

Lattice dynamics of ionic crystals in a model of “breathing” and polarizable ions

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An expression is written down for the dynamic matrix of ionic crystals in terms of a microscopic, parameterless model of “breathing” and polarizable ions. Results from a calculation of the complete spectrum of the lattice vibrations of ionic crystals having an NaCl structure are presented as an illustration. © 1998 American Institute of Physics. [S1063-7834(98)04202-6]

Recently Ivanov and Maksimov have presented^{1,2} microscopic justifications for a model of ionic crystals consisting of individual ions whose interaction also determines all the static and dynamic properties. This picture of ionic crystals is described rather completely by a simplified version of the functional density method proposed by Gordon and Kim.³ The later work^{1,2} generalizes the Gordon–Kim model so as to include the multipole polarizabilities of the ions. These must be included when calculating the electronic polarizability of the ions in the crystal, the dielectric permittivity, and the spectrum of the crystal lattice vibrations. The polarizability and deformability of the ions have been taken into account previously through a phenomenological model^{4–6} and an adequate description of the lattice dynamics of ionic crystals was obtained by including these effects. This approach, however, could only be used to calculate the lattice vibration frequencies of ionic crystals with a simple structure, since a large number of unknown parameters are involved. In Ivanov and Maksimov’s method^{1,2} there are no fit parameters and this method can be used for calculating the lattice vibrations of ionic crystals with a complicated crystalline structure. In it^{1,2} the lattice vibration frequencies are calculated by the frozen phonon method, which greatly limits the possible applications, since the whole frequency spectrum of the lattice vibrations cannot be calculated by the frozen phonon method.

In this paper the approach employed in Refs. 1 and 2 is used to derive expressions for the dynamic matrix and high-frequency dielectric constant and to calculate the complete phonon spectrum of the lattice vibrations of alkali halide crystals and alkaline earth oxides with an NaCl structure.

1. DYNAMIC MATRIX

An ionic crystal is treated as consisting of spherically symmetric overlapping ions and the total electron density can be written in the form

$$\rho(r) = \sum_i \rho_l(\mathbf{r}_i - \mathbf{R}_i). \quad (1)$$

The total energy of the crystal is given by^{1,2}

$$\begin{aligned} E = & \frac{1}{2} \sum_{ij} \frac{Z_i^{\text{ion}} Z_j^{\text{ion}}}{|\mathbf{R}_i - \mathbf{R}_j|} + \sum_i E_i^{\text{self}}(V_i) \\ & + \frac{1}{2} \sum_{ij} \Phi_{ij}(V_i, V_j, |\mathbf{R}_i - \mathbf{R}_j|) + \sum_i \frac{\mathbf{P}_i^2}{\alpha_i(V_i)} \\ & + \frac{1}{2} \sum_{ij} \mathbf{P}_i Q_{ij}(|\mathbf{R}_i - \mathbf{R}_j|) \mathbf{P}_j \\ & + \frac{1}{2} \sum_{ij} \mathbf{P}_i \Gamma_{ij}(V_i, V_j, |\mathbf{R}_i - \mathbf{R}_j|) \mathbf{P}_j - \sum_{ij} \mathbf{P}_i \mathbf{S}_j(i) \\ & - \sum_i \mathbf{P}_i \mathbf{E}_i, \end{aligned} \quad (2)$$

where the first term describes the Coulomb interaction of the nuclei and the second is the intrinsic energy of an ion, which depends on the potential V_i created by the crystalline environment. The pairwise interaction energy Φ_{ij} is defined as^{2,7}

$$\begin{aligned} \Phi_{ij} = & E[\rho_i(\mathbf{r}_i - \mathbf{R}_i) + \rho_j(\mathbf{r}_i - \mathbf{R}_j)] - E[\rho_i(\mathbf{r}_i - \mathbf{R}_i)] \\ & - E[\rho_j(\mathbf{r}_j - \mathbf{R}_j)]. \end{aligned} \quad (3)$$

