Multiple tunneling channels order-disorder ferroelectric model and field-induced phase transition in relaxors

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An improved eight-potential-well order-disorder ferroelectric model with isotropic distribution of random fields has been proposed and the field-induced phase transition and polarization behavior of relaxor ferroelectrics has been investigated. It was found that the type of phase transition, first order or second order, is independent of the random field width when the random field has an isotropic distribution. By introducing tunneling frequency between the nearest-neighbor wells, we observed a distinct threshold field and a corresponding nonzero phase transition temperature for field-induced phase transition, which is in good agreement with recent field-induced polarization measurement. Three kinds of dependence of polarization under an external electric field on temperature were demonstrated.

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Relaxor ferroelectrics have been extensively studied for more than 40 years since $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) was synthesized by Smolenske and Agranovskaya.[1] A typical relaxor displays a diffuse phase transition, a strong frequency dispersion of the dielectric properties, and an absence of macroscopic polarization at zero electric field, which are rather different from those of normal ferroelectrics.[2] Various models, such as the dipolar glass model, the quenched random-field model, and the random-band-random-field model, have been proposed to account for the unusual physical properties of relaxor ferroelectrics.[3–7] Glinchunk *et al.* revealed that the strong random fields can make the long-range order parameter disappear, and thus qualitatively explained the absence of the zero-field phase transition in relaxors.[8] Although relaxor ferroelectrics have no macroscopic phase transition at zero electric field, a ferroelectric phase can be induced by an electric field for some relaxors. For example, a first-order phase transition, from the pseudocubic phase to rhombohedral ferroelectric phase, occurs while cooling single crystal PMN in a $\langle 111 \rangle$ direction external field that is higher than the threshold field strength E_{th} (≈ 1.7 kV/cm).[9,10] Similar behavior is also found in $Pb_{0.91}La_{0.09}(Zr_{0.65}Ti_{0.35})_{0.978}O_3$ with $E_{th} \approx 5$ kV/cm.[11]

For order-disorder ferroelectrics such as KH_2PO_4, the active ion (H^+) has two equilibrum sites, and thus the phase transition can be well described by a pseudospin model.[12] Noting that each polar ion in PMN has eight equilibrum positions as allowed by the rhombohedral symmetry of the polar phase, an eight-potential-well ferroelectric model has recently been proposed.[13] Although only the two-body interactions are involved, both the second-order phase transition and first-order phase transition can be well described in that model, which is quite different from the case of the conventional pseudospin model.[12] Based on the calculation of the model, some characteristics of field-induced phase transition of relaxors were explained theoretically.[13] For simplicity, only the tunneling between wells with opposite directions was considered and random fields are projected in $\langle 111 \rangle$ direction in that model. The extraordinary feature of the field-induced phase-transition, i.e., the existence of a threshold field and the corresponding phase transition temperature, was not produced. In actual cases, other tunnelings, especially those between the nearest-neighbor wells, may be comparable with those between opposite wells, and thus cannot be ignored in analysis. Furthermore, the random fields may be distributed in random spatial directions rather than being limited to a $\langle 111 \rangle$ direction.

In this paper, an improved eight-potential-well ferroelectric model was proposed and the effects of random fields and external electric field on phase transition was investigated. The existence of the threshold field and the corresponding phase-transition temperature will be clearly demonstrated when considering the tunneling between the nearest-neighbor wells, which is in good agreements with the experiments of relaxors.[9,10]

For the ferroelectrics such as PMN, the polar phase has trigonal symmetry with point group $3m$, which suggests that for each polar ion there are eight potential wells along $\langle 111 \rangle$-equivalent directions (as shown in Fig. 1). When an external field is applied at any direction, the Hamiltonian matrix of the order-disorder system with eight potential wells is assumed to be

