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Some Aspects of Covalent Bonding in NaCl Structure Crystals: Application to the Lattice Dynamics of MgO[†]

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The lattice vibrational properties of heteropolar crystals of the NaCl structure are examined within the context of recent dielectric-screening theories of insulating crystals. Phillips's bond-charge approximation for the dielectric response of semiconductors with tetrahedral coordination is adapted to the treatment of partially covalent NaCl structure crystals. Application is made to MgO, where the gross violation of the Cauchy relation among the elastic constants points to the importance of noncentral forces arising from covalent effects. The bond-charge model in conjunction with a valence-force-field approximation for the short-range interactions is shown to provide an adequate description of the lattice spectrum in MgO.

I. INTRODUCTION

The character of the chemical bond which exists between the component atoms of a metallic or nonmetallic crystal is reflected in those properties of the crystal which depend directly on the electronic spectrum. These properties are, in turn, reflected in the linear dielectric-screening properties of the many-particle system consisting of the valence electrons alone. It is only natural, then, that recent advances in the understanding of the chemical bond[1-4] have been based on a dielectric-screening theory of the valence electrons of the crystal. Application of these ideas has met with considerable success in the understanding of the over-all trends of many of the physical properties of a large class of covalent and partially ionic diatomic crystals[5,6] with the formula $A_N B_{8-N}$. Of particular note is the successful correlation of a dielectric definition of electronegativity or ionicity[7] with the structure of the static electronic dielectric constant. This has led to the prediction, with good results, of ionization potentials and band structures of 68 binary compounds[6] of the form $A_N B_{8-N}$. Furthermore, a correlation has been shown to exist between the effective ionicity defined by Phillips and some of the regularities exhibited by the experimental elastic constants of ZnS structure semiconductors.[8]

The basic ideas which underlie the dielectric definition of electronegativity can be used to develop a model of lattice vibration spectra in covalent and partially ionic crystals. Such an extension was proposed by Phillips[4] and subsequently put on a more rigorous basis by Martin[9] in a dielectric-screening treatment of the lattice vibrations of silicon. It will be recalled that there have appeared recently several general formulations of the lattice vibration problem[10,11] which encompass in a unified manner the lattice dynamical description of both metallic and nonmetallic crystals. In his work on

Si, Martin succeeded in establishing the connection between Phillips's bond-charge model[4] and these general lattice dynamical formulations, thus justifying the bond-charge model within a rigorous context. The general lattice dynamical formulations focus on the problem of expressing the phonon self-energy function in terms of the response of the crystal electrons to an external probe. This so-called microscopic dielectric approach permits the complete solution of the lattice vibrational problem within the harmonic approximation[12] once a properly defined inverse screening matrix for the electrons, $\epsilon^{-1}(\vec{q}+\vec{K}, \vec{q}+\vec{K}')$, is known. A particularly noteworthy feature of the application of these ideas to insulating crystals is that the $\vec{K}\neq\vec{K}'$ elements of ϵ^{-1} are manifestly nonzero – indeed, these elements are necessary for the satisfaction of an exact sum rule[10–13] which ensures that all acoustic mode frequencies approach zero as the wave vector of the mode approaches zero. Previous pseudopotential treatments of the lattice dynamics of the simple metals are special cases of the more general microscopic dielectric formulation. In a metal, one neglects the $\vec{K}\neq\vec{K}'$ elements of $\epsilon^{-1}(\vec{q}+\vec{K}, \vec{q}+\vec{K}')$ and then approximates the diagonal part by $1/\epsilon_{\mathrm{RPA}}(\vec{q}+\vec{K})$, where ϵ_{RPA} represents the usual RPA (random-phase approximation) dielectric function appropriate to free-electron screening including exchange. Since $\epsilon_{\mathrm{RPA}}(\vec{q}) \sim 1/q^2$ as $q\rightarrow 0$, the acoustic sum rule places no constraint on the $\vec{K}\neq\vec{K}'$ terms and hence a diagonal-screening matrix is an acceptable choice for a metal. In insulating crystals on the other hand, $\epsilon^{-1}(\vec{q}, \vec{q})\rightarrow 1/\epsilon_0$ and the off-diagonal elements of ϵ^{-1} are necessarily nonzero if the acoustic sum rule is to be satisfied – the closer ϵ_0 is to the ideal insulating value of 1, the more important these off-diagonal elements become. Since the $\vec{K}\neq\vec{K}'$ elements of ϵ^{-1} are a manifestation of local field effects, one might anticipate that in those materials where the splitting between $\omega_{\mathrm{LO}}(\Gamma)$ and $\omega_{\mathrm{TO}}(\Gamma)$ is extremely large (hence implying a very polar material) these effects would be of primary importance.

Short of actually calculating $\epsilon(\vec{q}+\vec{K}, \vec{q}+\vec{K}')$ from the complete electronic spectrum of the crystal and inverting the full $N\times N$ matrix ϵ, a formidable job, one may proceed from a different point of view. Assuming a qualitatively reasonable model for ϵ based on a simplified description of the band structure, one might attempt to approximate the diagonal elements of $\epsilon^{-1}(\vec{q}+\vec{K}, \vec{q}+\vec{K}')$ by $1/\epsilon(\vec{q}+\vec{K},\vec{q}+\vec{K})$ and then proceed with an ansatz for the $\vec{K}\neq\vec{K}'$ elements of ϵ^{-1}, the choice of this ansatz being guided by the exact sum rule which ϵ^{-1} satisfies. This approach was adopted by Martin in a treatment of the vibrational spectrum of silicon.[9] In Martin's treatment the contribution to the dynamical matrix from the off-diagonal elements of ϵ^{-1} is approximated by the distortion energy associated with the displacement of point bond charges constrained to reside at points midway between nearest neighbor atoms. The phonon spectrum calculated in this way agrees well with the experimentally measured phonon spectrum of Si with a minimum number of adjustable parameters. Although the full calculation for Si utilized bare pseudopotential form factors together with a nonmetallic screening function, it was found that an effective "repulsive" contribution to the dynamical matrix could be isolated and approximated by a two-parameter nearest-neighbor interaction without altering the prominent qualitative features of the vibrational spectrum.

In the present paper we extend the ideas outlined above to the treatment of some of the vibrational properties of heteropolar crystals with octahedral coordination. It is true that covalent bonding is usually associated with tetrahedral coordination, whereas octahedrally coordinated materials are typically thought to be purely ionic in character. Nevertheless, there exists a class of NaCl-type crystals for which covalent effects are important. Let us recall that the simple picture one usually associates with a purely ionic material is that of individual ions existing at isolated lattice sites within the crystal. This picture, in fact, has little meaning unless the effective wave function for each ion exhibits negligible overlap with its neighbors. Such a situation is well approximated in an alkali halide such as KCl where the valence bandwidth is relatively narrow (~0.8 eV). Indeed, explicit APW (augmented-plane-wave) calculations of the band structure of KCl[14,15] indicate that the spatial distribution of electronic charge in the p valence bands is strongly ionic in character. Specifically, one finds that only 2.4% of the electronic charge is localized in the K sphere, whereas 89.0% is localized in the Cl sphere with the remaining 8.6% in the constant-potential region outside both spheres. In contrast to this, a material such as MgO has a very large bandwidth (~4 eV) and exhibits characteristics suggestive of covalent effects. A band-structure calculation[15] for MgO analogous to that for KCl reveals a significant decrease in the amount of electronic charge localized in the anion sphere, so that when compared to a material such as KCl, MgO exhibits the presence of a significant amount of valence charge in regions other than at lattice sites. This property might have been anticipated in view of the fact that MgO registers a value of 0.841 on the ionicity scale of Phillips and Van Vechtin,[5] in contrast to a value of 0.953 for KCl. The only other octahedrally coordinated $A_N B_{8-N}$ compound with an ionicity below MgO is CdO with an ionicity of 0.785, the critical value below which tetrahedral coordination dominates.

There exist other octahedrally coordinated materials for which the delocalization of electronic charge plays a dominant role and for which a partially covalent description may be appropriate. One such material is LiH. The results of x-ray and neutron diffraction studies[16] of the electron density in this compound suggest considerable overlap of the ionic wave functions. Finally, it should be noted that covalent bonding is vital to the understanding of many of the properties of the IV-VI compounds GeTe, SnTe, and PbTe.[17] Indeed, it is by now well established that the displacive phase transition exhibited by GeTe and $Ge_xSn_{1-x}Te$ involves a rhombohedral distortion which almost certainly is associated with covalent effects.[18,19]

The model which we introduce here is similar in its general features to the model employed by Martin in his treatment of the vibration spectra of the diamond-structure homopolar semiconductors. As in Martin's work the off-diagonal elements of the inverse screening matrix are related to the distortion energy associated with the displacement of the localized bond charges. There exist essential differences, nonetheless, between the analysis of the NaCl-type crystals and a similar analysis of the homopolar IV semiconductors. It is obvious that a homopolar NaCl-type crystal cannot exist. Indeed, it is the heteropolarity or partial ionicity which stabilizes the NaCl structure by preventing it from reverting to the simple cubic structure, which is known to be intrinsically unstable. Thus, the model must incorporate the possibility of there being unequal ionic changes on the two sublattices of the crystal. Furthermore, one can no longer impose the constraint of having the localized bond charges reside at the midpoint between nearest-neighbor ions as was assumed in Martin's treatment of Si. Indeed, in the present model, the splitting of the LO- and TO-phonon modes at the zone center is determined by an effective charge $q^* = \frac{1}{2} \times (z_1 - z_2) + \mu(z_1 + z_2)$, where μ represents the fractional deviation of the bond charge from a position midway between nearest neighbors in the instantaneous lattice configuration. The z_1, z_2 are related to the ionic charges associated with the two sublattices. The hypothetical homopolar case ($z_1 = z_2$, $\mu = 0$) yields $q^* = 0$, as it should.

With respect to the non-Coulombic contributions to the dynamical matrix, we restrict ourselves in the present paper to a detailed examination of the particular model in which the non-Coulombic contributions to the dynamical matrix are approximated by an effective short-range interaction. It is our basic purpose to explore in detail the content of the microscopic dielectric approach in its simplest possible form when applied to NaCl-type crystals. Except for a brief discussion in Sec. IV we do not concern ourselves in the present work with the detailed structure of the inverse screening matrix, reserving those considerations for a later paper.

In Sec. II we review briefly some of the basic ideas of the microscopic dielectric approach within the context of the present analysis. In Sec. III we introduce a prototype for a model of the lattice spectrum of a typical partially ionic NaCl-type crystal. Preliminary to the application of this prototype to a specific material, we consider in detail the dependence of the Coulombic contributions to the energy and elastic constants on bond-charge position and sublattice charge. After introducing a model for the short-range forces, we then discuss the validity of the model in the light of a specific application to MgO. How well the model works depends on several considerations. It should, in fact, be emphasized that the localized bond-charge model introduces valence distortion in an oversimplified manner through its restriction to point charges. In a material such as LiH, where ionic overlap is large, a proper description would require the introduction of form factors for the bonding charges. The consequences of our approximation will be discussed in Sec. IV.

