Soft modes in two- and eight-direction order-disorder ferroelectrics

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Abstract

The soft modes in the two- and eight-direction order-disorder ferroelectrics are calculated under the mean-field approximation. We find that the conventional method of the pseudospin model to calculate the soft-mode frequency is incorrect, and present a valid modified method. It is demonstrated that the conventional method does not show the soft-mode frequency going to zero at a critical temperature in the presence of random internal fields, while the frequency calculated by our modified method goes to zero in random fields at a critical temperature. In the eight-direction ferroelectrics, the soft-mode frequency decreases to zero at the first-order phase transition temperature though the symmetry has been destroyed at high temperatures under an ex-

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ternal field. The promotion effect of random fields on the phase transition is testified by the calculation results of the soft modes in the paraelectric phase.

PACS: 77.80.-e 64.60.-i 63.70.+h 77.80.Bh
I. INTRODUCTION

A pseudospin model is usually used to interpret the phase-transition phenomena of order-disorder ferroelectrics such as KH$_2$PO$_4$ in terms of the microscopic atomic interactions. The model describes the ferroelectric phenomena as the motion of active ions in the double-well type potential field. The dynamic properties are generally considered by calculating the frequency of the ferroelectric soft mode. It yields satisfactory results for the second-order ferroelectric phase transition: when the temperature increases, the frequency of the soft mode decreases below the critical temperature $T_c$ and increases above $T_c$. At the critical temperature $T_c$, the frequency is equal to zero, i.e., the ion vibration is frozen. In the previous works, the conventional equation to determine the frequency of the soft mode is expressed as

$$\frac{d\langle S_i \rangle_t}{dt} = -i\langle [S_i, H] \rangle_t,$$  \hspace{1cm} (1)

where $S_i$ is the pseudospin of the $i$-th ion, $H$ is the Hamiltonian of the system, and $t$ is the time. $\langle \ldots \rangle_t$ denotes the temporal thermal averaging. The equation (1) is obtained by making thermal averaging on the quantum mechanics equation

$$\frac{dS_i}{dt} = -i[S_i, H].$$  \hspace{1cm} (2)

To obtain Eq. (1) from Eq. (2), an assumption implied here is

$$d\langle S_i \rangle_t = \langle dS_i \rangle_t,$$  \hspace{1cm} (3)

i.e.,

$$d\langle S_i \rangle_t = \sum_\alpha \rho_\alpha dS_{i\alpha},$$  \hspace{1cm} (4)

where $S_{i\alpha}$ is the spin of the $\alpha$-th eigen state, and $\rho_\alpha$ is the statistic weight. However, starting from the original definition of $\langle S_i \rangle_t$, i.e.,

$$\langle S_i \rangle_t = \sum_\alpha \rho_\alpha S_{i\alpha},$$  \hspace{1cm} (5)
the correct equation should be

$$d\langle S_i \rangle_t = \sum_\alpha [\rho_\alpha dS_{i\alpha} + S_{i\alpha} d\rho_\alpha].$$

(6)

Therefore, one purpose of this article is to investigate the soft mode of the order-disorder ferroelectrics by using Eq. (6) and compare with the results of the conventional method.

Rather different from the normal ferroelectrics, relaxor ferroelectrics (relaxors) experience no macroscopic phase transition at zero external field. However, a strong external electric field can induce a first-order ferroelectric phase transition in the relaxors such as Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) (PMN). The phase transition and other special characteristics (such as the strong frequency dispersion and the history-dependent polarization behaviors) of relaxors are widely believed to be caused by the random interactions and the random electric fields in the system. Based on the experimental observation that the polar active ions in PMN shift along eight \(\{111\}\)-equivalent directions, an eight-direction order-disorder ferroelectric model was presented to explain the induced first-order phase transition. The dynamic properties, however, are not calculated in that work. So, another purpose of this article is to examine the dynamic properties of the phase transition in the eight-direction order-disorder ferroelectric system.

