[August, 1983] © *1983 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **56**, *2193—2197 (1983)*

Lattice Dynamical Analysis of MgO

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(Received December 4, 1981)

The lattice dynamical properties of MgO are studied using a model based on the Birman method, which is different from the conventional point-like atom model. The model includes three kinds of forces: the short-range, the long-range Coulomb, and the long-range polarization interactions. The long-range interactions are dependent on the magnitude of the expansion of the electron distribution. The degrees of the expansion for Mg and O (w_{Mg} and w_O) are estimated from the X-ray data. The calculated phonon dispersion curves agree with the observed curves in the case of $w_{Mg}=0.35$ Å and $w_O=0.73$ Å, which are nearly equal to the estimated values, 0.35 and 0.65 Å.

Many theoretical treatments have been accumulated in order to interpret and describe the dielectric and dynamical behavior of lattices observed by means of inelastic neutron scattering in ionic crystals. In these attempts, two processes of the theoretical treatments have been developed: (1) from the rigid-ion model (RIM) through the rigid-shell model to the three-body-force shell model;[1-7] (2) from the RIM through the polarizable-ion model (PIM) to the modified PIM.[8,9]

In the previous paper,[10] the lattice dynamics of wurzite has been studied on the basis of the PIM, which is a point-like atom model like the RIM. Later this model was modified by taking the expansion of the electron distribution (electron expansion or expansion of electrons) on the basis of the Birman method;[11,12] this new model was called the modified PIM,[9] where attention was paid only to the influence of the electron expansion on the macroscopic quantities.

Then this method was applied to CaO[13] in order to see the relation between the expansion estimated by the modified PIM method and that obtained by the X-ray analysis; discrepancy was found between them because only the electron expansion of one side of an ion pair in CaO was taken into account.

This paper, therefore, will be concerned with the lattice dynamics of MgO using further modified treatment regarding the electron expansion of both the Mg and O ions. On this occasion, since the Birman method includes many hard problems when it is applied explicitly to lattice dynamics, some assumptions are introduced into the practical treatment in order to simplify the procedure. The last section shows the relation between the further modified PIM treatment and the shell-model treatment, which has been the most frequently used one and which has achieved a close reproduction of the observed data.

Theoretical Treatment

The Modified PIM. In the conventional method of calculating the electrostatic lattice potential, called the Ewald method,[14] the contribution of any ion to the potential at a point in a crystal consists of the sum of two terms including a Gaussian function with a width parameter w for a rapid convergence on the evaluation of the crystal potential. These two terms we previously symbolized as Φ_r and Φ_t.[12] The potential $\Phi(=\Phi_r+\Phi_t)$ based on the Ewald method is independent of w after summation. Birman[11] noticed the physical meaning of the two terms and the Gaussian function: Φ_t represents the potential due to a neutral configuration (core plus compensating Gaussian), and Φ_r, the potential due to the unbalanced Gaussian charge, while a half-width parameter w of a Gaussian indicates the degree of electron expansion of an atom. Under the Birman method, two potentials are differently weighted with the ion and the core (nucleus and inner electrons) charge, z and q^c, and total:

$$\begin{aligned}\phi(w) &= z\Phi_r(w) + q^c\Phi_t(w), \text{ or} \\ &= q^v\Phi_r(w) + q^c\Phi, \end{aligned} \tag{1}$$

where q^v represents the valence-electron charge ($q^v=z-q^c$). The electron-charge distribution is assumed to be described by a single normalized Gaussian:

$$\rho(\mathbf{x}) = \exp[-\mathbf{x}^2/w^2]/w^3\pi^{3/2}. \tag{2}$$

The interaction energy between the kth and k'th ions is represented as the sum of the products of the charge and the potential, and expressed by:

