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Electric field dependence of the Curie temperature and microwave absorption in displacive ferroelectrics with impurities

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Abstract. The electric field dependence of the complex dielectric constant in an anharmonic defect ferroelectric crystal is calculated in its paraelectric phase from the Silverman-Joseph-Hamiltonian augmented with fourth-order phonon coordinates using double-time Green's functions. The field and impurity dependence of the shift in the Curie temperature is discussed. An expression is obtained for the electric field dependence of dielectric loss at microwave frequencies in defect ferroelectrics.

Keywords. Displacive ferroelectrics; anharmonicity; electric dipolemoment; microwave absorption; Curie temperature.

1. Introduction

It is well-known that several interesting temperature-dependent properties of ferroelectrics result from the temperature-dependence of the low lying transverse optic mode of vibration (Cochran 1969). Lattice defects in ferroelectrics have a major influence on the static dielectric constant in the paraelectric phase (Shirane and Jona 1962). The response of a crystal to an external electric field is conveniently described by the dielectric susceptibility. The Curie temperature is also affected by the electric field. Thus various impurities and different electric fields can change the Curie temperature T_c of the same material in different ways. The change in T_c cannot be accounted for simply by considering change in lattice constant or polarisability of the impurity ions.

Microwave losses in the presence of an electric field, in the pure and doped displacive ferroelectrics ($BaTiO_3$, $SrTiO_3$, etc) have been reported by many workers (Rupprecht *et al* 1961; Rupprecht and Bell 1962). Above the phase transition temperature, the results of loss measurements can be represented by the temperature and electric field dependence of the microwave loss tangent (tan δ) as

$$(T-T_c) \tan \delta = A+BT+CT^2, \tag{1}$$

where the parameter A depends strongly on the defect concentration. Parameters B and C are the results of anharmonicity. The present study shows that in response to the applied electric field, parameters B and C are modified (equation (27)). The loss tangent and therefore these parameters are proportional to the frequency ω. Vinogradov (1963) obtained a linear frequency dependence for these losses, if point

charged defects are present in the crystal. Silverman (1962) also showed a similar linear frequency dependence for microwave losses in $SrTiO_3$ using a linear chain model with defects consisting of changed force constants.

The defect dependence of the Curie temperature and microwave absorption in ferroelectric crystals is discussed by Bahadur and Sharma (1975) considering the changes in mass and harmonic force constants between the impurity atom and the host lattice atoms. We discuss n substitutional impurities ($N \gg n$) and neglect impurity-impurity interactions. The present study differs from that of Bahadur and Sharma (1975), in that the crystal is also subjected to an external electric field. We therefore discuss the defect dependence as well as the electric field dependence of Curie temperature and the microwave loss tangent in an anharmonic displacive ferroelectrics in the paraelectric phase. We make use of a unitary transformation discussed elsewhere (Gairola and Semwal 1977; Naithani and Semwal 1978), which renders the most significant first order dipole moment term ($-\hbar aEA_0^0$) to effect the Curie temperature and the microwave loss *via* the applied field E.

In § 2, the modified Hamiltonian for the problem is mentioned and the necessary Green's functions are evaluated. § 3 deals with the dependence of Curie temperature on the electric field and impurity. In § 4, an expression for the microwave loss tangent in the presence of impurity and electric field is given and its temperature, field and defect dependence are discussed.

2. Hamiltonian and the Green's functions

The real part of the dielectric constant and the microwave loss tangent tan δ are related (Bahadur and Sharma 1975) to the Green's function

$$G(\omega+i\epsilon) = \langle\langle A_0^0(t);\, A_0^0(t')\rangle\rangle_{\omega+i\epsilon} = G'(\omega) - iG''(\omega), \tag{2}$$

as
$$\epsilon'(\omega) - 1 = -8\pi^2 M_\mu^2(0) G'(\omega), \tag{3}$$

and
$$\tan\delta = G''(\omega)/G'(\omega). \tag{4}$$

The modified Silverman Hamiltonian used in the present study is exactly similar to equation (7) of Naithani (1978). Writing the equation of motion for the Green's function (2) with the help of this modified Hamiltonian, Fourier transforming and writing it in the Dyson's equation form, one obtains

$$G(\omega+i\epsilon) = \omega_0^0 / \pi[\omega^2 - \nu^2(\omega) + i\Gamma(\omega)], \tag{5a}$$