II. METHODS

In the eigen state space of the operator \(S^z\), the Hamiltonian of the two-direction pseudospin model can be equivalently expressed as

$$H = \begin{pmatrix}
-Ep_0 & \frac{\Omega}{2} \\
\frac{\Omega}{2} & Ep_0
\end{pmatrix},$$

(7)

where \(E\) is the electric field strength, and \(p_0\) is the magnitude of the dipole moment when an ion locates in a certain potential well. \(\Omega\) is the tunneling frequency between the two potential wells, whose magnitude is equal to the energy difference between the asymmetric
and the symmetric eigen states at zero field. The dipole moment $p$ is associated with $S^z$ through the relation

$$p = 2p_0 S^z.$$  \hfill (8)

Under the mean field approximation, the interactions upon a certain ion may be represented by an equivalent field, i.e.,

$$E p_0 = J \langle p \rangle p_0 + E_{\text{ext}} p_0 + E_{\text{rand}} p_0,$$  \hfill (9)

where $\langle p \rangle$ is the thermal average value of the dipole moment, and $J$ is the ferroelectric coupling energy between polar ions. $E_{\text{ext}}$ is the applied external electric field, and $E_{\text{rand}}$ is the internal random fields in the system. $E_{\text{rand}}$ is necessary to explaining the phase transitions in incipient ferroelectrics such as KTaO$_3$:Li,Nb,Na; SrTiO$_3$:Ca or PbTe:Ge with dipole impurities (active ions with random sites and orientations). It comes from the direct interactions of electric dipoles, fields created by point charge defects and aforementioned defects, etc. Random fields are also important to interpreting the special properties of relaxors such as PMN. The pinning effect in PMN was believed to be induced by the random fields of impurities in the system. In the process of the thermally activated flips of the local spontaneous polarization, the random interactions between polarization microregions are essential in producing the relaxor characteristics such as the diffused phase transition and the frequency dispersion. It is also revealed that the charged chemical defects and nano-domain textures originating from atomic ordering also give important contributions to the random fields. The real occurrence of long-range ordered phase depends on the competition of the constant-sign ferroelectric coupling and the alternating-sign random fields. The amplitude of random fields is mainly determined by the impurity and the microstructure inhomogeneity in the system. If there are more charge impurities or the microstructure is more inhomogeneous, the random fields are stronger. Random fields coming from different sources have different distribution but have similar influences. In this article, $E_{\text{rand}}$ is assumed to have a Gaussian distribution with a width $\sigma_e$ as
\[ \rho(E_{\text{rand}}) = \frac{1}{\sqrt{2\pi\sigma_e}} \exp \left[ -\frac{E_{\text{rand}}^2}{2\sigma_e^2} \right]. \]  

(10)

The static properties of the system can be easily determined from Eqs. (7-10), which have been discussed extensively previously.

To investigate the dynamic properties of the system, the fluctuation of the electric field

\[ dE(t) = dE \cdot \exp(i\omega t) \]  

(11)

is considered. The eigen energy and the eigen polarization (dipole moment) of the Hamiltonian in Eq. (7) are respectively expressed as

\[ E_\pm = \pm \sqrt{(E p_0)^2 + (\Omega/2)^2}, \]  

(12)

and

\[ p_\pm = \frac{E p_0}{E_\pm} p_0. \]  

(13)

The variation of \( p_\pm \) induced by \( dE(t) \) can be calculated in a linear perturbation method of the quantum mechanics, which yields

\[ dp_\pm(t) = \frac{\Omega^2}{(E p_0)^2} \cdot E_\pm p_0 dE(t) \]  

(14)

\[ \frac{4 E_\pm^2}{4 E_\pm^2 - (\hbar\omega)^2} \cdot p_0. \]

According to the conventional method [Eq. (4)], \( d\langle p \rangle_t \) reads as

\[ d\langle p \rangle_t = \int dp_+(t) \tanh \left( \frac{E_+}{k_B T} \right) \cdot \rho(E_{\text{rand}}) dE_{\text{rand}}, \]  

