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Microscopic theory of dielectric screening and lattice dynamics. II. Phonon spectra and effective charges*

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The factorization scheme for treating dielectric screening in solids, introduced in a previous paper, is here used to calculate the dynamical matrix for the phonon frequencies and eigenvectors. By considering the limit as $\vec{q} \to 0$ we derive explicit microscopic expressions for the effective-charge tensor, the optic modes, the low-frequency dielectric constant $\epsilon(\omega)$, the acoustic sum rules, and the elastic and piezoelectric constants. The Lyddane-Sachs-Teller relation is obeyed, and the deviation of the Szigeti charge from the ionic charge is discussed. We discuss the relationship to other models for the dynamics of insulators and semiconductors, and finally present results of explicit calculations for the phonon spectra of silicon and germanium.

I. INTRODUCTION

In the preceding paper[1] (hereafter called I) we presented a factorization scheme for the dielectric screening of a solid which enables one to calculate explicitly the electron response to an external perturbation. In this paper we consider the self-consistent response to a motion of the ions in a normal mode of the lattice. We calculate the expression for the dynamical matrix which yields the phonon frequencies and eigenvectors, and also obtain explicit microscopic expressions for the effective-charge tensor, the low-frequency dielectric constant $\epsilon(\omega)$, and the acoustic sum rules. We go on to compare our formalism with the model recently proposed by Martin (Sec. III) and with the shell model (Sec. IV). In Sec. V we consider the long-wavelength limit of the dynamical matrix and its relation to the elastic and piezoelectric properties of an insulating crystal. Finally in Sec. VI we present the results of calculations for the phonon-dispersion curves of silicon and germanium.

II. LATTICE DYNAMICS AND EFFECTIVE CHARGES

The dynamical matrix of the crystal is given by[2,3] $(M_\kappa M_{\kappa'})^{-1/2} D^{\kappa\kappa'}_{\alpha\beta}(\vec{q})$, where

$$D^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) = \Big(C^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) + \tilde{E}^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) - \delta_{\kappa\kappa'} \lim_{\vec{q}\to 0} \sum_{\kappa''} [C^{\kappa\kappa''}_{\alpha\beta}(\vec{q}) + \tilde{E}^{\kappa\kappa''}_{\alpha\beta}(\vec{q})] \Big) , \quad (1)$$

where M_κ is the mass of the ion at $\vec{r}_\kappa$, $C^{\kappa\kappa'}_{\alpha\beta}(\vec{q})$ is the usual Coulomb coupling coefficient between ions of charge $(Z_\kappa e)$, $(Z_{\kappa'} e)$ on the sublattices κ, κ', and $\tilde{E}^{\kappa\kappa'}_{\alpha\beta}(\vec{q})$ is the contribution of the valence electrons. We now restrict ourselves, for simplicity, to the case where these electrons may be treated in terms of a *local* pseudopotential. We thus rule out here any rigorous treatment of the noble or transition metals and restrict ourselves in particular to the case of semiconductors. If we ascribe to each ion at $\vec{r}_\kappa$ a pseudopotential form factor $W_\kappa(\vec{Q})$, the expression for $\tilde{E}^{\kappa\kappa'}_{\alpha\beta}(\vec{q})$ is[2,3]

$$\tilde{E}^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) = \sum_{\vec{G}\vec{G}'} (\vec{q}+\vec{G})_\alpha (\vec{q}+\vec{G}')_\beta W_\kappa(\vec{q}+\vec{G}) \times W_{\kappa'}(\vec{q}+\vec{G}') \chi(\vec{q}+\vec{G}, \vec{q}+\vec{G}') e^{i(\vec{G}\cdot\vec{r}_\kappa - \vec{G}'\cdot\vec{r}_{\kappa'})} , \quad (2)$$

where $\chi(\vec{Q}, \vec{Q}')$ is the electron density response function defined by Eq. (4) of I. Using Eq. (19) of I in Eq. (2), we obtain

$$\tilde{E}^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) = E^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) - (\underline{W}\underline{S}\underline{W}^\dagger)^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) , \quad (3)$$

where

$$E^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) = -\sum_{\vec{G}} \frac{(\vec{q}+\vec{G})_\alpha (\vec{q}+\vec{G})_\beta}{v(\vec{q}+\vec{G})} \left(1 - \frac{1}{\epsilon_0(\vec{q}+\vec{G})}\right) \times W_\kappa(\vec{q}+\vec{G}) W_{\kappa'}(\vec{q}+\vec{G}) e^{i\vec{G}\cdot\vec{r}_{\kappa\kappa'}} \quad (4)$$

and the matrix $\underline{W}$ is defined by

$$W^{\kappa s}_{\alpha\beta}(\vec{q}) = \sum_{\vec{G}} (\vec{q}+\vec{G})_\alpha (\vec{q}+\vec{G})_\beta \frac{W_\kappa(\vec{q}+\vec{G})}{\epsilon_0(\vec{q}+\vec{G})} \times f^s(\vec{q}+\vec{G}) e^{i\vec{G}\cdot\vec{r}_{\kappa s}} . \quad (5)$$

$\underline{W}$ is a $3r \times 3r'$ matrix (r is the number of atoms in the cell; r' is the number of chosen sites $\vec{r}_s$ in the cell) and is the coupling coefficient between the ion cores on sublattice κ with dipole distributions on sublattice s via a screened interaction $W_\kappa(\vec{Q})/\epsilon_0(\vec{Q})$. It is *not* in general a Hermitian matrix. The Hermitian matrix $\underline{S}$ is the inverse of the $(3r' \times 3r')$ matrix $[\underline{V} + \underline{a}^{-1}]$, as defined in I. It may be readily verified that the equations of motion resulting from Eqs. (1) and (3) are those which result from the set of equations

$$M_\kappa \omega^2 e_{\kappa\alpha} = \sum_{\kappa'\beta} (C^{\kappa\kappa'}_{\alpha\beta} + E'^{\kappa\kappa'}_{\alpha\beta}) e_{\kappa'\beta} + \sum_{s'\beta} W^{\kappa s'}_{\alpha\beta} w_{s'\beta} , \quad (6a)$$

$$0=\sum_{\kappa'\beta}(\underline{W}^{\dagger})^{s\kappa'}_{\alpha\beta}e_{\kappa'\beta}+\sum_{s'\beta}(\underline{V}+\underline{a}^{-1})^{ss'}_{\alpha\beta}w_{s'\beta}\ , \tag{6b}$$

where $E'^{\kappa\kappa'}_{\alpha\beta}$ means we have incorporated the last (constant) term in Eq. (1) into $E^{\kappa\kappa'}_{\alpha\beta}(\vec{q})$.

The above equations show a distinct resemblance to those of the dipolar models of lattice dynamics, but are far more general in the sense that (a) a "diagonal" electronic part is incorporated explicitly into the ion-ion coupling coefficient, (b) the "ion-dipole" and "dipole-dipole" interactions are screened by the function $\epsilon_0(\vec{Q})$, and (c) the dipoles are neither point dipoles nor need they be situated on the ion sites themselves. For homopolar semiconductors, we may confine ourselves to two cases: (i) situating the sites $\vec{r}_s$ on the ion sites in which case we obtain the *generalized shell model* (GSM), or (ii) situating the sites $\vec{r}_s$ at the centers of the covalent bonds, in which case we obtain the *bond-charge model* (BCM). If the function $\epsilon_0(\vec{Q})$ is an isotropic function of $\vec{Q}$ (a condition well satisfied in practice), then it may be seen that $(C^{\kappa\kappa'}_{\alpha\beta}+E'^{\kappa\kappa'}_{\alpha\beta})$ contributes only axially-symmetric-type force constants between the ions. The term $-(\underline{W}\underline{S}\underline{W}^{\dagger})^{\kappa\kappa'}_{\alpha\beta}$ in the dynamical matrix, however, contributes a more complicated kind of effective force constant which contains *bond-bending* forces also. This is physically obvious if we realize that this contribution couples two ions together via the polarization produced on a third ion (GSM) or on a bond-charge site (BCM). Mathematically, the result follows from the fact that $(\underline{W}\underline{S}\underline{W}^{\dagger})^{\kappa\kappa}_{\alpha\beta}$ contains a purely imaginary antisymmetric component in the coupling between ions on the same sublattice, which cannot be obtained from a bond-stretching-type interaction alone and therefore involves bond-bending forces also.

Let us now examine the analytic behavior of $\tilde{E}^{\kappa\kappa'}_{\alpha\beta}(\vec{q})$ as defined in Eq. (3) in the limit as $\vec{q}\to 0$. In Appendix A it is shown that

$$\lim_{\vec{q}\to 0}\tilde{E}^{\kappa\kappa'}_{\alpha\beta}(\vec{q})=\overline{E}^{(0)\kappa\kappa'}_{\alpha\beta}-(\overline{\underline{W}}^{(0)}\overline{\underline{S}}^{(0)}\overline{\underline{W}}^{(0)\dagger})^{\kappa\kappa'}_{\alpha\beta}+\lim_{\vec{q}\to 0}\left(\frac{4\pi e^2}{\Omega\epsilon_\infty}\sum_{\gamma\delta}(\tilde{Z}^{\kappa}_{\alpha\gamma})\frac{q_\gamma q_\delta}{q^2}(\tilde{Z}^{\kappa'}_{\delta\beta})^{\dagger}-\frac{4\pi e^2}{\Omega}Z_\kappa Z_{\kappa'}\frac{q_\alpha q_\beta}{q^2}\right), \tag{7}$$

where $\overline{E}^{(0)\kappa\kappa'}_{\alpha\beta}$ is the limit as $\vec{q}\to 0$ of

$$\overline{E}^{\kappa\kappa'}_{\alpha\beta}=-\sum_{\vec{G}}{}'\frac{(\vec{q}+\vec{G})_\alpha(\vec{q}+\vec{G})_\beta}{v(\vec{q}+\vec{G})}\left(1-\frac{1}{\epsilon_0(\vec{q}+\vec{G})}\right)\times W_\kappa(\vec{q}+\vec{G})W_{\kappa'}(\vec{q}+\vec{G})e^{i\vec{G}\cdot\vec{r}_{\kappa\kappa'}} \tag{8}$$

and $\overline{W}^{(0)\kappa s}_{\alpha\beta}$ is the limit as $\vec{q}\to 0$ of Eq. (5) with the term $\vec{G}=0$ excluded, as defined in Eq. (A4) of Appendix A. Similarly $\overline{\underline{S}}^{(0)}$ is the limit as $\vec{q}\to 0$ of the inverse of $[\overline{\underline{V}}+\underline{a}^{-1}]$, where the term $\vec{G}=0$ is excluded in $\overline{\underline{V}}$, as defined in Eq. (24) of I. The effective-charge tensor for the ion κ is defined by

$$\tilde{Z}^{\kappa}_{\alpha\beta}=Z_\kappa\delta_{\alpha\beta}+\sum_{s}(\overline{\underline{W}}^{(0)}\overline{\underline{S}}^{(0)})^{\kappa s}_{\alpha\beta}\ . \tag{9}$$

In Sec. IV we shall show that by rewriting Eq. (6) after explicitly separating out the macroscopic field, and eliminating the $w_{s'\beta}$ from the resulting equations, the tensor $\tilde{Z}^{\kappa}_{\alpha\beta}$ emerges naturally as a measure of the dipole moment generated per unit displacement of the ion κ, in the *absence* of the macroscopic field. It is thus the "Born" or transverse effective-charge tensor.

For tetrahedral and cubic crystals,

$$\lim_{\vec{q}\to 0}C^{\kappa\kappa'}_{\alpha\beta}(\vec{q})=-\frac{4\pi e^2}{3\Omega}Z_\kappa Z_{\kappa'}\delta_{\alpha\beta}+\lim_{\vec{q}\to 0}\frac{4\pi e^2}{\Omega}Z_\kappa Z_{\kappa'}\frac{q_\alpha q_\beta}{q^2}\ . \tag{10}$$

Adding Eqs. (7) and (10) we see that the only irregular part of the dynamical matrix as $\vec{q}\to 0$ is the third term on the right-hand side of Eq. (7), which completes the identification of $\tilde{Z}^{\kappa}_{\alpha\beta}$ with the effective-charge tensor. The existence of well-defined acoustic modes is assured if and only if the sum of the effective charges vanishes, i.e., if

$$\sum_{\kappa}\tilde{Z}^{\kappa}_{\alpha\beta}=0\ . \tag{11}$$

This is the well-known *acoustic sum rule* which has been discussed previously by several authors.[2–4] This sum rule is usually derived from the requirement that the macroscopic electric field resulting from a *uniform* displacement of the crystal must vanish. This condition may be written

$$\lim_{\vec{q}\to 0}\sum_{\kappa\vec{G}}q_\alpha(\vec{q}+\vec{G})_\beta W_\kappa(\vec{q}+\vec{G})\epsilon^{-1}(\vec{q},\vec{q}+\vec{G})e^{-i\vec{G}\cdot\vec{r}_\kappa}=0\ . \tag{12}$$

In Appendix B, it is shown that this is equivalent to condition (11).

For cubic and tetrahedral crystals, symmetry requires that $\sum_s(\overline{\underline{W}}^{(0)}\overline{\underline{S}}^{(0)})^{\kappa s}_{\alpha\beta}$ be a multiple of the unit tensor in (α,β) space, and the effective charges become scalars. Burstein[5] has discussed in detail the use of effective charges in treating the dielectric and optical properties of insulators. A conventional definition is

$$\tilde{Z}^{\kappa}=(Z_\kappa)^{*}_{s}[\tfrac{1}{3}(\epsilon_\infty+2)] \tag{13}$$

for ionic crystals, where $(Z_\kappa)^{*}_{s}$ is the *Szigeti charge*[6] which is supposed to account for mechanical-overlap distortion effects. For zinc-blende-type covalently bonded semiconductors, it has been customary[5] to write $\tilde{Z}^{\kappa}$ phenomenologically as the sum of a localized and a nonlocalized effective charge,

$$\tilde{Z}^{\kappa} = (Z_{\kappa})_l^* + (Z_{\kappa})_n^* \ . \tag{14}$$

Let us go back to the case of cubic ionic crystals where we may take the sites $\vec{r}_s$ to be the ion sites $\vec{r}_\kappa$, choose $\epsilon_0(\vec{Q}) = 1$, and assume that the form factors $f^{\kappa}(\vec{Q})$ are spherically symmetric and correspond to highly localized distributions on the ion sites so that they do not overlap in real space. This is really equivalent to the point-dipole model. Let us further assume that we have a local pseudopotential $W_\kappa(\vec{r})$ which is constant or zero near the ion but goes as $-(Z_\kappa e^2/r)$ at distances corresponding to the neighboring ions.

