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

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Abstract. Expressions for the complex dielectric constant, microwave absorption and the Curie temperature in doped displacive ferroelectrics, subjected to an external electric field are discussed, using the approach made in our previous study. A cross-term of defect parameters with electric field and anharmonic parameters is obtained. The intrinsic parameters B and C are modified by impurity terms. The qualitative E^3 dependence of tan δ is discussed.

Keywords. Displacive ferroelectrics; Curie temperature; tangent loss; dielectric constant.

1. Introduction

In a previous paper (Naithani and Semwal 1980, hereafter referred to as I), we discussed the complex dielectric constant, microwave absorption and the Curie temperature in doped displacive ferroelectrics, in the presence of an external electric field and higher order anharmonicities, by making use of a Hamiltonian proposed by Silverman and Joseph (1963) and the thermal Green's function technique (Zubarev 1960). The present study is an attempt to modify the expressions for the above mentioned properties, using the approach of I. The combined effect between the two dependences (the field and impurity) not shown in I, is observed in the presence of anharmonicity. It is shown that the parameters B and C (see equation (1) in I) are modified by the field and impurity terms but are non-zeros in the pure crystal, even in the absence of the external electric field. The modification in B and C due to impurity terms is missing in I. They represent the intrinsic properties of the crystal depending upon anharmonicity. The parameter A (see equation (1) in I) is mainly governed by the defect concentration and is zero for a pure crystal. It has been shown that the dielectric loss tangent increases with increasing external electric field. The loss tangent consists of a contribution which is quadratic in an applied biasing plus a field independent contribution, which agrees with the previous results (Rupprecht *et al* 1961). This variation of tan δ with applied field is noticeable in the vicinity of the Curie temperature. In the high temperature region, the field's effect ceases and the increase in loss arises mainly due to higher order anharmonic terms. We have shown the variation of tan δ with the electric field qualitatively. It is also shown that the expression for the shift in the Curie temperature (equation (22) in I) is also modified and the cross terms between the field and im-

purity parameters, in the presence of anharmonicity are obtained. These cross terms were missing in I.

2. Green's functions

In obtaining the values of $\Delta(\omega)$ and $\Gamma(\omega)$ (represented by equations (6) and (7) respectively in I), we start with the soft phonon Green's function (equation (2) in I), write its equation of motion, Fourier transform and write it in the Dyson's equation form. The process adopted was similar to our previous calculation. (Naithani and Semwal 1978). In this process we find $\Delta(\omega)$ and $\Gamma(\omega)$ to be the real and imaginary parts respectively of the response function for the soft phonon mode. The response function consists of higher order Green's functions, which are solved by the stabilised Hamiltonian. In I, we considered only the product of the direct terms in the expansion of the response function. If we also consider the product of the most dominating cross terms in the expansion of the response function, some additional Green's functions of the type $\langle\langle A_k^\lambda A_k^\lambda; A_{k'}^\lambda \rangle\rangle$ are obtained. These give zero contributions if we solve them without transformed Hamiltonian H_T (equation (7) in Naithani and Semwal 1978). Thus solving these Green's functions the additional terms in $\Delta(\omega)$ and $\Gamma(\omega)$ are obtained, which are the cross-terms of the electric field and defect parameters in the presence of anharmonicity. The new changed values of $\Delta(\omega)$ and $\Gamma(\omega)$ can be written as,

$$\Delta'(\omega) = \Delta(\omega) + \Delta_{DE}(\omega) \tag{1}$$

and $$\Gamma'(\omega) = \Gamma(w) + \Gamma_{DE}(\omega). \tag{2}$$

Here $\Delta(\omega)$ and $\Gamma(\omega)$ are still given by (6) and (7) respectively as in I and the values of $\Delta_{DE}(\omega)$ and $\Gamma_{DE}(\omega)$ are given by

$$\begin{aligned}\Delta_{DE}(\omega) = 48E^2\Big[&\Big\{\omega'^0_{k_1} \Big/ \Big(\omega^2 - \omega'^0_{k_1}\omega'^0_{k_2}\Big)\Big\} \sum_k D(k^0, 0) \\ &\times (B^0(k) - 4g\beta^0(k)) \sum_{k_1 k_2} \{D(k_1, k_2, -k) - 2g\,\Psi(k_1, k_2, -k)\} \\ &\times \sum_{\pm} \Big(\tilde{N}^0_{k_1} \pm \tilde{N}^0_{k_2}\Big)\Big(\tilde{\omega}^0_{k_1} \pm \tilde{\omega}^0_{k_2}\Big) \Big/ \Big(\omega^2 - \Big(\tilde{\omega}^0_{k_1} \pm \tilde{\omega}^0_{k_2}\Big)^2\Big)\Big],\end{aligned} \tag{3}$$

where $$\omega'^0_{k_1} = \omega^0_k + 4\sum_{k_1} C\Big(k^0_1, -k\Big)$$

and $$\omega'^0_{k_2} = \omega^0_k + 4\sum_{k_1} D\Big(k^0_1, -k\Big) + 8E^2\Big[2g^2 \sum_k B^0(k) - g\sum_k B^0(k)\Big].$$

