Dielectric Response in Microscopically Heterogeneous Dielectrics: Example of KTaO$_3$:Nb

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Abstract.

New experimental data on solid solutions of quantum paraelectrics with KTaO$_3$:Nb as an example are considered within a framework of a quantum theory of ferroelectric phase transitions. In order to describe the effect of local heterogeneities a percolation type theory together with a random field approach were employed.

I INTRODUCTION

Solid solutions of quantum paraelectrics exhibit a variety of intriguing properties, which have been attracting scientists for a long period of time [1] but, in spite of this fact, some important questions remain still under discussion. For example, it is known that the substitution of Nb for Ta in KTaO$_3$ results in the appearance of a strong temperature dielectric anomaly, which is regarded to a ferroelectric phase transition, but at the temperature of this anomaly and below manifestations of the glass-type behaviour have been often reported. We consider these effects in the framework of a random field approach combined with a percolation theory that includes zero-point quantum vibrations. New experimental data on the dielectric properties of the solid solution KTaO$_3$:Nb (KTN) with $x = 0.018$ (KTN 1.8) have been obtained and discussed in connection with this problem.

II QUANTUM EFFECTS

The quantum effect results in the following contribution to the soft mode frequency $\Omega_c$ at zero wave vector $k$ [2]
\[
\Omega_c^2 = \omega_c^2 + d(T)
\]
\[
\omega_c^2 = \omega_{c0}^2 + 3\beta P^2 + x\Xi
\]
\[
d(T) = \frac{g_0 V_c}{8\pi^2} \int_{BZ} d^3k \frac{1}{\omega_k} \left( \coth \frac{\hbar \omega_k}{2k_B T} - 1 \right)
\]  
\[
\frac{T_c^2}{T^2} - T^2
\]

where \(\omega_{c0}\) is the bare frequency at zero temperature and zero wave vector, \(P\) is polarization, \(\Xi\) is constant, \(x\) is the impurity concentration, \(\omega_k^2 = \omega_c^2 + c k^2 + \ldots\), \(g_0\) is a constant responsible for anharmonic interactions, \(V_c\) is the unit cell volume, and \(k_B\) is the Boltzmann constant. Just below the phase transition, one can neglect \(\omega_k^2\) in \(\omega_c^2\), due to a large spatial dispersion of the soft mode in KTaO\(_3\), and, in this case, the integral in (1) is proportional to \(T^2\). Thus the temperature dependence of \(\omega_c^2\) at \(T_c\) is: \(\omega_c^2 \sim T^2 - T_c^2\), and at \(T \ll \hbar \omega_c\) \(d(T) \sim T^{3/2} \exp \left(-\frac{\hbar \omega_c^2}{k_B T}\right)\). It is seen that the Currie-Weiss law is violated not only in a small vicinity above \(T_c\) as stressed in earlier studies [3] but also below \(T_c\).

Quantum effects can be observed in KTN 1.8 if one suppresses the contribution connected with heterogeneities by applying a field cooling procedure (see Fig 1). In this case a quadratic temperature decrease of \(\varepsilon(T)\) is obtained. Polarization in quantum ferroelectrics just below \(T_c\) should behave as \(P \sim \sqrt{T_c^2 - T^2}\) but at lower temperatures polarization should saturate due to the zero-point quantum vibrations [4]. Thus the zero-point quantum vibrations result in the saturation of the host-lattice polarization and dielectric permittivity in ferroelectrics at low temperatures.
III  LOCALLY HETEROGENEOUS SOLID SOLUTIONS

A  Percolation approach

The above analysis holds only for homogeneous ferroelectrics. In our opinion, KTN 1.8 is not microscopically uniform due to disorder in the impurity ion distribution over the corresponding crystallographic positions [5,6]. Indeed, since the impurity concentration is very small, the average distance among the impurities is rather large (e.g. in KTN 1.8 it is about 15.3 Å that is about 4 lattice parameters). In this case the fluctuations of the average distance can be rather large also that leads to percolative clustering of impurity ions and finally influences the phase diagram of the corresponding solid solutions [2,7,8]. Below we will discuss this behavior in terms of the theory of percolation.

