Effective Ionic Charges of Several Uniaxial Crystals

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A simple equation was derived for obtaining the effective ionic charges of uniaxial crystals on the basis of a rigid ion model by using the optically active lattice vibration frequencies of the TO and LO modes. It was applied to several uniaxial crystals such as wurtzite type (ZnO, ZnS, CdS, and BeO) and rutile type (ZnF_2, TiO_2, SnO_2, and GeO_2) crystals. Lattice vibration frequencies of orthorhombic hydrogen chloride crystal were calculated by means of a point charge model to estimate the effect of the long range Coulomb interaction on the vibrational frequencies of molecular crystals.

It is well-known that large frequency splittings between transverse and longitudinal modes are observed for infrared active lattice vibrations of ionic crystals.[1] The TO–LO splitting arises from long range electrostatic interactions. Kellermann calculated the frequency dispersion curves of the NaCl crystal on the basis of a rigid ion model.[2] The transverse ω(T) and longitudinal frequencies ω(L) near the center of the Brillouin zone (wave vector $\boldsymbol{y}\sim 0$) for the crystals of the NaCl type can be calculated from the equations

$$\omega^2(\mathrm{T}) = (1/m_{\mathrm{Na}}+1/m_{\mathrm{Cl}})[\beta-(4\pi/3)(Ze)^2/v_{\mathrm{a}}] \tag{1}$$

$$\omega^2(\mathrm{T}) = (1/m_{\mathrm{Na}}+1/m_{\mathrm{Cl}})[\beta+(8\pi/3)(Ze)^2/v_{\mathrm{a}}] \tag{2}$$

where m_{Na}, m_{Cl}, and v_{a} represent the masses of the Na^+ and Cl^- ions and the volume of the unit cell, respectively, and β the force constant due to the short range interaction. The ionic charges on the Na^+ and Cl^- ions are given by $+Ze$ and $-Ze$, respectively. In the case of the NaCl crystal, the values of Z, β, and $(4\pi/3)(Ze)^2/v_{\mathrm{a}}$ are calculated to be 0.73, 0.34 md/Å, and 0.11 md/Å, respectively, by using the values of ω(T) (164 cm^{-1}) and ω(L) (262 cm^{-1}).[1] The result indicates that the long range electrostatic interaction greatly affects the frequency of the lattice vibration of ionic crystals, so that the long range electrostatic interaction should be taken into account in the frequency calculation of the ionic crystals.

Many investigators[3] have calculated the frequencies of the lattice vibrations of ionic crystals on the basis of various models, such as the rigid ion model with effective ionic charges,[4] shell model[5] and deformation dipole model.[6] The calculations for partially ionic crystals, such as SiC, ZnTe, and CdS have also been made.[4,7] In the present work, simple equations were derived to obtain the values of the effective ionic charges of several crystals of wurtzite and rutile types on the basis of the rigid ion model. Usually the effective ionic charges are taken as a parameter to fit the observed frequencies. However, the values of the effective ionic charges can be obtained from the TO–LO splittings, which do not depend on a model of the short range interaction.

For molecular crystals, the lattice vibration frequencies are usually calculated without the long range interaction. The frequencies of the hydrogen chloride crystal was also calculated on the assumption of a point charge on each atom to estimate the amount of TO–LO splittings and the effect of the long range interaction on the lattice vibration frequencies of such a molecular crystal.

Rigid Ion Model and Effective Ionic Charge

In the harmonic approximation, the equation of motion of particles in the crystal is given by

$$\boldsymbol{M}\omega^2\boldsymbol{u} = (\boldsymbol{R}+\boldsymbol{ZCZ})\boldsymbol{u} \tag{3}$$

by the rigid ion model, where the matrices $\boldsymbol{R}$ and $\boldsymbol{C}$ represent the short range and long range electrostatic interactions, respectively. The normal frequencies can be obtained by solving the secular equation

$$|\boldsymbol{M}\omega^2\boldsymbol{I}-\boldsymbol{R}-\boldsymbol{ZCZ}| = 0 \tag{4}$$