II. FORMAL PRELIMINARIES

We begin this section by casting the results of the microscopic dielectric formulation[10] into a form suitable for our present purposes. We consider the situation in which a lattice of ions (consisting of nuclear charge plus tightly bound electronic charge) interacts with itself and with the remaining screening electrons. The core-core interaction energy is assumed to be purely Coulombic in nature, whereas the screening electrons interact with the cores via an effective potential $\sum_{l\sigma} U_\sigma(\vec{x} - \vec{r}_{l\sigma})$. Here $\vec{x}$ is an electron coordinate and $\vec{r}_{l\sigma}$ is the instantaneous position of an ion of type σ in lattice cell l. The bare ion-core form factor is defined by

$$U_\sigma(\vec{q}) \equiv \int d^3r\, e^{-i\vec{q}\cdot\vec{r}} U_\sigma(\vec{r}) , \tag{1a}$$

and satisfies

$$\lim_{q\to 0} [-(q^2/4\pi) U_\sigma(q)] = Z_\sigma , \tag{1b}$$

where Z_σ is the ionic charge associated with an ion of type σ.

The phonon frequencies $\omega_{q\lambda}$ and eigenvectors $\vec{\epsilon}^{\,\sigma}_{q\lambda}$ are derived from

$$\omega^2_{q\lambda} \epsilon^{s\sigma}_{q\lambda} = \sum_{s''\sigma''} D^{ss''}_{\sigma\sigma''}(\vec{q}) \epsilon^{s''\sigma''}_{q\lambda} , \tag{2a}$$

where (we specialize to the case of two atoms per unit cell)

$$(M_1 M_2)^{-1/2} D^{ss'}_{\sigma\sigma'}(\vec{q}) = (M_\sigma M_{\sigma'})^{-1/2} \times [A^{ss'}_{\sigma\sigma'}(\vec{q}) - \delta_{\sigma\sigma'} \sum_{\sigma''} A^{ss'}_{\sigma\sigma''}(0)] \tag{2b}$$

and

$$A^{ss'}_{\sigma\sigma'}(\vec{q})=\frac{4\pi}{a}\sum_{\vec{K}\vec{K}'}\exp(i\vec{K}'\cdot\vec{X}_{\sigma'}-i\vec{K}\cdot\vec{X}_{\sigma})\left(\frac{|q+\vec{K}|^2}{4\pi}U_{\sigma}(\vec{q}+\vec{K})\right)\frac{(\vec{q}+\vec{K})_s(\vec{q}+\vec{K}')_{s'}}{|\vec{q}+\vec{K}|\,|\vec{q}+\vec{K}'|}\left(\frac{|q+\vec{K}'|^2}{4\pi}U_{\sigma'}(\vec{q}+\vec{K}')\right)$$

$$\times\frac{|q+\vec{K}'|}{|\vec{q}+\vec{K}|}\left[\epsilon^{-1}_{K'K}(\vec{q})-\delta_{K'K}\right]+\frac{4\pi}{a}Z_{\sigma}Z_{\sigma'}\sum_{\vec{K}}e^{i\vec{K}\cdot\vec{x}_{\sigma'\sigma}}\frac{(\vec{q}+\vec{K})_s(\vec{q}+\vec{K})_{s'}}{|\vec{q}+\vec{K}|^2}\;. \tag{2c}$$

M_σ is the mass of an ion of type σ, and X_σ is the position of that ion in the unit cell. The ω^2 is given in units of the squared frequency $(me^4/2\hbar^2)/[r_0^2\times(M_1M_2)^{1/2}]$, where r_0 is the nearest-neighbor distance and $a=r_0/a_0$.

The last term in (2c) represents the direct Coulomb interaction between ion cores having charges $Z_\sigma e$ and $Z_{\sigma'}e$. The $\epsilon^{-1}_{KK'}(\vec{q})$ then represents the dressed inverse screening matrix of the valence electrons only. Now, in a crystal of cubic symmetry, the most general form that $A^{ss'}_{\sigma\sigma'}(\vec{q})$ can take in the $\vec{q}\sim 0$ limit is

$$A^{ss'}_{\sigma\sigma'}(\vec{q})\sim(\delta_{ss'}-q_sq_{s'}/q^2)A^{T}_{\sigma\sigma'}(q)$$
$$+(q_sq_{s'}/q^2)A^{L}_{\sigma\sigma'}(q)\;,$$

where the longitudinal and transverse parts

$$A^{L}_{\sigma\sigma'}(\vec{q})=q^{-2}\sum_{ss'}q_sA^{ss'}_{\sigma\sigma'}(\vec{q})q_{s'}\;,$$
$$A^{T}_{\sigma\sigma'}(\vec{q})=\tfrac{1}{2}\left[\sum_{s}A^{ss}_{\sigma\sigma'}(\vec{q})-q^{-2}\sum_{ss'}q_sA^{ss'}_{\sigma\sigma'}(\vec{q})q_{s'}\right] \tag{3}$$

are well defined as $q\to 0$ and are invariants of the full cubic group. The requirement that all acoustic modes become zero as $q\to 0$ takes the form

$$\lim_{q\to 0}\sum_{\sigma'}[A^{L}_{\sigma\sigma'}(q)-A^{T}_{\sigma\sigma'}(q)]=0\;. \tag{4}$$

This last allows us to write the total dynamical matrix for $q\sim 0$ as

$$(M_1/M_2)^{1/2}D^{ss'}_{11}(\vec{q})=(M_2/M_1)^{1/2}D^{ss'}_{22}(\vec{q})$$
$$=-D^{ss'}_{12}(\vec{q})$$
$$=(\delta_{ss'}-q_sq_{s'}/q^2)[-A^{T}_{12}(0)]$$
$$+(q_sq_{s'}/q^2)[-A^{L}_{12}(0)]\;. \tag{5}$$

It immediately follows that the $q=0$ optic modes are given by

$$\omega^2_{\rm LO}(0)=(M_1+M_2)(M_1M_2)^{-1/2}[-A^{L}_{12}(0)]\;,$$
$$\omega^2_{\rm TO}(0)=(M_1+M_2)(M_1M_2)^{-1/2}[-A^{T}_{12}(0)]\;. \tag{6}$$

The condition (4) can be shown to follow directly from the general sum rule established by Keating[13] together with the requirement of over-all charge neutrality

$$\int d^3r[\rho_{\rm el}(\vec{r})+\rho_{\rm ion}(\vec{r})]=0\;. \tag{7}$$

Once (7) has been assumed, the general sum rule yields, as a special case, the acoustic sum rule of Pick, Cohen, and Martin. As these authors point out, (4) is really a statement about the cancellation which occurs between the diagonal ($\vec{K}=\vec{K}'$) terms and the off-diagonal ($\vec{K}\neq\vec{K}'$) terms of ϵ^{-1}, as implied by the acoustic sum rule. With these last remarks in mind it is convenient to separate the expression (2c) into diagonal and off-diagonal parts, denoting the total contribution from all $\vec{K}\neq\vec{K}'$ terms by $\delta A^{ss'}_{\sigma\sigma'}(\vec{q})$. In addition, we denote that part of the dynamical matrix derivable from $\delta A^{ss'}_{\sigma\sigma'}(\vec{q})$ as $d^{ss'}_{\sigma\sigma'}(\vec{q})$; i.e., $d^{ss'}_{\sigma\sigma'}(\vec{q})$ is given by Eq. (2b) with $A^{ss'}_{\sigma\sigma'}(\vec{q})$ replaced by $\delta A^{ss'}_{\sigma\sigma'}(\vec{q})$. With these definitions, the condition (4) implies

$$(4\pi/a)Z_\sigma\epsilon^{-1}_{00}(0)\sum_{\sigma'}Z_{\sigma'}+(M_1M_2)^{-1/2}\lim_{q\to 0}\sum_{\sigma'}(M_\sigma)^{1/2}$$
$$\times[d^{L}_{\sigma\sigma'}(q)-d^{T}_{\sigma\sigma'}(q)](M_{\sigma'})^{1/2}=0\;. \tag{8}$$

Thus, whatever form the model for $d_{\sigma\sigma'}(q)$ takes, the necessary condition of translational invariance implies that it must satisfy (8).

III. MODEL

The choice of an approximation for the off-diagonal elements of $\epsilon^{-1}(\vec{q}+\vec{K},\,\vec{q}+\vec{K}')$ is guided by the ideas stressed in Phillips's theory of the covalent bond in diamond-type semiconductors. As in Martin's treatment of the homopolar semiconductor Si, one approximates the contributions from the off-diagonal part of the dynamical matrix by the Coulombic interaction of localized bond charges with themselves and with other "residual" charges located at the ion positions. Within the context of Phillips's theory, these residual charges arise because the ions are incompletely screened by the valence electrons. The fraction of the electronic charge not participating in the screening of the ions is localized in the covalent bond. Thus if an ion of type 1 exhibits a residual charge z_1, it contributes an amount of charge $\propto -z_1$ to each of its associated bonds. In the NaCl structure an ion of type 1 has only type-2 ions as its nearest neighbors. Thus, the total charge in each bond will be $z=-\frac{1}{6}(z_1+z_2)$. In the ideal covalent case both z_1 and z_2 would be separately positive and the ion cores would be well described by bare metallic form factors. However, in order to include the possibility of complete charge transfer, characteristic of ionic bonding, we impose no restrictions on the signs of z_1 and z_2. We would expect, however, that if this simple model of partially covalent bonding is to be qualitatively correct, one should have $z_1 + z_2 > 0$.

Now, within the framework of the model, the specific ansatz that one makes for the off-diagonal part of the dynamical matrix takes the form

$$\frac{1}{(M_1 M_2)^{1/2}}\, d_{\sigma\sigma'}^{ss'}(\vec{q}) = \frac{1}{(M_\sigma M_{\sigma'})^{1/2}} \left(\frac{\partial^2 E_C}{\partial u_{\vec{q}}^{s\sigma}\, \partial u_{-\vec{q}}^{s'\sigma'}} \right)_{u=0} . \tag{9}$$

Here, $u_q^{s\sigma}$ is related to the atomic displacement $u_l^{s\sigma}$ by the normal mode transformation

$$u_l^{s\sigma} = (N_C)^{-1/2} \sum_{\vec{q}} e^{i\vec{q}\cdot(\vec{R}_l + \vec{X}_\sigma)} u_{\vec{q}}^{s\sigma} ,$$

where $\vec{R}_l$ is a vector of the fcc space lattice and $\vec{X}_\sigma$ denotes the position of an ion of type σ in the primitive cell. N_C is the number of such cells. Finally, we have that E_C is a Coulombic energy consisting of two parts which we denote by E_{BB} and E_{BL}. The first part,

$$E_{BB} = \frac{1}{2} \sum_{lb,\, l'b'}{}' \frac{e^2 z^2}{|\vec{r}_{lb} - \vec{r}_{l'b'}|} , \tag{10}$$

represents the mutual interaction of all the bond charges in the crystal, assuming the same value z for each of these charges. Since each ion has as its nearest neighbors six ions of the opposite kind, we adopt the convention of associating all of the bond charges with a single sublattice and define their positions with respect to that sublattice. Thus,

$$\vec{r}_{lb} = \vec{R}_l + \vec{\tau}_b^{\,0} + \delta\vec{\tau}_b(l), \quad b = 1, 6 . \tag{11}$$

The $\vec{\tau}_b^{\,0}$ represents the bond-charge position in the undistorted lattice and is given by

$$\vec{\tau}_b^{\,0} = \alpha \vec{d}_b, \quad 0 < \alpha < 1$$

where $\vec{d}_b$ is one of the set of six-nearest-neighbor vectors (1, 0, 0), (0, 1, 0), (0, 0, 1), $(\bar{1}, 0, 0)$, $(0, \bar{1}, 0)$, and $(0, 0, \bar{1})$. For a given ion in the reference sublattice, the six bond charges associated with this ion are each located a fractional distance α along the respective nearest-neighbor vectors emanating from the ion. We assume that this holds true even in the distorted lattice. Thus $\delta\vec{\tau}_b(l)$, the displacement of the bond charge from its equilibrium position, depends linearly on α and has the form

$$\delta\vec{\tau}_b(l) = (1-\alpha)\vec{u}_l^{\,1} + \alpha \vec{u}_{l'}^{\,2} , \tag{12}$$

where $\vec{u}_l^{\,1}$, $\vec{u}_{l'}^{\,2}$ are the displacements associated with the reference ion and the appropriate nearest-neighbor ion, respectively.