$$\begin{aligned}\phi(kk') = {} & q_k^c\{z_{k'}\Phi_r(w_{k'},\mathbf{x}_{k'}) + q_{k'}^c\Phi_t(w_{k'},\mathbf{x}_{k'})\} \\ & + q_k^v\int\{z_{k'}\Phi_r(w_{k'},\mathbf{x}_{k'}-\mathbf{x}') + q_{k'}^c\Phi_t(w_{k'},\mathbf{x}_{k'}-\mathbf{x})\} \\ & \times \rho_k^v(\mathbf{x}_k-\mathbf{x}')d\mathbf{x}', \end{aligned} \tag{3}$$

where $\rho_k^v(\mathbf{x}_k-\mathbf{x}')$ denotes the valence-electron charge-density distribution of the kth ion, the center of which resides at the position $\mathbf{x}_k(=0)$.[11,13]

The dynamical matrix for the PIM is written by its constituents as:[8]

$$\boldsymbol{D}(\boldsymbol{y},kk') = \boldsymbol{D}^N(\boldsymbol{y},kk') + \boldsymbol{D}^C(\boldsymbol{y},kk') + \boldsymbol{D}^P(\boldsymbol{y},kk'), \tag{4}$$

where $\boldsymbol{y}$ is the wave vector. Three interaction terms, $\boldsymbol{D}^N$, $\boldsymbol{D}^C$, and $\boldsymbol{D}^P$, are concerned with the short-range force, the long-range Coulomb force, and the long-range polarization force respectively. In the MPIM, long-range interactions are dependent upon the degree of the width parameter w in a Gaussian related to the electron expansion. The model parameters are the effective ionic charge z, the polarizabilities α_+ and α_-, four short-range force coefficients, A, A', B, and B', and the width parameter w. The formulas for the calculation of macroscopic quantities, such as the wavenumbers and elastic constants in the MPIM, have been shown in previous papers.[9,10,13]

Electron Expansion of Both Side Ions. In a previous paper,[13] we assumed $\rho(\mathbf{x}_k-\mathbf{x}')=\delta(\mathbf{x}_k-\mathbf{x}')$ in Eq. 3, that is, in the interaction between k and k', one side of an ion pair is always assumed to be a point charge. This approximation is called the first approximation. Though the expansion of both ions is taken into account in the treatment, the overlap between two expanded ions is not considered. The present treatment is a PIM further modified by taking into consideration the overlap effect due to both sides of the Mg and O ions. This approximation is called the second approximation.

When $\phi^{(1)}$ denotes the first term of Eq. 3 with respect to the charge, it can be represented as:

$$\phi^{(1)} = q^{\mathrm{c}}_k q^{\mathrm{v}}_{k'} \times \mathrm{Gaussian}(w_{k'}) + q^{\mathrm{c}}_k q^{\mathrm{c}}_{k'} \times \mathrm{Dot(Point)}, \tag{5}$$

where the first Gaussian term represents the interaction between the dotty (point-like) core of k and the Gaussian valence electron of the k' ion, and the second, the Dot term between the dotty core of k and that of k'. The remaining interactions of $q^{\mathrm{v}}_k q^{\mathrm{c}}_k \times$ Gaussian and $q^{\mathrm{v}}_k q^{\mathrm{v}}_{k'} \times$ Gaussian are included in the second term of Eq. 3, $\phi^{(2)}$. This term is rewritten by means of the constitutive charge-density distributions as:

$$\phi^{(2)} = q^{\mathrm{v}}_k \iint \textstyle\sum_l \{[q^{\mathrm{v}}_k q^{\mathrm{v}}_{k'}(\mathbf{x}'' - \mathbf{x}_{lk'}) + q^{\mathrm{c}}_k q^{\mathrm{c}}_{k'}(\mathbf{x}'' - \mathbf{x}_{lk'})] \\ /|\mathbf{x}'' - \mathbf{x}'|\} \mathrm{d}\mathbf{x}'' \rho_k(\mathbf{x}_{lk} - \mathbf{x}') \mathrm{d}\mathbf{x}', \tag{6}$$

and hence:

