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Short-range Coulomb screening in a dielectric crystal

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We study the near dielectric screening of the Coulomb repulsion by a lattice of point polarizable elements. We find that the far screening factor (related to the static dielectric constant) persists even to distances of one or two lattice spacings. In some configurations the screening factor is enhanced by proximity, and we exhibit a case (two like charges at body-centered positions one spacing apart in a simple-cubic lattice) in which the screening factor exceeds 1 by $\sim 1\%$, although the polarizability is still below the Luttinger antiferroelectric threshold. Thus the dielectric screening overcomes the bare Coulomb repulsion in this case, and the net effect is attractive. Such considerations may play a part in explaining the mechanism of short-range pairing in cuprate superconductors. Incidentally we demonstrate that for the NaCl type of crystal there exists a small range of ratios of ionic polarizability for which a third configuration is preferred at $T=0$ K to both the ferroelectric and the Luttinger antiferroelectric spontaneous polarization.

I. INTRODUCTION

In any naïve model of electron or hole pairing in cuprate superconductors, the Coulomb repulsion is troublesome. The bare Coulomb energy between two electron charges 6 Å apart is about 2 eV, whereas the attractive energy available for pairing, which is usually supposed to arise from magnetic effects, is presumably $\sim 10^{-2}$ eV, comparable to kT_c. How can the latter overcome the former?

The problem is softened but not eliminated in the *s*-channel model for superconductivity.[1] There the net energy of the paired state is allowed to be positive; but for reasonable fits to data it should be only $\sim 10^{-2}$ eV, so that we still need a way to cancel or reduce the Coulomb repulsion. One possibility[2] is a capacitative effect between planes: The charged boson condensate in one plane is stabilized by a deficiency of that charge on another plane.

A different approach is to attribute the formation of bosons to the pairing of fermionic quasiparticles that carry no charge, as in the resonating-valence-bond (RVB) model.[3] Such models bypass the Coulomb difficulty in the insulating phase entirely, but it would seem to reappear in the superconducting phase since the current must be carried by a charged fluid.

Another way to reduce the Coulomb repulsion is by invoking the polarizability of the ions making up the crystal lattice. For two external charges far apart within the crystal, the effect simply reduces the Coulomb interaction by a factor equal to the dielectric constant of the crystal, which may be quite large. It is by no means evident, however, whether so great a reduction may be expected when the distance is only one or two lattice periods.

Accordingly we have undertaken to calculate Coulomb screening in an idealized crystal composed of identically inducible point dipoles. We do not take account of the complications due to ionic heterogeneity, nonpointlike polarization, and quantum and thermal effects. We take the naïve classical point of view commonly used in deriving the Causius-Mossotti law, except that we no longer assume that the polarization is uniform over the lattice.

We realize that the quantity we are calculating may be partly included in the more sophisticated arguments that ascribe pairing to the interaction of quantum orbitals, but such arguments normally do not take account of the self-interaction of the lattice as a whole. On the other hand, calculations in which everything is derived from properties of the phonon spectrum[4] may not take adequate account of the position of the paired objects in real space.

In the following section we show how the screened Coulomb potential may be expressed as an integral over the Brillouin zone, in which the integrand is a simple nonlinear function of certain sums of Madelung type. In Sec. III we apply the powerful extensions of Madelung's methods now available[5] to obtain quickly convergent transformations of these sums.

In Sec. IV we discuss implications for stability against antiferroelectric distortion: Briefly, the fact that a certain function over the Brillouin zone may reach its maximum at a nonvanishing wave vector implies that the "polarization catastrophe" can occur *nonuniformly* even when the dielectric constant remains finite. For the homogeneous simple-cubic (sc) lattice the principal instability is to the mode first described by Luttinger.[6] We show, however, that in a sc lattice with two alternating species there exists a narrow range of relative polarizability for which a different nonuniform mode predominates over both the Luttinger and the uniform mode.

In Sec. V we will present some results of numerical calculations for a simple-cubic lattice of identical point polarizable components. The main result is that the Coulomb potential can be strongly screened even for two charges in neighboring lattice cells. For some configurations the screening factor can be even larger than the bulk dielectric constant. In the last section we consider some of the simplifications we have made and discuss the implications of some of our more striking results.

II. GENERAL FORMALISM AND GREEN'S FUNCTION

Consider a lattice of points

$$\mathbf{r}_i = n_1\mathbf{a}^1 + n_2\mathbf{a}^2 + n_3\mathbf{a}^3 \ , \tag{1}$$

where n_1, n_2, n_3 are integers.

We assume that each lattice site carries an induced point dipole

$$\mathbf{p}_i = \alpha\mathbf{E}_i^{\text{loc}} \ , \tag{2}$$

where

$$\mathbf{E}_i^{\text{loc}} = \mathbf{E}_i^{\text{ext}} + \sum_j \mathbf{E}_i^j \ . \tag{3}$$

Here $\mathbf{E}_i^j$ is the field at $\mathbf{r}_i$ due to $\mathbf{p}_j$ at $\mathbf{r}_j$, and $\mathbf{E}_i^{\text{ext}}$ is the field at $\mathbf{r}_i$ due to sources other than induced dipoles.

The energy of the system in the given field $\mathbf{E}_i^{\text{ext}}$ is

$$\varepsilon = \sum_i \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2\alpha} - \sum_{i(\neq j)} \frac{\mathbf{p}_i\mathbf{p}_j}{2} : \nabla\nabla \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i \mathbf{p}_i \cdot \mathbf{E}_i^{\text{ext}} \ . \tag{4}$$

The notation $\mathbf{p}_i\mathbf{p}_j : \nabla\nabla[1/(\mathbf{r}_{\mathrm{i}} - \mathbf{r}_{\mathrm{j}})]$ means $(\mathbf{p}_i \cdot \nabla_r)(\mathbf{p}_j \cdot \nabla_r)[1/(|\mathbf{r}_i - \mathbf{r}_j + \mathbf{r})]|_{\mathbf{r}=0}$, similarly in later expressions.

The minimization of ε with respect to $\mathbf{P}_i$ yields the equilibrium relation

$$\frac{\mathbf{p}_i}{\alpha} = \mathbf{E}_i^{\text{ext}} + \sum_{j\,(\neq i)} (\mathbf{p}_j \cdot \nabla)\nabla \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{5}$$

equivalent to (2).

To solve this infinite set of equations, we introduce the Fourier expansion

$$\mathbf{p}(\mathbf{k}) = \sum_i \mathbf{p}_i e^{-i\mathbf{k}\cdot\mathbf{r}_i} \ , \tag{6}$$

$$\mathbf{E}^{\text{ext}}(\mathbf{k}) = \sum_i \mathbf{E}_i^{\text{ext}} e^{-i\mathbf{k}\cdot\mathbf{r}_i} \ , \tag{7}$$

in terms of which (4) and (5) become

$$\varepsilon = \int \frac{d^3k}{(2\pi)^3} \varepsilon(\mathbf{k}) \ , \tag{8}$$

where

$$\begin{aligned}\varepsilon(\mathbf{k}) = {} & \frac{1}{2}\frac{\mathbf{p}(\mathbf{k})\cdot[\mathbf{p}(\mathbf{k})]^*}{\alpha} - \frac{1}{2}\mathbf{p}(\mathbf{k})[\mathbf{p}(\mathbf{k})]^* : \overleftrightarrow{\mathbf{C}}(\mathbf{k})] \\ & - \{\mathbf{p}(\mathbf{k})[\mathbf{E}^{\text{ext}}(\mathbf{k})]^* + \text{c.c.}\}\end{aligned} \tag{9}$$

and

$$\frac{\mathbf{p}(\mathbf{k})}{\alpha} = \mathbf{E}^{\text{ext}}(\mathbf{k}) + \mathbf{p}(\mathbf{k}) \cdot \overleftrightarrow{\mathbf{C}}(\mathbf{k}) \ , \tag{10}$$

where

$$\overleftrightarrow{\mathbf{C}}(\mathbf{k}) = \sum_{\mathbf{r}_i\,(\neq 0)} e^{-i\mathbf{k}\cdot\mathbf{r}_i} \nabla\nabla \frac{1}{r_i} \ . \tag{11}$$

The integrals go over the unit cell in dual (i.e., reciprocal-lattice) space: $\mathbf{k} = k^1\mathbf{b}_1 + k^2\mathbf{b}_2 + k^3\mathbf{b}_3$, where $-\pi < (k^1, k^2, k^3) < \pi$, $\mathbf{b}_i\mathbf{a}^j = \delta_i{}^j$. The relation between **b**'s and **a**'s will be discussed in Sec. III.