The second contribution to the total Coulombic energy E_C consists of the interaction energy of the bond charges z with the residual charges z_1, z_2 located at the instantaneous ion positions in the two sublattices. As will be discussed in more detail later, z_1, z_2 are related through ϵ_0 to the ionic charges Z_1, Z_2. Thus,

$$E_{BL} = \sum_{l\sigma,\, l'b} \frac{z_\sigma z e^2}{|\vec{r}_{l\sigma} - \vec{r}_{l'b}|} , \tag{13}$$

where

$$\vec{r}_{l\sigma} = \vec{R}_l + \vec{X}_\sigma + \vec{u}_l^{\,\sigma}$$

and $\vec{r}_{l'b}$ is defined as before.

In Appendixes A and B we evaluate the expressions (10) and (13) for E_{BB} and E_{BL}, as well as the expression for $d_{\sigma\sigma'}^{ss'}(\vec{q})$. From Eqs. (B2)–(B4) in Appendix B we readily find that in the small q limit,

$$\begin{aligned}
(M_1/M_2)^{1/2} d_{11}^{ss'}(\vec{q}) &\sim (4\pi/a)(q_s q_{s'}/q^2) \\
&\quad \times \{[(1-\alpha)(6z) + z_1]^2 - z_1^2\} \\
&\quad + (4\pi/3a)[\alpha^2(6z)z_1 + (1-\alpha)^2(6z)z_2]\delta_{ss'} , \\
(M_2/M_1)^{1/2} d_{22}^{ss'}(\vec{q}) &\sim (4\pi/a)(q_s q_{s'}/q^2) \\
&\quad \times \{[\alpha(6z) + z_2]^2 - z_2^2\} \\
&\quad + (4\pi/3a)[\alpha^2(6z)z_1 + (1-\alpha)^2(6z)z_2]\delta_{ss'} , \\
d_{12}^{ss'}(\vec{q}) &\sim (4\pi/a)(q_s q_{s'}/q^2) \\
&\quad \times \{[(1-\alpha)(6z) + z_1][\alpha(6z) + z_2] - z_1 z_2\} \\
&\quad - (4\pi/3a)[\alpha^2(6z)z_1 + (1-\alpha)^2(6z)z_2]\delta_{ss'} .
\end{aligned} \tag{14}$$

From Eq. (14) one easily obtains expressions for $d_{\sigma\sigma'}^{L}(0)$ and $d_{\sigma\sigma'}^{T}(0)$, which can be inserted in the sum rule (8). When this is done, one readily finds that the sum rule will be satisfied for the following particular choice of z and z_1, z_2:

$$z = -\tfrac{1}{6}(z_1 + z_2) , \quad z_\sigma = Z_\sigma / \sqrt{\epsilon_0} . \tag{15}$$

This result is, of course, intuitively appealing. The amount of charge z associated with each bond agrees with our earlier speculation. Furthermore, the mutual interaction of the charges z_1, z_2 is proportional to $Z_1 Z_2/\epsilon_0$, which agrees with the interpretation of a bare ion of charge Z_1 interacting with the screened charge Z_2/ϵ_0. We may use (15) to rewrite the expression (14) as

$$\begin{aligned}
\left(\frac{M_1}{M_2}\right)^{1/2} d_{11}^{ss'}(\vec{q}) &\sim \frac{4\pi}{a} \frac{q_s q_{s'}}{q^2} [(q^*)^2 - z_1^2] \\
&\quad - \frac{4\pi}{3a} [(q^*)^2 + z_1 z_2]\delta_{ss'} , \\
\left(\frac{M_2}{M_1}\right)^{1/2} d_{22}^{ss'}(\vec{q}) &\sim \frac{4\pi}{a} \frac{q_s q_{s'}}{q^2} [(q^*)^2 - z_2^2] \\
&\quad - \frac{4\pi}{3a} [(q^*)^2 + z_1 z_2]\delta_{ss'} , \\
d_{12}^{ss'}(\vec{q}) &\sim -\frac{4\pi}{a} \frac{q_s q_{s'}}{q^2} [(q^*)^2 + z_1 z_2] \\
&\quad + \frac{4\pi}{3a} [(q^*)^2 + z_1 z_2]\delta_{ss'} ,
\end{aligned} \tag{16}$$

where the charge q^* is defined as

$$q^* = \alpha z_1 + (\alpha - 1) z_2 \ .$$

We will see shortly that q^* is the effective charge responsible for the splitting of the LO and TO modes at the zone center. The long-wavelength limit of the total dynamical matrix is found from (2c) and (16) to be given by

$$\left(\frac{M_1}{M_2}\right)^{1/2} D_{11}^{ss'}(\vec{q}) \sim \left(\frac{M_2}{M_1}\right)^{1/2} D_{22}^{ss'}(\vec{q}) \sim -D_{12}^{ss'}(\vec{q}) \sim \frac{4\pi}{a}\frac{q_s q_{s'}}{q^2}(q^*)^2 + (4\pi/3a)\delta_{ss'}\{Z_1 Z_2 - z_1 z_2 - (q^*)^2$$
$$-{\sum_{\vec{K}}}' e^{-i\vec{K}\cdot\vec{x}_{12}}[(K^2/4\pi)U_1(\vec{K})][(K^2/4\pi)U_2(\vec{K})][\epsilon_{KK}^{-1}(0) - 1]\} \ . \qquad (17)$$

The relation (5) permits the evaluation of $A_{12}^T(0)$ and $A_{12}^L(0)$ in a straightforward manner. The LO- and TO-mode frequencies at $q = 0$ are then given by (6). Of particular interest is the fact that

$$\omega_{\mathrm{LO}}^2(0) - \omega_{\mathrm{TO}}^2(0) = -\left[\frac{M_1 + M_2}{(M_1 M_2)^{1/2}}\right][A_{12}^L(0) - A_{12}^t(0)]$$
$$= \left[\frac{M_1 + M_2}{(M_1 M_2)^{1/2}}\right]\frac{4\pi}{a}(q^*)^2 \ , \qquad (18)$$

which justifies the earlier supposition of associating q^* with the macroscopic electric fields responsible for the splitting of the optic modes at $\vec{q} = 0$.

It is useful at this point to regroup the terms which appear in the expression for the total dynamical matrix. Thus, we rewrite (2c) as a sum of two terms:

$$A_{\sigma\sigma'}^{ss'}(\vec{q}) = C_{\sigma\sigma'}^{ss'}(\vec{q}) + F_{\sigma\sigma'}^{ss'}(\vec{q}) \ , \qquad (19)$$

where

$$C_{\sigma\sigma'}^{ss'}(\vec{q}) = \delta A_{\sigma\sigma'}^{ss'}(\vec{q}) + \frac{4\pi}{a} z_\sigma z_{\sigma'} \sum_{\vec{K}} e^{-i\vec{K}\cdot\vec{x}_{\sigma\sigma'}} \times \frac{(\vec{q}+\vec{K})_s(\vec{q}+\vec{K})_{s'}}{|\vec{q}+\vec{K}|^2}$$

and

$$F_{\sigma\sigma'}^{ss'}(\vec{q}) \equiv \frac{4\pi}{a}(Z_\sigma Z_{\sigma'} - z_\sigma z_{\sigma'}) \sum_{\vec{K}} e^{-i\vec{K}\cdot\vec{x}_{\sigma\sigma'}} \frac{(\vec{q}+\vec{K})_s(\vec{q}+\vec{K})_{s'}}{|\vec{q}+\vec{K}|^2} + \frac{4\pi}{a}\sum_{\vec{K}} e^{-i\vec{K}\cdot\vec{x}_{\sigma\sigma'}}\left[\frac{|\vec{q}+\vec{K}|^2}{4\pi} U_\sigma(\vec{q}+\vec{K})\right]$$
$$\times \frac{(\vec{q}+\vec{K})_s(\vec{q}+\vec{K})_{s'}}{|\vec{q}+\vec{K}|^2}\left[\frac{|\vec{q}+\vec{K}|^2}{4\pi} U_{\sigma'}(\vec{q}+\vec{K})\right][\epsilon_{KK}^{-1}(\vec{q}) - 1] \ . \qquad (20)$$

It is to be noted that $C_{\sigma\sigma'}^{ss'}(\vec{q})$ and $F_{\sigma\sigma'}^{ss'}(\vec{q})$ each separately satisfy the translational invariance condition (4). $C_{\sigma\sigma'}^{ss'}$ is, of course, that part of the dynamical matrix derivable from the Coulomb interaction of the electrically neutral system of charges z_1, z_2 and z, located at lattice sites and bond sites respectively. The remaining contribution to the dynamical matrix $F_{\sigma\sigma'}^{ss'}(\vec{q})$ may be termed the repulsive contribution, since it represents that part of the dynamical matrix arising from all non-Coulombic sources. [This is clear from (20) – the first term subtracts off the direct Coulomb part from the second term which contains both Coulombic and non-Coulombic contributions.] The model to be considered in the present work is that of approximating $F_{\sigma\sigma'}^{ss'}(\vec{q})$ by an effective short-range interaction, this being essentially the "simple bond charge model" employed by Martin in his calculations on Si and diamond. Martin was able to show in his calculation for Si that a direct evaluation of F employing a realistic model for $\epsilon(\vec{q}+\vec{K})$ yielded force constants which dropped off rapidly beyond the first-neighbor separation (thus justifying the approximation). We introduce the model here on an *ad hoc* basis – the major justification at this point being the extreme simplicity of the model. It might be anticipated that such a simple model would, at best, recapture only the qualitative features of the phonon spectrum. Interestingly enough, however, the model yields quite good results in that case which is treated in detail, i.e., MgO. Moreover, the overwhelming simplicity demands that the model be examined in detail – this is essentially the goal of the present work. We defer to Sec. IV a discussion of the more difficult task of calculating $F_{\sigma\sigma'}^{ss'}(\vec{q})$ from a model $\epsilon(\vec{q})$. Of immediate interest now, however, is an examination of the consequences of introducting an effective short-range interaction as the approximation for $F_{\sigma\sigma'}^{ss'}(\vec{q})$. We consider first the effect of nearest neighbors.

