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Electronic Contribution to Lattice Dynamics in Insulating Crystals*

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The electron contribution to the phonon spectrum is formulated in terms of the microscopic response function. The long-wavelength behavior of the lattice vibration is then investigated, with due attention to the long-range Coulomb interaction. An important quantity which emerges is the effective charge of the vibrating nuclei, which is shown to obey a sum rule. From this follows the existence of long-wavelength acoustic phonons. The infrared optical constants are also expressed in terms of the microscopic response function.

I. INTRODUCTION

It has been widely recognized that, in the lattice vibration of insulating crystals, the influence of the electronic motion is not negligible. Various models, such as the shell model and the deformation-dipole model, have been constructed to account for the electron contribution to the lattice dynamics. For references on these topics, see the paper by Sinha.[1] However, the values of the parameters in such models obtained by fitting to the experimental measurements do not agree with the physical interpretation of such parameters in some instances. Therefore, it is desirable to examine the role of electron dynamics in the lattice vibration from a more microscopic consideration. One approach is to write down first, in terms of electron response, its contribution to the lattice motion,[2–4] and then either to calculate the response in terms of the electronic band structure of the perfect crystal,[5] or to construct models more appropriate to the electron dynamics of the particular crystal, such as the covalent bond-charge model of Phillips[6] for the covalent crystals, or even to deduce the shell model from the microscopic basis.[1,4]

In this paper, we shall be concerned with the derivation of the long-wavelength behavior of the lattice vibration from the microscopic formulation of the lattice motion in terms of the ions and the response of the electrons.[2–4] It is of interest to see whether from this microscopic formulation follows the usual long-wavelength behavior,[7] such as the existence of acoustic modes (frequency proportional to wave vector), the Lyddane-Sachs-Teller relation for the optical modes,[8] and the appearance of the Szigeti charge in the infrared dielectric response.[9] The proof of these results is not as trivial as might appear at first sight because of the long-range Coulomb interaction between the particles in the insulating crystal. In a metal, the perfect screening of an ion by the conduction electrons renders the effective force between two ions to be short-ranged. It is then straightforward to see that there are acoustic modes with linear dispersion relation at long wavelength. For the point-ion model of an insulating crystal, the long-range interaction between the ions can be explicitly dealt with by the Edwald transformation and the long-wavelength behavior deduced.[7] With the inclusion of the electron response to the lattice vibration in an insulator which does not completely screen out the long-range Coulomb force between two ions, a careful investigation is needed. Indeed, Cohen *et al.*[10] were also aware of this problem but preferred to use the existence of the acoustic modes as the wave vector tends to impose certain conditions on the electron response in the insulator, which they called "sum rules." One of the results of this paper is a proof of such sum rules.

Another result of this study of the long-wavelength lattice vibrations is the formulas for the macroscopic optical constants (near infrared frequency) and the Szigeti charge (strictly speaking, the Born effective ion charge[11]) in terms of the microscopic quantities.

In Sec. II, the microscopic formulation of the dynamical matrix in terms of the electron response is included for the ease of following discussions. In Sec. III, an investigation of the small wave-vector limit of the formula for an insulator is given. Certain steps leading to the sum rule are more plausible arguments than rigorous, so as to make the physics involved easier to understand. A more rigorous proof is deferred to the Appendix. In Sec. IV, the results of Sec. III are utilized to express the macroscopic infrared optical properties in terms of microscopic quantities.

We shall restrict our consideration to normal insulators (as opposed to, say, excitonic insulators) for

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[2] L. J. Sham, Proc. Roy. Soc. (London) **A283**, 33 (1965).

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[9] B. Szigeti, Proc. Roy. Soc. (London) **A204**, 51 (1950).

[10] M. H. Cohen, R. M. Martin, and R. Pick, *Symposium on Inelastic Neutron Scattering* (International Atomic Energy Agency, Vienna, 1968), Vol. **1**, p. 119. *Note added in proof.* The same authors have given a proof of the sum rule similar to ours given here [Phys. Rev. (to be published)].

[11] M. Hass, *Physics of III-V Compounds*, edited by R. K. Willardson and A. C. Beer (Academic Press Inc., New York, 1967), Vol. 3, Chap. 1.

which the dielectric properties derived by perturbation theory of the electron-electron interaction[12] are valid. An interesting extension of this work is to the lattice dynamics of crystals with touching conduction and valence bands, such as grey tin,[13] which possess unusual dielectric properties.[14] In spite of the different dielectric properties, Sherrington[15] has been able to show the existence of the usual acoustic modes in grey tin using the method developed here.

II. DYNAMICAL MATRIX

Let the equilibrium lattice vectors be $\mathbf{x}_l$ and the equilibrium nucleus positions be $\mathbf{x}_{lk}=\mathbf{x}_l+\mathbf{x}_k$. Let the lk nucleus have charge $Z_k e$ and mass M_k, and let its displacement from equilibrium be denoted by $\mathbf{U}_{lk}$.

In the adiabatic and harmonic approximation, the force in the λ direction on the lk nucleus caused by the displacement $U_{l'k'\lambda'}$ of the $l'k'$ nucleus is linear in U and can be written as[7]

$$-\Phi_{\lambda\lambda'}(lk,l'k')U_{l'k'\lambda'}\,, \tag{2.1}$$

where the coefficient Φ is known as the force constant. Then, the equation of motion for the lattice vibration at frequency ω is given by

$$\sum_{l'k'\lambda'}\Phi_{\lambda\lambda'}(lk,l'k')U_{l'k'\lambda'}=M_k\omega^2U_{lk\lambda}\,. \tag{2.2}$$

From the lattice translational symmetry, we have

$$\Phi_{\lambda\lambda'}(lk,l'k')=\Phi_{\lambda\lambda'}(l-l'k,0k')\,; \tag{2.3}$$

hence, we can analyze the lattice vibration into normal modes of wave vector $\mathbf{q}$. For the normal modes with wave vector $\mathbf{q}$, the frequencies are determined by the dynamical matrix[7]

$$\Phi_{\lambda\lambda'}(\mathbf{q},kk')=(M_kM_{k'})^{-1/2}\sum_l e^{-i\mathbf{q}\cdot\mathbf{x}_l}\Phi_{\lambda\lambda'}(lk,0k')\,. \tag{2.4}$$

From the infinitesimal translational invariance of the crystal,[7] we have

$$\sum_{lk}\Phi_{\lambda\lambda'}(lk,0k')=0\,. \tag{2.5}$$

It follows that $\mathbf{q}=0$ acoustic modes, i.e., modes for which the displacements of nuclei in the same cell are in phase, have zero frequency ω.

We must make a careful distinction between $\mathbf{q}=0$ modes and small but nonzero $\mathbf{q}$ modes. The electrons and nuclei that make up the crystal interact with each other via the Coulomb potential. Its Fourier transform $4\pi/q^2$ diverges as $q\rightarrow0$. However, because the charged particles form a neutral system, the average interaction potential may be regarded as zero. This is the convention we shall adopt. For example, the interaction between two electrons at a distance r apart is

$$v_e(r)=e^2/r\,, \tag{2.6}$$

where $-e$ is the charge of an electron. Its Fourier transform is

$$\begin{aligned} v_e(q)&=4\pi e^2/q^2 \quad (q\neq0)\\ &=0 \qquad\qquad (q=0). \end{aligned} \tag{2.7}$$

In considering the small q limit of any quantity involving the Coulomb interaction, we shall be careful to bear this in mind.

To write down the formula for the force constants $\Phi_{\lambda\lambda'}(lk,l'k')$ or the dynamical matrix $\Phi_{\lambda\lambda'}(\mathbf{q},kk')$, we separate it into two contributions, (i) from the direct Coulomb interaction between nuclei, denoted by Φ^I, and (ii) from the direct interaction via the electrons, denoted by Φ^E.