Supposing $\overleftrightarrow{\mathbf{C}}(\mathbf{k})$ given, we may write the solution to (10) as

$$\mathbf{p}(\mathbf{k}) = \alpha\overleftrightarrow{\mathbf{g}}(\mathbf{k}) \cdot \mathbf{E}^{\text{ext}}(\mathbf{k}), \tag{12}$$

where

$$\overleftrightarrow{\mathbf{g}}(\mathbf{k}) = [1 - \alpha\overleftrightarrow{\mathbf{C}}(\mathbf{k})]^{-1} \ , \tag{13}$$

the inverse being taken by regarding the tensor as a linear operator on three-vectors. The integrand of (8) then becomes

$$\begin{aligned}\varepsilon(\mathbf{k}) &= -\frac{1}{2}\text{Re}[\mathbf{p}(\mathbf{k}) \cdot \mathbf{E}^{\text{ext}}(\mathbf{k})^*] \\ &= -\frac{\alpha}{2}\mathbf{E}^{\text{ext}}(\mathbf{k})\mathbf{E}^{\text{ext}}(\mathbf{k})^* : \overleftrightarrow{\mathbf{g}}(\mathbf{k}) \ .\end{aligned} \tag{14}$$

We shall calculate $\overleftrightarrow{\mathbf{C}}(\mathbf{k})$ for the simple cubic lattice in a later section. Here we point out that, at zero temperature and in the absence of any external field, the stability of the system against spontaneous ferroelectric or generalized antiferroelectric perturbation would require that $\partial^2\varepsilon(\mathbf{k})/\partial\mathbf{p}(\mathbf{k})\partial\mathbf{p}^*(\mathbf{k})$ be positive definite; in view of (9) this would require that *the eigenvalues of* $\overleftrightarrow{\mathbf{C}}(\mathbf{k})$ *be all less than* α^{-1} *for all* **k**. The consequences of this will be discussed in Sec. IV.

With $\overleftrightarrow{\mathbf{C}}(\mathbf{k})$ given, we may also evaluate the potential energy of the system plus two external point charges q, q' at $\mathbf{r}, \mathbf{r}'$:

$$\begin{aligned}\varepsilon_{\text{tot}} &= \varepsilon + \frac{qq'}{|\mathbf{r} - \mathbf{r}'|} \\ &= \frac{1}{2}q^2 G_{\text{pol}}(\mathbf{r}, \mathbf{r}) + \frac{1}{2}q'^2 G_{\text{pol}}(\mathbf{r}', \mathbf{r}') + qq'G(\mathbf{r}, \mathbf{r}') \ ,\end{aligned} \tag{15}$$

where

$$G_{\text{pol}}(\mathbf{r}, \mathbf{r}') = -\int \frac{d^3k}{(2\pi)^3} \alpha\overleftrightarrow{\mathbf{g}}(\mathbf{k}) : \nabla_{\mathbf{r}}\phi(\mathbf{k}, \mathbf{r})\nabla_{\mathbf{r}'}[\phi(\mathbf{k}, \mathbf{r}')]^* \tag{16}$$

and

$$G(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|} + G_{\text{pol}}(\mathbf{r}, \mathbf{r}') \ . \tag{17}$$

The function ϕ is defined by

$$\phi(\mathbf{k}, \mathbf{r}) = \sum \frac{e^{i\mathbf{k}\cdot\mathbf{r}_i}}{|\mathbf{r} - \mathbf{r}_i|} \ . \tag{18}$$

If we wish to place the point **r** directly on a lattice site $\mathbf{r}_{i_0}$, we shall adopt the convention that G_{pol} is to be averaged over values of **r** within a small sphere centered at $\mathbf{r}_{i_0}$. The effect of this is to remove the term with $i = i_0$ from the gradient of (18) and to replace **r** by $\mathbf{r}_{i_0}$ in all other expressions. The same is true of $\mathbf{r}'$.

III. LATTICE SUMS

We now derive rapidly convergent expressions for the functions $\phi(\mathbf{k}, \mathbf{r})$, its gradient, and $\overleftrightarrow{\mathbf{C}}(\mathbf{k})$ defined in Sec. II. We shall assume that the lattice in question is described by (1), where $\mathbf{a}^1,\mathbf{a}^2,\mathbf{a}^3$ are fixed vectors not necessarily orthogonal. We shall resolve the vector $\mathbf{r}$ as

$$\mathbf{r}=r_1\mathbf{a}^1+r_2\mathbf{a}^2+r_3\mathbf{a}^3 , \tag{19}$$

and $\mathbf{k}$ as

$$\mathbf{k}=k^1\mathbf{b}_1+k^2\mathbf{b}_2+k^3\mathbf{b}_3 ,$$

where $\mathbf{b}_1,\mathbf{b}_2,\mathbf{b}_3$ are basis vectors for the dual lattice:

$$\mathbf{b}_1=\frac{\mathbf{a}^2\times\mathbf{a}^3}{\mathbf{a}^1\cdot(\mathbf{a}^2\times\mathbf{a}^3)}, \quad \text{etc.}; \quad \mathbf{b}_l\cdot\mathbf{a}^{l'}=\delta_{ll'} .$$

To calculate $\phi_{\mathbf{k}}(\mathbf{r})$, we single out one direction, say the 1-direction, and write

$$\phi(\mathbf{k},\mathbf{r})=\sum_{n_1}\phi_{n_1}(\mathbf{r}) , \tag{20}$$

where (suppressing the argument $\mathbf{k}$)

$$\phi_{n_1}(\mathbf{r})=\sum_{n_2,n_3}\frac{e^{-i\mathbf{k}\cdot\mathbf{r}_i}}{|\mathbf{r}-\mathbf{r}_i|} . \tag{21}$$

For $r_1\neq n_1$, we notice that $\phi_{n_1}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$ is periodic. Fourier expansion on the 2,3 plane gives

$$\phi_{n_1}(\mathbf{r})=e^{-i\mathbf{k}\cdot\mathbf{r}}\sum_{m^2,m^3}V_{m^2,m^3}(r_1)e^{i\mathbf{m}\cdot\mathbf{r}} , \tag{22}$$

where

$$\mathbf{m}=m^2\mathbf{b}_2+m^3\mathbf{b}_3 ,$$

with $m^2,m^3=2\pi\times$integer. (From now on we shall use the shorthand "m" collectively for m^2,m^3 as in V_m, for example.)