Also

$$\begin{aligned}\Gamma_{DE}(\omega) = 48E^2\Big[&\sum_k D(k^0, 0)\,(B^0(k) - 4g\beta^0(k)) \\ &\times \sum_{k_1, k_2} \{D(k_1, k_2, -k) - 2g\,\Psi(k_1, k_2, -k)\} \sum_{\pm} \Big(\tilde{N}^0_{k_1} \pm \tilde{N}^0_{k_2}\Big)(1/(a^2 - b^2))\Big]\end{aligned}$$

$$\times \left[\frac{1}{a}\{\delta(x-a)-\delta(x+a)\}+\frac{1}{b}\{\delta(x-b)-\delta(x+b)\}\right], \tag{4}$$

where $a = \left(\omega'^{0}_{k_1}\,\omega'^{0}_{k_2}\right)^{\frac{1}{2}}$,

$x = \omega$

and $b = \left(\tilde{\omega}^{0}_{k_1} \pm \tilde{\omega}^{0}_{k_2}\right)$.

3. Conclusions

Thus $\Delta'(\omega)$ and $\Gamma'(\omega)$, shown by equations (1) and (2) respectively modifies the properties discussed in I. The combined effect of the defect and field dependences upon dielectric constant, microwave absorption and the Curie temperature (shown by equations (8), (28) and (22) respectively in I) is observed in the presence of anharmonicity. These effects cannot be explained without anharmonicity. The intrinsic parameters B and C are modified by the impurity terms in addition to the applied electric field. This modification is missing in the absence of an external electric field. The shift in the Curie temperature will now have cross-terms between the defect parameters, electric field and anharmonic parameters. In I we discussed the linear frequency dependence of tan δ. However, our expression for $\Gamma(\omega)$ (equation (7) in I) and hence for tan δ in the Debye approximation, besides containing a linear dependent term arising from force constant change scattering, also has ω^3 and ω^5 dependences when mass changes become appreciable. This result agrees with those of Bahadur and Sharma (1975) who also contend that the higher frequency dependences not observed so far in mixed polycrystalline materials may be detected in mixed single crystals of $M_xSr_{1-x}TiO_3$. Here M is of the type Ba, Fe or Gd and there is no scattering from grain boundaries, provided they lead to appreciable defect losses as compared to anharmonic losses. In general, our results give the combined effect of impurity and electric field in anharmonic ferroelectric crystal upon dielectric loss tangent. The presence of these parameters increases the tangent loss.

An investigation of the nature of the absorption should, in particular explain to what extent the observed absorption is due to " intrinsic " anharmonicity effects, which are present even in an ideal crystal and are caused by the ferroelectric effect itself, or whether the losses are due mainly to defects. If the latter is true, it should be possible to decrease losses by improving the quality of the crystal.

For a pure crystal at a constant temperature, in paraelectric phase the tangent loss (equation (28) in I) can be expressed as $\tan\delta = \tan\delta_0 + \tan\delta_F$, where $\tan\delta_0$ is the field independent tangent loss and $\tan\delta_F$ is the field-dependent loss. In this case the parameter A will vanish and the parameters B and C are modified by the electric field. The field-dependent part of tan δ is proportional to the square of the electric field and to the frequency of the microwave fields. This E^2 dependence (Rupprecht *et al* 1961) is valid for a frequency range 2·3 to 6·5 K Mc/sec and a temperature range of 90°K to 230°K. Here we also neglect the nonlinearity parameter ξ (equation (19c) in I) and the electric field dependence of T_c, to show the variation of $\tan\delta_F$ with the temperature. The variation of $\tan\delta_F$ with E will be

affected by change in T_c, due to the electric field. In a ferroelectric crystal the loss tangent increases with the applied electric field. The field's effect is noticeable near the Curie temperature and at high temperatures the E^2 effect of the field ceases and the anharmonicities are mainly responsible for the increase in loss tangent. In the vicinity of the Curie temperature the microwave loss increases anomalously. The soft mode frequency is responsible for this behaviour.

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