The construction of Φ^I by Ewald's method is well established.[7] Suffice it to write in the form

$$\begin{aligned} \Phi_{\lambda\lambda'}{}^I(\mathbf{q},kk')={}&e^{i\mathbf{q}\cdot(\mathbf{x}_k-\mathbf{x}_{k'})}(Z_kZ_{k'}e^2)/(M_kM_{k'})^{1/2}\\ &\times\bigg[\frac{4\pi}{\Omega_0}\frac{q_\lambda q_{\lambda'}}{q^2}-Q_{\lambda\lambda'}(\mathbf{q},kk')\\ &+\delta_{kk'}\sum_{k''}(Z_{k''}/Z_k)Q_{\lambda\lambda'}(0,kk'')\bigg]\,, \end{aligned} \tag{2.8}$$

Ω_0 being the volume of a unit cell. When the crystal is subjected to a distortion of wave vector $\mathbf{q}$, the most singular part of the dynamical matrix Φ^I, due to the long-range Coulomb singularity as $q\rightarrow0$, is isolated in the first term in the square brackets. $Q_{\lambda\lambda'}(\mathbf{q},kk')$ contains the rest of the response from the bare nuclei,[16] including Bragg-diffraction-like contributions, and is continuous at $q=0$. The dynamical matrix for the zero wave vector ($\mathbf{q}=0$), by our convention, does not possess the first term in the square brackets of Eq. (2.8). The third term in the square brackets is a consequence of the infinitesimal invariance relation for the force constants due to the bare nuclei only and it in turn guarantees zero contribution to ω^2 for the acoustic modes at $\mathbf{q}=0$.

In the adiabatic and harmonic approximation, the force constants between nuclei due to the mediation of electrons are derived from the effective nuclear potential energy due to the presence of electrons of second order in nuclear displacements $\mathbf{U}_{lk}$. These are due to the deviation of the electron-nucleus potential from the perfect crystal potential and consist of two types of terms[2]: (i) the second-order contribution from the deviation of the electron-nucleus potential of the first order in $\mathbf{U}$, and (ii) the first-order contribution from the deviation of the second order in $\mathbf{U}$.

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[12] L. J. Sham, Phys. Rev. **150**, 720 (1966).

[13] S. H. Groves and W. Paul, Phys. Rev. Letters **11**, 194 (1963).

[14] L. Liu and D. Brust, Phys. Rev. Letters **20**, 651 (1968); D. Sherrington and W. Kohn, Rev. Mod. Phys. **40**, 767 (1968).

[15] D. Sherrington (private communication).

[16] Reference 7, p. 254.

Thus, the electronic contribution to the force constants is

$$\Phi_{\lambda\lambda'}{}^{E}(lk,l'k')=\int\int d\mathbf{r}d\mathbf{r}'$$
$$\times\left(\frac{\partial v(\mathbf{r}-\mathbf{x}_{lk};k)}{\partial r_\lambda}\chi(\mathbf{r},\mathbf{r}')\frac{\partial v(\mathbf{r}'-\mathbf{x}_{l'k'};k')}{\partial r'_{\lambda'}}\right.$$
$$-\delta_{ll'}\delta_{kk'}\sum_{l''k''}\frac{\partial v(\mathbf{r}-\mathbf{x}_{lk};k)}{\partial r_\lambda}\chi(\mathbf{r},\mathbf{r}')$$
$$\left.\times\frac{\partial v(\mathbf{r}'-\mathbf{x}_{l''k''};k'')}{\partial r'_{\lambda'}}\right), \qquad (2.9)$$

where we have denoted the interaction between an electron at $\mathbf{r}$ and the nucleus at $\mathbf{x}_{lk}+\mathbf{U}_{lk}$ by

$$v(\mathbf{r}-\mathbf{x}_{lk}-\mathbf{U}_{lk};k)=-Z_ke^2/|\mathbf{r}-\mathbf{x}_{lk}-\mathbf{U}_{lk}| \qquad (2.10)$$

and the static electron density response function by χ.

The first term on the right of Eq. (2.9) is of type (i) mentioned above. The force on the nucleus is due to the redistribution of the electron density as a linear response to the distortion of the lattice. If we do not want to use the adiabatic condition, the density response function χ is then the real part of the dynamic response function at the normal mode frequency ω. For a more detailed discussion, see Ref. 4. In the adiabatic approximation, we take $\omega=0$ in the response function and neglect the phonon contribution to χ.

The second term on the right of Eq. (2.9) is of type (ii) mentioned above, which should be, accordingly,

$$\delta_{ll'}\delta_{kk'}\int d\mathbf{r}n^{(0)}(\mathbf{r})\partial^2v(\mathbf{r}-\mathbf{x}_{lk};k)/\partial r_\lambda\partial r_{\lambda'}, \qquad (2.11)$$

$n^{(0)}(\mathbf{r})$ being the electron density distribution for the perfect crystal. Now, if the whole crystal in moved bodily through a distance $\mathbf{U}$, then the first-order change in the electron-nucleus potential is

$$-\mathbf{U}\cdot\sum_{lk}\frac{\partial v(\mathbf{r}-\mathbf{x}_{lk};k)}{\partial\mathbf{r}}, \qquad (2.12)$$

and the first-order change in electron density,

$$-\mathbf{U}\cdot\partial n^{(0)}(\mathbf{r})/\partial\mathbf{r}. \qquad (2.13)$$

Hence,

$$\frac{\partial n^{(0)}(\mathbf{r})}{\partial r_\lambda}=\int d\mathbf{r}'\chi(\mathbf{r},\mathbf{r}')\sum_{lk}\frac{\partial v(\mathbf{r}'-\mathbf{x}_{lk};k)}{\partial r'_\lambda}, \qquad (2.14)$$

and combining with Eq. (2.11) gives the second term on the right of Eq. (2.9).

It is straightforward to show from Eq. (2.9) that the force constants Φ^E satisfy the translational symmetry relations (2.3) and (2.5). Together with the same properties possessed by Φ^I, we see that the total dynamical matrix will give zero frequency for the acoustic branches at $\mathbf{q}=0$.

Fourier transforming Eq. (2.9), we obtain the part of the dynamic matrix due to the electrons,

$$\Phi_{\lambda\lambda'}{}^{E}(\mathbf{q},kk')$$
$$=(M_kM_{k'})^{-1/2}\sum_{\mathbf{G},\mathbf{G}'}[X_{\lambda\lambda'}(\mathbf{q}+\mathbf{G}k,\mathbf{q}+\mathbf{G}'k')$$
$$-\delta_{kk'}\sum_{k''}X_{\lambda\lambda'}(\mathbf{G}k,\mathbf{G}'k'')], \qquad (2.15)$$

where $\mathbf{G}$ and $\mathbf{G}'$ are the reciprocal-lattice vectors and

$$X_{\lambda\lambda'}(\mathbf{q}+\mathbf{G}k,\,\mathbf{q}+\mathbf{G}'k')$$
$$=\Omega_0{}^{-1}e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{x}_k}v(-\mathbf{q}-\mathbf{G};k)(\mathbf{q}+\mathbf{G})_\lambda$$
$$\times\chi(\mathbf{q}+\mathbf{G},\,\mathbf{q}+\mathbf{G}')v(\mathbf{q}+\mathbf{G}';k')(\mathbf{q}+\mathbf{G}')_{\lambda'}$$
$$\times e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{x}_{k'}}, \qquad (2.16)$$

$v(\mathbf{q}+\mathbf{G};k)$ being the Fourier transform of the electron-nucleus potential $v(\mathbf{r};k)$. A formula of this form was first given in Ref. 2 with the Hartree approximation for the density response function. The more general form was written down independently in Refs. 3 and 4.

