Dielectric Losses in Ionic Crystals with Disordered Charge Distributions

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A theory of the dielectric losses to be expected in nonconducting, ionic crystals containing disordered charge distributions is described. In this theory the disorder in the distribution of mass and force constants (which accompanies the disordered charge distribution) is disregarded. Detailed results are derived for crystals with the inverse spinel structure. In such crystals two- and three-valent ions occupy equivalent sites (the "octahedral" sites) in a random fashion. The predicted loss tangent depends strongly on the spatial correlation between the charge deviations (the difference between the actual charge and the average charge corresponding to a given lattice site). If the charge deviations are substantially uncorrelated, the loss tangent is proportional to the frequency and approximately 5×10^{-4} at X band. However, if the charge deviations are strongly correlated in such a way that charge neutrality is maintained within each unit cell of the crystal, the loss tangent is proportional to the cube of the frequency and approximately 2×10^{-9} at X band. The theory is also applied to a discussion of the additional losses to be expected in polycrystals with very small grain size. It is concluded that this contribution to the loss tangent should be insignificant unless the grain size is extremely small.

I. INTRODUCTION

NONCONDUCTING, ionic crystals should, under ideal conditions, exhibit dielectric losses only in the vicinity of the limiting lattice frequencies, which are usually in the infrared region of the spectrum. If the charge distribution in these crystals deviates from perfect periodicity, however, dielectric losses may also occur at lower frequencies. The object of the present paper is to derive theoretical estimates of the dielectric losses attributable to various kinds of disorder in the charge distribution. An example for crystals with an inherently disordered charge distribution is provided by the inverse spinels. It is generally believed that in such crystals two- and three-valent ions are distributed over equivalent sites (the "octahedral" sites) in a random fashion.[1] It is shown below that this random distribution leads to dielectric losses even when electronic or ionic conduction are completely suppressed. Another type of disordered charge distribution occurs in polycrystals. It is shown below that the contribution to the dielectric losses arising from this disorder is insignificant unless the grain size is extremely small.

Similar problems have previously been discussed by Vinogradov.[2] His results are based on the assumption that no correlation exists between the charge deviations at different lattice sites. Here the charge deviation is defined as the difference between the actual charge and the average charge located at a given lattice site. Vinogradov's theory disregards the fact that the charge deviations will have a tendency to compensate each other. In the present theory the correlation between the charge deviations at different lattice sites is taken into account. The theory is thus more general than Vinogradov's theory, which is contained in it as a special case.

For the sake of simplicity it is assumed in the following discussion that the purely mechanical properties of the crystal are described by a primitive lattice (i.e., a lattice with one atom per unit cell). The completely ordered ionic crystal then corresponds to the case in which adjacent lattice sites carry charges of opposite sign. In addition to this completely ordered charge distribution, we shall also consider certain types of disordered charge distributions.

II. GENERAL THEORY[3]

Let $\mathbf{n}$, $\mathbf{n}'$ etc. be vectors with integer components, $\mathbf{r}^n$ the equilibrium site of the nth ion of the lattice, and $\mathbf{s}^n$ the deviation of the position of this ion from its rest position. For small deviations from equilibrium the potential energy of the lattice is, apart from a constant, given by

$$\phi(\cdots s_\nu{}^n \cdots) = \tfrac{1}{2} \sum_{\mathbf{nn}', \nu\nu'} \phi_{\nu\nu'}{}^{\mathbf{nn}'} s_\nu{}^n s_{\nu'}{}^{n'}, \tag{1}$$

where $s_\nu{}^n$ is the ν component of $\mathbf{s}^n$, and $\phi_{\nu\nu'}{}^{\mathbf{nn}'}$ are the force constants. If q^n is the charge of the ion $\mathbf{n}$ and m the mass of each ion, the equations of motion are

$$m\ddot{s}_\nu{}^n = - \sum_{\mathbf{n}', \nu'} \phi_{\nu\nu'}{}^{\mathbf{nn}'} s_{\nu'}{}^{n'} + q^n E_\nu, \tag{2}$$

where E_ν is the ν component of the electric field, which we assume to be uniform.

In the absence of an electric driving field E_ν the equations of motion have simple solutions of the form

$$s_\nu{}^n = \alpha_{\nu\lambda}{}^{\mathbf{k}} \exp i(\mathbf{k} \cdot \mathbf{r}^n - \omega_\lambda{}^{\mathbf{k}} t), \tag{3}$$

where $(\omega_\lambda{}^{\mathbf{k}})^2$ and $\alpha_{\nu\lambda}{}^{\mathbf{k}}$ are eigenvalues and eigenvectors,

[1] See for instance J. Smit and H. P. J. Wijn, *Ferrites* (John Wiley & Sons, Inc., New York, 1959), pp. 140–145.