where
$$\nu^2(\omega) = -(\omega_0^0)^2 + 4\omega_0^0 D(0,0)$$

$$+ \omega_0^0 E^2(96g^2V - 24gD_1') + 4\omega_0^0 \bar{Q} + \Delta(\omega), \tag{5b}$$

with $$\Delta(\omega)=\mathrm{Re}\,\omega_0^0\Bigg[2\sum_k |F(k)|^2 \sum_{\pm}(\tilde{N}_k^0 \pm \tilde{N}_k^a)\frac{(\tilde{\omega}_k^a \pm \tilde{\omega}_k^0)}{\omega^2-(\tilde{\omega}_k^a+\tilde{\omega}_k^0)^2}$$

$$+8\sum_{k,\lambda}|\beta^\lambda(k)|^2\Bigg([1+(\tilde{N}_k^\lambda)^2+2\tilde{N}_0^0\tilde{N}_k^\lambda]\frac{(\Omega+2\tilde{\omega}_k^\lambda)}{\omega^2-(\Omega+2\tilde{\omega}_k^\lambda)^2}$$

$$+[1+(\tilde{N}_k^\lambda)^2-2\tilde{N}_0^0\tilde{N}_k^\lambda]\frac{(\Omega-2\tilde{\omega}_k^\lambda)}{\omega^2-(\Omega-2\tilde{\omega}_k^\lambda)^2}-[1-(\tilde{N}_k^\lambda)^2]\frac{2\Omega}{\omega^2-\Omega^2}\Bigg)$$

$$+\sum_{k_1,k_2,k_3}\sum_{k_1',k_2',k_3'}\delta_{123}\,\Phi(k_1,k_2,k_3)\,\Phi(k_1',k_2',k_3')\Bigg([1+\tilde{N}_{k_1}^0\tilde{N}_{k_2}^a+\tilde{N}_{k_2}^a\tilde{N}_{k_3}^a$$

$$+\tilde{N}_{k_3}^a\tilde{N}_{k_1}^0]\frac{(\tilde{\omega}_{k_1}^0+\tilde{\omega}_{k_2}^a+\tilde{\omega}_{k_3}^a)}{\omega^2-(\tilde{\omega}_{k_1}^0+\tilde{\omega}_{k_2}^a+\tilde{\omega}_{k_3}^a)^2}+[1-\tilde{N}_{k_1}^0\tilde{N}_{k_2}^a+\tilde{N}_{k_2}^a\tilde{N}_{k_3}^a-\tilde{N}_{k_3}^a\tilde{N}_{k_1}^0]$$

$$\frac{(\tilde{\omega}_{k_1}^0-\tilde{\omega}_{k_2}^a-\tilde{\omega}_{k_3}^a)}{\omega^2-(\tilde{\omega}_{k_1}^0-\tilde{\omega}_{k_2}^a-\tilde{\omega}_{k_3}^a)^2}\Bigg)+\sum_{k_1,k_2,k_3}\sum_{k_1',k_2',k_3'}\delta\psi(k_1,k_2,k_3)\,\psi(k_1',k_2',k_3')$$

$$\times\Bigg([1+\tilde{N}_{k_1}^0\tilde{N}_{k_2}^0+\tilde{N}_{k_2}^0\tilde{N}_{k_3}^0+\tilde{N}_{k_3}^0\tilde{N}_{k_1}^0]\frac{(\tilde{\omega}_{k_1}^0+\tilde{\omega}_{k_2}^0+\tilde{\omega}_{k_3}^0)}{\omega^2-(\tilde{\omega}_{k_1}^0+\tilde{\omega}_{k_2}^0+\tilde{\omega}_{k_3}^0)^2}$$

$$+[1-\tilde{N}_{k_1}^0\tilde{N}_{k_2}^0+\tilde{N}_{k_2}^0\tilde{N}_{k_3}^0-\tilde{N}_{k_3}^0\tilde{N}_{k_1}^0]\frac{(\tilde{\omega}_{k_1}^0-\tilde{\omega}_{k_2}^0-\tilde{\omega}_{k_3}^0)}{\omega^2-(\tilde{\omega}_{k_1}^0-\tilde{\omega}_{k_2}^0-\tilde{\omega}_{k_3}^0)^2}\Bigg)$$