Equations (2.8) and (2.16) together give the dynamical matrix for a lattice vibration in terms of the interactions of its most fundamental constituents. These form the starting point for the discussion of small q behavior that follows.

III. ACOUSTIC PHONONS AT LONG WAVELENGTH

The expressions for the dynamical matrix written down in the last section apply to both conducting and insulating crystals. We now wish to examine the limit of the dynamical matrix for long wavelength, i.e., small but nonzero $\mathbf{q}$ for insulators, which, for our purpose, include intrinsic semiconductors at low temperatures.

In order to extract any singular terms in Eq. (2.15), we first review the behavior of the response function at long wavelength for an insulator.[12] The density response $\chi(\mathbf{q}+\mathbf{G},\,\mathbf{q}+\mathbf{G}')$ is the sum of all polarization diagrams. Let $\tilde{\chi}(\mathbf{q}+\mathbf{G},\,\mathbf{q}+\mathbf{G}')$ denote the proper polarization part.[17] In an insulator at zero temperature, for small q,

$$\tilde{\chi}(\mathbf{q},\,\mathbf{q})=q_\lambda\tilde{\chi}_{\lambda\lambda'}{}^{(2)}q_{\lambda'}+O(q^4), \qquad (3.1a)$$

$$\tilde{\chi}(\mathbf{q},\,\mathbf{q}+\mathbf{G})=q_\lambda\tilde{\chi}_\lambda{}^{(1)}(O,\mathbf{G})+O(q^2), \qquad (3.1b)$$

$$\tilde{\chi}(\mathbf{q}+\mathbf{G},\,\mathbf{q})=\tilde{\chi}_\lambda{}^{(1)}(\mathbf{G},O)q_\lambda+O(q^2), \qquad (3.1c)$$

$$\tilde{\chi}(\mathbf{q}+\mathbf{G},\,\mathbf{q}+\mathbf{G}')=\tilde{\chi}(\mathbf{G},\mathbf{G}')+O(q), \qquad (3.1d)$$

where the summations over repeated Greek indices are understood and $\mathbf{G},\mathbf{G}'$ are nonzero.

To isolate the leading term in χ for small q, we follow Ambegaokar and Kohn[18] in defining $P(\mathbf{q}+\mathbf{G},\,\mathbf{q}+\mathbf{G}')$ to

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[17] L. J. Sham and W. Kohn, Phys. Rev. **145**, 561 (1966).

[18] V. Ambegaokar and W. Kohn, Phys. Rev. **117**, 423 (1960).

be the sum of all polarization diagrams not containing the Coulomb line $v_e(\mathbf{q})$. Then, for small q, P has the same behavior as $\tilde{\chi}$, listed in Eqs. (3.1). It is a simple matter to express the full polarization χ in terms of P and thus to obtain the leading term for small q. For example,

$$\chi(\mathbf{q},\mathbf{q})=P(\mathbf{q},\mathbf{q})/[1-v_e(\mathbf{q})P(\mathbf{q},\mathbf{q})]$$
$$\simeq(q^2/4\pi e^2)[1/\epsilon_\infty(\hat{q})-1], \tag{3.2}$$

where

$$\epsilon_\infty(\hat{q})=1-4\pi e^2\hat{q}_\lambda P_{\lambda\lambda'}{}^{(2)}\hat{q}_{\lambda'}, \tag{3.3}$$

using Eq. (3.1a) with P in place of $\tilde{\chi}$. $\hat{q}$ stands for the unit vector in the direction of $\mathbf{q}$. As we shall see in the next section, $\epsilon_\infty(\hat{q})$ is indeed the macroscopic dielectric constant due to the polarization of electrons in a perfect and rigid crystal. The subscript ∞ means the response at frequency higher than where the lattice vibration will contribute.

Similarly, keeping only the leading terms, we have for small q,

$$\chi(\mathbf{q},\,\mathbf{q}+\mathbf{G})\simeq q_\lambda P_\lambda{}^{(1)}(O,\mathbf{G})/\epsilon_\infty(\hat{q}), \tag{3.2$'$}$$

$$\chi(\mathbf{q}+\mathbf{G},\,\mathbf{q})\simeq P_\lambda{}^{(1)}(\mathbf{G},0)q_\lambda/\epsilon_\infty(\hat{q}), \tag{3.2$''$}$$

$$\chi(\mathbf{q}+\mathbf{G},\,\mathbf{q}+\mathbf{G}')\simeq\chi(\mathbf{G},\mathbf{G}')+P_\lambda{}^{(1)}(\mathbf{G},0)$$
$$\times\hat{q}_\lambda[4\pi e^2/\epsilon_\infty(\hat{q})]\hat{q}_{\lambda'}P_{\lambda'}{}^{(1)}(0,\mathbf{G}'), \tag{3.2$'''$}$$

where the coefficients of P are defined in the same way as in Eqs. (3.1).

Knowing the leading terms of the response function, we can separate the irregular part of the electronic contribution to the dynamical matrix from the regular part, and by Eq. (2.16) write

$$\sum_{\mathbf{G},\mathbf{G}'} X_{\lambda\lambda'}(\mathbf{q}+\mathbf{G}k,\mathbf{q}+\mathbf{G}'k')$$
$$=e^{i\mathbf{q}\cdot(\mathbf{x}_k-\mathbf{x}_{k'})}\Bigg(-\frac{4\pi e^2 Z_k Z_{k'}}{\Omega_0}\frac{q_\lambda q_{\lambda'}}{q^2}$$
$$+\frac{4\pi e^2}{\Omega_0\epsilon_\infty(\hat{q})}[Z_k\delta_{\lambda\mu}-Z_{\lambda\mu}{}^\dagger(k)]$$
$$\times\frac{q_\mu q_{\mu'}}{q^2}[Z_{k'}\delta_{\mu'\lambda'}-Z_{\mu'\lambda'}(k')]+S_{\lambda\lambda'}(\mathbf{q},kk')\Bigg), \tag{3.4}$$

where

$$Z_{\mu\lambda}(k)=\sum_{\mathbf{G}} P_\mu{}^{(1)}(0,\mathbf{G})v(\mathbf{G},k)G_\lambda e^{-i\mathbf{G}\cdot\mathbf{x}_k}. \tag{3.5}$$

The first two terms on the right of Eq. (3.4) are irregular since they depend on the direction of $\mathbf{q}$ as $\mathbf{q}\rightarrow 0$. They are equal to zero if $\mathbf{q}=0$, by our convention, Eq. (2.7). The first term exactly cancels the irregular term in the direct nuclear part of the dynamical matrix, Eq. (2.8). The matrix $Z_{\mu\lambda}(k)$ in the second term is the effective charge acquired by the nuclei due to the drag of electrons by the displacement of the nuclei. The appearance of $\epsilon_\infty(\hat{q})$ here shows the macroscopic dielectric screening of the insulating medium. In the extreme tight-binding limit, $Z_k\delta_{\mu\lambda}-Z_{\mu\lambda}(k)$ is just the ionic charge and $\epsilon_\infty(\hat{q})$ is unity for the rigid ions.

