Proportion of frozen local polarization in relaxor ferroelectrics

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Abstract

A Landau-type phenomenological cluster theory was presented to model the freezing process of local polarization in relaxors. Based on the theory, the proportion of frozen polarization in Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ (PMNT) was calculated from the experiment of dielectric nonlinearity. The local polarization was shown to freeze continuously in a cooling process. The amount of frozen polarization increases with increasing the measuring frequency.

PACS: 77.22.Ej, 77.80.-e, 77.22.Ch, 77.84.Lf

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Typeset using REVTEX
Relaxor ferroelectrics (relaxors) have been showing great importance both for the fundamental solid state science and the applications to advanced technology. Relaxors experience no macroscopic phase transition at zero electric field until very low temperatures. However, local polarization exists at much higher temperatures, which is widely believed to be responsible for the special characteristics of relaxors. The concept of “polar micro region” in relaxors was firstly presented by Smolenskii in the chemical inhomogeneity theory. The presence of polar microregions was later confirmed by the experiments on the non-linear variation of the optical refractive index, the thermal strain, and the thermal expansion coefficient. The deviation from the paraelectric Curie-Weiss behavior of the dielectric permittivity also suggested the presence of polar regions. Cross presented in a superparaelectric model that the polar microregions (represented by independent dipoles) are able to switch between the equivalent orientation states and gave an appropriate picture of the nature of the micro polarization at high temperatures. When the temperature decreases, the coupling between the polar microregions controls the kinetics of the fluctuations and the system is frozen into a polar-glassy state. Gui et al. used the Monte Carlo method to simulate the freezing process in relaxors and showed that some dipoles are slowed or frozen due to the interactions. A special phase transition of ergodic space shrinking in succession was also proposed according to the freezing process. Kleemann et al., however, proposed that the polarization is frozen due to the quenched random electric fields.

Some works have been done to quantitatively analyze the freezing process of local polarization. Qian and Bursill developed a phenomenological theory to describe the interaction of polar domains and to simulate the dielectric relaxation and phase transition of relaxors. Nambu and Sugimoto proposed a Landau type mean field theory by considering a gradual condensation of local polarization and confirm a picture of diffuse phase transition in relaxors. In this paper, we propose a Landau-type phenomenological cluster theory of relaxors and calculate the proportion of frozen polarization from the experiments of dielectric nonlinearity.

A phenomenological free energy is defined as
\[ F = 2^{-1}N\alpha(T)P^2 + 4^{-1}N\alpha_1P^4 + 2^{-1}\gamma P^2 \sum_i n_i P^2_i + 2^{-1} \sum_i n_i \alpha_i(T) P^2_i + 4^{-1}\alpha'_{11} \sum_i n_i P^4_i, \]

where \( P \) is the uniform polarization and \( P_i \) is the \( i \)-th frozen local polarization. \( N \) is the total number of lattice sites, and \( n_i \) is the lattice-site number of the \( i \)-th local polarization. \( \alpha \) and \( \alpha_i \) are written as

\[ \alpha(T) = (T - T_0)/\varepsilon_0 C, \]  

\[ \alpha_i(T) = (T - T_i)/\varepsilon_0 C_i, \]

and \( \alpha_{11} \) and \( \alpha'_{11} \) are constants as the conventional Landau theory. The couplings between the global polarization and the local ones are written as \( \gamma P^2P^2_i \) from the symmetry consideration.

The equilibrium values of the frozen polarization \( \{P_i\} \) are determined by minimizing the free energy \( F \) in Eq. (1). Minimizing \( F \) with respect to \( \{P_i\} \) gives

\[ \frac{\partial F}{\partial P_i} = 0, \]  

i.e.,

\[ \gamma P^2 n_i P_i + n_i \alpha_i(T) P_i + \alpha'_{11} n_i P^3_i = 0. \]

Thus \( P_i \) is solved from Eq. (5) as

\[ P^2_i = -\alpha_i(T)/\alpha'_{11} - \gamma P^2/\alpha'_{11}. \]  

Define \( P_{i0} \) as

\[ P^2_{i0} = -\alpha_i(T)/\alpha'_{11} = (T_i - T)/\varepsilon_0 C_i \alpha'_{11}, \]  

and then \( P_i \) can be rewritten as

\[ P^2_i = P^2_{i0} - \gamma P^2/\alpha'_{11}. \]  

