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Impurity dependence of the Curie temperature and microwave absorption in ferroelectric crystals

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Using the method of double-time temperature-dependent Green's functions and Kubo formalism, a general expression is derived for the complex dielectric constant of a defect ferroelectric crystal in the paraelectric phase taking into account the change of mass as well as harmonic force constant between impurity atom and host-lattice atoms. The results are used to obtain an expression for the frequency and temperature dependence of the dielectric loss at microwave frequencies due to impurity and anharmonic scattering. Neglecting the polarization of ions it is shown that the influence of defects on the dielectric constant at low frequencies can be expressed by a change only in the Curie temperature, as is known experimentally. To a first-order approximation of the defect parameters, the Curie-temperature shift is found to depend only on the harmonic-force-constant changes between the impurity and host-lattice atoms, and is proportional to the concentration of defects, as has been experimentally established.

I. INTRODUCTION

It is now well known[1] that the lattice defects in ferroelectric materials greatly influence their static dielectric constant in the paraelectric phase. The effect of defects can generally be expressed by a change only in the Curie temperature T_C, without essentially changing the character of the temperature dependence of the dielectric constant, that is, the Curie-Weiss law remains valid with practically the same Curie constant. Various impurities change the Curie temperature of the same material in different ways. For example, on the substitution of Pb ions for Ba ions in $BaTiO_3$ the Curie temperature increases, while Sr ions decrease the T_C. On the other hand, the change in T_C when Ca ions are substituted for Ba ions is negligible. It has been shown[1] that these changes in T_C cannot be accounted for simply from considerations of change in lattice constant or polarizability of impurity ions.

Microwave losses in the pure and doped ferroelectric materials $BaTiO_3$ and $SrTiO_3$ as a function of temperature and frequency have been experimentally measured in the past by many workers.[2-4] Above the phase-transition temperature the results of loss measurements can be well represented by the temperature dependence of the microwave (dielectric) loss tangent $\tan\delta$ through the following relation:

$$(T-T_C)\tan\delta=\alpha+\beta T+\gamma T^2\,, \tag{1}$$

where T_C is the Curie temperature. The parameter α vanishes for pure single-crystalline materials, but in doped and polycrystalline samples, it depends strongly on the defect concentration. It is a measure of losses which are introduced by defects in the lattice. The parameters β and γ are unaffected by the defects added to the lattice and represent the intrinsic characteristics of the perfect lattice being determined by the anharmonic terms in the interionic potential. The loss tangent, and therefore the parameters α, β, and γ, is found to be proportional to frequency ω for all materials in the frequency range studied.

It is now clear on theoretical grounds that the absorption of microwaves cannot be due to absorption or creation of single phonons. Energy and momentum cannot be simultaneously conserved in the process, since the momentum of the microwave photon is negligible compared to that of excited phonon. It is possible, however, to excite a virtual phonon with energy equal to that of a microwave photon which subsequently decays into a real phonon due to interactions with lattice imperfections. The imperfections simply play the role of absorbing the excess momentum of the phonon. Owing to anharmonic interactions between the phonons, degradations into other vibrational modes of the material are also possible.

Recently Vinogradov[5] has calculated dielectric losses at superhigh frequencies in ionic crystals with various defects on a simplified model. He has shown that a linear frequency dependence for losses is obtained if point charged defects are present in the crystal. A similar frequency dependence for microwave losses in $SrTiO_3$ has been obtained by Silverman[6] using a linear chain model of a ferroelectric with defects consisting of changed force constants between the nearest ions distributed at random. However, if such defects are considered in a three-dimensional lattice, a cubic frequency dependence for α will be obtained which is contrary to the observations.

In this paper we present an explanation for the change in the Curie temperature caused by the substitutional defects, and the temperature and frequency dependence of microwave loss in ferroelectrics in the presence of defects, taking into consideration the detailed characteristics of the defect on the basis of its interactions with the other ions in the crystal. For this purpose at the first stage, using the method of time-dependent Green's functions,[7] we derive a general expression for the complex dielectric constant ϵ at frequency ω of a ferroelectric crystal having cubic symmetry in the paraelectric phase, involving anharmonicities up to fourth order with substitutional defects of low concentration distributed at random. The impurities introduced are characterized by a different mass than the host atoms and with modified nearest-neighbor harmonic-force constants around their sites. Their influence on the anharmonic coupling coefficients in the Hamiltonian is neglected. For the sake of simplicity the ions are assumed nonpolarizable. Such a formulation is particularly interesting as the real part of the dielectric constant, ϵ', will lead to an expression for the change in the Curie temperature resulting from the presence of the impurities. This combined with the expression for the imaginary part of the dielectric constant, ϵ'', would give the microwave loss tangent of the material in the presence of defects and anharmonicities.

In Sec. II, we give a general formalism of the dielectric constant in terms of double-time Green's functions. In Sec. III, we set up the Hamiltonian for a ferroelectric in the presence of defects. Section IV deals with the evaluation of Green's function for this Hamiltonian by the equation-of-motion method. In Sec. V, the results are used to obtain an expression for the impurity dependence of Curie temperature. In Sec. VI we treat the frequency and temperature dependence of microwave loss tangent in the presence of defects. Section VII summarizes the results.

II. COMPLEX DIELECTRIC CONSTANT

The response of a crystal to an externally applied electric field is most conveniently described by the dielectric susceptibility of the lattice. Using the Kubo formalism,[8] the general expression for the complex dielectric susceptibility tensor $\chi_{\mu\nu}(\omega)$ can be written

$$\chi_{\mu\nu}(\omega) = -\lim_{\epsilon \to 0} 2\pi G_{\mu\nu}(\omega + i\epsilon) \ , \tag{2}$$

where $G_{\mu\nu}(\omega)$ is the Fourier transform of the retarded double-time Green's function between the μth and νth components of the crystal dipole-moment operator $\vec{M}(t)$ in the Heisenberg representation defined by

$$G_{\mu\nu}(t-t') = \langle\langle M_\mu(t); M_\nu(t')\rangle\rangle_0 = -i\Theta(t-t')\langle[M_\mu(t), M_\nu(t')]\rangle_0 \ . \tag{3}$$

Here $\Theta(t-t')$ is the usual Heaviside step function and the symbol $\langle\cdots\rangle_0$ denotes the statistical average value for $\vec{E}=0$.