The last term on the right of Eq. (3.4) is the regular part. As $q\rightarrow 0$, $S_{\lambda\lambda'}(\mathbf{q},kk')$ tends to

$$S_{\lambda\lambda'}(0,kk')=\sum_{\mathbf{G},\mathbf{G},} X_{\lambda\lambda'}(\mathbf{G}k,\mathbf{G}'k'). \tag{3.6}$$

Putting all the previous results together, we can write the total dynamical matrix in the form

$$\Phi_{\lambda\lambda'}(\mathbf{q},kk')=(M_kM_{k'})^{-1/2}e^{i\mathbf{q}\cdot(\mathbf{x}_k-\mathbf{x}_{k'})}$$
$$\times\Bigg(\frac{4\pi e^2}{\Omega_0 q^2\epsilon_\infty(\hat{q})}[Z_k\delta_{\lambda\mu}-Z_{\lambda\mu}{}^\dagger(k)]q_\mu q_{\mu'}$$
$$\times[Z_{k'}\delta_{\mu'\lambda'}-Z_{\mu'\lambda'}(k')]+T_{\lambda\lambda'}(\mathbf{q},kk')$$
$$-\delta_{kk'}\sum_{k''}T_{\lambda\lambda'}(0,kk'')\Bigg), \tag{3.7}$$

where

$$T_{\lambda\lambda'}(\mathbf{q},kk')=-Z_kZ_{k'}e^2Q_{\lambda\lambda'}(\mathbf{q},kk')+S_{\lambda\lambda'}(\mathbf{q},kk'), \tag{3.8}$$

which is continuous at $\mathbf{q}=0$. Thus, we have separated the long-range interaction between the ions from the short-range part. In the former, the lk nucleus carries an effective charge matrix $eZ_k\delta_{\mu\lambda}-eZ_{\mu\lambda}(k)$ in the dielectric medium with dielectric constant $\epsilon_\infty(\hat{q})$. The last two terms on the right of Eq. (3.8) obey the infinitesimal translational invariance relation and contribute[7] terms of the order q^2 to ω^2 of the acoustic modes as $q\rightarrow 0$. No contribution to ω^2 of the order unity comes from the long-range part, if and only if the follow sum rule holds:

$$\sum_k Z_{\mu\lambda}(k)=\sum_k Z_k\delta_{\mu\lambda}. \tag{3.9}$$

A proof which will also exhibit the physical meaning of $Z_{\mu\lambda}(k)$ more clearly is as follows. Expanding, in powers of q, the Fourier transform,

$$\tilde{\chi}(\mathbf{q},\mathbf{q}+\mathbf{G})=\Omega^{-1}\int d\mathbf{r}\int d\mathbf{r}'e^{-i\mathbf{q}\cdot\mathbf{r}}\tilde{\chi}(\mathbf{r},\mathbf{r}')e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}, \tag{3.10}$$

Ω being the volume of the crystal, we have

$$\tilde{\chi}_\lambda{}^{(1)}(0,\mathbf{G})=\Omega^{-1}\int\int d\mathbf{r}d\mathbf{r}'(-ir_\lambda)\tilde{\chi}(\mathbf{r},\mathbf{r}')e^{i\mathbf{G}\cdot\mathbf{r}'}. \tag{3.11}$$

It may be questionable whether the expansion, under the integral on the right of Eq. (3.10), in powers of $\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')$ is valid. For a large crystal with periodic boundary conditions, we regard $\mathbf{r}$ as a position operator with the same boundary conditions. This can be defined either using the Wannier or the Bloch representation.[19] In the Appendix we shall give an alternative proof of the sum rule (3.9) without using this expansion.

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[19] E. I. Blount, Solid State Phys. **13**, 306 (1962).

From the definition of the polarization part $P(\mathbf{q}+\mathbf{G},\ \mathbf{q}+\mathbf{G}')$, we have

$$P_\mu^{(1)}(0,\mathbf{G}')=\sum_{\mathbf{G}}\tilde{\chi}_\mu^{(1)}(0,\mathbf{G})\epsilon^{-1}(\mathbf{G},\mathbf{G}'),\qquad(3.12)$$

where the inverse dielectric matrix is given by[17]

$$\epsilon^{-1}(\mathbf{G},\mathbf{G}')=\delta_{\mathbf{G},\mathbf{G}'}+v_e(\mathbf{G})\chi(\mathbf{G},\mathbf{G}').\qquad(3.13)$$

Hence, from Eq. (3.5),

$$Z_{\mu\lambda}(k)=\sum_{\mathbf{G},\mathbf{G}'}\tilde{\chi}_\mu^{(1)}(0,\mathbf{G})\epsilon^{-1}(\mathbf{G},\mathbf{G}')\times v(\mathbf{G}',k)G_\lambda' e^{-i\mathbf{G}'\cdot\mathbf{x}_k},\qquad(3.14)$$

$$=N^{-1}\int\int d\mathbf{r}d\mathbf{r}'r_\mu\chi(\mathbf{r},\mathbf{r}')\sum_l\frac{-\partial v(\mathbf{r}'-\mathbf{x}_{lk};k)}{\partial r_\lambda'}$$

$$\equiv N^{-1}\int d\mathbf{r}r_\mu\delta n_\lambda(\mathbf{r},k),\qquad(3.15)$$

N being the number of cells in the crystal.

If the sublattice of k-type nuclei is moved bodily through a small distance $\mathbf{U}$, by the same reasonings as those leading to Eq. (2.14), we see that the change in electron density distribution is just $\delta n_\lambda(\mathbf{r},k)U_\lambda$. Then, $-eZ_{\mu\lambda}(k)U_\lambda$ is the dipole moment of the displaced electron charge. $e[Z_k\delta_{\mu\lambda}-Z_{\mu\lambda}(k)]$ is the effective charge associated with the k-type nuclei when their sublattice is moved bodily relative to the rest of the crystal.[11] Equation (3.14) is the formula for this effective charge if we wish to calculate it from the band structure.

If the whole crystal is moved slowly through a small distance, then the shift of the electron distribution is given by Eq. (2.13) and hence

$$\sum_k Z_{\mu\lambda}(k)=N^{-1}\int d\mathbf{r}n^{(0)}(\mathbf{r})\delta_{\mu\lambda}=\sum_k Z_k\delta_{\mu\lambda}.\qquad(3.16)$$

IV. INFRARED OPTICAL PROPERTIES

In the microscopic formulation of the dynamical matrix, we have separated the irregular and the regular parts as a function of the wave vector $\mathbf{q}$, and have shown that the frequency of the acoustic modes tends to zero linearly in q as $q\rightarrow 0$. However, to find the sound velocity, we would need to carry the expansion of the electron density response function in powers of q further than in Sec. III. We would not gain much by doing so until we are ready to evaluate these formulas. On the other hand, the expansion in q which has already been made is sufficient to yield information on the long-wavelength optical modes.

We shall not include the retardation effect for a long-wavelength optical mode[20]; thus, we shall not obtain the hybrid mode of optical phonons and photons (polaritons). We shall restrict "long wavelength" to mean that the wave vector q is small compared with the Brillouin-zone boundary but large compared with ω/C, C being the speed of light. Having obtained the optical phonons for such wavelength from our microscopic formulation, we can simply follow Huang[20] to include the effects of the transverse electromagnetic fields.

The secular equations for the normal modes are[7]

$$\sum_{k'}C_{\lambda\lambda'}(\mathbf{q},kk')W_{\lambda'}(k'|\mathbf{q}j)=\omega_{\mathbf{q}j}^2W_\lambda(k|\mathbf{q}j),\qquad(4.1)$$

where

$$C_{\lambda\lambda'}(\mathbf{q},kk')=\Phi_{\lambda\lambda'}(\mathbf{q},kk')e^{-i\mathbf{q}\cdot(\mathbf{x}_k-\mathbf{x}_{k'})}\qquad(4.2)$$

and $W_\lambda(k|\mathbf{q}j)$ and $\omega_{\mathbf{q}j}$ are the polarization vector and frequency of the $(\mathbf{q}j)$ mode. Summation over λ' on the left-hand side is understood.