The $\boldsymbol{C}$ matrix can be calculated by using Ewald's transformation.[1,2,8] Using the notation of Born and Huang[1] Eq. (3) is written as

$$\begin{aligned}\omega^2\begin{pmatrix}\boldsymbol{y}\\ j\end{pmatrix}w_\alpha\left(k\middle|\begin{matrix}\boldsymbol{y}\\ j\end{matrix}\right) &= \sum_{k'\beta} C^{\mathrm{N}}_{\alpha\beta}\begin{pmatrix}\boldsymbol{y}\\ kk'\end{pmatrix}w_\beta\left(k'\middle|\begin{matrix}\boldsymbol{y}\\ j\end{matrix}\right) - e_kE_\alpha\sqrt{m_k}\\ &\quad+\sum_{k'\beta}(e_ke_{k'}/m_k)Q_{\alpha\beta}\begin{pmatrix}0\\ kk'\end{pmatrix}w_\beta\left(k\middle|\begin{matrix}\boldsymbol{y}\\ j\end{matrix}\right)\\ &\quad-\sum_{k'\beta}(e_ke_{k'}/\sqrt{m_km_{k'}})Q_{\alpha\beta}\begin{pmatrix}\boldsymbol{y}\\ kk'\end{pmatrix}w_\beta\left(k'\middle|\begin{matrix}\boldsymbol{y}\\ j\end{matrix}\right)\end{aligned} \tag{5}$$

where the α component of the displacement vector of the k-th particle in the l-th unit cell $u_\alpha(l/k)$ is given by

$$u_\alpha\begin{pmatrix}l\\ k\end{pmatrix} = (1/\sqrt{m_k})w_\alpha(k)\exp\left\{2\pi i\boldsymbol{y}\cdot\boldsymbol{x}\begin{pmatrix}l\\ k\end{pmatrix}-i\omega t\right\} \tag{6}$$

$\boldsymbol{x}(l/k)$ represents the Cartesian coordinate of the particle (l/k). The symlols e_k and m_k represent the ionic charge

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[8] R. A. Cowley, *Acta. Crystallogr.*, **15**, 687 (1962).

and mass of particle k, respectively. $C^N_{\alpha\beta}(\boldsymbol{y}/_{kk'})$ is a mass-adjusted matrix of R and $Q_{\alpha\beta}(\boldsymbol{y}/_{kk'})$ is a complicated function of k, k' and wave vector $\boldsymbol{y}$, and can be calculated if the crystal structure is known.[9] The macroscopic field

$$E_\alpha = -(4\pi/v_a)(y_\alpha/|\boldsymbol{y}|)\sum_\beta(y_\beta/|\boldsymbol{y}|)\sum_{k'}(e_{k'}/\sqrt{m_{k'}})w_\beta\left(k'\middle|\begin{matrix}\boldsymbol{y}\\ j\end{matrix}\right) \tag{7}$$

is not a regular function of $\boldsymbol{y}$ at $\boldsymbol{y}=0$. Its limiting value depends on the direction by which the point $\boldsymbol{y}=0$ is approached. It gives the TO–LO splittings of the frequencies of the infrared active vibrations.

When the matrices $\boldsymbol{R}$ and $\boldsymbol{C}$ are mass-adjusted, Eq. (4) is written as

$$|\omega^2\boldsymbol{I}-[\boldsymbol{R}+\boldsymbol{ZCZ}]| = 0 \tag{8}$$

where $\boldsymbol{I}$ represents an unit matrix. For a certain infrared active symmetry species at $\boldsymbol{y}\sim 0$, matrix $\boldsymbol{R}$ of the longitudinal mode is exactly the same as that of the transverse mode, while matrices $\boldsymbol{C}(\mathrm{L})$ and $\boldsymbol{C}(\mathrm{T})$, matrix $\boldsymbol{C}$ of the longitudinal and of the transverse modes, respectively, differ from each other, because of the existence of the macroscopic field. Equation (8) can then be given by

$$|\omega^2(\mathrm{L})\boldsymbol{I}-[\boldsymbol{R}+\boldsymbol{ZC}(\mathrm{L})\boldsymbol{Z}| = 0$$

and

$$|\omega^2(\mathrm{T})\boldsymbol{I}-[\boldsymbol{R}+\boldsymbol{ZC}(\mathrm{T})\boldsymbol{Z}| = 0 \tag{9}$$

