Macroscopic calculations of the electron polarizability and lattice dynamics of ionic crystals

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Microscopic calculations of the electron polarizability and lattice dynamics of ionic crystals are performed. The total electron density is represented as a superposition of overlapping densities of individual ions. In the spirit of Leontovich's method for nonequilibrium thermodynamics, the electron density distribution of an individual ion is calculated in the presence of auxiliary external fields which deform the electron density distribution of the ion. The deformation parameters are determined by minimizing the total energy of the crystal. The total energy of the crystal is regarded as a functional of the electron density, which is described by the local Thomas–Fermi approximation taking into account exchange effects. The computational results for the dielectric constants and phonon frequencies agree well with the experimental data. © *1995 American Institute of Physics.*

1. INTRODUCTION

The quantum theory of ionic crystals is one of the oldest, but still developing, fields of solid-state physics. By the beginning of the 1930s, Jensen and Lenz[1] had successfully used the newly formulated Thomas–Fermi statistical theory[2,3] to calculate the binding energy and equilibrium volume of alkali halide crystals. Later, starting with the classical works of Löwdin[4] and Tolpygo,[5] ionic crystals were widely investigated with the aid of the overlap model. On the basis of that model, an ionic crystal is regarded as consisting of individual ions at which the electron wave functions overlap slightly. The total energy of the crystal is determined by the Coulomb interactions of the ions and various overlap integrals of the electron wave functions of the individual ions. Among recent works in this direction we mention the investigations of the alkali halide crystals performed by Abarenkov and Antonova[6] and Zeyher (Ref. 7).

Until recently, however, many investigations of the electron polarizability and lattice dynamics of ionic crystals were based on various types of phenomenological models. For example, the well-known Clausius–Mossoti formula for the dielectric constant ε_∞

$$\epsilon_\infty = 1 + \frac{4\pi\alpha_s/v_0}{1-4\pi\alpha_s/3v_0}, \tag{1}$$

where v_0 is the unit-cell volume and α_s is the polarizability of a unit cell, was usually employed to describe the electron polarizability. In the case of diatomic cubic crystals, the standard expression was used for α_s

$$\alpha_s = \alpha_+ + \alpha_-, \tag{2}$$

where α_+ is the cation polarizability and α_- is the anion polarizability. As the analysis performed in Ref. 8 of the dielectric constant for a large number of ionic crystals showed, this approach makes it necessary to employ polarizabilities α_+ and α_- that differ substantially from their values for the free ions. Moreover, the corresponding polarizabilities, and especially α_-, are found to be different for different crystals, depending on the crystal environment, interionic distances, and so on. Later there appeared a large number of works[9–11] in which attempts were made to estimate or calculate the change in the electron polarizability of an ion placed in a crystal. In these works it was shown that the change in the polarizability of an ion in a crystal appears as a result of the long-range Madelung potential from other ions, as well as because of the short-range forces associated with the overlap of the electron densities of the nearest-neighbor ions.

Unfortunately, the possibility of representing the dielectric constant in the form of the Clausius–Mossotti formula with the electron polarizability defined to be the sum of the polarizabilities of the individual ions was not considered at all in these works. The problem is that Eqs. (1) and (2) are strictly valid only for systems of point-like ions, for which there exists a local relation between the induced dipole $\mathbf{P}_n$ and the local electric field $\mathbf{E}_n^{\mathrm{loc}}$ on the given ion:

$$\mathbf{P}_n = \alpha_n \mathbf{E}_n^{\mathrm{loc}}. \tag{3}$$

The local field $\mathbf{E}_n^{\mathrm{loc}}$ in turn can be expressed in terms of the external electric field $\mathbf{E}^{\mathrm{ext}}$ and the Lorentz field $(4\pi/3)\mathbf{P}$:

$$\mathbf{E}_n^{\mathrm{loc}} = \mathbf{E}^{\mathrm{ext}} + \frac{4\pi}{3}\mathbf{P}. \tag{4}$$

where $\mathbf{P}$ is the total polarization of the system

$$\mathbf{P} = \frac{1}{V}\sum_n \mathbf{P}_n, \tag{5}$$

and V is the volume of the system.

As shown in Ref. 12 for a simple model of overlapping oscillators, taking overlap into account does not simply lead to a change in the magnitude of the polarizability of an oscillator—it also leads to a nonlocal coupling between $\mathbf{P}_n$ and $\mathbf{E}_n^{\mathrm{loc}}$:

$$\mathbf{P}_n = \sum_{n'} \alpha_{nn'} \mathbf{E}_{n'}^{\mathrm{loc}}. \tag{6}$$

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The same nonlocal coupling also appears in the well-known shell model.[13] The existence of nonlocal polarizabilities $\alpha_{nn'}$ means that in the general case, the total electron polarizability of a crystal cannot be expressed solely in terms of the polarizabilities of individual ions. This problem will be discussed in detail below.

It is also very important to take the electron polarizability into account correctly in calculations of the lattice dynamics of ionic crystals. A substantial amount of work in this direction has been carried out using phenomenological models. These include the aforementioned shell model,[13] the deformed-ion model,[14] and the "breathing" ion model (Ref. 7 and 16). Attempts have been made to provide a microscopic justification for these models on the basis of a wave-function overlap scheme. Specific calculations for a number of coefficients appearing in these models have been carried out only for the simplest ionic crystal, LiH.[7] However, these investigations made it possible to formulate the most general phenomenological model of the lattice dynamics.[16] This model includes the dipole polarization of an ion as a result of the action of electric fields on the ion, as happens in the shell model. The dipole polarization resulting from the deformation of an ion by its immediate environment is also taken into account. In this model there is also the possibility of monopole polarization of an ion as a result of a change in the effective radius of the ion, i.e., the existence of a "breathing" ion. Unfortunately, in such a general model, there are a large number of unknown constants, and it is very difficult to choose these constants correctly.

There exists a formally rigorous microscopic theory, formulated more than 20 years ago, of the electron polarizability and lattice dynamics of ionic crystals[17] (see also the review in Ref. 18) that employs the dielectric constant matrix $\epsilon(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}')$ in the space of the reciprocal lattice vectors $\mathbf{K}$ and $\mathbf{K}'$. Since it is necessary to perform difficult calculations of a large number of matrix elements of the dielectric constant matrix, systematic microscopic calculations on the basis of this approach have been performed only for a very limited number of simple ionic crystals (see the review in Ref. 18). In the last few years, microscopic approaches based on the density functional method for the ground-state energy have been developed for calculating the polarization of ionic crystals and lattice dynamics (see the review in Ref. 19). This approach is in itself completely universal and can be used to calculate any type of crystal. However, its universality makes it necessary to carry out very complicated calculations of the electronic band structures and linear response functions. Actually, all of the calculations of the lattice dynamics based on this method have thus far been limited to an investigation of a small number of phonon modes, mainly at momentum $\mathbf{q}=0$. Specifically, this approach was employed to study the ferroelectric instability in perovskites[20,21] and IV–VI semiconductors (Ref. 22).

