Experimental and theoretical study of the influence of disorder on diffuse first-order phase transitions: NaNbO$_3$: Gd and KTaO$_3$: Li as examples

M.S. Prosandeeva

Institute of Theoretical and Experimental Biophysics, Puschino, Russia

S.I. Rayevskaya, S.A. Prosandeev, I.P. Raevski

Rostov State University, Rostov on Don, Russia

S.E. Kapphan

University of Osnabrueck, Osnabrueck, Germany

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Abstract

We consider consequences of local disorder in systems experiencing first order phase transitions. Such systems can be of rather different nature. For example, manganates showing gigantic magnetoelectric effect, doped antiferroelectrics or biomembranes. Monte-Carlo computations performed have shown that the disorder increases the temperature interval where the high- and low-temperature phases coexist and this provides thermodynamics in the disordered systems distinct from the thermodynamics of classical homogeneous systems.
I. INTRODUCTION

The effect of disorder on macroscopic properties of crystals is a topic of great interest because of fundamental problems, and due to numerous new physical phenomena evidenced in complex not fully ordered materials. For instance, PbMg$_{1/3}$Nb$_{2/3}$O$_3$-PbTiO$_3$ solid solutions show remarkable piezoelectric properties [1], which allow transforming the mechanical energy to electrical and back that is used in a wide spectrum of applications, from automobile industry to device implantations in human bodies. Other examples are perovskite-type manganates presenting giant magnetoresistant effect. The phase transition between the dielectric and metal phases is diffuse and contains some features (heat capacity) of first order phase transitions and some (strong fluctuations) of second order (see detailed discussion of this problem in Ref. [2]). We add to this list also a biological example, a lipid system in living cells. The main phase transition between the solid and gel states of the lipids is diffuse and the fluctuations are strong that reminds one of the case of manganates [3,4].

Recently, one more example was found in a solid solution of antiferroelectrics, NaNbO$_3$:Gd [5-7]. There are at least six first order phase transitions in pure NaNbO$_3$ but the main permittivity maximum corresponds to an antiferroelectric-to-antiferroelectric transition between two orthorhombic phases, P and R (Fig. 1). This peak in the dielectric permittivity is due to the coupling between the AFE and FE order parameters [5]. The thermal hysteresis appears at the P-R phase transition as straight vertical lines on the permittivity versus temperature dependence corresponding to abrupt change of the order parameter. Such a picture is classic. Doping NaNbO$_3$ with Gd results in changing the thermal hysteresis shape: the vertical lines on the permittivity versus temperature dependence become inclined and there appear tails at the bottom and top of these straight inclined lines (Fig. 1). It seems that the inclination of these lines can be a good measure of the degree of disorder. It is remarkable that there is a threshold Gd concentration at which the thermal hysteresis disappears abruptly and the dielectric permittivity maximum resembles one in relaxors [7] (Fig. 1c). In order to show that the phases coexist at the diffuse phase transition, a special experiment has been performed [6]. Dielectric permittivity was recorded in the cooling run until some temperature $T_t$ and, then the permittivity was measured in the heating rate. This experiment has shown that the thermal hysteresis loop area depends on $T_t$ that is consistent with the idea of phase coexistence. If the phase transition were sharp then one would expect the
form of the temperature hysteresis loop unchanged in the sense that the experimental points would follow the same path independently of $T_i$. This experiment resembles well-known results for the field hysteresis of magnetization in locally disordered magnetic systems studied by Preisah [16]. He assumed that there was a distribution function of local fields, and, due to this, the measured field hysteresis loops of permittivity were inclined and the slope of this inclination depended on the distribution function shape. We want to apply a similar idea in order to describe the temperature hysteresis loops in locally disordered systems like NaNbO$_3$:Gd.

The present study contains new experimental data on the systems experiencing a diffuse first order phase transition and we will provide a description of this diffuseness in the framework of the Monte Carlo computation and a mean field theory. We will consider two cases, NaNbO$_3$:Gd with the diffuse antiferroelectric - antiferroelectric phase transition and KTaO$_3$:Li with a diffuse first order paraelectric - ferroelectric phase transition. KTaO$_3$ is a quantum paraelectric. This means that the phase transition in it is suppressed by zero-point quantum atomic vibrations [8]. The substitution of K by Li results in a ferroelectric phase transition but, due to the Li impurity disorder, this phase transition is diffuse.