When relaxors stays in a unpolar state (\( P=0 \)), the frozen polarization \( P_i \) is equal to \( P_{i0} \). Substituting Eqs (7) and (8) into Eq. (1) yields the free energy
\[ \overline{F} = 2^{-1}NP^2 \left[ \alpha(T) + \gamma \frac{1}{N} \sum_i n_i P_{i0}^2 \right] + 4^{-1}NP^4 \left[ \alpha_{11} - \frac{\gamma^2}{\alpha'_{11}} \cdot \frac{1}{N} \sum_i n_i \right] + \text{const.} \quad (9) \]

Introduce

\[ q(T) = \frac{1}{N} \sum_i n_i P_{i0}^2 \quad (10) \]

and

\[ n(T) = \frac{1}{N} \sum_i n_i, \quad (11) \]

and then Eq. (9) can be expressed as

\[ \overline{F} = 2^{-1}Na(T)P^2 + 4^{-1}Nb(T)P^4 + \text{const}, \quad (12) \]

where

\[ a(T) = \alpha(T) + \gamma q(T), \quad (13) \]

\[ b(T) = \alpha_{11} - \frac{\gamma^2}{\alpha'_{11}} n(T). \quad (14) \]

For relaxors, the sum of local polarizations is equal to zero, while the sum of the square of local polarizations is not zero that can be measured in the nonlinear behaviors of optical refractive index and the thermal strain, etc.\[1\]–\[5\] So \( q(T) \) is the order parameter to represent the appearance of local polarizations. \( n(T) \) is the proportion of the lattice site of frozen polarization. It should be noted that Eq. (7) is valid only for \( T < T'_i \) (for \( T > T'_i, \, P_{i0} = 0 \), i.e., the \( i \)-th local polarization is not frozen), so the summarization in Eqs. (9-11) can be conducted only on the nonzero local polarization \( (P_{i0}^2 > 0) \), and \( n(T) \) and \( q(T) \) vary with temperatures.

The dielectric susceptibility is easily calculated from the thermodynamic relation between the dielectric field,

\[ E = \frac{1}{N} \cdot \frac{\partial \overline{F}}{\partial P} = a(T)P + b(T)P^3, \quad (15) \]

and the uniform polarization \( P \), i.e.,
$$\frac{1}{\varepsilon(T)} = \frac{\varepsilon_0 E}{P} \bigg|_{E=0} = \varepsilon_0 a(T) = \frac{T - T_0}{C} + \varepsilon_0 \gamma q(T). \quad (16)$$

It can be seen that the dielectric susceptibility deviates from the Curie-Weiss behavior due to the existence of the local order parameter $q(T)$. Schmitt and Kirsch gave the similar relation of Eq. (16) by simple phenomenology in $(\text{Pb,La})(\text{Zr,Ti})\text{O}_3$ (PLZT) system. Nambu and Sugimoto derived the same relation on the basis of a more general mean field theory and explained the difference of the phase transitions in PMN and Pb(Sc$_{1/2}$Ta$_{1/2}$)O$_3$ (PST).

The purpose of this work was to investigate $n(T)$, but not $q(T)$. So we consider the dielectric nonlinearity, i.e., the susceptibility corresponding to a nonzero electric field $E$,

$$\varepsilon_E(T) = \frac{P}{\varepsilon_0 E} = \frac{1}{\varepsilon_0} \cdot \frac{1}{a(T) + b(T)P^2} \approx \frac{1}{\varepsilon_0 a(T)} - \frac{b(T)}{\varepsilon_0 a^2(T)} P^2 = \varepsilon(T) - \varepsilon_0 E^2 \cdot \varepsilon^2(T) \varepsilon_E^2(T) \cdot b(T). \quad (17)$$

According to Eqs (17) and (14), $n(T)$ can be obtained as

$$n(T) = \frac{\alpha'_{11}}{\gamma^2} \left[ \alpha_{11} + \frac{1}{\varepsilon_0 E^2} \frac{\varepsilon_E(T) - \varepsilon(T)}{\varepsilon^2(T) \varepsilon_E^2(T)} \right]. \quad (18)$$

The value of $\alpha_{11}$ can be obtained from the experiment data at high temperatures by setting $n(T) = 0$ in Eq. (18) since there is no frozen polarization at high temperatures. So, by using Eq. (18), the proportion of frozen polarization, $n(T)$, can be determined except a constant coefficient $\alpha'_{11}/\gamma^2$ from the experiment of dielectric nonlinearity.