[2] V. S. Vinogradov, Fiz. Tverd. Tela **2**, 2622 (1960) [English transl.: Soviet Phys.—Solid State **2**, 2338 (1961)].

[3] For a detailed discussion of lattice dynamics the reader is referred to M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1954) or G. Leibfried in *Encyclopedia of Physics*, edited by S. Flügge (Springer Verlag, Berlin, 1955), Vol. VII, Part 1, Crystal Physics 1.

respectively, of the "frequency tensor"

$$l_{\nu\nu'}{}^{k}=\frac{1}{m}\sum_{n'}\phi_{\nu\nu'}{}^{nn'}\exp[-i\mathbf{k}\cdot(\mathbf{r}^{n}-\mathbf{r}^{n'})].\qquad(4)$$

It should be noticed that the right-hand side of Eq. (4) does not depend on $\mathbf{n}$ because the coupling matrix $\phi_{\nu\nu'}{}^{nn'}$ depends on $\mathbf{n}$ and $\mathbf{n'}$ only through the difference $\mathbf{n}-\mathbf{n'}$. In Eq. (3) the subscript λ labels the various solutions of the eigenvalue equation

$$(\omega^{k})^{2}\alpha_{\nu}{}^{k}=\sum_{\nu'}l_{\nu\nu'}{}^{k}\alpha_{\nu'}{}^{k},\qquad(5)$$

which defines the eigenfrequencies $\omega_{\lambda}{}^{k}$ and eigenvectors $\alpha_{\nu\lambda}{}^{k}$. The eigenvectors can be normalized in such a way that they form an orthonormal matrix.

We now assume periodic boundary conditions and introduce the Fourier components q^{k} of the charge distribution q^{n}.

$$q^{n}=N^{-1/2}\sum_{k}q^{k}\exp(i\mathbf{k}\cdot\mathbf{r}^{n}),$$
$$\qquad(6)$$
$$q^{k}=N^{-1/2}\sum_{n}q^{n}\exp(-i\mathbf{k}\cdot\mathbf{r}^{n}).$$

Here N is the number of lattice sites in the periodicity volume and the summation over $\mathbf{k}$ extends over N sites of the reciprocal lattice. Similarly we introduce normal coordinates $a_{\lambda}{}^{k}$ by means of the transformation

$$s_{\nu}{}^{n}=N^{-1/2}\sum_{k\lambda}a_{\lambda}{}^{k}\alpha_{\nu\lambda}{}^{k}\exp(i\mathbf{k}\cdot\mathbf{r}^{n}),$$
$$\qquad(7)$$
$$a_{\lambda}{}^{k}=N^{-1/2}\sum_{n\nu}s_{\nu}{}^{n}\alpha_{\nu\lambda}{}^{k}\exp(-i\mathbf{k}\cdot\mathbf{r}^{n}).$$

The equations of motion (2) expressed in terms of the normal coordinates now become

$$\ddot{a}_{\lambda}{}^{k}+(\omega_{\lambda}{}^{k})^{2}a_{\lambda}{}^{k}=m^{-1}q^{k}\sum_{\nu}\alpha_{\nu\lambda}{}^{k}E_{\nu}.\qquad(8)$$

Assume now that the driving field $\mathbf{E}$ has a periodic time dependence

$$\mathbf{E}=\bar{\mathbf{E}}\exp(i\omega t)\qquad(9)$$

and that the lattice oscillators $a_{\lambda}{}^{k}$ are slightly damped. This damping may be taken into account by adding to the left-hand side of Eq. (8) a damping term $\gamma\dot{a}_{\lambda}{}^{k}$. Later on, we shall consider the limit $\gamma\to0$.

The solution of the equations of motion (8) is obviously given by

$$a_{\lambda}{}^{k}=\frac{m^{-1}q^{k}\sum_{\nu}\alpha_{\nu\lambda}{}^{k}\bar{E}_{\nu}}{(\omega_{\lambda}{}^{k})^{2}-\omega^{2}+i\omega\gamma}\exp(i\omega t).\qquad(10)$$

The ν component of the polarization is

$$P_{\nu}=V^{-1}\sum_{n}s_{\nu}{}^{n}q^{n}=V^{-1}\sum_{k\nu}a_{\lambda}{}^{k}\alpha_{\nu\lambda}{}^{k}q^{k*},\qquad(11)$$

where we have used Eqs. (6) and (7), V is the periodicity volume, and the asterisk denotes the complex conjugate.