The understanding of the phenomena discussed above requires developing a model, which takes into account the degree of disorder and it should also describe the classic first order phase transition in the absence of the disorder. Semenovskaya and Khachaturyan [9] considered a two-dimensional dipole system containing defects influencing a phase transition between the paraelectric and ferroelectric phases. They found out that the defects help the system avoiding the hysteretic phenomena by finding passes over metastable states in a random network, which have only comparatively small potential barriers between each other. Further studies of Wang et al within the same approach [10] showed that dielectric permittivity diffuse in such a system, and there appears a number of relaxators, which produce a frequency dependence of dielectric permittivity. Qian and Bursill [11] considered the smoothening of the phase transition in PbMg$_{1/3}$Nb$_{2/3}$O$_3$ as a result of random fields on the Pb sites produced by Mg and Nb.

Khomskii and Khomskii [12] performed Monte-Carlo computations in which a correlated occupation was assumed (the probability for a defect to join a cluster depended on the local environment of this defect). They obtained that, under such a restriction, large clusters appear instead of a mist of small ones. In the author’s opinion, the distribution of
the percolation clusters by the size and shape may influence the macroscopic properties of manganates.

Smolenski et al [13] considered effects of disorder in ferroelectrics. They introduced a space distribution function of Curie temperatures, which allowed the authors to describe the main feature of the temperature dependence of dielectric permittivity in relaxors, the rounded dielectric permittivity peak. The starting point in their theory was a second order phase transition. A theory of a first order phase transition close to the second one [2] was also considered but without the disorder.

Doniah has proposed a useful mathematical approach to the problem of the description of the main phase transition in a lipid system [14]. He considered lipids as two-state (Ising) subsystems embedded into an effective field, which appears due to entropy contributions inside these subsystems. As a result, the effective Hamiltonian includes the field, which depends on temperature. This effective Hamiltonian allows describing the interacting lipids as a set of Ising subsystems in a temperature dependent field. The effective interaction was meant to be due to interchain interactions. Suger et al [3] and Heimburg [4] considered surface tension as the source of the interaction among the two-state subsystems. The disorder effects have not been addressed.

The disorder effect in NaNbO$_3$:Gd and KLT appears due to the randomness of the impurity distribution in the lattice, and the randomness of the local fields and strains [7]. In the case if one introduces a dependence of the soft-mode vibration frequency on the space coordinate then the soft-mode frequency at different coordinates can vanish at different temperatures. This fact provides an opportunity to introduce a distribution function of local Curie temperatures (the meaning of this term will be clarified below) that has been done by Smolenski et al. for relaxors [13] and we will extend this idea for the general case of diffuse first order phase transitions. The use of the Curie temperature distribution function allows one to substitute the complex problems of the real space averaging of macroscopic quantities in locally disordered media by configuration averaging. In the present study, we will explore this idea performing Monte-Carlo computations and deriving a mean field theory. Our goal is developing a simple model describing the main, most important features, of the diffuse first order phase transitions arising due to local disorder.
II. EXPERIMENTAL

Full details of the preparation of the NaNbO$_3$:Gd crystals and their characterization have been described elsewhere [5,15]. Fig. 1 shows the tendency in the dependence of the temperature hysteresis on the Gd concentration. In a first-order phase transition, the AFE order parameter experiences a jump and, as a result, the dielectric function exhibits a step seen in Fig. 1a. The diffusion of this step seen in Fig. 1b can be considered as a result of the distribution of the Curie temperatures (similar to the distribution of local fields in the Preisach model):

\[ f(T_c) = \frac{2}{\sqrt{\pi}} e^{-(T_c-T_{c0})^2/\Gamma^2} \]  

where $T_0$ is an average (macroscopic) Curie temperature, $T_c$ the local Curie temperature, and $\Gamma$ the distribution function width. The convolution of this function with the step function yields:

\[ \varepsilon'(T) = \varepsilon_0(T) + b(T) \int f(T_c) \theta(T-T_c) dT_c = \varepsilon_0 + \text{erf}\left[(T-T_{c0})/\Gamma\right] \]  

where $\varepsilon_0(T)$ and $B(T)$ are monotonic functions of temperature, which, in the first approximation (not far from the Curie temperature), can be given by linear functions; $\theta(x) = 0$ at $x < 0$ and 1 at $x > 0$; $\text{erf}(x)$ is the error function.