Substituting into Poisson's equation

$$\nabla^2\phi_{n_1}(\mathbf{r})=-4\pi\sum_{n^2,n^3}e^{-i\mathbf{k}\cdot\mathbf{r}_i}\delta(r_3-n_3)\times\delta(r_2-n_2)\delta(r_1-n_1) \tag{23}$$

and inverting the Fourier transform on the plane, we get

$$\left[\mathbf{b}_1\frac{\partial}{\partial r_1}-i\mathbf{K}_m\right]\cdot\left[\mathbf{b}_1\frac{\partial}{\partial r_1}-i\mathbf{K}_m\right]V_m=-4\pi\delta(r_1-n_1) , \tag{24}$$

where

$$\mathbf{K}_m=\mathbf{k}-\mathbf{m} .$$

Obviously $V_m(r_1)$ has the exponential form $e^{-\gamma_m(r_1-n_1)}$ for $r_1>n_1$, but $e^{-\gamma_m^*(n_1-r_1)}$ for $r_1<n_1$, where γ_m (with real part greater than 0) and $-\gamma_m^*$ are the roots of the equation

$$(\mathbf{b}_1\gamma_m+i\mathbf{K}_m)\cdot(\mathbf{b}_1\gamma_m+i\mathbf{K}_m)=0 . \tag{25}$$

This equation is satisfied by putting

$$\gamma_m=\frac{|\mathbf{K}_m\times\mathbf{b}_1|-i\mathbf{K}_m\cdot\mathbf{b}_1}{\mathbf{b}_1\cdot\mathbf{b}_1} , \tag{26}$$

as seen by direct substitution or, more laboriously, by solving (25) as a quadratic in γ_m.

To normalize V_m we integrate (24) through $r_1=n_1$. Substituting the result into (22) we have

$$\phi_{n_1}(\mathbf{r})=e^{-i\mathbf{k}\cdot\mathbf{r}}\sum_m\frac{2\pi}{\mathrm{Re}\gamma_m}e^{-\gamma_m(r_1-n_1)}e^{i\mathbf{m}\cdot\mathbf{r}} \tag{27}$$

for $r_1>n_1$, and

$$\phi_{n_1}(\mathbf{r})=e^{-i\mathbf{k}\cdot\mathbf{r}}\sum_m\frac{2\pi}{\mathrm{Re}\gamma_m}e^{-\gamma_m^*(n_1-r_1)}e^{i\mathbf{m}\cdot\mathbf{r}} \tag{28}$$

for $r_1<n_1$. As long as $r_1\neq n_1$, the series in m is exponentially convergent on account of (26). Thus, if $\mathbf{r}$ is not on a lattice site, we may obtain $\nabla_{\mathbf{r}}\phi(\mathbf{k},\mathbf{r})$ (from now on we shall write ∇ for $\nabla_{\mathbf{r}}$) by analytically differentiating each term of (27) or (28), summing over n_1—this sum is analytic!—and finally over m. [Note that the choice of the 1-direction in (20) was arbitrary. As long as $\mathbf{r}$ is off lattice, we can single out a j direction for which $\mathbf{r}_j\neq$integer.]

If $\mathbf{r}$ is on a lattice site (say $\mathbf{r}=\mathbf{0}$ without loss of generality) then we define ϕ by omitting the singular term from (18). But then, for $n_1=0$, $\phi_n(\mathbf{r})$ is no longer periodic and (22) does not hold. This is a serious difficulty.

It is absolutely necessary to confront this difficulty, because even if $\mathbf{r},\mathbf{r}'$ are not on lattice sites we cannot find $G(\mathbf{r},\mathbf{r}')$ without computing $C(\mathbf{k})$ [see (16) and (13)] which by (11) is just the double gradient of $\phi(\mathbf{k},\mathbf{r})$ at $\mathbf{r}=0$, with the singular term omitted.

To this end we use a device introduced by Mackenzie.[7] Notice that the Coulomb potential has the unique property

$$\frac{1}{|\mathbf{r}|}=-(\mathbf{r}\cdot\nabla)\frac{1}{|\mathbf{r}|} ,$$

$$\nabla\frac{1}{|\mathbf{r}|}=-\frac{1}{2}(\mathbf{r}\cdot\nabla)\nabla\frac{1}{|\mathbf{r}|} ,$$

$$\nabla\nabla\frac{1}{|\mathbf{r}|}=-\frac{1}{3}(\mathbf{r}\cdot\nabla)\nabla\nabla\frac{1}{|\mathbf{r}|} .$$

Changing $\mathbf{r}$ to $\mathbf{r}-\mathbf{r}_i$, we find

$$\phi(\mathbf{k},\mathbf{r})|_{\mathbf{r}\to 0}=\sum_{\mathbf{r}_i}e^{-i\mathbf{k}\cdot\mathbf{r}_i}\mathbf{r}_i\cdot\nabla\frac{1}{|\mathbf{r}-\mathbf{r}_i|}\Bigg|_{\mathbf{r}\to 0} .$$

But from (19) we have

$$\frac{\partial}{\partial r_l}=\mathbf{a}^l\cdot\nabla , \tag{29}$$

and hence

$$\mathbf{r}\cdot\nabla=\sum_l r_l\frac{\partial}{\partial r_l} , \tag{30}$$

so that

$$\phi(\mathbf{k},0)=\sum_l\sum_{\mathbf{r}_i}n_l\frac{\partial}{\partial r_l}\frac{1}{|\mathbf{r}_i|} . \tag{31}$$

In this sum we are still supposed to omit the term $\mathbf{r}_i=\mathbf{0}$. But now that causes no embarrassment because for each l the whole layer $n_l=0$ drops out of the sum.

Hence by choosing the special direction in (20) to be the l direction instead of the 1-direction we obtain ϕ in the form

$$\phi(\mathbf{k},0)=\sum_{l}\sum_{n_l\,(\neq 0)} n_l \frac{\partial}{\partial r_l}\phi_{n_l}^{(l)} , \tag{32}$$

where $\phi_{n_l}^{(l)}$ is given by a sum like (27) or (28) with $\mathbf{b}_l$ singled out in (26) instead of $\mathbf{b}_1$, and with $\mathbf{m}$ orthogonal to $\mathbf{a}^l$ instead of to $\mathbf{a}^1$.

Similarly we get

$$\nabla\phi(\mathbf{k},0)=\frac{1}{2}\sum_{l}\sum_{n_l\,(\neq 0)} n_l \frac{\partial}{\partial r_l}\nabla\phi_{n_l}^{(l)} , \tag{33}$$

$$\overleftrightarrow{\mathbf{C}}(\mathbf{k})=\frac{1}{3}\sum_{l}\sum_{n_l\,(\neq 0)} n_l \frac{\partial}{\partial r_l}\nabla\nabla\phi_{n_l}^{(l)} , \tag{34}$$

where it is understood that $\mathbf{r}$ is set equal to 0 after the gradients are taken. In all these expressions the "bad" layer $n_l=0$ does not enter.

This is a powerful method of great generality. It leads, however, to a large computation. For ϕ we must do three independent Madelung sums, each consisting of summing an expression like the summand of (27) over n_l (analytically) and over $\mathbf{m}$ (numerically). Likewise we must do nine Madelung sums to get the three components of $\nabla\phi$, and 15 Madelung sums to get the five independent components of $\overleftrightarrow{\mathbf{C}}=\overleftrightarrow{\nabla\nabla}\phi$.

(We say that $\overleftrightarrow{\mathbf{C}}$ has five components because its 3×3 components are subject to the three constraints of symmetry and one of tracelessness. For an oblique lattice these four constraints, though still present, are less convenient to apply since symmetry holds for the matrix elements $C^{ll'}=\partial^2\phi/\partial r_l\partial r_{l'}$, whereas tracelessness holes for the "mixed" matrix $C_l^{l'}=\sum_{l''}\mathbf{b}_l\cdot\mathbf{b}_{l''}C^{l'l''}$. Thus one might find it convenient to ignore the symmetry constraint and calculate independently eight components $C_l^{l'}$; this would require 24 Madelung sums.)