The dipole moment $\vec{M}$ of the crystal depends on the lattice configuration like the potential energy and can be expanded in a phonon series.[9,10] Neglecting the polarization of ions, the expansion contains only the linear dipole-moment coefficients $M_\mu(k)$. Because of cyclic boundary conditions imposed on the ionic motion, only the $\vec{k}=0$ optical mode has a nonzero polarization associated with it. Thus only the coefficients $M_\mu(\vec{0}j)$ contribute to the susceptibility, where j relates to the optic modes of the phonon spectrum. We shall consider only one transverse-optic branch (denoted by the index j) which is possible with ferroelectric crystals in the paraelectric phase. It is known that the dielectric properties of ferroelectrics are determined mainly by one Cochran soft (optic-transverse) mode with an anomalously low frequency in the neighborhood of the Curie temperature. With these considerations, for ferroelectric materials which have cubic symmetry in the paraelectric phase, the scalar susceptibility $\chi(\omega)=\chi_{\mu\mu}(\omega)$ can be written

$$\chi(\omega) = -2\pi M_\mu^2(0)\, G(\omega + i\epsilon) \ , \tag{4}$$

where the limit $\epsilon \to 0$ is understood, $M_\mu(0) = M_\mu(\vec{0}j)$, and

$$G(\omega + i\epsilon) = \langle\langle A_0^o(t); A_0^o(t')\rangle\rangle_{\omega+i\epsilon} = G'(\omega) - iG''(\omega), \tag{5}$$

A_0^o being the phonon operator for the Cochran soft mode. In the presence of relaxation effects the dielectric constant $\epsilon(\omega)$ can be separated into real $\epsilon'(\omega)$ and imaginary $\epsilon''(\omega)$ parts. Using the relation between the dielectric constant and susceptibility, we get the following expression for the real part of the dielectric constant:

$$\epsilon'(\omega) - 1 = -8\pi^2 M_\mu^2(0)\, G'(\omega) \ . \tag{6}$$

The microwave- or dielectric-loss tangent $\tan\delta$ for the dissipation of power, defined as the ratio of imaginary and real parts of the dielectric constant, can be written

$$\tan\delta(\omega) = G''(\omega)/G'(\omega) \ . \tag{7}$$

Thus it is enough to know only the retarded one-phonon Green's function $G(\omega)$ to determine the dielectric susceptibility and hence the dielectric constant and loss tangent.

III. HAMILTONIAN

The Hamiltonian of the defect ferroelectric crystal is constructed by a method similar to that used in another study,[11] from the crystal model proposed by Silverman and Joseph,[12] by augmenting it with fourth-order anharmonic interaction terms involving ferroelectric optic modes of lowest wave vector. It is known that this Hamiltonian provides a satisfactory interpretation of neutron scattering,[13,14] anomalous behavior of sound near the Curie points,[15] electric field dependence of Curie temperature,[16] and temperature dependence of thermal conductivity of ferroelectrics,[17-19] and contains essential characteristics of a displacive-type ferroelectric with perovskite structure. It is assumed that the introduction of defects in the lattice causes changes in the harmonic-force constants besides the mass change; their influence upon anharmonic coefficients is neglected. This is true for isovalent and nonpolarizable defects because they cause changes in the short-range forces only. For small concentration of defects the impurity-impurity interaction can be neglected.

Assuming that the doping of the crystal causes the modification of the harmonic-force constants only, i.e., neglecting entirely the changes of anharmonic coefficients due to defects, the Hamiltonian of a defect ferroelectric can be written

$$H = H_h + H_a \ . \tag{8}$$

The harmonic contribution H_h to the Hamiltonian, using the method of Ref. 11 is given by

$$\begin{aligned} H_h = {} & \sum_k \hbar\omega_k^a (a_k^{a\dagger} a_k^a + \tfrac{1}{2}) + {\sum_k}' \hbar\omega_k^o (a_k^{o\dagger} a_k^o + \tfrac{1}{2}) \\ & - \tfrac{1}{4}\hbar\omega_0^o (B_0^o B_0^o + A_0^o A_0^o) - \hbar C(0,0)\, B_0^o B_0^o \\ & + \hbar D(0,0) A_0^o A_0^o - \hbar B_0^o X + \hbar A_0^o Y + \hbar L \ , \end{aligned} \tag{9}$$

where we have put

$$\begin{aligned} X &= \sum_k [C(k_a, 0) B_k^a + C(k_o, 0) B_k^o] \\ &= \sum_{k,\lambda} C(k_\lambda, 0) B_k^\lambda \ , \end{aligned} \tag{10a}$$

$$\begin{aligned} Y &= \sum_k [D(k_a, 0) A_k^a + D(k_o, 0) A_k^o] \\ &= \sum_{k,\lambda} D(k_\lambda, 0) A_k^\lambda \ , \end{aligned} \tag{10b}$$

$$\begin{aligned} L = {} & \sum_{k',k''} [D(k_a', k_a'') A_{k'}^a A_{k''}^a + D(k_o', k_o'') A_{k'}^o A_{k''}^o \\ & + D(k_a', k_o'') A_{k'}^a A_{k''}^o - C(k_a', k_a'') B_{k'}^a B_{k''}^a \\ & - C(k_o', k_o'') B_{k'}^o B_{k''}^o - C(k_a', k_o'') B_{k'}^a B_{k''}^o] \\ = {} & \sum_{k',k'',\lambda} [D(k_\lambda', k_\lambda'') A_{k'}^\lambda A_{k''}^\lambda - C(k_\lambda', k_\lambda'') B_{k'}^\lambda B_{k''}^\lambda] \\ & + \sum_{k',k''} [D(k_a', k_o'') A_{k'}^a A_{k''}^o - C(k_a', k_o'') B_{k'}^a B_{k''}^o] \ , \end{aligned} \tag{10c}$$

with $\lambda = a, o, A_k = a_k + a_{-k}^\dagger$ and $B_k = a_k - a_{-k}^\dagger$, a_k and $a_k^\dagger$ being the annihilation and creation operators for the mode of wave vector k. All the long-wavelength soft modes which become unstable in the harmonic approximation are collectively lumped together into a single mode with zero wave vector and are assigned an imaginary frequency $i\omega_0^o$. The prime on the summation excludes this $\vec{k} = 0$ mode. The superscripts a and o denote the acoustical and optical modes, respectively, and we have used the abbreviations

$$C(0,0) = C(\vec{0}j; \vec{0}j); \quad D(0,0) = D(\vec{0}j, \vec{0}j) \ .$$

The parameters $C(k, k')$ and $D(k, k')$ depend upon changes in the mass and force constants due to substitutional impurities and are given by

$$C(q,q') = (\omega_q \omega_{q'})^{1/2} \frac{M_\rho^0}{4N\mu_\rho} \sum_\alpha \sigma_\alpha(\rho|q)\sigma_\alpha(\rho|q') \left(f \sum_s e^{i(\vec{q}+\vec{q}')\cdot\vec{x}(s)} - \sum_i e^{i(\vec{q}+\vec{q}')\cdot\vec{x}(i)} \right) \ , \tag{11a}$$

