

Dielectric Screening and the Phonon Spectra of Metallic and Nonmetallic Crystals*

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A quantum theory of the phonon excitation spectrum of a general crystal in the harmonic approximation is presented. Many-body perturbation theory is used to (i) generalize a result obtained by Baym relating the dielectric and lattice dynamical properties of a monoatomic metal to a general crystal, and (ii) show that Phillips's recent doubts regarding the applicability of linear screening theory to covalent crystals can be allayed. It is shown that a correct, "dressed" inverse screening tensor can be defined so as to make the linear-screening approach rigorous in the harmonic approximation and for wavelengths short enough so that relativistic effects are not important. An identity is also derived which allows the elimination of divergent self-interaction terms and provides an explicit demonstration that the acoustic-mode frequencies vanish in the long-wavelength limit.

I. INTRODUCTION

THE present theory of the lattice dynamics of metals is substantially different from the corresponding theory for nonmetallic crystals. A common and fruitful approach¹ to metals is afforded by means of a pseudopotential tensor involving the inverse dielectric-screening function of the Hartree approximation and a factor to correct this approximation. In nonmetals, however, the usual approach is via phenomenological interatomic force constants.² Recently, however, Phillips³ has applied some of his results, obtained from the application of the pseudopotential approach to covalent crystals, to the lattice dynamics of these crystals. Phillips³ finds contributions to the strain energy from changes in the screening due to changes in the energy gap and casts doubts on the applicability of linear-screening theory to the (harmonic) lattice dynamics of covalent crystals. In this article, we establish this applicability to all types of crystal by means of many-body perturbation theory. We shall thereby create a unified approach to the lattice dynamics of all types of crystal, metallic and nonmetallic, and find a simple and elegant general relation, which is a generalization of a result obtained by Baym⁴ for monoatomic metals, between the phonon excitation spectrum and a "dressed" inverse dielectric-screening function. The connection between this formal expression and the current pseudopotential approach to the phonon spectra of metals is established,

thus providing an alternative theoretical viewpoint of the latter.

The approach to be used in this article can be summarized as follows. We begin with a zero-order one-electron Hamiltonian, describing the system of an electron in a self-consistent field, and a zero-order nuclear Hamiltonian for the nuclei moving in a uniform background of charge together with additional forces analogous to a self-consistent field. The remaining interactions are treated as a perturbation by means of one-particle Green's functions and the resulting perturbation series is summed to infinite order by means of the Dyson procedure.

In the course of calculating the dressed phonon spectrum in the harmonic approximation, we consider the screening of a test charge by the electrons from an external potential in order to relate some of the diagrams which contribute to the phonon self-energy to screening effects. The general formal expression is finally considered in the approximation where the core electrons are assumed to provide a tight, spherically symmetric charge cloud which moves with the nucleus in order to relate the present approach to the pseudopotential type of calculation.

II. HAMILTONIAN AND PERTURBATION THEORY

We begin with the nonrelativistic Hamiltonian for the crystal:

$$H = \sum_i \frac{1}{2} p_i^2 + \sum_s (P_s^2/2M_s) + \sum_{i>j} r_{ij}^{-1} + \sum_{r>s} (Z_r Z_s/R_{rs}) - \sum_{i,s} (Z_s/|r_i - R_s|), \quad (1)$$

in atomic units, where p_i and r_i are electron momentum and position operators, P_s and R_s those for the nuclei, and M_s , Z_s are the mass and charge number of the s th nucleus in electron units. We re-

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¹ See, for example, S. H. Vosko, R. Taylor, and G. H. Keech, *Can. J. Phys.* **43**, 1187 (1965), and references therein; see, also, Ref. 2.

² See, for example, W. Cochran, in *Phonons in Perfect Lattices and in Lattices with Point Imperfections*, edited by R. W. H. Stevenson (Plenum Press, Inc., New York, 1966), and references therein. An exception is the work of D. R. Fredkin and N. R. Werthamer [*Phys. Rev.* **138**, A1527 (1965)] and N. S. Gillis and N. R. Werthamer [*Phys. Rev.* **167**, 607 (1968)].

³ J. C. Phillips, *Phys. Rev.* **168**, 917 (1968).

⁴ G. Baym, *Ann. Phys. (N. Y.)* **14**, 1 (1961).

write this as

$$H = H_e + H_N + H_I = H_0 + H_I,$$

where

$$\begin{aligned} H_e &= \sum_i \left\{ \frac{1}{2} p_i^2 - \sum_s [Z_s / |\mathbf{r}_i - \mathbf{R}_s(0)|] + V_{SF}(\mathbf{r}_i) \right\}, \\ H_N &= \sum_s (P_s^2 / 2M_s) + \frac{1}{2} \sum_{r \neq s} [(Z_r Z_s / R_{rs}) + f(\mathbf{R}_{rs})], \\ H_I &= \sum_{i>j} r_{ij}^{-1} - \sum_{i,s} Z_s [|\mathbf{r}_i - \mathbf{R}_s|^{-1} - |\mathbf{r}_i - \mathbf{R}_s(0)|^{-1}] \\ &\quad - \sum_i V_{SF}(\mathbf{r}_i) - \frac{1}{2} \sum_{r \neq s} f(\mathbf{R}_{rs}), \quad (2) \end{aligned}$$

where $\mathbf{R}_s(0)$ is the equilibrium position of nucleus s . To ensure that the different terms are finite, the interaction with a uniform charge distribution is added and subtracted in the manner given by Bardeen and Pines.⁵ The terms $V_{SF}(\mathbf{r}_i)$, $f(\mathbf{R}_{rs})$ are terms added to and subtracted from the Hamiltonian to ensure that the zero-order Hamiltonian is an accurate one so that the zero-order eigenstates are close to the dressed eigenstates.⁶

The eigenstates of H_e are Bloch functions, since the potential in H_e is periodic, and \mathbf{k} is a good quantum number. We thus expand the electron field in terms of the wave-vector eigenstates of H_e :

$$\Psi = \sum_{\mathbf{k}} c_{\mathbf{k}} \psi_{\mathbf{k}},$$

where the $\psi_{\mathbf{k}}$ are the eigenstates of H_e and the $c_{\mathbf{k}}$ are the corresponding field amplitudes, or destruction operators. The $c_{\mathbf{k}}$, $c_{\mathbf{k}}^\dagger$ satisfy the usual equal-time anticommutation relations for fermion operators. We thus have

$$H_e = \sum_{\mathbf{k}} \epsilon(\mathbf{k}) c_{\mathbf{k}}^\dagger c_{\mathbf{k}}, \quad (3)$$

where the $\epsilon(\mathbf{k})$ are the eigenvalues of H_e .

Within the harmonic approximation, H_N can be written as

$$H_N = \sum_s (P_s^2 / 2M_s) + \frac{1}{2} \sum_{r,s} K_{rs} \alpha_r^\beta u_{rs}^\alpha u_{rs}^\beta \quad (4)$$

and thence as

$$H_N = \sum_{j,q} \Omega_{qj} (a_{qj}^\dagger a_{qj} + \frac{1}{2}),$$

following the well-known normal-coordinate transformation and quantization of the resulting field.⁷ The a_{qj} , a_{qj}^\dagger satisfy⁷ the usual equal-time commutation relations appropriate to boson operators. The sum

over j is a sum over branches, and the sum over \mathbf{q} is only over points in the first Brillouin Zone.⁸

The electron-electron Coulomb interaction [Eq. (2)] can be written in the form

$$\begin{aligned} H_{ee} &= \frac{1}{2} \sum_{\mathbf{Q}} \left\{ \sum_{\mathbf{k}\mathbf{k}'} v_{\mathbf{Q}}^* B_{\mathbf{Q}+\mathbf{k}'}^*(\mathbf{k}, \mathbf{k}') c_{\mathbf{k}}^\dagger c_{\mathbf{k}+\mathbf{Q}+\mathbf{k}'} \right\} \\ &\quad \times \left\{ \sum_{\mathbf{k}'\mathbf{k}''} v_{\mathbf{Q}} B_{\mathbf{Q}+\mathbf{k}'}(\mathbf{k}', \mathbf{k}'') c_{\mathbf{k}'+\mathbf{Q}+\mathbf{k}'}^\dagger c_{\mathbf{k}''} \right\}, \quad (5) \end{aligned}$$

where $B_{\mathbf{Q}+\mathbf{k}}(\mathbf{k}, \mathbf{k}') = \langle \psi_{\mathbf{k}+\mathbf{Q}+\mathbf{k}} | \exp(i\mathbf{Q} \cdot \mathbf{r}) | \psi_{\mathbf{k}} \rangle$ and \mathbf{k} is a reciprocal-lattice vector. All quantities are normalized to unit volume.