(15)

while in the modified method, \( d\langle p \rangle_t \) reads as

\[ d\langle p \rangle_t = \int \left\{ dp_+(t) \tanh \left( \frac{E_+}{k_B T} \right) + p_+ \left[ 1 - \tanh^2 \left( \frac{E_+}{k_B T} \right) \right] \frac{E p_0^2 dE(t)}{k_B T E_+} \right\} \rho(E_{\text{rand}}) dE_{\text{rand}}. \]  

(16)

Thus the frequency of the soft mode, \( \omega \), can be determined from the self-consistent equation

\[ p_0 dE(t) = J \frac{d\langle p \rangle_t}{p_0}. \]  

(17)

The dynamic properties of the pseudospin model have been investigated in details by using the conventional method when there is no random field.
For the eight-direction order-disorder ferroelectric model, there are eight potential wells along \(\{111\}\)-equivalent directions, and the Hamiltonian is assumed to be the direct sum of four groups of double-well matrix, i.e.,

\[
H = \begin{bmatrix}
-E_{p_0} & \frac{\Omega}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{\Omega}{2} & E_{p_0} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -\frac{1}{3}E_{p_0} & \frac{\Omega}{2} & 0 & 0 & 0 & 0 \\
0 & 0 & \frac{\Omega}{2} & \frac{1}{3}E_{p_0} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -\frac{1}{3}E_{p_0} & \frac{\Omega}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{\Omega}{2} & \frac{1}{3}E_{p_0} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{3}E_{p_0} & \frac{\Omega}{2} \\
0 & 0 & 0 & 0 & 0 & 0 & \frac{\Omega}{2} & \frac{1}{3}E_{p_0}
\end{bmatrix},
\]

where the factor 1/3 is the cosine of the angle between the dipole moment and the external field when they are not parallel to each other. Other equations similar to the two-direction cases can also be obtained, which are not listed here in order to keep the article concise.

### III. RESULTS AND DISCUSSIONS

#### A. Two-direction pseudospin model

In order to demonstrate the different effects of the conventional and the modified methods, the soft-mode frequency of the two-direction pseudospin model corresponding to \(\Omega = J\) is shown in Fig. 1 when there are no external field and random fields. The dashed line represents the calculation results by using the conventional method, and the solid line represents those calculated by using the modified method. We can see that both the conventional method and the modified method yield the same frequencies of the paraelectric phases \((T > T_c)\). The reason is that the polarization and \(z\)-spin of the eigen states in the paraelectric phase are zero \([p_\pm = 0\) while \(E = 0\). See Eq. (13)], so the Eq. (4) is equivalent to Eq. (6) in this case. For the ferroelectric phase, \((h\omega)^2\) in the conventional method is proportional to the polarization of the system; \((h\omega)^2\) in the modified method is smaller than
that in the conventional method. The feature can be understood as follows: under the same drive $dE(t)$, the “displacement” $d\langle S_i \rangle_t$ calculated by Eq. (4) is smaller than that calculated by Eq. (6), i.e., the “elastic” coefficient of the conventional method is larger than that of the modified method, so the vibration frequency in the conventional method is higher than that in the modified method. It should be noted that the frequency decreases to zero at the critical temperature, which is just a unique characteristic of the soft mode theory.

Figure 2 shows the polarization and the soft-mode frequency of the system under a weak external field $E_{\text{ext}} = 0.005 J/p_0$ when $\Omega = J$. It can be seen that the polarization increases continuously when the temperature decreases. The soft-mode frequency does not decrease to the zero value but reach a nonzero minimum. The minimal value of the frequency in the modified method is closer to zero than that in the conventional method. The frequency calculated in the modified method reaches its minimum at $T_m' = 0.95 J/k_B$, which is a little larger than the temperature at which the polarization changes most quickly, $T_m = 0.91 J/k_B$.