$$+4\sum_{k,\lambda}D^2(k_\lambda,0)\frac{\tilde{\omega}_k^\lambda}{\omega^2-(\tilde{\omega}_k^\lambda)^2}-4(\omega/\omega_0^0)^2\sum_{k,\lambda}C^2(k_\lambda,0)\frac{\tilde{\omega}_k^\lambda}{\omega^2-(\tilde{\omega}_k^\lambda)^2}$$

$$+4(\omega/\omega_0^0)\sum_{k,\lambda}C(k_\lambda,0)\,D^*(k_\lambda,0)\frac{\tilde{\omega}_k^\lambda}{\omega^2-(\tilde{\omega}_k^\lambda)^2}-4(\omega/\omega_0^0)\sum_{k,\lambda}C^*(k_\lambda,0)$$

$$\times D(k_\lambda,0)\frac{\tilde{\omega}_k^\lambda}{\omega^2-(\tilde{\omega}_k^\lambda)^2}+8E^2\sum_{k,\lambda}|B^\lambda(k)|^2\sum_k\tilde{N}_k^\lambda\frac{\tilde{\omega}_k^\lambda}{\omega^2-(2\tilde{\omega}_k^\lambda)^2}$$

$$+128\,g^2E^2\sum_k|\beta^\lambda(k)|^2\sum_k\tilde{N}_k^\lambda\frac{\tilde{\omega}_k^\lambda}{\omega^2-(2\tilde{\omega}_k^\lambda)^2}+48\,V^2$$

$$\times\Bigg([1+3(\tilde{N}_0^0)^2]\frac{3\Omega}{\omega^2-(3\Omega)^2}-[1-(\tilde{N}_0^0)^2]\frac{\Omega}{\omega^2-\Omega^2}\Bigg)$$

$$+(6D_1'-48\,g\,V)^2E^2\tilde{N}_0^0\frac{4\Omega}{\omega^2-(2\Omega)^2}\Bigg], \qquad (6)$$

and $$\Gamma(\omega)=\omega_0^0\pi\Big[\sum_k |F(k)|^2 \sum_{\pm}(\tilde{N}_k^0 \pm \tilde{N}_k^a)\{\delta(\omega-\tilde{\omega}_k^a \mp \tilde{\omega}_k^0)$$

$$-\delta(\omega+\tilde{\omega}_k^a \pm \tilde{\omega}_k^0)\} + 4\sum_{k,\lambda} |\beta^\lambda(k)|^2 ([1+(\tilde{N}_k^\lambda)^2+2N_0^0\tilde{N}_k^\lambda]$$

$$\times \{\delta(\omega-\Omega-2\tilde{\omega}_k^\lambda)-\delta(\omega+\Omega+2\tilde{\omega}_k^\lambda)\}+[1+(\tilde{N}_k^\lambda)^2-2N_0^0\tilde{N}_k^\lambda]$$

$$\times \{\delta(\omega-\Omega+2\tilde{\omega}_k^\lambda)-\delta(\omega+\Omega-2\tilde{\omega}_k^\lambda)\}-[1-(\tilde{N}_k^\lambda)^2]$$

$$\times \{\delta(\omega-\Omega)-\delta(\omega+\Omega)\})+\sum_{k_1,k_2,k_3}\sum_{k_1',k_2',k_3'}(1/2)\delta_{123}\,\Phi(k_1,k_2,k_3)$$

$$\times \Phi(k_1',k_2',k_3')\,([1+\tilde{N}_{k_1}^0\tilde{N}_{k_2}^a+\tilde{N}_{k_2}^a\tilde{N}_{k_3}^a+\tilde{N}_{k_3}^a\tilde{N}_{k_1}^0]$$

$$\times \{\delta(\omega-\tilde{\omega}_{k_1}^0-\tilde{\omega}_{k_2}^a-\tilde{\omega}_{k_3}^a)-\delta(\omega+\tilde{\omega}_{k_1}^0+\tilde{\omega}_{k_2}^a+\tilde{\omega}_{k_3}^a)\}$$

$$+[1-\tilde{N}_{k_1}^0\tilde{N}_{k_2}^a+\tilde{N}_{k_2}^a\tilde{N}_{k_3}^a-\tilde{N}_{k_3}^a\tilde{N}_{k_1}^0]\{\delta(\omega-\tilde{\omega}_{k_1}^0+\tilde{\omega}_{k_2}^a+\tilde{\omega}_{k_3}^a)$$