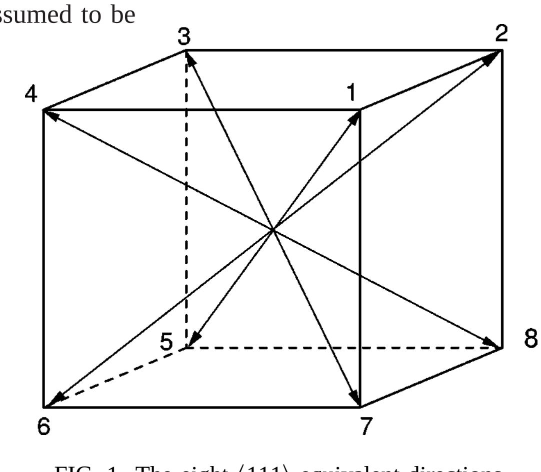

FIG. 1. The eight $\langle 111 \rangle$-equivalent directions.

$$H=\begin{bmatrix} -\mathbf{E}\cdot\mathbf{p}_1 & \frac{\Omega_1}{2} & \frac{\Omega_2}{2} & 0 & 0 & \frac{\Omega_2}{2} & \frac{\Omega_2}{2} & 0 \\ \frac{\Omega_1}{2} & -\mathbf{E}\cdot\mathbf{p}_5 & 0 & \frac{\Omega_2}{2} & \frac{\Omega_2}{2} & 0 & 0 & \frac{\Omega_2}{2} \\ \frac{\Omega_2}{2} & 0 & -\mathbf{E}\cdot\mathbf{p}_2 & \frac{\Omega_1}{2} & \frac{\Omega_2}{2} & 0 & 0 & \frac{\Omega_2}{2} \\ 0 & \frac{\Omega_2}{2} & \frac{\Omega_1}{2} & -\mathbf{E}\cdot\mathbf{p}_6 & 0 & \frac{\Omega_2}{2} & \frac{\Omega_2}{2} & 0 \\ 0 & \frac{\Omega_2}{2} & \frac{\Omega_2}{2} & 0 & -\mathbf{E}\cdot\mathbf{p}_3 & \frac{\Omega_1}{2} & \frac{\Omega_2}{2} & 0 \\ \frac{\Omega_2}{2} & 0 & 0 & \frac{\Omega_2}{2} & \frac{\Omega_1}{2} & -\mathbf{E}\cdot\mathbf{p}_7 & 0 & \frac{\Omega_2}{2} \\ \frac{\Omega_2}{2} & 0 & 0 & \frac{\Omega_2}{2} & \frac{\Omega_2}{2} & 0 & -\mathbf{E}\cdot\mathbf{p}_4 & \frac{\Omega_1}{2} \\ 0 & \frac{\Omega_2}{2} & \frac{\Omega_2}{2} & 0 & 0 & \frac{\Omega_2}{2} & \frac{\Omega_1}{2} & -\mathbf{E}\cdot\mathbf{p}_8 \end{bmatrix}, \tag{1}$$

where $\mathbf{p}_i$ is the dipole moments when an ion locates in well i $(i=1,\cdots,8)$. $\mathbf{p}_i$ have the same magnitude p_0 and their directions are along eight $\langle 111\rangle$ directions (see Fig. 1). Ω_1 and Ω_2 are, respectively, the tunneling frequencies between wells with opposite directions and between the nearest-neighbor wells. Under the mean-field approximation, the polar interactions upon a certain ion may be represented by an equivalent field, i.e.,

$$\mathbf{E}=\frac{J}{p_0^2}\langle\mathbf{p}\rangle+\mathbf{E}_{\text{ext}}+\mathbf{E}_{\text{ran}}, \tag{2}$$

where $\langle\mathbf{p}\rangle$ is the thermal average value of the dipole moment and J is the coupling energy, which comes from the dipole interaction. $\mathbf{E}_{\text{ext}}$ is the applied external electric field. $\mathbf{E}_{\text{ran}}$ is the internal random field in the system, which originates from charged compositional fluctuations and the point-charge defect, etc. $\mathbf{E}_{\text{ran}}$ is assumed to have equal probability in any direction and a Gaussian distribution in magnitude