We therefore have sought to reduce the number of sums to be performed, while still omitting the "bad" layer from the calculation. Let us note that the gradient operator can be written not only as

$$\nabla=\sum_{l}\mathbf{b}_l\frac{\partial}{\partial r_l} , \tag{35}$$

consistent with (19), but also has

$$\nabla=\sum_{l}\mathbf{a}^l\frac{\partial}{\partial r^l} \tag{36}$$

where we define

$$\frac{\partial}{\partial r^l}=\mathbf{b}_l\cdot\nabla=\sum_{l'}\mathbf{b}_l\cdot\mathbf{b}_{l'}\frac{\partial}{\partial r_{l'}} . \tag{37}$$

Then we have

$$\frac{\partial}{\partial r^l}(r^2)=2r_l , \tag{38}$$

as easily seen by substituting into (27). Hence

$$\frac{\partial}{\partial r^l}\frac{1}{r}=-\frac{r_l}{r^3} . \tag{39}$$

But this quantity vanishes if $\mathbf{r}$ lies in the plane $r_l=0$.

It follows that we can return to (21) [not (31)] and write

$$\left.\frac{\partial}{\partial r^1}\phi(\mathbf{k},\mathbf{r})\right|_{\mathbf{r}\to 0}=\sum_{n_1\,(\neq 0)}\left.\frac{\partial}{\partial r^1}\phi_{n_1}(\mathbf{r})\right|_{\mathbf{r}\to 0} , \tag{40}$$

since

$$\frac{\partial}{\partial r^1}\phi_{n_1}(\mathbf{r})=\sum_{n_2,n_3}e^{-i\mathbf{k}\cdot\mathbf{r}_i}\frac{n_1}{|n_1\mathbf{a}^1+n_2\mathbf{a}^2+n_3\mathbf{a}^3|^3} , \tag{41}$$

which vanishes for $n_1=0$.

The individual terms on the right side of (40) can be written with the help of (27) and (28) as

$$\left.\frac{\partial}{\partial r^1}\phi_{n_1}(\mathbf{r})\right|_{\mathbf{r}\to 0}=e^{-i\mathbf{k}\cdot\mathbf{r}}\sum_{m}\mathbf{b}_1\cdot(-\gamma_m\mathbf{b}_1-i\mathbf{K}_m)\frac{2\pi}{\mathrm{Re}\gamma_m}e^{-\gamma_m^* n_1}e^{i\mathbf{m}\cdot\mathbf{r}} \tag{42}$$

for $n_1>0$, and the same with $-\gamma_m^*$ replaced by γ_m for $n_1<0$. (Note that $\mathbf{b}_1\cdot\mathbf{m}=0$ for rectangular lattices but not in general for oblique ones.)

This whole procedure can be repeated for $l=2,3$ instead of $l=1$, and in this way the three quantities $\partial\phi(\mathbf{k},\mathbf{r})/\partial r^l|_{\mathbf{r}=0}$ can be calculated by performing only three Madelung sums instead of nine.

The off-diagonal components of $\overleftrightarrow{\mathbf{C}}$ can be found in a similar manner; for example,

$$\frac{\partial}{\partial r_2}\frac{\partial}{\partial r^1}\phi_{n_1}(\mathbf{r})=\sum_{n_2n_3}e^{-i\mathbf{k}\cdot\mathbf{r}_i}\frac{\partial}{\partial n_2}\frac{-n_1}{|n_1\mathbf{a}^1+n_2\mathbf{a}^2+n_3\mathbf{a}^3|^3} , \tag{43}$$

which also vanishes when $n_1=0$. Therefore we can write

$$\left.\frac{\partial}{\partial r_2}\frac{\partial}{\partial r^1}\phi(\mathbf{k},\mathbf{r})\right|_{\mathbf{r}\to 0}=\sum_{n_1\,(\neq 0)}\left.\frac{\partial}{\partial r_2}\frac{\partial}{\partial r^1}\phi_{n_1}(\mathbf{r})\right|_{\mathbf{r}\to 0} \tag{44}$$

and similarly for other $C_l^{l'}$, $l\neq l'$. Thus we obtain the off-diagonal components from only three instead of nine Madelung sums if the lattice is rectangular, or 6 instead of 18 if it is oblique and we do not use the symmetry constraint.

For the diagonal components, we observe first that

$$\nabla^2=\sum_{l}\frac{\partial}{\partial r_l}\frac{\partial}{\partial r^l} , \tag{45}$$

and so

$$C_l^{l'}=(\partial/\partial r_{l'})(\partial/\partial r^l)\phi$$

is traceless because $\nabla^2\phi=0$. It therefore suffices to calculate two differences, for example, $C_1^1-C_2^2$ and $C_1^1-C_3^3$.

We now consider the quantity

$$r_1\frac{\partial}{\partial r_1}\frac{\partial}{\partial r_2}\frac{\partial}{\partial r^2}\frac{1}{|\mathbf{r}|}=r_1\frac{\partial}{\partial r_1}\frac{\partial}{\partial r_2}\frac{-r_2}{|\mathbf{r}|^3}$$
$$=\left[-r_1\frac{\partial}{\partial r_1}-r_1r_2\frac{\partial}{\partial r_1}\frac{\partial}{\partial r_2}\right]\frac{1}{|\mathbf{r}|^3}\ . \tag{46}$$

Since the second term is symmetric under interchange of 1 and 2, we have

$$\left[r_1\frac{\partial}{\partial r_1}\frac{\partial^2}{\partial r_2\partial r^2}-r_2\frac{\partial}{\partial r_2}\frac{\partial}{\partial r_1\partial r^1}\right]\frac{1}{|\mathbf{r}|}$$
$$=\left[-r_1\frac{\partial}{\partial r_1}+r_2\frac{\partial}{\partial r_2}\right]\frac{1}{|\mathbf{r}|^3}$$
$$=-\frac{\partial}{\partial r_1}\frac{r_1}{|\mathbf{r}|^3}+\frac{\partial}{\partial r_2}\frac{r_2}{|\mathbf{r}|^3}$$
$$=\left[\frac{\partial^2}{\partial r_1\partial r^1}-\frac{\partial^2}{\partial r_2\partial r^2}\right]\frac{1}{|\mathbf{r}|}\ . \tag{47}$$

Replacing $\mathbf{r}$ by $\mathbf{r}-\mathbf{r}_i$ and summing over $\mathbf{r}_i$ we find on setting $\mathbf{r}=0$

$$C_1^1-C_2^2=-\sum_{n_1}n_1\frac{\partial}{\partial r_1}\frac{\partial^2}{\partial r_2\partial r^2}\phi_{n_1}^{(1)}$$
$$+\sum_{n_2}n_2\frac{\partial}{\partial r_2}\frac{\partial^2}{\partial r_1\partial r^1}\phi_{n_2}^{(2)}\ . \tag{48}$$

This and a similar formula for $C_1^1-C_3^3$ enables us to find all the diagonal elements $C_l^{l'}$ by means of four Madelung sums instead of six.

Since for any vector $\mathbf{q}=\sum_l q_l\mathbf{a}^l$ we have $\overleftrightarrow{\mathbf{C}}\cdot\mathbf{q}=\sum_l t_l\mathbf{a}^l$, where $t_l=\sum_{l'}C_l^{l'}q_l$, can regard the $C_l^{l'}$ as matrix elements of a *linear operator*. Hence the inversion indicated in (31) can be carried out as a matrix inversion using these elements. This means that (suppressing the argument $\mathbf{k}$)

$$\overleftrightarrow{\mathbf{g}}=\sum_{l,l'}g_l^{l'}\mathbf{a}^l\mathbf{b}_{l'}\ , \tag{49}$$

where $g_l^{l'}$ are given by

$$\sum_{l''}g_l^{l''}(\delta_{l''}^{l'}-\alpha C_{l''}^{l'})=\delta_l{}^{l'}\ . \tag{50}$$

We may then write (16) as

$$G_{\text{pol}}(\mathbf{r},\mathbf{r}')=-\int\int\int\frac{dk^1dk^2dk^3}{(2\pi)^3}\alpha g_{l''}^{l}\mathbf{a}^{l'}\cdot\mathbf{a}^{l''}\frac{\partial}{\partial r^l}\phi\frac{\partial}{\partial r^{l'}}\phi. \tag{51}$$

In Sec. V we shall discuss an explicit computation of (51) for the simple cubic lattice.