$$-\delta(\omega+\tilde{\omega}_k^0-\tilde{\omega}_{k_2}^a-\omega_{k_3}^a)\})+(1/2)\sum_{k_1,k_2,k_3}\sum_{k_1',k_2',k_3'}\delta\psi(k_1,k_2,k_3)$$

$$\times \psi(k_1',k_2',k_3')\,([1+\tilde{N}_{k_1}^0\tilde{N}_{k_2}^0+\tilde{N}_{k_2}^0\tilde{N}_{k_3}^0+\tilde{N}_{k_3}^0\tilde{N}_{k_1}^0]\{\delta(\omega-\omega_{k_1}^0$$

$$-\tilde{\omega}_{k_2}^0-\tilde{\omega}_{k_3}^0)-\delta(\omega+\tilde{\omega}_{k_1}^0+\tilde{\omega}_{k_2}^0+\tilde{\omega}_{k_3}^0)\}+[1-\tilde{N}_{k_1}^0\tilde{N}_{k_2}^0$$

$$+\tilde{N}_{k_2}^0\tilde{N}_{k_3}^0-\tilde{N}_{k_3}^0\tilde{N}_{k_1}^0]\{\delta(\omega-\tilde{\omega}_{k_1}^0+\tilde{\omega}_{k_2}^0+\tilde{\omega}_{k_3}^0)-\delta(\omega+\tilde{\omega}_{k_1}^0$$

$$-\tilde{\omega}_{k_2}^0-\tilde{\omega}_{k_3}^0)\})+2\sum_{k,\lambda}D^2(k_\lambda,0)\{\delta(\omega-\tilde{\omega}_k^\lambda)-\delta(\omega+\tilde{\omega}_k^\lambda)\}$$

$$-2(\omega/\omega_0^0)^2\sum_{k,\lambda}C^2(k_\lambda,0)\{\delta(\omega-\tilde{\omega}_k^\lambda)-\delta(\omega+\tilde{\omega}_k^\lambda)\}+2(\omega/\omega_0^0)$$

$$\times\sum_{k,\lambda}D^*(k_\lambda,0)\,C(k_\lambda,0)\{\delta(\omega-\tilde{\omega}_k^\lambda)-\delta(\omega+\tilde{\omega}_k^\lambda)\}-2(\omega/\omega_0^0)$$

$$\times \sum_{k,\lambda} C^*(k_\lambda, 0)\, D(k_\lambda, 0) \{\delta(\omega - \tilde{\omega}_k^\lambda) - \delta(\omega + \tilde{\omega}_k^\lambda)\}$$

$$+ 4E^2 \sum_{k,\lambda} [|B^\lambda(k)|^2 + 16g^2 |\beta^\lambda(k)|^2] \sum_k \tilde{N}_k^\lambda \{\delta(\omega - 2\tilde{\omega}_k^\lambda)$$

$$- \delta(\omega + 2\tilde{\omega}_k^\lambda)\} + (6D_1' - 48gV)^2 E^2 \tilde{N}_0^0 \{\delta(\omega - 2\Omega)$$

$$- \delta(\omega + 2\Omega)\} + 24V^2 ([1 + 3(N_0^0)^2] \{\delta(\omega - 3\Omega)$$

$$- \delta(\omega + 3\Omega)\} - [1 - (N_0^0)^2] \{\delta(\omega - \Omega) - \delta(\omega + \Omega)\})], \tag{7}$$

where $\delta = \delta_{123} + \delta_{213} + \delta_{321}$,

with $\delta_{123} = \delta_{k_1 - k_1'} (\delta_{k_2 - k_2'} \delta_{k_3 - k_3'} + \delta_{k_2 - k_3'} \delta_{k_3 - k_2'})$,

also $\tilde{N}_0^0 = \cot h\,(\hbar\Omega / 2k_B T)$

and $\tilde{N}_k^\lambda = \cot h\,(\hbar\tilde{\omega}_k^\lambda / 2k_B T)$.