$$D(q,q') = (\omega_q \omega_{q'})^{-1/2} \frac{1}{4N} \sum_{s\kappa\alpha} \sum_{s'k'\beta} (M^\kappa M^{\kappa'})^{-1/2} \sigma_\alpha(\kappa|q)\sigma_\beta(\kappa'|q')\, \Delta\Phi_{\alpha\beta}(s\kappa; s'\kappa')\, e^{i[\vec{q}\cdot\vec{x}(s) + \vec{q}'\cdot\vec{x}(s')]} (\delta_{si}\delta_{\kappa\rho} + \delta_{s'i}\delta_{\kappa'\rho}) \ , \tag{11b}$$

where N is the number of unit cells in the lattice, $\vec{x}(s)$ gives the position vector of the sth unit cell, the symbol $(i\rho)$ identifies the position of an impurity atom in the ith unit cell, $\Delta\Phi_{\alpha\beta}(s\kappa; s'\kappa')$ represents the change in the harmonic force constant between atoms at $(s\kappa)$ and $(s'\kappa')$ when one of these sites is occupied by an impurity atom. ω_k is the circular frequency of the normal mode described by $k = (\vec{k}j)$, $\vec{k}$ being the phonon wave vector and j the branch index of the phonon dispersion spectrum, and $\vec{\sigma}(\kappa|k)$ is the associated unit polarization vector (eigenvector) of the lattice mode belonging to the sublattice κ. M_ρ^0 is the weighted harmonic mean of the masses of atoms of the type ρ defined by

$$1/M_\rho^0=f/M'_\rho+(1-f)/M_\rho;\quad f=n/N\,, \tag{12}$$

n being the number of impurities, $\mu_\rho=M_\rho M'_\rho/(M'_\rho-M_\rho)$ and

$$M^\kappa=M_\kappa+(M_\rho^0-M_\kappa)\,\delta_{\kappa\rho}\,. \tag{13}$$

M_ρ and M'_ρ are the masses of host and impurity atoms of the ρth kind.

Using Szigeti's[20] theorem which asserts that for a crystal with a center of inversion symmetry the coordinates of optical modes come in pairs, the anharmonic contribution H_a which includes dominant third- and fourth-order anharmonic interaction terms in the lattice potential-energy expansion can be written as

$$H_a=\hbar A_0^o P+\hbar A_0^o A_0^o Q+\hbar A_0^o R+\hbar A_0^o S\;, \tag{14}$$

where

$$P=\sum_k \alpha(k)A_k^{a\dagger}A_k^o\;, \tag{15a}$$

$$Q=\sum_{k,\lambda}\beta^\lambda(k)A_k^{\lambda\dagger}A_k^\lambda\,,\quad \lambda=a,o \tag{15b}$$

$$R=\sum_{k_1,k_2,k_3}\gamma(k_1,k_2,k_3)A_{k_1}^o A_{k_2}^a A_{k_3}^a\;, \tag{15c}$$

$$S=\sum_{k_1,k_2,k_3}\mu(k_1,k_2,k_3)A_{k_1}^o A_{k_2}^o A_{k_3}^o\;. \tag{15d}$$

Here $\alpha(k)$, $\beta^o(k)$, $\beta^a(k)$, $\gamma(k_1,k_2,k_3)$, and $\mu(k_1,k_2,k_3)$ are Fourier-transformed third- and fourth-order anharmonic coupling constants. The three- and four-phonon processes generated by these terms are dominant among those which involve the ferroelectric mode ω_0^o. The definition (11a) shows that the coefficient $C(00,00)$ vanishes. In Eqs. (10) the summations over optic modes excludes the Cochran mode of lowest transverse-optic-branch frequency.

IV. GREEN'S FUNCTIONS

We now come to the evaluation of the Fourier component of retarded Green's function $G(t-t')$ defined in Eq. (5). Differentiating the expression for $G(t-t')$ with respect to time argument t and Fourier transforming the result, the equation of motion of $G(\omega)$ is obtained as

$$(\omega^2+\omega_1\omega_2)G(\omega)=\frac{\omega_1}{\pi}+\langle\langle F_1(t);A_0^o(t')\rangle\rangle_\omega\;, \tag{16}$$

where

$$F_1=4\omega_1A_0^oQ+2\omega_1Z+2\omega X\,, \tag{17}$$

$$\omega_1=\omega_0^o+4C(0,0)=\omega_0^o\,, \tag{18}$$

$$\omega_2=\omega_0^o-4D(0,0)\,, \tag{19}$$

with $Z=Y+P+R+S$. The equation of motion of $\langle\langle F_1(t);A_0^o(t')\rangle\rangle$ with respect to time argument t' gives

$$(\omega^2+\omega_1\omega_2)\langle\langle F_1(t);A_0^o(t')\rangle\rangle_\omega=\frac{4\omega_1{}^2\overline{Q}}{\pi}+\langle\langle F_1(t);F_2(t')\rangle\rangle_\omega\;, \tag{20}$$

where

$$F_2=4\omega_1A_0^oQ+2\omega_1Z-2\omega X \tag{21}$$

and

$$\overline{Q}=\sum_{k,\lambda}\beta^\lambda(k)\langle A_k^{\lambda}{}^\dagger A_k^\lambda\rangle=\sum_{k,\lambda}\beta^\lambda(k)\eta_k^\lambda\,. \tag{22}$$

Combining Eqs. (16) and (20) the equation of motion for $G(\omega)$ can be written in the form of a Dyson equation:

$$\begin{aligned}G(\omega)&=g(\omega)+g(\omega)\tilde{P}(\omega)g(\omega)\\&=g(\omega)+g(\omega)\Pi(\omega)G(\omega)\,,\end{aligned} \tag{23}$$

where

$$g(\omega)=\omega_1/\pi(\omega^2+\omega_1\omega_2)\,, \tag{24}$$

$$\tilde{P}(\omega)=4\pi\overline{Q}+(\pi^2/\omega_1^2)\langle\langle F_1(t);F_2(t')\rangle\rangle_\omega\,. \tag{25}$$

From Eq. (23) the expression for the polarization operator can be written

$$\Pi(\omega)=\tilde{P}(\omega)/[1+\tilde{P}(\omega)g(\omega)]\,. \tag{26}$$

At frequencies far enough from the poles of the denominator, one may expand the latter in a power series of $\tilde{P}$ and retain the first term in the lowest approximation, i.e., $\Pi(\omega)\simeq\tilde{P}(\omega)$. This gives for $G(\omega)$ the following expression:

$$\begin{aligned}G(\omega)&=\omega_1/\pi[\omega^2+\omega_1\omega_2-4\omega_1\overline{Q}-f(\omega)]\\&=\omega_0^o/\pi[\omega^2+(\omega_0^o)^2-4\omega_0^oD(0,0)-4\omega_0^o\overline{Q}-f(\omega)]\,,\end{aligned} \tag{27}$$

with

$$f(\omega)=(\pi/\omega_0^o)\langle\langle F_1(t);F_2(t')\rangle\rangle_\omega\,. \tag{28}$$