$$\rho(|\mathbf{E}_{\text{ran}}|)=\frac{1}{\sqrt{2\pi}\sigma_e}\exp\left[\frac{-|\mathbf{E}_{\text{ran}}|^2}{2\sigma_e^2}\right], \tag{3}$$

where σ_e is the distributive width. From Eqs. (1)–(3), the thermal average value of dipole moments $\langle\mathbf{p}\rangle$ can be calculated at any temperature. It was observed in our calculation that $\langle\mathbf{p}\rangle$ is always along one of the eight $\langle 111\rangle$-equivalent direction if no external field or a $\langle 111\rangle$-equivalent direction external field is applied.

First, the effect of the isotropic distribution of random fields on the phase transition was investigated. We only considered the tunneling between wells with opposite directions (i.e., Ω_2 is taken to be 0) in order to compare with the previous work[13] where random fields are limited in the $\langle 111\rangle$ direction. In Fig. 2, the calculated phase-transition temperatures versus random field width σ_e were given for $\Omega_1=0.7J$ and $\Omega_2=0$. We can see that the overheated and overcooled temperatures have different behavior while increasing the random fields. The overheated temperature decreases monotonously from 0.18 at $\sigma_e=0$ to 0 at $\sigma_e=1.05J/p_0$. The overcooled temperature first increases and reaches its maximum at $\sigma_e=0.27J/p_0$, and then decreases to 0 at $\sigma_e=0.72J/p_0$. Although enough high random field indeed inhibits the macroscopic phase transition, proper random fields can prompt the spontaneous first-order phase transition by increasing the overcooled temperature. The features mentioned above are qualitatively consistent with previous works.[13]

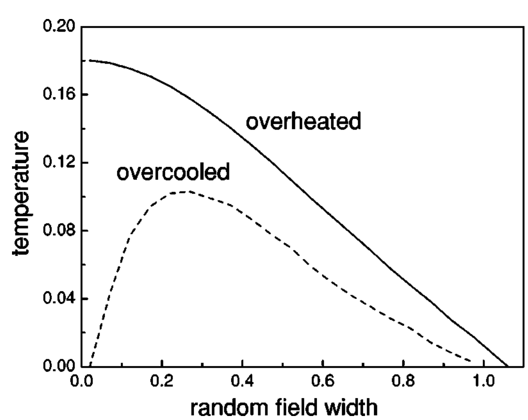

FIG. 2. Phase transition temperatures (in units of J/k_B) versus random-field width (in units of J/p_0) when $\Omega_1=0.7J$. The solid and dotted lines represent the overheated and the overcooled temperatures, respectively.

The difference between our results and the previous work is also obvious. In Ref. 13, a first-order phase transition is evolved into a second-order transition with increasing random fields. Nevertheless, Fig. 2 indicates that the overheated and overcooled temperature curves do not intersect at any random fields width while $\Omega_1=0.7J$ and $\Omega_2=0$, which means that only the first-order phase transition could occur. The discrepancy results from different spatial distribution of random fields: the $\langle 111\rangle$ direction in the previous work[13] and the isotropic distribution in this work. For the latter, the first-order phase transition is more distinct when $1.1J<\Omega_1<2J$, where the spontaneous polarization does not appear in the cooling process at any random-field width. It is known that the random field can be modulated with doping. For many ferroelectrics such as $BaTiO_3$, $PbTiO_3$, and $Pb(Zr_{1-x}Ti_x)O_3$,[15,16] the spontaneous macroscopic phase transition can be inhibited and relaxor behavior appears by properly doping. However, the doping does not change the type of the normal ferroelectric phase transition, first-order or second-order. For example, $Pb_{1-x}La_x\,(Zr_{0.4}Ti_{0.6})_{1-x}O_3$ exhibits, respectively, the first-order normal ferroelectric phase transition for La content below 10%, the first-order normal to relaxor transformation for La content between 10%–12%, and relaxor phase transition for La content above 12%.[17] During the doping process, a normal ferroelectric phase transition of the second-order type does not appear. Therefore, the present results are more consistent with the experiment.