Consider now the susceptibility tensor $\chi_{\nu\nu'}{}^{(0)}$ defined by

$$P_{\nu}=\sum_{\nu'}\chi_{\nu\nu'}{}^{(0)}\bar{E}_{\nu\;\text{eff}}(e^{i\omega t}),\qquad(12)$$

where $\bar{\mathbf{E}}_{\text{eff}}$ is the effective electric field acting on each ion of the crystal. The effective field is the sum of the applied electric field and a contribution arising from the polarization of the crystal. For this reason $\chi^{(0)}$ is not the actual susceptibility χ. The relation between $\chi^{(0)}$ and χ is discussed in Sec. V. We find from Eqs. (10), (11), and (12)

$$\chi_{\nu\nu'}{}^{(0)}=\frac{1}{Vm}\sum_{k\lambda}\frac{|q^{k}|^{2}\alpha_{\nu\lambda}{}^{k}\alpha_{\nu'\lambda}{}^{k}}{(\omega_{\lambda}{}^{k})^{2}-\omega^{2}+i\gamma\omega}.\qquad(13)$$

If the material is macroscopically isotropic, all diagonal elements of the susceptibility tensor are equal, and hence also equal to one-third of the trace of the susceptibility tensor. Thus the scalar susceptibility is under these conditions

$$\chi_{0}=\tfrac{1}{3}\sum_{\nu}\chi_{\nu\nu}{}^{(0)}=\frac{1}{3Vm}\sum_{k\lambda}\frac{|q^{k}|^{2}}{(\omega_{\lambda}{}^{k})^{2}-\omega^{2}+i\gamma\omega}.\qquad(14)$$

Here we have used the orthonormality of the matrix $\alpha_{\nu\lambda}{}^{k}$.

Consider now the (negative) imaginary part χ_{0}'' of the susceptibility as a function of frequency. According to Eq. (14) it consists of a sum of resonance curves corresponding to the various normal modes. The width of these individual resonance curves depends on the damping constant γ whereas the total area under each curve is substantially independent of γ. Since the imaginary part of the susceptibility is a superposition of many closely spaced resonance curves, it is primarily determined by the area associated with each individual curve (rather than the width or the peak height). Thus it is permissible for the purpose of evaluating Eq. (14) to consider the limit of vanishing damping constant. The results obtained in this way are reliable as long as the Q of the individual resonances ($Q\sim\omega_{\lambda}{}^{k}/\gamma$) is reasonably high ($Q\geq5$ say).

In the limit of zero damping χ_{0}'' approaches a sum of delta functions, because for $\omega>0$

$$\lim_{\gamma\to0}\mathrm{Im}[(\omega_{\lambda}{}^{k})^{2}-\omega^{2}+i\gamma\omega]^{-1}=-\tfrac{1}{2}\pi\omega^{-1}\delta(\omega_{\lambda}{}^{k}-\omega).\qquad(15)$$

Thus

$$\chi_{0}''=(\pi/6Vm\omega)\sum_{k\lambda}|q^{k}|^{2}\delta(\omega_{\lambda}{}^{k}-\omega).\qquad(16)$$

For further progress it is obviously necessary to know $|q^{k}|^{2}$, i.e., the "spectrum" of the charge distribution q^{n}. If the statistical laws that govern the distribution of charge over the lattice sites are known, the spectrum can be calculated from the correlation function

$$\phi^{m}=N^{-1}\sum_{n}\langle q^{n+m}q^{n}\rangle.\qquad(17)$$

Here the angular brackets denote an ensemble average. After introduction of the Fourier transform of q^n the correlation function becomes according to Eq. (6)

$$\phi^m = N^{-1} \sum_k \langle |q^k|^2 \rangle \exp(i\mathbf{k} \cdot \mathbf{r}^m). \quad (18)$$

Hence

$$\langle |q^k|^2 \rangle = \sum_m \phi^m \exp(-i\mathbf{k} \cdot \mathbf{r}^m). \quad (19)$$

If the correlation function is known, we may thus calculate the ensemble average of the susceptibility according to Eqs. (16) and (19).

III. APPLICATION TO SINGLE CRYSTALS WITH INTERNAL DISORDER

It is convenient to express the charge distribution q^n as

$$q^n = q_0^n + q_1^n, \quad (20)$$

where q_0^n is the average charge and q_1^n the deviation from the average charge. Thus

$$\langle q_1^n \rangle = 0. \quad (21)$$

The correlation function is similarly expressed as

$$\phi^m = \phi_0^m + \phi_1^m, \quad (22)$$

where

$$\phi_0^m = N^{-1} \sum_n q_0^{n+m} q_0^n,$$

$$\quad (23)$$

$$\phi_1^m = N^{-1} \sum_n \langle q_1^{n+m} q_1^n \rangle.$$

Similarly,

$$\langle |q^k|^2 \rangle = |q^k|_0^2 + \langle |q^k|_1^2 \rangle,$$

$$|q^k|_0^2 = \sum_m \phi_0^m \exp[-i\mathbf{k} \cdot \mathbf{r}^m],$$

$$\quad (24)$$

$$\langle |q^k|_1^2 \rangle = \sum_m \phi_1^m \exp[-i\mathbf{k} \cdot \mathbf{r}^m].$$

$|q_0^k|^2$ is nonzero only for the limiting lattice frequencies and is of no further interest for the present problem.