For the NaCl structure, a nearest-neighbor interaction involves only atoms of opposite kind and hence only contributes to $A_{12}^{ss'}(\vec{q})$. We have that

$$F_{11}^{ss'}(\vec{q}) = F_{22}^{ss'}(\vec{q}) = 0 \ ,$$
$$F_{12}^{ss'}(\vec{q}) = -\sum_{\vec{\tau}} \cos \vec{q}\cdot\vec{\tau}\, \varphi_{12}^{ss'}(\vec{\tau}) \ , \qquad (21)$$

where

$$\varphi_{12}^{ss'}(\vec{\tau}) = (\delta_{ss'} - \tau_s \tau_{s'}/\tau^2)\varphi_t(|\vec{\tau}|)$$
$$+ (\tau_s \tau_{s'}/\tau^2)\varphi_l(|\vec{\tau}|)$$

and the sum on lattice vectors $\vec{\tau}$ is taken only over near-neighbor atoms.

In the simple bond-charge model, the expressions for $A^T_{12}(0)$ and $A^L_{12}(0)$ are found to be

$$\begin{aligned} A^T_{12}(0) &= (4\pi/3a)(q^*)^2 - 2\varphi_l - 4\varphi_t \ , \\ A^L_{12}(0) &= -(8\pi/3a)(q^*)^2 - 2\varphi_l - 4\varphi_t \ , \end{aligned} \tag{22}$$

from which we obtain the optic mode frequencies at $q=0$. The condition that the crystal be in equilibrium at zero pressure allows us to eliminate the transverse component of the near-neighbor force in favor of the Coulomb energy per particle. Thus, we have

$$\varphi_t = \tfrac{1}{3}\epsilon_C \ ,$$

where ϵ_C is the Coulomb energy per particle of the system of charges z_1, z_2, and z arranged at lattice and bond sites, respectively. The calculation of ϵ_C is carried out in Appendix A where it is shown that ϵ_C may be expressed as a sum of two parts:

$$\begin{aligned} \epsilon_C &= \epsilon_C^{(1)} + \epsilon_C^{(2)}(\alpha) \ , \\ \epsilon_C^{(1)} &= (1/a)\left[(z_2+z_1)^2 \bar{M}_1 + (z_2-z_1)^2 \bar{M}_2\right] \ , \\ \epsilon_C^{(2)}(\alpha) &= (1/a)[(z_2+z_1)^2 \bar{M}_3(\alpha) \\ &\quad + (z_2+z_1)(z_1-z_2)\bar{M}_4(\alpha)] \ . \end{aligned} \tag{23}$$

Here $\epsilon_C^{(1)}$ represents the Coulomb energy per particle in Ry for the array of charges z_1, z_2 immersed in a uniform compensating background. We have that

$$\bar{M}_1 = -0.709\,32 \ , \quad \bar{M}_2 = -0.436\,89 \ ,$$

and note that $(-4\bar{M}_2)$ is the usual Madelung constant associated with the NaCl structure. The term $\epsilon_C^{(2)}$ represents the energy of interaction of bond charges z with the charges z_1, z_2 at lattice sites in the presence of a uniform compensating background of charge. The $\bar{M}_3$ and $\bar{M}_4$ depend on the bond-charge parameter α and satisfy

$$\bar{M}_3(\alpha) = \bar{M}_3(1-\alpha) \ , \quad \bar{M}_4(\alpha) = -\bar{M}_4(1-\alpha) \ .$$

Table I tabulates M_3 and M_4 as functions of α.

TABLE I. The parameters which enter into the expression for the Coulomb energy as functions of the bond position α.

α	$\bar{M}_3(\alpha)$	$\bar{M}_4(\alpha)$
0.10	−1.954 06	−4.126 04
0.15	−1.212 68	−2.458 64
0.20	−0.843 61	−1.623 32
0.25	−0.625 17	−1.119 09
0.30	−0.484 39	−0.777 93
0.35	−0.390 95	−0.526 68
0.40	−0.330 67	−0.327 34
0.45	−0.296 61	−0.157 09
0.50	−0.285 56	0

TABLE II. The parameters which enter into the expressions for the elastic constants as functions of the bond position α.

α	$\bar{C}_{11}^{(1)}(\alpha)$	$\bar{C}_{11}^{(3)}(\alpha)$	$\bar{C}_{44}^{(1)}(\alpha)$	$\bar{C}_{44}^{(3)}(\alpha)$	$\bar{C}_{s}^{(1)}(\alpha)$	$\bar{C}_{s}^{(3)}(\alpha)$
0.10	−3.2631	−2.0973	1.6316	1.0487	−1.5581	−0.1935
0.15	−2.3299	−1.0312	1.1649	0.5162	−1.1056	0.0487
0.20	−1.8269	−0.5376	0.9133	0.2684	−0.8516	0.1411
0.25	−1.4935	−0.2785	0.7466	0.1397	−0.6744	0.1691
0.30	−1.2479	−0.1558	0.6240	0.0785	−0.5373	0.1625
0.35	−1.0620	−0.0778	0.5309	0.0395	−0.4288	0.1359
0.40	−0.9273	−0.0333	0.4635	0.0172	−0.3475	0.0973
0.45	−0.8457	−0.0110	0.4229	0.0058	−0.2988	0.0448
0.50	−0.8186	0	0.4092	0	−0.2825	0

The long-wavelength limit of the dynamical matrix yields expressions for the elastic constants whose dependence on sublattice charge and bond position is similar to that exhibited by ϵ_C. Indeed, we find that

$$\begin{aligned} \bar{C}_{11} &= (z_2+z_1)^2 \bar{C}_{11}^{(1)}(\alpha) + (z_2-z_1)^2 \bar{C}_{11}^{(2)} \\ &\quad + (z_2+z_1)(z_1-z_2)\bar{C}_{11}^{(3)}(\alpha) + a\varphi_l \ , \\ \bar{C}_{44} &= (z_2+z_1)^2 \bar{C}_{44}^{(1)}(\alpha) + (z_2-z_1)^2 \bar{C}_{44}^{(2)} \\ &\quad + (z_2+z_1)(z_1-z_2)\bar{C}_{44}^{(3)}(\alpha) + \tfrac{1}{3}a\epsilon_C \ , \\ \bar{C}_s &\equiv \tfrac{1}{2}(\bar{C}_{11} - \bar{C}_{12}) \\ &= (z_2+z_1)^2 \bar{C}_s^{(1)}(\alpha) + (z_2-z_1)^2 \bar{C}_s^{(2)} \\ &\quad + (z_2+z_1)(z_1-z_2)\bar{C}_s^{(3)}(\alpha) + \tfrac{1}{2}a(\varphi_l + \tfrac{1}{3}\epsilon_C) \ . \end{aligned} \tag{24}$$

In the above, $\bar{C}$ represents a dimensionless quantity defined in terms of the usual elastic constant C as

$$\bar{C} \equiv (2r_0^4/e^2)C \ .$$

The parameters $\bar{C}_{11}^{(1)}$, $\bar{C}_{44}^{(1)}$, $\bar{C}_s^{(1)}$ are symmetric under $\alpha \longleftrightarrow 1-\alpha$, whereas $\bar{C}_{11}^{(3)}$, $\bar{C}_{44}^{(3)}$, and $\bar{C}_s^{(3)}$ are antisymmetric under this same interchange. The values of these parameters are tabluated in Table II. Furthermore, we have

$$\bar{C}_{11}^{(2)} = -0.6390 \ , \quad \bar{C}_{44}^{(2)} = 0.3195 \ , \quad \bar{C}_s^{(2)} = -0.3336 \ ,$$

independent of α.

It is instructive to plot the reduced elastic constants as functions of z_1 and α for fixed q^*. First, however, note that the dynamical matrix is invariant under the transformation $z_1 \rightarrow -z_1$, $z_2 \rightarrow -z_2$, as well as being invariant under the simultaneous interchanges $M_1 \longleftrightarrow M_2$, $z_1 \longleftrightarrow z_2$, $\alpha \longleftrightarrow 1-\alpha$. Either of these transformations results in a change in the sign of q^*. Thus, only $|q^*|$ is relevant and this may be determined from the zone-center optic mode splitting. If we arbitrarily choose the sign of q^* to be positive and allow z_1 to range over positive and negative values, we find that $z_2 \gtrless 0$ for $\alpha z_1 \lessgtr q^*$. Imposing the constraint that the charge in each bond be negative restricts the range of z_1 values to be considered to $z_1 > q^*$. The short-range parameter φ_l appearing in Eq. (24) is determined through a fit to the zone-center TO mode – a convenient pro-

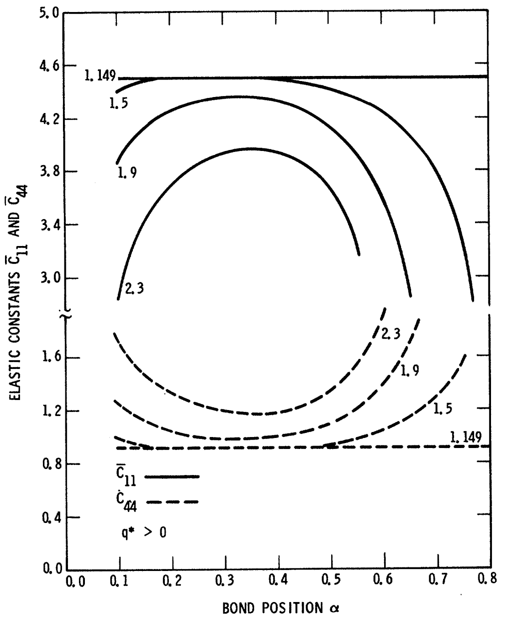

FIG. 1. Plot of the reduced elastic constants $\bar{C}_{11}$ and $\bar{C}_{44}$ vs bond position α. The curves are labeled by the value of the parameter z_1. The rigid-ion model ($z_1 = 1.149$) is represented by a horizontal straight line.

cedure, since it permits the introduction of second-neighbor forces in a straightforward manner at a later point. This last conclusion follows if we recall that second-neighbor forces act only between like atoms, so that the placement of the zone-center optic modes and, hence, the value assigned to $\varphi_l + 2\varphi_t$ will be unaffected by the introduction of these forces. Furthermore, the second-neighbor parameters can be chosen in such a way as to be consistent with the zero-pressure condition in the presence of nearest-neighbor forces only, thus leaving the determination of φ_t and φ_l separately unchanged.

In Figs. 1 and 2 the reduced elastic constants as given by Eq. (24) are plotted as functions of z_1 and α for the case $q^* > 0$ and in the region $z_1 \geq q^*$. The value chosen for $|q^*|$ is that appropriate to the zone-center optic mode splitting[20] in MgO, i.e., $|q^*| = 1.149$. For each value of z_1 and α, the short-range parameter φ_t was determined from the zero-pressure condition whereas the parameter φ_l was determined from a fit to the zone-center TO mode frequency[20] in MgO, i.e., $\omega_{\mathrm{TO}}(\Gamma) = 1.354$.