3. Curie temperature

The real part of the complex dielectric constant in eq. (3) now takes the form,

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

In the presence of electric field, in a defect ferroelectric crystal, the real part of the Green's function given by (5a), gives Cochran's temperature-dependent frequency $\Omega(T)$ as the self-consistent solution of the equation,

$$\Omega^2 = -(\omega_0^0)^2 + 4\omega_0^0 D(0, 0) + \omega_0^0 E^2 (96 g^2 V - 24 g D_1')$$

$$+ 4\omega_0^0 \bar{Q} + \Delta(\Omega). \tag{9}$$

$\Delta(\omega)$ is given by (6). Hence by comparing (9) and (5b), one can approximate $\nu(\omega)$ as Ω. For a ferroelectric having cubic symmetry, the Cochran mode frequency Ω is very high compared to the microwave frequency ω, so that $\nu(\omega) \gg \omega$ and no relaxation effects are observed. In paraelectrics the value of $\epsilon'(\omega)$ is very high compared to those in alkali halides, so that $\epsilon'(\omega) \gg 1$. Equation (8) thus becomes

$$\epsilon'(\omega) = 8\pi M_\mu^2(0)\, \omega_0^0 / \nu^2(\omega). \tag{10}$$

In a pure crystal we have,

$$\epsilon_0'(\omega) = 8\pi M_\mu^2(0)\,\omega_0^0 / \nu_0^2(\omega), \tag{11}$$

where, $$\nu_0^2(\omega) = -(\omega_0^0)^2 + 4\omega_0^0 \bar{Q} + \Delta_0(\omega). \tag{12}$$

$\Delta_0(\omega)$ corresponds to a pure crystal and is given by (6) in the absence of defects and the electric field. For an impure crystal, with the help of (5b) we write,

$$\nu^2(\omega) = \nu_0^2(\omega) + \Delta(\nu^2(\omega)), \tag{13}$$

where
$$\Delta(\nu^2(\omega)) = 4\omega_0^0 D(0,0) + 4\omega_0^0 \sum_{k,\lambda} D^2(k_\lambda, 0) \frac{\tilde{\omega}_k^\lambda}{\omega^2 - (\tilde{\omega}_k^\lambda)^2}$$

$$- 4(\omega^2/\omega_0^0) \sum_{k,\lambda} C^2(k_\lambda, 0) \frac{\tilde{\omega}_k^\lambda}{\omega^2 - (\tilde{\omega}_k^\lambda)^2} + 4\omega \sum_{k,\lambda} C(k_\lambda, 0)\, D^*(k_\lambda, 0)$$

$$\times \frac{\tilde{\omega}_k^\lambda}{\omega^2 - (\tilde{\omega}_k^\lambda)^2} - 4\omega \sum_{k,\lambda} C^*(k_\lambda, 0)\, D(k_\lambda, 0) \frac{\tilde{\omega}_k^\lambda}{\omega^2 - (\tilde{\omega}_k^\lambda)^2} + 8E^2\omega_0^0$$

$$\times \sum_k |B^\lambda(k)|^2 \sum_k \tilde{N}_k^\lambda \frac{\tilde{\omega}_k^\lambda}{\omega^2 - (2\tilde{\omega}_k^\lambda)^2} + 128 g^2 E^2 \omega_0^0 \sum_k |\beta^\lambda(k)|^2 \sum_k \tilde{N}_k^\lambda$$

$$\times \frac{\tilde{\omega}_k^\lambda}{\omega^2 - (2\tilde{\omega}_k^\lambda)^2} + \omega_0^0 (6D_1' - 48 g V)^2 E^2 \tilde{N}_0^0 \frac{4\Omega}{\omega^2 - (2\Omega)^2} + 96 V^2$$

$$\times \omega_0^0 \left([1 + 3(\tilde{N}_0^0)^2] \frac{3\Omega}{\omega^2 - (3\Omega)^2} - [1 - (\tilde{N}_0^0)^2] \frac{\Omega}{\omega^2 - \Omega^2} \right), \tag{14}$$

and
$$\nu_0^2(\omega) = -(\omega_0^0)^2 + \frac{4\omega_0^0}{\pi} \sum_k |\beta^\lambda(k)|\, \tilde{N}_k^\lambda + \Delta_0(\omega). \tag{15}$$

With the help of (14) and (15) the temperature-dependence of $\nu^2(\omega)$ can be written as,

$$\nu^2(\omega) = -(\omega_0^0)^2 + \gamma_1 T + \gamma_2 T^2 + \gamma_3 E^2 T + \omega_0^0 E^2$$

$$\times (96 g^2 V - 24 g D_1') + \Delta(\nu_D^2), \tag{16}$$

where $\Delta(\nu_D^2)$ is the temperature independent part of equation (14) due to defect and γ_i's (i=1, 2, 3) denote the temperature and electric field-independent terms in $\nu^2(\omega)$

and depend on the anharmonic force constants and electric dipole moment terms. The T and T^2 dependence of $\nu^2(\omega)$ are due to third and fourth-order anharmonicities respectively.