If the charge deviations are uncorrelated, it follows that

$$\phi_1^m = \langle q_1^2 \rangle \quad \text{for} \quad \mathbf{m} = 0,$$

$$\quad = 0 \quad \text{for} \quad \mathbf{m} \neq 0. \quad (25)$$

This implies that the spectrum is "white" (i.e., independent of $\mathbf{k}$)

$$\langle |q^k|_1^2 \rangle = \langle q_1^2 \rangle. \quad (26)$$

The susceptibility is according to Eqs. (16) and (26) in this case

$$\chi_0'' = (\langle q_1^2 \rangle \omega / 12\pi m) \sum_\lambda 1/c_\lambda^3, \quad (27)$$

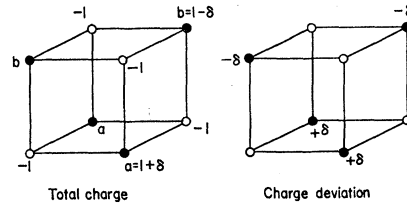where c_λ is the sound velocity for the three branches of

FIG. 1. Disordered charge distribution in an Na–Cl lattice. "a" and "b" ions are randomly distributed over the black sites, with two "a" and two "b" ions falling into each cell.

the spectrum and it has been assumed that the phonon frequencies ω_λ^k are proportional to the wave number $k = |\mathbf{k}|$ in the frequency region of interest.

$$\omega_\lambda^k = c_\lambda k. \quad (28)$$

This approximation is valid as long as the measuring frequency is small compared to the limiting lattice frequencies. The summation over $\mathbf{k}$ in Eq. (16) has been replaced by an integration according to the rule

$$\sum_k = \frac{V}{(2\pi)^3} \int d^3\mathbf{k}. \quad (29)$$

In order to arrive at an estimate of the absorption to be expected in inverse spinels, we note that the unit cell contains 14 sites, on four of which there is a charge deviation of $\pm \frac{1}{2}$ electron charge. Thus

$$\langle q_1^2 \rangle = (1/14)e^2 \simeq 1.8 \times 10^{-20} \text{ erg cm}.$$

Inserting for m the average mass of the ions ($m \simeq 46 \times 10^{-24}$ g), and replacing $\sum_\lambda c_\lambda^{-3}$ by $2c_t^{-3}$, where $c_t \simeq 4 \times 10^5$ cm sec^{-1} is the velocity of transverse sound, one obtains for $\omega/2\pi = 10^{10}$ sec^{-1}

$$\chi_0'' \simeq 2 \times 10^{-5}. \quad (30)$$

Consider now a case of strong correlation between the charge deviations. As an example, we shall discuss crystals with an NaCl-lattice structure assuming that charge neutrality is maintained within each cubic unit cell, which contains 4 positive and 4 negative ions. Figure 1 shows the lattice structure and the distribution of positive and negative ions over the available sites. The negative ions are assumed to have equal charge, but the positive ions are of two kinds with unequal charge. Charge neutrality requires that each of the lattice cells contains 2 each of the two kinds of positive ions. It is shown in Appendix 1 that the correlation function for this case is given by

$$\phi_1^m = \langle q_1^2 \rangle \quad \mathbf{m} = 0,$$
$$\quad = -\tfrac{1}{12}\langle q_1^2 \rangle \quad \mathbf{m} = [110], [1-10], \quad (31)$$
$$\quad \quad \quad \quad \quad [-110], \cdots, [01-1],$$
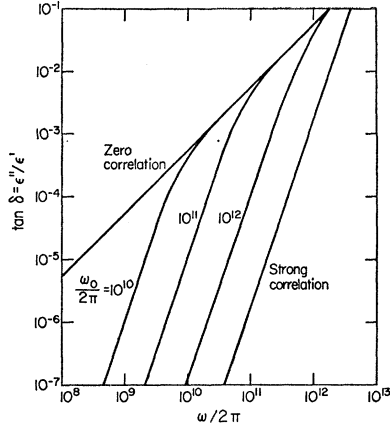$$\quad = 0 \quad \text{otherwise}.$$

FIG. 2. Predicted dielectric loss tangent of inverse spinels as a function of frequency for various correlation frequencies ω_0. Only the contribution arising from the disordered charge distribution is plotted.

It should be noticed that

$$\sum_m \phi_1^m = 0 \qquad (32)$$

as required by charge neutrality.