In such a case,

$$\overline{W}_{\alpha\beta}^{(0)\kappa\kappa'} = (4\pi e^2/3\Omega) Z_\kappa \delta_{\alpha\beta} \quad \text{for all } \kappa' \tag{15}$$

and $\overline{S}_{\alpha\beta}^{(0)\kappa\kappa'}$ is given by Eq. (35) of I.

It may be verified that in this case

$$\tilde{Z}^{\kappa} = Z_\kappa [\tfrac{1}{3}(\epsilon_\infty + 2)] \tag{16}$$

with ϵ_∞ given by Eqs. (39) and (40) of I. Thus we have the apparently paradoxical result that the Szigeti charge $(Z_\kappa)_s^*$ which appears in Eq. (13) comes out to be the charge Z_κ of the *ion core*, instead of the total ionic charge Z_κ^I. This is due to the fact that in the (tightly bound) ionic-crystal limit a weak local pseudopotential of the assumed form does not correctly represent the perturbation of the valence-electron distribution due to a lattice displacement. In Ref. 7 a reformulation of the electron-ion interaction for this case was developed and it was shown that the above treatment is valid also for tightly bound electrons *provided that* in Eq. (15) we replace $\overline{W}_{\alpha\beta}^{(0)\kappa\kappa'}$ by

$$[(4\pi e^2/3\Omega) Z_\kappa^I + (\underline{J}\,\underline{a}^{-1})^{(0)\kappa\kappa'}]\delta_{\alpha\beta} \ , \tag{17}$$

where Z_κ^I is the *total* ionic charge on the κth ion and $\underline{J}$ is an "overlap" matrix which depends on the overlap of the atomic wave functions on the ions. It may then be shown that Eq. (16) is modified to

$$\tilde{Z}^{\kappa} = \Big(Z_\kappa^I + \sum_{\kappa'} J^{(0)\kappa\kappa'} \Big) [\tfrac{1}{3}(\epsilon_\infty + 2)] \ . \tag{18}$$

Thus the overlap terms cause the Szigeti charge to deviate from the total ionic charge. In addition, if the dipole distributions themselves overlap, Eq. (35) of I is no longer valid, and the $\frac{1}{3}(\epsilon_\infty + 2)$ factor in Eq. (18) will also be modified, causing a further deviation of the Szigeti charge—expressed as $[3/(\epsilon_\infty + 2)]\tilde{Z}^{\kappa}$—from Z_κ^I.

For covalently bonded crystals, $\epsilon_0(\vec{Q})$ deviates from unity, and the form factors will certainly not be well localized on the ion sites so that Eqs. (33) of I and (15) for $\overline{V}_{\alpha\beta}^{(0)\kappa\kappa'}$ and $\overline{W}_{\alpha\beta}^{(0)\kappa\kappa'}$ will no longer be valid. On the other hand, $(\underline{\overline{W}}^{(0)}\underline{\overline{S}}^{(0)})_{\alpha\beta}^{\kappa s}$ does not split naturally into a localized and a delocalized part as assumed in Eq. (14). Instead, the effective charge should be calculated directly from Eq. (9).

We may derive explicit expressions for the effective charge for the case of crystals of the NaCl or zinc-blende structure if we again situate the sites $\vec{r}_s$ at the ion sites $\vec{r}_\kappa$. Then, in addition to the $a_{\alpha\beta}^{(0)\kappa\kappa'}$ and $\overline{V}_{\alpha\beta}^{(0)\kappa\kappa'}$ being diagonal with respect to (α, β), so is $\overline{W}_{\alpha\beta}^{(0)\kappa\kappa'}$, i.e.,

$$\overline{W}_{\alpha\beta}^{(0)\kappa\kappa'} = \delta_{\alpha\beta} \overline{W}^{(0)\kappa\kappa'} \ , \tag{19a}$$

where

$$\overline{W}^{(0)\kappa\kappa'} = \frac{1}{3} \sum_{\vec{G}}{}' G^2 \frac{W_\kappa(\vec{G})}{\epsilon_0(\vec{G})} f_{\kappa'}^*(\vec{G}) e^{i\vec{G}\cdot\vec{r}_{\kappa\kappa'}} \ . \tag{19b}$$

Let us define

$$\kappa_{11} = \overline{V}^{(0)11} + (a^{(0)-1})^{11}$$
$$= \overline{V}^{(0)11} + (a^{(0)22}/\Delta) \ ,$$

etc., where $\overline{V}^{(0)\kappa\kappa'}$ and Δ are defined in Eqs. (42) and (44) of I. Then using Eq. (9) we get

$$\tilde{Z}^{(1)} = Z_1 + \frac{\overline{W}^{(0)12}(\kappa_{11} - \kappa_{12}) + \overline{W}^{(0)11}(\kappa_{22} - \kappa_{12}^*)}{\kappa_{11}\kappa_{22} - |\kappa_{12}|^2} \tag{20a}$$

and

$$\tilde{Z}^{(2)} = Z_2 + \frac{\overline{W}^{(0)21}(\kappa_{22} - \kappa_{12}^*) + \overline{W}^{(0)22}(\kappa_{11} - \kappa_{12})}{\kappa_{11}\kappa_{22} - |\kappa_{12}|^2} \ , \tag{20b}$$

and the sum rule becomes

$$Z_1 + Z_2 + \frac{(\overline{W}^{(0)12} + \overline{W}^{(0)22})(\kappa_{11} - \kappa_{12}) + (\overline{W}^{(0)21} + \overline{W}^{(0)11})(\kappa_{22} - \kappa_{12}^*)}{\kappa_{11}\kappa_{22} - |\kappa_{12}|^2} = 0 \ , \tag{21}$$

which may be regarded as imposing a restriction on a^{11}, a^{22}, a^{12}. For homopolar crystals (atom 1 the same as atom 2 in the unit cell), Eq. (21) yields

$$a^{(0)11} + a^{(0)12} = -[(\overline{W}^{(0)11} + \overline{W}^{(0)12}/Z + \overline{V}^{(0)11} + \overline{V}^{(0)12}]^{-1} \ . \tag{22}$$

In the approximation where the "interference" term a_{12} is neglected, the sum rule thus serves to determine a^{11} as was done for the calculations described in Sec. VI.

For crystals such as Si and Ge, symmetry requires the effective charges on all the ions to be equal, so that they must all vanish by the effective-charge sum rule. Some homopolar crystals such as Se and Te, on the other hand, do not posses the symmetry requirement that $\bar{Z}^{\kappa}_{\alpha\beta}=\bar{Z}^{\kappa'}_{\alpha\beta}(\kappa\neq\kappa')$, in which case the effective charge can be nonzero and the crystals may exhibit infrared activity.

In addition to the acoustic sum rule, there is another set of related sum rules (first stated explicitly by Keating[4]) which state that in the limit $\vec{q}=0$, corresponding to rigid translation of the whole crystal, the electron-density response to the lattice perturbation for *all* wave vectors must correspond to the rigid translation of the total valence-electron density.

This may be written as

$$\lim_{\vec{q}\to 0}\sum_{\kappa\vec{G}'}\chi(\vec{q}+\vec{G},\vec{q}+\vec{G}')(\vec{q}+\vec{G}')_{\alpha}W_{\kappa}(\vec{q}+\vec{G}')e^{-i\vec{G}'\cdot\vec{r}_{\kappa}}$$

$$=-\Omega\sum_{\kappa}(\vec{q}+\vec{G})_{\alpha}\rho_{\kappa}(\vec{q}+\vec{G})e^{-i\vec{G}\cdot\vec{r}_{\kappa}}\quad(\vec{G}\neq 0)\ ,\qquad(23)$$

where the total valence-electron density is regarded as made up of a superposition of densities $\rho_{\kappa}(\vec{r})$ centered on the sites $\vec{r}_{\kappa}$. This division is somewhat arbitrary, but the right-hand side of Eq. (23) is unique, even if the $\rho_{\kappa}(\vec{Q})$ are not. Using Eq. (5) of I for $\chi(\vec{Q},\vec{Q}')$, and the results of Eqs. (45)-(47) of I, we obtain the result that, within the framework of our model, the left-hand side of (23) splits into a singular part as $\vec{q}\to 0$ and a regular part.

The singular part is

$$-\frac{4\pi e^2}{\Omega\epsilon_{\infty}}\frac{1}{\epsilon_0(\vec{G})}\sum_{\substack{\beta\gamma\delta\\ ss'}}G_{\beta}f^{s}(\vec{G})e^{-\vec{G}\cdot\vec{r}_s}S^{ss'}_{\beta\gamma}q_{\gamma}\sum_{\kappa}\Big(Z_{\kappa}\delta_{\delta\alpha}$$

$$+\sum_{s''}(\overline{\underline{S}}^{(0)}\overline{\underline{W}}^{(0)\dagger})^{s''\kappa}_{\delta\alpha}\Big)\frac{q_{\delta}}{q^2}$$

where we have used the fact that

$$W_{\kappa}(\vec{q})\to-(4\pi e^2/\Omega q^2)Z_{\kappa}\quad\text{as } q\to 0\ .$$

If the acoustic sum rule [Eqs. (9) and (11)] is satisfied, this part vanishes identically.

The regular part yields, on equating both sides of Eq. (23),

$$\frac{1}{v(\vec{G})}\left(1-\frac{1}{\epsilon_0(\vec{G})}\right)\sum_{\kappa}W_{\kappa}(\vec{G})e^{-i\vec{G}\cdot\vec{r}_{\kappa}}G_{\alpha}+\frac{1}{\epsilon_0(\vec{G})}\sum_{\kappa s\beta}G_{\beta}(\overline{\underline{S}}^{(0)}\overline{\underline{W}}^{(0)\dagger})^{s\kappa}_{\beta\alpha}f^{s}(\vec{G})e^{-i\vec{G}\cdot\vec{r}_s}=-\Omega\sum_{\kappa}\rho_{\kappa}(\vec{G})e^{-i\vec{G}\cdot\vec{r}_{\kappa}}G_{\alpha}\quad(\vec{G}\neq 0)\ .\qquad(24)$$

For the case where the $\vec{r}_s$ are chosen as the ion sites $\vec{r}_{\kappa}$ and the matrix $(\overline{\underline{S}}^{(0)}\overline{\underline{W}}^{(0)})^{\kappa\kappa'}_{\beta\alpha}$ becomes diagonal with respect to (α,β), an allowed solution to Eq. (24) (although not necessarily the *only* solution) is

$$f^{\kappa}(\vec{G})=\left(\epsilon_0(\vec{G})\Big/\sum_{\kappa'}(\overline{\underline{S}}^{(0)}\overline{\underline{W}}^{(0)\dagger})^{\kappa\kappa'}\right)\left[-\Omega\rho_{\kappa}(\vec{G})-\frac{1}{v(\vec{G})}\left(1-\frac{1}{\epsilon_0(\vec{G})}\right)W_{\kappa}(\vec{G})\right]\qquad(25)$$

which would determine the form factors introduced in the factorization *ansatz* [Eq. (16) of I] at the reciprocal-lattice points. Note that the condition that $f_{\kappa}(\vec{Q})\to 1$ as $\vec{Q}\to 0$ now fixes uniquely the fraction of the true valence charge to be associated with the ion of type κ. By Eq. (25) this is given by

$$\Omega\rho_{\kappa}(0)=Z_{\kappa}\left(1-\frac{1}{\epsilon_0}\right)-\frac{1}{\epsilon_0}\sum_{\kappa'}(\overline{\underline{S}}^{(0)}\overline{\underline{W}}^{(0)\dagger})^{\kappa\kappa'}\ .\qquad(25a)$$

This is consistent with the requirement of charge neutrality and the effective-charge sum rule [Eq. (11)]. It is interesting to note that Phillips[8] has obtained an equation for the valence-charge density in a semiconductor very similar to Eq. (25a) based on intuitive physical arguments. The second term on the right-hand side of Eq. (25a) is to be identified in this case with the "bond charges," which is correct if the sites s in our model are chosen as the bond-charge sites. They can also, however, correspond to localized distributions on the ionic sites. The first term on the right-hand side of Eq. (25a) represents that part of the valence-charge density associated with the "diagonal" part of the screening. As stated previously, there is no analog of this in the conventional shell model,[9] which corresponds to the choice $\epsilon_0(\vec{Q})\equiv 1$. In such a case, Eq. (25a) may be taken as defining the *shell charge* on the site κ, which as expected turns out to be the total valence-electron charge associated with the site κ. In Sec. IV we shall show by comparing our equations with those of the shell model that the shell charge must be identified with the quantity

$$-|e|\sum_{\kappa'}(\overline{\underline{S}}^{(0)}\overline{\underline{W}}^{(0)\dagger})^{\kappa\kappa'}\ .$$

By Eq. (9) it follows that the effective-charge sum rule is then identically satisfied if the sum of the core and shell charges in a unit cell is zero. Note also that in the case $\epsilon_0(\vec{Q})=1$, Eq. (25) implies that the form factors $f^{\kappa}(\vec{G})$ are *proportional* to those of the valence-electron distribution around each ion. This is physically obvious in the sense that if the crystal as a *whole* is rigidly displaced, the linear electron response must correspond to dipole distributions with a form factor given by the valence-electron-density form factor. For $\vec{Q} \neq \vec{G}$ there is no such restriction. It is currently not clear how seriously to take the restriction on the form factors provided by Eqs. (24), in the sense that they may be inconsistent with the form factors $f^{\kappa}(\vec{Q})$ used to fit the actual dielectric function $\epsilon(\vec{Q}, \vec{Q}')$ within the framework of our factorization scheme. We note that even if the sum rules given by Eq. (24) are not exactly satisfied, but Eq. (11) *is* satisfied, no catastrophe results in the sense that well-defined acoustic modes still exist. On the other hand, one may regard Eqs. (24) and (25) as providing an important clue as to the nature of the required form factors $f^{\kappa}(\vec{Q})$. Thus calculations of the valence-electron densities in the covalently bonded semiconductors[10] show areas of piled-up density at the "bond-charge" sites. This implies that the sum of the real-space distributions corresponding to the form factors $f^{s}(\vec{Q})/\epsilon_0(\vec{Q})$ must simulate such piling up of density, which may be done either by situating the distributions on the bond-charge sites (bond-charge model) or by letting the distributions on the ion sites overlap appreciably. In the calculations on silicon and germanium described below, the best fit to the lattice-dynamical data did indeed correspond to such overlapping form factors. It should be emphasized, however, that a superposition of *spherically symmetric* overlapping charge distributions on the ions lacks the essential tetrahedral distortion required to give, for instance, scattering from the "forbidden" (222) reflection in the diamond type structures. Thus the form factors used in the calculations described below must be regarded as an approximation.

