	29.8	40.8
	c_{13}	11.9	20.9	25.0	27.0	35.1
	c_{33}	49.3	44.7	46.7	47.7	50.9
	c_{44}	15.3	15.9	13.0	11.9	8.1

is thus advantageous because it brings the effect of the radius ratio into operation.

Table 3 gives the results obtained against several values of B_0 at $B_{+-}=0.1$. If we assume that the Coulomb force and the repulsive force are balanced at the equilibrium (because the covalent-bond force is not regarded as such a force as to take part in an ionic balance), $B_0=3.53$ is obtained. If we assume that the lattice energy can be represented as the sum of the Coulomb and the repulsive energies, the result is too small in comparison with the observation for the wurtzite structure. In the case of NaCl, on the contrary, the reproduction is very good. We regard the difference between the calculated and the observed values as the covalency.

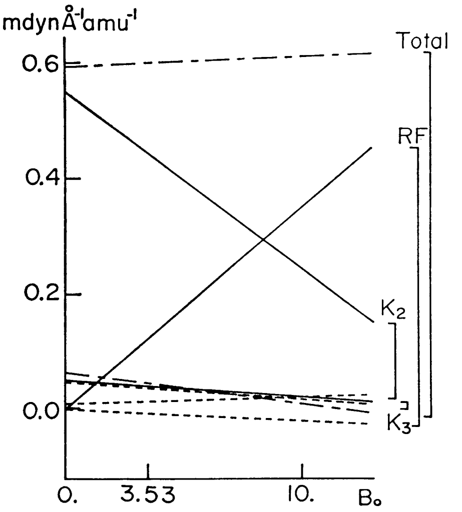

Fig. 5. The contribution of each short-range force to e_2-mode frequencies.

The increased B_0 value causes the contribution of RF to increase and the value of the force constants to decrease. The calculated results also vary appreciably in reproduction in terms of the increase. This evidence indicates that the manner of the contribution of RF is peculiar to itself. The contribution of RF and each force constant in VF to the e_2-mode frequencies is shown in Fig. 5, as examples. As can also be seen in it, RF makes a contribution not only so as to compensate VF, but also so as to give a peculiar feature.

Discussion

The short-range force was separated into the covalent-bond force and the repulsive force in the preceding chapter. On this occasion, the Born-type central-force model was employed for the repulsive force. As for the covalent-bond force, on the other hand, the valence force was employed. On Born's notation, the force field occurring between the two particles of k and k' is described by the matrix elements α and β, $\phi_{\alpha\beta}(kk')$, denoting the coefficients of the derivatives with respect to the direction of the displacement, α and $\beta=x, y$, and z; the coefficients of the matrix elements are force constants. Accordingly, 3×3 kinds of force constants with respect to α and β are distinguished against each pair of atoms, k and k', —the number of them is reduced through symmetry operations. Among them, we distinguished the constants connected with the difference in the pair of particles, but identified those with a difference in the direction: as the most characteristic feature of the covalent-bond forces is their directional nature, a characteristic of this kind, expected to be involved in Born's notation in terms of the α and β elements, was considered to be put into the covalent-bond force collectively.

As can be seen in Table 3, the increased RF caused the VF to decrease; this resulted in a split of the e_2-mode frequencies and in an increase in the c_{12} and c_{13} species. Thus, the ionicity in the crystal-force field was emphasized according to the increase in RF. Even without RF, a lack of the covalent-bond force, that is, a lack of the rigidity in direction, can be observed in the calculated results, as shown in the fourth column in Table 3. However the value of H, which has been expected to represent an angular rigidity, became zero; this result reproduced the calculated results satisfactorily, but this matter seems strange. This evidence seems to indicate that each force constant in VF, which reasonably been defined by means of molecular spectroscopy, does not give the same meaning in such a crystal as a wurtzite structure forming a coordination lattice. The increase in RF causing a decrease of VF also indicates that the VF used here involves not only the covalent-bond force, but also a force similar to RF. VF is thus an inclusive force including not only the covalent-bond force, but also several other kinds of forces. Hence, we can scarcely make any progress in separating the short-range forces as long as we use an ambigous valence-force-field model. It may be supposed that we had better distinguish constants in terms of their α and β elements rather than use those defined on the basis of the molecular theory.

Conclusion

We have separated the short-range forces into various kinds of forces according to their characteristics in order to establish a suitable treatment which is applicable to any crystal with any character. By the use of an inclusive valence force, we can scarcely make any progress in separation.

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