We consider the crystals M_nX_m which contain only two different particles such as ZnO and TiO_2. The effective ionic charge on particle M can be written as Ze. The effective charge on particle X is then $-(n/m)Ze$, since the crystal should be electrically neutral. In Eq. (9), $\boldsymbol{Z}$ is a diagonal matrix, the elements of which are effective ionic charges of particles. When matrix $\boldsymbol{C}$ is taken to include the constants e and $-(n/m)e$, we can write matrix $\boldsymbol{ZCZ}$ as $\boldsymbol{Z}^2\boldsymbol{C}$. Thus Eq. (9) becomes

$$\mathrm{Tr}\cdot[\boldsymbol{R}+\boldsymbol{Z}^2\boldsymbol{C}(\mathrm{L})] = \sum_i\omega_i^2(\mathrm{L})$$

and

$$\mathrm{Tr}\cdot[\boldsymbol{R}+\boldsymbol{Z}^2\boldsymbol{C}(\mathrm{T})] = \sum_i\omega_i^2(\mathrm{T}) \tag{10}$$

the value of Z being obtained from the equation

$$Z^2 = [\sum_i\omega_i^2(\mathrm{L})-\sum_i\omega_i^2(\mathrm{T})]/[\mathrm{Tr}\cdot\boldsymbol{C}(\mathrm{L})-\mathrm{Tr}\cdot\boldsymbol{C}(\mathrm{T})] \tag{11}$$

where Tr. $\boldsymbol{C}$ represents the trace of the matrix $\boldsymbol{C}$.

Effective Ionic Charges of Several Wurtzite and Rutile Type Crystals

We apply Eq. (11) to crystals of wurtzite and rutile type, the transverse and longitudinal frequencies of which are all known.

Wurtzite Type Crystals. The space group of the wurtzite type ZnO crystal is C^4_{6v}-$P6_3mc$ and the unit cell contains two formula units as shown in Fig. 1. At $\boldsymbol{y}\sim 0$, by factor group analysis the lattice vibrations can be classified into $2a_1+2b_1+2e_1+2e_2$. The vibrations of the symmetry species a_1 and e_1 are active in both infrared and Raman spectra, those of e_2 species are only Raman active, and those of b_1 species are optically inactive. The Cartesian symmetry coordinates are shown in Table 1. The acoustic modes belong to a_1 and e_1 species. When the point $\boldsymbol{y}=0$ is approached by 001 direction, $\boldsymbol{C}(\mathrm{L})a_1$ and $\boldsymbol{C}(\mathrm{T})e_1$ are obtained, where $\boldsymbol{C}(\mathrm{L})a_1$ represents matrix $\boldsymbol{C}$ of the longitudinal mode of a_1 species *etc.* On the other hand, when approached by 100 direction, we can get $\boldsymbol{C}(\mathrm{T})a_1$ and $\boldsymbol{C}(\mathrm{L})e_1$. The $\boldsymbol{C}$ matrices of b_1 and e_2 species are

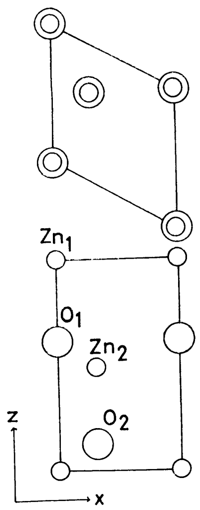

Fig. 1. Crystal structure of ZnO (wurtzite type). The upper figure represents the projection on the ab plane.

TABLE 1. CARTESIAN SYMMETRY COORDINATES FOR ZnO (zincite)

a_1	$s_1=[z(Zn_1)+z(Zn_2)]/\sqrt{2}$
	$s_2=[z(O_1)+z(O_2)]/\sqrt{2}$
b_1	$s_1=[z(Zn_1)-z(Zn_2)]/\sqrt{2}$
	$s_2=[z(O_1)-z(O_2)]/\sqrt{2}$
e_1	$s_1=[x(Zn_1)+x(Zn_2)]/\sqrt{2}$
	$s_2=[x(O_1)+x(O_2)]/\sqrt{2}$
	$s_1'=[y(Zn_1)+y(Zn_2)]/\sqrt{2}$
	$s_2'=[y(O_1)+y(O_2)]/\sqrt{2}$
e_2	$s_1=[x(Zn_1)-x(Zn_2)]/\sqrt{2}$
	$s_2=[x(O_1)-x(O_2)]/\sqrt{2}$
	$s_1'=[y(Zn_1)-y(Zn_2)]/\sqrt{2}$
	$s_2'=[y(O_1)-y(O_2)]/\sqrt{2}$

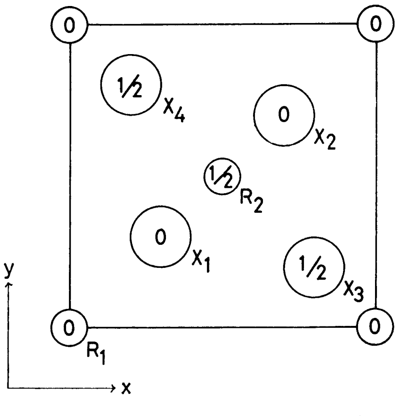

Fig. 2. Crystal structure of rutile type crystals. The figure represents the projection on the ab plane. The numbers in the circles mean the height along c axis.