$$\phi^{(2)} = q^{\mathrm{v}}_k \textstyle\sum_l \iint \{q^{\mathrm{v}}_k q^{\mathrm{v}}_{k'}(\mathbf{x}'' - \mathbf{x}_{lk'})/|\mathbf{x}'' - \mathbf{x}'|\} \mathrm{d}\mathbf{x}'' \rho_k(\mathbf{x}') \mathrm{d}\mathbf{x}' \\ + q^{\mathrm{v}}_k q^{\mathrm{c}}_{k'} \textstyle\sum_l \int \rho_k \{(\mathbf{x}_k - \mathbf{x}')/(\mathbf{x}_{lk} - \mathbf{x}')\} \mathrm{d}\mathbf{x}', \tag{7}$$

where l indicates the cell index. The second term in this equation represents the contribution to the potential field at $\mathbf{x}_{lk}$ due to the Gaussian charge distribution, the center of which resides at $\mathbf{x}_k$ and the sum of which as regards l is represented by means of Φ_{r}.

The double integrals appearing in the first term in Eq. 7 are troublesome or scarcely calculable. A practical treatment is, therefore, carried out as follows. The overlap integral of the charge distributions $\rho(\mathbf{x})$ between the ions is given as:

$$\int \{\exp[-(\mathbf{x}_k - \mathbf{x}')^2/w_k{}^2]/w_k{}^2\pi^{3/2} \\ \times \{\exp[-(\mathbf{x}_{k'} - \mathbf{x}')^2/w_{k'}{}^2]/w_{k'}{}^3\pi^{3/2}\} \mathrm{d}\mathbf{x}' \\ = \exp[-(\mathbf{x}_k - \mathbf{x}_{k'})^2/(w_k{}^2 + w_{k'}{}^2)]/[(w_k{}^2 + w_{k'}{}^2)\pi]^{3/2}. \tag{8}$$

This result can be considered to represent the charge density at the point $\mathbf{x}_k$ due to the Gaussian residing at $\mathbf{x}_{k'}$ and with the width parameter of $(w_k{}^2 + w_{k'}{}^2)^{1/2}$. Accordingly, the double integral term is approximately represented by means of Φ_{r} with the with the width parameter of $(w_k{}^2 + w_{k'}{}^2)^{1/2}$. Though this approximation is mathematically not valid, this simplifies Eq. 3 to:

$$\phi(kk') = q^{\mathrm{c}}_k[z_{k'}\Phi_{\mathrm{r}}(w_{k'},\mathbf{X}) + q^{\mathrm{c}}_{k'}\Phi_{\mathrm{t}}(w_{k'},\mathbf{X})] \\ + q^{\mathrm{v}}_k q^{\mathrm{c}}_{k'}\Phi_{\mathrm{r}}(w_k,\mathbf{X}) + q^{\mathrm{v}}_k q^{\mathrm{v}}_{k'}\Phi_{\mathrm{t}}(\sqrt{w_k{}^2 + w_{k'}{}^2},\mathbf{X}) \\ = (z_k z_{k'} - q^{\mathrm{v}}_k q^{\mathrm{c}}_{k'} - q^{\mathrm{v}}_k q^{\mathrm{v}}_{k'})\Phi_{\mathrm{r}}(w_{k'},\mathbf{X}) \\ + q^{\mathrm{c}}_k q^{\mathrm{c}}_{k'}\Phi_{\mathrm{t}}(w_{k'},\mathbf{X}) + q^{\mathrm{v}}_k q^{\mathrm{c}}_{k'}\Phi_{\mathrm{r}}(w_k,\mathbf{X}) \\ + q^{\mathrm{v}}_k q^{\mathrm{v}}_{k'}\Phi_{\mathrm{t}}(\sqrt{w_k{}^2 + w_{k'}{}^2},\mathbf{X}), \tag{9}$$

where $\mathbf{X} = \mathbf{x}_k - \mathbf{x}_{k'}$. The signs of the terms with regard to the interaction between the valence charges of different kinds of ions have to be inverted. Though a physical reason for this inversion can not yet be given explicitly, it seems that the interaction between the valence charges of different kinds of ions makes a different contribution in comparison with that of the same kind.