There are several general features of the plots in Figs. 1 and 2 which are relatively independent of the values chosen for $|q^*|$ and $\omega_{\mathrm{TO}}(\Gamma)$. Let us note that the amount of charge in each bond varies linearly as z_1 for fixed α and inversely as $(1-\alpha)$ for fixed z_1. Then, for fixed $\alpha \neq 0$ or 1, if we increase the amount of charge in each bond by increasing z_1, the reduced elastic constants $\bar{C}_{11}$ and $\bar{C}_{44}$, respectively, decrease and increase from their purely ionic values ($z_1 = q^*$, $z_1 + z_2 = 0$). Thus, the introduction of bond charge tends to soften the longitudinal vibration along [100], at the same time strengthening the [100] direction against shear. Furthermore, the [110] shear mode is softened. Fixing z_1 and varying the bond-charge position α reveals broad maxima in $\bar{C}_{11}$ and $\bar{C}_s$ as well as a broad minimum in $\bar{C}_{44}$.

If we note the experimental values for the elastic constants[21] in MgO:

$$\bar{C}_{11} = 4.93, \quad \bar{C}_{44} = 2.64, \quad \bar{C}_{12} = 1.49\ , \tag{25}$$

we see that the best fit to $\bar{C}_{11}$ and $\bar{C}_s$ is given by a nearly ionic description, although such a description yields a crystal which is nearly unstable to shear along [100]. It is not surprising that the rigid ion model is not satisfactory; the Cauchy relation $\bar{C}_{12} = \bar{C}_{44}$ is satisfied for such a model, yet it is clear from (25) that such is not the case in MgO. The violation of the Cauchy relation may be interpreted as a manifestation of the presence of noncentral forces, arising from covalent effects. It is a feature of the bond-charge model in the present context that the inclusion of charge along the octahedral bonds stiffens the [100] shear mode through the introduction of noncentral forces. We will see in what follows that by employing a simple second-neighbor force we will be able to retain this desirable feature of the bond-charge model and at the same time make a fit to $\bar{C}_{11}$ and $\bar{C}_s$.

Second-neighbor interactions in crystals of the NaCl structure involve only like atoms. If these second-neighbor forces are important in MgO it is

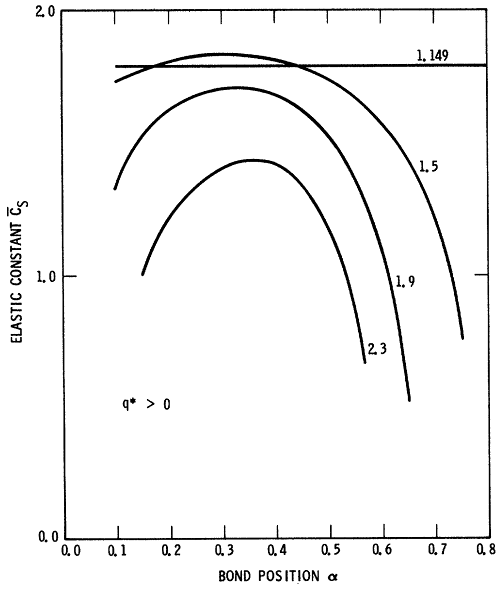

FIG. 2. Same as Fig. 1, but for the reduced elastic constant $\bar{C}_s$.

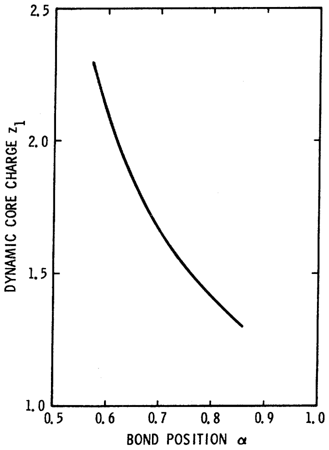

FIG. 3. Plot of the range of values of the bond parameters z_1 and α for which a fit was obtained to the long-wavelength optical properties and elastic constants of MgO.

reasonable to assume that they act between O ions only, since the sum of ionic radii for two Mg ions is much less than the second-neighbor separation, whereas the sum of radii for two O ions is almost equal to this separation.[22] With Mg ions labeled $\sigma = 1$ and the O ions labeled $\sigma = 2$, we have the following form for the second-neighbor contribution to $F_{\sigma\sigma'}^{ss'}(q)$:

$$F_{11}^{ss'}(\vec{q}) = F_{12}^{ss'}(\vec{q}) = 0 \;, \qquad (26)$$
$$F_{22}^{ss'}(\vec{q}) = (M_1/M_2)^{1/2} \sum_{\vec{\tau}}{}' (1 - \cos \vec{q}\cdot\vec{\tau})\, \varphi_{22}^{ss'}(\vec{\tau}) \;.$$

The sum on lattice vectors $\vec{\tau}$ is taken over the 12 second-neighbor ions. For $\vec{\tau} = (1, 1, 0)$, the most general form of $\varphi_{22}^{ss'}(\vec{\tau})$ allowable by symmetry is

$$\varphi_{22}^{ss'}(110) = \begin{pmatrix} \varphi_{22}^{11}(110) & \varphi_{22}^{12}(110) & 0 \\ \varphi_{22}^{12}(110) & \varphi_{22}^{11}(110) & 0 \\ 0 & 0 & \varphi_{22}^{33}(110) \end{pmatrix} . \qquad (27)$$

Setting $\varphi_{22}^{33}(110) = 0$ in the above achieves consistency with the previously imposed zero-pressure condition. The resulting form of the matrix may then be related to a valence-force-field[8, 23] approximation appropriate to the NaCl structure. In the valence-force-field approximation $\varphi_{22}^{11} \propto 2k_{r\theta}$ and $\varphi_{22}^{12} \propto k_\theta - 2k_{rr}$. Here k_θ denotes a bond-bending constant for the angle O – Mg – O, k_{rr} is a bond pair interaction constant and $k_{r\theta}$ represents a cross-coupling constant between the bond and the angle of which the bond forms one arm. The equivalent of the zero-pressure condition implies $k_{r\theta} = k_\theta$ in addition to $\varphi_{11}^{33} = 0$. The valence-force-field picture, first employed in the description of molecular binding, has the advantage that force constants are easily interpretable in reasonable physical terms.

The contributions to the elastic constants, $\Delta\overline{C}$, arising from the second-neighbor interaction alone are easily shown to be

$$\Delta\overline{C}_{11} = 2a\varphi_{22}^{11}, \;\; \Delta\overline{C}_{44} = a\varphi_{22}^{11}, \;\; \Delta\overline{C}_s = \tfrac{1}{2}a(3\varphi_{22}^{11} - 2\varphi_{22}^{12}) \;. \qquad (28)$$

As far as the long-wavelength elastic properties are concerned, it makes no difference which second neighbors interact; i.e., one cannot distinguish O-O interactions from Mg-Mg interactions from the long-wavelength properties alone. It is instructive, then, to examine the consequences of assuming only O-O interactions by considering the phonon frequencies at the zone boundary. At the L-symmetry point of the Brillouin zone the second-neighbor interactions contribute additively to the frequencies squared. Indeed, we find that second-neighbor forces between O ions affect only the high frequency (optic) modes at the L point. The second-neighbor contributions to these frequencies are given by

$$\Delta\omega_{\mathrm{LO}}^2(L) = (M_1/M_2)^{1/2} 8(\varphi_{22}^{11} + \varphi_{22}^{12}) \;, \qquad (29)$$
$$\Delta\omega_{\mathrm{TO}}^2(L) = (M_1/M_2)^{1/2} 8(\varphi_{22}^{11} - \tfrac{1}{2}\varphi_{22}^{12}) \;.$$

Similarly, second-neighbor forces between Mg ions affect only the low-frequency (acoustic) modes at L with the contributions to these modes being given by formulas identical to (29) but with $\varphi_{22}^{ss'}$ replaced by $\varphi_{11}^{ss'}$ and $M_1 \leftrightarrow M_2$.

The relations (28) suggest that we search for a range of values of z_1 and α for which

$$\overline{C}_{11}(\text{calc}) - \overline{C}_{11}(\text{expt}) = 2[\overline{C}_{44}(\text{calc}) - \overline{C}_{44}(\text{expt})] \;, \qquad (30)$$

where $\overline{C}$(calc) denotes values calculated from (24). If such a range of z_1 and α exists, then it follows that within that range a fit can be made to both $\overline{C}_{11}$ and $\overline{C}_{44}$ employing the single second-neighbor constant φ_{11}. If one plots the left-hand side (lhs) of (30) and the right-hand side (rhs) of (30) in a combined plot similar to Fig. 1, it becomes clear that there does indeed exist a relatively large range of values of z_1 and α for which the equality in (30) is satisfied. Furthermore, the locus of the points of intersection of $[\overline{C}_{11}(\text{expt}) - \overline{C}_{11}(\text{calc})]$ with $2[\overline{C}_{44}(\text{expt}) - \overline{C}_{44}(\text{calc})]$ is to a good approximation a straight line with zero slope; i.e., the lhs (or rhs) of (30) is essentially a constant for those values of z_1 and α for which the equality is satisfied. We have plotted a subset of these values in Fig. 3. For $z_1 > 2.8$ the relation (30) cannot be satisfied for any α. However, in the interval $2.8 > z_1 > 2.3$ there actually exist two possible solutions α_1, α_2 with $\alpha_1 \sim 0.4$ and $\alpha_2 \sim 0.2$. We have chosen to examine the interval $2.3 > z_1 > 1.3$ as that which is physically most reasonable. For $z_1 < 1.3$ the Coulomb contribution to the total energy becomes positive. In the ionic limit ($z_1 = q^* = -z_2$) Eq. (30) cannot be satisfied at all, indeed, the lhs of (30) has the value 0.43,

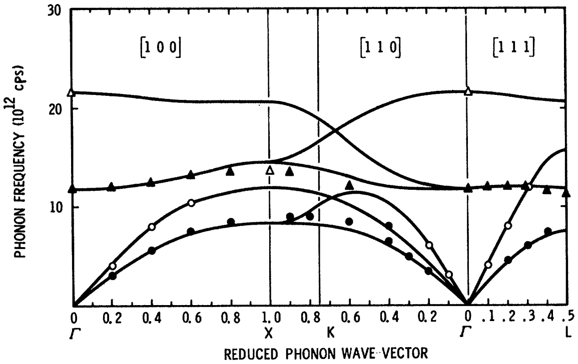

FIG. 4. Calculated phonon dispersion curves in MgO. Experimental points are from the inelastic neutron scattering data of Peckham (Ref. 24). The optic branch is represented by triangles; the acoustic branch by circles. Open symbols denote longitudinal polarizations; solid symbols denote transverse polarizations.

whereas the rhs has the value 3.44. Finally, we point out that within the parameter range depicted in Fig. 3, $\overline{C}_s(\text{expt}) - \overline{C}_s(\text{calc})$ is constant, so that $\overline{C}_s(\text{expt})$ can be fit with a value of φ_{22}^{12} independent of z_1 and α. The final values of φ_{22}^{11} and φ_{22}^{12} employed in obtaining a fit to all elastic constants are

$$\varphi_{22}^{11} = 0.244, \quad \varphi_{22}^{12} = 0.100 . \qquad (31)$$

We can now ask what effect the variation of z_1 and α within the range depicted in Fig. 3 has on the phonon frequencies throughout the Brillouin zone. Complete phonon dispersion curves were calculated employing a sampling of the z_1 and α values depicted in Fig. 3 and using the values of φ_{22}^{11} and φ_{22}^{12} given in (31). Over this complete range of values, zone boundary frequencies changed by no more than 10%. The best fit, obtained with $z_1 \sim 1.9$ and $\alpha \sim 0.64$ is shown in Fig. 4 together with the experimental data of Peckham,[24] obtained from inelastic neutron scattering. Agreement between the calculated curves and the experimental points is quite satisfactory, although the lack of more extensive experimental data on the LO and LA branches precludes the making of any definitive statements. This is especially true in view of the fact that a shell-model calculation[24] yields comparable agreement with experiment, yet differs in several important aspects from the present calculation. A comparison of the present calculated curves with those obtained from a shell-model calculation reveals important differences with respect to the LO and LA branches near X as well as the TO branch near X, K, and L. In particular, we note that the shell-model TO branch is too low, whereas the TO branch of the present model is too high. Furthermore, the LA and TO branches cross near X in the shell-model calculation, whereas this crossing does not occur in the present model.