For crystals of the NaCl or zinc-blende structure, we obtain from Eqs. (1), (7), and (10), assuming the acoustic sum rule Eq. (11) is satisfied,

$$\lim_{\vec{q}\to 0} D_{\alpha\beta}^{\kappa\kappa'} = \lim_{\vec{q}\to 0} \Big\{ \frac{4\pi e^2}{\Omega\epsilon_\infty} \tilde{Z}^{\kappa}\tilde{Z}^{\kappa'} \frac{q_\alpha q_\beta}{q^2} + \delta_{\alpha\beta}\Big[\overline{E}^{(0)\kappa\kappa'} - (\underline{\overline{W}}^{(0)} \underline{\overline{S}}^{(0)} \underline{\overline{W}}^{(0)\dagger})^{\kappa\kappa'} - \frac{4\pi e^2}{3\Omega} Z_\kappa Z_{\kappa'} - \delta_{\kappa\kappa'}$$

$$\times \sum_{\kappa''} \Big(\overline{E}^{(0)\kappa\kappa''} - (\underline{\overline{W}}^{(0)} \underline{\overline{S}}^{(0)} \underline{\overline{W}}^{(0)\dagger})^{\kappa\kappa''} - \frac{4\pi e^2}{3\Omega} Z_\kappa Z_{\kappa''} \Big) \Big] \Big\} , \qquad (26)$$

where

$$\overline{E}^{(0)\kappa\kappa'} = -\frac{1}{3} \sum_{\vec{G}}{}' \frac{G^2}{v(\vec{G})} \left(1 - \frac{1}{\epsilon_0(\vec{G})} \right) W_\kappa(\vec{G}) W_{\kappa'}(\vec{G}) e^{i\vec{G}\cdot\vec{r}_{\kappa\kappa'}} . \qquad (27)$$

Let us define a constant

$$B = \frac{4\pi e^2}{3\Omega} Z_1 Z_2 - \overline{E}^{(0)12} + (\overline{W}^{(0)} \overline{S}^{(0)} \overline{W}^{(0)\dagger})^{12} . \qquad (28)$$

Then Eq. (26) yields for the longitudinal- and transverse-optical frequencies at $\vec{q} = 0$,

$$\omega_{\mathrm{TO}}^2 = (1/\overline{M}) B \qquad (29a)$$

$$\omega_{\mathrm{LO}}^2 = (1/\overline{M})[B + (4\pi e^2/\Omega\epsilon_\infty)\tilde{Z}^2] , \qquad (29b)$$

where $\overline{M}$ is the reduced mass of the two ions in the unit cell and $\tilde{Z}$ is the magnitude of the effective charge on each ion.

We remark here that in the case of metals in which the contribution of the conduction electrons to $\epsilon(\vec{Q}, \vec{Q}')$ is supposed to be purely diagonal and enters as a free-electron-like contribution to $\epsilon_0(\vec{Q})$, as discussed in I, ϵ_∞ becomes infinite. The acoustic sum rule (11) is now unnecessary to ensure the existence of acoustic modes owing to the presence of $1/\epsilon_\infty$ in the singular part of the dynamical matrix. It is interesting to note, however, that an effective ionic charge can still be defined via Eq. (9) and will be different from the ion-core charge due to the second term in Eq. (9) if appreciable interband transitions not included in $\epsilon_0(\vec{Q})$ contribute to $\epsilon(\vec{Q}, \vec{Q}')$. Since ϵ_∞ becomes infinite, Eqs. (29) show that the ω_{LO} and ω_{TO} modes at the zone center become degenerate—a well-known result which is physically caused by the screening of the macroscopic field by the conduction electrons. For metals with a small number of conduction electrons, or semiconductors with a small number of carriers in the conduction band, $\epsilon_0(\vec{Q})$ will rapidly increase to infinity only for $|\vec{Q}| < k_{\mathrm{FT}}$, the Fermi-Thomas wave vector of the "free" electrons. Thus the ω_{LO} and ω_{TO} modes will be forced to be degenerate rapidly for $q < k_{\mathrm{FT}}$, a phenomenon observed experimentally in PbTe,[11] $\mathrm{Mg_2Pb}$[12] and the transition-metal carbides.[13] This point has also been discussed by Weber *et al.*[14]

By imagining a time-dependent applied field $\vec{D}(\vec{q}) e^{i(\vec{q}\cdot\vec{r}-\omega t)}$ acting on the system, and suitably modifying the lattice equations of motion (6a) and the electron-density response equation (6b), it may be shown that in the limit of $\vec{q}\to 0$, the frequency-dependent dielectric tensor *including* the lattice contribution is given for the general case by

$$\epsilon_{\alpha\beta}(\omega)=\epsilon_{\alpha\beta}(\infty)+\frac{4\pi e^2}{\Omega}\times\sum_{\substack{\kappa\kappa'\\ \gamma\lambda\\ j}}\frac{\tilde{Z}^{\kappa}_{\gamma\alpha}e^{*}_{\kappa\gamma}(j)e_{\kappa'\lambda}(j)\tilde{Z}^{\kappa'}_{\lambda\beta}}{\omega(j)^2-\omega^2}, \qquad (30)$$

where the sum over the dispersion frequencies $\omega(j)$ includes contribution from the optic modes only. The high-frequency limit of the dielectric tensor is

$$\epsilon_{\alpha\beta}(\infty)=\epsilon_0\delta_{\alpha\beta}+\frac{4\pi e^2}{\Omega}\sum_{ss'}\bar{S}^{(0)ss'}_{\alpha\beta}, \qquad (31)$$

which has been given in Eq. (30a) of I. For crystals of rocksalt or zinc-blende structure, Eq. (30) simplifies to

$$\epsilon(\omega)=\epsilon_\infty+\frac{4\pi e^2}{\Omega\bar{M}}\frac{\tilde{Z}^2}{(\omega_{\mathrm{TO}}^2-\omega^2)}. \qquad (32)$$

From Eqs. (29) and (32), the Lyddane-Sachs-Teller relation[15] follows:

$$\omega_{\mathrm{LO}}^2/\omega_{\mathrm{TO}}^2=\frac{\epsilon(0)}{\epsilon_\infty}, \qquad (33)$$

which can easily be generalized to more general structures.

The formal justification of Eqs. (32) and (33) from a quantum-mechanical theory has been given previously by several authors.[2,16] We have derived them here on the basis of our factorization *ansatz* which, however, as discussed in I, can be made as general as we wish. Furthermore, our model yields explicit results for ϵ_∞, $\tilde{Z}$, ω_{TO}^2 and ω_{LO}^2 in terms of microscopic quantities.

III. RELATION TO MARTIN MODEL

In this section we discuss the relationship of our model to the lattice-dynamical bond-charge model of Martin.[17] As stated previously, a choice of the sites $\vec{r}_s$ in our factorization *ansatz* [Eq. (16) of I] as the bond-charge sites yields a lattice-dynamical model via Eq. (6) which is a very general bond-charge model, in the sense that the $w_{s\alpha}/\epsilon_0$ which are obtained from Eq. (6) represent the dipole-polarization vectors which may pictorially be associated with the displacement of a "bond-charge" at site $\vec{r}_s$ in the unit cell. Equation (6) then allows a very general set of displacements for the bond charges in each unit cell. Here we have to regard each bond charge as being a "basis atom" in the crystallographic unit cell so that in a lattice of the diamond structure there are four bond charges associated with each unit cell, which we may take as the four sites $\{\frac{1}{8}a(1,1,1),\ \frac{1}{8}a(1,-1,-1),\ \frac{1}{8}a(-1,1,-1),\ \frac{1}{8}a(-1,-1,1)\}$. Thus the calculation of the bond-charge displacements in terms of the ionic displacements from Eq. (6b) requires the inversion of a 12×12 matrix. Martin's model, on the other hand, assumes that the four bond charges in the unit cell may be regarded as carrying a charge of magnitude $-Z|e|/2\epsilon_0$ (Z is the valence of the ion), and that each bond charge moves in such a way that it remains at the midpoint of the bond joining the two ions it is associated with. If we assume for the moment that the bond charges are really point charges, then we may take the form factors in our *ansatz*, Eq. (16) of I, to be $\epsilon_0(\vec{Q})/\epsilon_0$. Martin's constraint on the distribution of dipoles in the unit cell due to the lattice motion may then be written as

$$w_{s\alpha}e^{i\vec{q}\cdot\vec{r}_s}=(\tfrac{1}{2}Z)\tfrac{1}{2}(e_{1\alpha}+e_{2\alpha}e^{i\vec{q}\cdot\vec{r}_{l,2}(s)}), \qquad (34)$$

where $\vec{r}_{l,2}(s)$ is the position of the other atom of basis type 2 associated with the bond charge at $\vec{r}_s$ and may be in another unit cell. [We have assumed that the four bond charges are each associated with bonds between the atom at the origin (basis type 1) and its four nearest neighbors.]

The phase convention for the polarization vectors $e_{\kappa\alpha}$ and $w_{s\alpha}$ in Eq. (34) has been chosen to be consistent with the form for the dynamical matrix given in Eq. (2).

Since $\vec{r}_{l,2}(s)=2\vec{r}_s$, Eq. (34) may be rewritten as

$$w_{s\alpha}=\tfrac{1}{4}Z(e_{1\alpha}e^{-i\vec{q}\cdot\vec{r}_s}+e_{2\alpha}e^{i\vec{q}\cdot\vec{r}_s}), \qquad (35)$$

which by Eqs. (6) is equivalent to the postulate that

$$[\underline{S}\underline{W}^{\dagger}]^{s\kappa}_{\alpha\beta}(\vec{q})=-\delta_{\alpha\beta}\tfrac{1}{4}Ze^{-i\vec{q}\cdot\vec{r}_{s\kappa}}, \qquad (36)$$

where

$$\vec{r}_{s\kappa}=\vec{r}_s \quad \text{if } \kappa=1$$
$$=-\vec{r}_s \quad \text{if } \kappa=2\ .$$

It should be noted that the assumption (36) causes the acoustic sum rule (11) to be satisfied identically, a fact which is also intuitively obvious from the nature of the model.

From Eq. (36), we obtain

$$(\underline{W}\underline{S}\underline{W}^{\dagger})^{\kappa\kappa'}_{\alpha\beta}(\vec{q})=-\tfrac{1}{4}Z\sum_{s'}W^{\kappa s'}_{\alpha\beta}(\vec{q})e^{-i\vec{q}\cdot\vec{r}_{s'\kappa'}}\ . \qquad (37)$$

Again from (36) we have

$$W^{\kappa s'}_{\alpha\beta}(\vec{q})=-\tfrac{1}{4}Z\sum_{s''}e^{i\vec{q}\cdot\vec{r}_{s''\kappa}}\times[V^{s''s'}_{\alpha\beta}(\vec{q})+(\underline{a}^{-1})^{s''s'}_{\alpha\beta}(\vec{q})], \qquad (38)$$

which we may rewrite as

$$W^{\kappa s'}_{\alpha\beta}(\vec{q})=2W^{\kappa s'}_{\alpha\beta}(\vec{q})+\tfrac{1}{4}Z\sum_{s''}e^{i\vec{q}\cdot\vec{r}_{s''\kappa}}\times[V^{s''s'}_{\alpha\beta}(\vec{q})+(\underline{a}^{-1})^{s''s'}_{\alpha\beta}(\vec{q})]\ . \qquad (39)$$

Substituting in Eq. (37), we get

$$(\underline{\mathrm{W}}\underline{\mathrm{S}}\underline{\mathrm{W}}^{\dagger})^{\kappa\kappa'}_{\alpha\beta}(\vec{\mathrm{q}}) = -\tfrac{1}{2}Z\sum_{s'} W^{\kappa s'}_{\alpha\beta}(\vec{\mathrm{q}})e^{-i\vec{\mathrm{q}}\cdot\vec{\mathrm{r}}_{s'\kappa'}} - \tfrac{1}{16}Z^2\sum_{s's''} V^{s''s'}_{\alpha\beta}(\vec{\mathrm{q}})e^{i\vec{\mathrm{q}}\cdot(\vec{\mathrm{r}}_{s''\kappa}-\vec{\mathrm{r}}_{s'\kappa'})} - \tfrac{1}{16}Z^2\sum_{s's''}(\underline{\mathrm{a}}^{-1})^{s''s'}_{\alpha\beta}(\vec{\mathrm{q}})e^{i\vec{\mathrm{q}}\cdot(\vec{\mathrm{r}}_{s''\kappa}-\vec{\mathrm{r}}_{s'\kappa'})} \quad . \tag{40}$$

Hence, the dynamical matrix obtained from Eqs. (6) becomes

$$D^{\kappa\kappa'}_{\alpha\beta}(\vec{\mathrm{q}}) = C^{\kappa\kappa'}_{\alpha\beta}(\vec{\mathrm{q}}) + E'^{\kappa\kappa'}_{\alpha\beta}(\vec{\mathrm{q}}) + \tfrac{1}{2}Z\sum_{s'} W^{\kappa s'}_{\alpha\beta}(\vec{\mathrm{q}})e^{-i\vec{\mathrm{q}}\cdot\vec{\mathrm{r}}_{s'\kappa'}} + \tfrac{1}{16}Z^2\sum_{s's''} V^{s''s'}_{\alpha\beta}(\vec{\mathrm{q}})e^{i\vec{\mathrm{q}}\cdot(\vec{\mathrm{r}}_{s''\kappa}-\vec{\mathrm{r}}_{s'\kappa'})}$$

$$- \tfrac{1}{16}Z^2\sum_{s's''}(\underline{\mathrm{a}}^{-1})^{s''s'}_{\alpha\beta}(\vec{\mathrm{q}})e^{i\vec{\mathrm{q}}\cdot(\vec{\mathrm{r}}_{s''\kappa}-\vec{\mathrm{r}}_{s'\kappa'})} \quad . \tag{41}$$