This is the general form for the unretarded electron-electron Coulomb interaction for electrons in a periodic potential and reduces to the form used in previous work^{5,9} in the case $B_{\mathbf{Q}+\mathbf{k}}(\mathbf{k}, \mathbf{k}') = \delta_{\mathbf{k},0}$, appropriate to the case of the electron gas. In the case of non-metals, it is necessary to use the general form since $B_{\mathbf{Q}+\mathbf{k}}(\mathbf{k}, \mathbf{k}')$ for $\mathbf{k} \neq 0$ approaches the $\mathbf{k} = 0$ value in magnitude when $\epsilon(\mathbf{k})$ is near a band edge. The coefficient $v_{\mathbf{Q}}$ is

$$v_{\mathbf{Q}} = i(2\pi^{1/2}/|\mathbf{Q}|) \quad \text{or} \quad |v_{\mathbf{Q}}|^2 = 4\pi/\mathbf{Q}^2$$

if we ignore retardation. We note that Eq. (5) includes self-interaction effects.

We now consider the electron-phonon interaction term in H_I . To lowest order, this is

$$H_{ep}^{(1)} = - \sum_{is} Z_s \mathbf{u}_s \cdot \nabla [|\mathbf{r}_i - \mathbf{R}_s(0)|]^{-1},$$

which can be written

$$H_{ep}^{(1)} = \sum_{\mathbf{k}\mathbf{k}'} \sum_{\mathbf{q}\mathbf{j}} \{ U_{\mathbf{q}+\mathbf{k}}(\mathbf{k}) a_{\mathbf{q}} c_{\mathbf{k}+\mathbf{q}+\mathbf{k}'}^\dagger c_{\mathbf{k}} + \text{H.c.} \},$$

where

$$\begin{aligned} U_{\mathbf{q}+\mathbf{k}}(\mathbf{k}) &= i \sum_{\mathbf{k}'} |v_{\mathbf{q}+\mathbf{k}'}|^2 B_{\mathbf{q}+\mathbf{k}}(\mathbf{k}-\mathbf{k}', \mathbf{k}) \\ &\quad \times \sum_n Z_n (2M_n V_A \Omega_{\mathbf{q}})^{-1/2} \mathbf{e}_{\mathbf{q}}^n \cdot (\mathbf{q}+\mathbf{k}') \exp(-i\mathbf{k}' \cdot \mathbf{x}_n) \end{aligned}$$

if V_A is the cell volume, n ranges over the nuclei in a unit cell, $\mathbf{e}_{\mathbf{q}}^n$ is the orthonormal polarization vector for the n th species, \mathbf{x}_n is the equilibrium position of this species in the unit cell, and we have suppressed the label j for notational convenience. It is convenient to rewrite this as

$$U_{\mathbf{q}+\mathbf{k}}(\mathbf{k}) = \sum_{\mathbf{k}'} A(\mathbf{q}, \mathbf{k}') B_{\mathbf{q}+\mathbf{k}}(\mathbf{k}-\mathbf{k}'; \mathbf{k}) v_{\mathbf{q}+\mathbf{k}'}, \quad (6)$$

⁸ In this article, we use the extended zone scheme and \mathbf{Q} , \mathbf{k} are summed always over all points in reciprocal space, whereas \mathbf{q} is always confined to the first zone. The vector \mathbf{k} always denotes a reciprocal-lattice vector.

⁹ See, for example, D. Pines, *The Many Body Problem* (W. A. Benjamin, Inc., New York, 1962), and references and reprints therein; and J. J. Quinn, in *Phonons and Phonon Interactions*, edited by T. Bak (W. A. Benjamin, Inc., New York, 1964).

⁵ J. Bardeen and D. Pines, Phys. Rev. **99**, 1140 (1955).

⁶ The V_{SF} term has been discussed in some detail by Vosko *et al.* (Ref. 1) and J. Hubbard, Proc. Roy. Soc. (London) **244**, 199 (1958). The $f(\mathbf{R}_{rs})$ term is analogous.

⁷ A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation*, (Academic Press Inc., New York, 1963), Solid State Physics Suppl. No. 3.

where

$$A(\mathbf{q}, \boldsymbol{\kappa}') = (2\pi/V_A\Omega_q)^{1/2} \times \sum_n Z_n M_n^{-1/2} \mathbf{e}_q^n \cdot [\mathbf{q} + \mathbf{k}'] \exp(-i\boldsymbol{\kappa}' \cdot \mathbf{x}_n)$$

if $[\mathbf{a} + \mathbf{b}]$ represents the unit vector $(\mathbf{a} + \mathbf{b})/|\mathbf{a} + \mathbf{b}|$.

It is usual^{5,9,10} to use $H_{ep}^{(1)}$ as the total electron-phonon interaction but we shall find that it is necessary to include the next-order term in the general case. For the electron-phonon gas, the second-order contribution to the phonon self-energy is unimportant, but for real crystals it is a necessary term. As we shall see later, it actually subtracts out the ultraviolet divergence due to $H_{ep}^{(1)}$. It can be written as

$$H_{ep}^{(2)} = \sum L_{qq'}(\boldsymbol{\kappa}') B_{\mathbf{k}+\mathbf{q}-\mathbf{q}'}(\boldsymbol{\kappa}-\boldsymbol{\kappa}', \mathbf{k}) c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'}^\dagger c_{\mathbf{k}} \times (a_{\mathbf{q}}^\dagger + a_{-\mathbf{q}})(a_{\mathbf{q}'} + a_{-\mathbf{q}'})^\dagger, \quad (7)$$

where

$$L_{qq'}(\boldsymbol{\kappa}') = \frac{-\pi}{V_A(\Omega_q\Omega_{q'})^{1/2}} \sum_n Z_n M_n^{-1} (\mathbf{e}_q^n \cdot [\mathbf{q} - \mathbf{q}' + \boldsymbol{\kappa}']) \times (\mathbf{e}_{q'}^{n*} \cdot [\boldsymbol{\kappa}' + \mathbf{q} - \mathbf{q}']) \exp(i\boldsymbol{\kappa}' \cdot \mathbf{x}_n).$$

Thus the total electron-phonon interaction term with in the harmonic approximation is

$$H_{ep} = \sum \{U_{\mathbf{q}+\boldsymbol{\kappa}}(\mathbf{k}) a_{\mathbf{q}} c_{\mathbf{k}+\mathbf{q}+\boldsymbol{\kappa}}^\dagger c_{\mathbf{k}} + \text{H.c.}\} + H_{ep}^{(2)}, \quad (8)$$

where $U_{\mathbf{q}+\boldsymbol{\kappa}}(\mathbf{k})$ is given by Eq. (6) and $H_{ep}^{(2)}$ is given by Eq. (7). The total Hamiltonian to be used is thus

$$H = H_0 + H_I,$$

where $H_0 = H_e + H_N$ is given by Eqs. (3) and (4), respectively, and

$$H_I = H_{ee} + H_{ep} - V_{SF} - f$$

is given by Eqs. (5), (7), and (8). In lowest order, the V_{SF} and f terms will automatically cancel with the corresponding terms in H_0 .⁶

We intend to employ $H_e + H_N$ as the zero-order Hamiltonian and use H_I as the interaction term in a perturbation theory. It is well known that successive terms in the perturbation series for the electron-electron interaction invariably get larger and it is necessary to sum the perturbation series to infinite order to get meaningful results. We shall, therefore, necessarily carry out the perturbation theory to infinite order and will thus use diagrams to facilitate the calculations. We shall carry out the perturbation calculation by evaluating the diagrams according to the following rules:

(1) Assign a different four-vector $k = (\mathbf{k}, \epsilon)$ to each solid (bare-electron) line. For each such internal line a factor $iG_0(k)$ enters, where $G_0(k)$ is the bare-

electron propagator

$$G_0(\mathbf{k}, \epsilon) = [\epsilon - \epsilon(\mathbf{k}) + i\delta_k]^{-1}$$

and where δ_k is greater or less than zero according to whether $\epsilon(\mathbf{k})$ is greater or less than the chemical potential.