Thus from eq. (16) we conclude that,

$$\nu^2(\omega)/\gamma = -\frac{(\omega_0^0)^2}{\gamma} + T + [\Delta(\nu_D^2) + \omega_0^0 (96\, g^2\, V - 24\, g\, D_1')\, E^2 + \gamma_2\, T^2]\,(1/\gamma), \tag{17}$$

where $\gamma = \gamma_1 + E^2\, \gamma_3$.

Using (10) and (17) one gets

$$\epsilon'(\omega) = C/[T - T_c + \xi\, T^2 + (1/\gamma)\{\Delta(\nu_D^2) + \omega_0^0 (96\, g^2 V - 24\, g\, D_1')\, E^2\}], \tag{18}$$

where $C = 8\pi\, M_\mu^2(0)\, \omega_0^0 / \gamma$, (19a)

$T_c = (\omega_0^0)^2/\gamma$, (19b)

and $\xi = \gamma_2/\gamma$. (19c)

Equation (18) can be rewritten as,

$$\epsilon'(\omega) = C/[T - T_c' + \xi T^2], \tag{20}$$

where $T_c' = T_c + \Delta(T_c)$, (21)

with $$\Delta(T_c) = -\frac{\Delta(\nu_D^2)}{\gamma} + \{[24 g D_1' - 96 g^2 V]\, [(\omega_0^0 E^2)/\gamma]\}. \tag{22}$$

Expression (22) shows that the change in the Curie temperature depends both on the impurities and the external electric field. $\gamma(=\gamma_1 + E^2\gamma_3)$ depends on the anharmonic coupling constants and electric field. It is evident from (22) that the change in Curie temperature $\Delta(T_c)$ is a function of mass change due to defect, anharmonic force constants and the applied electric field. In the absence of electric field ($E=0$), $\Delta(T_c)$ depends on the defects and anharmonicities present in the crystal. Clearly this is a combined effect of defects and anharmonicity in the lattice. The term in curly bracket in (22) gives the influence of external field on $\Delta(T_c)$, and depends on α (first order dipole moment coefficient), D_1' (third order dipole moment coefficient), γ, and V (fourth order soft phonon anharmonic coefficient). In a pure crystal [$\Delta(\nu_D^2)=0$] the relative magnitudes of these anharmonic coefficients determine the change in Curie temperature in the presence of an electric field. This field dependence is a consequence of the transformation used (Gairola and Semwal 1977; Naithani *et al* 1977 and Naithani and Semwal 1978).

We have so far not considered the influence of defects on the dipole moment coefficients, and have assumed that the introduction of defects changes only the nearest neighbour harmonic force constants as mentioned in Naithani (1978). It is clear from (22) that the change in Curie temperature is dependent upon impurity and electric field terms in the presence of anharmonicity. Since we are discussing the displacive ferroelectrics in the paraelectric phase, one can see that the change in Curie temperature $\Delta(T_c)$ cannot be explained without anharmonicity.

4. Microwave absorption

For a defect ferroelectric crystal, in the presence of electric field, using the Green's function given by (5a) for microwave photons $[\omega \ll \nu(\omega)]$ we write the expression for loss tangent as,

$$\tan \delta(\omega) = -\Gamma(\omega)/\nu^2(\omega). \tag{23}$$

$\Gamma(\omega)/2\nu(\omega)$ corresponds to the half-width associated with the damping of Cochran soft mode. The damping of microwaves therefore arises from the creation of a virtual Cochran polarisation mode excited by the transverse electromagnetic radiation and the subsequent decay into real phonon by scattering from lattice imperfections and third- and fourth-order anharmonicity in the presence of electric field.