The impurity ions being close each other are correlated at distances lower than

\[ R_{\text{cut-off}} \sim \left( V_0 + k_B T \right)^{-1/3} \]

where \( V_0 \) is proportional to the sum of the energies of the dipole-dipole and elastic impurity–impurity interactions. At small impurity concentrations, which we consider in the present study, the impurity clusters can appear only at low temperatures where the cut-off radius is comparatively large. It explains the experiment performed with KTN under high pressure [9]. When the pressure is normal the phase transition occurs at large temperatures, at which the Nb clusters do not appear, and, as a result, a frequency dispersion of the dielectric permittivity is absent. When pressure is applied the soft mode frequency increases and the phase transition temperature is reduced to the region where the Nb clusters can already appear; as a result, there appears a frequency dispersion of the permittivity.

The average cluster size \( <s> \) for interacting spheres with fixed radii is usually given by a critical dependence [10]. We consider the case when the interaction radius is temperature dependent. In order to take this fact into account we introduce the following dependence:

\[ <s> \sim \frac{1}{\left( (R_{\text{cut-off}}/a)^3 x - c \right)^\gamma} \]  

where \( \gamma \) is a critical exponent; \( c \) is constant and can be calculated on the basis of the percolation theory for different lattices [10] (it equals 0.35 in the continual percolation approach); the critical concentration can be found from:

\[ x_c = \left( a/R_{\text{cut-off}} \right)^3 c. \]

It is seen that the critical concentration can be very small if the cut-off radius is large enough. This finding corresponds to experimental data for dilute solid solutions of quantum paraelectrics according to which cluster phenomena appear in them already at a very small impurity concentrations [7,2] that is a consequence of a large cut-off radius. Note that the cut-off radius can increase not only due to a straight dipole-dipole and quadrupole-quadrupole interactions but also because of...
an indirect interaction over the soft mode. The latter interaction can even diverge if the soft mode frequency approaches zero but we do not consider this case here (see [7]).

It follows from (3) that when the cut-off radius increases this can be considered as an increase of the unit volume (at constant cut-off radius) and the effective concentration also increases: \( x_{\text{eff}} = (R_{\text{cut-off}}/a)^3 x \). For us it is easier to consider the percolation for spheres with the same (temperature independent) radius but with the concentration of the spheres effectively dependent on temperature instead of considering a fixed impurity concentration but varying the sphere radius. In this case a temperature decrease results in an increase of the effective impurity concentration and due to this a percolation phase transition can happen at some temperature.

After the substitution of the temperature dependent cut-off radius value to (2) one can see that at the phase transition point the average cluster size behaves as \( |T - T_{\text{cp}}|^{-\gamma} \) (where \( T_{\text{cp}} \sim x^{1/3} - \text{const} \) and \( T > T_{\text{cp}} \)). The most interesting result is that the critical exponent \( \gamma \) known in the theory of percolation as the exponent for the critical concentration dependence coincides with the critical exponent for the critical temperature dependence. This exponent should be close to \( \gamma = 1.8 \) as obtained in the theory of percolation that can be a key to decide if the percolation approach is suitable or not to describe concrete experimental data.

In reality expression (2) is invalid for finite-size heterogeneities. Unfortunately there is no analytical description of such a situation although computations showed that the singularity is diffused in this case [10]. In the vicinity of the singularity one can try using the expression:

\[
\langle s \rangle \sim \frac{1}{| (R_{\text{cut-off}}/a)^3 x - c |^{-\gamma} + b^2 }
\]

This expression differs from (2) only in a vicinity of the percolation threshold where the critical dependence is replaced by a diffused anomaly.

### B Heterogeneity size

Similar to (4) the dielectric permittivity has rather a rounding peak instead of a keen anomaly. It can be explained by reaching the correlation radius the heterogeneity size. The correlation radius, \( r_c \), is the characteristic size of the polarization fluctuation in the lattice. In uniform ferroelectrics, when lowering temperature approaching \( T_c \), this radius increases as \( r_c \sim \sqrt{\varepsilon} \). We consider locally nonuniform ferroelectrics in the regime where the main contribution to the dielectric permittivity stems from local heterogeneities (for example in KTN these are regions enriched with Nb) and where these heterogeneities can be considered, at first glance, as independent. In this case the correlation radius is not able to exceed the heterogeneity size, which can be defined as the maximal size of the polar regions. It implies that the correlation radius will saturate at lower temperatures. Such a reason for this
saturation differs from the zero-point quantum vibrations: it is connected with a finite heterogeneity size.

There are different possibilities to interpolate the temperature dependence of the correlation radius described above from the Curie-Weiss dependence at high temperatures to the constant behavior at low temperatures. Earlier we used the Barrett formula for this purpose [2,11].