(2) Assign a different four-vector $q = (\mathbf{q}, \omega)$ to each wavy (bare-phonon) line and enter a factor $-iD_0(q)$, where $D_0(q)$ is the bare-phonon propagator

$$D_0(\mathbf{q}, \omega) = (\omega - \Omega_q + i\delta)^{-1} - (\omega + \Omega_q - i\delta)^{-1}.$$

(3) For each vertex (type A) involving a phonon line and two electron lines, enter a factor

$$\sum_{\boldsymbol{\kappa}'} v_{\mathbf{q}+\boldsymbol{\kappa}'} A(\mathbf{q}, \boldsymbol{\kappa}') B_{\mathbf{q}+\boldsymbol{\kappa}}(\boldsymbol{\kappa}-\boldsymbol{\kappa}', \mathbf{k})$$

or its Hermitian conjugate, according to whether the phonon is annihilated or created at the vertex; the two electron lines have four-vectors k and $k + q + \kappa$ [where $\kappa = (\boldsymbol{\kappa}, 0)$].

(4) For each vertex (type B) involving two phonon lines q, q' and two electron lines $k, k \pm q \mp q' + \kappa$, enter a factor

$$\sum_{\boldsymbol{\kappa}'} L_{\pm q \pm q'}(\boldsymbol{\kappa}') B_{\mathbf{k}+\mathbf{q} \mp \mathbf{q}'}(\boldsymbol{\kappa}-\boldsymbol{\kappa}', \mathbf{k}),$$

where the signs on q, q' are appropriate to whether the phonons are created or annihilated at the vertex.

(5) For each dotted line, representing the electron-electron Coulomb interaction, assign a four-vector $Q = (\mathbf{Q} + \boldsymbol{\kappa}, \omega)$ and enter a factor $-i$. For each vertex (type C) involving a dotted line Q and two electron lines $k, k + Q + \kappa$, enter a factor

$$v_Q B_{\mathbf{Q}+\boldsymbol{\kappa}}(\boldsymbol{\kappa}, \mathbf{k})$$

or its conjugate, according to whether the dotted line begins^m or ends at the vertex.

(6) The four-vectors are to be conservedⁿ at each vertex (modulo κ) and there are summations over all free reciprocal-lattice vectors κ and integration over all free variables k, q , and Q according to

$$\int \frac{d^4 k}{(2\pi)^4} \quad \text{and} \quad \int_{\text{zone}} \frac{d^4 q}{(2\pi)^4}.$$

A factor 2 is introduced when a sum over spins is necessary and a factor (-1) for each closed loop.

III. FORMAL DEVELOPMENT

We shall begin by calculating several important subdiagrams which will arise frequently in the later stages.

We begin with the diagram shown in Fig. 1(a), which is a polarization part representing "scattering" of the Coulomb interaction by electron-hole pair production. Using the rules given, this is readily

¹⁰ S. Engelsberg and J. R. Schrieffer, Phys. Rev. 131, 993 (1963); A. Migdal, Zh. Eksperim. i Teor. Fiz. 34, 1438 (1958) [English transl.: Soviet Phys.—JETP 7, 996 (1958)].

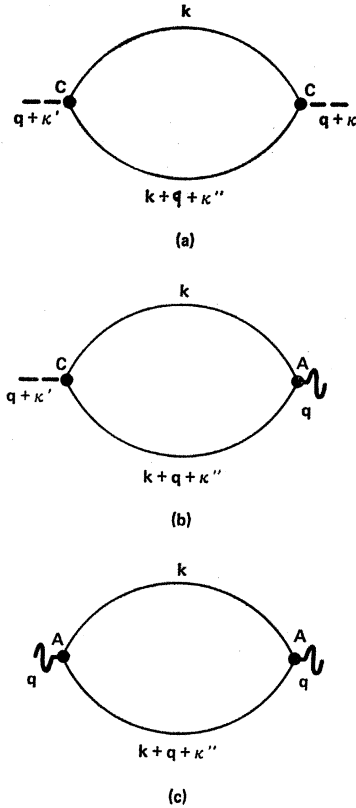


FIG. 1. Some low-order polarizationlike diagrams.

calculated as

$$\begin{aligned}
 -i\phi_1^{(0)}(q; \kappa, \kappa') &= -i\pi_1^{(0)}(q; \kappa, \kappa') v_{q+\kappa}^* v_{q+\kappa'} \\
 &= v_{q+\kappa}^* v_{q+\kappa'} 2 \sum_{\kappa''} \int \frac{d^4k}{(2\pi)^4} \\
 &\quad \times G_0(k) G_0(k+q+\kappa'') \\
 &\quad \times B_{q+\kappa''}^*(\kappa''-\kappa, k) B_{q+\kappa''}(\kappa''-\kappa', k),
 \end{aligned}$$

where the quasiparticles are considered as propagating from right to left in the diagrams. Similarly, the diagram of Fig. 1(b) is

$$\begin{aligned}
 -i\phi_2^{(0)}(q, \kappa) &= \sum_{\kappa'} A(q, \kappa') v_{q+\kappa}^* v_{q+\kappa'} \\
 &\times 2 \sum_{\kappa''} \int \frac{d^4k}{(2\pi)^4} G_0(k) G_0(k+q+\kappa'') \\
 &\quad \times B_{q+\kappa''}^*(\kappa''-\kappa, k) B_{q+\kappa''}(\kappa''-\kappa', k)
 \end{aligned}$$

and we readily note the relation

$$\phi_2^{(0)}(q, \kappa) = \sum_{\kappa'} A(q, \kappa') \phi_1^{(0)}(q; \kappa, \kappa').$$

Similarly, Fig. 1(c) gives

$$\phi_3^{(0)}(q) = \sum_{\kappa, \kappa'} A^*(q, \kappa) A(q, \kappa') \phi_1^{(0)}(q; \kappa, \kappa').$$

The three diagrams of Fig. 1 are merely low-order terms in an infinite series of terms, but we can readily

generalize these results to diagrams in which the series is summed, such as that given in Fig. 2(a). We have

$$\begin{aligned}
 -i\pi_1(q, \kappa, \kappa') &= 2 \sum_{\kappa''} \int \frac{d^4k}{(2\pi)^4} G_0(k) G_0(k+q+\kappa'') \\
 &\quad \times B_{q+\kappa''}^*(\kappa''-\kappa, k) B_{q+\kappa''}(\kappa''-\kappa', k) \\
 &\quad \times \Gamma(k, k+q+\kappa''), \quad (9)
 \end{aligned}$$

where $\Gamma(k, k+q+\kappa'')$ includes all those subdiagrams which begin with a vertex of types A or C and end with two external electron lines $k, k+q+\kappa''$; those subdiagrams which can be split into two parts by cutting a single phonon or Coulomb interaction line are to be excluded. Some low-order contributions to Γ , including an exchange term, are shown in Fig. 2(b). We can rewrite Eq. (9) in a convenient form if we note that many of the terms in Γ , such as the last two of Fig. 2(b), involve electron self-energy contributions. Equation (9) then becomes

$$\begin{aligned}
 -i\pi_1(q; \kappa, \kappa') &= 2 \sum_{\kappa''} \int \frac{d^4k}{(2\pi)^4} G(k) G(k+q+\kappa'') \\
 &\quad \times B_{q+\kappa''}^*(\kappa''-\kappa, k) B_{q+\kappa''}(\kappa''-\kappa', k) \bar{\Gamma}(k, k+q+\kappa''),
 \end{aligned}$$

where the proper vertex part $\bar{\Gamma}$ does not include the self-energy contributions to the two propagators and $G(k), G(k+q+\kappa'')$ are the dressed electron propagators. We note that the very useful relations

$$\begin{aligned}
 \phi_2(q, \kappa) &= \sum_{\kappa'} A(q, \kappa') \phi_1(q; \kappa, \kappa'), \\
 \phi_3(q) &= \sum_{\kappa, \kappa'} A^*(q, \kappa) A(q, \kappa') \phi_1(q; \kappa, \kappa') \quad (10)
 \end{aligned}$$

remain valid when we consider the more general subdiagrams. We also note that

$$\pi_1(q; \kappa, \kappa') = \pi_1^*(q; \kappa', \kappa), \quad \phi_1(q; \kappa, \kappa') = \phi_1^*(q; \kappa', \kappa)$$

if Γ is real.