Equation (27) can be rewritten

$$G(\omega+i\epsilon)=\omega_0^o/\pi[\omega^2-\nu^2(\omega)+i\Gamma(\omega)]\,, \tag{29}$$

with

$$\nu^2(\omega)=-(\omega_0^o)^2+4\omega_0^oD(0,0)+4\omega_0^o\overline{Q}+\Delta(\omega)\,, \tag{30}$$

$$\Delta(\omega)=\mathcal{P}(\pi/\omega_0^o)\langle\langle F_1(t);F_2(t')\rangle\rangle_{\omega+i\epsilon}\;, \tag{31}$$

and

$$\Gamma(\omega)=-\operatorname{Im}(\pi/\omega_0^o)\langle\langle F_1(t);F_2(t')\rangle\rangle_{\omega+i\epsilon}\;. \tag{32}$$

The self-energy function $f(\omega)$ defined by Eq. (28)

can be evaluated in successive approximations of the perturbation. It is determined here to second-order in the defect and anharmonicity parameters. In this approximation one can write, from (17) and (21),

$$\langle\langle F_1(t);F_2(t')\rangle\rangle_\omega = 4(\omega_0^o)^2G_1(\omega)+16(\omega_0^o)^2G_2(\omega) + 4(\omega_0^o)^2G_3(\omega)+4(\omega_0^o)^2G_4(\omega)+4(\omega_0^o)^2G_5(\omega) - 4\omega^2G_6(\omega)+4\omega\omega_0^o\,G_7(\omega)-4\omega\omega_0^o\,G_8(\omega)\,, \tag{33}$$

where the Green's function $G_i(t-t')$, $i=1,\ldots,8$, are defined by

$$G_1(t-t')=\sum_{k,k'}\alpha(k)\alpha(k')\langle\langle A_k^{a\dagger}A_k^o;A_{k'}^{a\dagger}A_{k'}^o\rangle\rangle, \tag{34a}$$

$$G_2(t-t')=\sum_{k,k',\lambda}\beta^\lambda(k)\beta^\lambda(k')\langle\langle A_0^oA_k^{\lambda\dagger}A_k^\lambda;A_0^oA_{k'}^{\lambda\dagger}A_{k'}^\lambda\rangle\rangle \tag{34b}$$

$$G_3(t-t')=\sum_{k_1,k_2,k_3}\sum_{k_1',k_2',k_3'}\gamma(k_1,k_2,k_3)\gamma(k_1',k_2',k_3') \times\langle\langle A_{k_1}^oA_{k_2}^aA_{k_3}^a;A_{k_1'}^oA_{k_2'}^aA_{k_3'}^a\rangle\rangle\,, \tag{34c}$$

$$G_4(t-t')=\sum_{k_1,k_2,k_3}\sum_{k_1',k_2',k_3'}\mu(k_1,k_2,k_3)\mu(k_1',k_2',k_3') \times\langle\langle A_{k_1}^oA_{k_2}^oA_{k_3}^o;A_{k_1'}^oA_{k_2'}^oA_{k_3'}^o\rangle\rangle\,, \tag{34d}$$

$$G_5(t-t')=\sum_{k,k',\lambda}D(k_\lambda,0)D(k_\lambda',0)\langle\langle A_k^\lambda;A_{k'}^\lambda\rangle\rangle\,, \tag{34e}$$

$$G_6(t-t')=\sum_{k,k',\lambda}C(k_\lambda,0)C(k_\lambda',0)\langle\langle B_k^\lambda;B_{k'}^\lambda\rangle\rangle\,, \tag{34f}$$

$$G_7(t-t')=\sum_{k,k',\lambda}C(k_\lambda,0)D(k_\lambda',0)\langle\langle B_k^\lambda;A_{k'}^\lambda\rangle\rangle\,, \tag{34g}$$

$$G_8(t-t')=\sum_{k,k',\lambda}D(k_\lambda,0)C(k_\lambda',0)\langle\langle A_k^\lambda;B_{k'}^\lambda\rangle\rangle\,. \tag{34h}$$

In writing these Green's functions we have suppressed the time arguments t and t' on the right-hand side of Eqs. (34) for brevity. The Green's functions appearing on the right-hand side of Eqs. (34) can be conveniently evaluated via the zeroth-order stabilized Hamiltonian given by[19]

$$H_0=\hbar\sum_k\omega_k^a(a_k^{a\dagger}a_k^a+\tfrac{1}{2})+\hbar\sum_k{}'\,\omega_k^o(a_k^{o\dagger}a_k^o+\tfrac{1}{2}) +\hbar\Omega(a_o^\dagger a_o+\tfrac{1}{2})\,, \tag{35}$$

where Ω is the effective temperature-dependent frequency of the anomalous transverse-optic mode, and a_o and $a_o^\dagger$ are the annihilation and creation operators for this soft mode.

V. CURIE TEMPERATURE

Using Eqs. (6) and (29), the temperature dependence of the dielectric constant can be written as

$$\epsilon'(\omega)-1=-8\pi M_\mu^2(0)\,\frac{\omega_0^o[\omega^2-\nu^2(\omega)]}{[\omega^2-\nu^2(\omega)]^2+\Gamma^2(\omega)}\;. \tag{36}$$

The real part of the pole of $G(\omega+i\epsilon)$ in Eq. (29) would give the temperature-dependent frequency $\Omega(T)$ of the Cochran mode in the presence of defects as the self-consistent solution of the equation

$$\Omega^2=-(\omega_0^o)^2+4\omega_0^oD(0,0)+4\omega_0^o\overline{Q}+\Delta(\Omega)\;. \tag{37}$$

We will see that $\Delta(\omega)$ is of second order in the defect and anharmonicity parameters. Hence comparing (30) and (37) we can approximate $\nu(\omega)$ as Ω. For cubic ferroelectrics, the microwave frequency ω is much smaller than the Cochran-mode frequency Ω, so that $\omega\ll\nu(\omega)$ and no relaxation effects will be observed as established experimentally. Further, the half-width $\Gamma(\omega)/2\nu(\omega)$ is such that $\Gamma(\omega)\ll\nu^2(\omega)$. Due to the anomalously low value of Ω, paraelectric materials have high value of $\epsilon'(\omega)$ as compared to alkali halides, so that $\epsilon'(\omega)\gg 1$. With these considerations the expression (36) for $\epsilon'(\omega)$ becomes

$$\epsilon'(\omega)=8\pi M_\mu^2(0)\omega_0^o/\nu^2(\omega)\;. \tag{38}$$

In the case of pure crystals we have

$$\epsilon_0'(\omega)=8\pi M_\mu^2(0)\omega_0^o/\nu_0^2(\omega)\,, \tag{39}$$

where

$$\nu_0^2(\omega)=-(\omega_0^o)^2+4\omega_0^o\overline{Q}+\Delta_0(\omega)\,, \tag{40}$$

with

$$\Delta_0(\omega) =\pi\omega_0^o\mathcal{P}[G_1(\omega+i\epsilon)+4G_2(\omega+i\epsilon) +G_3(\omega+i\epsilon)+G_4(\omega+i\epsilon)]\;. \tag{41}$$