In Eq. (1) $\mathbf{R}_i = \mathbf{R}_i^0 - \mathbf{u}_i$, \mathbf{u}_i is the displacement of an ion from its equilibrium position, \mathbf{P}_i and α_i are the dipole moment and polarizability of the i -th ion, respectively, and \mathbf{E}_i is the electric field at the i -th ion owing to the displacement of the atoms from their equilibrium position, i.e.,

$$\mathbf{E}_i = - \sum_j Q_{ij} Z_j^{\text{ion}} \mathbf{u}_j. \quad (4)$$

The matrices Q_{ij} and Γ_{ij} describe the long and short range parts, respectively, of the dipole-dipole interaction, $\mathbf{S}_j(i) = \sum_k m_{jk} \mathbf{u}_k$, and the matrix m_{jk} describes the deformability of an ion. Expanding the first three terms in Eq. (1) in terms of the small displacements \mathbf{u}_i , eliminating \mathbf{P}_i from the minimum energy condition, and transforming to normal coordinates, we obtain an expression for the dynamic matrix,

$$\begin{aligned} D_{\alpha k, \beta k'}(\mathbf{q}) = & (D_{\alpha k, \beta k'}^{\text{pib}}(\mathbf{q}) + D_{\alpha k, \beta k'}^{\text{pol}}(\mathbf{q}))(m_k m_{k'})^{-1/2}, \\ D_{\alpha k, \beta k'}^{\text{pib}}(\mathbf{q}) = & \frac{1}{2} Z_k Q_{\alpha k, \beta k'}(\mathbf{q}) Z_{k'} \end{aligned}$$

TABLE I. Cell parameters, dielectric constants, limiting phonon frequencies, and dynamic charges.

Crystal	$\alpha, \text{\AA}$		ε_∞		$\omega_{T0}, \text{cm}^{-1}$		$\omega_{L0}, \text{cm}^{-1}$		Z_{eff}	
	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.
LiF	4.03	4.02	1.9	1.71	308	343	636	536	1.0	0.70
NaF	4.63	4.66	1.7	1.54	239	229	413	338	1.02	0.72
KF	5.34	5.24	1.5	1.69	191	127	323	269	1.01	0.95
RbF	5.60	5.61	1.9	1.84	154	156	286	277	1.25	1.16
LiCl	5.14	4.5	2.7	3.36	191	364	398	557	1.15	1.27
NaCl	5.64	5.4	2.3	2.30	164	161	265	239	1.13	0.9
KCl	6.29	5.92	2.1	2.25	143	102	212	180	1.11	0.99
RbCl	6.60	6.24		2.32	124	112	172	169	1.13	1.08
LiBr	5.50	5.03	3.2	3.25	159	319	323	466	1.18	1.25
NaBr	6.00	5.82	2.6	2.38	133	139	207	193	1.14	0.88
KBr	6.60	6.24	2.4	2.36	120	111	166	154	1.11	0.94
RbBr	6.88	6.56		2.38		82		115		0.96
LiI	6.00	5.32		3.91		326		506		1.72
NaI	6.48	6.14	2.9	2.70	120	169	170	216	1.07	1.06
KI	7.06	6.59	2.7	2.58	101	109	138	150	1.14	1.10
RbI	7.34	6.88	2.6	2.58	74	76	101	102	1.13	1.01
MgO	4.21	4.21	3.0	2.83	400	476	750	617	1.15	0.98
CaO	4.81	4.79	3.4	2.95	300	350	574	516	1.26	1.28
SrO	5.16	5.10	3.3	3.09	240	330	495	474	1.40	1.41
BaO	5.54	5.50	3.3	3.32	150	222	430	418	1.45	1.75

$$\begin{aligned}
 & + \sum_{\mathbf{n}j} \frac{\partial}{\partial V_k} \Phi \begin{pmatrix} 0 & \mathbf{n} \\ k & j \end{pmatrix} Q_{\alpha k, \beta k'}(\mathbf{q}) Z_{k'} \\
 & + \frac{\partial E_k^{\text{self}}}{\partial V_k} Q_{\alpha k, \beta k'}(\mathbf{q}) Z_{k'} \\
 & + T_{\gamma i, \alpha k}^*(\mathbf{q}) R_{\gamma i, \gamma' i'}(\mathbf{q}) Q_{\gamma' i', \beta k'}(\mathbf{q}) Z_{k'} \\
 & + Z_k Q_{\gamma i, \alpha k}^*(\mathbf{q}) R_{\gamma i, \gamma' i'}(\mathbf{q}) T_{\gamma' i', \beta k'}(\mathbf{q}) \\
 & + T_{\gamma i, \alpha k}^*(\mathbf{q}) R_{\gamma l, \gamma' l'}(\mathbf{q}) T_{\gamma' i', \beta k'}(\mathbf{q}), \quad (6)
 \end{aligned}$$