When the crystal is vibrating with a small wave vector $\mathbf{q}$, the microscopic electric field excited in the crystal has components $\mathbf{q}+\mathbf{G}$ for all reciprocal-lattice vectors $\mathbf{G}$. We follow Born and Huang in defining the macroscopic electric field as the $\mathbf{q}$ component,[21] given by

$$E_\lambda=-(4\pi q_\lambda q_{\lambda'}/q^2)P_{\lambda'},\qquad(4.3)$$

where $\mathbf{P}$ is the macroscopic polarization (dipole moment per unit volume). The contribution from the bare nuclei per unit amplitude of the normal mode $\mathbf{q}j$ is

$$P_\lambda{}^I=\Omega_0^{-1}\sum_k Z_keW_\lambda(k|\mathbf{q}j)M_k^{-1/2}.\qquad(4.4)$$

The $\mathbf{q}$ component of the first-order change in electron density distribution is

$$n^{(1)}(\mathbf{q})=-i\Omega_0^{-1}\sum_{k\mathbf{G}}\chi(\mathbf{q},\mathbf{q}+\mathbf{G})e^{-i\mathbf{G}\cdot\mathbf{x}_k}\times v(\mathbf{q}+\mathbf{G};k)(\mathbf{q}+\mathbf{G})\cdot\mathbf{W}(k|\mathbf{q}j)M_k^{-1/2}.\qquad(4.5)$$

Keeping only the leading term for small q by using the results in Sec. III, we obtain

$$-en^{(1)}(\mathbf{q})=-i\mathbf{q}\cdot\mathbf{P}^E,\qquad(4.6)$$

where the electronic contribution to the macroscopic polarization is

$$P_\mu{}^E=-e\Omega_0^{-1}\sum_k\{Z_k\delta_{\mu\lambda}-[Z_k\delta_{\mu\lambda}-Z_{\mu\lambda}(k)]/\epsilon_\infty(\hat{q})\}\times W_\lambda(k|\mathbf{q}j)M_k^{-1/2}.\qquad(4.7)$$

Hence

$$P_\mu=\frac{e}{\Omega_0\epsilon_\infty(\hat{q})}\sum_k[Z_k\delta_{\mu\lambda}-Z_{\mu\lambda}(k)]W_\lambda(k|\mathbf{q}j)M_k^{-1/2}.\qquad(4.8)$$

For the acoustic modes, $W_\lambda(k|\mathbf{q}j)M_k^{-1/2}$ is independent of k, and from the sum rule (3.9) follows the reasonable conclusion that no macroscopic polarization is induced.

From Eq. (3.7) for the dynamical matrix, it follows that the secular equations (4.1) can be written in the

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[20] K. Huang, Proc. Roy. Soc. (London) **A208**, 352 (1951).

[21] See Ref. 7, p. 249.

form

$$\omega_{\mathbf{q}j}{}^2 W_\lambda(k|\mathbf{q}j)=\sum_{k'}\bar{C}_{\lambda\lambda'}(\mathbf{q},kk')W_{\lambda'}(k|\mathbf{q}j)$$
$$-e[Z_k\delta_{\lambda\mu}-Z_{\lambda\mu}{}^\dagger(k)]M_k{}^{-1/2}E_\mu. \quad (4.9)$$

Now Born and Huang[22] have given a treatment of the optical properties starting from the macroscopic energy density

$$U=\tfrac{1}{2}\sum_{kk'} f(k\lambda,k'\lambda')u_\lambda(k)u_{\lambda'}(k')$$
$$+\sum_k f(k\lambda,\mu)u_\lambda(k)E_\mu-\tfrac{1}{2}f(\lambda\mu)E_\lambda E_\mu. \quad (4.10)$$

From this density, follow the equations of motion and polarization which can be compared with Eqs. (4.8) and (4.9), whence we obtain the identification

$$f(k\lambda,k'\lambda')=\bar{C}_{\lambda\lambda'}(0,kk')(M_kM_{k'})^{1/2}/\Omega_0, \quad (4.11)$$

$$f(k\lambda,\mu)=-e[Z_k\delta_{\lambda\mu}-Z_{\lambda\mu}(k)]/\Omega_0, \quad (4.12)$$

$$f(\lambda\mu)=-e^2P_{\lambda\mu}{}^{(2)}. \quad (4.13)$$

These relations are the extension of similar ones given by Born and Huang[22] for the rigid-ion and polarizable-ion models to general electron redistribution.

As a consequence, $\bar{C}_{\lambda\lambda'}(0,kk')$ determines a set of normal modes with frequencies ω_j and polarization vectors $\mathbf{e}(k|j)$, three of which have zero frequency (the acoustic branches). The macroscopic dielectric tensor, as a function of frequency, is given by

$$\epsilon_{\lambda\mu}(\omega)=\delta_{\lambda\mu}-4\pi\left(e^2P_{\lambda\mu}{}^{(2)}+\sum_j\frac{M_\lambda(j)M_\mu{}^\dagger(j)}{\omega^2-\omega_j{}^2}\right), \quad (4.14)$$

where the electric dipole moment $M_\lambda(j)$ is given by

$$M_\lambda(j)=\Omega_0{}^{-1/2}e\sum_k[Z_k\delta_{\lambda\mu}-Z_{\lambda\mu}(k)]$$
$$\times M_k{}^{-1/2}e_\mu(k|j). \quad (4.15)$$

In particular, let us record the results for the important class of diatomic crystals with tetrahedral symmetry, which includes NaCl, ZnS, diamond, etc. By symmetry,[23] we have

$$Q_{\lambda\lambda'}(0,kk')=\delta_{\lambda\lambda'}\times 4\pi/3\Omega_0, \quad (4.16)$$

$$S_{\lambda\lambda'}(0,kk')=\delta_{\lambda\lambda'}s, \quad k\neq k' \quad (4.17)$$

$$Z_{\lambda\mu}(k)=\delta_{\lambda\mu}z_k, \quad (4.18)$$

$$P_{\lambda\mu}{}^{(2)}=\delta_{\lambda\mu}p. \quad (4.19)$$

Hence, the transverse-optical mode frequency is given by

$$\omega_0{}^2=M^{-1}[s-(4\pi e^2/3\Omega_0)Z_1Z_2], \quad (4.20)$$

where M is the reduced mass of the two nuclei in the unit cell. The "high-frequency" dielectric constant is

$$\epsilon_\infty=1-4\pi e^2p, \quad (4.21)$$

and the infrared dielectric constant,

$$\epsilon(\omega)=\epsilon_\infty+4\pi e^2(Z_1-z_1)^2/\Omega_0M(\omega_0{}^2-\omega^2). \quad (4.22)$$

The appearance of $(Z_1-z_1)e$ in the expression of the dielectric constant shows that it can be regarded as the dynamical charge of the ions in the sublattice $k=1$. The sum rule (3.9) ensures that the dynamical charge on the other sublattice is equal in magnitude and opposite in sign. It follows easily that, for the diamond lattice, the dynamical charge is zero, i.e., it is not infrared-active.[7] From Eq. (4.9), we have the longitudinal-optical mode frequency,

$$\omega_l=(\epsilon_0/\epsilon_\infty)^{1/2}\omega_0. \quad (4.23)$$

This constitutes a microscopic proof of the Lyddane-Sachs-Teller relation.[8]

APPENDIX: PROOF OF THE EFFECTIVE-CHARGE SUM RULE

We shall give here a more careful proof of the sum rule (3.9). This involves a more careful consideration of the coefficient $\tilde{\chi}_\mu{}^{(1)}(0,\mathbf{G})$ of the power expansion in q of the proper polarization part, although the underlying physical meaning remains the same, namely, that $-eZ_{\mu\lambda}(k)$ is a measure of the electric dipole moment per unit displacement of the k sublattice. We do this by examining the complete perturbation series of the proper polarization part in terms of the electron-electron interaction, following closely the method of Kohn.[24]

Let the zeroth-order single-particle state of the insulator have the wave function

$$\psi_{\nu k}(\mathbf{r})=e^{i\mathbf{k}\cdot i}u_{\nu k}(\mathbf{r}). \quad (\mathrm{A}1)$$