We emphasize that all of the foregoing first-principles microscopic methods for calculating the electron polarizability and lattice dynamics of ionic crystals have, besides complexity and awkwardness, one other important deficiency. In these methods, we lose the physically transparent and attractive picture of an ionic crystal consisting of individual ions whose interaction determines all static and dynamic properties of these crystals. This is especially important, because a great deal of experimental and theoretical evidence supports this picture of an ionic crystal.

One objective of the present work will be to justify this picture. To this end, a simplified version of the density functional method, first proposed by Gordon and Kim, is employed.[23] In the next section a detailed exposition of the initial idea of Ref. 23 and an elaboration of this idea that makes it possible to take into account multipole polarizabilities of ions, necessary for calculating the electron polarizability and lattice dynamics, will be given. In Sec. 3, a method for calculating ionic crystals taking into account the dipole polarization of the ions is described. In Sec. 4, the principles for calculating the electronic dielectric constant and the phonon spectra are formulated and computational results are presented. Some problems requiring further investigation are discussed in the concluding section.

The atomic system of units is used throughout.

2. GENERALIZED GORDON–KIM MODEL

In the Gordon–Kim model,[23] an ionic crystal consists of individual overlapping spherically symmetric ions. The total electron density can be written in the form

$$\rho(\mathbf{r})=\sum_i \rho_i(\mathbf{r}-\mathbf{R}_i), \tag{7}$$

where the summation extends over all ions in the crystal. The electron density distribution $\rho_i(\mathbf{r})$ of an individual free ion can be calculated using any atomic program. Specifically, in Ref. 23, the Hartree–Fock values of $\rho_i(r)$ were used. We note immediately that accurate experimental measurements of the electron density distribution $\rho(\mathbf{r})$ in alkali halide crystals[24,25] confirm that $\rho(\mathbf{r})$ can be represented in the form (7). The experimental data show, however, that the electron density on a negative ion is slightly compressed compared with its distribution on a free ion. The same result was also obtained in Ref. 26, where careful microscopic calculations of the function $\rho(\mathbf{r})$ were carried out by the Hartree–Fock method for alkali halide crystals.

Using Eq. (7) for $\rho(\mathbf{r})$, the total energy of the crystal in the density functional method can be represented in the form

$$E^{\mathrm{cr}}=E\left\{\sum_i \rho_i(\mathbf{r}-\mathbf{R}_i)\right\}-\sum_i E\{\rho_i(\mathbf{r}-\mathbf{R}_i)\}+E^N$$
$$+\sum_i E\{\rho_i(\mathbf{r}-\mathbf{R}_i)\}. \tag{8}$$

Here E^N is the interaction energy of the nuclei, which can be written as

$$E^N=\frac{1}{2}\sum_{i,i'}\frac{Z_i^N Z_{i'}^N}{|\mathbf{R}_i-\mathbf{R}_{i'}|}, \tag{9}$$

where Z_i^N is the nuclear charge of the i-th ion. The quantity $E\{\rho\}$ is the electron density functional and, in accordance with the work of Hohenberg and Kohn,[28] can be represented as

$$E\{\rho\}=\int d^3\mathbf{r}\rho(\mathbf{r})V^{\mathrm{ext}}(\mathbf{r})+\frac{1}{2}\int d^3\mathbf{r}\int d^3\mathbf{r}'\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$
$$+\int d^3\mathbf{r}F\{\rho(\mathbf{r})\}. \tag{10}$$

Here $V^{\mathrm{ext}}(\mathbf{r})$ is the external potential, which in the crystal is simply the Coulomb potential of the nuclei

$$V^{\mathrm{ext}}(\mathbf{r})=\sum_i \frac{Z_i^N}{|\mathbf{r}-\mathbf{R}_i|}. \tag{11}$$

The quantity $F\{\rho\}$ is a universal density functional, describing the contribution of the kinetic energy $T\{\rho\}$ and the exchange energy $E^{\mathrm{ex}}\{\rho\}$ of the electrons. In Ref. 23 it was suggested that the standard local Thomas–Fermi approximation, extended in order to take into account exchange and correlation, be used for $F\{\rho\}$.

Neglecting the overlap of more than two ions at the same time and the self-energy of the ions, Eq. (8) for the energy of the crystal can be rewritten in the form

$$E^{\mathrm{cr}}=\frac{1}{2}\sum_{i\neq i}\frac{Z_i^N Z_{i'}^N}{|\mathbf{R}_i-\mathbf{R}_{i'}|}+\frac{1}{2}\sum_{i\neq i'}V_{i,i'}, \tag{12}$$

where $V_{i,i'}$ has the form

$$V_{i,i'}=E\{\rho_i(\mathbf{r}-\mathbf{R}_i)+\rho_{i'}(\mathbf{r}-\mathbf{R}_{i'})\}-E\{\rho_i(\mathbf{r}-\mathbf{R}_i)\}$$
$$-E\{\rho_{i'}(\mathbf{r}-\mathbf{R}_{i'})\}. \tag{13}$$

Using Eq. (10), $V_{i,i'}$ can be rewritten as

$$V_{i,i'}=\int d^3\mathbf{r}\rho_i(\mathbf{r}-\mathbf{R}_i)\frac{Z_{i'}^N}{|\mathbf{r}-\mathbf{R}_{i'}|}+\int d^3\mathbf{r}\rho_{i'}(\mathbf{r}-\mathbf{R}_{i'})\frac{Z_i^N}{|\mathbf{r}-\mathbf{R}_i|}$$
$$+\frac{1}{2}\int d^3\mathbf{r}\int d^3\mathbf{r}'\frac{\rho_i(\mathbf{r}-\mathbf{R}_i)\rho_{i'}(\mathbf{r}'-\mathbf{R}_{i'})}{|\mathbf{r}-\mathbf{r}'|}$$
$$+\int d^3\mathbf{r}[F\{\rho_i(\mathbf{r}-\mathbf{R}_i)+\rho_{i'}(\mathbf{r}-\mathbf{R}_{i'})\}-F\{\rho_i(\mathbf{r}-\mathbf{R}_i)\}-F\{\rho_{i'}(\mathbf{r}-\mathbf{R}_{i'})\}]. \tag{14}$$