The spectrum of the charge distribution is in this case

$$\langle |q^k|_1^2 \rangle = \tfrac{1}{6}\langle q_1^2 \rangle [6 - \cos(k_x + k_y)d - \cos(k_x - k_y)d$$
$$- \cos(k_y + k_z)d - \cos(k_y - k_z)d$$
$$- \cos(k_x + k_z)d - \cos(k_x - k_z)d], \quad (33)$$

where d is the lattice constant. In the microwave and millimeter wave region $|\mathbf{k}|d \ll 1$, so that to a good approximation

$$\langle |q^k|_1^2 \rangle = \tfrac{1}{3}\langle q_1^2 \rangle \cdot d^2(k_x^2 + k_y^2 + k_z^2). \quad (34)$$

Thus according to Eq. (16) for this case

$$\chi_0'' = \frac{\langle q_1^2 \rangle d^2 \omega^3}{36\pi m} \sum_\lambda \frac{1}{c_\lambda^5}. \quad (35)$$

Comparison of Eqs. (27) and (35) shows that the imposition of charge neutrality within each lattice cell reduces the absorption coefficient by a factor of approximately $(1/3)(d\omega/c_t)^2$. At X-band this factor is typically of the order of 3×10^{-6}.

The two preceding examples (zero correlation and strong correlation) should be considered as limiting cases. The actual physical reality may be expected to fall between these two extremes. Charge neutrality is certainly realized on a macroscopic level, so that the assumption of uncorrelated charge deviations is highly suspect. On the other hand, charge neutrality may not necessarily be maintained within each lattice cell, but only over a larger volume. The correlation function for such a case will have finite values at larger distances than the correlation function corresponding to charge neutrality within each lattice cell [Eq. (31)]. It appears reasonable to assume that the correlation function ϕ_1^m

decreases exponentially with distance. Thus

$$\phi_1^m = \langle q_1^2 \rangle \qquad\qquad\qquad m = 0,$$
$$= -c\langle q_1^2 \rangle \exp(-|\mathbf{r}^m|/l) \quad m \neq 0, \qquad (36)$$

where the "correlation distance" l characterizes the strength of the correlation and c is a normalization constant defined by

$$c \sum_{m \neq 0} \exp(-|\mathbf{r}^m|/l) = 1. \qquad (37)$$

The spectrum of the charge distribution can be calculated easily if the correlation distance l is large compared with the lattice constant. Under these conditions the summation over $\mathbf{m}$ may be replaced by an integration, and one finds

$$|q^k|_1^2 = \langle q_1^2 \rangle g(kl), \qquad (38)$$

where

$$g(x) = 1 - (1 + x^2)^{-2}. \qquad (39)$$

Inserting Eq. (39) into Eq. (16) and neglecting the contribution from the longitudinal branch of the spectrum (which is approximately correct since $c_l^{-3} \ll c_t^{-3}$) one obtains

$$\chi_0'' = (\langle q_1^2 \rangle \omega / 6\pi m c_t^3) g(\omega/\omega_0), \qquad (40)$$

where

$$\omega_0 = c_t / l. \qquad (41)$$

For $\omega \gg \omega_0$ the result for intermediate correlation (40) approaches the previously derived result for zero correlation [Eq. (27)]. For $\omega \ll \omega_0$, on the other hand, χ_0'' is according to Eq. (40) proportional to ω^3 as was previously shown for the case of strong correlation [Eq. (35)]. For this case the correlation length is of the order of the lattice constant. Quantitative numerical agreement between the two results cannot be expected because of the approximations involved in the derivation of Eq. (40).

In Fig. 2 the dielectric loss tangent to be expected in inverse spinels is plotted versus frequency for different values of the correlation frequency ω_0. The loss tangent is proportional to χ_0''; the constant of proportionality is derived in Sec. V [Eq. (53)].

The assumption of an exponentially decreasing correlation function is somewhat arbitrary. It can be shown, however, that the end result is not sensitively dependent upon the finer details of the correlation function. The frequency dependence of the loss tangent has also been calculated for the case in which the correlation function is constant within a sphere of radius l (excepting the origin) and zero outside of this sphere. The results obtained in this way are qualitatively very similar to those summarized in Fig. 2.

IV. APPLICATION TO POLYCRYSTALS

A rigorous theory of the electrical properties of polycrystalline materials is obviously an extremely difficult task. The discussion presented in this section is,

therefore, based on a simple theoretical model of polycrystalline materials. This model, though not rigorously correct, is believed to reflect fairly well those properties of polycrystals which lead to dielectric loss at frequencies between 10^{10} and 10^{12} sec^{-1}.

Consider first a one-dimensional analogy. A single crystal corresponds to a long chain of ions with alternating charges. (For the sake of simplicity we assume that the masses are equal.) The model of a polycrystal on which the subsequent discussion is based consists of a similar chain of ions except that the proper charge sequence is not always rigorously maintained. We shall assume, in fact, that at the edges of smaller sections of the chain (which correspond to the grains in a three-dimensional crystal) the proper charge sequence is interrupted with a probability of one-half. Figure 3 demonstrates this theoretical model. The discontinuity of the charge distribution to be expected at the grain boundaries is reasonably well taken into account in this theoretical model. On the other hand, the discontinuity of the mechanical properties of the crystal (such as mass, force constants, and equilibrium position of the ions) is not taken into account at all.