The proper polarization part may be written as

$$\tilde{\chi}(\mathbf{r},\mathbf{r}')=\sum_{\nu_1k_1\cdots\nu_4k_4}\psi_{\nu_1k_1}(\mathbf{r})\psi_{\nu_2k_2}{}^*(\mathbf{r})$$
$$\times\tilde{\chi}_{\nu_1k_1,\nu_2k_2,\nu_3k_3,\nu_4k_4}\psi_{\nu_3k_3}(\mathbf{r}')\psi_{\nu_4k_4}{}^*(\mathbf{r}'), \quad (\mathrm{A}2)$$

and the Fourier transform, from Eq. (3.10), is

$$\tilde{\chi}(\mathbf{q},\mathbf{q}+\mathbf{G})=\Omega^{-1}\sum_{\nu_1\cdots\nu_4}\sum_{k_1k_3}\langle\psi_{\nu_2k_1-q}|e^{-i\mathbf{q}\cdot\mathbf{r}}|\psi_{\nu_1k_1}\rangle$$
$$\times\tilde{\chi}_{\nu_1k_1,\nu_2k_1-q,\nu_3k_3,\nu_4k_3+q}\langle\psi_{\nu_4k_3+q}|e^{i(\mathbf{q}+\mathbf{G})\cdot r}|\psi_{\nu_3k_3}\rangle. \quad (\mathrm{A}3)$$

Now we expand each of the three factors in the summand in powers of q. From the properties of the Bloch waves,[19] we have[24]

$$\langle\psi_{\nu_2k_1-q}|e^{-i\mathbf{q}\cdot\mathbf{r})}|\psi_{\nu_1k_1}\rangle=\delta_{\nu_2\nu_1}+(1-\delta_{\nu_1\nu_2})$$
$$\times\langle u_{\nu_2k_1}|\mathbf{q}\cdot\partial u_{\nu_1k_1}/\partial\mathbf{k}_1\rangle+O(q^2) \quad (\mathrm{A}4)$$

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[22] Reference 7, p. 265 ff.

[23] Reference 7, Appendix VI.

[24] W. Kohn, Phys. Rev. **110**, 857 (1958).

and

$$\langle\psi_{\nu_4k_3+q}|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|\psi_{\nu_3k_3}\rangle=\langle\psi_{\nu_4k_3}|e^{i\mathbf{G}\cdot\mathbf{r}}|\psi_{\nu_3k_3}\rangle +\langle\mathbf{q}\cdot\partial u_{\nu_4k_3}/\partial\mathbf{k}_3|e^{i\mathbf{G}\cdot\mathbf{r}}|u_{\nu_3k_3}\rangle+O(q^2)\,. \quad \text{(A5)}$$

The zeroth order of (A3) is, therefore,

$$\tilde{\chi}(0,\mathbf{G})=\Omega^{-1}\sum_{\nu_1\nu_3\nu_4}\sum_{k_1k_3}\tilde{\chi}_{\nu_1k_1,\nu_1k_1,\nu_3k_3,\nu_4k_3} \times\langle\psi_{\nu_4k_3}|e^{(i\mathbf{G}\cdot\mathbf{r})}|\psi_{\nu_3k_3}\rangle\,, \quad \text{(A6)}$$

which vanishes[24,12]. The first-order term $q_\lambda\tilde{\chi}_\lambda{}^{(1)}(0,\mathbf{G})$ consists of three types of terms, each composed of the product of a first-order term from one factor and zeroth-order terms from the other two factors.

If the whole crystal is moved through a small distance $\mathbf{u}$, then the change in the lattice potential has the Fourier transform

$$\delta v(\mathbf{G})=\sum_k v(\mathbf{G};k)(-i\mathbf{G}\cdot\mathbf{u})e^{-i\mathbf{G}\cdot\mathbf{x}_k}\,, \quad \text{(A7)}$$

and the change in the screened self-consistent field is[17]

$$\delta\varphi(\mathbf{G})=\sum_{\mathbf{G}'}\epsilon^{-1}(\mathbf{G},\mathbf{G}')\delta v(\mathbf{G}')\,. \quad \text{(A8)}$$

From Eq. (3.14), we have

$$-i\sum_k q_\mu Z_{\mu\lambda}(k)u_\lambda=\sum_{\mathbf{G}} q_\mu\tilde{\chi}_\mu{}^{(1)}(0,\mathbf{G})\delta\varphi(\mathbf{G})\,, \quad \text{(A9)}$$

which is the sum of three types of terms:

$$\text{(I)} \quad \Omega^{-1}\sum_{\nu_1\cdots\nu_4}\sum_{k_1k_3}(1-\delta_{\nu_1\nu_2})\langle u_{\nu_2k_1}|\mathbf{q}\cdot\partial u_{\nu_1k_1}/\partial\mathbf{k}_1\rangle \times\tilde{\chi}_{\nu_1k_1,\nu_2k_1,\nu_3k_3,\nu_4k_3}\langle\psi_{\nu_4k_3}|\delta\varphi|\psi_{\nu_3k_3}\rangle\,, \quad \text{(A10)}$$

$$\text{(II)} \quad \Omega^{-1}\sum_{\nu_1\nu_3\nu_4}\sum_{k_1k_3}\left[\mathbf{q}\cdot\left(\frac{\partial}{\partial\mathbf{k}_4}-\frac{\partial}{\partial\mathbf{k}_2}\right) \times\tilde{\chi}_{\nu_1k_1,\nu_1k_2,\nu_3k_3,\nu_4k_4}\right]_{k_2=k_1,k_4=k_3} \times\langle\psi_{\nu_4k_3}|\delta\varphi|\psi_{\nu_3k_3}\rangle\,, \quad \text{(A11)}$$

$$\text{(III)} \quad \Omega^{-1}\sum_{\nu_1\nu_3\nu_4}\sum_{k_1k_3}\tilde{\chi}_{\nu_1k_1,\nu_1k_1,\nu_3k_3,\nu_4k_3} \times\langle\mathbf{q}\cdot\partial u_{\nu_4k_3}/\partial\mathbf{k}_3|\delta\varphi|u_{\nu_3k_3}\rangle\,. \quad \text{(A12)}$$

On the other hand, using the one-particle density matrix,

$$n(\mathbf{r},\mathbf{r}')=\sum_{\nu\nu'k}\psi_{\nu k}(\mathbf{r})n_{\nu\nu'k}\psi_{\nu'k}{}^*(\mathbf{r}')\,, \quad \text{(A13)}$$

we have

$$\Omega^{-1}\sum_{\nu\nu'k}\langle\psi_{\nu'k}|[i\mathbf{u}\cdot\mathbf{p},e^{-i\mathbf{q}\cdot\mathbf{r}}]|\psi_{\nu,k+q}\rangle n_{\nu\nu'k} =-i\mathbf{q}\cdot\mathbf{u}\Omega^{-1}\sum_{\nu k}n_{\nu\nu k}+O(q^2) =-i\mathbf{q}\cdot\mathbf{u}\frac{N}{\Omega}\sum_k Z_k+O(q^2)\,, \quad \text{(A14)}$$

where $\mathbf{p}$ is the momentum operator $-i\partial/\partial\mathbf{r}$. The sum rule (3.9) would be proven if we could show the equality of Eq. (A14) with Eq. (A9), to terms linear in q.

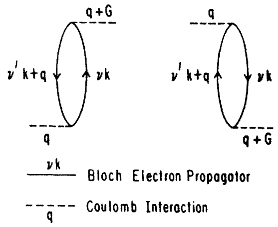

FIG. 1. Random-phase approximation for the proper polarization part.