Here $\mathcal{P}$ stands for the principal value of the quantity in the brackets. Substituting for the Green's functions from Eqs. (34a)–(34d) into (41) we obtain for $\Delta_0(\omega)$

$$\begin{aligned}\Delta_0(\omega)=\omega_0^o\mathcal{P}\Bigg[&-2\sum_k\alpha^2(k)\left((N_k^a+N_k^o)\frac{\omega_k^a+\omega_k^o}{\omega^2-(\omega_k^a+\omega_k^o)^2}-(N_k^a-N_k^o)\frac{\omega_k^a-\omega_k^o}{\omega^2-(\omega_k^a-\omega_k^o)^2}\right)\\
&+8\sum_{k,\lambda}[\beta^\lambda(k)]^2\Bigg([1+(N_k^\lambda)^2+2N_0N_k^\lambda]\frac{\Omega+2\omega_k^\lambda}{\omega^2-(\Omega+2\omega_k^\lambda)^2}\\
&\qquad+(1+N_k^\lambda-2N_0N_k^\lambda)\frac{\Omega-2\omega_k^\lambda}{\omega^2-(\Omega-2\omega_k^\lambda)^2}-[1-(N_k^\lambda)^2]\frac{2\Omega}{\omega^2-\Omega^2}\Bigg)\\
&+\sum_{k_1,k_2,k_3}\sum_{k_1',k_2',k_3'}\delta_{123}\gamma(k_1,k_2,k_3)\gamma(k_1',k_2',k_3')\\
&\times\Bigg((1+N_{k_2}^aN_{k_3}^a+N_{k_3}^aN_{k_1}^o+N_{k_1}^oN_{k_2}^a)\frac{\omega_{k_1}^o+\omega_{k_2}^a+\omega_{k_3}^a}{\omega^2-(\omega_{k_1}^o+\omega_{k_2}^a+\omega_{k_3}^a)^2}\\
&\quad+\left\{(1+N_{k_2}^aN_{k_3}^a-N_{k_3}^aN_{k_1}^o-N_{k_1}^oN_{k_2}^a)\frac{\omega_{k_1}^o-\omega_{k_2}^a-\omega_{k_3}^a}{\omega^2-(\omega_{k_1}^o-\omega_{k_2}^a-\omega_{k_3}^a)^2}\right\}+\{\omega_{k_1}^o\leftrightarrow\omega_{k_2}^a\}+\{\omega_{k_1}^o\leftrightarrow\omega_{k_3}^a\}\Bigg)\\
&+\sum_{k_1,k_2,k_3}\sum_{k_1',k_2',k_3'}(\delta_{123}+\delta_{213}+\delta_{312})\mu(k_1,k_2,k_3)\mu(k_1',k_2',k_3')\\
&\qquad\times\Bigg((1+N_{k_2}^oN_{k_3}^o+N_{k_3}^oN_{k_1}^o+N_{k_1}^oN_{k_2}^o)\frac{\omega_{k_1}^o+\omega_{k_2}^o+\omega_{k_3}^o}{\omega^2-(\omega_{k_1}^o+\omega_{k_2}^o+\omega_{k_3}^o)^2}\\
&\quad+\left\{(1+N_{k_2}^oN_{k_3}^o-N_{k_3}^oN_{k_1}^o-N_{k_1}^oN_{k_2}^o)\frac{\omega_{k_1}^o-\omega_{k_2}^o-\omega_{k_3}^o}{\omega^2-(\omega_{k_1}^o-\omega_{k_2}^o-\omega_{k_3}^o)^2}\right\}+\{\omega_{k_1}^o\leftrightarrow\omega_{k_2}^o\}+\{\omega_{k_1}^o\leftrightarrow\omega_{k_3}^o\}\Bigg)\Bigg]\,,\end{aligned}\tag{42}$$

where

$$\begin{aligned}&\delta_{123}=\delta_{k_1,-k_1'}(\delta_{k_2,-k_2'}\delta_{k_3,-k_3'}+\delta_{k_2,-k_3'}\delta_{k_3,-k_2'})\,,\\
&N_0=\coth(\hbar\Omega/2k_BT)\ \text{ and }\ N_k^\lambda=\coth(\hbar\omega_k^\lambda/2k_BT)\,,\end{aligned}\tag{43}$$

and we have used the relations $\alpha(-k)=-\alpha(k)$ and $\beta^\lambda(-k)=\beta^\lambda(k)$. With the approximation $\eta_k^\lambda=\langle A_k^{\lambda\dagger}A_k^\lambda\rangle\simeq N_k^\lambda$, in the high-temperature classical limit, Eq. (40) can be written in the form

$$\nu_0^2(\omega)=-(\omega_0^o)^2+\gamma_1T+\gamma_2T^2\,,\tag{44}$$

where

$$\gamma_1=\frac{4k_B\omega_0^o}{\hbar}\left[-\mathcal{P}\sum_k\frac{\alpha^2(k)}{\omega_k^a\omega_k^o}\left(\frac{(\omega_k^a+\omega_k^o)^2}{\omega^2-(\omega_k^a+\omega_k^o)^2}+\frac{(\omega_k^a-\omega_k^o)^2}{\omega^2-(\omega_k^a-\omega_k^o)^2}\right)+2\sum_{k,\lambda}\frac{\beta^\lambda(k)}{\omega_k^\lambda}\right]\,,\tag{45a}$$