The random fields existing in the system have great influence on the properties of disordered ferroelectrics. They can make the critical temperature decrease, and even inhibit the phase transition. The polarization is calculated for the two-direction model with distribution width of random fields $\sigma_e = 0$ and $0.3 J/p_0$, respectively, and the results are presented in Fig. 3(a). It is demonstrated that the critical temperature $T_c$ decreases from 0.911 to 0.802 $J/k_B$ when the random field width increases from 0 to 0.3 $J/p_0$. The figure 3(b) shows the calculated results of the soft-mode frequency when $\sigma_e = 0.3 J/p_0$ and $\Omega = J$. We observe an extraordinary difference between the results calculated by the two methods: the frequency in the conventional method keeps nonzero while the frequency in the modified method decreases to zero at the critical temperature. From the curve of the polarization in Fig. 3(a) we know that the phase transition is of the second-order type and the symmetry of the system changes at the critical temperature. A zero frequency at the critical temperature is required by the soft mode theory. Thus, Eqs. (1) and (4) used in the past to calculate the frequency are incorrect, while Eq. (6) produces the physically reasonable results.
B. Eight-direction order-disorder ferroelectric model

Under the two-body couplings, there is only the second-order phase transition in the two-direction ferroelectric system, while both the second-order and the first-order phase transitions can exist in the eight-direction ferroelectrics. The polarization and the soft-mode frequency in both cooling and heating processes are shown in Fig. 4 for the eight-direction model when $\Omega = 0.63J$. Fig. 4(a) clearly demonstrates the jump of the polarization and the difference of the phase transition temperature between the cooling and heating processes, which indicates that the phase transition is of the first-order type. In a cooling process, the soft mode frequency decreases to zero at the phase transition temperature (overcooled temperature) and suddenly jumps to the nonzero frequency value of the ferroelectric phase. In a heating process, the cases are similar except that the phase transition occurs at a higher temperature (overheated temperature).

For the relaxor ferroelectrics such as PMN, an external field with proper strength will induce a first-order phase transition. The second-order phase transition occurs in stronger field ranges, and the phase transition vanishes when the field increases further. The curves of the soft-mode frequency at different external fields are depicted in Fig. 5 when $\Omega = J$. At the external fields $E = 0.075$ and $0.095 \, J/p_0$, the phase transition is of the first-order type (see Ref. 12). There is a jump of frequency at the phase-transition temperature, and a down-pulse reaching the zero value exists above the phase transition temperature. When an external field is applied, the symmetry of the system has already been lowered at high temperatures, and the high and low temperature phases can not be distinguished from the symmetry changing. However, the zero soft-mode frequency at the critical temperature clearly indicates the existence of the phase transition. For $E = 0.115J/p_0$, the phase transition is of the second-order type, and a down-peak of the frequency is easy to be identified. It is not a “real” phase transition in the sense that the soft-mode frequency does not decrease to zero. The phase transition can only be approximately defined from the rapid change of the polarization or from the minimum of the soft-mode frequency. For a strong field $E = 0.15J/p_0$, the soft-
mode frequency varies rather smoothly, and the softness of frequency is indefinite. In this case, it is difficult to identify any phase transition; in other words, the transition does not exist.

Rather different from the common sense, the random fields with proper distribution width will promote the spontaneous phase transition in the eight-direction ferroelectric system. In Fig. 6, the soft-mode frequencies of the paraelectric phase at different temperatures when Ω = J are given as functions of the width of random fields. With increasing width of the random fields, the frequency decreases first, and then increases. The minimal frequency is reached at a nonzero width. The promotion effect of random fields on the phase transition is demonstrated most clearly in the case of T = 0.085 J/k_B: the random fields with distribution width 0.276 J/p_0 < σ_e < 0.436 J/p_0 induce the spontaneous appearance of the ferroelectric phase.

The original motivation of the eight-direction order-disorder ferroelectric model is to predict the phase transition in relaxors, but not to explore the dielectric mechanism. It is known that relaxors have a rather broad and smooth spectrum of the relaxation times, and the relaxation time shows a progressive slowing down upon cooling, which results in a transition into a glassy state. A distribution of relaxation time instead of a single frequency of the soft mode should be introduced for fully describing the dielectric properties of relaxors such as the frequency dispersion. The Monte Carlo simulation on the two-direction pseudospin model has been done to explain the dielectric behaviors of relaxors. Thus further works of simulation on the eight-direction model may be helpful for understanding the characteristics of relaxors.