It is important to notice that the considered saturation of the correlation radius is a general property of locally heterogeneous ferroelectrics: for example, we believe that it holds in relaxors like PMN. Indeed, at temperatures above the Burns temperature a Curie-Weiss behavior was evidenced but below the Burns temperature and above the $T_m$ dielectric permittivity maximum temperature rather a quadratic temperature dependence was observed. We have found the following form of the dielectric permittivity suitable in the whole temperature region [12]

$$\frac{1}{\chi} = A(T - T_0)^2/T + f$$

where $f$ is constant. At temperatures close to $T_0$ this expression gives a quadratic temperature dependence, which has zero derivative at $T = T_0$. At high temperatures this expression gives the Curie-Weiss behavior. It is interesting to notice that the same expression can be considered as a sum of a linear temperature term, $A(T - 2T_0)$, and an inverse temperature term, $(AT_0^2 + f)/T$.

Hence there is a temperature interval where the correlation radius reaches the heterogeneity size and saturates thereafter (at lower temperatures). In this interval there is a deviation from the Curie-Weiss law due to the saturation of the correlation radius. Additional (hydrodynamic) fluctuations appear at these temperatures, which we consider in the next subsection.

### C Orientable Polar Regions

The main difference of the dielectric response in a nonuniform dielectric media relative the uniform one, besides the appearance of precursors described above in subsection A, is the existence of added polarizability due to the polar microregions. This new feature of the nonuniform media manifests itself by a very peculiar temperature dependence of the dielectric permittivity below $T_c$. In Fig. 2 we plot the temperature dependence of the inverse dielectric permittivity of KTN 1.8 obtained on heating. It is seen that the low-temperature behavior is given by a straight line, the inclination of which is noticeably lower than one for the high-temperature branch but according to the theory of ferroelectrics [13], below $T_c$, it should be two times larger than above $T_c$. This contradiction can be explained if one takes into account the saturation of the correlation radius at $T_c$ and a contribution of the polar microregions to the dielectric permittivity below $T_c$. The latter contribution can originate from ordering of the polar region dipole moments in external field and due to the interactions among the polar regions.
Indeed, consider random fields $\mathbf{e}$ (see for definitions and experimental studies of the random fields Refs. [14,15]) and merged to their directions local dipole moments $\mu$. In the field $\mathbf{E} = \mathbf{E}_0 + \eta\mathbf{P}$, where $\mathbf{E}_0$ is the external field and $\mathbf{P}$ being the polarization, the dipole moments are directed along $\mathbf{E} + \mathbf{e}$. It results in the following polarization

$$P = n\mu g(E) = \frac{n\mu}{2} \int_0^\pi \sin \vartheta d\vartheta \left[ \frac{E + e \cos \theta}{\sqrt{E^2 + e^2 + 2Ee \cos \theta}} - \cos \theta \right] =$$

$$= \begin{cases} n\mu(1 - e^2/3E^2) & E > e \\ 2n\mu E/3e & E < e \end{cases}$$

(6)

where $e = |\mathbf{e}|$. It follows from this result that the susceptibility of noninteracting polar regions can be found from the expression (see Fig. 3):

$$\chi_0 = 1 \frac{dP}{\varepsilon_0 dE} \bigg|_{E=0} = \begin{cases} 2n\mu/3\varepsilon_0 & E < e \\ 2n\mu e^2/3\varepsilon_0 E^3 & E > e \end{cases}$$

(7)

where $n$ is the dipole (heterogeneity) concentration. The temperature dependence of the dipole moment can be found from the expression: $\mu = \mu_0 \tanh[(\mu_0 e)/k_B T]$ where $\mu_0$ is the dipole moment magnitude. This derivation explains the existence of the large contribution to the dielectric permittivity of KTN 1.8 below $T_c$ due to the Nb related heterogeneities.

In the presence of macroscopic polarization the linear susceptibility depends on the $P_0$ value, which can be found from: $P_0 = \mu g(P_0)$ and it appears at the condition
2nµη/3ε = 1, which provides $T_{c2} \sim \mu_0^2 n\eta/k_B$. At large $E + \eta P_0$ the contribution of the polar region dipole moments to the dielectric permittivity rapidly decreases, as $(E + \eta P_0)^{-\frac{3}{2}}$. This explains the absence of this contribution in our experimental data when the sample was field cooled.