The first term in Eq. (A14) is the sum of two types of terms:

$$\text{(IV)} \quad \Omega^{-1}\sum_{\nu\nu'k}(1-\delta_{\nu\nu'})\langle u_{\nu'k}|\mathbf{q}\cdot\partial u_{\nu k}/\partial\mathbf{k}\rangle\delta n_{\nu\nu'k}\,, \quad \text{(A15)}$$

where the first-order change in the one-particle density matrix due to a displacement $\mathbf{u}$ of the whole crystal is given by

$$\delta n_{\nu\nu'k}=\langle\psi_{\nu k}|-\mathbf{u}\cdot(\partial/\partial\mathbf{r}+\partial/\partial\mathbf{r}')n(\mathbf{r},\mathbf{r}')|\psi_{\nu'k}\rangle\,, \quad \text{(A16)}$$

$$\text{(V)} \quad \Omega^{-1}\sum_{\nu\nu'k}[\mathbf{q}\cdot\partial/\partial\mathbf{k}n_{\nu\nu'k}]\langle\psi_{\nu'k}|i\mathbf{u}\cdot\mathbf{p}|\psi_{\nu k}\rangle\,. \quad \text{(A17)}$$

We shall prove that

$$\text{(I)}=\text{(IV)}\,, \quad \text{(A18)}$$

$$\text{(II)}=\text{(V)}\,, \quad \text{(A19)}$$

and

$$\text{(III)}=0\,. \quad \text{(A20)}$$

(III) is of the same form as $\tilde{\chi}(0,\mathbf{G})$ in Eq. (A6) and vanishes for the same reason.[24,12]

When the whole crystal is moved through a small distance $\mathbf{u}$ the change in the one-particle density matrix is[17]

$$\delta n_{\nu\nu'k}=\sum_{\nu_3\nu_4k_3}\tilde{\chi}_{\nu k,\nu'k,\nu_3k_3,\nu_4k_3}\langle\psi_{\nu_4k_3}|\delta\varphi|\psi_{\nu_3k_3}\rangle\,. \quad \text{(A21)}$$

Equation (A18) follows from this equation and Eq. (A16).

Before we go on to the rather involved proof of Eq. (A19), let us illustrate the preceding steps by verifying the sum rule for the lowest-order contribution to the proper polarization part (namely, the Hartree or random-phase approximation), as represented by the time-ordered Feynman diagrams[25] in Fig. 1.

$$\tilde{\chi}(\mathbf{q},\mathbf{q}+\mathbf{G})=\Omega^{-1}\sum_{\nu\nu'k}\langle\psi_{\nu k}|e^{-i\mathbf{q}\cdot\mathbf{r}}|\psi_{\nu'k+q}\rangle \times\langle\psi_{\nu'k+q}|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|\psi_{\nu k}\rangle \times(n_{\nu k}-n_{\nu'k+q})\;(\epsilon_{\nu k}-\epsilon_{\nu'k+q})\,, \quad \text{(A22)}$$

where $n_{\nu k}$ and $\epsilon_{\nu k}$ are the occupation number and energy, respectively. In this particular case, since the electrons

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[25] J. M. Luttinger, Phys. Rev. **121**, 942 (1961).

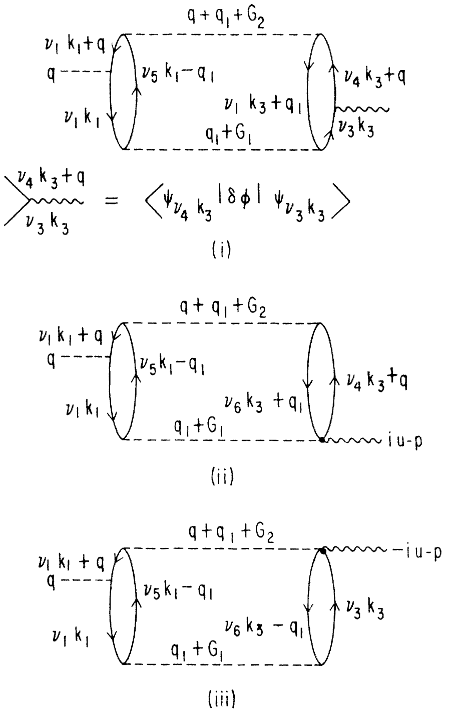

FIG. 2. A typical term for the proper polarization part.

and holes which are polarized belong to different bands, there are no contributions to (II), (III), and (V). Hence,

$$
\begin{aligned}
(\mathrm{I}) &= \Omega^{-1}\sum_{\nu\nu' k} \langle u_{\nu k}|\,\mathbf{q}\cdot\partial u_{\nu' k}/\partial\mathbf{k}\rangle \frac{n_{\nu k}-n_{\nu' k}}{\epsilon_{\nu k}-\epsilon_{\nu' k}} \langle\psi_{\nu' k}|\,\delta\varphi\,|\psi_{\nu k}\rangle \\
&= \Omega^{-1}\sum_{\nu\nu' k} \langle u_{\nu k}|\,\mathbf{q}\cdot\partial u_{\nu' k}/\partial\mathbf{k}\rangle (n_{\nu' k}-n_{\nu k}) \langle\psi_{\nu' k}|\,i\mathbf{u}\cdot\mathbf{p}\,|\psi_{\nu k}\rangle \\
&= (\mathrm{IV}).
\end{aligned}
\qquad (\mathrm{A}23)
$$

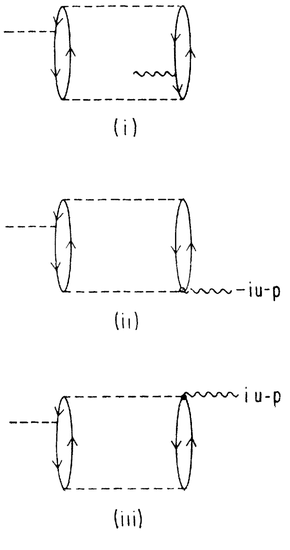

FIG. 3. Another perturbation term for the proper polarization part.

To prove Eq. (A19), we introduce the one-electron Green's function for the Bloch electron in the self-consistent field $\varphi(\mathbf{r})$, given by[12]

$$
\begin{aligned}
G(\mathbf{r},\mathbf{r}';\xi) &= \sum_{\nu k} \psi_{\nu k}(\mathbf{r})\psi_{\nu k}^{*}(\mathbf{r}')G_{\nu k}(\xi) \\
&= \sum_{\nu k} \psi_{\nu k}(\mathbf{r})\psi_{\nu k}^{*}(\mathbf{r}')/(\xi-\epsilon_{\nu k}),
\end{aligned}
\qquad (\mathrm{A}24)
$$

and the vertex part $\tilde{\Lambda}$ given by

$$
\begin{aligned}
\tilde{\chi}_{\nu_1 k+q,\nu_2 k,\nu_3 k',\nu_4 k'+q} &= \frac{1}{2\pi i}\oint d\xi \\
&\quad\times \tilde{\Lambda}_{\nu_1 k+q,\nu_2 k,\nu_3 k',\nu_4 k'+q}(\xi) G_{\nu_3 k'}(\xi) G_{\nu_4 k'+q}(\xi),
\end{aligned}
\qquad (\mathrm{A}25)
$$

where the contour of integration over the complex energy variable ξ is $\mathrm{Re}\,\xi=\mu$, where μ is the chemical potential,[12] plus a large semicircle closing to the left. The vertex part is slightly different from the usual one[17] because the Green's functions used here are not fully dressed.