IV. DISCUSSION

In previous sections we have made a detailed study of a covalent-bond-charge model of the lattice vibrational properties of heteropolar NaCl-type crystals. The conclusion was reached that a simple bond-charge description of the dielectric response is capable of describing satisfactorily the lattice spectrum of a heteropolar crystal such as MgO, a material in which covalent effects are thought to be important. Although comparable agreement with experiment has been obtained within the context of a shell model, the physical interpretation of the parameters appearing in the bond model is clearer. To reinforce this point we would now like to summarize and discuss in detail some of the more important points arrived at in the present work.

In Sec. III we considered in detail the behavior of the elastic constants for a simple model of a heteropolar-structure NaCl crystal. This model included Coulomb forces arising from point bond charges and ion charges, together with a nearest-neighbor repulsive interaction. Two parameters were important here – the dynamic core charge z_1 for the "cation" and the bond-position parameter α. The dynamic core charge z_2 of the "anion" was determined from z_1 and α once the effective charge q^* was fixed by the optic mode splitting at the zone center. Eliminating the tangential near-neighbor force constant through the zero-pressure condition left only the longitudinal force constant φ_l to be determined, and this was done through a fit to the zone-center TO mode. With this fit to the long-wavelength optical properties accomplished, the trends in the elastic constants were examined with respect to variations in z_1 and α. Equations (23) and (24), together with Tables I and II, summarize the information necessary to apply this procedure to any NaCl-type crystal. In our considerations we confined ourselves to the region of positive z_1, a reasonable choice, as well as to that range of z_1 for which the charge in each bond $-\frac{1}{6}(z_1 + z_2)$ was negative. It was argued that several general features of the plots in Figs. 1 and 2 were not dependent on the fit made to the zone-center optical properties. These features included: (a) For fixed z_1, a broad maximum and a broad minimum appear in $\overline{C}_{11}$ and $\overline{C}_{44}$, respectively, as α is varied; (b) the strengthening (softening) of the [100] transverse (longitudinal) mode with an increase in bond charge. Within the framework of a specific application to MgO, these two general properties permitted a range of z_1 and α to be found such that the introduction of a single second-neighbor force constant, independent of z_1 and α, yielded agreement with the experimental $\overline{C}_{11}$ and $\overline{C}_{44}$. This force constant φ_{22}^{11} was interpreted as a bond-bending constant for the angle O – Mg – O. The inclusion of an additonal sec-

TABLE III. Values of some relevant quantities entering into the bond-charge model for the range of z_1 and α depicted in Fig. 3.

α	z_1	z_2	z	φ_l	Z_{eff}
0.808	1.4	−0.093	−0.218	1.648	2.43
0.761	1.5	−0.031	−0.245	1.804	2.60
0.723	1.6	0.028	−0.271	1.934	2.78
0.694	1.7	0.101	−0.300	2.062	2.95
0.665	1.8	0.143	−0.324	2.184	3.12
0.643	1.9	0.204	−0.351	2.314	3.30
0.620	2.0	0.240	−0.373	2.445	3.47
0.603	2.1	0.296	−0.399	2.588	3.64
0.585	2.2	0.326	−0.421	2.732	3.82
0.566	2.3	0.352	−0.442	2.884	3.99

ond-neighbor parameter φ_{22}^{12} – again independent of z_1 and α – yielded agreement with the experimental value of $\bar{C}_s$. This latter parameter was related to the coupling between bond pairs. The fact that φ_{22}^{11} and φ_{22}^{12} were essentially independent of z_1 and α implied that all implicit dependence on parameters relating directly to the bond was absorbed into the radial nearest-neighbor constant φ_l. Finally, it was pointed out that the rigid-ion model, represented by $z_1 = q^* = -z_2$, provided an unsatisfactory description of the crystal.

Having established the long-wavelength elastic and optical properties of our prototype of a partially covalent crystal, the stage was set for a calculation of the complete dispersion curves in MgO. Having constrained the six available parameters through a fit to the two zone-center optical constants plus the three macroscopic elastic constants, considerable latitude remained in the choice of z_1 and α. A sampling of the values of z_1 and α plotted in Fig. 3 together with other relevant quantities is given in Table III. The trends exhibited in Table III are what one might expect on simple physical grounds. We see that the amount of electronic charge in each bond z increases in absolute value from 0.22 to 0.44 as one increases the value of z, from 1.4 to 2.3. Over this same range the first-neighbor radial force constant φ_l increases in value in order to keep in line with the increased importance of the Coulomb forces. The effective ionic charge Z_{eff} for the cation [see Eq. (1b)] is defined in terms of z_1 as $Z_{\text{eff}} = \sqrt{\epsilon_0}\, z_1$, where ϵ_0 is the high-frequency long-wavelength dielectric constant. Using the value[20] $\epsilon_0 = 3.01$ for MgO, we see that Z_{eff} increases from a value of 2.41 to a value 3.96. For the value of z_1 used in the calculation of the dispersion curves shown in Fig. 4, Z_{eff} has the value 3.30. This is to be compared with $Z_{\text{eff}} = 2$, which one would expect for a rigid-ion model with no valence distortion effects. One should not place an undue amount of significance on the particular value of z_1 used in the final calculation, especially in view of the fact that the over-all dispersion curves were relatively insensitive to the values chosen within the range depicted in Fig. 3. It is to be expected that the $q \neq 0$ phonon frequencies would be relatively unaffected by variations in z_1 and α – the point bond-charge approximation is essentially a long-wavelength approximation. Hence, once the $q \sim 0$ lattice properties have been used to constrain the range of variation of the parameters relating directly to the bond charge, there should be little effect on the $q \neq 0$ properties when these parameters are varied. Further improvements would require the introduction of a form factor for the bond charge as well as an ion-core form factor calculated from first principles. In lieu of this one is forced to resort to the simplest approximation – that of using point charges. This is probably not an entirely satisfactory approximation in MgO, in spite of the agreement with the experimental dispersion curves shown in Fig. 4.

There are several differences which exist between the present approach and the more common shell-model approach which should be emphasized. First, and most obvious, is the fact that valence distortion is included in the bond-charge model through the introduction of charge into the octahedral bonds, rather than through electronic "shells" located at lattice sites. Second, the nearest-neighbor tangential force constant is eliminated through the stability condition in the present approach rather than being treated as an additional adjustable parameter. Third, the covalent bond model places physical significance on the second-neighbor forces through the introduction of a valence-force-field matrix, rather than treating these parameters in an *ad hoc* manner as in the shell model.

We would now like to confine the remaining discussion in this section to a consideration of one of the major approximations involved in the present work. In Sec. III we saw that by approximating the non-Coulombic part of the dynamical matrix $F_{\sigma\sigma'}^{ss'}(\vec{q})$ by an effective short-range interaction extending to second neighbors, an adequate description of the dispersion curves in MgO could be obtained. The question now arises whether an effective diagonal-screening function $\epsilon_{\text{eff}}(\vec{q}+\vec{K})$ can be constructed from a simplified model of the band structure such that the approximation

$$\epsilon^{-1}(\vec{q}+\vec{K},\ \vec{q}+\vec{K}) \approx 1/\epsilon_{\text{eff}}(\vec{q}+\vec{K})$$

will suffice for a calculation of $F_{\sigma\sigma'}^{ss'}(\vec{q})$. Our considerations will only be qualitative and will be based on an examination of the expression for the zone-center TO mode frequency:

$$\omega^2_{\mathrm{TO}}(\Gamma)=\left[\left(\frac{M_1}{M_2}\right)^{1/2}+\left(\frac{M_2}{M_1}\right)^{1/2}\right]\left[-\frac{4\pi}{3a}(q^*)^2+\frac{4\pi}{3a}z_1z_2(\epsilon_0-1)-\frac{4\pi}{3a}\sum_K{}' \cos\vec{\mathrm{K}}\cdot\vec{\mathrm{X}}_{12}\left(\frac{K^2}{4\pi}U_1(K)\right)\left(\frac{1}{\epsilon_{\mathrm{eff}}(K)}-1\right)\left(\frac{K^2}{4\pi}U_2(K)\right)\right]. \tag{32}$$

Lacking a better description, we consider a model for $\epsilon_{\mathrm{eff}}(q+K)$ similar to that used by Penn[25] and Srinivasan[26]:

$$\epsilon_{\mathrm{eff}}(q)=1+\frac{16}{3\pi}\left(\frac{k_F}{a}\right)^3\frac{1}{\Delta^2}\left[1+B\frac{2}{\Delta}\left(\frac{q}{a}\right)^2+\frac{1}{\Delta^2}\left(\frac{q}{a}\right)^4\right]^{-1}. \tag{33}$$

In the above expression Δ is an effective energy gap which is to be chosen so that $\epsilon_{\mathrm{eff}}(q=0)$ agrees with the experimental ϵ_0. The k_F is a dimensionless Fermi wave vector, and B is to be treated as an adjustable parameter. Fixing the value of q^* through the optic mode splitting, the first two terms on the rhs of (32) were evaluated for a range of values of z_1 and α. For each value of z_1 and α the third term in (32) was then evaluated for a range of B values. As a first approximation the form factors were taken to be purely Coulombic; i.e.,

$$U_\sigma(q)\approx -4\pi Z_\sigma/q^2\ . \tag{34}$$

The value for k_F chosen corresponded to eight electrons per unit cell. With $B=1$ (Penn model) no range of z_1 and α values could be found such that Eq. (32) yielded agreement with the experimental value of $\omega^2_{\mathrm{TO}}(\Gamma)$, indeed, the calculated $\omega^2_{\mathrm{TO}}(\Gamma)$ was always too soft. The situation improved, however, for $B>1$. A value of $B\sim 2.5$ yielded a satisfactory range of z_1 and α values qualitatively similar to the range depicit in Fig. 3 but with $z_1>1.6$ and $\alpha>0.65$. Admittedly, the approximation (34) for the form factors is crude; however, it is doubtful that the over-all qualitative dependence of Eq. (32) on the parameters involved would be grossly altered through the introduction of realistic form factors. Thus, on the basis of these qualitative considerations we can tentatively conclude that at least the zone-center optical properties can be fit with a qualitatively reasonable choice for $\epsilon_{\mathrm{eff}}(q)$. However, a satisfactory calculation of the complete dispersion curves would require a more detailed knowledge of the exact structure of $\epsilon_{\mathrm{eff}}(q)$ based on the actual band structure of MgO.