IV. STABILITY AGAINST SPONTANEOUS POLARIZATION

The eigenvalues of $\overleftrightarrow{\mathbf{C}}(\mathbf{k})$ are connected with the well-known "polarization catastrophe".[8] Suppose that there is no external field ($\mathbf{E}_i^{\text{ext}}=0$, all i). Then (9) becomes a homogeneous quadratic form in the $\mathbf{p}_i$. If this form is not positive definite (i.e., if it has even one negative eigenvalue) then the configuration with all $\mathbf{p}_i=0$ is not the ground state, and the system (considered ideally at zero temperature) will polarize spontaneously until it is stabilized at some nonzero configuration of $\mathbf{p}_i$'s by nonlinear restoring forces not considered here.

By translation symmetry the quadratic form in question is diagonal in $\mathbf{k}$, and so its eigenvalues are those of the matrices

$$\overleftrightarrow{\mathbf{Q}}(\mathbf{k})=\tfrac{1}{2}[\alpha^{-1}\overleftrightarrow{\mathbf{I}}-\overleftrightarrow{\mathbf{C}}(\mathbf{k})] \tag{52}$$

for individual values of $\mathbf{k}$. Hence the polarization catastrophe arises whenever *any* $\overleftrightarrow{\mathbf{C}}(\mathbf{k})$ has an eigenvalue greater than $1/\alpha$.

For $\mathbf{k}\to 0$ we have $\overleftrightarrow{\mathbf{C}}\to 4\pi(\frac{1}{3}\overleftrightarrow{\mathbf{I}}-\hat{\mathbf{k}}\hat{\mathbf{k}})$ for any cubically symmetric crystal. [The term $-4\pi\hat{\mathbf{k}}\hat{\mathbf{k}}$ is the result of replacing (11) by an integral, while $\frac{4}{3}\pi\overleftrightarrow{\mathbf{I}}$ is the Clausius-Mossotti correction; the latter becomes anisotropic in crystals of lower symmetry.] Since the highest eigenvalue is $4\pi/3$, one might conclude that at zero temperature a cubically symmetric crystal will develop spontaneous ferroelectricity if $4\pi\alpha/3>1$. In fact, the threshold value of α is just that which makes the dielectric constant $\kappa=1+4\pi\alpha/(1-\frac{4}{3}\pi\alpha)$ infinite.

This simple conclusion must, however, be modified in two ways. First, there may be values of $\mathbf{k}\neq\mathbf{0}$ for which $\overleftrightarrow{\mathbf{C}}(\mathbf{k})$ has an eigenvalue greater than $4\pi/3$. This holds for the simple cubic lattice, in which the maximum eigenvalue is attained for $\mathbf{k}=(\pi,\pi,0)$. The eigenconfiguration is that in which each dipole points along the z axis in the same sense as its z neighbors, but in the opposite sense from its x and y neighbors. The eigenvalue was first calculated as $2\times 2.676=5.352$ by Luttinger[6] in 1946; we find (see (Table I) $4\pi\times 0.42602=5.3533$. This is greater than the positive eigenvalue of $\overleftrightarrow{\mathbf{C}}(0)$, $4\pi/3=4.18879$.

One would thus expect a crystal of this type to become antiferroelectric rather than ferroelectric at zero temperature. Moreover, by setting $1/4\pi\alpha=0.42602$ we obtain the critical value of the dielectric constant,

$$\left[1+\frac{8\pi\alpha}{3}\right]\left[1-\frac{4\pi\alpha}{3}\right]=11.789\ .$$

Simple cubic crystals *not* antiferroelectric at zero temperature, one would expect, must have a dielectric constant less than this number. By contrast, for the face-centered-cubic lattice there is no eigenvalue higher than $4\pi/3$. Such a crystal could be ferroelectric at zero temperature, and the critical dielectric constant is infinity.

But second, the above reasoning assumes that all the atoms are equally polarizable, and for typical ionic crystals this is not true. If, for example, alternate sites have two different polarizabilities, α_1 and α_2, the three-vector $\mathbf{p}(\mathbf{k})$ is replaced by a six-component pair $(\mathbf{p}_1(\mathbf{k}),\mathbf{p}_2(\mathbf{k}))$, and $\overleftrightarrow{\mathbf{Q}}$ by a 6×6 matrix. Nevertheless, many of the above conclusions remain true qualitatively.

In particular, for the NaCl type of crystal, (52) becomes

$$(Q)(\mathbf{k})=\frac{1}{2}\begin{bmatrix}\alpha_1^{-1}\overleftrightarrow{\mathbf{I}}-\overleftrightarrow{\mathbf{C}}_+ & -\overleftrightarrow{\mathbf{C}}_- \\ -\overleftrightarrow{\mathbf{C}}_- & \alpha_2^{-1}\overleftrightarrow{\mathbf{I}}-\overleftrightarrow{\mathbf{C}}_+\end{bmatrix}, \tag{53}$$

where $\overleftrightarrow{\mathbf{C}}_\pm=\frac{1}{2}\overleftrightarrow{\mathbf{C}}(\mathbf{k})\pm\frac{1}{2}\overleftrightarrow{\mathbf{C}}(\mathbf{k}+\boldsymbol{\pi})$, $\boldsymbol{\pi}=(\pi,\pi,\pi)$. For $\mathbf{k}=(\pi,\pi,0)$, $\mathbf{k}+\boldsymbol{\pi}=(0,0,\pi)$, we have

$$\overleftrightarrow{\mathbf{C}}_\pm=4\pi c_\pm\begin{bmatrix}-\frac{1}{2} & 0 & 0\\ 0 & -\frac{1}{2} & 0\\ 0 & 0 & 1\end{bmatrix}, \tag{54}$$

where from Table I

$$2c_\pm=0.426\,02\pm(-0.770\,90)\ . \tag{55}$$

Since $\overleftrightarrow{\mathbf{C}}_+$ and $\overleftrightarrow{\mathbf{C}}_-$ are simultaneously diagonal, (Q) can be reorganized as

$$(Q)=2\pi\begin{bmatrix}(\gamma)+\frac{1}{2}(c) & 0 & 0\\ 0 & (\gamma)+\frac{1}{2}(c) & 0\\ 0 & 0 & (\gamma)-(c)\end{bmatrix}, \tag{56}$$

where

$$(c)=\begin{bmatrix}c_+ & c_-\\ c_- & c_+\end{bmatrix}, \tag{57}$$

$$(\gamma)=\begin{bmatrix}\gamma_1 & 0\\ 0 & \gamma_2\end{bmatrix}, \tag{58}$$

and

$$\gamma_i=(4\pi\alpha_i)^{-1}\ . \tag{59}$$

Let us now designate by H the configuration in which all dipoles point in the same direction and by L the alternating configuration described by Luttinger,[6] which corresponds to the z sector of (56). As discussed above, if the two species of ion are identical the favored instability is to L polarization, but if one species is totally unpolarizable than the other will form a fcc lattice which prefers to undergo H polarization. The condition for H stability is $4\pi\alpha/3<1$ where $\alpha=\frac{1}{2}(\alpha_1+\alpha_2)$, or

$$D_H\equiv\gamma_1\gamma_2-\tfrac{1}{6}(\gamma_1+\gamma_2)>0\ ; \tag{60}$$

the condition for L stability is

$$D_L\equiv\gamma_1\gamma_2-c_+(\gamma_1+\gamma_2)-s>0\ , \tag{61}$$

where $s=c_-^2-c_+^2$.