A. Dielectric-Screening Tensor and Effective Electron-Phonon Interaction

The inverse dielectric-screening tensor is defined by the relation between the "bare" and "screened"

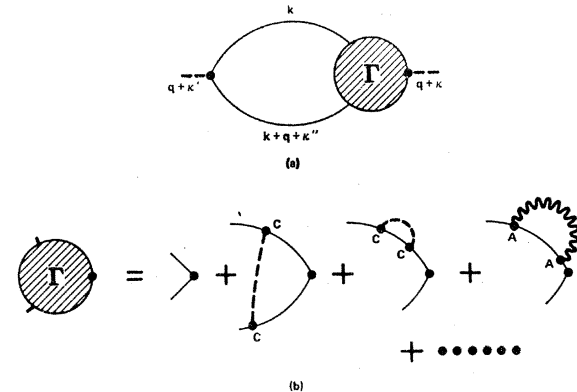


FIG. 2. The full polarization part.

Coulomb interaction between a test charge and an "external" potential:

$$\mathcal{V}_{q+\kappa}^{(so)} = \sum_{\kappa'} \mathcal{K}_{\kappa\kappa'}(q) \mathcal{V}_{q+\kappa'}^{(0)}.$$

Now the full inverse dielectric-screening tensor $\mathcal{K}_{\kappa\kappa'}(q)$ includes the effect of lattice polarization as well as the effect of polarization of the electrons. In other words, the diagrammatic equation for $\mathcal{K}_{\kappa\kappa'}(q)$ includes phonon lines as well as Coulomb lines. However, as will become evident later, we shall actually be interested only in a "reduced" inverse screening function $\mathcal{K}_{\kappa\kappa'}(q)$, where those diagrams which can be disconnected by cutting a single phonon line are excluded.¹¹ If we put $\Gamma=1$, this becomes the screening function which has been considered by Falk¹² within the Hartree approximation and by Penn¹³ for semiconductors. If the off-diagonal elements are negligible, as in the electron-gas case, we have

$$\mathcal{K}_{\kappa\kappa}(q) = [\epsilon(q+\kappa)]^{-1}, \quad \mathcal{V}_Q^{(so)} = \mathcal{V}_Q^{(0)}/\epsilon(Q),$$

which are familiar results. In the general case, however, we must consider the off-diagonal elements also.

The diagonal contribution $\mathcal{K}_{\kappa\kappa}(q)v_{q+\kappa}$ is given by the diagrammatic equation of Fig. 3(a), which is

$$\mathcal{K}_{\kappa\kappa}(q)v_{q+\kappa} = v_{q+\kappa} - v_{q+\kappa} \sum_{\kappa''} \mathcal{K}_{\kappa\kappa''}(q) |v_{q+\kappa''}|^2 \pi_1(q; \kappa'', \kappa)$$

if only linear-response diagrams are retained.

The off-diagonal contribution is given by the equation of Fig. 3(b) or

$$\mathcal{K}_{\kappa\kappa'}(q)v_{q+\kappa'} = -v_{q+\kappa'} \sum_{\kappa''} \mathcal{K}_{\kappa\kappa''}(q) |v_{q+\kappa''}|^2 \pi_1(q; \kappa'', \kappa') \quad (\kappa \neq \kappa').$$

Thus, we have the set of equations

$$\begin{aligned} \mathcal{K}_{\kappa\kappa'} &= \delta_{\kappa\kappa'} - \sum_{\kappa''} \mathcal{K}_{\kappa\kappa''}(q) |v_{q+\kappa''}|^2 \pi_1(q; \kappa'', \kappa') \\ &= \delta_{\kappa\kappa'} - \sum_{\kappa''} \mathcal{K}_{\kappa\kappa''}(q) \frac{|v_{q+\kappa''}|}{|v_{q+\kappa'}|} \phi_1(q; \kappa'', \kappa') \end{aligned} \quad (11)$$

for the reduced inverse screening tensor. These equations are a generalization of Eq. (29) of Falk's article,¹² where $\phi_1^{(0)}$ is treated within the Hartree approximation. They are actually equivalent to a double Fourier transform of Eq. (6.62) of Martin and Schwinger¹⁴ in the case of a periodic structure.

If we rewrite $|v_{q+\kappa'}|^2 \pi_1(q; \kappa'', \kappa')$ as $P_{\kappa''\kappa'}(q)$, we note that the reduced screening tensor is

$$\mathbf{K}^{-1}(q) = \boldsymbol{\epsilon}(q) = \mathbf{1} + \mathbf{P}(q).$$

¹¹ Such diagrams are excluded so that the phonon self-energy (see Sec. III B) is proper; their exclusion corresponds to considering only the electron polarization.

¹² D. S. Falk, Phys. Rev. **118**, 105 (1960). The properties of the inverse dielectric-screening function have also been discussed in Ref. 14, below, and by S. L. Adler [Phys. Rev. **126**, 413 (1962)] and N. Wiser [Phys. Rev. **129**, 62 (1963)].

¹³ D. R. Penn, Phys. Rev. **128**, 2093 (1963).

¹⁴ P. C. Martin and J. Schwinger, Phys. Rev. **115**, 1342 (1959).

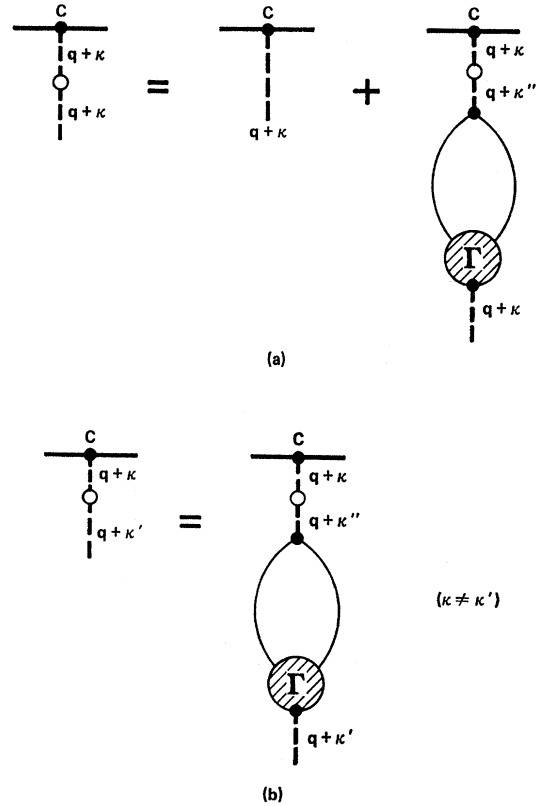


FIG. 3. The screening equations.

In the case of the electron gas, the off-diagonal elements vanish and we have the familiar result

$$\epsilon(Q) = 1 + \phi_1(q; \kappa, \kappa) = 1 + |v_Q|^2 \pi'(Q),$$

where

$$Q = q + \kappa, \quad \pi'(Q) = \pi_1(q; \kappa, \kappa).$$

It is convenient for the remainder of this article to define a new tensor

$$S_{\kappa\kappa'}(q) = [|\mathbf{q} + \boldsymbol{\kappa}| / |\mathbf{q} + \boldsymbol{\kappa}'|] \mathcal{K}_{\kappa\kappa'}(q), \quad (12)$$

so that Eq. (11) becomes

$$S_{\kappa\kappa'}(q) = \delta_{\kappa\kappa'} - \sum_{\kappa''} S_{\kappa\kappa''}(q) \phi_1(q; \kappa'', \kappa'). \quad (13)$$

This tensor has the advantage of being Hermitian if Γ is real, whereas $\mathcal{K}_{\kappa\kappa'}(q)$ does not have this property. Because of its Hermiticity, the treatment of screening can be carried out in a more elegant manner if we use $S_{\kappa\kappa'}$ instead of $\mathcal{K}_{\kappa\kappa'}$; we can readily rewrite our results in terms of the more familiar $\mathcal{K}_{\kappa\kappa'}$ at the end. It is readily seen that the diagonal elements are equal:

$$S_{\kappa\kappa}(q) = \mathcal{K}_{\kappa\kappa}(q).$$

We now turn our attention to the effect of polarization on the electron-phonon interaction. As we might expect, the problem of calculating the screened electron-phonon interaction is very similar to the

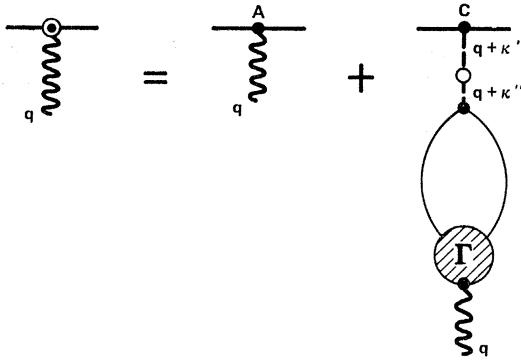


FIG. 4. The screened electron-phonon interaction, without vertex corrections.

previous problem of the screened Coulomb interaction. The screened electron-phonon interaction without the vertex correction is given by the diagrammatic equation of Fig. 4, which is

$$\bar{U}_{q+\kappa}(k) = U_{q+\kappa} - \sum_{\kappa', \kappa''} \phi_2(q, \kappa'') S_{\kappa', \kappa''}(q) B_{q+\kappa}(\kappa - \kappa', k) v_{q+\kappa'}.$$

On comparing this with Eq. (6) we have

$$\bar{U}_{q+\kappa}(k) = \sum_{\kappa'} \bar{A}(q; \kappa') B_{q+\kappa}(\kappa - \kappa', k) v_{q+\kappa'},$$

where

$$\begin{aligned} \bar{A}(q; \kappa') &= A(q; \kappa') - \sum_{\kappa''} S_{\kappa', \kappa''} \phi_2(q, \kappa'') \\ &= \sum_{\kappa} S_{\kappa', \kappa}(q) A(q; \kappa) \end{aligned}$$

if we use Eqs. (10) and (13).