We take a typical and well-known relaxors, Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ (PMNT), as an example to analyze the proportion of frozen polarization. The samples were prepared by two-stage calcination method. The magnesium niobate is synthesized by calcining MgCO$_3$·Mg(OH)$_2$·6H$_2$O and Nb$_2$O$_5$ at 1000$^\circ$C for 6 h. The columbite phase was then mixed with lead oxide and titanium oxide to form the composition 0.96PMN-0.04PT. Excess PbO (0.3 wt%) was added to compensate for PbO loss during heat treatment. The mixture was ball-milled and calcined again at 800$^\circ$C for 2 h. A 10 mm uniaxial steel die was employed to produce green pellets from the calcined powder, using a pressure of 100 MPa. The pressed pellets were subsequently sintered in a covered alumina crucible at 1200$^\circ$C for
1 h. After sintering, the pellets were polished to a thickness of 0.6 mm and silver paste was applied and fired at 600°C to achieve a conductive and adherent coating. The dielectric susceptibility was measured at various frequencies with an LCR precision meter (Model HP 4284A, Hewlett Packard, Palo Alto, CA) remotely controlled through a desktop computer. A temperature chamber (Model 2300, Delta Design, San Diego, CA) was interfaced to the computer to allow measurement of dielectric properties at various temperatures. The amplitude of the ac measurement field was 0.05 and 0.25 kV/cm.

An illustration of the temperature dependence of the dielectric response at a low frequency 100 Hz is shown in Fig. 1(a), and the corresponding calculated proportion of frozen polarization is given in Fig. 1(b). The curves in Fig. 1(a) demonstrate typical dielectric nonlinear behavior with the magnitude of the susceptibility increasing with increasing the field amplitude and the maximum shifting to lower temperatures, which is consistent with the previous observations. The curve of the proportion of frozen polarization, \( n(T) \), is determined with an arbitrary factor. It can be seen that \( n(T) \) is equal to zero at high temperatures, which means that the local polarization is all dynamic. When the temperature decreases to approach the temperature of the susceptibility maximum \( (T_m) \), \( n(T) \) starts to increase, i.e., some local polarization is frozen. After crossing \( T_m \), \( n(T) \) increases rapidly with decreasing temperature, and an extrapolation of the slope at the inflection point to zero yielded a critical temperature \( T_p = 8.3°C \). The monotonous increasing of \( n(T) \) with decreasing temperature in Fig. 1(b) shows that the calculation is physically realistic.

In the works of other researchers, the calculated quantity is the local order parameter \( q(T) \) that is determined from the temperature dependence of zero-field susceptibility [see Eq. (16)]. The increase of \( q(T) \) with decreasing temperature is ensured by the decrease of susceptibility at low temperatures. However, the quantity investigated here, \( n(T) \), is calculated from the nonlinear effect [see Eq. (18)]. It should be noted that the dielectric nonlinearity is the strongest when the temperature is near \( T_m \) while the proportion of frozen polarization is not large at that temperature range. It seems to be conflict with the thought that the frozen polarization is the origin of the dielectric nonlinearity. The key to answer
this problem is that the nonlinearity is approximately proportional to the forth power of the susceptibility [see Eq. (17)]. The susceptibility reaches the maximum at $T_m$, so the nonlinear is strong near $T_m$. This can also explain the weakening of the nonlinearity when the proportion of frozen polarization increases in further decreasing the temperature.

Another feature of Fig. 1 is that the frozen polarization, i.e., the local polarization which experiences a phase transition and loses the ergodicity, does not appear suddenly, but increases continuously, which is accompanied with the decreasing of the susceptibility. It is a kind of phase transition where the ergodic space shrinks in succession.[1] A few sentences can be presented here to explore the origin of the effect of dielectric amplitude on the susceptibility. From Eq. (8) one knows that the magnitude of frozen polarization decreases with increasing external field. In other words, the driving forces on the polarization is enhanced when the ac field amplitude increases, so the frozen polarization is forced to flip faster, and some frozen polarization is unfrozen and gives contribution to the polarization process. Thus the susceptibility increases with increasing the field amplitude.