One could arrange γ_1 and γ_2 so that both D_H and D_L vanish, and thus describe a hypothetical crystal representing a "boundary" between H- and L-polarizing substances. It may be seen, though, that this boundary does not really exist because there is a third configuration L' which preempts both H and L within a narrow range of the parameters. The L' configuration corresponds to the x or y sector of (56). The condition for L' stability is

$$D_{L'}\equiv\gamma_1\gamma_2+\tfrac{1}{2}c_+(\gamma_1+\gamma_2)-\tfrac{1}{4}s>0\ . \tag{62}$$

To exhibit the existence of a region dominated by L', we choose γ_1 and γ_2 so that

$$\gamma_1\gamma_2=\tfrac{1}{6}(\gamma_1+\gamma_2)=\tfrac{1}{2}s\ ; \tag{63}$$

this is possible since $s>\frac{2}{9}$ by (55). We now have

$$\begin{gathered}D_H=0,\quad D_L=s(-\tfrac{1}{2}-3c_+)\ ,\\ D_{L'}=s(\tfrac{1}{4}+\tfrac{3}{2}c_+)=-\tfrac{1}{2}D_L\ .\end{gathered} \tag{64}$$

But from (55) we see that $2c_+=-0.34488<-\frac{1}{3}$, so that $D_L>0$ and $D_{L'}<0$. Thus this crystal would be stable against L polarization but unstable to L' polarization. By increasing either γ_i slightly we could render it also stable against H polarization. Therefore there is a finite region in the γ_1-γ_2 plane representing ionic crystals of the NaCl type which (if they exist) should be H and L stable but L' unstable at zero temperature.

V. NUMERICAL CALCULATION OF GREEN'S FUNCTION FOR A SIMPLE CUBIC LATTICE

We have carried out a sample calculation of $G_{\rm pol}$ for the simple cubic lattice. The basic formula (16) involves an integral which we have done by fast Fourier transform (FFT); in this way we obtain the values of $G_{\rm pol}$ simultane-

TABLE I. For the simple-cubic lattice, we show all six components of $\overleftrightarrow{c}=\overleftrightarrow{\mathbf{C}}/4\pi$ for all $\mathbf{k}\neq 0$ having all three components divisible by $\pi/2$.

k_x	k_y	k_z	c_{xx}	c_{yy}	c_{zz}	$c_{xy}=c_{yx}$	$c_{yz}=c_{zy}$	$c_{zx}=c_{xz}$
$\frac{\pi}{2}$	0	0	−0.718 96	0.359 48	0.359 48	0.000 00	0.000 00	0.000 00
$\frac{\pi}{2}$	$\frac{\pi}{2}$	0	−0.191 34	−0.191 34	0.382 69	−0.275 34	0.000 00	0.000 00
$\frac{\pi}{2}$	$\frac{\pi}{2}$	$\frac{\pi}{2}$	0.000 00	0.000 00	0.000 00	−0.143 84	−0.143 84	−0.143 84
π	0	0	−0.770 90	0.385 45	0.385 45	0.000 00	0.000 00	0.000 00
π	$\frac{\pi}{2}$	0	−0.468 48	0.062 71	0.405 77	0.000 00	0.000 00	0.000 00
π	$\frac{\pi}{2}$	$\frac{\pi}{2}$	−0.276 18	0.138 09	0.138 09	0.000 00	−0.064 05	0.000 00
π	π	0	−0.213 01	−0.213 01	0.426 02	0.000 00	0.000 00	0.000 00
π	π	$\frac{\pi}{2}$	−0.104 05	−0.104 05	0.208 09	0.000 00	0.000 00	0.000 00
π	π	π	0.000 00	0.000 00	0.000 00	0.000 00	0.000 00	0.000 00

ously for a whole family of positions $\mathbf{r}'=\mathbf{s}+\mathbf{n}$, where $\mathbf{s}$ is fixed and $\mathbf{n}$ is any lattice vector in (1).

For simplicity we have restricted ourselves to the case $\mathbf{s}=\mathbf{r}$, $\mathbf{r}'=\mathbf{r}+\mathbf{n}$; then $\phi(\mathbf{k},\mathbf{r}')=e^{-i\mathbf{k}\cdot\mathbf{n}}\phi(\mathbf{k},\mathbf{r})$, and (16) can be written

$$G_{\text{pol}}(\mathbf{r},\mathbf{r}+\mathbf{n}) = -\int\frac{d^3k}{(2\pi)^3}e^{i\mathbf{k}\cdot\mathbf{n}}\alpha\overleftrightarrow{\mathbf{g}}(\mathbf{k}):\boldsymbol{\nabla}_r\phi(\mathbf{k},\mathbf{r})\boldsymbol{\nabla}_r\phi(\mathbf{k},\mathbf{r})^* \ . \tag{65}$$

The FFT requires us to evaluate $\alpha\overleftrightarrow{\mathbf{g}}:\boldsymbol{\nabla}\phi\boldsymbol{\nabla}\phi^*$ on a set of $(2^q)^3$ points evenly spaced in the $\mathbf{k}$ cube $-\pi<k_i<\pi$, where q is some integer. We find, however, that there is a singularity at $\mathbf{k}\to 0$. In fact, we have $\phi\sim 4\pi/k^2$, $\boldsymbol{\nabla}_r\phi\sim 4\pi i\mathbf{k}/k^2$, and $\overleftrightarrow{\mathbf{C}}\approx 4\pi(\frac{1}{3}\overleftrightarrow{\mathbf{I}}-\mathbf{k}\mathbf{k}/k^2)$ by the Clausius-Mossotti argument. [The continuum approximation gives $-4\pi\mathbf{k}\mathbf{k}/k^2$, and the lattice correction is $\frac{4}{3}\pi\overleftrightarrow{\mathbf{I}}$; note that $\overleftrightarrow{\mathbf{C}}$ is strictly traceless by (11).] Hence

$$\alpha\overleftrightarrow{\mathbf{g}}:\boldsymbol{\nabla}_r\phi\boldsymbol{\nabla}_r\phi^*\sim\frac{\alpha}{1+\frac{8}{3}\pi\alpha}\frac{(4\pi)^2}{k^2} \quad \text{as } \mathbf{k}\to\mathbf{0} \ . \tag{66}$$

This singularity does not spoil the convergence of the integral in three dimensions, but it makes it impossible to sample the integrand at $\mathbf{k}\to 0$. Even if the $\mathbf{k}$ mesh is staggered so as to miss the origin, the result will be unreliable.

We resolve this difficulty by noting that the singularity arises from the distant behavior of G_{pol}, which is already known from the Clausius-Mossotti law. Therefore we can mitigate the singularity by subtracting a known term. From (18) we have

$$\int\frac{d^3k}{(2\pi)^3}\phi(\mathbf{k},0)e^{i\mathbf{k}\cdot\mathbf{n}}=\frac{1}{|\mathbf{n}|} \tag{67}$$

for any lattice vector $\mathbf{n}$. Hence we may rewrite (65) as

$$G_{\text{pol}}(\mathbf{r},\mathbf{r}+\mathbf{n}) = -\frac{4\pi\alpha}{1+\frac{8}{3}\pi\alpha}\frac{1}{|\mathbf{n}|} - \int\frac{d^3k}{(2\pi)^3}F(\mathbf{k},\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{n}} \ , \tag{68}$$

where

$$F(\mathbf{k},\mathbf{r})=\alpha\overleftrightarrow{\mathbf{g}}(\mathbf{k}):\boldsymbol{\nabla}_r\phi\boldsymbol{\nabla}_r\phi^*-\frac{4\pi\alpha}{1+\frac{8}{3}\pi\alpha}\phi(\mathbf{k},0) \ . \tag{69}$$

Combining (68) with (17) we have

$$G(\mathbf{r},\mathbf{r}+\mathbf{n})=\left[\frac{1-\frac{4}{3}\pi\alpha}{1+\frac{8}{3}\alpha}\right]\frac{1}{|\mathbf{n}|}-\int\frac{d^3k}{(2\pi)^3}Fe^{i\mathbf{k}\cdot\mathbf{n}} \ , \tag{70}$$

where we recognize

$$\frac{1+\frac{8}{3}\pi\alpha}{1-\frac{4}{3}\pi\alpha}=1+\frac{4\pi\alpha}{1-\frac{4}{3}\pi\alpha}$$

as the long-range dielectric constant.