We now introduce the quantity Z_i^e, which characterizes the total number of electrons in a given ion,

$$Z_i^e=\int d^3\mathbf{r}\rho_i(\mathbf{r}). \tag{15}$$

Adding and subtracting $Z_i^e\delta(\mathbf{r}-\mathbf{R}_i)$ in the first two terms of Eq. (14), we can finally rewrite the expression for the energy of the crystal in the form

$$E^{\mathrm{cr}}=E^M+\frac{1}{2}\sum_{i,i'}\tilde{V}_{i,i'}. \tag{16}$$

Here E^M is the Madelung energy of point-like ions

$$E^M=\frac{1}{2}\sum_i Z_i^{\mathrm{ion}}V_i^M, \tag{17}$$

where Z_i^{ion} is the nominal charge of the i-th ion $Z_i^{\mathrm{ion}}=-(Z_i^N+Z_i^e)$ (its sign is the same as for the standard chemical definition), and V_i^M is the Madelung potential of the i-th ion

$$V_i^M=\sum_{i'}\frac{Z_{i'}^{\mathrm{ion}}}{|\mathbf{R}_i-\mathbf{R}_{i'}|}. \tag{18}$$

The interaction $\tilde{V}_{i,i'}$ can be expressed as follows:

$$\tilde{V}_{i,i'}=\int d^3\mathbf{r}(\rho_i(\mathbf{r}-\mathbf{R}_i)-Z_i^e\delta(\mathbf{r}-\mathbf{R}_i))\frac{Z_{i'}^{\mathrm{ion}}}{|\mathbf{r}-\mathbf{R}_{i'}|}$$
$$-\int d^3\mathbf{r}(\rho_i(\mathbf{r}-\mathbf{R}_{i'})-Z_{i'}^e\delta(\mathbf{r}-\mathbf{R}_{i'}))\frac{Z_i^{\mathrm{ion}}}{|\mathbf{r}-\mathbf{R}_i|}$$
$$+\frac{1}{2}\int d^3\mathbf{r}\int d^3\mathbf{r}'\frac{1}{|\mathbf{r}'-\mathbf{r}|}(\rho_{i'}(\mathbf{r}'-\mathbf{R}_{i'})-Z_{i'}^e\delta$$
$$\times(r'-\mathbf{R}_{i'}))(\rho_i(\mathbf{r}-\mathbf{R}_i)-Z_i^e\delta(\mathbf{r}-\mathbf{R}_i))$$
$$+\int d^3\mathbf{r}(F\{\rho_i(\mathbf{r}-\mathbf{R}_i)+\rho_{i'}(\mathbf{r}-\mathbf{R}_{i'})\}$$
$$-F\{\rho_i(\mathbf{r}-\mathbf{R}_i)\}-F\{\rho_{i'}(\mathbf{r}-\mathbf{R}_{i'})\}). \tag{19}$$

The interaction $\tilde{V}_{i,i'}$ can be obtained numerically, and is a short-range repulsive potential.

Thus, the Gordon–Kim model in its original form reduces, in accordance with Eq. (16), to the well-known rigid-ion model. The calculations in Ref. 27 show that this model, which does not employ any adjustable parameters, describes fairly well the static properties of alkali halide crystals. Like any rigid-ion model, however, it has a number of well-known drawbacks, since it completely neglects deformations in the electron-density distribution. The experimental data show that even in the equilibrium state, the electron density on a negative ion is compressed compared to a free ion. When an external electric field is applied to the crystal, induced dipole moments and therefore a dipole-type deformation of the electron density arise on the ions. In addition, the Gordon–Kim model does not enable one to calculate many ionic crystals, specifically oxides, since the O^{2-} ion does not exist in vacuum, and is stabilized only by the crystalline environment. Before we present possible extensions of the Gordon–Kim model, we discuss the problem of calculating the function $\rho(r)$ for one ion.

As we have already mentioned, in the original Gordon–Kim work,[23] the Hartree–Fock method was used to calculate $\rho(r)$. In the present work, as in most other work in this field, we employ the density functional method in the form presented by Kohn and Sham.[29] In this approach, the energy functional for the system (in this case, for the ion) can be written in the form

$$E=T_0\{\rho(r)\}+\int d^3\mathbf{r}\rho(r)\frac{Z^N}{r}$$
$$+\frac{1}{2}\int d^3\mathbf{r}\int d^3\mathbf{r}'\frac{\rho(r)\rho(r')}{|\mathbf{r}-\mathbf{r}'|}+E^{xc}\{\rho(r)\}. \tag{20}$$

Here T_0 is the kinetic energy of the noninteracting electrons, which have the same density $\rho(r)$ as the original system. The second term in Eq. (20) is the Coulomb interaction of electrons with the nuclear charge Z^N. The third term is the Hartree contribution of the interelectronic Coulomb interaction, and the fourth term is the exchange energy. Representing the desired density as the density of a system of noninteracting electrons

$$\rho(r)=\sum_n |\psi_n(r)|^2 \tag{21}$$

the Kohn–Sham equation for the wave functions $\psi_n(r)$ describing a free ion can be derived by minimizing the functional (20) with respect to $\delta\rho$:

$$(-(1/2)\nabla^2+V^{\text{eff}}(r))\psi_n(r)=\epsilon_n\psi_n(r), \tag{22}$$

where

$$V^{\text{eff}}(r)=\frac{Z^N}{r}+\int\frac{\rho(r')dr'}{|r-r'|}+\frac{\delta E^{xc}\{\rho(r)\}}{\delta\rho(r)}. \tag{23}$$

As a rule, in calculations employing the Kohn–Sham equation, a local approximation is used for the exchange energy:

$$E^{xc}=\int\rho(r)\epsilon^{xc}(\rho(r))dr. \tag{24}$$

Here $\epsilon^{xc}(\rho)$ is the exchange energy of an interacting electron gas of density ρ. This quantity is quite well known, and there are a multitude of interpolation expressions for it. A detailed review of all advantages and disadvantages of the local approximation can be found in Ref. 30. A significant drawback of the local approximation, especially important for our purposes, is that the free negative ions are unstable. This instability arises because the asymptotic behavior of the exchange correlation potential

$$V^{xc}(r)=\frac{\delta E^{xc}\{\rho(r)\}}{\delta\rho(r)}$$

at large distances r from the nucleus is incorrect. In a crystal, the electrons in a given ion are influenced by the ions surrounding them at distances much closer than the distances where $V^{xc}(r)$ exhibits incorrect asymptotic behavior. It is reasonable to allow at the outset for some part of the crystal potential in the equation for an individual ion. Such an approach to studying O^{2-} ions was proposed by Watson in Ref. 31. The electron-density distribution was calculated not for a free ion, but rather for an ion located inside a charged sphere. The charge on this sphere was chosen by requiring electrical neutrality, and therefore is equal in magnitude and opposite in sign to the charge of the ion. The choice of the radius of the sphere is a difficult problem, and we shall examine it in detail below. From what has been said above, it follows that we must add to Eq. (22) the potential of the Watson sphere

$$V^W(r)=\begin{cases} Z_i^{\text{ion}}/R_W & \text{for } r<R_W \\ Z_i^{\text{ion}}/r & \text{for } r>R_W \end{cases}. \tag{25}$$

Solving Eq. (22) with the additional potential $V^W(r)$, we can determine ρ for any radius R_W.