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[9] See the chapter V of Ref. 1.

TABLE 2. EFFECTIVE IONIC CHARGES OF SEVERAL WURTZITE TYPE CRYSTALS

	Symmetry species	Observed frequencies (cm^{-1}) IR	Raman LO	Raman TO	Z	Z_{av}[d]
ZnO	a_1	(414)[a]	574[b]	380	1.07	1.05
	e_1		583	407	1.04	
ZnS	a_1	(274)[c]	352[b]	274	0.91	0.91
	e_1		352	274	0.91	
CdS	a_1	234[c]	305[b]	228	1.02	1.00
	e_1	241	305	235	0.98	
BeO	a_1		1081[b]	678	1.05	1.04
	e_1		1097	722	1.03	

a) Ref. 10. b) Ref. 11. c) Ref. 12.
d) The average value of Z obtained from a_1 and e_1 species.

independent of the direction of approach. For certain symmetry species $\mathrm{Tr}\cdot\boldsymbol{C}(\mathrm{L})-\mathrm{Tr}\cdot\boldsymbol{C}(\mathrm{T})$ in Eq. (11) can be calculated by use of the macroscopic field, Eq. (7) and the symmetry coordinates shown in Table 1. The results are

$$\mathrm{Tr}\cdot\boldsymbol{C}(\mathrm{L})-\mathrm{Tr}\cdot\boldsymbol{C}(\mathrm{T}) = 8\pi(1/m_{\mathrm{Zn}}+1/m_{\mathrm{O}})e^2/v_a \quad (12)$$

for both a_1 and e_1 species, where the effective ionic charges on Zn and O are $+Ze$ and $-Ze$, respectively. It is not necessary to calculate the complicated function $Q_{\alpha\beta}(\boldsymbol{y}/_{kk'})$. The values of Z obtained from Eqs. (11) and (12) for several wurtzite type crystals are summarized in Table 2.

Rutile Type Crystals. The space group of the rutile type crystal RX_2 is $D_{4h}^{14}-P4_2/mnm$ and the unit cell contains two formula units as shown in Fig. 2. At $\boldsymbol{y}\sim 0$, the lattice vibrations are classified by the

TABLE 3. CARTESIAN SYMMETRY COORDINATES FOR RUTILE TYPE CRYSTALS

a_{1g}	$s_1=[x(X_1)+y(X_1)-x(X_2)-y(X_2)+x(X_3)-y(X_3)-x(X_4)+y(X_4)]/2\sqrt{2}$
b_{1g}	$s_1=[x(X_1)-y(X_1)-x(X_2)+y(X_2)+x(X_3)+y(X_3)-x(X_4)-y(X_4)]/2\sqrt{2}$
a_{2g}	$s_1=[x(X_1)-y(X_1)-x(X_2)+y(X_2)-x(X_3)-y(X_3)+x(X_4)+y(X_4)]/2\sqrt{2}$
b_{2g}	$s_1=[x(X_1)+y(X_1)-x(X_2)-y(X_2)-x(X_3)+y(X_3)+x(X_4)-y(X_4)]/2\sqrt{2}$
a_{2u}	$s_1=[z(R_1)+z(R_2)]/\sqrt{2}$ $s_2=[z(X_1)+z(X_2)+z(X_3)+z(X_4)]/2$
b_{2u}	$s_1=[z(R_1)-z(R_2)]/\sqrt{2}$ $s_2=[z(X_1)+z(X_2)-z(X_3)-z(X_4)]/2$
e_g	$s_1=[z(X_1)-z(X_2)]/\sqrt{2}$ $s_1'=[z(X_3)-z(X_4)]/\sqrt{2}$
e_u	$s_1=[x(R_1)+y(R_1)]/\sqrt{2}$ $s_2=[x(R_2)+y(R_2)]/\sqrt{2}$ $s_3=[x(X_1)+y(X_1)+x(X_2)+y(X_2)]/2$ $s_4=[x(X_3)+y(X_3)+x(X_4)+y(X_4)]/2$ $s_1'=[x(R_1)-y(R_1)]/\sqrt{2}$ $s_2'=[x(R_2)-y(R_2)]/\sqrt{2}$ $s_3'=[x(X_1)-y(X_1)+x(X_2)-y(X_2)]/2$ $s_4'=[x(X_3)-y(X_3)+x(X_4)-y(X_4)]/2$