The phonon dispersion is calculated by means of Eq. 9, where the calculation is performed by assuming $\phi(kk') = \phi(k'k)$.

Calculation and Results

Determination of w and q^{c}. In the Birman method, the electrons of an ion are divided into two parts, the "inner" (tightly bound) and the "valence" (loosely bound) parts.[11] The inner-core part is built of the nucleus and the inner electrons, while the electron expansion is formed of the outer, valence electrons. The division of electrons into the valence and the core may be unequivocal. In this paper the electrons are divided in accordance with the experimental charge-density distribution, though in the case of CaO[13] the division was based on the atomic arrangement of the neighbors.

Vidal-Valat *et al.*[16] have determined the atomic charge-density distribution for MgO by means of X-ray analysis, as is shown in Fig. 1. The dense inner distributions are assigned to the core electrons, shown by the shadow in the figure. The partitions of the electrons are illustrated in Fig. 2, together with their charges. The integration of these distributions leads to the findings that the total charge of the inner electrons of Mg is nearly equal to $4e$ and that of O to $2e$. Accordingly, the core charges, q^{c}, become $8|e|$ and $6|e|$ for Mg and O respectively. The dense outer distributions are assigned to the valence electrons. The width parameter w of the normalized Gaussian function for each ion is determined so as to reproduce the corresponding dense outer distributions. The results are that the w for Mg

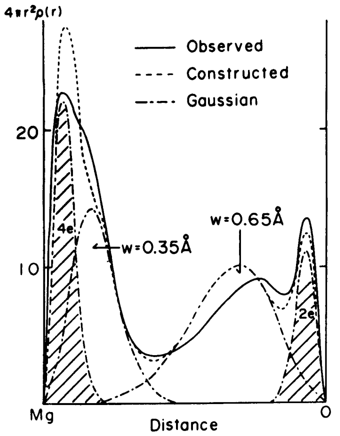

Fig. 1. The radial charge-density distribution for MgO. Shaded part indicate the inner electrons.

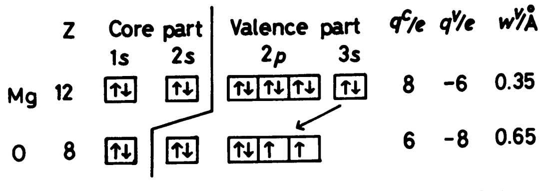

Fig. 2. Partitions of the electrons of Mg^{2+} and O^{2-}.

Table 1. Macroscopic quantities of MgO.

Lattice parameter	a/Å	4.21	Ref. 3a
High-frequency dielectric constant	ε_∞	2.96	Ref. 3a
Wave numbers	ν_{LO}/cm^{-1}	730	Ref. 3b
	ν_{TO}/cm^{-1}	400	Ref. 3b
Elastic constants	c_{11}/GPa	294	Ref. 17
	c_{12}/GPa	93	Ref. 17
	c_{44}/GPa	155	Ref. 17

Table 2. The model parameters determined for MgO on the first approximation

w_O/Å	z/e	α_-/Å^3	A/mdyn Å^{-1}	B/mdyn Å^{-1}	A'/mdyn Å^{-1}	B'/mdyn Å^{-1}
0.65	1.22	1.64	0.935	0.076	0.105	−0.029
0.90	1.40	1.67	0.910	0.018	0.080	−0.019
1.00	1.57	1.71	0.840	−0.020	0.050	−0.011
1.10	1.81	1.76	0.740	−0.065	0.007	0.

α_+ is fixed as 0.12 Å^3.

(w_{Mg}) is equal to 0.35 Å, while the w for O (w_O) is 0.65 Å. The effective ionic charge determined roughly by the use of this experimental charge distribution is nearly equal to the formal charge. The manner in which the experimental charge distribution is reconstructed with the Gaussian having these w values is shown in Fig. 1 by broken curves. Though the charge distribution constructed of the Gaussian in this way does not closely reproduce the observations up to the inner part, this is not important, for the interaction due to the electronic overlap occurs mostly in the outer part.