Fig 2 shows the fit of expression (2) to the experimentally observed $\varepsilon'(T)$ in NaNbO$_3$:Gd for $x=0.09$. The dashed lines present the dependence that one would expect if the phase transition were not diffuse. The fit (solid lines in Fig. 2) shows that the width of the distribution function for $x=0.09$ is about 27 K on heating and 35 K on cooling, which is nearly comparable with the hysteresis width, 44 K. We found that the distribution function width decreases with decreasing Gd concentration. For pure NaNbO$_3$, the width of the distribution function is negligible. Notice that the distribution function width can be easily found from the slope of the thermal hysteresis lines: $\text{ctg}\alpha = \Gamma / (T - T_{c0})$.

We have measured also the temporal dependence of the temperature hysteresis and found that the hysteresis width and slopes depend on the time but the tendencies obtained remain valid even after rather large measuring time. This point will be a subject of a separate publication.
Our second experiment is for $K_{1-x}Li_xTiO_3$ (KLT) single crystals. The samples and setup have been characterized in [17]. The integral Second Harmonic Generation (SHG) intensities were obtained for different KLT single crystals with $x=0.022, 0.036, 0.043$ and $0.063$ in the melt (Fig. 3). The present study treats the data obtained with the help of the expression, which is similar to expression (2):

$$S(T) = S_0(T) + B(T)erf\left(\frac{T - T_{c0}}{\Gamma}\right)$$

where $S_0$ and $\Gamma$ are monotonic (in our case, linear) functions of temperature. The fit of this expression is shown in Fig. 3. One can see that, in all the studied cases, there is a temperature interval, at which two phases (high-temperature and low-temperature) coexist. The distribution function width is especially large on cooling at $x = 0.063$, and it is much smaller on heating at the same $x$.

III. THE MODEL

1. Monte-Carlo computations

We consider a two-state system in a temperature dependent field as it was introduced by Suger et al [3] and Heimburg [4]:

$$H = \sum_i \Delta_i s_i^z - \gamma \sum_{ij} \left| s_i^z - s_j^z \right|$$

where $\Delta_i = (T - T_{0i})$, $T_{0i}$ is a local Curie temperature at which the first-order phase transition would happen if the Ising two-state subsystems were not interacting, $s^z$ is a $z$-component of the spin operator corresponding to the $i$-th site. The difference of our approach from that used by Suger et al [3] and Heimburg [4] is the distribution of $T_c$ with a given Gauss type function $f(T_{0i})$.

The first term in (4) describes the chemical potential of a subsystem at the $i$-th site in the Ising network. The second term is the energy arising due to the boundary between the old and new phases.

The computation within the Metropolis scheme has been done for a two-dimensional triangular lattice, 500x500. The results are shown in figure 4. One can see that smoothening the phase transition results in a larger inclination of the dependence of the order parameter...
on temperature. The inclination of the order parameter dependence on temperature implies that there is a temperature interval, in which the high- and low-temperature phases coexist. This interval can be estimated as $\Gamma$. Figure 5 shows snapshots obtained for $\Delta = 0.1k_B T$, $\gamma = 0.4k_B T$, $\Gamma = 0.1k_B T$ (a), and $\Gamma = 0$ (b). One can see that the cluster’s size obtained with the Gauss smoothing is larger than that without it. In order to find an analytical criteria, in the next section, we consider a mean field approximation of the model considered.