The quantity F remains finite at $\mathbf{k}\to 0$, and therefore it is more suitable for FFT. It is, however, discontinuous. To establish this, we may write (for $\mathbf{r}\neq 0$)

$$\phi(\mathbf{k},\mathbf{r})=e^{-i\mathbf{k}\cdot\mathbf{r}}\left[\frac{4\pi}{k^2}+\eta(\mathbf{k},\mathbf{r})\right] , \tag{71}$$

where η is finite and well behaved at all $\mathbf{k}$, and

$$\eta(-\mathbf{k},\mathbf{r})=\eta^*(\mathbf{k},\mathbf{r}) \ . \tag{72}$$

Then

$$\begin{aligned}\boldsymbol{\nabla}_r\phi\boldsymbol{\nabla}_r\phi^* &= \frac{(4\pi)^2}{k^4}\mathbf{k}\mathbf{k} \\ &\quad +\frac{4\pi}{k^2}[-i\mathbf{k}(\boldsymbol{\nabla}_r+i\mathbf{k})\eta^*+(\boldsymbol{\nabla}_r-i\mathbf{k})\eta i\mathbf{k}] \\ &\quad +\boldsymbol{\nabla}_r\eta\boldsymbol{\nabla}_r\eta^* \ .\end{aligned} \tag{73}$$

When substituted into (69), the first term of (73) yields

$$\frac{\alpha}{1+\frac{8}{3}\pi\alpha}(4\pi)^2k^2/k^4 \ ,$$

which cancels the singularity in the second term of (69). The second term of (73) does not give rise to any infinity $\sim\mathbf{k}/k^2$, because $\boldsymbol{\nabla}_r\eta$ is real at $\mathbf{k}=\mathbf{0}$ on account of (72).

TABLE II. G_{pol} and G for on-site charges. For three values of $4\pi\alpha$ and for several values of the separation vector $\mathbf{n}=\mathbf{r}-\mathbf{r}'$ we show the continuum shielding function $G_{\text{pol}}^{\text{cont}}=|\mathbf{n}|^{-1}4\pi\alpha/(1+\frac{8}{3}\pi\alpha)$ and the true lattice shielding function G_{pol}. The charges are at the on-site position in a simple-cubic lattice of polarizability α at each site.

		$4\pi\alpha=1.75$		$4\pi\alpha=2.00$		$4\pi\alpha=2.25$	
$\mathbf{n}$	$\lvert\mathbf{n}\rvert^{-1}$	$G_{\text{pol}}^{\text{cont}}$	G_{pol}	$G_{\text{pol}}^{\text{cont}}$	G_{pol}	$G_{\text{pol}}^{\text{cont}}$	G_{pol}
(0,0,0)	∞	∞	1.669 90	∞	1.787 67	∞	1.893 99
(0,0,1)	1.000 00	0.807 69	0.759 81	0.857 15	0.809 68	0.900 00	0.854 54
(0,0,2)	0.500 00	0.403 85	0.370 12	0.428 57	0.392 93	0.450 00	0.415 37
(0,0,3)	0.333 33	0.269 23	0.252 56	0.285 71	0.265 61	0.300 00	0.276 43
(0,0,4)	0.250 00	0.201 92	0.193 92	0.214 29	0.203 61	0.225 00	0.210 56
(0,1,1)	0.707 11	0.571 13	0.579 75	0.606 09	0.613 39	0.636 40	0.640 28
(0,2,2)	0.353 55	0.285 56	0.285 91	0.303 04	0.303 06	0.318 20	0.318 10
(0,3,3)	0.235 70	0.190 37	0.190 52	0.202 03	0.201 96	0.212 13	0.211 75
(0,4,4)	0.176 78	0.142 78	0.142 92	0.151 53	0.151 57	0.159 10	0.158 95
(1,1,1)	0.577 35	0.466 32	0.482 33	0.494 87	0.509 82	0.519 62	0.532 96
(2,2,2)	0.288 68	0.233 16	0.236 38	0.247 44	0.250 73	0.259 81	0.263 04
(3,3,3)	0.192 45	0.155 44	0.156 54	0.164 96	0.166 12	0.173 20	0.174 38
(4,4,4)	0.144 34	0.116 58	0.117 08	0.123 72	0.124 26	0.129 91	0.130 46

However, if we write

$$\nabla_r \eta = \mathbf{M}_0 + i\mathbf{k}\cdot\overleftrightarrow{\mathbf{M}}_1 + O[k^2], \tag{74}$$

where $\mathbf{M}_0, \overleftrightarrow{\mathbf{M}}_1$ are real, then we get a finite term $4\pi(\mathbf{k}/k^2)\overleftrightarrow{\mathbf{M}}\cdot\mathbf{k}$ in (73), leading to a discontinuous term $\sim\overleftrightarrow{\mathbf{M}}_1\mathbf{kk}/k^2$ in F. The other terms in (73) behave smoothly in F; but the expansion of $\overleftrightarrow{\mathbf{g}}(\mathbf{k})$ has the form

$$\overleftrightarrow{\mathbf{g}}(\mathbf{k}) = \overleftrightarrow{\mathbf{g}}(0) + \underline{\overleftrightarrow{\mathbf{g}}}_2^{(4)}:\mathbf{kk} + \cdots, \tag{75}$$

and this leads to a finite discontinuity $\sim\underline{\overleftrightarrow{\mathbf{g}}}_2^{(4)}:\mathbf{kkkk}/k^4$ in F. For the case $\mathbf{r}=0$ the result is the same, since we define $\nabla_r\phi$ by averaging in the neighborhood $\mathbf{r}\neq 0$.

To avoid the ambiguous value of F at $\mathbf{k}=\mathbf{0}$, we stagger our FFT mesh by giving each k^i the values $2\pi/2^{q+1}, 3\times 2\pi/2^{q+1}, 5\times 2\pi/2q^{q+1}, \ldots$. Nevertheless, because of the discontinuity we should not expect our error to diminish exponentially in the parameter 2^q as would be usual in integrating a periodic function. In fact, we may predict the error as follows.

Our choice of mesh $\mathbf{k}$ space ensures that the Fourier transform of F, as we calculate it, will be antiperiodic in $\mathbf{n}$, with antiperiod 2^q in each Cartesian direction. In fact, if $\tilde{F} = \int [d^3k/(2\pi)^3] e^{i\mathbf{k}\cdot\mathbf{n}} F$ is the true transform, then what we are calculating is really $\sum_{\mathbf{n}'}(-1)^{n'_1+n'_2+n'_3}\tilde{F}(\mathbf{n}+2^q\mathbf{n}')$. Therefore the error consists of the $\mathbf{n}'\neq\mathbf{0}$ terms. For fixed $\mathbf{n}$ and increasing 2^q, the error will diminish essentially as $\tilde{F}(2^q,0,0)$.