and

$$\begin{aligned}\gamma_2=\frac{4k_B^2\omega_0^o}{\hbar^2}\mathcal{P}\Bigg[&8\sum_{k,\lambda}\frac{[\beta^\lambda(k)]^2}{(\omega_k^\lambda)^2}\left(\frac{(\Omega+2\omega_k^\lambda)^2/\Omega}{\omega^2-(\Omega+2\omega_k^\lambda)^2}+\frac{(\Omega-2\omega_k^\lambda)^2/\Omega}{\omega^2-(\Omega-2\omega_k^\lambda)^2}+\frac{2\Omega}{\omega^2-\Omega^2}\right)\\
&+\sum_{k_1,k_2,k_3}\sum_{k_1',k_2',k_3'}\delta_{123}\frac{\gamma(k_1,k_2,k_3)\gamma(k_1',k_2',k_3')}{\omega_{k_1}^o\omega_{k_2}^a\omega_{k_3}^a}\\
&\qquad\times\left(\frac{(\omega_{k_1}^o+\omega_{k_2}^a+\omega_{k_3}^a)^2}{\omega^2-(\omega_{k_1}^o+\omega_{k_2}^a+\omega_{k_3}^a)^2}+\left\{\frac{(\omega_{k_1}^o-\omega_{k_2}^a-\omega_{k_3}^o)^2}{\omega^2-(\omega_{k_1}^o-\omega_{k_2}^a-\omega_{k_3}^a)^2}\right\}+\{\omega_{k_1}^o\leftrightarrow\omega_{k_2}^a\}+\{\omega_{k_1}^o\leftrightarrow\omega_{k_3}^a\}\right)\\
&+\sum_{k_1,k_2,k_3}\sum_{k_1',k_2',k_3'}(\delta_{123}+\delta_{231}+\delta_{312})\frac{\mu(k_1,k_2,k_3)\mu(k_1',k_2',k_3')}{\omega_{k_1}^o\omega_{k_2}^o\omega_{k_3}^o}\Bigg(\frac{(\omega_{k_1}^o+\omega_{k_2}^o+\omega_{k_3}^o)^2}{\omega^2-(\omega_{k_1}^o+\omega_{k_2}^o+\omega_{k_3}^o)^2}\\
&\qquad+\left\{\frac{(\omega_{k_1}^o-\omega_{k_2}^o-\omega_{k_3}^o)^2}{\omega^2-(\omega_{k_1}^o-\omega_{k_2}^o-\omega_{k_3}^o)^2}\right\}\\
&\qquad+\{\omega_{k_1}^o\leftrightarrow\omega_{k_2}^o\}+\{\omega_{k_1}^o\leftrightarrow\omega_{k_3}^o\}\Bigg)\Bigg]\,.\end{aligned}\tag{45b}$$

Hence at temperatures higher than the Curie temperature T_C, the dielectric constant obeys the law

$$\epsilon_0'(\omega)=C/(T+\zeta T^2-T_C)\,,\tag{46}$$

with

$$C=8\pi M_\mu{}^2(0)\omega_0^o/\gamma_1\,,\tag{47a}$$

$$\zeta=\gamma_2/\gamma_1\,,\tag{47b}$$

$$T_C=(\omega_0^o)^2/\gamma_1\,.\tag{47c}$$

Equation (46) shows that in pure ferroelectric crystals, the Curie-Weiss law $\epsilon = T/(T-T_C)$ is strictly obeyed only so long as the parameter ζ is small. If this is not the case then deviations from the Curie-Weiss law may be expected for highly anharmonic crystals at high temperatures. The nonlinearity constant ζ characterizing the deviation of the temperature dependence of the dielectric constant from Curie-Weiss behavior is related to the third- and fourth-order anharmonic coupling coefficients and is unaffected by the presence of impurities.

For an impure crystal we can write from Eqs. (28), (30), and (33)

$$\nu^2(\omega) = \nu_0{}^2(\omega) + \Delta\nu^2 , \tag{48}$$

where

$$\Delta\nu^2 = 4\omega_0^o D(0,0) + (4\pi/\omega_0^o)\mathcal{P}[(\omega_0^o)^2 G_5(\omega+i\epsilon) - \omega^2 G_6(\omega+i\epsilon) + \omega\omega_0^o G_7(\omega+i\epsilon) - \omega\omega_0^o G_8(\omega+i\epsilon)] . \tag{49}$$

After substituting $\mathcal{P}G_i(\omega+i\epsilon)$, $i = 5, 6, 7, 8$, from definitions (34) we have

$$\Delta\nu^2 = 4\omega_0^o D(0,0) + \frac{4}{\omega_0^o}\mathcal{P}\sum_{k,\lambda}\frac{1}{\omega^2(\omega_k^\lambda)^2}\{(\omega_0^o)^2\omega_k^\lambda D^2(k_\lambda,0) + \omega^2\omega_k^\lambda C^2(k_\lambda,0) + \omega^2\omega_0^o[C(k_\lambda,0)D^*(k_\lambda,0) + C^*(k_\lambda,0)D(k_\lambda,0)]\} . \tag{50}$$

The change in ν^2 due to defects is independent of temperature and will lead to a change in the Curie temperature T_C only. For an anharmonic defect crystal using Eq. (48) we obtain

$$\epsilon'(\omega) = C/(T - T_C' + \zeta T^2) , \tag{51}$$

where $T_C' = T_C + \Delta T_C$. The change ΔT_C in the Curie temperature caused by the defects is given by

$$\Delta T_C = -\Delta\nu^2/\gamma_1 . \tag{52}$$

The parameters C and ζ have the same values as in a pure crystal, as the influence of defects upon anharmonic coefficients is not considered. The first term in Eq. (52) in reality does not depend on ω_0^o as follows from Eq. (45a).

We thus see that the influence of defects on the dielectric constant of a ferroelectric crystal in the paraelectric phase appears only in the shift of the Curie temperature, as is found experimentally. In the first approximation, for the crystal model considered here, it follows from Eqs. (50) and (52) that the shift in the Curie temperature caused by the impurity depends only on the changes in the harmonic force constants between the impurity and host lattice ions and can be positive or negative. It thus explains different signs of ΔT_C. This agrees with the calculations of Dvorăk and Glogar[21] in the harmonic approximation. However, to second order in defect parameters, ΔT_C depends on both C and D which may lead to either cancelling or reinforcing effects in the shift. Another new result is that ΔT_C depends also on the microwave frequency employed. For the static dielectric constant, the Curie temperature shift is solely determined by the parameter D, i.e., force-constant changes.

A word may be said for the dependence of ΔT_C on the concentration of randomly distributed defects in a crystal. For changes in the short-range forces between the ions, Eq. (11b) shows that $D(0,0)$ is nonvanishing only for those values of $(s\kappa)$ which represent the lattice sites in the immediate neighborhood of defect at the site $(s'\kappa')$. If the concentration of defects is such that the range of influence of the different defects is smaller than the average distance between them, we obtain n equal terms when summed over $(s\kappa)$. In such a case the shift of T_C will be proportional to the concentration of defects (n/N). Similar considerations show that even the second term in the expression (50), representing the shift of Curie temperature in the next approximation, is proportional to the concentration of defects. Thus a linear concentration dependence of the Curie-temperature shift can be expected in a broad range of concentrations of substitutional isovalent defects, which has experimentally been established.[1] However, for the purpose of a quantitative comparison, there are difficulties in the calculation of the Curie temperature shift from Eqs. (50) and (52), as it requires a detailed knowledge of the forces between the ions in a perfect as well as in an imperfect crystal.