As we must expect, this result reduces to the electron-phonon gas result^{5,9} when $S_{\kappa', \kappa}$ is diagonal (and thus $S_{\kappa\kappa} = \mathcal{K}_{\kappa\kappa}$):

$$\bar{A}(q, \kappa) = A(q, \kappa) \mathcal{K}_{\kappa\kappa}(q) = A(q, \kappa) / \epsilon(q + \kappa).$$

The inclusion of vertex corrections to the electron-phonon interaction is trivially accomplished by replacing the simple vertices at the top of each of the diagrams of Fig. 4 by the proper vertex part $\bar{\Gamma}$. In other words,

$$B_{q+\kappa}(\kappa - \kappa', k) \rightarrow \bar{\Gamma}(k, k + q + \kappa) B_{q+\kappa}(\kappa - \kappa', k)$$

and

$$U_{q+\kappa}(k) \rightarrow \bar{U}_{q+\kappa}(k) \bar{\Gamma}(k, k + q + \kappa).$$

It is worth noting that the upper part of the last diagram of Fig. 4 (if we cut across the loop) is just the electron-hole scattering kernel, proper with respect to phonon lines.

B. Dressed Phonon Spectrum

The calculation of the dressed phonon propagator $D(q)$, whose poles give the dressed phonon excitation spectrum, requires the summation of all diagrams

which begin and end with the same bare-phonon propagator $D_0(q)$. This series is conveniently summed by means of the Dyson procedure, whence we obtain the diagrammatic equation shown in Fig. 5, where the third and fourth terms arise from the $H_{ep}^{(2)}$ interaction and the double wavy line represents the dressed phonon propagator. The last term is just the lowest-order contribution f_H from the harmonic part of $f(R_{rs})$. The Dyson equation represented by Fig. 5 is

$$D(q) = D_0(q) + D_0(q) \Pi(q) D(q), \quad (14)$$

where

$$\Pi(q) = -\phi_3(q) + \sum_{\kappa, \kappa'} S_{\kappa', \kappa}(q) \phi_2^*(q, \kappa') \phi_2(q, \kappa) + \Pi' - f_H \quad (15)$$

if

$$\begin{aligned} \Pi'(q) &= 2 \sum_{\kappa, \kappa', \kappa''} L_{q\kappa}(\kappa) \pi_1(0, \kappa, \kappa') S_{\kappa', \kappa''}(0) |v_{\kappa'}| |v_{\kappa''}| \\ &\times \int \frac{d^3k}{(2\pi)^3} n_k B_0(-\kappa'', k) \\ &- 2 \sum_{\kappa} L_{q\kappa}(\kappa) \int \frac{d^3k}{(2\pi)^3} n_k B_0(-\kappa, k). \end{aligned}$$

The quantity n_k is unity for occupied states and zero for unoccupied states. It will be noted that we have neglected certain contributions to the proper self-energy Π which are of higher order in the phonon field amplitudes and represent anharmonic contributions. Equation (15) can be simplified by the use of Eqs. (10), (11), and (13):

$$\Pi(q) = \sum_{\kappa, \kappa'} A^*(q, \kappa) A(q, \kappa') [S_{\kappa\kappa'}(q) - \delta_{\kappa\kappa'}] + \Pi' - f_H,$$

while Π' , the term which corrects for the action of a nucleus on itself, reduces to

$$\Pi' = -2 \sum_{\kappa, \kappa'} L_{q\kappa}(\kappa) \mathcal{K}_{\kappa\kappa}^*(0) \int \frac{d^3k}{(2\pi)^3} n_k B_0(-\kappa', k),$$

with the help of Eqs. (12) and (13).

It is worth noting that $\Pi(q)$ may also be calculated by using the effective electron-phonon interaction evaluated earlier. In other words, we should

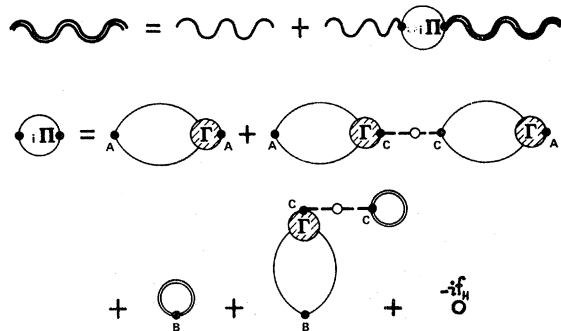


FIG. 5. The dressed phonon propagator.

obtain $\Pi(q)$ if we drop the second term in Fig. 5 and replace the bare electron-phonon interaction vertex on the right of the first diagram by the screened interaction vertex [i.e., in which $A(q, \kappa) \rightarrow \bar{A}(q, \kappa)$]. One can readily show that the same result for Π is obtained from this approach when Eqs. (10), (11), and (13) are used.

The Dyson equation (14) can be rearranged to

$$D^{-1}(q) = D_0^{-1}(q) - \Pi(q)$$

and, since the dressed phonon propagator has poles at the dressed phonon excitation frequencies, the phonon spectrum is given by the solutions of

$$\omega^2 = \Omega_q^2 + 2\Omega_q \Pi(q). \quad (16)$$

Now the zero-order phonon spectrum is given by

$$\Omega_q^2 = 2\Omega_q \sum_{\kappa} |A(q, \kappa)|^2 - (4\pi/V_A) \sum_{n, n', \kappa} Z_n Z_{n'} |\mathbf{u}_n \cdot [\boldsymbol{\kappa}]|^2 \exp(i\boldsymbol{\kappa} \cdot \mathbf{x}_{nn'}) + 2\Omega_q f_H,$$

where $\mathbf{u}_n = \mathbf{e}_q^n M_n^{-1/2}$ and $[\boldsymbol{\kappa}] \equiv [\mathbf{q}]$ when $\boldsymbol{\kappa} = 0$ and we have allowed the background to move so as to cancel the macroscopic charge density of the nuclei. Thus, Eq. (16) becomes

$$\omega^2 = (4\pi/V_A) \sum_{n, n'} Z_n Z_{n'} \sum_{\kappa, \kappa'} \exp[i(\boldsymbol{\kappa}' \cdot \mathbf{x}_{n'} - \boldsymbol{\kappa} \cdot \mathbf{x}_n)] \times (\mathbf{u}_n \cdot [\mathbf{q} + \boldsymbol{\kappa}']) (\mathbf{u}_{n'} \cdot [\mathbf{q} + \boldsymbol{\kappa}']) S_{\kappa'\kappa}(\mathbf{q}, \omega) + C(\mathbf{q}, \omega),$$

where

$$C(\mathbf{q}, \omega) = 2\Omega_q \Pi' - (4\pi/V_A) \sum_{n, n', \kappa} Z_n Z_{n'} \times \exp(i\boldsymbol{\kappa} \cdot \mathbf{x}_{nn'}) |\mathbf{u}_n \cdot [\boldsymbol{\kappa}]|^2.$$