When the whole crystal is moved through a small distance $\mathbf{u}$, the change in the one-electron Green's function is given by

$$
\begin{aligned}
\delta G_{\nu\nu' k}(\xi) &= G_{\nu k}(\xi)\langle\psi_{\nu k}|\,\delta\varphi\,|\psi_{\nu' k}\rangle G_{\nu' k}(\xi) = \langle\psi_{\nu k}|\,-i\mathbf{u}\cdot\mathbf{p}\,|\psi_{\nu' k}\rangle \\
&\quad\times G_{\nu' k}(\xi) + G_{\nu k}(\xi)\langle\psi_{\nu k}|\,i\mathbf{u}\cdot\mathbf{p}\,|\psi_{\nu' k}\rangle.
\end{aligned}
\qquad (\mathrm{A}26)
$$

Hence,

$$
\begin{aligned}
(\mathrm{II}) = \frac{1}{2\pi i}\oint d\xi\,\Omega^{-1}\sum_{\nu_1\nu_3\nu_4}\sum_{k_1 k_3} \Bigg\{ &\bigg[\mathbf{q}\cdot\left(\frac{\partial}{\partial\mathbf{k}_2}+\frac{\partial}{\partial\mathbf{k}_4}\right) \\
&\times \tilde{\Lambda}_{\nu_1 k_2,\nu_1 k_1,\nu_3 k_3,\nu_4 k_4}(\xi) G_{\nu_3 k_3}(\xi)\bigg]_{k_2=k_1,k_4=k_3} \\
&\times \langle\psi_{\nu_4 k_3}|\,-i\mathbf{u}\cdot\mathbf{p}\,|\psi_{\nu_3 k_3}\rangle + \bigg[\mathbf{q}\cdot\left(\frac{\partial}{\partial\mathbf{k}_2}+\frac{\partial}{\partial\mathbf{k}_4}\right) \\
&\times \tilde{\Lambda}_{\nu_1 k_2,\nu_1 k_1,\nu_3 k_3,\nu_4 k_4}(\xi) G_{\nu_4 k_4}(\xi)\bigg]_{k_2=k_1,k_4=k_3} \\
&\times \langle\psi_{\nu_4 k_3}|\,i\mathbf{u}\cdot\mathbf{p}\,|\psi_{\nu_3 k_3}\rangle \Bigg\}.
\end{aligned}
\qquad (\mathrm{A}27)
$$

An example of the perturbation terms that contribute to (II) is given in Fig. 2(i). The diagram is evaluated to the first order in q by the usual rules except that the electrons or holes transferring crystal momentum $\mathbf{q}$ are in the same band (ν_1) and that the vertex containing the self-consistent potential $\delta\varphi$ has no change in crystal momentum. By Eq. (A27), Fig. 2(i) is the sum of Figs. 2(ii) and 2(iii), where the vertex with $i\mathbf{u}\cdot\mathbf{p}$ (or $-i\mathbf{u}\cdot\mathbf{p}$) means the matrix element with this operator as in Eq. (A27). Similarly, the diagram Fig. 3(i) can also be broken up into Figs. 3(ii) and 3(iii). We note that the sum of Fig. 2(ii) and Fig. 3(ii) gives the same term as each except that the vertex with the wavy line has a factor

$$\langle\psi_{\nu_4 k_3}|[i\mathbf{u}\cdot\mathbf{p},e^{i(\mathbf{q}_1+\mathbf{G}_1)\cdot\mathbf{r}}]|\psi_{\nu_6 k_3-q_1}\rangle$$
$$=\langle\psi_{\nu_4 k_3}|i\mathbf{u}\cdot(\mathbf{q}_1+\mathbf{G}_1)e^{i(\mathbf{q}_1+\mathbf{G}_1)\cdot\mathbf{r}}|\psi_{\nu_6 k_3-q_1}\rangle. \quad \text{(A28)}$$

It is a general property that for every diagram with a vertex $i\mathbf{u}\cdot\mathbf{p}$ acting on the outgoing propagator there is a diagram with the same vertex associated with $-i\mathbf{u}\cdot\mathbf{p}$ acting on the incoming propagator and that their sum is a vertex like (A28), which we shall just denote by a wavy line in Fig. 4. The only exception is at the vertex $\mathbf{q}$, where we do not use Eq. (A28).

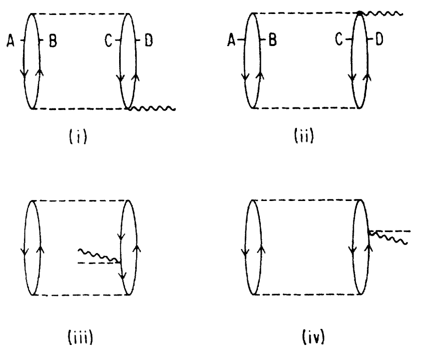

FIG. 4. Perturbation contributions to the effective charge.

For diagrams such as Figs. 4(i) and 4(ii), the external interaction line with momentum $\mathbf{q}$ can be attached at A, B, C, or D. The sum of all these contributions to (II) is zero, leaving only the two diagrams given in Figs. 4(iii) and 4(iv), which give the corresponding term in the perturbation series for (V) in (A17). In the same way we can consider other terms in the perturbation series of $\tilde{\chi}$ and prove Eq. (A19).

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Formation of F_3^+ Centers in KI

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When undoped KI is x-rayed at 130°K and then irradiated with F light at 275°K, the M, R, and N centers are formed. Subsequent irradiation at 78°K with F-aggregate light or R_2 light results in the formation of an optical-absorption band at 1125 nm at the expense of the R bands. Studies suggest that it is associated with F_3^+ centers (formerly called R^+), which are formed at 78°K by (1) $V+F_3+h\nu_R \rightarrow V^-+F_3^+$ (where $h\nu_R$ represents light absorbed only by the R bands) and destroyed by x rays at 78°K by (2) $V^-+F_3^+ +(\text{x rays}) \rightarrow V+F_3$, where V^- is an electron center containing a halogen (V) center core. F_3^+ centers may also be destroyed at 78°K by F light, by (3) $V^-+F_3^++F+h\nu_F \rightarrow V^-+F_3+\alpha$. The F_3^+ and V^- centers are also formed thermally by heavily x-ray coloring the crystal at 130°K and by warming it to room temperature in the dark. The suggested mechanism which involves the mobility of α (not F) centers is (4a) $F+F \rightarrow \alpha+e+F \rightarrow F_2^++e \rightarrow F_2$ (by diffusion), (4b) $F_2+F \rightarrow F_2+e+\alpha$, (4c) $V+e \rightarrow V^-$, (4d) $F_2+\alpha \rightarrow F_3^+$. (4a) is in accordance with Delbecq's mechanism. Studies show that the F_3^+ is not formed optically as a result of V_K excitation but only by direct ionization. The formation of F_3^+ centers in x-rayed crystals seems to depend on the existence of V centers which act as special electron traps. Thus far, F_3^+ centers have not been found in additively colored crystals.

I. INTRODUCTION

It is well known that F-band irradiation of alkali halides near room temperature results in the formation of M, R, and N bands. The M, R, and N bands are called F-aggregate centers and are formed on the longer-wavelength side of the F band.[1] Van Doorn and Haven[2] first suggested that the M center is an F_2 center composed of two nearest-neighbor F centers lying along a $\langle 110\rangle$ lattice direction. The model of the M center seems to be well established. The R center is supposed to be an F_3 center consisting of three nearest-neighbor F centers in a plane.[3] The N center, according to Pick, is an F_4 center consisting of four (aggregated) F centers, aggregating in two distinct ways, to give rise to N_1 and N_2 bands. Although these centers are now interpreted as aggregates of F centers, the mechanism of coagulation F centers is not well understood.

The various F-aggregate centers so far mentioned are electrically neutral clusters of anion vacancies and trapped electrons. If additional electrons are trapped (by F-aggregate centers), one would have F_2', F_3', and F_4' centers (where the prime denotes an additional electron) having an effective negative charge.[4] On the other

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[1] J. H. Schulman and W. D. Compton, *Color Centers in Solids* (The Macmillan Co., New York, 1962).

[2] C. Z. Van Doorn and Y. Haven, Philips Res. Rept. **11**, 479 (1956).

[3] H. Pick, Z. Physik **159**, 69 (1960).

[4] M. Hirai, M. Ikezawa, and M. Ueta, J. Phys. Soc. Japan **17**, 1483 (1962).