The first term on the right-hand side represents the ion-ion Coulomb coupling coefficient, the second term the "diagonal" contribution of the valence electrons [Eq. (4)], the third term is the coupling coefficient between ions and bond charges, and the fourth term is the coupling coefficient between bond charges. If in the last term we arbitrarily set the $(\underline{\mathrm{a}}^{-1})^{s''s'}_{\alpha\beta}(\vec{\mathrm{q}})$ to be diagonal in s', s'' and independent of $\vec{\mathrm{q}}$, then these may be obtained from $\vec{\mathrm{q}}=0$ limit of the regular part of Eq. (38), namely,

$$(\underline{\mathrm{a}}^{-1})^{s''s'}_{\alpha\beta} = -\,\delta_{s''s'}\left(\sum_{s''}\overline{V}^{(0)s''s'}_{\alpha\beta} + \frac{4}{Z}\,\overline{W}^{(0)\kappa s'}_{\alpha\beta}\right) \quad . \tag{42}$$

For $\kappa=\kappa'$, the last term of Eq. (41) then gives a constant ($\vec{\mathrm{q}}$-independent) term which may be absorbed into the constant term in $E^{\kappa\kappa'}_{\alpha\beta}$; whereas for $\kappa=1$, $\kappa'=2$, the last term of Eq. (41) gives

$$\tfrac{1}{16}Z^2\sum_{s} e^{2i\vec{\mathrm{q}}\cdot\vec{\mathrm{r}}_s}\left(\sum_{s''}\overline{V}^{(0)s''s}_{\alpha\beta} + \frac{4}{Z}\,\overline{W}^{(0)1s}_{\alpha\beta}\right) \quad . \tag{43}$$

This term may be identified with the term Martin obtains from considering classically the motion of one bond-charge "against" the rest of the lattice. Equation (41) represents a model which very closely resembles Martin's model. However, his exact model is not obtained unless one further (a) sets $\epsilon_0=\epsilon_\infty$, i.e., sets the $\vec{\mathrm{Q}}=0$ limit of $\epsilon_0(\vec{\mathrm{Q}})$ to be equal to ϵ_∞; (b) assumes that the effective electron-electron interaction $v(\vec{\mathrm{Q}})$ and the electron-ion pseudopotential $W_\kappa(\vec{\mathrm{Q}})$ [which enter into the expressions for $V^{ss'}_{\alpha\beta}(\vec{\mathrm{q}})$ and $W^{\kappa s}_{\alpha\beta}(\vec{\mathrm{q}})$, respectively] are pure Coulomb-like at distances equal to or greater than that between an ion and its neighboring bond charge, and zero or constant at distances less than this (so that self-interaction terms are removed); (c) assumes that $\epsilon_0(\vec{\mathrm{Q}})$ is equal to ϵ_∞ for *all* $\vec{\mathrm{Q}}$ in the expressions for $W^{\kappa s}_{\alpha\beta}(\vec{\mathrm{q}})$ and $V^{ss'}_{\alpha\beta}(\vec{\mathrm{q}})$; and (d) assumes that in the expression for $E^{\kappa\kappa'}_{\alpha\beta}(\vec{\mathrm{q}})$, $\epsilon_0(\vec{\mathrm{Q}})$ may be taken equal to $\epsilon(\vec{\mathrm{Q}},\vec{\mathrm{Q}})$, the total diagonal part of the dielectric function. Further, in his calculation, Martin uses Srinivasan's calculated $\epsilon(\vec{\mathrm{Q}},\vec{\mathrm{Q}})$ which was constrained to be equal to ϵ_∞ at $\vec{\mathrm{Q}}=0$. From our discussion of local-field corrections [Eqs. (31) and (32) of I] we see that there are a number of inconsistencies in this procedure. Approximations (a), (c), and (d) above are strictly speaking inconsistent within the framework of our general factorization scheme, and further, given Eq. (42) it is almost certainly impossible to satisfy Eq. (38) for all $\vec{\mathrm{q}}$. Thus, it may be concluded that while the microscopic formalism developed in this paper can lead [under the further basic assumption represented by Eqs. (36) or (38)] to a model formally very similar to Martin's model, it is not consistent with the exact form of his model. It is possible of course that a different kind of factorization scheme for $\epsilon(\vec{\mathrm{Q}},\vec{\mathrm{Q}}')$ could lead exactly to Martin's model.

It should be pointed out that although the assumption Eq. (36) does appear to be somewhat restrictive in forcing the bond charges to move always with the center of mass of their two adjoining ions, it may be a useful starting point in guessing at the nature of the $a^{ss'}_{\alpha\beta}(\vec{\mathrm{q}})$ that appear as arbitrary functions in the general factorization scheme appropriate to a bond-charge model. The symmetry of the bond-charge lattice is low enough so that even at $\vec{\mathrm{q}}=0$, the $a^{ss'}_{\alpha\beta}(0)$ do not have to be diagonal and this in general leads to a large number of undetermined parameters which enter into the microscopic theory. Martin's formalism provides, via Eq. (42), a means of determining all these parameters. There is nothing in our factorization scheme to disallow us from then choosing these as constants independent of $\vec{\mathrm{q}}$ since, as stated, the acoustic sum rule is then automatically satisfied, although strictly speaking this would not yield Martin's assumed form of the bond-charge motion for all $\vec{\mathrm{q}}$ since Eq. (35) would not necessarily be satisfied for all $\vec{\mathrm{q}}$. Calculations based on this kind of model are discussed in Sec. VI.

IV. RELATION TO SHELL MODEL

In this section the equations of motion given by Eq. (6) are related to those of the conventional shell model.[9,18–20] We situate the dipoles on general sites $\vec{\mathrm{r}}_s$. As $\vec{\mathrm{q}}\to 0$, the matrices $\underline{\mathrm{C}}$, $\underline{\mathrm{E}}'$, $\underline{\mathrm{S}}^{-1}$, and $\underline{\mathrm{W}}$ have the limiting form

$$C^{\kappa\kappa'}_{\alpha\beta} \to \overline{C}^{\kappa\kappa'}_{\alpha\beta} + \lim_{\vec{\mathrm{q}}\to 0}\frac{4\pi e^2}{\Omega}Z_\kappa Z_{\kappa'}\frac{q_\alpha q_\beta}{q^2} \ , \tag{44}$$

$$E'^{\kappa\kappa'}_{\alpha\beta} \to \overline{E}'^{\kappa\kappa}_{\alpha\beta} - \lim_{\vec{\mathrm{q}}\to 0}\frac{4\pi e^2}{\Omega}\left(1-\frac{1}{\epsilon_0}\right)Z_\kappa Z_{\kappa'}\frac{q_\alpha q_\beta}{q^2} \ , \tag{45}$$

$$(\underline{S}^{-1})^{ss'}_{\alpha\beta} = (\underline{V} + \underline{a}^{-1})^{ss'}_{\alpha\beta} \rightarrow (\underline{\overline{S}}^{-1})^{ss'}_{\alpha\beta} + \lim_{\vec{q}\to 0} \frac{4\pi e^2}{\Omega\epsilon_0} \frac{q_\alpha q_\beta}{q^2} , \tag{46}$$

$$W^{\kappa s'}_{\alpha\beta} \rightarrow \overline{W}^{\kappa s'}_{\alpha\beta} - \lim_{\vec{q}\to 0} \frac{4\pi e^2}{\Omega} \frac{Z_\kappa}{\epsilon_0} \frac{q_\alpha q_\beta}{q^2} . \tag{47}$$

The barred symbols refer to the regular parts of their unbarred equivalents at $\vec{q}=0$. [$\underline{\overline{S}}$, $\underline{\overline{W}}$ and $\overline{E}$ have already been defined in Eqs. (24) of I, (A4), and (8), respectively]. Equation (44) is a well-known result[21] while the other three equations are evident from the structures of Eqs. (4), (18) of I and (5), respectively. The equations of motion, Eq. (6), can be rewritten in terms of these regular matrices and the macroscopic electric field $\mathcal{E}_\alpha$:

$$M_\kappa \omega^2 e_{\kappa\alpha} = \sum_{\kappa'\beta} (\overline{C}^{\kappa\kappa'}_{\alpha\beta} + \overline{E}'^{\kappa\kappa'}_{\alpha\beta}) e_{\kappa'\beta} + \sum_{s'\beta} \overline{W}^{\kappa s'}_{\alpha\beta} w_{s'\beta} - Z_\kappa |e| \mathcal{E}_\alpha , \tag{48a}$$

$$0 = \sum_{\kappa'\beta} (\underline{\overline{W}}^\dagger)^{s\kappa'}_{\alpha\beta} e_{\kappa'\beta} + \sum_{s'\beta} (\underline{\overline{S}}^{-1})^{ss'}_{\alpha\beta} w_{s'\beta} + |e| \mathcal{E}_\alpha , \tag{48b}$$

where e is the charge on the electron and

$$\mathcal{E}_\alpha = -\frac{4\pi|e|}{\Omega\epsilon_0} \sum_\beta \frac{q_\alpha q_\beta}{q^2} \left(\sum_{\kappa'} Z_{\kappa'} e_{\kappa'\beta} - \sum_{s'} w_{s'\beta} \right) . \tag{49}$$

The macroscopic field $\vec{\mathcal{E}}$ is related to the polarization $\vec{\mathcal{P}}$ by the usual relation

$$\mathcal{E}_\alpha = -4\pi \sum_\beta \frac{q_\alpha q_\beta}{q^2} \mathcal{P}_\beta , \tag{50a}$$

where $\vec{\mathcal{P}}$ can be written as the sum of a part due to the localized dipoles and a part due to the "diagonal" part of the dielectric matrix which arises directly from the macroscopic field:

$$\mathcal{P}_\beta = \frac{|e|}{\Omega} \left(\sum_{\kappa'} Z_{\kappa'} e_{\kappa'\beta} - \sum_{s'} w_{s'\beta} \right) + \frac{1}{4\pi} (\epsilon_0 - 1) \mathcal{E}_\beta . \tag{50b}$$

Solving for the $w_{s'\beta}$ from Eq. (48b) and substituting in Eqs. (48a) and (50) leads again to the identification of the effective-charge tensor as defined in Eq. (9).

Since the presence of the "purely diagonal" part $\epsilon_0(\vec{Q})$ of the dielectric matrix intrinsically distinguishes our formalism from that of the shell model, for purposes of comparison with the shell model we take $\epsilon_0(Q) \equiv 1$ and place the dipoles on the ion sites $\vec{r}_\kappa$. We shall return to the more general case in Sec. V. In the conventional shell model,[9,18–20] the dipole $-|e|w_{\kappa'\beta}$ developed during the motion is described by the motion of a "shell" of charge $Y_{\kappa'}$ with an amplitude $v_{\kappa'\beta}$. The latter is written as the sum of the "core" amplitude $e_{\kappa'\beta}$ and the amplitude $p_{\kappa'\beta}$ of the relative shell-core motion. Thus the shell-model equations are obtained by substituting in Eq. (48),

$$-|e| w_{\kappa'\beta} = Y_{\kappa'} (e_{\kappa'\beta} + p_{\kappa'\beta}) , \tag{51}$$

$$Z_{\kappa'} |e| = Z^I_{\kappa'} - Y_{\kappa'} , \tag{52}$$

where $Z^I_{\kappa'}$ is the total "ionic" charge associated with the site κ'. The resulting equations are

$$M_\kappa \omega^2 e_{\kappa\alpha} = \sum_{\kappa'\beta} (A^{\kappa\kappa'}_{\alpha\beta} e_{\kappa'\beta} + B^{\kappa\kappa'}_{\alpha\beta} p_{\kappa\beta}) - Z^I_\kappa \mathcal{E}_\alpha , \tag{53a}$$

$$0 = \sum_{\kappa'} [(\underline{B}^\dagger)^{\kappa\kappa'}_{\alpha\beta} e_{\kappa'\beta} + G^{\kappa\kappa'}_{\alpha\beta} p_{\kappa'\beta}] - Y_\kappa \mathcal{E}_\alpha , \tag{53b}$$

where

$$A^{\kappa\kappa'}_{\alpha\beta} = \overline{C}^{\kappa\kappa'}_{\alpha\beta} + \overline{E}'^{\kappa\kappa'}_{\alpha\beta} - \overline{W}'^{\kappa\kappa'}_{\alpha\beta} (Y_{\kappa'}/|e|) - (Y_\kappa/|e|)(W^\dagger)^{\kappa\kappa'}_{\alpha\beta} + (Y_\kappa/|e|)(\underline{\overline{S}}^{-1})^{\kappa\kappa'}_{\alpha\beta}(Y_{\kappa'}/|e|) , \tag{54a}$$

$$B^{\kappa\kappa'}_{\alpha\beta} = -\overline{W}^{\kappa\kappa'}_{\alpha\beta}(Y_{\kappa'}/|e|) + (Y_\kappa/|e|)(\underline{\overline{S}}^{-1})^{\kappa\kappa'}_{\alpha\beta}(Y_{\kappa'}/|e|) , \tag{54b}$$

$$G^{\kappa\kappa'}_{\alpha\beta} = (Y_\kappa/|e| (\underline{\overline{S}}^{-1})^{\kappa\kappa'}_{\alpha\beta}(Y_{\kappa'}/|e|) , \tag{54c}$$

and $\mathcal{E}_\alpha$ is given by Eq. (50a) with

$$\mathcal{P}_\beta = \sum_{\kappa'} \frac{Z^I_{\kappa'} e_{\kappa'\beta} + Y_{\kappa'} p_{\kappa'\beta}}{\Omega} . \tag{55}$$

Eqs. (53) and (55) are the conventional shell-model equations of motion as given, for example, in Eqs. (2.3) and (2.4) of Ref. 20.