This is actually the term which cancels out the divergent self-interaction part and also ensures that ω^2 goes to zero for acoustic modes as $\mathbf{q} \rightarrow 0$.¹⁵ In the present article, we show explicitly that this cancellation does in fact occur, a demonstration which has so far been carried out only for the special case of the diamond structure and the Hartree approximation.¹⁶ In the Appendix, we derive a new identity

$$\lim_{\mathbf{q}, \omega \rightarrow 0} \left\{ \sum_{n, \kappa'} Z_n \exp(i\boldsymbol{\kappa}' \cdot \mathbf{x}_n) [\boldsymbol{\kappa}' + \mathbf{q}] [S_{\kappa'\kappa}(\mathbf{q}, \omega) - \delta_{\kappa'\kappa}] + [\boldsymbol{\kappa}' + \mathbf{q}] \sum_{\kappa'} \mathcal{K}_{\kappa'\kappa}(\mathbf{q}, \omega) \int \frac{d^3k}{(2\pi)^3} n_{\mathbf{k}} B_0(+\boldsymbol{\kappa}', \mathbf{k}) \right\} = 0, \quad (17)$$

¹⁵ This limit $\mathbf{q} \rightarrow 0$ is not strictly valid in polyatomic crystals for optical modes. We have used an unretarded Coulomb interaction which is only valid for $|\mathbf{q}| \gg \omega_0/c$, where ω_0 is the optical phonon frequency and c is the velocity of light. Thus, the limit $\mathbf{q} \rightarrow 0$ must be interpreted as $qa \ll 1$ but $qc \gg \omega_0$, where a is the lattice constant. Because $\omega_0 a/c$ is very small (10^{-4} – 10^{-5}), the inequalities are consistent and the limit $\mathbf{q} \rightarrow 0$ is to be interpreted in this way everywhere in this article. A rigorous calculation would include retardation and thus use photon propagators; however, the optical phonon quasiparticle concept breaks down for $|\mathbf{q}| \sim \omega_0/c$, as discussed classically by K. Huang [Proc. Roy. Soc. (London) A208, 352 (1951)].

¹⁶ A. A. Maradudin (to be published).

which allows the divergence to be subtracted out, and thereby show that

$$\omega^2 = (4\pi/V_A) \sum_{n, n'} Z_n Z_{n'} \sum_{\kappa, \kappa'} \exp[i(\boldsymbol{\kappa}' \cdot \mathbf{x}_{n'} - \boldsymbol{\kappa} \cdot \mathbf{x}_n)] \times \{ S_{\kappa'\kappa}(\mathbf{q}, \omega) (\mathbf{u}_n \cdot [\mathbf{q} + \boldsymbol{\kappa}']) (\mathbf{u}_{n'} \cdot [\mathbf{q} + \boldsymbol{\kappa}']) - S_{\kappa'\kappa}(0) (\mathbf{u}_n \cdot [\boldsymbol{\kappa}']) (\mathbf{u}_{n'} \cdot [\boldsymbol{\kappa}']) \}, \quad (18)$$

where¹⁷ $S_{\kappa'\kappa}(0) = \lim_{\mathbf{q}, \omega \rightarrow 0} S_{\kappa'\kappa}(\mathbf{q}, \omega)$ and $[\boldsymbol{\kappa}'] = \lim_{\mathbf{q} \rightarrow 0} [\mathbf{q} + \boldsymbol{\kappa}']$.

Thus, the phonon excitation spectrum, within the harmonic approximation and for $|\mathbf{q}| \gg \omega_0/c$,¹⁵ is given by Eq. (18) and, because of the orthogonality of the \mathbf{e}_q^n ,⁷ is also given as the solution of

$$\omega^2 \mathbf{e}_q^n = \sum_{n'} \mathbf{D}_{nn'}(\mathbf{q}, \omega) \cdot \mathbf{e}_q^{n'}, \quad (19)$$

where

$$\mathbf{D}_{nn'}(\mathbf{q}, \omega) = \mathbf{A}_{nn'}(\mathbf{q}, \omega) - \delta_{nn'} \sum_m (M_m/M_n)^{1/2} \mathbf{A}_{nm}(0)$$

and

$$\mathbf{A}_{nn'}(\mathbf{q}, \omega) = \frac{4\pi}{V_A} Z_n Z_{n'} \sum_{\kappa, \kappa'} \exp[i(\boldsymbol{\kappa}' \cdot \mathbf{x}_{n'} - \boldsymbol{\kappa} \cdot \mathbf{x}_n)] \times S_{\kappa'\kappa}(\mathbf{q}, \omega) \frac{[\mathbf{q} + \boldsymbol{\kappa}'] [\mathbf{q} + \boldsymbol{\kappa}']}{(M_n M_{n'})^{1/2}}.$$

It is necessary to reemphasize that the tensor $S_{\kappa'\kappa}$ appearing in these expressions is related to that inverse screening tensor which does not include *direct* phonon contributions (i.e., lattice polarization) but does include the phonon exchange contributions to the electron self-energy. In other words, the calculation of $\mathcal{K}_{\kappa'\kappa}$ must exclude those diagrams which can be cut by cutting only a phonon line [otherwise $\Pi(q)$ is not the proper phonon self-energy] but the electron propagators used must be the dressed propagators, i.e., dressed by phonon exchange effects as well as the other interactions, and vertex corrections should be included. In this case, the linear-screening approach to the lattice dynamics of covalent crystals is rigorous and the additional terms noted by Phillips³ are included and his doubts³ are no longer appropriate.

It should also be noted that ω^2 will, in general, be complex and Eqs. (18) and (19) must be solved for both real and imaginary parts. The Born-Oppenheimer adiabatic approximation corresponds to the neglect of any ω dependence in the real part of $S_{\kappa'\kappa}(\mathbf{q}, \omega)$.

IV. DISCUSSION OF RESULTS

It is of interest to investigate the formal expression (18) for ω^2 in the limit of the "monatomic" electron-phonon gas, which is frequently used as a first approximation to an alkali metal.^{5,9} For a mon-

¹⁷ It should be noted that this limit does not strictly exist and $S_{\kappa'\kappa}(0)$ depends on \mathbf{q} .

atomic crystal, Eq. (18) reduces to

$$\omega^2 = \frac{4\pi Z^2}{MV_A} \sum_{\kappa\kappa'} \{ (\mathbf{e} \cdot [\mathbf{q} + \boldsymbol{\kappa}]) (\mathbf{e}^* \cdot [\mathbf{q} + \boldsymbol{\kappa}']) S_{\kappa'\kappa}(\mathbf{q}, \omega) - (\mathbf{e} \cdot [\boldsymbol{\kappa}]) (\mathbf{e}^* \cdot [\boldsymbol{\kappa}']) S_{\kappa'\kappa}(0) \},$$

where, for $\boldsymbol{\kappa} \equiv 0$, $\mathbf{e} \cdot [\boldsymbol{\kappa}]$ is understood to be $\mathbf{e} \cdot [\mathbf{q}]$. If we neglect the off-diagonal components of $\mathcal{K}_{\kappa\kappa'}$ (i.e., the umklapp contributions to the screening) and note that, for an electron-phonon gas (and any normal metal), $\epsilon^{-1}(0) = 0$, we obtain

$$\omega^2 = \frac{4\pi Z^2}{MV_A} \left\{ \frac{|\mathbf{e} \cdot [\mathbf{q}]|^2}{\epsilon(\mathbf{q}, \omega)} + \sum_{\kappa \neq 0} \left[\frac{|\mathbf{e} \cdot [\mathbf{q} + \boldsymbol{\kappa}]|^2}{\epsilon(\mathbf{q} + \boldsymbol{\kappa}, \omega)} - \frac{|\mathbf{e} \cdot [\boldsymbol{\kappa}]|^2}{\epsilon(\boldsymbol{\kappa}, 0)} \right] \right\}.$$

This is to be contrasted with the existing expression^{5,9} for an electron-phonon gas:

$$\omega^2 = \Omega_q^2 / \epsilon(\mathbf{q}, \omega) = (4\pi Z^2 / MV_A) [\epsilon(\mathbf{q}, \omega)]^{-1} \times \{ |\mathbf{e} \cdot [\mathbf{q}]|^2 + \sum_{\kappa \neq 0} [|\mathbf{e} \cdot [\boldsymbol{\kappa} + \mathbf{q}]|^2 - |\mathbf{e} \cdot [\boldsymbol{\kappa}]|^2] \},$$

which is obtained by ignoring the periodicity of the lattice completely.^{5,9} This is not a physically meaningful procedure because the periodic structure is a necessary consequence of the presence of nuclei, which necessarily accompanies the existence of phonons.