The accuracy of these evaluated w values is governed by the experimental error allowed for the X-ray measurements. By taking into account the experimental error and assuming that the charge distribution is represented by the Gaussian with only one parameter, the error of these w values was estimated at about ±0.1 Å.

Reproduction of Macroscopic Quantities. The macroscopic quantities are tabulated in Table 1. The effective ionic charge, $z(=q^c+q^v)$, and the electronic polarizability, α, are determined respectively from the observed *TO-LO* splitting and high-frequency dielectric constants.[10] The Coulomb and the polarization force terms in the dynamical matrix in Eq. 4 are estimated from z and α. The short-range force coefficients are adjusted towards agreement between the calculated and observed Γ-point optical mode wavenumbers and the elastic constants by successive approximations.

To make it clear that the second approximation is reasonable, the result calculated by means of the first approximation is given. Table 2 summarizes reasonable parameter sets producing observed macroscopic quantities against several different values of w_O, fixing $w_{Mg}=$ 0.35 Å. In order to examine the reasonableness of the parameters determined, the phonon dispersions are calculated by the use of these parameters, where $w_{Mg}=$ 0.35 Å and $w_O=0.65$ Å, both determined by the X-ray analysis, are adopted. However, certain marked discrepancies in the acoustic-branch mode towards higher wave vectors along the [y00] and [yy0] directions are seen (dotted curves in Fig. 3) and are improved by taking into account the further electron expansion, that is, when the w_O is expanded so far as to 1.1 Å (full curves in Fig. 3).

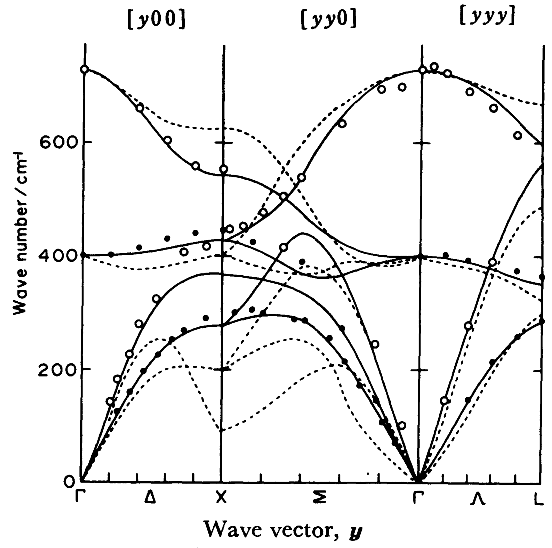

Fig. 3. The dispersion curves of MgO along three symmetry directions using the modified PIM on the assumption $\rho(\mathbf{x}_k-\mathbf{x}')=\delta(\mathbf{x}_0-\mathbf{x}')$. ------ Calculated results for $w_{Mg}=0.35$ Å and $w_O=0.65$ Å; —— those for $w_{Mg}=0.35$ Å and $w_O=1.1$ Å. Observation; ○ transverse branches; ● longitudinal branches.

Under the second approximation, where the overlap effect is due to both side ions, Mg and O, a closer reproduction of the phonon dispersion is given, as can be seen in Fig. 4, when the w_{Mg} and w_O are equal to 0.35 Å and 0.73 Å respectively, which are nearly equal to the values determined by the X-ray analysis. Even if the w_O changes from 0.65 Å to 0.73 Å, the total density is not far different from the observation. The model parameters for the further modified PIM are as follows: z/e, 1.97; α_-/Å^3, 1.82; A, A', B, and B'/mdyn Å^{-1}, 0.76, −0.14, −0.012, and 0.0025. Table 3 gives the calculated macroscopic quantities and the contributions of each kind of force to them. The value of the effective ionic charge, z, increases toward the formal charge with an increase in the value of w_O (see Table 2). The increase in the z value may be interpreted as indicating that all the electrons, spreading in accordance with the width parameter, can be explicitly assigned to each domain of