VI. MICROWAVE ABSORPTION

For the defect model of a ferroelectric considered here, the Green's function $G(\omega)$ is given by Eq. (29). Using this expression, the loss tangent (7) equals.

$$\tan\delta(\omega) = \Gamma(\omega)/[\omega^2 - \nu^2(\omega)] , \tag{53}$$

which for microwave photons, $\omega \ll \nu$, becomes

$$\tan\delta(\omega) = -\Gamma(\omega)/\nu^2(\omega) . \tag{54}$$

As shown earlier, $\Gamma(\omega)/2\nu(\omega)$ corresponds to the half-width associated with the damping of the Cochran soft mode. Hence in conformity with the suggestion of Silverman,[6] the damping of microwaves may be understood to arise due to the creation of a virtual Cochran polarization mode excitation by the transverse electromagnetic radiation and the subsequent decay into real phonons by scattering from lattice imperfections and third- and fourth-order anharmonicity. Defining

$$\Gamma_i(\omega) = -\mathrm{Im}G_i(\omega + i\epsilon);\ i = 1, \ldots, 8 \tag{55}$$

where the Green's functions $G_i(\omega)$ are given in Eqs. (34), we can write from Eqs. (32) and (33)

$$\Gamma(\omega) = \Gamma_{\mathrm{anh}}(\omega) + \Gamma_d(\omega), \tag{56}$$

with

$$\Gamma_{\mathrm{anh}}(\omega) = 4\pi\omega_0^o[\Gamma_1(\omega) + 4\Gamma_2(\omega) + \Gamma_3(\omega) + \Gamma_4(\omega)], \tag{57}$$

and

$$\Gamma_d(\omega) = (4\pi/\omega_0^o)[(\omega_0^o)^2\Gamma_5(\omega) - \omega^2\Gamma_6(\omega) + \omega\omega_0^o\Gamma_7(\omega) - \omega\omega_0^o\Gamma_8(\omega)]. \tag{58}$$

Considering three- and four-phonon energy-conserving processes giving rise to damping of microwaves, the expressions for $\Gamma_i(\omega)$ $(i = 1, 2, 3, 4)$, where ω is the microwave photon frequency corresponding to which a polarization-mode phonon of frequency ω is virtually excited, are obtained as

$$\Gamma_1(\omega) = -\frac{1}{4}\sum_k \alpha^2(k)(N_k^a - N_k^o)\delta(\omega + \omega_k^a - \omega_k^o), \tag{59a}$$

$$\Gamma_2(\omega) = \frac{1}{8}\sum_k [\beta^a(k)]^2[1 + (N_k^a)^2 - 2N_0 N_k^a]\{\delta(\omega + 2\omega_k^a - \Omega) - \delta(\omega - 2\omega_k^a + \Omega)\}, \tag{59b}$$

$$\begin{aligned}\Gamma_3(\omega) = \sum_{k_1,k_2,k_3}\ \sum_{k_1',k_2',k_3'} \delta_{123}\,\gamma(k_1, k_2, k_3)\gamma(k_1', k_2', k_3')((1 + N_{k_2}^a N_{k_3}^a - N_{k_3}^a N_{k_1}^o - N_{k_1}^o N_{k_2}^a)\\ \times[\delta(\omega - \omega_{k_1}^o + \omega_{k_2}^a + \omega_{k_3}^a) - \delta(\omega + \omega_{k_1}^o - \omega_{k_2}^a - \omega_{k_3}^a)]\\ - \{(1 - N_{k_2}^a N_{k_3}^a + N_{k_3}^a N_{k_1}^o - N_{k_1}^o N_{k_2}^a)\delta(\omega - \omega_{k_1}^o + \omega_{k_2}^a - \omega_{k_3}^a)\} - \{\omega_{k_2}^a \leftrightarrow \omega_{k_3}^a\}),\end{aligned} \tag{59c}$$

and

$$\begin{aligned}\Gamma_4(\omega) = \sum_{k_1,k_2,k_3}\ \sum_{k_1',k_2',k_3'} (\delta_{123} + \delta_{231} + \delta_{312})\mu(k_1, k_2, k_3)\mu(k_1', k_2', k_3')\\ \times(\{(1 + N_{k_2}^o N_{k_3}^o - N_{k_3}^o N_{k_1}^o - N_{k_1}^o N_{k_2}^o)[\delta(\omega - \omega_{k_1}^o + \omega_{k_2}^o + \omega_{k_3}^o) - \delta(\omega + \omega_{k_1}^o - \omega_{k_2}^o - \omega_{k_3}^o)]\}\\ + \{\omega_{k_1}^o \leftrightarrow \omega_{k_2}^o\} + \{\omega_{k_1}^o \leftrightarrow \omega_{k_3}^o\}).\end{aligned} \tag{59d}$$

For $\Gamma_5(\omega)$ to $\Gamma_8(\omega)$ due to impurity scattering, we find correspondingly

$$\Gamma_5(\omega) = \frac{1}{2}\sum_k D^2(k_a, 0)\delta(\omega - \omega_k^a), \tag{60a}$$

$$\Gamma_6(\omega) = \frac{1}{2}\sum_k C^2(k_a, 0)\delta(\omega - \omega_k^a), \tag{60b}$$

$$\Gamma_7(\omega) = \frac{1}{2}\sum_k C(k_a, 0)D^*(k_a, 0)\delta(\omega - \omega_k^a), \tag{60c}$$

$$\Gamma_8(\omega) = -\frac{1}{2}\sum_k C^*(k_a, 0)D(k_a, 0)\delta(\omega - \omega_k^a). \tag{60d}$$

Substituting for $\nu^2(\omega)$ from Eq. (48) into Eq. (54) we have

$$\gamma_1(T - T_C' + \zeta T^2)\tan\delta = -\Gamma(\omega), \tag{61}$$

where

$$\gamma_1 = \frac{8k_B\omega_0^o}{\hbar}\left(\sum_k \frac{\alpha^2(k)}{\omega_k^a\omega_k^o} + \sum_{k,\lambda}\frac{\beta^\lambda(k)}{\omega_k^\lambda}\right). \tag{62}$$

As is evident from (60), $\Gamma_d(\omega)$ is independent of temperature. In the high-temperature limit, $\Gamma_{\mathrm{anh}}(\omega)$ from Eqs. (57) and (59) has the form

$$\Gamma_{\mathrm{anh}}(\omega) = AT + BT^2, \tag{63}$$

where

$$A = -\frac{2\pi k_B\omega_0^o}{\hbar}\omega\sum_k \frac{\alpha^2(k)}{\omega_k^a\omega_k^o}\delta(\omega + \omega_k^a - \omega_k^o) \tag{64a}$$

and

$$B=\frac{4\pi k_B{}^2\omega_0^o}{\hbar^2}\,\omega\Bigg(8\sum_k[\beta^a(k)]^2\frac{1}{(\omega_k^a)^2\Omega}[\delta(\omega+2\omega_k^a-\Omega)-\delta(\omega-2\omega_k^a+\Omega)]+2\sum_{k_1,k_2,k_3}\sum_{k_1',k_2',k_3'}\delta_{123}\frac{\gamma(k_1,k_2,k_3)\gamma(k_1',k_2',k_3')}{\omega_{k_1}^o\omega_{k_2}^a\omega_{k_3}^a}$$