where

$$\begin{aligned}
 p_{\alpha k}^j(\mathbf{q}) &= \sum_{\mathbf{n}} \left[\frac{\partial^2}{\partial V_k \partial R_\alpha} \Phi \begin{pmatrix} \mathbf{n} & 0 \\ k & k' \end{pmatrix} \right] \exp(-i\mathbf{q}\mathbf{n}), \\
 d_{\alpha k} &= - \sum_{\mathbf{n}j} \left[\frac{\partial^2}{\partial V_k \partial R_\alpha} \Phi \begin{pmatrix} 0 & \mathbf{n} \\ k & j \end{pmatrix} \right], \\
 g_{k, k'}(\mathbf{q}) &= \sum_{\mathbf{n}} \left[\frac{\partial^2}{\partial V_k \partial V_{k'}} \Phi \begin{pmatrix} \mathbf{n} & 0 \\ k & k' \end{pmatrix} \right] \exp(-i\mathbf{q}\mathbf{n}), \\
 i_k &= - \sum_{\mathbf{n}j} \left[\frac{\partial^2}{\partial V_k^2} \Phi \begin{pmatrix} 0 & \mathbf{n} \\ k & j \end{pmatrix} \right] + \frac{\partial^2 E_k^{\text{self}}}{\partial V_k^2}, \\
 \hat{R} &= (\hat{\Gamma} + \hat{Q} + \hat{\alpha})^{-1}, \quad (\hat{\alpha})_{\gamma i, \gamma' i'} = \delta_{\gamma \gamma'} \delta_{i i'} \alpha_i,
 \end{aligned}$$

TABLE II. Electronic polarizabilities of oxygen, halogens, and metals in compounds with an NaCl structure.

Crystal	$\alpha_M, \text{\AA}^3$	$\alpha_x, \text{\AA}^3$	Crystal	$\alpha_M, \text{\AA}^3$	$\alpha_x, \text{\AA}^3$
LiF	0.02	0.71	KI	0.71	5.09
NaF	0.12	0.79	RbI	1.29	5.24
KF	0.73	0.86	LiBr	0.02	3.21
RbF	1.36	0.89	NaRb	0.12	3.58
LiCl	0.02	2.35	KBr	0.71	3.76
NaCl	0.12	2.69	RbBr	1.3	3.88
KCl	0.71	2.89	MgO	0.06	1.6
KbCl	1.32	2.99	CaO	0.38	2.03
LiI	0.02	4.38	SrO	0.75	2.28
NaI	0.12	4.84	BaO	1.3	2.63