For the sake of simplicity we assume that all grains are equally large, containing (in the one-dimensional case) L ions. It should be noticed that charge neutrality is maintained within each grain if L is even, whereas it is not if L is odd. It may therefore be anticipated that the dielectric losses as calculated on the basis of this model will be considerably larger if L is odd. We shall return to this question later.

The charge correlation function ϕ^m is calculated in Appendix 2, where it is shown that for the one-dimensional case,

$$\phi^m = e^2(-1)^m(1-|m|/L) \quad \text{for} \quad |m| \leq L,$$
$$= 0 \quad \text{for} \quad |m| \geq L, \quad (42)$$

where e is the charge of each ion. The spectrum of the charge distribution is calculated in Appendix 3, with the result

$$|q^k|^2 = \frac{e^2}{L}\left[\frac{\sin(\frac{1}{2}Lkd)}{\cos(\frac{1}{2}kd)}\right]^2 \quad L = \text{even},$$

$$= \frac{e^2}{L}\left[\frac{\cos(\frac{1}{2}Lkd)}{\cos(\frac{1}{2}kd)}\right]^2 \quad L = \text{odd}. \quad (43)$$

So far we have assumed that all grains have equal size. This is certainly unrealistic. In an actual polycrystal the grain sizes will be distributed over a finite range. We may take this into account by taking an average of the spectrum (43) with respect to the grain size. We assume for simplicity that the distribution of grain sizes has a relatively sharp peak at the average grain size L_0.

Under these conditions the average spectrum is obtained from (43) by replacing the sin^2 and cos^2 factors in

FIG. 3. Theoretical model of polycrystals. One-dimensional case; $L=6$.
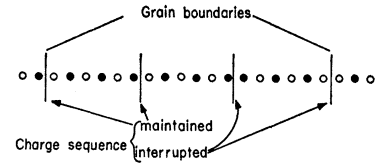
the numerator by $\frac{1}{2}$ and L by L_0. Thus

$$\langle|q^k|^2\rangle_{\text{av}} = \frac{e^2}{2L_0\cos^2(\frac{1}{2}kd)}. \quad (44)$$

The results obtained for the one-dimensional case can easily be generalized to three dimensions. In our theoretical model of a polycrystal the grains now consist of cubic blocks, containing L ions along each side. If the charge sequence is rigorously maintained within each grain, but interrupted or maintained with equal probability at the grain boundary, the three-dimensional correlation function is (apart from constant factors) the product of three one-dimensional correlation functions

$$\phi^m = e^2(-1)^{m_x+m_y+m_z}\left(1-\frac{|m_x|}{L}\right)$$
$$\times\left(1-\frac{|m_y|}{L}\right)\left(1-\frac{|m_z|}{L}\right). \quad (45)$$

Similarly the three-dimensional spectrum is a product of three one-dimensional spectra

$$\langle|q^k|^2\rangle_{\text{av}} = e^2/$$
$$(2L_0)^3\cos^2(\frac{1}{2}k_xd)\cos^2(\frac{1}{2}k_yd)\cos^2(\frac{1}{2}k_zd). \quad (46)$$

If the frequency is much less than the limiting lattice frequency, the cosine factors in Eq. (46) are approximately unity. Under these conditions the contribution of polycrystallinity to the dielectric loss is given by Eq. (27) with $\langle q_1^2\rangle$ replaced by $e^2/(2L_0)^3$.

V. DIELECTRIC LOSS TANGENT

For cubic materials the effective field E_{eff} is related to the applied field E and the polarization P by

$$E_{\text{eff}} = E + (4\pi/3)P. \quad (47)$$

Thus the true susceptibility χ is related to χ_0 by

$$\chi = \chi_0/(1-\tfrac{4}{3}\pi\chi_0). \quad (48)$$

If the imaginary part χ_0'' of χ_0 is small compared to the real part χ_0' and compared to $1-\tfrac{4}{3}\pi\chi_0'$ it follows that

$$\chi' \simeq \chi_0'/(1-\tfrac{4}{3}\pi\chi_0'), \quad (49)$$

$$\chi'' \simeq \chi_0''/(1-\tfrac{4}{3}\pi\chi_0')^2. \quad (50)$$

Since χ' can be measured directly, it is convenient to express χ'' in terms of χ_0'' and χ' rather than in terms of

χ_0'' and χ_0'. From Eqs. (49) and (50)

$$\chi'' \simeq \chi_0''(1 + \tfrac{4}{3}\pi\chi')^2. \tag{51}$$

The dielectric loss tangent as expressed in terms of χ_0'' and the real part of the dielectric constant

$$\epsilon' = 1 + 4\pi\chi' \tag{52}$$

is

$$\tan\delta = \frac{4\pi\chi''}{\epsilon'} \simeq \frac{(\epsilon'+2)^2}{9\epsilon'} 4\pi\chi_0''. \tag{53}$$

For magnetic spinels the dielectric constant is of the order of 15. The curves shown in Fig. 2 have been calculated using this numerical value.