It is also interesting to compare our results (in the special case of a monatomic metal) with the results of Vosko *et al.*¹ In the case of a monatomic metal in the adiabatic approximation, the real part of Eq. (18) reduces to

$$\text{Re}\omega_q^2 = \frac{4\pi Z^2}{MV_A} \{ |\mathbf{e} \cdot [\mathbf{q}]|^2 S_{00}(\mathbf{q}) + \sum'_{\kappa, \kappa'} [(\mathbf{e} \cdot [\mathbf{q} + \boldsymbol{\kappa}]) (\mathbf{e}^* \cdot [\mathbf{q} + \boldsymbol{\kappa}']) S_{\kappa'\kappa}^{(\text{Re})}(\mathbf{q}) - (\mathbf{e} \cdot [\boldsymbol{\kappa}]) (\mathbf{e}^* \cdot [\boldsymbol{\kappa}']) S_{\kappa'\kappa}^{(\text{Re})}(0)] \}.$$

Vosko *et al.*¹ obtained an expression for a monatomic metal of the form

$$\omega_q^2 = \frac{4\pi Z_0^2}{MV_A} \sum_{\kappa} \{ |\mathbf{e} \cdot [\mathbf{q} + \boldsymbol{\kappa}]|^2 [1 - F(\mathbf{q} + \boldsymbol{\kappa})] - |\mathbf{e} \cdot [\boldsymbol{\kappa}]|^2 [1 - F(\boldsymbol{\kappa})] \}$$

[where Z_0 is the charge on the ion with the valence electrons removed and where $F(0) = 1$] from a theory based on the adiabatic approximation. Thus,

$$Z_0^2 [\mathbf{e}^* \cdot [\mathbf{q} + \boldsymbol{\kappa}]] [1 - F(\mathbf{q} + \boldsymbol{\kappa})]$$

is to be identified with

$$Z^2 \sum_{\kappa'} \mathbf{e}^* \cdot [\mathbf{q} + \boldsymbol{\kappa}'] S_{\kappa'\kappa}(\mathbf{q})$$

or, if one assumes that the off-diagonal contributions from $\mathcal{K}_{\kappa\kappa'}$ can be neglected, as suggested by Phillips,¹⁸ we have the identification

$$Z_0^2 F(\mathbf{q} + \boldsymbol{\kappa}) \equiv Z_0^2 - Z^2 \mathcal{K}_{\kappa\kappa}(\mathbf{q}) = [Z_0^2 \epsilon(\mathbf{q} + \boldsymbol{\kappa}) - Z^2] / \epsilon(\mathbf{q} + \boldsymbol{\kappa}).$$

However, although the off-diagonal contributions are likely to be small, their contribution may not be negligible because of the sum over $\boldsymbol{\kappa}'$. Furthermore, Phillips's pseudopotential argument¹⁸ for the smallness of the off-diagonal elements is reasonable for the valence electrons but becomes less valid for the core-electron contribution to the screening, of course.

We can, however, reduce the problem to the evaluation of the response of the valence electrons only, by making the common approximation that the core electrons form nonoverlapping spherically symmetric charge clouds. In this case, the integral over $\int d^3k / (2\pi)^3$ which arises in calculating the screening tensor is reduced to an integral only over \mathbf{k} values corresponding to the valence Brillouin zone. The remaining Brillouin-zone contributions to the screening are approximated by assuming that the core charge clouds move completely with the nucleus. In this approximation, Eq. (18) retains its form but Z is replaced by Z_0 and the full screening tensor $\mathcal{K}_{\kappa'\kappa}(\mathbf{q})$ is replaced by the screening due only to the valence electrons. This would normally be calculated by means of a pseudopotential approach. In this approximation, the problem becomes exactly that considered by Vosko *et al.*,¹ for example, as discussed above. The approximation might be improved, if necessary, by the inclusion of small core-polarization effects of a simple dipole nature to take account of the fact that the core electrons will not follow the nuclei completely.

In the case of nonmetallic crystals, where, invariably, $\hbar\omega_0$ is very much less than Δ , the average direct gap between conduction and valence bands, the inverse screening tensor becomes essentially independent of ω and is real in the range of interest.¹³ This is just a demonstration of the validity of the Born-Oppenheimer approximation for nonmetallic crystals. In this case, the solution of Eq. (18) for ω^2 becomes trivial. The reality of ω^2 for nonmetallic crystals in the phonon frequency range implies that there is no ultrasonic attenuation in the absence of anharmonic interactions and impurities. On the other hand, in metals $S_{\kappa'\kappa}$ is complex and there is the possibility of ultrasonic attenuation via scattering from the electrons near the Fermi surface.¹⁰ We note from

¹⁸ J. C. Phillips, *Phys. Rev.* **123**, 420 (1961).

Eq. (18) the close relationship between the imaginary part of ω^2 and the imaginary part of the screening function, which has already been established from a somewhat different point of view in Migdal's work,¹⁰ for example. In fact, as our results show, there is a very close basic relationship between the lattice dynamical and dielectric properties of a solid.

We have shown that linear-screening theory can be applied to the problem of the harmonic phonon spectra of nonmetallic crystals if the correct inverse screening tensor is used. The arguments used by Migdal¹⁰ to show that $\tilde{\Gamma} \simeq 1$ to within terms of order $(m/M)^{1/2}$ for metals appear to be generalizable to nonmetals also and, in this case, the phonon proper vertex corrections may be dropped. However, the self-energy part of Γ cannot be dropped because there can be an important contribution from that part of the self-energy of the electrons due to the exchange of phonons with frequency and wave vector close to that of the phonon connecting the polarization bubbles. This contribution is actually the contribution noted by Phillips³ as due to the change in energy gap produced by the lattice vibrations and which caused his doubts³ regarding linear-screening theory. We see that these doubts can be put to rest by noting that dressed electron propagators are to be used in calculating the inverse screening tensor (i.e., dressed with phonon exchange contributions, also).

Note added in proof. We have recently become aware of work by R. Pick, M. H. Cohen, and R. M. Martin (to be published), who have independently derived essentially Eq. (18) of this work within the adiabatic approximation.

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APPENDIX

We consider the potential in a crystal in which an infinitesimally small, very-long-wavelength periodic displacement of the nuclei is present. This device allows us to avoid difficulties with translational invariance but gives an electron and nucleus distribution which is essentially undisturbed. The "bare" potential due to the nuclei is

$$V_0(\mathbf{r}, t) = \lim_{\mathbf{q}, \omega \rightarrow 0} \sum_{n, \kappa} \frac{4\pi Z_n}{V_A(\boldsymbol{\kappa} + \mathbf{q})^2} \times \exp(-i\boldsymbol{\kappa} \cdot \mathbf{x}_n) \exp\{i[(\boldsymbol{\kappa} + \mathbf{q}) \cdot \mathbf{r} - \omega t]\}.$$

If we subtract this from the screened potential it

generates, we have

$$V_e(\mathbf{r}, t) = \lim_{\mathbf{q}, \omega \rightarrow 0} \sum_{n, \kappa, \kappa'} \frac{4\pi Z_n}{V_A(\boldsymbol{\kappa} + \mathbf{q})^2} [\mathcal{K}_{\kappa'\kappa}(\mathbf{q}, \omega) - \delta_{\kappa'\kappa}] \times \exp(-i\boldsymbol{\kappa} \cdot \mathbf{x}_n) \exp\{i[(\boldsymbol{\kappa}' + \mathbf{q}) \cdot \mathbf{r} - \omega t]\},$$

which is just the contribution provided by the electrons, of course. The change from this value when we consider the nuclei displaced by a finite amount $\mathbf{u} \exp\{i[\mathbf{q} \cdot \mathbf{x}_n(t) - \omega t]\}$, where \mathbf{q}, ω are again small, is

$$\delta V_e(\mathbf{r}, t) = \lim_{\mathbf{q}, \omega \rightarrow 0} \sum_{n, \kappa, \kappa'} \frac{4\pi i Z_n}{V_A} \frac{[(\boldsymbol{\kappa} + \mathbf{q}) \cdot \mathbf{u}]}{|\boldsymbol{\kappa}' + \mathbf{q}|} \times \exp(-i\boldsymbol{\kappa} \cdot \mathbf{x}_n) [\mathcal{S}_{\kappa'\kappa}(\mathbf{q}, \omega) - \delta_{\kappa'\kappa}] \times \exp\{i[(\boldsymbol{\kappa}' + \mathbf{q}) \cdot \mathbf{r} - \omega t]\}, \quad (\text{A1})$$

where we have used Eq. (12).