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APPENDIX A

In this Appendix we employ Ewald techniques to evaluate the energy E_C for an instantaneous configuration of the lattice. In everything that follows, energies will be expressed in rydbergs, distances in units of the nearest-neighbor distance r_0, and wave vectors in units of $1/r_0$.

The first term entering into the expression for E_C is E_{BB}, which we evaluate as the mutual interaction energy of all the bond charges in the crystal immersed in a uniform compensating background. This takes the form

$$\begin{aligned}E_{BB}/N=&(4\pi/a)z^2\sum_{\vec{\mathrm{k}}}{}' k^{-2}e^{-k^2/4\eta}N^{-2}\sum_{lb,\,l'b'} e^{-i\vec{\mathrm{k}}\cdot(\vec{\mathrm{r}}_{lb}-\vec{\mathrm{r}}_{l'b'})}\\&+a^{-1}z^2N^{-1}\sum_{lb,\,l'b'}{}' G(|\vec{\mathrm{r}}_{lb}-\vec{\mathrm{r}}_{l'b'}|)\\&-(\eta^{1/2}/a\pi)(6z^2)-(\pi/4\eta a)(6z)^2\ .\end{aligned} \tag{A1}$$

In the above $\sum_k'$ denotes a sum on all wave vectors $\vec{\mathrm{k}}\neq 0$. Furthermore, we have that $a=r_0$ in a.u., N is the total number of atoms in the crystal, z is the value of the total bond charge at each bond site and $\vec{\mathrm{r}}_{lb}$ is defined by Eq. (12) in the main text. Finally,

$$G(|\vec{\mathrm{r}}|)=(1/|\vec{\mathrm{r}}|)\,\mathrm{Erfc}(\eta^{1/2}|\vec{\mathrm{r}}|)$$

with η being the usual Ewald convergence constant.

The second contribution to E_C consists of the Coulomb energy of the bond charges z interacting with the charges z_1, z_2 located at the instantaneous ion positions in sublattices 1 and 2, the whole array being immersed in a uniform compensating background. This contribution is given as

$$\begin{aligned}E_{BL}/N=&(8\pi/a)\sum_{\vec{\mathrm{k}}}{}' k^{-2}e^{-k^2/4\eta}N^{-2}\sum_{l\sigma,\,l'b'} z_\sigma z\, e^{-i\vec{\mathrm{k}}\cdot(\vec{\mathrm{r}}_{l\sigma}-\vec{\mathrm{r}}_{l'b'})}\\&+(2/a)N^{-1}\sum_{l\sigma,\,l'b'} z_\sigma z\, G(|r_{l\sigma}-r_{l'b'}|)\\&-(\pi/4\eta)\,2(z_1+z_2)(6z)\ .\end{aligned} \tag{A2}$$

A third contribution which we will need is the mutual interaction energy of the charges z_1, z_2 at the instantaneous lattice positions and immersed in a compensating background. Denoting this contribution by E_{LL}, we have that

$$\begin{aligned}E_{LL}/N=&(4\pi/a)\sum_{\vec{\mathrm{k}}}{}' k^{-2}e^{-k^2/4\eta}\\&\times N^{-2}\sum_{l\sigma,\,l'\sigma'} z_\sigma z_{\sigma'}\, e^{-i\vec{\mathrm{k}}\cdot(\vec{\mathrm{r}}_{l\sigma}-\vec{\mathrm{r}}_{l'\sigma'})}\\&+(aN)^{-1}\sum_{l\sigma,\,l'\sigma'} z_\sigma z_{\sigma'}\, G(|\vec{\mathrm{r}}_{l\sigma}-\vec{\mathrm{r}}_{l'\sigma'}|)\\&-(\eta^{1/2}/a\sqrt{\pi})(z_1^2+z_2^2)-(\pi/4\eta a)(z_1+z_2)^2\ .\end{aligned} \tag{A3}$$

Evaluating (A1)–(A3) for $\vec{\mathrm{u}}=0$, yields the expressions necessary for the calculation of the static lattice energy ϵ_C. We have that

$$\epsilon_C = \epsilon_C^{(1)} + \epsilon_C^{(2)} ,$$

with

$$\epsilon_C^{(1)} = (E_{LL}/N)_{u=0} ,$$

$$\epsilon_C^{(2)} = (E_{BB}/N)_{u=0} + (E_{BL}/N)_{u=0} . \tag{A4}$$

Using (A1)–(A4) and the fact that $z = -\frac{1}{6}(z_1 + z_2)$, it is a straightforward matter to express the $\overline{M}_1$, $\overline{M}_2$, $\overline{M}_3$, and $\overline{M}_4$ defined in (25) as

$$\overline{M}_1 = \pi \sum_{K_e}{}' K^{-2} \exp(-K^2/4\eta) + \frac{1}{4}\left[\sum_{\vec{\tau}}{}' G(|\vec{\tau}|) + \sum_{\vec{\tau}} G(|\vec{\tau} + \vec{X}_{12}|)\right] - \left(\frac{\eta^{1/2}}{2\sqrt{\pi}}\right) - \left(\frac{\pi}{4\eta}\right) ,$$

$$\overline{M}_2 = \pi \sum_{K_0} K^{-2} e^{-K^2/4\eta} + \tfrac{1}{4}\left[\sum_{\vec{\tau}}{}' G(|\vec{\tau}|) - \sum_{\vec{\tau}} G(|\vec{\tau} + \vec{X}_{12}|)\right] ,$$

$$\overline{M}_3(\alpha) = \pi \left\{ \sum_{K_0} K^{-2} e^{-K^2/4\eta} \left(\frac{1}{3}\sum_{i=1}^{3} \cos \alpha K_i\right)^2 + \sum_{K_e}{}' \left(\frac{1}{K^2}\right) e^{-K^2/4\eta} \left[\left(\frac{1}{3}\sum_{i=1}^{3} \cos\alpha K_i - 1\right)^2 - 1\right]\right\} \tag{A5}$$

$$+ \frac{1}{2}\left\{\frac{1}{6}\sum_{\vec{\tau}}{}' G(|\vec{\tau}|) + \frac{1}{36}\sum_{b,b'}{}' \sum_{\vec{\tau}} G(|\vec{\tau} + \alpha\vec{d}_{bb'}|) - \frac{1}{6}\left[\sum_b \sum_{\vec{\tau}} G(|\vec{\tau} + \alpha\vec{d}_b|) + \sum_b \sum_{\vec{\tau}} G(|\vec{\tau} + \vec{X}_{12} + \alpha\vec{d}_b|)\right]\right\} - \left(\frac{\eta^{1/2}}{6\pi}\right) + \left(\frac{\pi}{4\eta}\right) ,$$

$$\overline{M}_4(\alpha) = -2\pi \sum_{K_0} K^{-2} e^{-K^2/4\eta} \left(\frac{1}{3}\sum_{i=1}^{3} \cos\alpha K_i\right) - \frac{1}{12}\left[\sum_b \sum_{\vec{\tau}} G(|\vec{\tau} + \alpha\vec{d}_b|) - \sum_b \sum_{\vec{\tau}} G(|\vec{\tau} + \vec{X}_{12} + \alpha\vec{d}_b|)\right] .$$

In the above $\vec{K}$ denotes a vector of the reciprocal lattice, i.e., $\vec{K} = \pi(l_1, l_2, l_3)$, where for the NaCl structure the set of integers (l_1, l_2, l_3) are either all even or all odd. Thus, $\sum_{Ke}$ denotes a sum over the subset of $\vec{K}$ for which the l_i are all even, whereas $\sum_{K0}$ denotes a sum over the subset for which the l_i are all odd. The $\vec{\tau}$ denotes a vector of the fcc space lattice $\vec{\tau} = (m_1, m_2, m_3)$, where the sum of the integers m_i must be even. Finally, $\vec{X}_{12} = (1, 1, 1)$. The α, $\vec{d}_b$ are defined in the main text.

APPENDIX B

Starting from Eq. (9) of the main text we proceed to evaluate the contribution $d_{\sigma\sigma'}^{ss'}(\vec{q})$ to the total dynamical matrix. We have that

$$(M_1 M_2)^{-1/2} d_{\sigma\sigma'}^{ss'}(\vec{q}) = (N_C)^{-1} \sum_{ll'} e^{-iq\cdot(\vec{R}_{ll'} + \vec{X}_{\sigma\sigma'})} \frac{1}{(M_\sigma M_{\sigma'})^{1/2}} \left(\frac{\partial^2 E_C}{\partial u_{ls}^{\sigma}\, \partial u_{l's'}^{\sigma'}}\right)_{u=0} . \tag{B1}$$

Considering first the contribution to E_C arising from E_{BL}, we find using (B1) and (A2) that

$$\left(\frac{M_1}{M_2}\right)^{1/2} d_{11,BL}^{ss'}(\vec{q}) = z_1 z \left[2(1-\alpha)\sum_{\vec{\tau}} (1 - e^{i\vec{q}\cdot\vec{\tau}}) \sum_b \varphi_{ss'}(\vec{\tau} + \alpha\vec{d}_b) + \alpha^2 \sum_{\vec{\tau}} \sum_b \varphi_{ss'}(\vec{\tau} + \alpha\vec{d}_b)\right]$$
$$+ z_2 z (1-\alpha)^2 \sum_{\vec{\tau}} \sum_b \varphi_{ss'}[\vec{\tau} + (1-\alpha)\vec{d}_b] ,$$

$$\left(\frac{M_2}{M_1}\right)^{1/2} d_{22,BL}^{ss'}(\vec{q}) = \left(\frac{M_1}{M_2}\right)^{1/2} d_{11,BL}^{ss'}(\vec{q}) \text{ with } z_1 \longleftrightarrow z_2, \quad \alpha \longleftrightarrow 1 - \alpha ,$$

$$d_{12,BL}^{ss'}(\vec{q}) = z_1 z \left\{\alpha \sum_{\vec{\tau}} \sum_b [e^{i\vec{q}\cdot\vec{d}_b} - e^{i\vec{q}\cdot(\vec{\tau} + \vec{d}_b)}]\varphi_{ss'}(\vec{\tau} + \alpha\vec{d}_b) - \alpha^2 \sum_{\vec{\tau}} \sum_b e^{i\vec{q}\cdot\vec{d}_b}\varphi_{ss'}(\vec{\tau} + \alpha\vec{d}_b)\right\}$$
$$+ z_2 z \left\{(1-\alpha) \sum_{\vec{\tau}} \sum_b [e^{i\vec{q}\cdot\vec{d}_b} - e^{i\vec{q}\cdot(\vec{\tau} + \vec{d}_b)}]\varphi_{ss'}[\vec{\tau} + (1-\alpha)\vec{d}_b] - (1-\alpha)^2 \sum_{\vec{\tau}} \sum_b e^{i\vec{q}\cdot\vec{d}_b}\varphi_{ss'}[\vec{\tau} + (1-\alpha)\vec{d}_b]\right\} , \tag{B2}$$

where

$$\varphi_{ss'}(\vec{\tau} + \alpha\vec{d}_b) \equiv -(8\pi/aN) \sum_{\vec{k}}{}' (k_s k_{s'}/k^2) e^{-k^2/4\eta} e^{i\vec{k}\cdot(\vec{\tau} + \alpha\vec{d}_b)} + (2/a)\nabla_s \nabla_{s'} G(|\vec{\tau} + \alpha\vec{d}_b|) . \tag{B3}$$

The nomenclature is the same as that which was introduced in Appendix A.