But $\tilde{F}(\mathbf{n})$ is the difference between $G(\mathbf{r},\mathbf{r}+\mathbf{n})$ and its continuum approximation. For general $\mathbf{r},\mathbf{r}'$ this difference should decrease as $1/|\mathbf{n}|^2$, since each charge induces nearby dipoles that affect the other charge to this order. When, however, $\mathbf{r}'=\mathbf{r}+\mathbf{n}$, then the environment of one charge is the inversion of that of the other. Hence (taking two equal charges without loss of generality) they induce opposite dipole moments, and the leading effects cancel, leaving a discrepancy $\sim 1/|\mathbf{n}|^3$ due to induced quadrupole moments in the near environment. Dipoles at $\mathbf{r}''$ far from both $\mathbf{r}$ and $\mathbf{r}'$ contribute to G in proportion to $1/r_1^2 r_2^2$, where $\mathbf{r}_1 = |\mathbf{r}-\mathbf{r}''|$, $\mathbf{r}_2 = |\mathbf{r}'-\mathbf{r}''|$. The discrepancy between this and the result of spreading the dipole into a continuous cube is down by another factor $1/r_1^2$ or $1/r_2^2$. Therefore the "far" contribution to $\tilde{F}$ is of order $\int (d^3r''/r_1^4 r_2^2) \sim 1/|\mathbf{n}|^3$ also.

We conclude that the error in our calculation should diminish as the cube of 2^q. This was confirmed by comparing our value of $\tilde{F}(0)$ for different values of q.

From the definition we see that F is real [as expected since $G(\mathbf{r},\mathbf{r}+\mathbf{n})$ is even in $\mathbf{n}$] and that F is even in $\mathbf{k}$ (as expected since G is real). Hence there are really only $(2^{q-1})^3$ real quantities in the FFT, related moreover by permutation of axes. By transforming one layer at a time, we are able to profit partly from the permutation symmetry and the fit the FFT into $\frac{1}{2}(2^{q-1})^3$ words of double precision, or 2^{3q-1} bytes (where 1 byte$\equiv 2^3$ binary digits).

In evaluating sums of the type (27) and (28), we kept 25 terms, those having all $|m^i|^2 \leq 2$. This yielded an accuracy of $\sim 10^{-5}$. Since the sums must be repeated for each $\mathbf{k}$, we saved computer time by tabulating the required exponential functions in advance, and by avoiding various redundancies associated with permutations of axes. For $q=6$ the computation (error $\sim 10^{-5}$) required about 400×10^3 bytes and 4 min. CPU time (Digital Equipment Corporation VAX 11-780 computer) for each value of $\mathbf{r}$. Typical results are shown in Tables II and III.

VI. DISCUSSION

We have presented in Sec. III a system of calculation applicable to any three-dimensional lattice, but our numerical results (Sec. V) pertain only to the simple cubic. Hence we can answer our original questions (Sec. I) only in a way which indicates roughly what may be expected in other lattices.

We find that the dielectric screening is indeed effective at distances of the order of a lattice spacing. In the most unfavorable case studied, where the two charges are on

TABLE III. G_{pol} and G for off-site charges. For three values of $4\pi\alpha$ and for several values of the separation vector $\mathbf{n}=\mathbf{r}-\mathbf{r}'$ we show the continuum shielding function $G_{\text{pol}}^{\text{cont}} = |\mathbf{n}|^{-1} 4\pi\alpha/(1+\frac{8}{3}\pi\alpha)$ and the true lattice shielding function G_{pol}. The charges are at the body-centered position in a simple-cubic lattice of polarizability α at each site.

		$4\pi\alpha=1.75$		$4\pi\alpha=2.00$		$4\pi\alpha=2.25$	
$\mathbf{n}$	$\lvert\mathbf{n}\rvert^{-1}$	$G_{\text{pol}}^{\text{cont}}$	G_{pol}	$G_{\text{pol}}^{\text{cont}}$	G_{pol}	$G_{\text{pol}}^{\text{cont}}$	G_{pol}
(0,0,0)	∞	∞	1.669 90	∞	1.787 67	∞	1.893 99
(0,0,1)	1.000 00	0.807 69	0.900 12	0.857 15	0.957 81	0.900 00	1.008 99
(0,0,2)	0.500 00	0.403 85	0.390 91	0.428 57	0.412 05	0.450 00	0.403 06
(0,0,3)	0.333 33	0.269 23	0.263 78	0.285 71	0.279 67	0.300 00	0.293 70
(0,0,4)	0.250 00	0.201 92	0.197 97	0.214 29	0.209 53	0.225 00	0.219 37
(0,1,1)	0.707 11	0.571 13	0.580 86	0.606 09	0.616 98	0.636 40	0.648 58
(0,2,2)	0.353 55	0.285 56	0.287 42	0.303 04	0.305 11	0.318 20	0.320 30
(0,3,3)	0.235 70	0.190 37	0.190 83	0.202 03	0.202 41	0.212 13	0.212 38
(0,4,4)	0.176 78	0.142 78	0.142 99	0.151 53	0.151 70	0.159 10	0.159 21
(1,1,1)	0.577 35	0.466 32	0.444 49	0.494 87	0.472 47	0.519 62	0.496 68
(2,2,2)	0.288 68	0.233 16	0.235 82	0.247 44	0.250 32	0.259 81	0.262 75
(3,3,3)	0.192 45	0.155 44	0.156 45	0.164 96	0.166 05	0.173 20	0.174 31
(4,4,4)	0.144 34	0.116 58	0.117 05	0.123 72	0.124 23	0.129 91	0.130 45

adjacent lattice sites (0,0,1 of Table II), the screening is 94–95% of that expected in a continuous dielectric. In the most favorable case, where the two charges are at adjacent body-centered positions (0,0,1 of Table III), the screening is 11–12% *greater* than in the continuum. This is sufficient, when $4\pi\alpha = 2.25$, to make the screening stronger than the bare repulsion, so that from classical electrostatics alone one can actually obtain an attractive force between two like charges. We note that the Luttinger instability discussed in Sec. IV comes into play only at $4\pi\alpha = 1/0.42602 = 2.347$.

This result is extremely encouraging for the possibility of short-range pairing mechanisms between electrons or holes leading to boson formation, as it suggests that under favorable circumstances the Coulomb repulsion might be wholly or nearly nullified by dielectric effects.

Our other striking result (Sec. IV) is the existence of the L' configuration as the ground state of binary simple cubic crystals in a narrow range of polarizabilities. In view of Eqs. (63), one species of ion should have $4\pi\alpha$ near 3 and the other near $\frac{1}{6}$. Since the preference for L' depends on the inequality $0.34488 > \frac{1}{3}$, we may estimate a tolerance of a few percent in the tuning of ionic polarizabilities to obtain this ground state. We note that negative ions normally have much greater polarizabilities (on account of greater volume) than positive ones, and so the needed ratio of 15–20:1 might not be impossible.

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[1] R. Friedberg and T. D. Lee, Phys. Lett. A **138**, 423 (1989).

[2] R. Friedberg and T. D. Lee, Phys. Rev. B **39**, 482 (1989).

[3] P. W. Anderson, Mater. Res. Bull. **8**, 153 (1973); G. Baskaran, Z. Zhou, and P. W. Anderson, Solid State Commun. **63**, 973 (1987).

[4] Werner Weber, Phys. Rev. Lett. **58**, 1371 (1987).

[5] M. L. Glasser and I. J. Zucker, Theor. Chem. Adv. Persp. **9**, 67–139 (1980).

[6] J. M. Luttinger, Phys. Rev. **70**, 954 (1946).

[7] J. K. Mackenzie, Can. J. Phys. **35**, 500 (1957); J. Chem. Phys. **26**, 1769 (1957).

[8] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1986), p. 378.