We now calculate this electronic contribution explicitly. In the system with infinitesimally small nuclear displacements, the electron density is

$$\rho(\mathbf{r}, t) = \lim_{\mathbf{q}, \omega \rightarrow 0} V_A^{-1} \sum_{\kappa} \exp\{i[(\boldsymbol{\kappa} + \mathbf{q}) \cdot \mathbf{r} - \omega t]\} \times \int \frac{d^3k}{(2\pi)^3} n_{\mathbf{k}} B_{\mathbf{q}}^*(\boldsymbol{\kappa}, \mathbf{k}),$$

which acts as an "external" source to set up the potential

$$V_e(\mathbf{r}, t) = \lim_{\mathbf{q}, \omega \rightarrow 0} \sum_{\kappa, \kappa'} \frac{-4\pi}{V_A(\boldsymbol{\kappa} + \mathbf{q})^2} \mathcal{K}_{\kappa'\kappa}(\mathbf{q}, \omega) \times \int \frac{d^3k}{(2\pi)^3} n_{\mathbf{k}} B_{\mathbf{q}}^*(\boldsymbol{\kappa}, \mathbf{k}) \exp\{i[(\boldsymbol{\kappa}' + \mathbf{q}) \cdot \mathbf{r} - \omega t]\}.$$

The change from this value when the electron distribution suffers a finite displacement $\mathbf{r} \rightarrow \mathbf{r} + \mathbf{u} \exp[i(\mathbf{q} \cdot \mathbf{r} - \omega t)]$ is

$$\delta V_e(\mathbf{r}, t) = \lim_{\mathbf{q}, \omega \rightarrow 0} \sum_{\kappa, \kappa'} \frac{-4\pi i}{V_A} \frac{[(\boldsymbol{\kappa}' + \mathbf{q}) \cdot \mathbf{u}]}{|\boldsymbol{\kappa} + \mathbf{q}|} \mathcal{S}_{\kappa'\kappa}(\mathbf{q}, \omega) \times \int \frac{d^3k}{(2\pi)^3} n_{\mathbf{k}} B_{\mathbf{q}}^*(\boldsymbol{\kappa}, \mathbf{k}) \exp\{i[(\boldsymbol{\kappa}' + \mathbf{q}) \cdot \mathbf{r} - \omega t]\},$$

since changes in $B_{\mathbf{q}}(\boldsymbol{\kappa}, \mathbf{k})$ are of higher order in \mathbf{q} . If we recall the Hermitian nature of $\mathcal{S}_{\kappa'\kappa}$ and use Eq. (12) again, we obtain

$$\delta V_e(\mathbf{r}, t) = \lim_{\mathbf{q}, \omega \rightarrow 0} \sum_{\kappa, \kappa'} \frac{-4\pi i}{V_A} \frac{[(\boldsymbol{\kappa}' + \mathbf{q}) \cdot \mathbf{u}]}{|\boldsymbol{\kappa}' + \mathbf{q}|} \mathcal{K}_{\kappa\kappa'}^*(\mathbf{q}, \omega) \times \int \frac{d^3k}{(2\pi)^3} n_{\mathbf{k}} B_{\mathbf{q}}^*(\boldsymbol{\kappa}, \mathbf{k}) \exp\{i[(\boldsymbol{\kappa}' + \mathbf{q}) \cdot \mathbf{r} - \omega t]\}. \quad (\text{A2})$$

We now equate expressions (A1) and (A2) for the electron contribution, make an interchange $\boldsymbol{\kappa} \leftrightarrow \boldsymbol{\kappa}'$, and take the complex conjugate to obtain the identity given as Eq. (17) in the main text.

We continue by calculating $C(\mathbf{q}, \omega)$, which is

$$C = \lim_{\mathbf{q}, \omega \rightarrow 0} \frac{4\pi}{V_A} \left\{ \sum_{\kappa, \kappa'} \mathcal{K}_{\kappa' \kappa}^*(\mathbf{q}, \omega) \int \frac{d^3k}{(2\pi)^3} n_{\mathbf{k}} B_{\mathbf{q}}(-\kappa', \mathbf{k}) \right. \\ \times \sum_n Z_n \exp(-i\kappa \cdot \mathbf{x}_n) | \mathbf{u}_n \cdot [\mathbf{k} + \mathbf{q}]|^2 \\ \left. - \sum_{n, n'} Z_n Z_{n'} \exp(-i\kappa \cdot \mathbf{x}_{nn'}) | \mathbf{u}_n \cdot [\mathbf{k} + \mathbf{q}]|^2 \right\}.$$

With the help of Eq. (17), this can be rewritten as

$$C = - \lim_{\mathbf{q}, \omega \rightarrow 0} \frac{4\pi}{V_A} \sum_{n, n'} Z_n Z_{n'} \sum_{\kappa, \kappa'} \exp[i(\kappa' \cdot \mathbf{x}_{n'} - \kappa \cdot \mathbf{x}_n)] \\ \times S_{\kappa' \kappa}(\mathbf{q}, \omega) (\mathbf{u}_n \cdot [\mathbf{q} + \kappa]) (\mathbf{u}_{n'} \cdot [\mathbf{q} + \kappa']),$$

so that we obtain Eq. (18) of the main text, and $\omega^2 \rightarrow 0$ in the $\mathbf{q} \rightarrow 0$ limit for those modes (i.e., the acoustic modes) for which \mathbf{u}_n becomes independent of n in this limit.

Long-Wavelength Optical Lattice Vibrations in Mixed KMgF_3 - KNiF_3 Crystals

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Infrared reflection and transmission data are analyzed to give the transverse and longitudinal phonons in mixed KNiF_3 - KMgF_3 crystals for seven concentrations ranging from 0 to 100% Ni. Both one- and two-mode behavior are observed. A point-ion model is developed patterned on earlier work on simpler mixed-crystal systems. The model assumes randomly distributed impurity ions and nearest-neighbor forces. The model gives good agreement with the observed mode frequencies, and in particular it fits the observed splitting of one of the reststrahlen bands at intermediate compositions.

I. INTRODUCTION

WELL-DEFINED infrared- and Raman-active phonon modes have been seen in several mixed-crystal systems of the type $A_y B_{1-y}$.¹⁻³ Near the ends of the composition range of a mixed crystal one ion can be viewed as an impurity and connections can be made with the theories of local modes and impurity resonance modes,¹ but for intermediate compositions no first-principles theories exist. The extra degrees of freedom resulting from the presence of the impurity can lead to two extremes of behavior that have been observed experimentally. These have been called one- and two-mode behavior.¹ A mixed crystal $A_{0.5} B_{0.5}$ that shows one-mode behavior typically has one strong phonon mode in its infrared spectrum occurring at a frequency intermediate to the relevant mode frequencies ω_A and ω_B of the pure crystals A and B . If $A_y B_{1-y}$ exhibits two-mode behavior, then $A_{0.5} B_{0.5}$ will have two strong modes whose frequencies are close to ω_A and ω_B . The present study of $\text{KNi}_y \text{Mg}_{1-y} \text{F}_3$ examines the infrared modes in a mixed perovskite that has three infrared-active modes at $y=0$ and at $y=1$. For intermediate y

two of these show one-mode behavior and one of these shows two-mode behavior. This is the first report of a systematic study of a system that simultaneously exhibits both kinds of behavior.

A simple model that includes effective charges and inter-ion force constants but neglects local-field effects is used to analyze the results. This model leads quite naturally to the behavior observed experimentally with a minimum number of special assumptions.

In Sec. II, the experimental methods and results are described. Section III presents the model of the long-wavelength lattice vibrations in the mixed crystal and the method for calculating the corresponding dielectric function for analysis of the optical properties. In Sec. IV, the model is compared with experiment and a discussion is given of the model parameters and normal modes.

II. EXPERIMENTAL METHODS AND RESULTS

A. Sample Preparation

The crystals were grown by a modified Stockbarger method in sealed platinum systems.⁴ Single crystals of KNiF_3 and KMgF_3 were used as starting material. These materials form solid solutions at all concentrations and single crystals $12 \times 12 \times 5$ mm were easily obtained.

¹ H. W. Verleur and A. S. Barker, Jr., *Phys. Rev.* **164**, 1169 (1967).

² I. F. Chang and S. S. Mitra, *Phys. Rev.* **172**, 924 (1968).

³ In addition to Refs. 1 and 2, review papers on mixed crystals appear in *Proceedings of International Conference on Localized Excitation in Solids*, edited by R. F. Wallis (Plenum Press, Inc., New York, 1968).

⁴ H. J. Guggenheim, *J. Phys. Chem.* **64**, 938 (1960).