The most systematic approach to the choice of R_W is to determine it by minimizing the total energy of the crystal E^{cr}. In allowing for the potential of the Watson sphere, the energy E^{cr} can be written in the form

$$E^{cr}=E_M+\sum_i\tilde{E}_i(R_W^i)+\frac{1}{2}\sum_{i,i'}\tilde{V}_{i,i'}(R_W^i,R_W^{i'}). \tag{26}$$

Here $\tilde{V}_{i,i'}(R_W^i,R_W^{i'})$ is determined by the relation (19) and depends on the radii of the Watson spheres. $\tilde{E}_i(R_W^i)$ is the self-energy of the i-th ion, and depends on R_W^i. In contrast to the case of a rigid ion, the self-energy can no longer be neglected, as it was in the derivation of Eq. (16).

Just as in the case of a rigid ion, $\tilde{V}_{i,i'}(R_W^i,R_W^{i'})$ is determined by short-range forces and can be obtained by numerical methods. To verify this, we shall examine the change produced in the interaction energy by a change in R_W^i. The charge distribution of an ion varies in a spherically symmetric manner

$$\rho(r)=\rho_0(r)+\delta\rho(r),$$

where

$$\int\delta\rho(r)dr=0. \tag{27}$$

Using Eq. (19), we can calculate the change in the interaction energy of the ions as

$$\begin{aligned}\delta\sum_{i,i'}\tilde{V}_{i,i'}=&-\sum_i\int d^3\mathbf{r}(\delta\rho_i(\mathbf{r}-\mathbf{R}_i)-Z_i^e\delta(\mathbf{r}\\&-\mathbf{R}_i))\sum_{i'}\frac{Z_{i'}^{\text{ion}}}{|\mathbf{r}-\mathbf{R}_{i'}|}-\sum_{i'}\int d^3\mathbf{r}(\delta\rho_{i'}(\mathbf{r}\\&-\mathbf{R}_{i'})-Z_{i'}^e\delta(\mathbf{r}-\mathbf{R}_{i'}))\sum_i\frac{Z_i^{\text{ion}}}{|\mathbf{r}-\mathbf{R}_i|}\\&+\left(\frac{1}{2}\right)\sum_{i,i'}\int d^3\mathbf{r}\int d^3\mathbf{r}'\frac{1}{|\mathbf{r}'-\mathbf{r}|}(\delta\rho_i(\mathbf{r}-\mathbf{R}_i)\\&-Z_i^e\delta(\mathbf{r}-\mathbf{R}_i))(\delta\rho_{i'}(\mathbf{r}'-\mathbf{R}_{i'})\\&-Z_{i'}^e\delta(\mathbf{r}'-\mathbf{R}_{i'}))+\sum_{i,i'}\int d^3\mathbf{r}\delta\rho_i(r)\\&\times\left(\frac{\partial F\{\rho_i(\mathbf{r}-\mathbf{R}_i)+\rho_{i'}(\mathbf{r}-\mathbf{R}_{i'})\}}{\partial\rho}\right.\\&\left.-\frac{\partial F\{\rho_i(\mathbf{r}-\mathbf{R}_i)\}}{\Omega\rho}-\frac{\partial F\{p_{i'}(\mathbf{r}-\mathbf{R}_{i'})\}}{\Omega\rho}\right).\end{aligned} \tag{28}$$

We now consider the first and second terms in Eq. (28). These terms represent the interaction energy of a spherically symmetric change $\delta\rho(r)$ in the charge density with all point-like ions in the crystal. It is the existence of this term that might have motivated the authors of Ref. 32 to suggest the following procedure for choosing the quantities R_W^i.

The radii R_W^i are chosen by requiring that the potential Z/R_W^i inside the Watson sphere equal the Madelung potential V_i^M on a given ion due to all other point-like ions. It is easy to verify that this approach has no physical basis, since the value of the Madelung potential at a given ion bears no relation whatever to the spherically symmetric variation of the electron density. Indeed, noting that $\delta\rho(r)$ is spherically symmetric, we can rewrite the first and second terms in Eq. (28) in the form

$$\sum_i \int r^2 dr\, \delta\rho_i(\mathbf{r}-\mathbf{R}_i) \int d\Omega \sum_{i'} \frac{Z_{i'}}{|\mathbf{r}-\mathbf{R}_{i'}|}. \tag{29}$$

It is easy to show that the spherically averaged potential of point ions can be rewritten as

$$\frac{1}{4\pi}\int d\Omega \sum_{i'} \frac{Z_{i'}}{|\mathbf{r}-\mathbf{R}_{i'}|} = V_i^M + \sum_{R_{i'}<r} Z_{i'}^{\text{ion}}\left(\frac{1}{r}-\frac{1}{R_{i'}}\right). \tag{30}$$

As one can clearly see from the expressions (27), (29), and (30), the Madelung potential itself has been completely eliminated from the problem at hand. Therefore the spherically symmetric distribution of the charge density is determined completely by short-range forces.

The variational approach to determining R_W^i was studied previously in Refs. 33 and 34, where it was was based on a variational determination of R_W^i derived by minimizing the total energy of the crystal. The self-energy E_i^{self} of an ion was defined to be the difference in the total energy of the ion in the potential of the Watson sphere after subtracting the interaction energy of the electron density with that potential and the energy of the free ions:

$$E_i^{\text{self}}(R_W^i) = E_i(R_W^i) - E_i^{\text{free}}.$$

This definition of the free energy is very uncertain for ions that do not exist in a free state, and in any case it is inconvenient for numerical calculations.

Indeed, the potential of the Watson sphere is introduced as an auxiliary potential that makes it possible to alter the electron density distribution of the ion. The total energy of an ion with the potential $V^W(R_W,r)$ is a functional of this potential. In using the Legendre transformation, we must first of all change variables from V to ρ in the definition of the energy, since the interaction energy defined by Eq. (26) depends on the latter. Then we must eliminate the "excess" energy associated with the potential of the Watson sphere. We write the change in the energy of the ion as the potential varies in the form

$$\delta E\{V^W(r,R_W)\} = \int \rho(r)\,\delta V^W(r,R_W)\,d^3r. \tag{31}$$

Then, in accordance with the Legendre transformations, the change in the energy of an ion as a functional of the change in density will have the form

$$\begin{aligned}\delta E\{\rho(r)\} &= \delta E\{V^W(r,R_W)\} - \delta\int \rho(r)V^W(r,R_W)\,d^3r\\ &= -\int \delta\rho(r)V^W(r,R_W)\,d^3r.\end{aligned} \tag{32}$$

It follows from Eq. (32) that

$$\frac{\partial E}{\partial R_W} = -\int \frac{\partial\rho(r)}{\partial R_W} V^W(r,R_W)\,d^3r \tag{33}$$

and, accordingly, the self-energy of the ion can be written in the form

$$E^{\text{self}}(R_W) = E^0 - \int_{R_W^0}^{R_W} dX \int \frac{\partial\rho(r)}{\partial X} V^W(r,X)\,d^3r, \tag{34}$$

where E^0 is an unimportant constant. We can choose as the starting point R_W^0 of the integration any value of the radius of the Watson sphere, up to an unimportant constant, that lies in the range of interest. The procedure described above corresponds exactly to Leontovich's principle for determining the energy of nonequilibrium states.[35]

In an actual calculation of $E^{\text{self}}(R_W)$, the density $\rho(r)$ and its derivative $\partial\rho(r)/\partial R_W$ must be calculated over some range of R_W using the Kohn–Sham equation (22) with the potential of the Watson sphere included in it. The program developed in Ref. 37 was used for the numerical calculation of the ions.