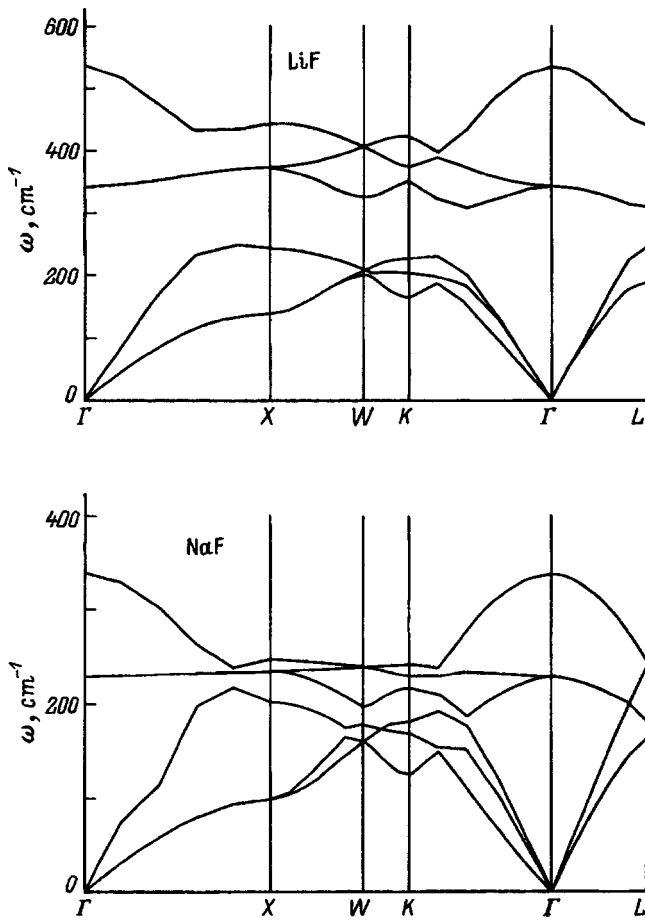


FIG. 1. Phonon dispersion in MF (calculated).

$$\begin{aligned}
 T_{\alpha k, \beta k'}(\mathbf{q}) = & \left\{ \sum_{\mathbf{n}j} \left[\frac{\partial}{\partial V_k} S_{\alpha} \begin{pmatrix} 0 & \mathbf{n} \\ k & j \end{pmatrix} \right] \frac{\partial V_k}{\partial R_{\beta}} \exp(i\mathbf{q}\mathbf{n}) \right. \\
 & + \sum_{\mathbf{n}j} \left[\frac{\partial}{\partial V_j} S_{\alpha} \begin{pmatrix} \mathbf{n} & 0 \\ k & j \end{pmatrix} \right] \frac{\partial V_j}{\partial R_{\beta}} \\
 & \left. + \sum_{\mathbf{n}} \left[\frac{\partial}{\partial R_{\beta}} S_{\alpha} \begin{pmatrix} \mathbf{n} & 0 \\ k & k' \end{pmatrix} \right] \exp(-i\mathbf{q}\mathbf{n}) \right\} \\
 & \times \exp(-i\mathbf{q}(\mathbf{r}_k - \mathbf{r}_{k'}))
 \end{aligned}$$

An expression for the dynamic matrix D^{pib} in the “breathing” ion model has been obtained in Ref. 7.

2. LATTICE DYNAMICS OF CRYSTALS WITH AN NaCl STRUCTURE

We shall use this expression for the dynamic matrix to calculate the lattice dynamics of alkali halide crystals and alkaline earth oxides with an NaCl structure. The calculated equilibrium values of the unit cell parameters, limiting vibration frequencies, high-frequency dielectric constant, and dynamic Born charges, as well as experimental data for comparison, are listed in Table I. The calculated polarizabilities of the metals, oxygen, and halogens are given in Table II. Dispersion curves together with available experimental data for the symmetric directions of the Brillouin zone are shown in Figs. 1–5. As can be seen from Table I and the figures, the