A number of invariance conditions must be satisfied by these matrices. These relate various terms in the small $\vec{q}$ expansion of the matrices which are given, e.g., by

$$A^{\kappa\kappa'}_{\alpha\beta}(\epsilon\vec{q}) = A^{(0)\kappa\kappa'}_{\alpha\beta} + i\epsilon \sum_\gamma A^{(1)\kappa\kappa'}_{\alpha\beta,\gamma} q_\gamma + \tfrac{1}{2}\epsilon^2 \sum_{\gamma\lambda} A^{(2)\kappa\kappa'}_{\alpha\beta,\gamma\lambda} q_\gamma q_\lambda + \cdots , \tag{56}$$

where the wave vector is now written as $(\epsilon\vec{q})$. They were first discussed by Born and Huang[22] and subsequently by Cowley[20] in connection with the shell model. In this section we refer only to the conditions on the zero-order matrices, which specify that the equations of motion and dipole moments remain invariant under uniform translations:

$$\sum_\kappa (\underline{A} - \underline{B}\underline{G}^{-1}\underline{B}^\dagger)^{(0)\kappa\kappa'}_{\alpha\beta} = \sum_{\kappa'} (\underline{A} - \underline{B}\underline{G}^{-1}\underline{B}^\dagger)^{(0)\kappa\kappa'}_{\alpha\beta} = 0 \tag{57}$$

and

$$\sum_\kappa B^{(0)\kappa\kappa'}_{\alpha\beta} = 0 . \tag{58}$$

By substituting Eq. (54b) in (58) it can be seen that the latter is satisfied if

$$\sum_\kappa \left(-\overline{W}^{(0)\kappa\kappa'}_{\alpha\beta} + \frac{Y_\kappa}{|e|} (\underline{\overline{S}}^{-1})^{(0)\kappa\kappa'}_{\alpha\beta} \right) = 0 ,$$

i.e., if

$$Y_{\kappa'}\delta_{\alpha\beta} = |e| \sum_{\kappa} (\overline{\underline{W}}\,\overline{\underline{S}})^{(0)\kappa\kappa'}_{\alpha\beta} \ . \tag{59}$$

Equation (59) defines the "charges on the shells" in terms of our formulation. Note that in the conventional shell model, Y_κ is a redundant parameter. Further, a constant term is introduced in $\underline{B}$ so as to automatically satisfy Eq. (58). This, together with the total charge neutrality of the unit cell, automatically ensures the satisfaction of the effective-charge sum rule, which states that no macroscopic field can arise as a result of uniform translation of the crystal. In the *microscopic* derivation of the shell model as presented above, however, we *define* Y_κ by the microscopic expression in Eq. (59). Equation (58) is then automatically satisfied. The effective-charge sum rule [Eqs. (9) and (11)] is then equivalent to the condition that the sum of the core and shell charges in a unit cell vanish. [The Keating sum rule, Eq. (25a), if satisfied, automatically ensures this since the shell charge then becomes equal to the total valence-electron charge associated with the ion, and the Fourier transform of the latter becomes the "shell form factor."]

V. ELASTIC AND PIEZOELECTRIC PROPERTIES

It is convenient to return to the equations of motion in our original notation as given in Eq. (48), and to define the regular part of the full dynamical matrix

$$\overline{\underline{D}} = \overline{\underline{C}} + \overline{\underline{E}}' - \overline{\underline{W}}\,\overline{\underline{S}}\,\overline{\underline{W}}^\dagger \ . \tag{60}$$

The invariance relation (57) can then be expressed as

$$\sum_{\kappa} \overline{D}^{(0)\kappa\kappa'}_{\alpha\beta} = \sum_{\kappa'} \overline{D}^{(0)\kappa\kappa'}_{\alpha\beta} = 0 \ . \tag{61}$$

This is satisfied because $\underline{E}'$ was defined in Eq. (6) to incorporate the constant term

$$-\delta_{\kappa\kappa'} \lim_{\vec{q}\to 0} \sum_{\kappa'} D^{\kappa\kappa'}_{\alpha\beta} \ .$$

The condition represented by Eq. (58) in the shell model is no longer required. However, there are two conditions on the first-order dynamical matrix. The first is a condition of invariance against infinitesimal rotations:

$$\sum_{\kappa'} \overline{D}^{(1)\kappa\kappa'}_{\alpha\beta,\gamma} = \sum_{\kappa'} \overline{D}^{(1)\kappa\kappa'}_{\alpha\gamma,\beta} \ , \tag{62}$$

while the second is one of translational invariance for a homogeneously deformed lattice:

$$\sum_{\kappa\kappa'} \overline{D}^{(1)\kappa\kappa'}_{\alpha\beta,\gamma} = 0 \ . \tag{63}$$

There are also (in general, 15) conditions involving the second-order terms, the "Born-Huang conditions,"[22] which must be satisfied in order for the elastic constants to have the correct symmetry:

$$\sum_{\kappa\kappa'} \overline{D}^{(2)\kappa\kappa'}_{\alpha\beta,\gamma\lambda} = \sum_{\kappa\kappa'} \overline{D}^{(2)\kappa\kappa'}_{\gamma\lambda,\alpha\beta} \ . \tag{64}$$

The conditions given in Eqs. (62)–(64) do not appear to be satisfied in general for this formulation. They are, however, satisfied identically for lattices of tetrahedral and cubic symmetry, as shown below. Note that if all interactions in the formulation are rotationally invariant, the end result must of course be rotationally invariant. Thus, analogous to Eq. (24) and the effective-charge sum rule, there will presumably exist conditions which ensure that, for an infinitesimal rotation of the crystal, the electron-density response will also correspond to an infinitesimal rotation of the valence-charge density. Such conditions will automatically ensure that conditions such as those required by Eq. (62) are satisfied.

We may now proceed with a perturbation expansion for the acoustic modes in terms of $(\epsilon\vec{q})$ along the lines of Born and Huang[22] and Cowley.[20] The matrices $\overline{\underline{C}}$, $\overline{\underline{E}}$, $\overline{\underline{W}}$, and $\overline{\underline{S}}$ are expanded according to Eq. (56). The vectors $\vec{e}$, $\vec{w}$, $\vec{\mathcal{E}}$, and $\vec{\mathcal{P}}$ are expanded in a similar way. For the acoustic modes the expansion for the frequency starts with the first-order term

$$\omega = \epsilon\omega^{(1)} + \cdots \ . \tag{65}$$

The zero-order equations of motion obtained from the expansion of Eq. (48) are

$$\sum_{\kappa'\beta} \overline{D}^{(0)\kappa\kappa'}_{\alpha\beta} e^{(0)}_{\kappa'\beta} = \sum_{\beta} \tilde{Z}^{\kappa}_{\alpha\beta} |e| \mathcal{E}^{(0)}_{\beta} \ , \tag{66}$$

where $\tilde{Z}^{\kappa}_{\alpha\beta}$ is the effective-charge tensor defined in Eq. (9). By virtue of the relation Eq. (61) and the acoustic sum rule, Eq. (11), Eq. (66) has the solution

$$\vec{\mathcal{E}} = \vec{0} \tag{67}$$

and

$$e^{(0)}_{\kappa\alpha} = u_\alpha, \quad a \text{ constant} \tag{68}$$

while

$$w^{(0)}_{s\alpha} = -\sum_{\kappa\beta} (\overline{\underline{S}}\,\overline{\underline{W}}^\dagger)^{(0)s\kappa}_{\alpha\beta} e^{(0)}_{\kappa\beta} \ . \tag{69}$$

The first-order equations of motion are

$$\sum_{\kappa'\beta} \overline{D}^{(0)\kappa\kappa'}_{\alpha\beta} e^{(1)}_{\kappa'\beta} = -\sum_{\kappa'\beta\gamma} \overline{D}^{(1)\kappa\kappa'}_{\alpha\beta,\gamma} q_\gamma e^{(0)}_{\beta\kappa'} + \sum_{\beta} \tilde{Z}^{\kappa}_{\alpha\beta} |e| \mathcal{E}^{(1)}_{\beta} \ . \tag{70}$$

The solubility condition for this equation, that the inhomogeneous part be orthogonal to the solution of the homogeneous part, is satisfied by virtue of Eq. (63) and the acoustic sum rule. The solution can be written

$$e_{\kappa\alpha}^{(1)} = -\sum_{\kappa'\beta} (\underline{\bar{D}}^{(0)-1})_{\alpha\beta}^{\kappa\kappa'} \left(\sum_{\kappa''\gamma\lambda} \bar{D}_{\beta\gamma,\lambda}^{(1)\kappa'\kappa''} q_\lambda e_{\kappa''\gamma}^{(0)} + \sum_\gamma \tilde{Z}_{\beta\gamma}^{\kappa'} |e| \mathcal{E}_\gamma^{(1)} \right) , \tag{71}$$

where, although the matrix $\underline{\bar{D}}^{(0)}$ is singular, an effective inverse can be defined in the sense of Eq. (26.27) of Ref. 22 or Appendix 1 of Ref. 20. The second-order equations of motion are

$$\sum_{\kappa'\beta} \bar{D}_{\alpha\beta}^{(0)\kappa\kappa'} e_{\kappa'\beta}^{(2)} = \left\{ M_\kappa \omega^2 - \sum_{\kappa'\beta\gamma\lambda} (\underline{\bar{D}}_\gamma^{(1)} \underline{\bar{D}}^{(0)-1} \underline{\bar{D}}_\lambda^{(1)} + \tfrac{1}{2} \underline{\bar{D}}_{\gamma\lambda}^{(2)})_{\alpha\beta}^{\kappa\kappa'} q_\gamma q_\lambda \right\} e_{\kappa'\beta}^{(0)}$$

$$+\sum_{\beta\gamma} \left(\sum_{\kappa'\lambda} (\underline{\bar{D}}_\gamma^{(1)} \underline{\bar{D}}^{(0)-1})_{\alpha\lambda}^{\kappa\kappa'} \tilde{Z}_{\lambda\beta}^{\kappa'} - \sum_s (\underline{\overline{WS}})_{\alpha\beta,\gamma}^{(1)\kappa s} \right) q_\gamma |e| \mathcal{E}_\beta^{(1)} + \sum_\beta \tilde{Z}_{\alpha\beta}^\kappa |e| \mathcal{E}_\beta^{(2)} , \tag{72}$$

where $\underline{\bar{D}}_\gamma^{(1)}$ and $\underline{\bar{D}}_{\gamma\lambda}^{(2)}$ refer to $(3r \times 3r)$ matrices whose $(\alpha\beta, \kappa\kappa')$ components are $\bar{D}_{\alpha\beta,\gamma}^{(1)\kappa\kappa'}$ and $\bar{D}_{\alpha\beta,\gamma\lambda}^{\kappa\kappa'}$, respectively. The solubility condition for this equation gives

$$\sum_\kappa M_\kappa \omega^2 e_{\kappa\alpha}^{(0)} = \sum_{\substack{\kappa\kappa' \\ \beta\gamma\lambda}} (\underline{\bar{D}}_\gamma^{(1)} \underline{\bar{D}}^{(0)-1} \underline{\bar{D}}_\lambda^{(1)} + \tfrac{1}{2} \underline{\bar{D}}_{\gamma\lambda}^{(2)})_{\alpha\beta}^{\kappa\kappa'} q_\gamma q_\lambda e_{\kappa'\beta} - \sum_{\substack{\kappa \\ \beta\gamma}} \left(\sum_{\kappa'\lambda} (\underline{\bar{D}}_\gamma^{(1)} \underline{\bar{D}}^{(0)-1})_{\alpha\lambda}^{\kappa\kappa'} \tilde{Z}_{\lambda\beta}^{\kappa'} - \sum_s (\underline{\overline{WS}})_{\alpha\beta,\gamma}^{(1)\kappa s} \right) q_\gamma |e| \mathcal{E}_\beta^{(1)} \tag{73}$$

since the term in $\mathcal{E}_\beta^{(2)}$ drops out because of the acoustic sum rule.

Let us define

$$c_{\alpha\gamma,\beta\lambda} = [\alpha\beta, \gamma\lambda] + [\beta\gamma, \alpha\lambda] - [\beta\lambda, \alpha\gamma] + (\alpha\gamma, \beta\lambda) , \tag{74a}$$

$$e_{\beta,\gamma\lambda} = [\beta, \alpha\gamma] , \tag{74b}$$

where the brackets are defined by the expressions

$$[\alpha\beta, \gamma\lambda] = \frac{1}{2\Omega} \sum_{\kappa\kappa'} \bar{D}_{\alpha\beta,\gamma\lambda}^{(2)\kappa\kappa'} , \tag{75a}$$

$$(\alpha\gamma, \beta\lambda) = \frac{1}{\Omega} \sum_{\kappa\kappa'} (\underline{\bar{D}}_\gamma^{(1)} \underline{\bar{D}}^{(0)-1} \underline{\bar{D}}_\lambda^{(1)})_{\alpha\beta}^{\kappa\kappa'} , \tag{75b}$$

$$[\beta, \alpha\gamma] = \frac{|e|}{\Omega} \left(\sum_{\kappa\kappa'\lambda} (\underline{\bar{D}}_\gamma^{(1)} \underline{\bar{D}}^{(0)-1})_{\alpha\lambda}^{\kappa\kappa'} \times \tilde{Z}_{\lambda\beta}^{\kappa'} - \sum_{\kappa s} (\underline{\overline{WS}})_{\alpha\beta,\gamma}^{(1)\kappa s} \right) . \tag{75c}$$

Note that the last two expressions represent internal-strain contributions and are absent in the case of centrosymmetric crystals. The $c_{\alpha\gamma,\beta\lambda}$ will shortly be identified with the elastic constants, and the $e_{\beta,\alpha\gamma}$ with the piezoelectric constants. The latter are made up of two terms, the first representing the displacement of the effective changes with the internal strains and the second the electronic-deformation contribution through the dipole distributions.