The interaction energy can also be calculated as a function of R_W, and R_W^{min}, corresponding to the minimum total energy of the crystal, can be determined for any interionic distance. For many ionic crystals the energy minimum in this method is very smooth, and it is this chance circumstance that makes it possible in Refs. 32–34 to calculate many of the properties of ionic crystals to reasonable accuracy, even with an improper choice of R_W. There are, however, many ionic crystals—especially those with strongly polarizing positive ions—where accurate determination of the self-energy of an ion is crucial, most notably at high pressures. This problem is also under investigation, and will not be considered here.

3. DIPOLAR DEFORMATION OF THE IONS

In the preceding section we presented the generalized Gordon–Kim model and described in detail a method for calculating ionic crystals that takes into account the spherically symmetric deformation of the ions. Here we present a method for calculating the static and dynamic properties of ionic crystals in the presence of dipolar deformation of the ions.

In the spirit of the Gordon–Kim method, we must first calculate the behavior of an isolated ion in an external electric field E^{ext}. To this end, we employ the Kohn–Sham equation (22), which we rewrite in the form

$$\begin{aligned}&((-1/2)\nabla^2 + V^{\text{eff}}(\mathbf{r}) + V^W(R_W,\mathbf{r}) - \mathbf{r}E^{\text{ext}})\psi_n(\mathbf{r})\\ &\quad = \epsilon_i\psi_n(\mathbf{r}),\end{aligned} \tag{35}$$

where the potential of the Watson sphere corresponds to the radius R_W that minimizes the energy of the equilibrium state in the absence of an external electric field. We take into account the effect of the electric field on the ion by perturbation theory. To first order in $\mathbf{E}^{\text{ext}}$, we obtain

$$\psi_n(\mathbf{r}) = \psi_n(\mathbf{r}) + \delta\psi_n(\mathbf{r}), \tag{36}$$

and

$$\rho(\mathbf{r}) = \rho^0(r) + \delta\rho(\mathbf{r}), \tag{37}$$

where

$$\delta\rho(\mathbf{r})=\sum_{n}\psi_n(\mathbf{r})\delta\psi_n(\mathbf{r}). \tag{38}$$

In calculating the change $\delta\psi_n(\mathbf{r})$ in the wave function, we must bear in mind that in Eq. (35), the total potential changes not only as a result of the potential of the external field $\delta V^{\mathrm{ext}}=-\mathbf{r}\cdot\mathbf{E}^{\mathrm{ext}}$, but also as a result of the change in the self-consistent effective potential δV^{eff}, which can be written in the form

$$\delta V^{\mathrm{eff}}(\mathbf{r})=\int d^3\mathbf{r}\frac{\delta\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}+\int d^3\mathbf{r}\delta\rho(\mathbf{r})\frac{\partial V^{\mathrm{exc}}(\rho(\mathbf{r}))}{\partial\rho}. \tag{39}$$

The change $\delta\psi_n(\mathbf{r})$ can be calculated using the standard quantum-mechanical formula, which expresses $\delta\psi_n(\mathbf{r})$ as a sum over all occupied and vacant electron states determined by Eq. (35) in the absence of the field $\mathbf{E}^{\mathrm{ext}}$. There are, however, a number of reasons why this method is inconvenient. It is much more convenient to directly solve the differential equation for $\delta\psi_n(\mathbf{r})$,

$$\begin{aligned}((-1/2)\nabla^2+V^{\mathrm{eff}}(\mathbf{r})+V^{W}(R_W,\mathbf{r})-\epsilon_i)\delta\psi_n(\mathbf{r})\\=-(\mathbf{r}\mathbf{E}^{\mathrm{ext}}+\delta V^{\mathrm{eff}}(\mathbf{r}))\psi_n^0(\mathbf{r}),\end{aligned} \tag{40}$$

in a self-consistent manner. This approach to the calculation of atomic polarizabilities was proposed back in 1954 by Sternheimer,[36] the only difference being that he neglected the change produced by the field in the self-consistent potential.

Once the change $\delta\psi_n(\mathbf{r})$ in the wave function is known, it is easy to calculate the change in the electron density $\delta\rho(\mathbf{r})$, and therefore the dipole moment $\mathbf{P}$ induced at an ion by the external electric field $\mathbf{E}^{\mathrm{ext}}$

$$\mathbf{P}=\int d^3\mathbf{r}\delta\rho(\mathbf{r})\mathbf{r}. \tag{41}$$

The dipolar polarizability α of an ion is defined by

$$\mathbf{P}=\alpha\mathbf{E}. \tag{42}$$

It follows from Eqs. (40), (41), and (42) that

$$\delta\rho^1(r)=\frac{\mathbf{r}\mathbf{E}}{r}\rho^{-1}(r), \tag{43}$$

$$\alpha=\frac{4\pi}{3}\int_0^\infty\rho^{-1}(r)r^3dr. \tag{44}$$

Our calculations of the polarizabilities of the atoms were published previously in Ref. 38, and we do not discuss them in detail here. We merely note that in the calculations, we used improperly determined values of R_W for the ions in accordance with Ref. 32, and we point out below the changes introduced in the polarizabilities when R_W is properly chosen.

The next step is to calculate the interaction energy of two ions with fixed dipole moments $\mathbf{P}_i$ and $\mathbf{P}_{i'}$. Before doing so, we note that just as in the case of a spherically symmetric density distribution, we must change variables from $\mathbf{E}$ to $\mathbf{P}$ when we determine the self-energy of an ion. The Legendre transformations for this case are trivial, and the self-energy of an ion in an electric field as a functional of the polarization $\mathbf{P}$ takes the form

$$E=E^0+\frac{P^2}{2\alpha}-\mathbf{P}\mathbf{E}, \tag{45}$$

where E^0 is the polarization-independent part of the self energy. Representing the electron density distribution in the given field in the form (43), we can rewrite it as a function of the dipole moment,

$$\delta\rho^1(\mathbf{P},\mathbf{r})=\frac{\mathbf{r}\mathbf{P}}{r}\rho^1(r), \tag{46}$$

where

$$\rho^1(r)=\frac{\rho^{-1}(r)}{\alpha}.$$

All of these quantities are known from the solution for the behavior of one ion in an external field. The key idea for subsequent analysis is that the form of the polarization of an ion in a crystal is the same as in an isolated ion, and the amplitude of the polarization must be determined self-consistently by minimizing the total energy of the crystal.