From (17) we can write,

$$\nu^2(\omega)=\gamma(T-T_c'+\xi T^2) \tag{24}$$

Hence $$\gamma(T-T_c'+\xi T^2)\tan\delta=-\Gamma(\omega) \tag{25}$$

or $$\gamma(T-T_c'+\xi T^2)\tan\delta=a+b'T+d'T^2, \tag{26}$$

with $$b'=b+cE^2 \tag{27}$$

Where b' and d' are the coefficients of T and T^2 terms, and a is a temperature-independent term in (17). Equation (26) can also be rewritten as,

$$(T-T_c'+\xi T^2)\tan\delta=A+B'T+D'T^2 \tag{28}$$

where $$A=a/\gamma,\ B'=b'/\gamma \text{ and } D'=d'/\gamma. \tag{29}$$

Equation (28) gives the microwave tangent loss in a defect ferroelectric crystal subjected to external electric field. The parameter A depends on the impurity contents in the anharmonic crystal and is zero for a pure crystal. The expression (28) is similar to that obtained by Bahadur and Sharma (1975) excepting that B' and D' are now modified by the applied electric field, as evident from (27) and (29).

5. Discussion

The dependence of Cochran's frequency Ω gives the dependence of the Curie temperature ($\Omega \alpha (T - T_c)^{1/2}$, in the paraelectric phase). Our results show that the Curie temperature changes due to the presence of defects and external electric field in the anharmonic ferroelectric crystal. We shall separately discuss the impurity and field dependence of $\Delta(T_c)$. Anharmonicity is necessary in the crystal to observe this dependence. The field dependence is a consequence of the transformation used (Gairola 1977). In the absence of electric field the change in T_c caused by impurity depends on the changes in harmonic force constants between the impurity and host lattice atoms and mass change due to impurity and can be positive or negative (Bahadur and Sharma 1975). For a pure crystal placed in an external field E, the shift in Curie temperature will depend on the relative magnitudes of the anharmonic coupling coefficients and will have different signs for different crystals (Worlock and Fleury 1967; Kanzig and Maikoff 1951). However in a defect crystal in the presence of electric field E, the effect of these two dependence is observed (equations (22) and (28)) in the presence of anharmonicity.

The impurity, field and the temperature dependence of the complex dielectric constant can be explained with the help of (18), (19), (20) and (21) exactly on the above grounds. In the pure crystal, in the absence of field, the deviations from the Curie-Weiss law at high temperature are characterised by the parameter ξ. The introduction of defects and the presence of electric field in the crystal changes the Curie temperature T_c to T_c'; the Curie law remains valid in the paraelectric phase. In the temperature region where the phonon occupation number deviates from the classical values deviations from Curie-Weiss behaviour of the dielectric constant are observed (Barrett 1952).

The microwave loss tangent similarly depends on the electric field and the impurity contents in the lattice. From (27) and (28), it can be seen that the tangent loss increases with the increase in electric field. The loss tangent consists of a contribution which is quadratic in an applied biasing field plus a field-independent contribution, which agrees with previous results (Rupprecht *et al* 1961). It follows from (28) that the microwave loss tangent strictly depends on the anharmonicity and electric field through γ, and the defects and field affect tan δ only in the presence of the anharmonicity. The temperature-dependence of loss tangent is of the form $A + BT + CT^2$ (Silverman 1962). We have discussed the impurity and field dependence of $\Delta(T_c)$, tan δ and complex dielectric constant of an anharmonic ferroelectric in a qualitative manner using the lattice dynamical approach with the help of thermodynamic soft phonon Green's function. The quantitative variation requires specific models which is being studied separately.

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References

Barrett J H 1952 *Phys. Rev.* **86** 118
Bahadur R and Sharma P K 1975 *Phys. Rev.* **12** 448
Cochran W 1969 *Adv. Phys.* **18** 157
Gairola R P and Semwal B S 1977 *J. Phys. Soc. Jpn.* **42** 975
Kanzig W and Maikoff N 1951 *Helv. Phys. Acta* **24** 343
Naithani U C, Gairola R P and Semwal B S 1977 *J. Phys. Soc. Jpn.* **43** 204
Naithani U C and Semwal B S 1978 *Pramana* **11** 423
Rupprecht G and Bell R O 1962 *Phys. Rev.* **125** 1915
Rupprecht G, Bell R O and Silverman B D 1961 *Phys. Rev.* **123** 97
Silverman B D 1962 *Phys. Rev.* **125** 1921
Shirane G and Jona F 1962; *Some aspects on ferroelectricity* (London: Pergamon Press)
Vinogradov V S 1963 in *Proc. Int. Conf. Lattice Dynamics, Copenhagen* ed. R F Wallis (New York: Pergamon) p. 421
Worlock J M and Fleury P A 1967 *Phys. Rev. lett.* **19** 1176