VI. DISCUSSION

The previous calculation has shown that the contributions to the loss tangent arising from internal disorder in single crystals (such as occurs in inverse spinels) may be expected to be significant at high microwave frequencies provided that the charge deviations are not strongly correlated. This contribution will be sharply reduced if the charge distribution is subject to correlations such as imposed by the tendency for charge neutrality.

The distribution of the ions over the available sites depends on the preparation of the crystal. The correlated distribution discussed in Sec. III [Eq. (35)], in which charge neutrality is maintained within each lattice cell, is very likely energetically favored over the uncorrelated distribution [Eq. (27)]. One may thus expect a tendency towards a strongly correlated distribution at low temperatures provided that the equilibrium distribution corresponding to a given temperature has been established. On the other hand, a high-temperature distribution can probably be "frozen in" by rapid cooling.

The contribution to the loss tangent arising from polycrystallinity assuming an average grain size of 10^{-6} cm is of the order of 10^{-8} at X band. Thus this contribution is probably insignificant, at this frequency, even for materials with very fine grains.

ACKNOWLEDGMENTS

APPENDIX 1. CHARGE CORRELATION FUNCTION IN SINGLE CRYSTALS WITH INTERNAL DISORDER

We assume that the charge distribution in different cells (such as shown in Fig. 1) are statistically independent. Since all cells are equivalent the correlation function may be expressed as

$$\phi_1{}^m = \tfrac{1}{8} \sum_n \langle q_1{}^{n+m} q_1{}^n \rangle, \tag{A1}$$

where the summation over n extends only over the 8 sites of the fundamental cell. By reference to Fig. 1, it is easily seen that $\phi_1{}^{100}$, $\phi_1{}^{010}$, etc., and $\phi_1{}^{111}$, $\phi_1{}^{-111}$, etc., vanish because they are proportional to the ensemble average of the charge deviation. On the other hand, $\phi_1{}^{000}$ and $\phi_1{}^{110}$, $\phi_1{}^{1-10}$, etc., are nonzero and given by

$$\phi_1{}^{000} = \tfrac{1}{2}e^2\delta^2,$$

$$\phi_1{}^{110} = -\frac{1}{8}e^2\left(\frac{2}{6} - \frac{4}{6}\right)\delta^2 = -\frac{1}{24}e^2\delta^2 = -\frac{1}{12}\phi_1{}^{000}. \tag{A2}$$

Here we have used the fact that only one term in the summation of Eq. (A1) contributes to $\phi_1{}^{110}$. This term arises from an aa or a bb pair with a probability of 2/6 and from an ab pair with a probability of 4/6.

The correlation function vanishes for larger distances because of the assumed statistical independence of the charge distributions in different cells.

APPENDIX 2. CHARGE CORRELATION FUNCTION IN POLYCRYSTALS

One-dimensional case: Because all grains are equivalent the correlation function can be written as

$$\phi^m = (1/L)\sum_{n=1}^{L} \langle q^{n+m} q^n \rangle. \tag{A3}$$

In this sum only those terms are nonzero for which $n+m$ and n lie within the same grain. Thus

$$\begin{aligned}
\phi^0 &= (e^2/L)L, \\
\phi^{\pm 1} &= -(e^2/L)(L-1), \\
\phi^{\pm 2} &= (e^2/L)(L-2), \\
&\vdots \qquad \vdots
\end{aligned} \tag{A4}$$

which is equivalent to Eq. (42).

Two-dimensional case: By the same arguments as above, one finds

$$\begin{aligned}
\phi^{00} &= (e^2/L^2)LL, \\
\phi^{10} &= -(e^2/L^2)(L-1)L, \\
\phi^{20} &= (e^2/L^2)(L-2)L, \\
\phi^{21} &= -(e^2/L^2)(L-2)(L-1).
\end{aligned} \tag{A5}$$

Thus, in general,

$$\phi^{n_x n_y} = (e^2/L^2)(-1)^{n_x+n_y}(1 - |n_x|/L)(1 - |n_y|/L);$$
$$\qquad\qquad |n_x| \text{ and } |n_y| \leq L, \quad \text{(A6)}$$
$$= 0; \qquad\qquad |n_x| \text{ or } |n_y| \geq L.$$