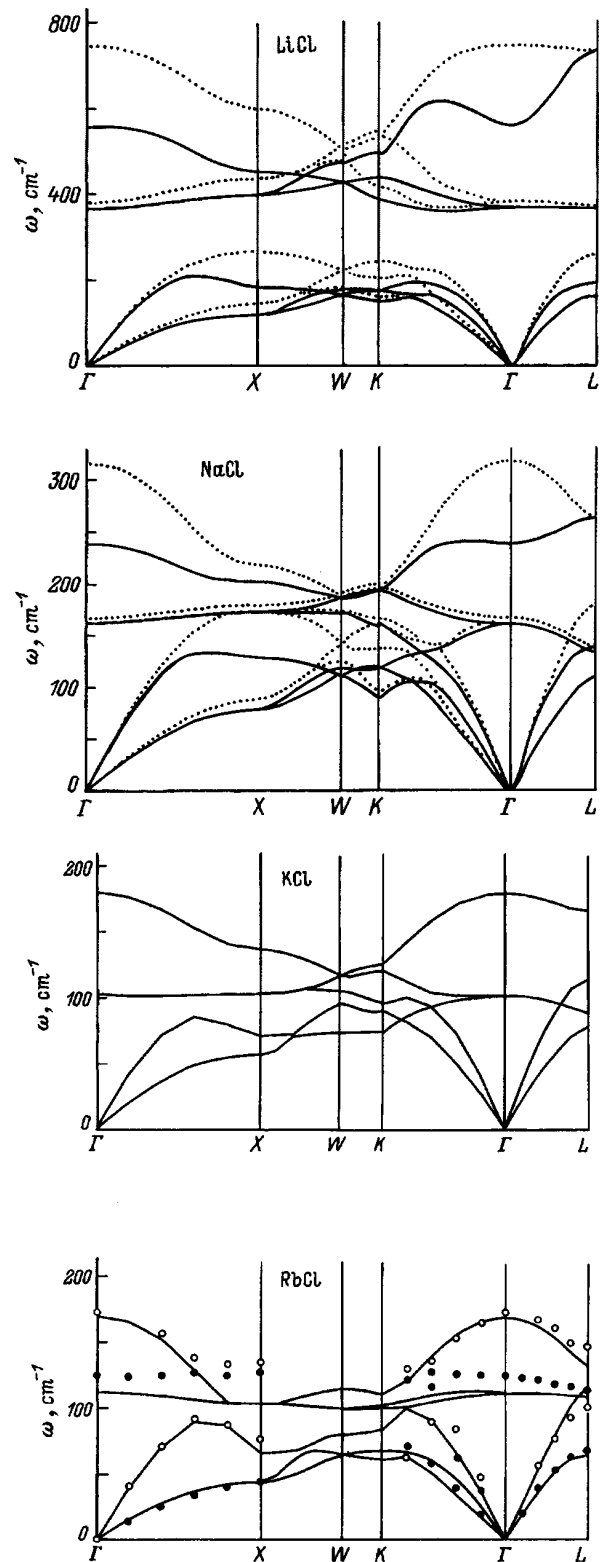


FIG. 2. Phonon dispersion in MCl. The smooth curves are calculated. For comparison, the results of a “breathing”-ion-model calculation neglecting the ion polarizability are shown as dotted curves. The hollow and solid circles are the experimental dependences for the longitudinal and transverse branches, respectively.¹³

agreement between the calculated and experimental values and dependences is quite satisfactory, except for LiCl and LiBr crystals, for which the calculated transverse optical mode frequencies are 2 times the experimental values.

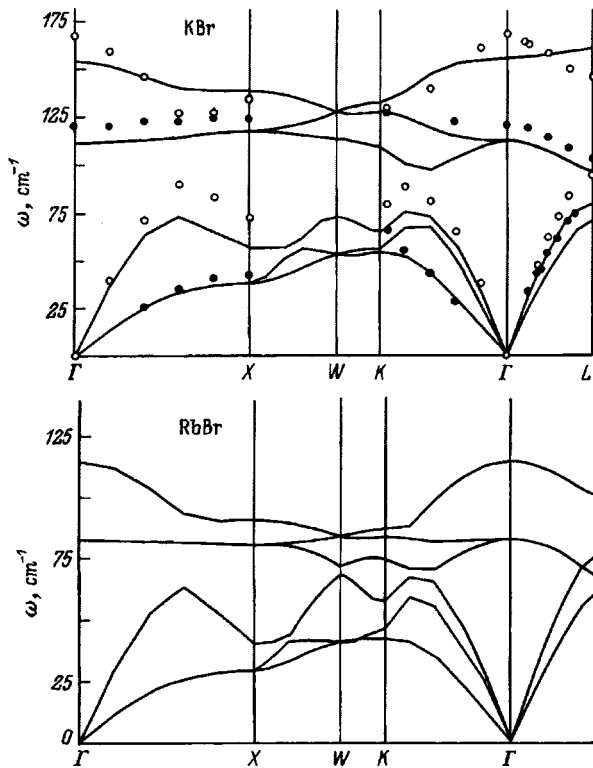


FIG. 3. Phonon dispersion in MBr. The smooth curves are calculated. The hollow and solid circles are the experimental dependences for the longitudinal and transverse branches, respectively.¹⁴