Let us observe that

$$f_{ss'}(\vec{\tau}) \equiv \textstyle\sum_b \varphi_{ss'}(\vec{\tau} + \alpha\vec{d}_b)$$

may be interpreted as contributing to an effective force acting between an ion located at the origin and an ion located at $\vec{\tau}$. The $f_{ss'}(\vec{\tau})$ possesses the full symmetry of the lattice, i.e.,

$$f_{ss'}(R\vec{\tau}) = \sum_{tu} R_{st} f_{tu}(\vec{\tau}) R_{us'}^{-1} ,$$

where R is an operator of the full cubic group.

Note, however, that in $d^{ss'}_{12,BL}$ there appear other nonconventional terms of the form

$$g_{ss'}(\vec{q},\vec{\tau}) \equiv \textstyle\sum_b e^{i\vec{q}\cdot\vec{d}_b}\varphi_{ss'}(\vec{\tau}+\alpha\vec{d}_b) ,$$

which cannot be interpreted as a force constant depending only on $\vec{\tau}$. This, of course, is a manifestation of the noncentral forces arising from the interaction of bond charges located at points other than lattice sites. Since $g_{ss'}$ satisfies

$$g_{ss'}(R^{-1}\vec{q}, R\vec{\tau}) = \sum_{tu} R_{st}\, g_{tu}(\vec{q},\vec{\tau}) R^{-1}_{us'} ,$$

the dynamical matrix has the correct symmetry as it should.

The calculation of the contribution to $d^{ss'}_{\sigma\sigma'}(\vec{q})$ arising from E_{BB} proceeds as above. We now employ (A1) in conjunction with (B1) to obtain

$$\left(\frac{M_1}{M_2}\right)^{1/2} d^{ss'}_{11,BB}(\vec{q}) = (1-\alpha)^2(6z)^2 \sum_{\vec{\tau}}{}' [1-e^{-i\vec{q}\cdot\vec{\tau}}] \times \frac{1}{36}\sum_{b,b'} \varphi_{ss'}(\vec{\tau}+\alpha\vec{d}_{bb'}) ,$$

$$\left(\frac{M_2}{M_1}\right)^{1/2} d^{ss'}_{22,BB}(\vec{q}) = \left(\frac{M_1}{M_2}\right)^{1/2} d^{ss'}_{11,BB}(\vec{q}) \quad \text{with } z_1 \leftrightarrow z_2,\ \alpha \leftrightarrow 1-\alpha , \tag{B4}$$

$$d^{ss'}_{12,BB}(\vec{q}) = \alpha(1-\alpha)(6z)^2 \sum_{\vec{\tau},b,b'}{}' [e^{-i\vec{q}\cdot\vec{d}_b} - e^{-i\vec{q}\cdot(\vec{\tau}+\vec{d}_b)}]\varphi_{ss'}(\vec{\tau}+\alpha\vec{d}_{bb'}) ,$$

where $\vec{d}_{bb'} \equiv \vec{d}_b - \vec{d}_{b'}$.

Considerable simplification results if we combine $d^{ss'}_{\sigma\sigma',BL}(\vec{q})$ with $d^{ss'}_{\sigma\sigma',BB}(\vec{q})$ and insert the value $-\frac{1}{6}(z_1+z_2)$ for z. We have that

$$\frac{1}{(M_1M_2)^{1/2}} d^{ss'}_{\sigma\sigma}(\vec{q}) = \frac{1}{M_\sigma}\left[\frac{4\pi}{a}\sum_{\vec{K}} \frac{(\vec{q}+\vec{K})_s(\vec{q}+\vec{K})_{s'}}{|\vec{q}+\vec{K}|^2} e^{-|\vec{q}+\vec{K}|^2/4\eta} F_\sigma(\vec{q}+\vec{K}) - \sum_{\vec{\tau}}{}' \cos(\vec{q}\cdot\vec{\tau})\Psi^{ss'}_\sigma(\vec{\tau}) + f_\sigma\delta_{ss'}\right] ,$$

$$d^{ss'}_{12}(\vec{q}) = \frac{4\pi}{a}\sum_{\vec{K}} \frac{(\vec{q}+\vec{K})_s(\vec{q}+\vec{K})_{s'}}{|\vec{q}+\vec{K}|^2} \cos(\vec{K}\cdot\vec{X}_{12}) F_{12}(\vec{q}+\vec{K}) - \sum_{\vec{\tau}} \cos[\vec{q}\cdot(\vec{\tau}+\vec{X}_{12})]\Psi^{ss'}_{12}(\vec{\tau}+\vec{X}_{12}) + R^{ss'}(\vec{q}) , \tag{B5}$$

where

$$F_1(\vec{q}+\vec{K}) = \left\{(1-\alpha)(z_1+z_2)\frac{1}{3}\sum_{i=1}^{3}\cos[\alpha(\vec{q}+\vec{K})_i] - z_1\right\}^2 - z_1^2 , \qquad F_2(\vec{q}+\vec{K}) = F_1 \text{ with } z_1 \leftrightarrow z_2,\ \alpha \leftrightarrow 1-\alpha ,$$

$$f_1 = -\frac{4\pi}{3a} z_1(z_1+z_2) - \frac{8}{3a}\frac{\eta^{3/2}}{\sqrt{\pi}}(1-\alpha)(z_1+z_2)\{(1-\alpha)(z_1+z_2)\tfrac{1}{6}[1+e^{-4\eta\alpha^2}+4e^{-2\eta\alpha^2}] - 2z_1e^{-\eta\alpha^2}\} ,$$

$$f_2 = f_1 \text{ with } z_1 \leftrightarrow z_2,\ \alpha \leftrightarrow 1-\alpha ,$$

$$\Psi^{ss'}_1(\vec{\tau}) = (1-\alpha)^2(z_1+z_2)^2\tfrac{1}{36}\sum_{bb'}(2/a)\nabla_s\nabla_{s'}G(|\vec{\tau}+\alpha\vec{d}_{bb'}|) - 2(1-\alpha)z_1(z_1+z_2)\tfrac{1}{6}\sum_b(2/a)\nabla_s\nabla_{s'}G(|\vec{\tau}+\alpha\vec{d}_b|) ,$$

$$\Psi^{ss'}_2(\vec{\tau}) = \Psi^{ss'}_1 \text{ with } z_1 \leftrightarrow z_2,\ \alpha \leftrightarrow 1-\alpha ,$$

$$F_{12}(\vec{q}+\vec{K}) = \left[(1-\alpha)(z_1+z_2)\frac{1}{3}\sum_{i=1}^{3}\cos(\alpha(q+K)_i) - z_1\right]\left\{\alpha(z_1+z_2)\frac{1}{3}\sum_{i=1}^{3}\cos[(1-\alpha)(q+K)_i] - z_2\right\} - z_1z_2 ,$$

$$\begin{aligned}\Psi^{ss'}_{12}(\vec{\tau}+\vec{X}_{12}) = {}& \alpha(1-\alpha)(z_1+z_2)^2\tfrac{1}{36}\left[\sum_b{}''(2/a)\nabla_s\nabla_{s'}G(|\vec{\tau}+\vec{X}_{12}-\vec{d}_b|) + \sum_{b,b'}{}'(2/a)\nabla_s\nabla_{s'}G(|\vec{\tau}+\vec{X}_{12}-\vec{d}_b+\alpha\vec{d}_{bb'}|)\right] \\ & - \alpha z_1(z_1+z_2)\tfrac{1}{6}\sum_b(2/a)\nabla_s\nabla_{s'}G(|\vec{\tau}+\vec{X}_{12}+(1-\alpha)\vec{d}_b|) \\ & - (1-\alpha)z_2(z_1+z_2)\tfrac{1}{6}\sum_b(2/a)\nabla_s\nabla_{s'}G(|\vec{\tau}+\vec{X}_{12}+\alpha\vec{d}_b|) .\end{aligned}$$

The double prime on $\sum_b$ in the first term in the above expression means that when $\vec{\tau}+\vec{X}_{12}$ is a nearest-neighbor vector, the term $\vec{d}_b = \vec{\tau}+\vec{X}_{12}$ is to be excluded. Finally, we have that $R^{ss'}(\vec{q})$ is given in terms of $R^{ss'}_{BL}$ and $R^{ss'}_{BB}$ by

$$R^{ss'}(\vec{q}) = \alpha(1-\alpha)(z_1+z_2)[z_1R^{ss'}_{BL}(1-\alpha) + z_2R^{ss'}_{BL}(\alpha)] - \alpha(1-\alpha)(z_1+z_2)^2R^{ss'}_{BB}(\alpha) ,$$

where

$$\begin{aligned}R^{ss'}_{BL}(\alpha) = {}& (4\pi/a)\textstyle\sum'_{\vec{K}}(K_sK_{s'}/K^2)\cos(\vec{K}\cdot\vec{X}_{12})\, e^{-K^2/4\eta}\tfrac{1}{6}\displaystyle\sum_b\cos(\vec{q}\cdot\vec{d}_b+\alpha\vec{K}\cdot\vec{d}_b) \\ & - (2/a)\sum_{\vec{\tau}}\tfrac{1}{6}\sum_b\cos(\vec{q}\cdot\vec{d}_b)\nabla_s\nabla_{s'}G(|\vec{\tau}+\vec{X}_{12}+\alpha\vec{d}_b|) ,\end{aligned}$$

and

$$R_{BB}^{ss'}(\alpha) = (4\pi/a) \sum_{\vec{K}} (K_s K_{s'}/K^2) e^{-K^2/4\eta} \tfrac{1}{36} \sum_{bb'} \cos(\vec{q}\cdot\vec{d}_b + \alpha\vec{K}\cdot\vec{d}_{b'b})$$

$$- \tfrac{1}{36}\{[\sum_b \cos(\vec{q}\cdot\vec{d}_b)](2/a) \sum_{\vec{\tau}} \nabla_s\nabla_{s'} G(|\tau|) + \sum_{b\neq b'} \cos(\vec{q}\cdot\vec{d}_b)\,(2/a) \sum_{\vec{\tau}} \nabla_s\nabla_{s'} G(|\vec{\tau} + \alpha\vec{d}_{bb'}|)\} \;.$$

It is easily found that

$$R^{ss'}(\vec{q}) = 0, \quad s \neq s'$$

and that the diagonal elements have the form

$$R_{11}(\vec{q}) = (\cos q_1) r_l + (\cos q_2 + \cos q_3) r_t \;,$$

$$R_{22}(\vec{q}) = (\cos q_2) r_l + (\cos q_1 + \cos q_3) r_t \;,$$

$$R_{33}(\vec{q}) = (\cos q_3) r_l + (\cos q_1 + \cos q_2) r_t \;.$$

Furthermore,

$$\tfrac{1}{3}\mathrm{Tr}[R^{ss'}(\vec{q})] = -\tfrac{1}{3}(\cos q_1 + \cos q_2 + \cos q_3)\,\alpha(1-\alpha)$$

$$\times \tfrac{1}{6}(z_1 + z_2)^2 (8/3a)(\eta^{3/2}/\sqrt{\pi})$$

$$= \tfrac{1}{3}(\cos q_1 + \cos q_2 + \cos q_3)(r_l + 2r_t) \;.$$

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