$$\times[\delta(\omega-\omega_{k_1}^o+\omega_{k_2}^a+\omega_{k_3}^a)-\delta(\omega+\omega_{k_1}^o-\omega_{k_2}^a-\omega_{k_3}^a)-\delta(\omega-\omega_{k_1}^o+\omega_{k_2}^a-\omega_{k_3}^a)-\delta(\omega-\omega_{k_1}^o-\omega_{k_2}^a+\omega_{k_3}^a)]$$

$$+3\sum_{k_1,k_2,k_3}\sum_{k_1',k_2',k_3'}(\delta_{123}+\delta_{231}+\delta_{312})\frac{\mu(k_1,k_2,k_3)\mu(k_1',k_2',k_3')}{\omega_{k_1}^o\omega_{k_2}^o\omega_{k_3}^o}$$

$$\times[\{\delta(\omega-\omega_{k_1}^o+\omega_{k_2}^o+\omega_{k_3}^o)-\delta(\omega+\omega_{k_1}^o-\omega_{k_2}^o-\omega_{k_3}^o)\}+\{\omega_{k_1}^o\leftrightarrow\omega_{k_2}^o\}+\{\omega_{k_1}^o\leftrightarrow\omega_{k_3}^o\}]\Bigg)\,. \qquad (64b)$$

The factors A and B depend linearly on the frequency ω and may be related to the parameters β and γ of the dielectric loss equation.

The expression for $\Gamma_d(\omega)$ from (58) and (60) is given by

$$\Gamma_d(\omega)=\frac{2\pi}{\omega_0^o}\sum_k[(\omega_0^o)^2D^2(k_a,0)+\omega^2C^2(k_a,0)+\omega\omega_0^oC(k_a,0)D^*(k_a,0)+\omega\omega_0^oC^*(k_a,0)D(k_a,0)]\,\delta(\omega-\omega_k^a)\,. \qquad (65)$$

Setting

$$C(k_a,0)=(\omega_k^a\omega_0^o)^{1/2}C'(k_a,0)$$

and

$$D(k_a,0)=(\omega_k^a\omega_0^o)^{-1/2}D'(k_a,0)\,,$$

Eq. (65) can be rewritten

$$\Gamma_d(\omega)=2\pi\sum_k\left[\frac{1}{\omega}D'^2(k_a,0)+\omega^3C'^2(k_a,0)+\omega C'(k_a,0)D'^*(k_a,0)+\omega C'^*(k_a,0)D'(k_a,0)\right]\delta(\omega-\omega_k^a)\,. \qquad (66)$$

The occurrence of the factor $\delta(\omega-\omega_k^a)$ in Eq. (66) justifies the physical interpretation of the mechanism responsible for the attenuation of electromagnetic waves caused by the presence of defects given by Vinogradov.[5] It is suggested that the polarization-mode wave connected with the electromganetic wave is scattered from the defects by the creation of phonons with different directions of wave vectors whose frequency is equal to the electromagnetic wave frequency, i.e., $\omega_k^a=\omega$, and these are acoustic phonons. The excess momentum, for momentum conservation in the process, is assumed to be supplied by the defects.

Equation (61) expresses the loss tangent of a ferroelectric crystal with defects. Neglecting the change in the Curie temperature due to defects, from Eqs. (56), (63), and (66), the expression for the loss tangent has the form (1). The parameters α, β, and γ are given by

$$\alpha=-\Gamma_d/\gamma_1\,,$$
$$\beta=-A/\gamma_1\,,$$
$$\gamma=-B/\gamma_1\,. \qquad (67)$$

As follows from (64) and (67) the parameters β and γ arise due to three- and four-phonon anharmonic interaction terms of the lattice. They have the same values in the pure and doped materials and very linearly with ω. The parameter α depends only on the impurity content of the material and vanishes for pure single crystals. These predictions are in agreement with the experimental observations.

Experiments give a linear ω dependence for the temperature-independent term in the expression for $(T-T_C)\tan\delta$. Summing over $\vec{k}$ in Eq. (66) in the Debye approximation, this is found to be the case in our expression for α when the introduction of impurities results in a force-constant change only. When mass changes also become appreciable, terms with ω^3 and ω^5 dependences would also occur. The reason why the higher-frequency dependences have not been experimentally observed is that these experiments were performed on mixed polycrystalline materials for which the contribution Γ_{imp} for scattering from lattice imperfections, namely, grain boundaries and lattice defects within the grains, dominates over the contribution Γ_d for scattering from foreign defect atoms. The parameter α is composed of defect Γ_d/γ_1, and imperfection $\Gamma_{\text{imp}}/\gamma_1$ parts. We have calculated only Γ_d. We contend that in single mixed crystals of $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$, where the contribution Γ_{imp} would vanish, the nonlinear frequency terms in Γ_d could be experimentally detected, provided they lead to losses appreciable compared to anharmonic losses. This might be also the case for the system SrTiO_3 doped with Fe^{+3} or Gd^{+3} ions.

We have obtained a linear ω dependence for the loss tangent for a three-dimensional crystal when there is a force-constant change only. As mentioned earlier, an extension of the linear-chain model of Silverman[6] to a three-dimensional lattice would lead to the loss tangent being proportional to the cube of the frequency, contrary to experiments. Silverman has argued that frequency dependences higher than linear were unlikely to be observed, as in the expression for α each extra ω would come with a factor ω_0^0 in the denominator. The parameter α is therefore reduced by the factor $(\omega/\omega_0^0)^3 \simeq 10^{-9}$. This is not valid here as in our case the higher ω terms do not occur with ω_0^0 in the denominator.

VII. SUMMARY

In the present paper, we have developed a theory for the influence of isovalent impurities on the Curie temperature, and the frequency and temperature dependence of microwave loss in ferroelectrics due to impurity and anharmonic scattering taking into consideration the detailed characteristics of the defects. The treatment is based on the double-time thermal Green's function and the Kubo formalism for the Silverman and Joseph Hamiltonian augmented with dominant four-phonon processes by including both mass and harmonic-force-constant changes. It is shown that the effect of defects on the real part of the dielectric constant at low frequencies appears only in shift of the Curie temperature. In the first-order approximation of defect parameters, the defect-induced Curie-temperature shift depends only on the force-constant changes and is proportional to the concentration of defects, in conformity with the experimental results. For the crystal model considered here, the expression for the microwave-loss tangent has the same form as the empirical result obtained from experiments. A plausible description of the microwave absorption is obtained when defects produce appreciable changes in the harmonic force constants linking their host neighbors. However, detailed quantitative calculations of the Curie-temperature shift and microwave-loss tangent are extremely complicated as they require a knowledge of the lattice dynamics of defect ferroelectrics on some specific model of the

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