Equation (73) now takes the form

$$\frac{1}{\Omega} \sum_\kappa M_\kappa \omega^2 e_{\kappa\alpha}^{(0)} = \sum_{\kappa\gamma\lambda\beta} [c_{\alpha\gamma,\beta\lambda} q_\gamma q_\lambda] e_{\kappa\beta}^{(0)} - \sum_\gamma [e_{\beta,\alpha\gamma} q_\gamma] \mathcal{E}_\beta^{(1)} . \tag{76}$$

On the other hand, the solution of the first-order equation for the polarization is, by Eq. (50b),

$$\mathcal{P}_\alpha^{(1)} = \frac{|e|}{\Omega} \left(\sum_\kappa Z_\kappa e_{\kappa\alpha}^{(1)} - \sum_s w_{s\alpha}^{(1)} \right) + \frac{1}{4\pi} (\epsilon_0 - 1) \mathcal{E}_\alpha^{(1)} , \tag{77}$$

which by Eq. (71) and the corresponding first-order solution for $w_{s\beta}^{(1)}$ may be shown to be

$$\mathcal{P}_\alpha^{(1)} = \left(\sum_{\kappa\beta} [e_{\alpha,\beta\gamma} q_\gamma] e_{\kappa\beta}^{(0)} + \sum_\beta \tilde{\alpha}_{\alpha\beta} \bar{\mathcal{E}}_\beta^{(1)} \right) , \tag{78}$$

where the total polarizability $\tilde{\alpha}_{\alpha\beta}$ (including a lattice contribution) is given by

$$\tilde{\alpha}_{\alpha\beta} = \frac{e^2}{\Omega} \left(\sum_{ss'} \bar{S}_{\alpha\beta}^{(0)ss'} + \sum_{\substack{\kappa\kappa' \\ \gamma\lambda}} \tilde{Z}_{\gamma\alpha}^\kappa (\underline{\bar{D}}^{(0)-1})_{\gamma\lambda}^{\kappa\kappa'} \tilde{Z}_{\lambda\beta}^{\kappa'} \right) + \frac{1}{4\pi} (\epsilon_0 - 1) \delta_{\alpha\beta} . \tag{79}$$

The total static dielectric tensor is given by

$$\epsilon_{\alpha\beta}(0) = \delta_{\alpha\beta} + 4\pi \tilde{\alpha}_{\alpha\beta} \tag{80}$$

$$= \epsilon_0 \delta_{\alpha\beta} + \frac{4\pi e^2}{\Omega} \left(\sum_{ss'} \bar{S}_{\alpha\beta}^{(0)ss'} + \sum_{\substack{\kappa\kappa' \\ \gamma\lambda}} \tilde{Z}_{\gamma\alpha}^\kappa (\underline{\bar{D}}^{(0)-1})_{\gamma\lambda}^{\kappa\kappa'} \tilde{Z}_{\lambda\beta}^{\kappa'} \right) , \tag{81}$$

which is consistent with the expression derived earlier in Eq. (30). Equations (76) and (78) yield equations identical to the usual macroscopic equations relating stress, strain, polarization, and macroscopic field in an insulator.

We have now completed the identification of $c_{\alpha\gamma,\beta\lambda}$ and $e_{\beta,\alpha\gamma}$ with the elastic and piezoelectric constant, respectively. Equations (75a) and (75b) are of course expected results since the long-wavelength acoustic modes must be related to the elastic waves in this way.[22] Equation (75c) is more interesting because, in contrast to earlier treatments of piezoelectricity, it relates the piezoelectric constants to fundamental microscopic quantities.

Specific forms can be written down for the expansion matrices. For example, the components of $\underline{\overline{\mathrm{E}}}'$ are given by

$$E'^{\kappa\kappa'}_{\alpha\beta} = -\sum_{\vec{G}}{}' \frac{(\vec{q}+\vec{G})_\alpha(\vec{q}+\vec{G})_\beta}{v(\vec{q}+\vec{G})}\left(1-\frac{1}{\epsilon_0(\vec{q}+\vec{G})}\right)W_\kappa(\vec{q}+\vec{G})W_{\kappa'}(\vec{q}+\vec{G})e^{i\vec{G}\cdot\vec{r}_{\kappa'\kappa}}+\text{constant}$$

$$=\sum_{\vec{G}}{}'(\vec{q}+\vec{G})_\alpha(\vec{q}+\vec{G})_\beta f^{\kappa\kappa'}_{\mathrm{E}}(\vec{q}+\vec{G})e^{i\vec{G}\cdot\vec{r}_{\kappa'\kappa}}+\text{constant}\ , \tag{82}$$

where, as long as $\epsilon_0(\vec{Q})$ is isotropic, $f_E^{\kappa\kappa'}$ is a function of $|\vec{Q}|$ only. The expansion matrices are given by

$$\overline{E}'^{\kappa\kappa'(0)}_{\alpha\beta} = -\sum_{\vec{G}}{}' G_\alpha G_\beta f_E^{\kappa\kappa'}(G)e^{i\vec{G}\cdot\vec{r}_{\kappa'\kappa}}+\text{constant}\ , \tag{83a}$$

$$E'^{\kappa\kappa'(1)}_{\alpha\beta,\gamma} = i\sum_{\vec{G}}{}'\left((G_\alpha\delta_{\beta\gamma}+G_\beta\delta_{\alpha\gamma})f_E^{\kappa\kappa'}(G)+\frac{G_\alpha G_\beta G_\gamma}{G}\frac{\partial f_E^{\kappa\kappa'}}{\partial Q}\bigg|_G\right)e^{i\vec{G}\cdot\vec{r}_{\kappa'\kappa}}\ , \tag{83b}$$

$$E'^{\kappa\kappa'(2)}_{\alpha\beta,\gamma\lambda} = \sum_{\vec{G}}{}'\Bigg[(\delta_{\alpha\lambda}\delta_{\beta\gamma}+\delta_{\beta\lambda}\delta_{\alpha\gamma})f_E+\left(\frac{G_\alpha G_\lambda}{G}\delta_{\beta\gamma}+\frac{G_\beta G_\lambda}{G}\delta_{\alpha\gamma}+\frac{G_\beta G_\gamma}{G}\delta_{\alpha\lambda}+\frac{G_\alpha G_\gamma}{G}\delta_{\beta\lambda}+\frac{G_\alpha G_\beta}{G}\delta_{\gamma\lambda}\right)\frac{\partial f_E^{\kappa\kappa'}}{\partial Q}\bigg|_G$$

$$+\left(\frac{G_\alpha G_\beta G_\gamma G_\lambda}{G^2}\right)\frac{\partial^2 f_E}{\partial Q^2}\bigg|_G\Bigg]e^{i\vec{G}\cdot\vec{r}_{\kappa'\kappa}}\ . \tag{83c}$$

Similar expressions can be written down for the matrices $\underline{\overline{\mathrm{C}}}$, $\underline{\overline{\mathrm{W}}}$, and $\underline{\overline{\mathrm{V}}}$ by defining functions $f_C^{\kappa\kappa'}(Q)$, $f_W^{\kappa s'}(Q)$, and $f_V^{ss'}(Q)$ in the appropriate way; the expansion matrices for $a^{ss'}_{\alpha\beta}(q)$ must also be derived. The expression for the expansion matrices for the full dynamical matrix $\underline{\overline{\mathrm{D}}}$ can then be obtained by the usual chain rules for differentiation.

Let us now specialize to lattices of tetrahedral or cubic symmetry and take the dipole sites to be the ion positions $\underline{r}_\kappa$. Similar results may be established for the case where the dipoles are on the bond charge sites. Then $\overline{E}'^{(0)\kappa\kappa'}_{\alpha\beta}$ is proportional to $\delta_{\alpha\beta}$ and the first term on the right-hand side of Eq. (83b) vanishes, whereas the second term is proportional to

$$|e_{\alpha\beta\gamma}| = 1 \quad \text{if } \alpha\neq\beta\neq\gamma\neq\alpha$$

$$= 0 \quad \text{otherwise.} \tag{84}$$

Similarly the various terms Eq. (83c) are proportional to terms involving either products of two δ matrices or

$$\eta_{\alpha\beta\gamma\lambda} = 1 \quad \text{if } \alpha=\beta=\gamma=\lambda$$

$$= 0 \quad \text{otherwise.} \tag{85}$$

Equations (83a)–(83c) can then be written

$$\overline{E}'^{(0)\kappa\kappa'}_{\alpha\beta} = \delta_{\alpha\beta}\overline{E}'^{(0)\kappa\kappa'}\ , \tag{86a}$$

$$\overline{E}'^{(1)\kappa\kappa'}_{\alpha\beta,\gamma} = |\epsilon_{\alpha\beta\gamma}|E'^{(1)\kappa\kappa'}\ , \tag{86b}$$

$$\overline{E}'^{(2)\kappa\kappa'}_{\alpha\beta,\gamma\lambda} = (\delta_{\alpha\lambda}\delta_{\beta\gamma}+\delta_{\beta\lambda}\delta_{\alpha\gamma})\overline{E}'^{(2a)\kappa\kappa'}$$

$$+\delta_{\alpha\beta}\delta_{\gamma\lambda}\overline{E}'^{(2b)\kappa\kappa'}+\eta_{\alpha\beta\gamma\lambda}\overline{E}'^{(2c)\kappa\kappa'}\ , \tag{86c}$$

where

$$\overline{E}'^{(0)\kappa\kappa'} = -\frac{1}{3}\sum_{G}{}' G^2 f_E^{\kappa\kappa'}(G)e^{i\vec{G}\cdot\vec{r}_{\kappa'\kappa}}+\text{constant}\ , \tag{87a}$$

$$\overline{E}'^{(1)\kappa\kappa'} = i\sum_{G}{}'\frac{G_1G_2G_3}{G}\frac{\partial f_E^{\kappa\kappa'}}{\partial Q}\bigg|_G e^{i\vec{G}\cdot\vec{r}_{\kappa'\kappa}}\ , \tag{87b}$$

$$\overline{E}'^{(2a)\kappa\kappa'} = \sum_{G}{}'\left(f_E+\tfrac{2}{3}G\frac{\partial f_E\kappa\kappa'}{\partial Q}\bigg|_G+\frac{G_2^2G_3^2}{G^2}\frac{\partial^2 f_E^{\kappa\kappa'}}{\partial Q^2}\bigg|_G\right)e^{i\vec{G}\cdot\vec{r}_{\kappa'\kappa}}$$

$$\overline{E}'^{(2b)\kappa\kappa'} = \sum_{G}{}'\left(\tfrac{1}{3}G\frac{\partial f_E^{\kappa\kappa'}}{\partial Q}\bigg|_G+\frac{G_2^2G_3^2}{G^2}\frac{\partial^2 f_E^{\kappa\kappa'}}{\partial Q^2}\bigg|_G\right)e^{i\vec{G}\cdot\vec{r}_{\kappa'\kappa}}\ , \tag{87c}$$

$$\overline{E}'^{(2c)\kappa\kappa'} = \sum_{G}{}'\frac{(G_1^4-3G_2^2G_3^2)}{G^2}\frac{\partial^2 f_E^{\kappa\kappa'}}{\partial Q^2}\bigg|_G e^{i\vec{G}\cdot\vec{r}_{\kappa'\kappa}}\ .$$

Analogous expressions can be written down for the expansion matrices for $\underline{\bar{C}}$, $\underline{\bar{W}}$, $\underline{\bar{V}}$, and $\underline{a}$.

We may now prove that conditions (62)–(64) are satisfied for the full dynamical matrix in the case of this special symmetry. Since the full dynamical matrix is

$$\underline{\bar{\mathrm{D}}}=\underline{\bar{\mathrm{C}}}+\underline{\bar{\mathrm{E}}}-\underline{\bar{\mathrm{W}}}\,\underline{\bar{\mathrm{S}}}\,\underline{\bar{\mathrm{W}}}^{\dagger}\ , \tag{88}$$

the first order matrix $D^{(1)\kappa\kappa'}_{\alpha\beta,\gamma}$ is the sum of terms of the form given either by Eq. (86b) or by the product of one term like Eq. (86b) and two terms like Eq. (86a). In either case they are all proportional to $|\epsilon_{\alpha\beta\gamma}|$, so that Eq. (62) is immediately satisfied and Eq. (63) is satisfied because

$$\bar{D}^{(1)\kappa'\kappa}_{\alpha\beta,\gamma}\equiv-\bar{D}^{(1)\kappa\kappa'}_{\beta\alpha,\gamma}=-\bar{D}^{(1)\kappa\kappa'}_{\alpha\beta,\gamma}\ . \tag{89}$$

Similarly, $D^{(2)\kappa\kappa'}_{\alpha\beta,\gamma\lambda}$ is the sum of terms of the form given either by Eq. (86c), or by the product of one term like Eq. (86c) and two terms like Eq. (86a), or by the product of two terms like Eq. (86b) and one term like Eq. (86a). In the first case, Eq. (64) is clearly satisfied. In the second case the product is composed of terms proportional to either $(\delta_{\alpha\lambda}\delta_{\beta\gamma}+\delta_{\beta\lambda}\delta_{\alpha\gamma})$, or $\delta_{\alpha\beta}\delta_{\gamma\lambda}$, or $\eta_{\alpha\beta\gamma\lambda}$, which again must satisfy Eq. (64). In the third case the product is proportional to

$$\sum_{\delta}\left(|\epsilon_{\delta\alpha\gamma}|\ |\epsilon_{\delta\beta\lambda}|+|\epsilon_{\delta\alpha\lambda}|\ |\epsilon_{\delta\beta\gamma}|\right)\ ,$$

which can be shown to be equal to

$$2\delta_{\alpha\beta}\delta_{\gamma\lambda}+\delta_{\alpha\lambda}\delta_{\gamma\beta}+\delta_{\alpha\gamma}\delta_{\beta\lambda}-4\eta_{\alpha\beta\gamma\lambda}\ ,$$

which also satisfies Eq. (64). Thus all the invariance relations discussed in this section are identically satisfied for crystals of tetrahedral or cubic symmetry.