2. A mean field approximation

It is assumed in the mean field approximation that each molecule is in an average field, which substitutes the complex two-particle interactions. The local field can be obtained as a derivative of the energy of the system with respect to the site occupation number, $n_i$, which takes one of the two possible values, 0 and 1 (for the high-temperature and low-temperature states, correspondingly). The total energy of the system as a function of the occupation numbers can be written in the form

$$H = \delta \sum n_i + \gamma \sum (n_i + n_j - 2n_i n_j) \tag{5}$$

The interaction term here is written in the form suggested by Doniah [11]. This term gives the same values as $|n_i - n_j|$ in expression (4) at the values 0 and 1 for the occupation numbers, $n_i$ and $n_j$. The average local field can be found now by differentiating:

$$h = -\left(\frac{dH}{dn_i}\right) = -\Delta - \gamma \sum (1 - 2n_j) = -\Delta - 2\gamma z \left(\frac{1}{2} - n\right) \tag{6}$$

where $z$ is the coordination number, the number of the nearest neighbors, $n$ is the average occupation number (the order parameter):

$$n = \frac{1}{1 + e^{-h/k_B T}} \tag{7}$$

As the average field depends on $n$ [see expression (6)], equation (7) provides a possibility to find $n$ as a function of temperature. Solutions of this equation are shown in Fig. 6. At $\gamma > 2k_B T/z$, $n(T)$ does not exhibit a jump and continuous changing the order parameter takes place. Above this critical point, there appears an abrupt change of the order parameter and the phase transition becomes first-order.
In order to study the solutions obtained, we computed the free energy

\[ F = -k_B T \ln Z + \langle H - H_0 \rangle \]  

(8)

where \( H_0 = -hn \), and \( Z \) is the partition function:

\[ Z = 1 + e^{h/k_B T} \]  

(9)

\[ \langle H - H_0 \rangle = \gamma zn^2 \]  

(10)

Fig. 7 shows the dependence of the averaged free energy on \( n \) at different values of the model parameters. One can see that disordering results in the vanishing of the double-well behavior of the free energy. In other words, disordering removes the average barrier between the ground and metastable states. This is in very good agreement with results of Semenovskaya and Khachaturyan [9] who showed that disordering stabilizes connected chains of metastable states having comparatively small barriers between each other. Disorder also decreases the slope of the \( n(T) \) dependence that is in excellent agreement with experiments shown in Fig. 1 and with the results of the Monte-Carlo computations presented in the previous section.

IV. SUMMARY

The present study has shown that the two-state model supplemented with a temperature dependent field gives reasonable explanation of the diffusion of first order phase transitions. The general trend is that disordering smoothes the abrupt temperature dependence of the order parameter and this dependence becomes inclined instead of vertical lines. The model gives a satisfactory fit to the experimental data discussed.

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CAPTIONS

Fig. 1. Temperature dependence of the $\varepsilon'$ for single crystal NNG with $x = 0$ (1), $x = 0.09$ (2), $x = 0.10$ (3) and $x = 0.12$ (4) measured at 100 kHz. Filled symbols correspond to heating, empty symbols to cooling.

Fig. 2. The temperature hysteresis loop for NaNbO$_3$:Gd at $x=0.09$. The symbols are experimental points, the solid line the result of the fit. The dashed lines are guides to the eye.

Fig. 3. Temperature dependence of SHG intensity for K$_{1-x}$Li$_x$TiO$_3$ single crystals with different Li content. Symbols correspond to the experimental data and solid lines show the best fits of expression (3).

Fig. 4. The dependence of the order parameter, $n$, on $\Delta/k_BT_{c0}$ obtained in the Monte Carlo computation: 1. $\gamma/k_BT_{c0} = 0.5$, $\Gamma/k_BT_{c0} = 0$, 2. $\gamma/k_BT_{c0} = 0.4$, $\Gamma/k_BT_{c0} = 0$, 3. $\gamma/k_BT_{c0} = 0.5$, $\Gamma/k_BT_{c0} = 1$, 4. $\gamma/k_BT_{c0} = 0.4$, $\Gamma/k_BT_{c0} = 1$.

Fig. 5. The snapshots obtained in the Monte Carlo computation with $\Gamma = 0.1k_BT$ (a) and $\Gamma = 0$ (b).

Fig. 6. The dependence of the order parameter on the reduced temperature in the mean field model.

Fig. 7. The dependence of the average free energy on the order parameter at $\gamma z/k_BT = 2.4$, $\Gamma/k_BT = 0.1$ (1), $\Gamma/k_BT = 1.0$ (2), and $\Gamma/k_BT = 1.5$ (3).