Now we investigated the relation of polarization with the temperature when an external field along direction 1 (as shown in Fig. 1) is applied. It was found that the tunneling frequency strongly influences the polarization behavior. Figure 3 shows three kinds of behavior mode for different tunneling frequencies Ω_1 between wells with opposite directions and Ω_2 between nearest-neighbor wells. In Fig. 3(a), only the tunneling between wells with opposite directions is considered ($\Omega_2=0$). We can see a distinct field-induced transition. A very small external field ($<0.001J/p_0$) can yield a rapid increase of polarization at $T\approx 0$; the transition temperature increases with increasing field strength. If we only consider the tunneling frequency Ω_2 between the nearest-neighbor wells, then a completely different behavior appears, which is shown in Fig. 3(b) for $\Omega_1=0$ and $\Omega_2=1.2J$. With decreasing temperature, the polarization slowly increases at high temperature and is saturated at low temperature. There is no field-induced phase transition at the external field from 0 to $0.4J/p_0$. It is interesting to compare the magnitude of $\langle p\rangle$ in Fig. 3(a) with that in Fig. 3(b). The field-induced $\langle p\rangle$ is close to p_0 at low temperature in Fig. 3(a), which means that most of the polar ions locate in well 1, while the thermal average polarization $\langle p\rangle$ in Fig. 3(b) reveals that even at high external field, quite a few polar ions locate in the three nearest-neighbor wells of well 1 at low temperature. The discrepancy can be qualitatively understood. When no tunneling exists, all polar ions locate in well 1 at low temperature if the external field is along the direction of well 1. With increasing tunneling frequency, many polar ions would tunnel from well 1 to other wells. The number of polar ions tunneling from well 1 to another well is determined by both the tunneling frequency and the energy difference between two wells. Under the same external field and the average polarization, the energy difference between well 1 and its opposite direction well is about three times of that between well 1 and its nearest-neighbor well. Noting that the number of polar ions tunneling from well 1 to another well exponentially decreases with increasing energy difference between wells, we can see that two kinds of tunneling have different effects under the external field: the Ω_1 prompts the field-induced phase transition while Ω_2 inhibits