Obviously the macroscopic polarization obtained on field cooling is larger than one got on zero field cooling. Hence the appearance of macroscopic polarization suppresses the additional contribution connected with the polar microregions. It implies that the new phenomenon seen in the dielectric data of KTN 1.8 at low temperatures can be explained by a very low value of macroscopic polarization appeared on zero field cooling below $T_c$ because of clustering the Nb impurities but without the appearance of the connected cluster on the one hand and because of quantum effects leading to suppression of the polarization growth at low temperatures on the other hand. This peculiar situation results in a random distribution of the local polarization over the polar microregions merged to local random field directions and, as a consequence, in an additional contribution to the dielectric permittivity connected with the ordering of the polar region dipole moments.

Our experimental data show a hysteresis phenomenon at low temperatures, which can be explained within a Landau-type theory if one assumes the existence of strong electrostriction interaction in KTN 1.8 in agreement with experimental finding [16]. The final Hamiltonian can be written in the form

$$H = \left( \frac{2\mu_0 n}{3\epsilon} \coth \frac{\mu_0 e}{k_B T} - \eta \right) \delta P^2 + \frac{1}{4} \tilde{\beta} P^4 + \frac{1}{6} \xi P^6 + v (\nabla P)^2 - EP$$

where $\tilde{\beta} = \beta - 4\lambda/\kappa$, $\lambda$ is the electrostriction constant and $\kappa$ being the elastic
constant. A large value of the electrostriction constant leads to negative values of the nonlinearity constant \( \tilde{\beta} \) and, consequently, to the phase transition of the first order.

To take into account the scattering of the random field magnitude we used the following distribution function for a reorientable part of the random fields [15]

\[
 f(e) = \frac{1}{(\sqrt{\pi a})^3} e^{-|e-\eta P|^2/a^2}
\]  

(9)

By integrating (7) with this distribution function we obtained at \( E < e \)

\[
 \chi_0 = \frac{4n\mu}{3\varepsilon_0 P} erf(\eta P/a) \approx \frac{4n\mu}{3\sqrt{\pi\varepsilon_0 a}} \left[ 1 - \frac{\eta^2 P^2}{3a^3} + ... \right]
\]  

(10)

It is seen that the bare susceptibility (7) decreases with the width of the distribution function (9) and with polarization \( P \).

The phase transition in the system consisting of polar regions can be whether of the glass-type or ferroelectric. In order to decide, which type of the phase transition will occur one can employ the percolation technique again but on the next, nanoscale level (see also a consideration in the framework of a Random-Field-Random-Bond model in [17]). One can introduce a cut-off interaction radius for interactions among the polar regions and obtain that if the polar region concentration exceeds a critical concentration then a connected cluster appears and the steady state is ferroelectric but in the reverse case only finite clusters made of polar regions exist and the steady state is of the glass nature.

Our experimental data show a strong frequency dependence of the dielectric permittivity at \( T_c \). We regard this finding to potential barriers separating different positions of the random fields. For example for Li impurities a six-well model can be suitable to describe this situation [18]. This model considers dipoles embedded into elongated random fields having six possible directions, which provides a description of a phase transition when temperature or field are changed. In the electric field this model gives a critical point. One can consider the random fields coupled to the soft vibrations and these random fields can be polarized by external field according to the distribution function (9). The existence of the potential barriers for the local random fields results in the following frequency dependence of the dielectric permittivity [2,11]:

\[
 \varepsilon' \sim \frac{1}{\omega_c^2(T) - \lambda^2 n F(\omega)}
\]  

(11)

where \( F(\omega) = \left[ 4k_B T \left( 1 - i(\omega \tau)^{1-\alpha} \right) \right]^{-1} \). We introduced here the Cole-Cole type frequency dependence bearing in mind a relaxation time distribution. Here \( \lambda \) is a coupling constant. Expression (11) at large temperature above \( T_c \) shows the Curie-Weiss behavior but at low temperatures there is frequency dependent contribution,
IV CONCLUSIONS

We showed that the striking dielectric properties of KTN 1.8 can be understood and described on the basis of assumption that in highly polarizable quantum para-electrics even a small concentration of dipolar impurity centres can form nano-scale polar regions (clusters). The main addition to the dielectric permittivity at high temperatures originates from these local heterogeneities. At high temperatures, when the correlation radius is larger than the heterogeneity radius, the heterogeneities provide a Curie-Weiss law and an average over the bulk Curie temperature governs the temperature dependence of the total dielectric permittivity. When approaching the Curie temperature the correlation radius increases but it saturates when reaching the heterogeneity size. Together with quantum effects this leads to the appearance of an intermediate state, in which the dielectric permittivity is saturated. The orientation of the cluster dipole moments as well as local random fields in an external field results in the appearance of an additional contribution to
the dielectric permittivity in the low temperature ferroelectric phase as it has been observed for KTN 1.8.

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