Substituting the expression for $\delta\rho_i^1(\mathbf{P}_i,\mathbf{r})$ into Eq. (19), we can calculate the interaction energy $\tilde{V}_{i,i'}$ of two ions with prescribed dipole moments $\mathbf{P}_i$ and $\mathbf{P}_{i'}$. As shown in our previous work,[38] $\tilde{V}_{i,i'}$ can be represented in the form

$$\tilde{V}_{i,i'}=\tilde{V}^0_{i,i'}+\mathbf{P}_i\Phi_{i,i'}\mathbf{P}_{i'}+\mathbf{P}_i\Gamma_{i,i'}\mathbf{P}_{i'}-\mathbf{P}_i\mathbf{S}_{i,i'}-\mathbf{P}_{i'}\mathbf{S}_{i',i}. \tag{47}$$

Here $\tilde{V}^0_{i,i'}$ is the part of the interaction that does not depend on the polarization, and $\Phi_{i,i'}$ is the matrix of the interaction of point dipoles. The matrix $\Gamma_{i,i'}$ represents the difference between the true interaction of distributed dipoles and the interaction of point dipoles. This is a short-range matrix, and must be calculated numerically only for the nearest neighbors.

The vector $\mathbf{S}_{i,i'}$ describes the interaction of the dipoles with the electric field induced by the spherically symmetric distribution of electron density. Formally, the matrices $\Psi_{i,i'}$ and $\Gamma_{i,i'}$ and the vector $\mathbf{S}_{i,i'}$ can be represented in the form

$$\Gamma_{i,i'}+\Psi_{i,i'}=\frac{\partial^2}{\partial\mathbf{P}_i\partial\mathbf{P}_{i'}}[E\{\rho_i(\mathbf{P}_i,\mathbf{r})+\rho_{i'}(\mathbf{P}_{i'},\mathbf{r})\}], \tag{48}$$

and

$$\mathbf{S}_{i,i'}=-\frac{\partial}{\partial\mathbf{P}_i}[E\{\rho_i(\mathbf{P}_i,\mathbf{r})+\rho^0_{i'}(\mathbf{r})\}-E\{\rho_i(\mathbf{P}_i,\mathbf{r})\}], \tag{49}$$

where $\rho_i(\mathbf{P}_i,\mathbf{r})$ is the electron density distribution of an ion and $\rho^0_{i'}(\mathbf{r})$ is its spherically symmetric part. To calculate these quantities numerically, the expression for $E\{\cdot\}$ must be expanded, as was done in the case of a spherically symmetric distribution of the electron density of the ions, using Eq. (19).

Then the total energy of the crystal in an external electric field can be written in the form

$$E^{cr}=E_0^{cr}+\sum_i \frac{P^2}{2\alpha_i}+\frac{1}{2}\sum_{i,i'} \mathbf{P}_i\Phi_{i,i'}\mathbf{P}_{i'}+\frac{1}{2}\sum_{i,i'}\mathbf{P}_i\Gamma_{i,i'}\mathbf{P}_{i'}$$

$$-\sum_{i,i'}\mathbf{P}_i\mathbf{S}_{i,i'}-\sum_i \mathbf{P}_i\mathbf{E}^{\mathrm{ext}}. \qquad (50)$$

Minimizing the energy as a function of the dipole moments,

$$\frac{\partial E^{cr}}{\partial \mathbf{P}_i}=0 \qquad (51)$$

we obtain a linear equation for these quantities:

$$\mathbf{P}_i=\alpha_i\mathbf{E}^{\mathrm{ext}}-\sum_{i'}(\Phi_{i,i'}+\Gamma_{i,i'})\mathbf{P}_{i'}-\sum_{i'}\mathbf{S}_{i,i'}. \qquad (52)$$

This equation can be solved numerically.

4. DIELECTRIC POLARIZATION AND LATTICE DYNAMICS OF IONIC CRYSTALS

The extension of the Gordon–Kim model developed in the preceding sections can be used to calculate the electron contribution to the dielectric constant ϵ_∞ of ionic crystals, as well as the lattice dynamics. First of all, we examine the expression for ϵ_∞, employing a definition which for cubic crystals can be written in the form

$$\mathbf{D}=\epsilon_\infty\mathbf{E}=\mathbf{E}+4\pi\mathbf{P}=\mathbf{E}+\frac{4\pi}{v_0}\sum_i \mathbf{P}_i. \qquad (53)$$

Here $\mathbf{D}$ is the electric displacement vector, $\mathbf{P}$ is the total dipole moment of the crystal, and $\mathbf{E}$ is the electric field inside the crystal. The summation in Eq. (53) extends over a unit cell of volume v_0. We then consider a crystal wafer in an electric field oriented parallel to the surface of the wafer. In this case the electric field $\mathbf{E}$ inside the wafer will equal the external field $\mathbf{E}^{\mathrm{ext}}$. Now, passing to the limit of infinite volume of the wafer, we can replace $\mathbf{E}$ by $\mathbf{E}^{\mathrm{ext}}$ in Eq. (53) and obtain the final expression for the dielectric constant,

$$\epsilon_\infty=1+\frac{4\pi}{v_0\mathbf{E}^{\mathrm{ext}}}\sum_i \mathbf{P}_i. \qquad (54)$$

We use this formula in the calculations.

The dipole moments can be calculated using Eq. (52) derived in the preceding section. We rewrite it in the form

$$\mathbf{P}_i=\alpha_i\mathbf{E}^{\mathrm{ext}}-\sum_{i,i'}(\Psi_{i,i'}+\Gamma_{i,i'})\mathbf{P}_{i'}. \qquad (55)$$

In writing this expression, we neglected the vector $\mathbf{S}_{i,i'}$, since in cubic crystals it vanishes in the absence of permanent dipoles.