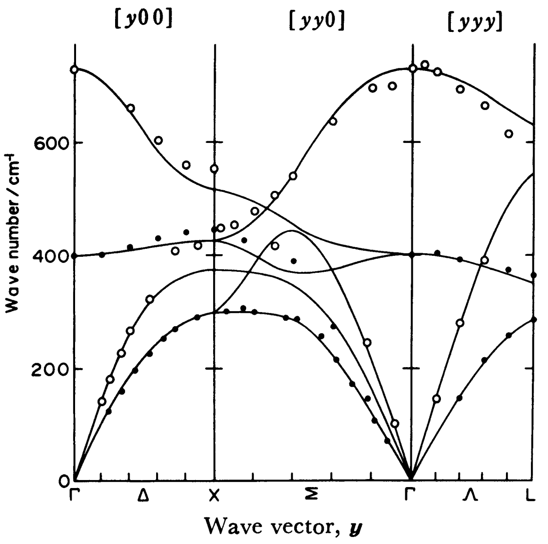

Fig. 4. The dispersion curves of MgO for $w_{Mg}=0.35$ and $w_0=0.73$ Å using the further modified PIM taking account of valence electron expansion of both the side ions.

TABLE 3. CALCULATED MACROSCOPIC QUANTITIES AND CONTRIBUTION OF EACH KIND OF FORCE TO THEM UNDER THE SECOND APPROXIMATION

	Calcd	Contribution (%)		
		D^N	D^C	D^P
ν	400.4	105	−5	−0
c_{11}	282	125	−25	
c_{12}	98	56	44	
c_{44}	163	−42	142	

an expanded ion. Usually the z value is smaller than the formal charge because of the neglect of the overlap or because of the interaction between the valence electrons. In the present treatment, as can be seen, by taking the electron expansion explicitly into account the z is estimated as the formal charge.

Thus, we have improved the previous finding that the electron expansion determined on the basis of the assumption that one side of an ion pair is a point charge is larger than that expected from the experimental data, and the w values determined from the phonon dispersion agree with those determined by means of the X-ray data.

Discussion

The origin of the polarization has been assumed to be the effective field at the lattice sites, which is composed of the externally applied field and the field due to the point dipoles of the crystal.[8] Woods *et al.*[12] have given an extended treatment so as to consider the short-range interaction causing the polarization—a treatment which has been termed the shell-model method. In this model, the polarizability is made finite by an arbitrary short-range harmonic restoring force with a spring constant k that acts between the core and the shell of an ion, while the relative displacement between the shell and the core produces a dipole moment at the ion site. The calculated phonon dispersions given by Sangster *et al.* on the basis of the shell model have reproduced the observed values very closely.[3b]

The value of k represents the strength of the bond between the core and the shell. If $k\rightarrow\infty$, the shell shrinks down to the core and the ion, therefore, becomes rigid. This rigid-shell model corresponds to the PIM. This feature of k is just the same as that of the width parameter w in the modified PIM, which can be determined by the X-ray data. As has been mentioned previously in the study on CaO[13] the shell charge, the core-shell coupling parameters, *etc.*, are the adjustable parameters in the shell model, whereas in the modified PIM treatment the only adjustable parameters are four short-range force coefficients. The other parameters, w, z, and a, can be determined independently from the results of the electron-charge distribution by means of the X-ray analysis, the *TO-LO* splitting phenomenon, and the dielectric property respectively. In conclusion, the further modified PIM treatment deserves well of the examination of lattice dynamics as well as the shell model because the parameter w reproducing the observed phonon dispersion curve agrees with the one estimated from the electron-density distribution. This treatment has, moreover, two advantages; the ease of handling because of the less adjustable parameters and the electronic overlap effect obtained by describing the valence-electron expansion by the Gaussian function.

The author wish to express their thanks to Professor Yosio Sakamoto and Mr. Hitoshi Arimori, Hiroshima University, for their indespensable help in the preparation of this paper.

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