TABLE 4. EFFECTIVE IONIC CHARGES OF SEVERAL RUTILE TYPE CRYSTALS

	Symmetry species	Infrared (cm^{-1}) LO	Infrared (cm^{-1}) TO	Z	Z_{av}[f]
TiO_2[a]	a_{2u}	811	167	1.38	
	e_u	806	500		1.35
		458	388	1.31	
		373	183		
SnO_2[b]	a_{2u}	704	465	1.13	
	e_u	757	605		1.13
		368	284	1.13	
		273	243		
GeO_2	a_{2u}[c]	755	455	1.07	
	e_u[c]	815	635		1.08
		470	370	1.08	
		345	300		
	a_{2u}[d]	816	522	1.11	
	e_u[d]	852	709		1.10
		680	652	1.09	
		484	334		
ZnF_2[e]	a_{2u}	488	294	0.80	
	e_u	498	380		0.78
		264	244	0.76	
		227	173		

a) Ref. 13. b) Ref. 15. c) Ref. 16. d) Ref. 17.
e) Ref. 14. f) The average value of Z obtained from species a_1 and e_1.

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factor group analysis into $a_{1g}+b_{1g}+a_{2g}+2a_{2u}+b_{2g}+2b_{2u}+e_g+4e_u$. The vibrations of the gerade symmetry species except for a_{2g} are Raman active, those of a_{2u} and e_u species infrared active, and those of b_{2u} and a_{2g} species optically inactive. The Cartesian symmetry coordinates are shown in Table 3. The acoustic modes are included in a_{2u} and e_u species. As in the case of wurtzite type crystals, $\mathrm{Tr}\cdot\boldsymbol{C}(\mathrm{L})-\mathrm{Tr}\cdot\boldsymbol{C}(\mathrm{T})$ can be obtained by using the macroscopic field and the symmetry coordinates. The result is given by

$$\mathrm{Tr}\cdot\boldsymbol{C}(\mathrm{L}) - \mathrm{Tr}\cdot\boldsymbol{C}(\mathrm{T}) = 16\pi(2/m_\mathrm{R}+1/m_\mathrm{X})e^2/v_\mathrm{a} \qquad (13)$$

for both a_{2u} and e_u species, where the effective ionic charges on R and X are $+2Ze$ and $-Ze$, respectively. The values of Z obtained from Eqs. (11) and (13) for several rutile type crystals are listed in Table 4. For the crystal GeO_2, two different sets of frequencies were reported.[16,17] Table 4 includes the vlaues of the effective charges on the basis of the two sets.

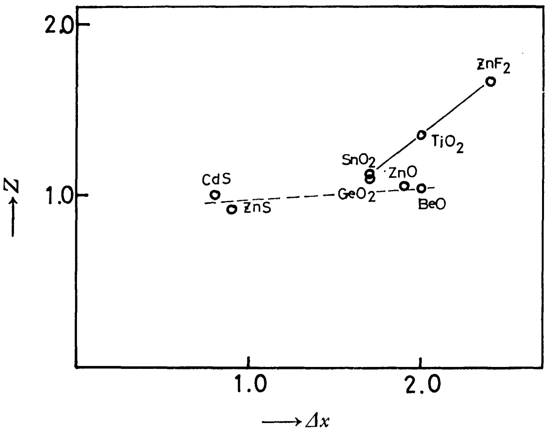

Fig. 3. The relation between the values of the effective ionic charges, Z, and the difference of the Pauling's electronegativity of the positive and negative ions, Δx.