Before presenting the results of the numerical calculations of ϵ_∞, we discuss some general results that follow from Eqs. (53) and (54). Neglecting the short-range interaction matrix $\Gamma_{i,i'}$, we rewrite Eq. (55) in the form

$$\mathbf{P}_i=\alpha_i\mathbf{E}_i^{\mathrm{loc}}. \qquad (56)$$

Introducing an expression for the local field at site i,

$$\mathbf{E}_i^{\mathrm{loc}}=\mathbf{E}^{\mathrm{ext}}-\sum_{i'}\Phi_{i,i'}\mathbf{P}_{i'} \qquad (57)$$

and noting that for cubic crystals with NaCl-type structure, the local field has the form

$$\mathbf{E}_i^{\mathrm{loc}}=\mathbf{E}^{\mathrm{ext}}+\frac{4\pi}{3}\mathbf{P}, \qquad (58)$$

we easily obtain for ϵ_∞ the standard Clausius–Mossotti formula

$$\epsilon_\infty=1+\frac{4\pi\alpha_s/v_0}{1-4\pi\alpha_s mh;1.5q/3v_0}, \qquad (59)$$

where α_s is the polarizability of the cell, in this case equal to the sum of the polarizabilities of the individual ions.

Making use of $\Gamma_{i,i'}$, we can also solve Eq. (55) for the local field $\mathbf{E}^{\mathrm{loc}}$, which yields

$$\mathbf{P}_i=\sum_{i'}\alpha_{i,i'}\mathbf{E}_{i'}^{\mathrm{loc}}, \qquad (60)$$

where $\alpha_{i,i'}$ is the nonlocal polarizability:

$$\alpha_{i,i'}=(\delta_{i,i'}+\alpha_i\Gamma_{i,i'})^{-1}\alpha_{i'}. \qquad (61)$$

The nonlocal relationship between the dipole moment $\mathbf{P}_i$ at a site and the local field in all surrounding sites was previously proposed[12] on the basis of a simple phenomenological model. The derivation presented above demonstrates the universality of the relationship between $\mathbf{P}_i$ and $\mathbf{E}_i^{\mathrm{loc}}$ in ionic crystals. We emphasize that in spite of the nonlocal character of the relation between $\mathbf{P}_i$ and $\mathbf{E}_i^{\mathrm{loc}}$, an expression that is formally identical to the Clausius–Mossotti relation can be derived, as before, for the dielectric constant. Taking advantage of Eq. (58) for $\mathbf{E}_i^{\mathrm{loc}}$, we can easily solve Eq. (60) and directly obtain for ϵ_∞ an expression of the Clausius–Mossotti type, but the polarizability α_s of a cell will now take the form

$$\alpha_s=\sum_{i,i'}(\delta_{i,i'}+\alpha_i\Gamma_{i,i'})^{-1}\alpha_{i'}. \qquad (62)$$

In this formula the summation extends over all ions in a unit cell and over all nearest neighbors.

This result provides direct confirmation of the general statement, proved in Ref. 39, that the Clausius–Mossotti formula is of a very general nature, and derives from the presence of long-range dipole–dipole interactions between unit cells. The polarizability of a unit cell itself must be calculated with allowance for all short-range interactions, and thus exhibits an entirely nonuniversal dependence on the properties of the constituent ions, the cell volume, and so on. Formally, we can determine the polarizability of each ion in a cell using the formula

$$\tilde{\alpha}_i=\sum_{i'\neq i}(\delta_{i,i'}+\alpha_i\Gamma_{i,i'})^{-1}\alpha_{i'}. \qquad (63)$$

But this is really just a formal definition, since the corresponding quantity α_i is not a response of the ion to some external or local electric field. As one can see from Eq. (60) and the site-independence of E_i^{loc} for crystals with NaCl structure, α_i is the response of an ion at the site i to local fields generated by all nearest neighbors.

TABLE I. Dielectric constants.

	α_0	α_m	$\tilde{\alpha}_0$	$\tilde{\alpha}_m$	ϵ_∞ (theor.)	ϵ_∞ (exp.)
MgO	3.82	0.08	2.73	0.06	4.60	3.01
CaO	4.41	0.47	3.22	0.34	4.40	3.38
SrO	4.58	0.78	3.47	0.60	4.05	3.27
BaO	5.03	1.58	3.71	1.18	4.47	3.34

As can be easily verified from Eq. (54), ϵ_∞ can be expressed much more simply as

$$\epsilon_\infty = 1 + \frac{4\pi}{v_0} \sum_i \breve{\alpha}_i , \tag{64}$$

which has the form of the dielectric constant of a system of noninteracting dipoles. The polarizability $\breve{\alpha}_i$ of the i-th ion relates the dipole moment $\mathbf{P}_i$ to the external electric field $\mathbf{E}^{\mathrm{ext}}$:

$$\mathbf{P}_i = \breve{\alpha}_i \mathbf{E}^{\mathrm{ext}}. \tag{65}$$

The polarizability $\breve{\alpha}_i$ and the polarizability $\tilde{\alpha}_i$, which is defined by Eq. (63), are related by

$$\breve{\alpha}_i = \frac{\breve{\alpha}_i}{1 - \frac{4\pi}{3v_0} \sum_i \tilde{\alpha}_i} . \tag{66}$$

In deriving the dielectric constant ϵ_∞, we have thus determined three quantities that characterize the polarizability of an ion in a crystal. First there is the polarizability α_i of an individual ion in the potential of the Watson sphere, which takes the crystalline environment into account approximately. This is the quantity calculated previously (see, for example, Refs. 9–11) in various approximations to the polarizability of an ion in a crystal, and then substituted into the Clausius–Mossotti formula (59) in order to calculate ϵ_∞.

As one can see from the above analysis, this approach to determining ϵ_∞ is totally unjustified, since it completely neglects the short-range dipole–dipole interaction. The formal polarizability $\tilde{\alpha}_i$ of an ion, which must be used in the Clausius–Mossotti formula (59), is defined by Eq. (63). As one can see from Table I, in oxides α_i is substantially different from $\tilde{\alpha}_i$. These differences, as we show in Ref. 38, are small for alkali halide compounds, so that the calculations of ϵ_∞ performed for them in Ref. 11 are in good agreement with the experimental data. The difference between α_i and $\tilde{\alpha}_i$ relates to the fact that in calculating them, differing methods are used to allow for electric fields in the system. Although it is physically impossible to separate the long-range field of a point dipole from the short-range field, it is often convenient to study them separately. Specifically,[38] this makes it possible to obtain a number of rigorous relationships among phonon frequencies.

The numerical results for ϵ_∞ in Table I are in good agreement with existing experimental data. The fact that the theoretical values of ϵ_∞ are somewhat higher than the experimental derives mainly from the well-known fact that the density functional approach using the local density approximation for the exchange overestimates the polarizabilities of individual ions.

The generalized Gordon–Kim model can also be used to calculate the lattice dynamics. In this case, the electric field induced by ion displacement plays the role of the external electric field. Once again, the variation in the interaction energy of the ions with fixed dipole moments can be calculated using Eq. (19). To calculate the phonon spectra for the deformed crystal, the first-order terms in $\delta\rho$, which vanished in the total interaction energy for an ideal crystal in the calculation of the electron polarizability, can no longer be neglected. Specifically, the first and second terms in Eq. (19) give precisely the interaction of the dipole moments with the electric field of the point ions. The third and fourth terms lead to an interaction between distributed dipoles and the spherically symmetric electron density distribution of neighboring ions.