APPENDIX 3. SPECTRUM OF THE CHARGE DISTRIBUTION IN POLYCRYSTALS

From Eqs. (19) and (42) for the one-dimensional case

$$|q^k|^2/e^2 = 1 + \sum_{m=1}^{L} (1-m/L)\{\exp[i(\kappa-\pi)m] + \text{c.c.}\}, \quad \text{(A7)}$$

where $\kappa = kd$. Using the relations

$$\sum_{m=1}^{L} \exp(imx)$$

$$= \exp[\tfrac{1}{2}ix(L+1)] \sin(\tfrac{1}{2}xL)/\sin(\tfrac{1}{2}x), \quad \text{(A8)}$$

$$\sum_{m=1}^{L} m \exp(imx)$$

$$= \frac{\exp[\tfrac{1}{2}ix(L+1)]}{2\sin^2(\tfrac{1}{2}x)}\{(L+1)\sin(\tfrac{1}{2}xL)\sin(\tfrac{1}{2}x)$$

$$-i[L\cos(\tfrac{1}{2}xL)\sin(\tfrac{1}{2}x) - \sin(\tfrac{1}{2}xL)\cos(\tfrac{1}{2}x)]\}, \quad \text{(A9)}$$

one finds after trivial calculations

$$|q^k|^2/e^2 = \sin^2\tfrac{1}{2}L(\kappa-\pi)/L\cos^2\tfrac{1}{2}\kappa, \quad \text{(A10)}$$

which is equivalent to Eq. (43).

Energy Levels of Polarons in a Magnetic Field

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A variational method closely related to the intermediate coupling method of Lee, Low, and Pines is used to calculate the ground-state energy and low-lying excited states of the Fröhlich Hamiltonian with a uniform time-independent magnetic field. The energy is calculated in a power series in ω_c/ω to order $(\omega_c/\omega)^2$, where ω_c is the cyclotron resonance frequency of the electron in the absence of electron-phonon interaction and ω is the frequency of the longitudinal optical phonons. It is shown that in the presence of electron-phonon interaction the energy of the nth magnetic level is no longer proportional to n and that the effective mass for motion along the direction of the magnetic field is a function of n. The calculated variational energies approach the weak field result expected from the calculation of Lee, Low, and Pines (LLP) when $\omega_c/\omega \to 0$, and in the weak coupling limit the ground-state energy becomes exact to order $(\omega_c/\omega)^2$.

INTRODUCTION

IT is well known that if one wishes to compute the energy spectrum of a spinless electron of mass m in a magnetic field, $\mathbf{H}$, with associated vector potential $\mathbf{A}$, one replaces the energy operator $p^2/2m$ for the free electron by $(\mathbf{p}-e\mathbf{A}/c)^2/2m$ and solves the resulting Schrödinger equation. The energy spectrum so obtained can be written

$$(p_z^2/2m) + (n+\tfrac{1}{2})\hbar\omega_0, \quad \text{(1)}$$

where $\omega_0 = eH/mc$, p_z is the component of electron momentum along $\mathbf{H}$, e is the magnitude of the electron charge, and n takes on values $(0,1,2,\cdots)$.

In this paper we shall discuss what happens to the energy of an electron (more precisely, a polaron) in a polarizable but magnetically inert crystal when a relatively weak magnetic field is turned on. Polaron theory[1-3] predicts that in the absence of external fields

the polaron energy spectrum has the form

$$p^2/2m^* + (\bar{K}p^4/4m^2\hbar\omega) + O(p^6/m^3(\hbar\omega)^2), \quad \text{(2)}$$

if $(p^2/2m) \ll \hbar\omega$, where ω is the frequency of the longitudinal optical phonons and m is now and henceforth the band mass of the electron. In (2) m^* is the "effective mass" of the polaron and $\bar{K}$ is a dimensionless constant.

If we could proceed in analogy to the free electron we would regard (2) as the energy operator for the polaron, replace $p^2/2m$ in (2) by $(\mathbf{p}-e\mathbf{A}/c)^2/2m$ and solve the resulting Schrödinger equation. The energy levels of the polaron in the magnetic field would then take the form

$$\mu[(n+\tfrac{1}{2})\hbar\omega_c + p_z^2]$$
$$+ (\bar{K}/\hbar\omega)[(n+\tfrac{1}{2})\hbar\omega_c + (p_z^2/2m)]^2$$
$$+ O[((n+\tfrac{1}{2})\hbar\omega_c + p_z^2/2m)^3/(\hbar\omega)^2], \quad \text{(3)}$$

where

$$\mu = m/m^* \quad \text{(4)}$$

and

$$\omega_c = eH/mc.$$

At this point (3) is only suggestive; it motivates the more careful study of low-lying polaron energy levels to be undertaken in the present paper. We shall show, to the accuracy of our calculation, that in fact (3) becomes

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[1] H. Fröhlich, *Advances in Physics* (Taylor & Francis, Ltd., London, 1954), Vol. 3, p. 325. We use the notation of Fröhlich unless otherwise specified.

[2] T. D. Lee, F. E. Low, and D. Pines, Phys. Rev. 90, 297 (1953). This paper will henceforth be referred to as LLP.

[3] Particularly useful as a survey of the entire subject of polarons is the book *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Oliver & Boyd, Ltd., Edinburgh, 1963).