IV. SUMMARIES

In summary, the soft modes in the two-direction and eight-direction order-disorder ferroelectric systems are studied in this article. We indicate that the conventional method yields incorrect soft-mode frequency of the pseudospin model, and present the valid modified equa-
tion. The soft-mode frequency of the ferroelectric phase calculated by the modified method is smaller than the conventional values, while the critical temperature does not vary. When there exists random electric fields, the frequency calculated by the conventional method does not decrease to zero at the critical temperature, which is physically unreasonable. In contrast, the modified method yields the reasonable results. In the eight-direction ferroelectrics, the soft mode of paraelectric phase decreases to zero at the over-cooled temperature. The calculation of the soft modes under external electric fields shows that the frequency decreases to zero at the first-order phase transition temperature although the symmetry of the system has been destroyed at high temperatures. We find that the soft-mode frequency decreases first and then increases with increasing distribution width of the random fields, which testifies the promotion effect of random fields on the spontaneous appearance of the ferroelectric phase.

ACKNOWLEDGMENT

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 R. Blinc and B. Zeks, *Soft Modes in Ferroelectrics and Antiferroelectrics* (North-Hollad, Amsterdam, 1974).

2 M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon Press, Oxford, 1977).

3 L. E. Cross, Ferroelectrics *76*, 241 (1987).

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

5 Z. G. Ye and H. Schmid, Ferroelectrics *145*, 83 (1993).

6 G. Calvarin E. Husson, and Z. G. Ye, Ferroelectrics *165*, 349 (1995).

7 D. Viehland, S. J. Jang, and L. E. Cross, J. Appl. Phys. *68*, 2916(1990).

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

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

10 M. D. Glinchuk and V. A. Stephanovich, J. Phys.: Condens. Matter *6*, 6317 (1994).

11 N. de Mathan, E. Husson, G. Calvarin, J. R. Gavarri, A. W. Hewat, and A. Morell, J. Phys.: Condens. Matter *3*, 8159 (1991).

12 Z. R. Liu, B. L. Gu, and X. W. Zhang, Appl. Phys. Lett. *77*, 3447 (2000).

13 H. Qian and L. A. Bursill, Int. J. Mod. Phys. B *10*, 2027 (1996).

14 Z. R. Liu, B. L. Gu, and X. W. Zhang, Phys. Rev. B *62*, 1 (2000).
FIGURES

FIG. 1. Soft-mode frequency of the two-direction pseudospin model as function of temperature when $\Omega = J$. The dashed and the solid lines represent the results in the conventional and the modified methods, respectively. The temperatures is measured in unit of $J/k_B$, and $\hbar\omega$ in unit of $J$.

FIG. 2. Temperature dependence of the polarization and the soft-mode frequency of the two-direction ferroelectrics at an external field $E_{\text{ext}} = 0.005J/p_0$ when $\Omega = J$. The polarization $\langle p \rangle$ is measured in unit of $p_0$. The dashed and the solid lines represent the results in the conventional and the modified methods, respectively.

FIG. 3. (a) The polarization of the two-direction ferroelectrics when $\sigma_e = 0$ (dot-dashed) and $0.3J/p_0$ (solid), respectively. (b) Soft-mode frequency of the two-direction ferroelectrics as function of temperature when $\Omega = J$ and $\sigma_e = 0.3J/p_0$, where the dashed and the solid lines represent the results in the conventional and the modified methods, respectively.

FIG. 4. Temperature dependence of (a) the polarization and (b) the soft-mode frequency of the eight-direction ferroelectric when $\Omega = 0.63J$. The solid and dashed lines represent the results in a cooling process and a heating process, respectively.

FIG. 5. Soft-mode frequency of the eight-direction ferroelectrics as function of temperature at a cooling process when $\Omega = J$. Curves 1-4 correspond to $E_{\text{ext}}=0.075$, 0.095, 0.115, and 0.15 $J$, respectively.

FIG. 6. Soft-mode frequency of the eight-direction ferroelectrics as function of random field distribution width when $\Omega = J$. The solid, dashed, and dot-dashed lines correspond $T=0.1$, 0.09, and 0.08 $J/k_B$, respectively.