The complete expression for the energy of the crystal can be written in the form

$$\begin{aligned} E^{\mathrm{cr}} = {} & \frac{1}{2} \sum_{i,i'} \frac{Z_i^{\mathrm{ion}} Z_{i'}^{\mathrm{ion}}}{|\mathbf{R}_i + \mathbf{R}_{i'}|} + \sum_i E_i^{\mathrm{self}}(R_W^0) + \frac{1}{2} \sum_{i,i'} \tilde{V}_{i,i'} \\ & + \sum_i \frac{\mathbf{P}_i^2}{\alpha_i} + \frac{1}{2} \sum_{i,i'} \mathbf{P}_i \Psi_{i,i'} \mathbf{P}_{i'} + \frac{1}{2} \sum_{i,i'} \mathbf{P}_i \Gamma_{i,i'} 2b P_{i'} \\ & - \sum_{i,i'} \mathbf{P}_i \mathbf{S}_{i,i'} - \sum_i \mathbf{P}_i \mathbf{E}_i . \end{aligned} \tag{67}$$

Representing $\mathbf{R}_i$ as

$$\mathbf{R}_i = \mathbf{R}_i^0 + u_i , \tag{68}$$

where $\mathbf{R}_i^0$ is the equilibrium position of the i-th ion and u_i is a small displacement of the ion from equilibrium, we can write the expression for the electric field $\mathbf{E}_i$ as

$$\mathbf{E}_i = - \sum_{i'} \Psi_{i,i'} Z_{i'}^{\mathrm{ion}} u_{i'} \tag{69}$$

and the vector $\mathbf{S}_{i,i'}$ as

$$\mathbf{S}_{i,i'} = m_{i,i'} u_{i'} . \tag{70}$$

The deformability matrix $m_{i,i'}$ is therefore short-range, and can be calculated numerically with Eq. (19). Minimizing with respect to $\mathbf{P}_i$ we obtain the following equation for the dipole moment:

$$\mathbf{P}_i = \alpha_i \left(E_i - \sum_{i'} (\Psi_{i,i'} + \Gamma_{i,i'}) \mathbf{P}_{i'} + \sum_{i'} m_{i,i'} u_{i'} \right). \tag{71}$$

Introducing the local field $\mathbf{E}_i^{\mathrm{loc}}$ as in the preceding section, we can rewrite the equation for $\mathbf{P}_i$:

$$\mathbf{P}_i = \alpha_i \left(\sum_{i'} \alpha_{i,i'} \mathbf{E}_i^{\mathrm{loc}} + \sum_{i'} m_{i,i'} u_{i'} \right). \tag{72}$$

Here $\alpha_{i,i'}$ is the nonlocal polarizability matrix defined by Eq. (61).

Equation (72) for the induced dipole moment was proposed in Ref. 40 as a phenomenological nonlocal extension of the shell and deformed-ion models. Our result can there-

TABLE II. Phonon frequencies.

			Γ point		X point			
		Z^{eff}	ω_{TO}, cm^{-1}	ω_{LO}, cm^{-1}	ω_1, cm^{-1}	ω_2, cm^{-1}	ω_3, cm^{-1}	ω_4, cm^{-1}
CaO	theor.	2.43	265	524	213	286	318	433
	exp.		300	574	210	290	320	400
SrO	theor.	2.39	248	461	143	196	297	389
	exp.		240	495	130	200	250	350

fore be regarded as a microscopic substantiation of this model. Moreover, in our approach, all matrices are calculated without recourse to adjustable parameters.

Expanding the first three terms to second order in the small displacements u_i, and the second and third terms in powers of the small deviations of the Watson radius R_W from its equilibrium lattice value R_W^0, we can represent the expression (53) for E^{cr} in a form corresponding to the most general phenomenological model of an ionic crystal.[16,40] This model takes into account both the spherically symmetric variation of the effective radius of the ion ("breathing") and the nonlocal polarizability and deformability of the ions. There is no reason, in principle, why one cannot then calculate the modal matrix of the oscillations and the phonon frequency spectrum. Here, however, we shall not calculate the complete phonon spectrum, but instead restrict ourselves to calculations of some phonon frequencies at the center of the Brillouin zone and at its boundaries by the "frozen-in" phonon method (see Ref. 41).

This method makes it possible to obtain the phonon frequencies from the energy difference between the ideal and deformed lattices. We shall not describe here the details of this well-known method, but merely consider the calculation of the frequency of the longitudinal optical mode with $q=0$. To this end, we first determine, by the method of frozen-in phonons, the frequency ω_{TO} of the transverse optical mode. We can then determine the resulting total polarization **P** of the crystal with a lattice displacement corresponding to the transverse optical mode with $q=0$:

$$\mathbf{P}=\sum_i Z^{\text{ion}}u_i+\sum_i \mathbf{P}_i. \tag{73}$$

Knowing **P**, we can easily find the dynamical Born charge Z^{eff}, which is defined by[19]

$$\mathbf{P}=\sum_i Z_i^{\text{eff}}u_i. \tag{74}$$

We can then also easily determine the frequency ω_{LO} of the longitudinal optical mode at $q=0$ from the splitting of the optical phonon frequencies for longitudinal and transverse vibrations,

$$\omega_{\text{LO}}^2-\omega_{\text{TO}}^2=\frac{4\pi(Z^{\text{eff}})^2}{\mu v_0\epsilon_\infty}, \tag{75}$$

where μ is the reduced mass of the ions.

The numerical results for the phonon frequencies at the center (Γ point) and boundary (X point) of the Brillouin zone are presented in Table II. Since there are no adjustable parameters in our calculations, we can regard the agreement with the experimental data to be highly satisfactory.

5. CONCLUSION

In summary, in the present paper we have presented a simple microscopic approach to calculating the static and dynamical properties of ionic crystals. This approach is based on an extension of the Gordon–Kim model that makes it possible to take into account the monopole and dipole polarizabilities of each ion. In principle, this approach can also be extended to take into account the higher-order multipole polarizabilities or static distortions of electron density in an ion. This is important in studying ions with unfilled electron shells. Our results for the lattice dynamics yield an expression for the energy of the crystal that is formally identical to the most general phenomenological model of lattice dynamics, which assumes both the spherical symmetry of the electron density and the presence of nonlocal polarizabilities and deformabilities of the ions.

The numerical results for the electron polarizability of the ions show that it is necessary to improve upon the local approximation for the exchange energy. This is especially important in calculations of a light negative ions, such as O^{2-}, for which the local approximation overestimates the ionic polarizability substantially.

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