Figure 2 shows the curves of frozen polarization proportion at different measuring frequencies. When the frequency increases, the curve of the proportion shifts slightly towards higher temperatures. It implies that the time scale of polarization flipping is shortened when the frequency increases, so more polarization cannot reach the equilibrium states in the observation time, i.e., more polarization is frozen. The slight increase of frozen polarization would result in the decreasing of susceptibility at higher frequency, which is known as the frequency dispersion in relaxors. The curve of $T_p$ [$T_p$ is defined in Fig. 1(b)] is depicted in Fig. 3 together with the curve of $T_m$ for comparison. It clearly demonstrates the increment of $T_p$ with increasing frequency. And we can see that $T_m$ increases more rapidly than $T_p$ does.

There are several points that should be discussed here. Firstly, the couplings between local polarization are not included in Eq. (1). However, if the couplings between polarization are considered, through the similar solving procedure as that in Ref. 15, the results presented in this paper is still valid by redefining the parameters. Secondly, we only consider the forth-
power terms in the free energy and ignore the influence of the higher terms in this work. And the coefficients $\alpha_{11}$, $\alpha'_{11}$ and $\gamma$ are considered as temperature-independent. All these defects restrict the applications of the theory. At last, in this paper the local properties are included within the Landau expansion by introducing the local changing quantities $n_i$. Consequently, one expects the appearance of a distribution for $n_i$ which is missed in the model. As the result all quantities should be averaged on such a distribution.

In summary, a Landau-type phenomenological cluster theory of relaxors is proposed in this paper to evaluate the influence of frozen polarization. The proportion of frozen polarization in PMNT is calculated from the experimental data of dielectric nonlinearity. It is shown that the frozen polarization starts to appear when the temperature decreases near to $T_m$, and increases rapidly after crossing $T_m$. When the ac field frequency increases, the amount of frozen polarization arises too.

This work was supported by the Chinese National Science Foundation (Grant NO. 59995520) and State Key Program of Basic Research Development (Grant No. G2000067108).
REFERENCES

1 L. E. Cross, Ferroelectrics 76, 241 (1987).

2 Z. G. Ye, Key Eng. Mater. 155-156, 81 (1998).

3 G. H. Haertling, J. Am. Ceram. Soc. 82, 797 (1999).

4 G. A. Smolenskii, J. Phys. Soc. Japan 28 suppl., 26 (1970).

5 G. Burns and F. H. Dacol, Solid State Commun. 48, 853 (1983).

6 P. Bonneau, P. Garnier, G. Calvarin, E. Husson, J. R. Gavarri, A. W. Hewat, and A. Morell, J. Solid State Chem. 91, 350 (1991).

7 H. Arndt and G. Schmidt, Ferroelectrics 79, 149 (1988).

8 D. Viehland, S. J. Jang, L. E. Cross, and M. Wuttig, J. Appl. Phys. 68, 2916 (1990).

9 D. Viehland, S. J. Jang, L. E. Cross and M. Wuttig, Phys. Rev. B 46, 8003 (1992).

10 H. Gui, B. L. Gu, and X. W. Zhang, Phys. Rev. B 52, 3135 (1995).

11 X. W. Zhang, H. Gui, Z. R. Liu, and B. L. Gu, Phys. Lett. A 251, 219 (1999).

12 V. Westphal, W. Kleemann, and M. D. Glinchuk, Phys. Rev. Lett. 68, 847 (1992).

13 Kleemann, Int. J. Mod. Phys. B 7, 2469 (1993).

14 H. Qian and L. A. Bursill, Int. J. Mod. Phys. B 10, 2007 (1996).

15 S. Nambu and K. Sugimoto, Ferroelectrics 198, 11 (1997).

16 H. Schmitt and B. Kirsch, Ferroelectrics 124, 225 (1991).

17 A. E. Glazounov, A. K. Tagantsev, and A. J. Bell, Phys. Rev. B 53, 11281 (1996).
FIGURES

FIG. 1. (a) The dielectric permittivity of PMNT as functions of temperature at various drive amplitudes when the frequency is fixed as 100 Hz. (b) The proportion of frozen polarization (arbitrary unit) in PMNT calculated from the data in Fig. 1(a) by Eq.(18).

FIG. 2. The proportion of frozen polarization in PMNT for different measurement frequencies.

FIG. 3. The curves of $T_m$ (temperature of susceptibility maximum) and $T_p$ (defined in Fig. 1) as functions of measurement frequency.