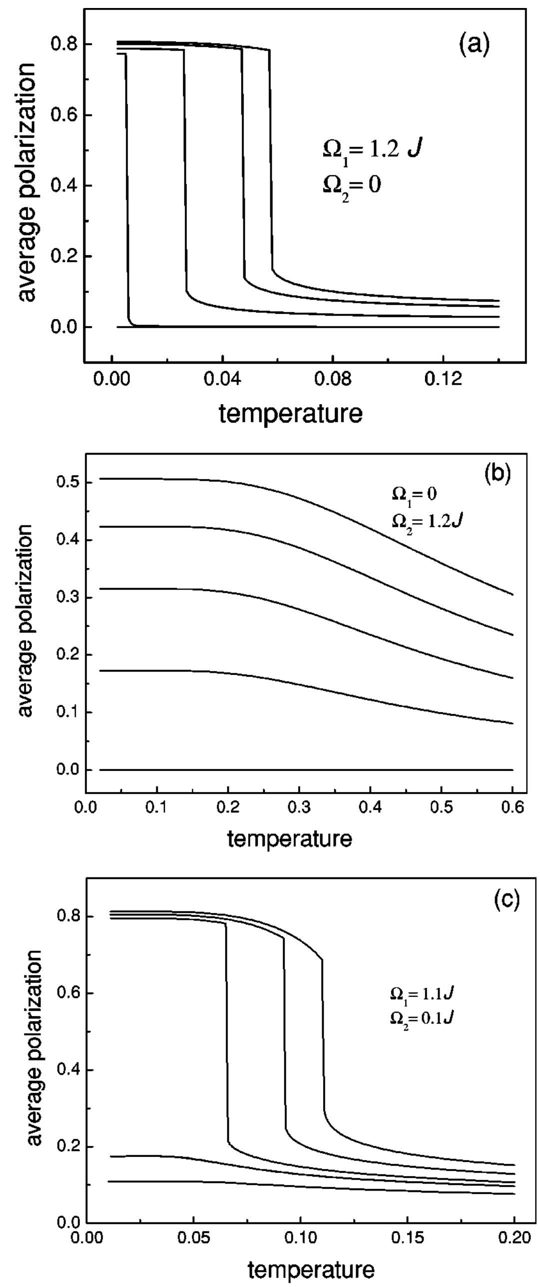

FIG. 3. The dependence of average polarization $\langle p\rangle$ (in units of p_0) on temperature (in units of J/k_B) in cooling processes at $\sigma_e=0.25J/p_0$, (a) $\Omega_1=1.2J$ and $\Omega_2=0$. The external fields are, from the bottom up, 0, 0.001, 0.02, 0.04, and $0.05J/p_0$. (b) $\Omega_1=0$ and $\Omega_2=1.2J$. The external fields are, from the bottom up, 0, 0.1, 0.2, 0.3, and $0.4J/p_0$. (c) $\Omega_1=1.1J$ and $\Omega_2=0.1J$. The external fields are, from the bottom up, 0.04, 0.05, 0.055, 0.065, and $0.075J/p_0$.

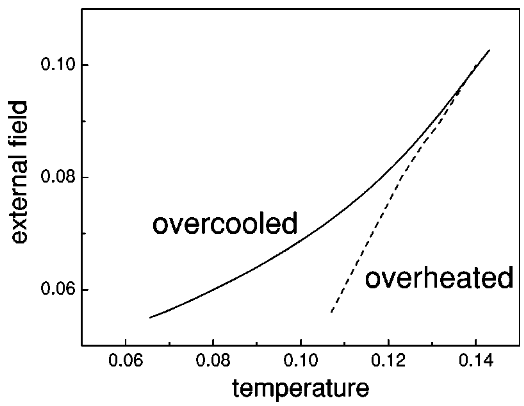

FIG. 4. Phase-transition temperatures (in units of J/k_B) as functions of the external field (in units of J/p_0) when $\Omega_1=1.1J$, $\Omega_2=0.1J$, and $\sigma_e=0.25J/p_0$. The solid and dash lines represent, respectively, the overcooled and overheated temperatures.

the field-induced transition. It would be interesting to study the case where both kinds of tunneling exist. When the ratio of Ω_1 to Ω_2 is proper, the third kind of behavior mode appears. The polarization curves at different external fields are shown in Fig. 3(c) for $\Omega_1=1.1J$ and $\Omega_2=0.1J$. When the external field E is lower than the threshold field ($E_{\mathrm{th}}\approx 0.055J/p_0$), the average polarization is weak and slowly increases with decreasing temperature. When $E>E_{\mathrm{th}}$, the polarization has a sharp variation at a temperature T_c and saturates at low temperature. The saturation value of polarization is weakly dependent on the electric field. A distinct difference between Fig. 3(c) and Fig. 3(a) is that the phase transition temperature in Fig. 3(c) is not zero at the threshold field E_{th}. The phenomena we predicted here, i.e., the existence of a threshold electric field for induced phase transition, is in good accord with experiments.[10]

The third mode of behavior was discussed in detail. In Fig. 4, the phase-transition temperatures T_c are given as functions of the external field E for $\Omega_1=1.1J$, $\Omega_2=0.1J$, and $\sigma_e=0.25J/p_0$. There exists a threshold field $E_{\mathrm{th}}\approx 0.055J/p_0$, which corresponds to a overcooled temperature $T_{\mathrm{th}}=0.065J/k_B$. The overcooled and overheated temperatures increase with enhancing field strength. The higher the