For these crystals there is a single piezoelectric constant given by

$$e_{14}=\frac{|e|}{\Omega}\sum_{\kappa\kappa'}\left[(\bar{D}^{(1)}\bar{D}^{(0)-1})^{\kappa\kappa'}\tilde{Z}^{\kappa'}-(\overline{\mathrm{W}}\overline{\mathrm{S}})^{(1)\kappa\kappa'}\right]\ , \tag{90}$$

where the matrices are in (κ,κ') space only, as in Eq. (87). For a system with two atoms per unit cell,

$$\bar{D}^{(0)11}=\bar{D}^{(0)22}=-\bar{D}^{(0)12}$$
$$=-\bar{D}^{(0)21}=B\ ,$$

where

$$B=M\omega^2_{\mathrm{TO}}\ , \tag{91}$$

as defined in Eqs. (28) and (29a). Then Eq. (90) becomes

$$e_{14}=\frac{|e|}{\Omega}\,\frac{\tilde{Z}(\bar{D}^{(1)11}+\bar{D}^{(1)21})}{\bar{M}\omega^2_{\mathrm{TO}}}-\left(\sum_{\kappa\kappa'}(\underline{\overline{\mathrm{W}}}\,\underline{\overline{\mathrm{S}}})^{(1)\kappa\kappa'}\right)\ . \tag{92}$$

Thus the piezoelectric constant is composed of two terms, one representing the motion of the effective charge with the internal strains and the other the distortion of the electronic charge distribution. In the case of the bond-charge model, Eq. (92) can be readily generalized by writing the last term as a sum over κ and s' and using the appropriately defined matrices $\underline{\bar{W}}$ and $\underline{\bar{S}}$.

VI. CALCULATIONS FOR SILICON AND GERMANIUM

The formalism developed above has been applied to the case of the homopolar semiconductors silicon, germanium, and grey tin. The equivalence of the two types of ion in the unit cell reduces the number of parameters involved in the factorization *ansatz*. Two different models were studied, namely, the generalized shell model (GSM) where the sites $\vec{r}_s$ were chosen as the ion sites $\vec{r}_\kappa$, and the bond-charge model (BCM) where the sites $\vec{r}_s$ were chosen at the bond charge sites.

a. GSM calculations. The functions $f^{\kappa}(\vec{Q})$ were chosen to be the Fourier transforms of a real-space distribution which was characterized by being constant for $r <$ a characteristic cut-off radius r_G and zero for $r > r_G$. Thus

$$f^{\kappa}(\vec{Q})=3(\sin x-x\cos x)/x^3,\quad x=Qr_G\ . \tag{93}$$

For simplicity, the $a^{\kappa\kappa'}_{\alpha\beta}(\vec{q})$ were taken to be constants and diagonal in both (α,β) and (κ,κ'),

$$a^{\kappa\kappa'}_{\alpha\beta}(\vec{q})=a_1\delta_{\alpha\beta}\delta_{\kappa\kappa'}\ . \tag{94}$$

The pseudopotentials due to the ions were taken to be $-Ze^2/r$ for $r\geq r_c$ and constant at a value of $-Ze^2/r_c$ for $r<r_c$. Thus

$$W_\kappa(\vec{Q})=-(4\pi Ze^2/\Omega Q^2)\sin(Qr_c)/Qr_c\ . \tag{95}$$

The above form of the pseudopotential form factor provides a simple and reasonably close analytic representation to the pseudopotential form factor for silicon as given by Heine and Abarankov (HA) and modified by Shaw.[23] The value of r_c was chosen to be very close to the value required to make the first node of $W_\kappa(\vec{Q})$ coincide exactly with that of the HA pseudopotential. The calculated dispersion curves, however, did show some sensitivity to the value of r_c and as a result r_c was very slightly varied in order to obtain the "best" fit. Figures 1 and 2 illustrate the pseudopotential form factors for silicon and germanium corresponding to the "best" values for r_c used in the calculations (see Table I). Also shown in Figs. 1 and 2 are the "best" values for $W_\kappa(\vec{Q})$ at the reciprocal-lattice points obtained from electronic band-structure data and tabulated by Cohen and Heine.[24] It may be seen that the pseudopotentials used in the calculations are not inconsistent with the latter, considering the wide spread in pseudopotential form factors obtained by different methods.[24] The pseudopotential form factors in Eq. (95) were also truncated smoothly to zero at the fifth node.

TABLE I. Parameters used for the generalized-shell-model calculations for silicon and germanium.

	Si	Ge
Lattice constant (Å)	5.417	5.647
r_c/a	0.209	0.209
r_G/a	0.26	0.26
$[(4\pi e^2/\Omega)a_1]$ (from sum rule)	2.24	2.19
ϵ_0	6.8	9.6
ϵ_∞ (calculated)	9.3	12.0
ϵ_∞ (experiment)	11.7	16.0
$\epsilon(0,0)$ (Ref. 25)	11.3	14.0

In order to use the factorization scheme [Eq. (16) of I] we also need to know something about $\epsilon(\vec{Q},\vec{Q}')$, the actual dielectric matrix for the solid. Fortunately, the diagonal elements $\epsilon(\vec{Q},\vec{Q})$ for Si and Ge have been calculated recently within the framework of the random-phase approximation (RPA) by Walter and Cohen[25] using actual energy bands and wave functions. In their calculation, Walter and Cohen neglected exchange and correlation effects, i.e., $v(\vec{Q})$ was taken to be simply $4\pi e^2/\Omega Q^2$. In our calculation, $v(\vec{Q})$ has been taken to be of the form given in Eq. (2) to allow approximately for exchange and correlation effects. The expression used for $f(Q)$ was that given by Singwi *et al.*[26] for a free-electron gas with the same density as the average valence-electron density in the solid in question. Therefore, Walter and Cohen's $\epsilon(\vec{Q},\vec{Q})$ was first corrected for exchange and correlation. Their calculations also showed that $\epsilon(\vec{Q},\vec{Q})$ is quite isotropic as a function of the direction of $\vec{Q}$, and hence a suitably averaged isotropic function was chosen to represent $\epsilon(Q,Q)$.

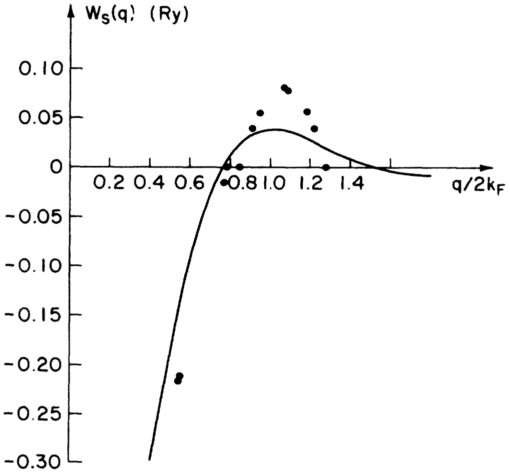

FIG. 1. Pseudopotential form factor for silicon calculated from Eq. (95) using the value of r_c fitted to the phonon spectrum. The curve shown corresponds to the bare-ion pseudopotential screened by a free-electron gas of equivalent density to that of the valence electrons in silicon. The points represent best fits to the band-structure data as given by Cohen and Heine (Ref. 24).

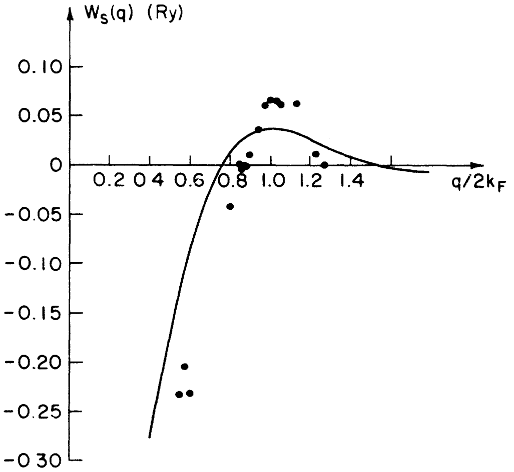

FIG. 2. Pseudopotential form factor for germanium calculated from Eq. (95) using the value of r_c fitted to the phonon spectrum. The curve shown corresponds to the bare-ion pseudopotential screened by a free-electron gas of equivalent density to that of the valence electrons in germanium. The points represent best fits to the band-structure data as given by Cohen and Heine (Ref. 24).

From $\epsilon(Q,Q)$ and the acoustic sum rule which takes-the simple form Eq. (22) for the GSM applied to homopolar semiconductions, the constant a_1 and the function $\epsilon_0(Q)$ were obtained by means of the following iterative procedure. First, a value for a_1 was assumed and using Eq. (93) and Eq. (16) of I, $\epsilon_0(\vec{Q})$ was calculated. This was then used to calculate $\overline{W}^{(0)11}$, $\overline{W}^{(0)12}$, $\overline{V}^{(0)11}$, and $\overline{V}^{(0)12}$ from Eqs. (19) and Eq. (42) of I, and then, using the sum rule Eq. (22), a_1 was recalculated. This new value of a_1 was then chosen to recalculate $\epsilon_0(\vec{Q})$ and to process repeated until it converged, thus providing a consistent solution for a_1 and $\epsilon_0(\vec{Q})$. The calculation was repeated for different values of r_G in Eq. (93), r_G being regarded as a parameter to obtain the best fit to the experimental dispersion curves. The values of the parameters used are given in Table I.

The calculated dispersion curves for silicon and germanium are shown in Figs. 3 and 4 together with the experimental data of Dolling[27] and Nilsson and Nelin[28] for silicon and Nilsson and Nelin[29] for germanium. The results for grey tin will be published separately.[30] For silicon, it may be seen that the agreement is quite reasonable considering the crudeness of the assumptions (93)–(95). The LA modes show a remarkable lack of dispersion which is also borne out by experimental observa-

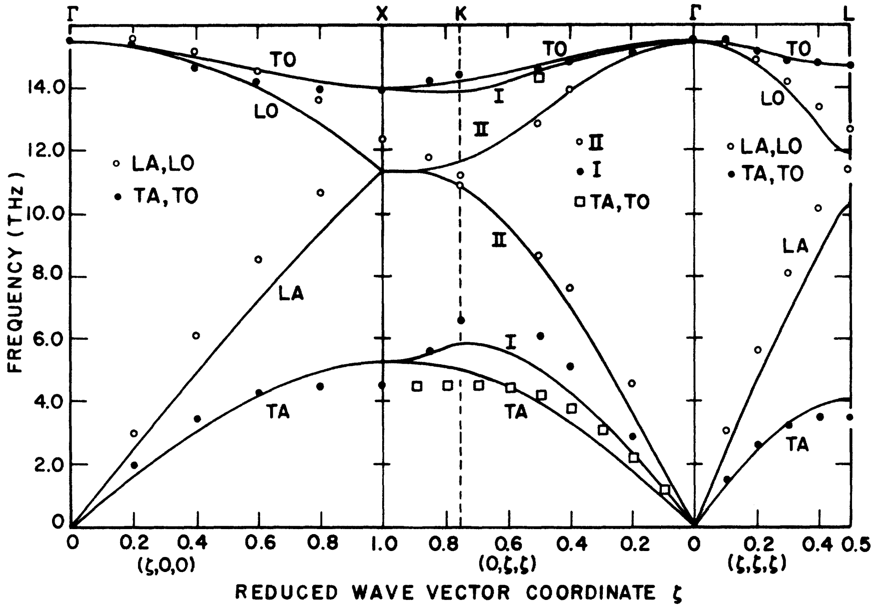

FIG. 3. Phonon-dispersion curves for silicon calculated from the generalized shell model. The experimental points refer to the data of Dolling (Ref. 27), except for the [110] TA and TO points which are taken from Nilsson and Nelin (Ref. 28).

tions. The flatness of the TA modes from halfway to the zone edge outwards, however, is not reproduced and probably requires a more accurate representation of the form factors $f_\kappa(\vec{Q})$. For germanium, the "best" values of r_G and r_c turned out to be very close to those for silicon scaled by the ratio of their lattice constants. The agreement with experiment for germanium is, however, appreciably worse. This may possibly be due to the effect of the *d* bands in this material which were not taken into account in the calculations of Walter and Cohen.

The induced dipolar distributions in real space are, as discussed in Sec. I, the Fourier transforms of $\epsilon_0 f_\kappa(\vec{Q})/\epsilon_0(\vec{Q})$ and turn out to be mainly contained inside spheres of radius r_G centered on the ion sites with a discontinuity at r_G and a small oscillatory tail outside r_G. The discontinuity and oscillations are a consequence of our simplifying assumption for $f_\kappa(\vec{G})$. It should be noted that the values for r_G obtained from our fit correspond to overlapping spherical distributions which thus would tend to approximate a build up of dipole distributions at the bond charge sites in describing the electron response.

Also listed in Table I are the values of ϵ_∞ calculated from the parameters of the model by using Eq. (43) of I. It may be seen that according to our model the local-field corrections decrease ϵ_∞ from $\epsilon(0,0)$ instead of increasing them to the slightly greater experimental values. We believe this to be a consequence of our approximations for exchange and correlation effects in $v(\vec{Q})$ which could rather sensitively affect the $\overline{V}^{(0)\kappa\kappa'}$ defined in Eq. (42) of I. The results do indicate that further refinements need to be made on our model before a completely satisfactory explanation of both the lattice-dynamical and dielectric properties of these materials is established.

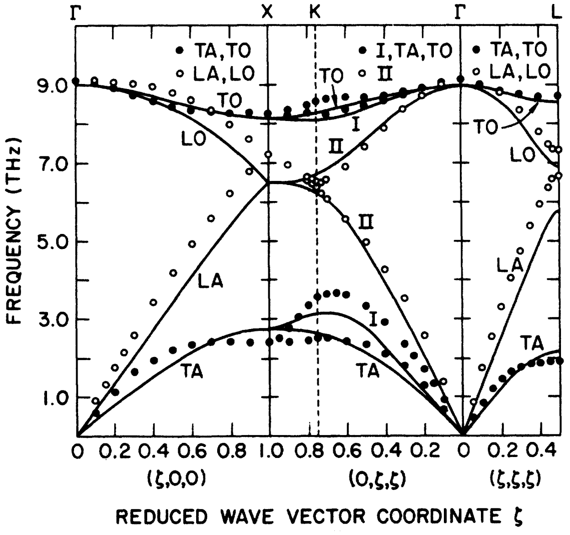

FIG. 4. Phonon-dispersion curves for germanium calculated from the generalized shell model. The experimental points refer to the data of Nilsson and Nelin (Ref. 29).

b. BCM calculations. As discussed in Sec. II, the symmetry of the lattice of bond charges is lower than that of a cubic lattice. As a result, even if the $a_{\alpha\beta}^{ss'}(\vec{q})$ in the factorization *ansatz*, Eq. (16) of I, were assumed to be constants and diagonal in (s, s'), they are still not diagonal in (α, β) and consequently one needs more than a single parameter to characterize them, unlike Eq. (94). To reduce the number of parameters, Eq. (42) was used to determine the $a_{\alpha\beta}^{ss'}$ and thus automatically satisfy the acoustic sum rule. The form factors associated with the bond-charge sites were taken to be of the form given in Eq. (93) with r_G again being regarded as a variable parameter. As in the case of the GSM calculations, an iterative procedure was followed to determine the functions $\epsilon_0(\vec{Q})$ and the $a_{\alpha\beta}^{ss'}$ self-consistently. The values of r_c characterizing the pseudopotential form factors were kept close to the values used for the GSM. Surprisingly, no satisfactory agreement was obtained with experiment using such a model for any value of r_G. This does not necessarily mean that a BCM is invalid for these materials, but rather that the simple form factors [Eq. (93)] and the particular assumptions represented by Eq. (42) for the $a_{\alpha\beta}^{ss'}$ probably do not well represent the dielectric matrix for these solids.