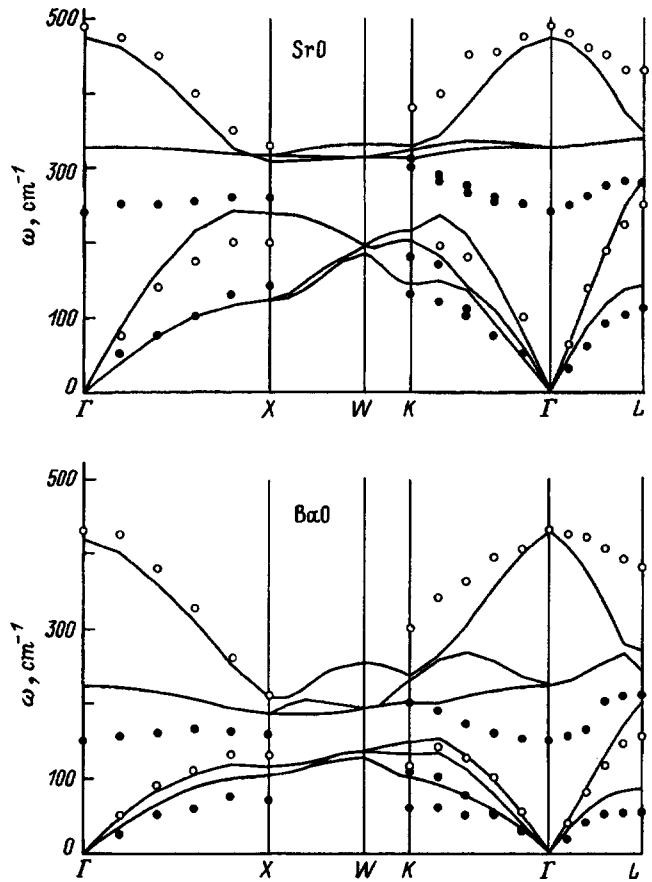


FIG. 5. Phonon dispersion in MO. The smooth curves are calculated. The hollow and solid circles are the experimental dependences for the longitudinal and transverse branches, respectively.⁹⁻¹²

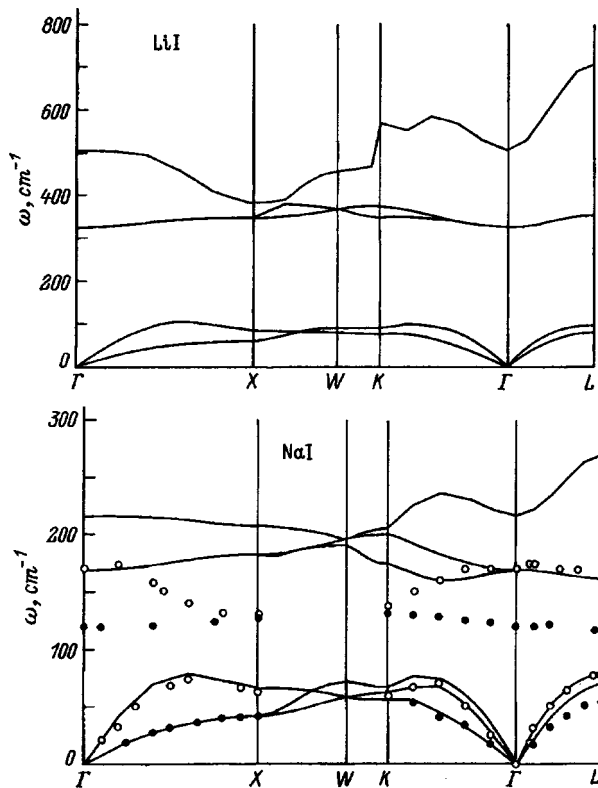


FIG. 4. Phonon dispersion in MI. The smooth curves are calculated. The hollow and solid circles are the experimental dependences for the longitudinal and transverse branches, respectively.¹⁴

Thus, the calculations made here show that a rather simple microscopic model of ionic crystals including the monopole and dipole polarizability of the ions can be used successfully to calculate the static and dynamic properties. The advantage of this method is that the time to compute the complete phonon spectrum is several orders of magnitude shorter than for the other known methods of calculating the crystal lattice vibrational frequencies based on first principles and this offers the possibility of calculating the lattice dynamics of compounds having a complicated crystalline structure.

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