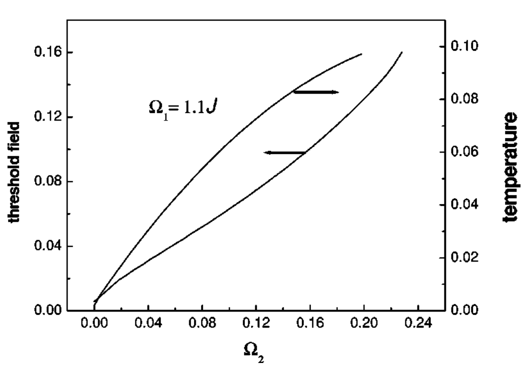

FIG. 5. The dependence of the threshold field (in units of J/p_0) and the corresponding overcooled temperature (in units of J/k_B) on the nearest-neighbor tunneling frequency Ω_2 (in units of J) when $\Omega_1=1.1J$, and $\sigma_e=0$.

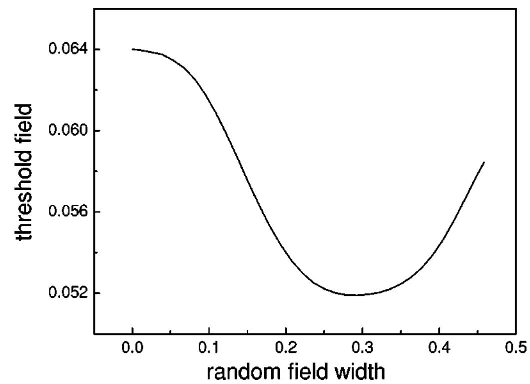

FIG. 6. The threshold field (in units of J/p_0) vs the random-field width (in units of J/p_0) when $\Omega_1=1.1J$, and $\Omega_2=0.1J$.

field, the more slowly the overcooled temperature increases. The phase transition appears to be of first order at low E and is evolved into a second-order transition for $E>0.1J/p_0$. When the electric field is smaller than the threshold value, the induced phase transition dose not appear even if the temperature decreases to zero. These features of $E-T_c$ curves are consistent with experimental observations.[9]

Two of the essential parameters of field-induced transition are the threshold field and the corresponding temperature, which are determined by the tunneling frequency and random fields. The dependence of the threshold field E_{th} and the corresponding overcooled temperature on Ω_2 is demonstrated in Fig. 5 when $\Omega_1=1.1J$, $\sigma_e=0$. We can see that for $\Omega_2<0.24J$, the larger the Ω_2, the higher the E_{th}. The overcooled temperature is almost zero when $\Omega_2=0$, and increases with enhancing Ω_2. The characteristics of field-induced phase transition become more vague with increasing Ω_2. When $\Omega_2>0.24J$, the polarization behavior is similar to that of only Ω_2 considered and no field-induced phase transition occurs. This indicates that E_{th} can appear only at the proper ratio of Ω_1 and Ω_2. Our result may explain why no field-induced phase transition was observed in some relaxors such as $Pb(Mg_{1/3}Ta_{2/3})O_3$ under an applied external field up to $E=8$ kV/cm.[18]

The effects of random fields on the threshold field E_{th} are shown in Fig. 6 while $\Omega_1=1.1J$ and $\Omega_2=0.1J$. The threshold field first decreases and then increases with increasing random field. This indicates that proper random field can facilitate the field-induced phase transition by decreasing the threshold field E_{th}, which supports the mechanism of stochastic resonance revealed recently in ferroelectric systems.[14]

In summary, by generalizing the eight-potential-well model by introducing isotropic random fields and considering two kinds of tunnelings, we investigated field-induced phase transition and polarization behavior of ferroelectrics under an external field. The type of the phase transition, the first-order or second-order, is almost independent of the random-field width. When a moderate nearest-neighbor well tunneling frequency is considered, the behavior of average polarization with temperature at an external field, including the existence of the threshold field and the corresponding temperature, can be well described for the relaxors with field-induced phase transition. Many important features of field-induced phase transition and the behavior of polarization with temperature revealed in this work are in agreement with the experimental measurements.

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