More detailed calculations of the off-diagonal elements of $\epsilon(\vec{Q}, \vec{Q}')$ will be required before the parameters of a BCM type of factorization scheme may be determined and the model successfully tested in the manner described in this paper.

VII. SUMMARY AND DISCUSSION

In this paper the scheme presented in I for calculating the local-field corrections to the dielectric screening in a solid has been applied to the problem of lattice dynamics. The general expression is given for the equations of motion representing the ion displacements and the dipoles developed during the motion. Explicit microscopic expressions are also derived for the effective-change tensor, and it is shown that the deviation of the "Szigeti charge" from the ionic charge is due to (a) overlap of the induced-dipole distributions and (b) "mechanical-overlap" effects resulting from nonlocal components of the electron-ion pseudopotential or deviations of the latter from a Coulomb potential. For covalent solids it is seen that no simple separation of the effective charge into a local and a nonlocal part is possible. The restrictions on the parameters involved in the factorization scheme imposed by the sum rules which result from the vanishing of the macroscopic field in the limit $\vec{q} \to 0$ are discussed in detail. Expressions are derived for the longitudinal- and transverse-optic-mode frequencies at the zone center for cubic and tetrahedral crystals, and for the low-frequency dielectric constant $\epsilon(\omega)$. It is shown that the Lyddane-Sachs-Teller relation follows.

The bond-charge model is next considered and it is shown that Martin's original lattice-dynamical bond-charge model follows as a special case if certain assumptions are met. The relation to the conventional "shell model" is discussed, and an expression is derived for the "charge on the shell" in terms of our formulation. The elastic and dielectric properties are derived from the long-wavelength limit of the dynamical matrix, and an expression for the piezoelectric constant is obtained in terms of microscopically defined quantities.

Explicit calculations are made for the phonon frequencies of silicon and germanium, using both the generalized shell model and the bond-charge model, with rather satisfactory results for the former. The bond-charge model, however, contains too many parameters for a reliable first-principles calculation. A simple assumption for these parameters does not yield good agreement with experiment, and it seems clear that information about the off-diagonal elements from band-structure calculations is required for the input to this particular model.

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APPENDIX A

We note that

$$W_\kappa(\vec{q}) \to -4\pi Z_\kappa e^2/\Omega q^2 \quad \text{as } \vec{q} \to 0 \tag{A1}$$

and

$$v(\vec{q}) \to 4\pi e^2/\Omega q^2 \quad \text{as } \vec{q} \to 0 \; .$$

From Eq. (2) and Eq. (5) of I, we have

$$\tilde{E}_{\alpha\beta}^{\kappa\kappa'}(q) = \sum_{\vec{G}\vec{G}'} \frac{1}{v(\vec{q}+\vec{G})} [\delta_{\vec{G}\vec{G}'} - \epsilon^{-1}(\vec{q}+\vec{G}, \vec{q}+\vec{G}')](\vec{q}+\vec{G})_\alpha (\vec{q}+\vec{G}')_\beta W_\kappa(\vec{q}+\vec{G}) W_{\kappa'}(\vec{q}+\vec{G}) e^{i(\vec{G}\cdot\vec{r}_\kappa - \vec{G}'\cdot\vec{r}_{\kappa'}} \; ,$$

therefore,

$$\lim_{\vec{q}\to 0}\tilde{E}^{\kappa\kappa'}_{\alpha\beta}(\vec{q})=-\lim_{\vec{q}\to 0}\Bigg(\frac{1}{v(\vec{q})}\,[1-\epsilon^{-1}(\vec{q},\vec{q})]q_\alpha q_\beta W_\kappa(\vec{q})W_{\kappa'}(\vec{q})-\sum_{\vec{G}}{}'\,\frac{1}{v(\vec{q})}\,\epsilon^{-1}(\vec{q},\vec{G})q_\alpha G_\beta W_\kappa(\vec{q})W_{\kappa'}(\vec{G})e^{-i\vec{G}\cdot\vec{r}_{\kappa'}}$$
$$-\sum_{\vec{G}}{}'\,\frac{1}{v(\vec{G})}\,\epsilon^{-1}(\vec{G},\vec{q})G_\alpha q_\beta W_\kappa(\vec{G})W_{\kappa'}(\vec{q})e^{i\vec{G}\cdot\vec{r}_\kappa}+\sum_{\vec{G}\vec{G}'}{}'\,\frac{1}{v(\vec{G})}\,[\delta_{\vec{G}\vec{G}'}-\epsilon^{-1}(\vec{G},\vec{G}')]G_\alpha G'_\beta W_\kappa(\vec{G})W_{\kappa'}(\vec{G}')$$
$$\times e^{i(\vec{G}\cdot\vec{r}_\kappa-\vec{G}'\cdot\vec{r}_{\kappa'})}\Bigg)\,, \qquad \text{(A2)}$$

where the primes over the summations imply the exclusion of $\vec{G}$, $\vec{G}'=0$ from the sum. Using Eqs. (20) and (45)–(47) of I and Eq. (A1), we obtain

$$\lim_{\vec{q}\to 0}\tilde{E}^{\kappa\kappa'}_{\alpha\beta}(q)=-\lim_{\vec{q}\to 0}\Bigg[\frac{4\pi Z_\kappa Z_{\kappa'}e^2}{\Omega q^2}\,q_\alpha q_\beta\left(1-\frac{1}{\epsilon_\infty}\right)-\frac{4\pi e^2 Z_\kappa}{\Omega\epsilon_\infty}\sum_{\substack{\vec{G}\\ \gamma\delta\\ ss'}}{}'\frac{q_\alpha q_\gamma}{q^2}\,G_\delta f^{*s'}(\vec{G})\overline{S}^{ss'}_{\gamma\delta}e^{i\vec{G}\cdot\vec{r}_s}G_\beta\,\frac{W_{\kappa'}(\vec{G})}{\epsilon_0(\vec{G})}\,e^{-i\vec{G}\cdot\vec{r}_{\kappa'}}$$
$$-\frac{4\pi e^2 Z_{\kappa'}}{\Omega\epsilon_\infty}\sum_{\substack{\vec{G}\\ \gamma\delta\\ ss'}}{}'\frac{q_\beta q_\delta}{q^2}\,f^s(\vec{G})\overline{S}^{ss'}_{\gamma\delta}e^{-i\vec{G}\cdot\vec{r}_s}G_\alpha\,\frac{W_\kappa(\vec{G})}{\epsilon_0(\vec{G})}\,e^{i\vec{G}\cdot\vec{r}_\kappa}$$
$$+\sum_{\vec{G}\vec{G}'}{}'\,\frac{1}{v(\vec{G})}\,\delta_{\vec{G}\vec{G}'}\left(1-\frac{1}{\epsilon_0(\vec{G})}\right)G_\alpha G'_\beta W_\kappa(\vec{G})W_{\kappa'}(\vec{G}')e^{i(\vec{G}\cdot\vec{r}_\kappa-\vec{G}'\cdot\vec{r}_{\kappa'})}$$
$$+\sum_{\vec{G}\vec{G}'}{}'\,\frac{W_\kappa(\vec{G})}{\epsilon_0(\vec{G})}\,\frac{W_{\kappa'}(\vec{G}')}{\epsilon_0(\vec{G}')}\,G_\alpha G'_\beta e^{i(\vec{G}\cdot\vec{r}_\kappa-\vec{G}'\cdot\vec{r}_{\kappa'})}\sum_{\substack{\gamma\delta\\ ss'}}G_\gamma f^s(\vec{G})\left[\overline{S}^{ss'}_{\gamma\delta}-\lim_{\vec{q}\to 0}\sum_{\substack{\epsilon\nu\\ tt'}}\left(\frac{4\pi e^2}{\Omega\epsilon_\infty}\,\frac{q_\epsilon q_\nu}{q^2}\,\overline{S}^{st}_{\gamma\epsilon}\,\overline{S}^{s't'}_{\nu\delta}\right)\right]$$
$$\times f^{*s'}(\vec{G}')G'_\delta e^{-i(\vec{G}\cdot\vec{r}_s-\vec{G}'\cdot\vec{r}_{s'})}\Bigg]\,. \qquad \text{(A3)}$$

If we define $\overline{W}^{(0)\kappa s}_{\alpha\beta}$ to be the limit as $\vec{q}\to 0$ of

$$\overline{W}^{\kappa s}_{\alpha\beta}=\sum_{\vec{G}}{}'\,(\vec{q}+\vec{G})_\alpha(\vec{q}+\vec{G})_\beta\,\frac{W_\kappa(\vec{q}+\vec{G})}{\epsilon_0(\vec{q}+\vec{G})}\,f^s(\vec{q}+\vec{G})e^{i\vec{G}\cdot\vec{r}_{\kappa s}}\,, \qquad \text{(A4)}$$

then Eq. (A3) becomes

$$\lim_{\vec{q}\to 0}\tilde{E}^{\kappa\kappa'}_{\alpha\beta}(q)=\lim_{\vec{q}\to 0}\Bigg[-\frac{4\pi Z_\kappa Z_{\kappa'}e^2}{\Omega}\left(1-\frac{1}{\epsilon_\infty}\right)\frac{q_\alpha q_\beta}{q^2}+\frac{4\pi e^2}{\Omega}\,\frac{Z_\kappa}{\epsilon_\infty}\sum_{\gamma s}\frac{q_\alpha q_\gamma}{q^2}\,(\underline{\overline{S}}^{(0)}\underline{\overline{W}}^{(0)\dagger})^{s\kappa'}_{\gamma\beta}+\frac{4\pi e^2}{\Omega}\,\frac{Z_{\kappa'}}{\epsilon_\infty}\sum_{\gamma s}(\underline{\overline{W}}^{(0)}\underline{\overline{S}}^{(0)})^{\kappa s}_{\alpha\gamma}\,\frac{q_\gamma q_\beta}{q^2}$$
$$+\overline{E}^{(0)\kappa\kappa'}_{\alpha\beta}-(\underline{\overline{W}}^{(0)}\underline{\overline{S}}^{(0)}\underline{\overline{W}}^{(0)\dagger})^{\kappa\kappa'}_{\alpha\beta}+\frac{4\pi e^2}{\Omega\epsilon_\infty}\sum_{\substack{\gamma\delta\\ ss'}}(\underline{\overline{W}}^{(0)}\underline{\overline{S}}^{(0)})^{\kappa s}_{\alpha\gamma}(\underline{\overline{S}}^{(0)}\underline{\overline{W}}^{(0)\dagger})^{s'\kappa'}_{\alpha\beta}\frac{q_\gamma q_\delta}{q^2}\Bigg]\,, \qquad \text{(A5)}$$

where $\overline{E}^{(0)\kappa\kappa'}_{\alpha\beta}$ has been defined in the text [Eq. (8)]. Equation (A5) simplifies to the form Eq. (7) given in the text.

APPENDIX B

The left-hand side of the acoustic sum rule as given in Eq. (12) is

$$X\equiv\lim_{\vec{q}\to 0}\sum_{\kappa\vec{G}}q_\alpha(\vec{q}+\vec{G})_\beta W_\kappa(\vec{q}+\vec{G})\epsilon^{-1}(\vec{q},\vec{q}+\vec{G})e^{-i\vec{G}\cdot\vec{r}_\kappa}$$
$$=\lim_{\vec{q}\to 0}\left(-\frac{4\pi e^2}{\Omega\epsilon_\infty}\sum_\kappa Z_\kappa\,\frac{q_\alpha q_\beta}{q^2}+\sum_{\vec{G}\kappa}{}'q_\alpha G_\beta W_\kappa(\vec{G})\epsilon^{-1}(\vec{q},\vec{G})e^{-i\vec{G}\cdot\vec{r}_\kappa}\right)\,, \qquad \text{(B1)}$$

where the prime over the summation excludes $\vec{G}=0$ from the sum. Using Eq. (45) of I, we obtain

$$X=-\frac{4\pi e^2}{\Omega\epsilon_\infty}\lim_{\vec{q}\to 0}\sum_\kappa\left(Z_\kappa\,\frac{q_\alpha q_\beta}{q^2}+q_\alpha\sum_G{}'\frac{q_\gamma}{q^2}\,G_\delta f^{*s}(\vec{G})\overline{S}^{ss'}_{\gamma\delta}e^{i\vec{G}\cdot\vec{r}_{s'}}G_\beta\,\frac{W_\kappa(\vec{G})}{\epsilon_0(\vec{G})}\,e^{-i\vec{G}\cdot\vec{r}_\kappa}\right)$$
$$=-\frac{4\pi e^2}{\Omega\epsilon_\infty}\lim_{\vec{q}\to 0}\sum_\kappa\left(Z_\kappa\,\frac{q_\alpha q_\beta}{q^2}+\frac{q_\alpha q_\gamma}{q^2}\sum_s(\underline{\overline{S}}\underline{\overline{W}}^\dagger)^{s\kappa}_{\gamma\beta}\right)=-\frac{4\pi e^2}{\Omega\epsilon_\infty}\lim_{\vec{q}\to 0}\sum_\kappa[q_\alpha\;\tilde{Z}^\kappa_{\alpha\beta}q_\beta\,] \qquad \text{(B2)}$$

using the definition of Eq. (9), since $\tilde{Z}^\kappa_{\alpha\beta}$ is a symmetric matrix. The acoustic sum rule $X=0$ is satisfied if

$$\sum_\kappa\tilde{Z}^\kappa_{\alpha\beta}=0\,,$$

as given in Eq. (11) of the text.

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