The effective ionic charges on Zn for ZnO, ZnS, and ZnF_2 were found to be 1.05, 0.91, and 1.56 (2× 0.78), respectively. The results indicate that the nature of the ionic bonds of oxide and sulfide is more covalent than that of fluoride. Table 4 also shows that the values of Z for the three rutile type oxides increases in the order of $GeO_2<SnO_2<TiO_2$. TiO_2 has a large ionic character, which gives rise to a large TO–LO splitting in the frequencies of a_{2u} species. Figure 3 shows the relation between the values of the effective ionic charges Z and the difference of Pauling's electronegativity[18] of the positive and negative ions $\Delta\chi$. For rutile type crystals a fairly good linear relation is found between Z and $\Delta\chi$. However, for the wurtzite type crystals the values of Z are almost constant.

The values of the effective ionic charges were obtained on the basis of the rigid ion model. However, the ions are not rigid, that is, polarizable. In order to estimate the effect of the polarizable ion, we consider the following two examples, for which the values of the ionic charges were obtained by a model which contained the polarization of ions. For CdS, Nusimovici and Balkanski[7] calculated the phonon frequencies to fit the observed phonon dispersion curves. On the basis of a model which includes valence-bond forces, rigid ion Coulomb forces and electronic and ionic polarization, they gave 1.02*e* as the value of the ionic charge which was very close to the value 1.00*e* in Table 2. Traylor *et al.*[3d] studied the phonon dispersion relation of rutile (TiO_2) and obtained the value −1.26*e* as Z_0 on the basis of shell model. The value 1.26*e* is also close to the value 1.35*e* given in Table 4.

Orthorhombic Hydrogen Chloride Crystal

In ionic crystals long range interaction is of importance, but in molecular crystals it is usually omitted in the calculation of lattice vibration frequency. We tried to estimate its effect on the lattice vibration frequencies in molecular crystals, and chose orthorhombic hydrogen chloride crystal, since the system is simple and the frequency calculation at $y\sim0$ was already made by Ito *et al.*[19] on the basis of the force field only due to short range interactions.

The space group of the crystal is C_{2v}^{12}—$Bb2_1m$ and the Bravais cell contains two HCl molecules.[20] Factor group analysis gives the result $4a_1+4b_1+2a_2+2b_2$. The a_1, b_1, and b_2 species contain one acoustic mode each, and can be expected to have different frequencies in transverse and longitudinal modes. The frequencies were calculated by Eq. (4). Matrix $\boldsymbol{R}$ was constructed by the same force field as that adopted by Ito *et al.*[19] Matrix $\boldsymbol{C}$ was set up according to the method of Kellermann[2] on the assumption that the hydrogen atom has an electric charge $+Ze$ and the chlorine atom $-Ze$. The value of Z was determined to be 0.18 from the distance between H and Cl atoms (1.27 Å) and the dipole moment (1.085 D) of the gaseous hydrogen chloride molecule. The distance between D and Cl atoms in the orthorhombic DCl crystal is 1.25 Å,[21] so that the value of Z in the crystal

TABLE 5. THE CALCULATED FREQUENCIES FOR ORTHORHOMBIC HYDROGEN CHLORIDE CRYSTAL (IN cm^{-1})

Symmetry species	Calculation 1	Calculation 2	
		TO	LO
a_1	2727	2699	2703
	297	377	401
	97	93	93
b_1	2732	2709	2713
	501	574	593
	109	112	112
a_2	213	303	303
	54	56	56
b_2	215	316	375

a) The values differ slightly from those reported by Ito *et al.*[19], who assumed $F'_{\mathrm{HH}}=-0.1F_{\mathrm{HH}}$. In the present work F'_{HH} was assumed to be zero.

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21) E. Sándor and R. F. C. Farraw, *ibid.*, **213**, 171 (1967).

can not differ much from the value obtained from gas. The values of the force constants due to the short range interaction were taken to be the same as those by Ito *et al.* The calculated results are shown in Table 5 in which 1 gives the frequencies without long range interaction and 2 those obtained with long range interaction.

As expected the effect of long range interaction in the case of the hydrogen chloride crystal is not so large as that in ionic crystals. The TO–LO splittings of the internal H–Cl stretching vibrations are 4 cm^{-1}. The largest TO–LO splitting of the lattice vibrations is 59 cm^{-1} which was obtained for the librational mode of b_2 species. The vibrational modes of the lowest frequencies of a_1, b_1, and a_2 species are approximately the translational modes of the HCl molecules. It is concluded that their frequencies do not depend on the long range interaction, since the frequencies of calculation 1 and TO and LO frequencies of calculation 2 are about the same. However, for the frequencies of the librational modes, which have the second lowest frequency of all symmetry species, the effect of long range interaction is much larger than that for translational modes.