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Effect of tunneling frequency on relaxor behavior

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Abstract

A main characteristic of typical relaxor ferroelectrics distinguished from normal ferroelectric is the diffuse phase transition (DPT), i.e. the dielectric constant slowly varies nearby the temperature of the dielectric peak. DPT behavior can be well described by a modified Curie–Weiss formula. Dependence of the critical exponent on the tunneling frequency has been investigated with the eight-potential-well order–disorder ferroelectric model. For low tunneling frequency, the ferroelectric phase transition is of second-order and the system conforms to the Curie–Weiss law. The critical exponent departs significantly from the Curie–Weiss value of unity and increases with increasing tunneling frequency at the region of the first-order phase transition, which is a typical diffuse phase transition behavior. Our work is useful for understanding the phenomena that some normal ferroelectrics show pressure-induced crossover from normal ferroelectric to relaxor.

Keywords: Ferroelectric; Tunneling frequency; Relaxors

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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 Smolenskii and Agranovska [1]. Besides a strong frequency dispersion of the dielectric properties, and an absence of macroscopic polarization at zero electric field, the diffuse phase transition (DPT) is another typical characteristic of the relaxor ferroelectric distinguished from normal ferroelectric: the dielectric constant varies slowly nearby the temperature of the dielectric peak [2]. The temperature dependence of the dielectric constant does not comply with the Curie–Weiss law. DPT behavior can be described by a modified Curie–Weiss formula, $1/\epsilon - 1/\epsilon_m = c^{-1}(T - T_m)^{\gamma}$ when $T > T_m$, where c is the diffuseness parameter and γ is the critical exponent. For relaxor ferroelectric, $1 < \gamma \leq 2$. For example, γ is equal to 1.66 for PMN and 1.76 for $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) [3]. Many normal ferroelectrics can be transformed into relaxors by doping [4–6] or pressure [7]. The critical exponent γ is sensitive to doping or pressure. For

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example, the critical exponent γ increases from 1.2 to 1.86 when increasing Ca content from 0.04 to 0.16 for $Ba_{1-x}Ca_xTiO_4$ [4].

In this paper, we investigated DPT behavior with the eight-potential-well ferroelectric model, which has been recently proposed [8–10]. For the ferroelectrics such as PMN, the polar phase has trigonal symmetry with point group 3*m* [11], which suggests that for each polar ion there are eight potential wells along ⟨111⟩-equivalent directions (as shown in Fig. 1). The Hamiltonian matrix of the order–disorder system with eight potential wells is

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

where $\mathbf{p}_i$ is the dipole moment when an ion locates in well i ($i = 1,\cdots,8$). $\mathbf{p}_i$ have the same

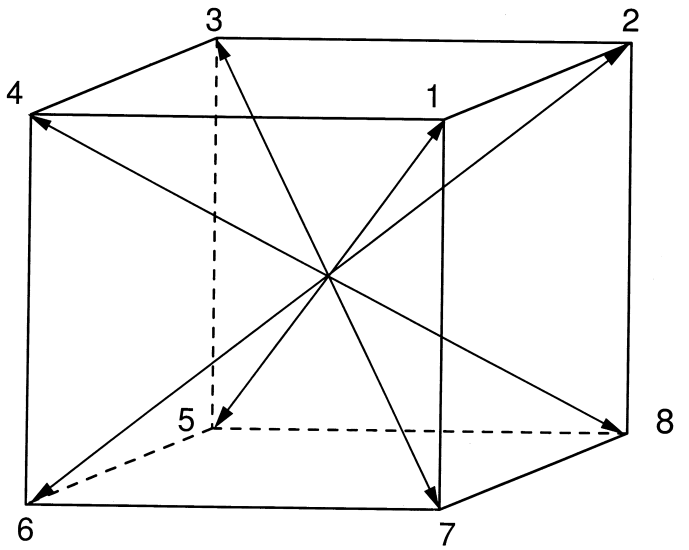

Fig. 1. The eight ⟨111⟩-equivalent directions.

magnitude p_0 and their directions are along eight ⟨111⟩-directions (see Fig. 1). Ω is the tunneling frequency. Only the tunneling between wells with opposite directions is considered here. 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 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 the equal probability in any direction and a Guassian distribution in magnitude

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

where σ_e is the distributive width. From Eqs. (1)–(3), the thermal average value of dipole moments $\langle \mathbf{p} \rangle$ and the static dielectric constant can be calculated at any temperature. The phase transition temperature, the overheated temperature T_+ or overcooled temperature T_-, can be further determined on the basis of the thermal average value of dipole moments $\langle \mathbf{p} \rangle$.

Unchio et al. have shown that the critical exponent γ, the important parameter denoting the diffuseness, is insensitive to the frequency change [3]. Therefore, it is feasible to investigate the DPT within the eight-potential-well ferroelectric model, in spite of that only the static dielectric constant can be calculated in this case. In order to depict the plot of $\ln(1/\varepsilon - 1/\varepsilon_{\text{m}})$ and $\ln(T - T_{\text{m}})$ by which the critical exponent γ can be determined, firstly we must make sure what T_{m} is (note: no dielectric peak exists for the calculated static dielectric constant). Herein, we take the overheated temperature T_+ as T_{m} for the following reasons: (i) When ε is the static dielectric constant, T_{m} is just the freezing temperature T_{f}. The data of (ω, T_{m}) can be well fitted with the Vogel–Fulcher relationship [12]

$$\omega = \omega_0 \exp\left[-\frac{E_{\text{a}}}{k_{\text{B}}(T_{\text{m}} - T_{\text{f}})} \right], \tag{4}$$

where T_{f} is the freezing temperature. Obviously T_{m} is equal to T_{f} when $\omega = 0$. (ii) T_{f} could be regarded as the overheated temperature T_+ to some extent, since the induced polar state should disappear nearby T_{f} in the heating process.

It is well known that in the two-direction pseudospin model [13], the phase transition is of the second-order type if only the coupling of two spins is considered. Within the present model, however, both the second- and first-order phase transitions can exist although only the coupling of two spins is included. This is clearly shown from the dependence of the phase transition temperatures on the tunneling frequency (Fig. 2). The system is sensitive to the tunneling frequency. The long-range order can appear only while $\Omega < 2J$. The tricritical point between the second- and first-order phase transitions is determined as $\Omega_{\text{tri}} = 0.56J$ and $T_{\text{tri}} = 0.23J/k_{\text{B}}$. When $\Omega > \Omega_{\text{tri}}$, the overcooled temperature T_- decreases rapidly with increasing Ω and vanishes at $\Omega = 0.9J$. For $0.9J < \Omega < 2J$, the overcooled temperature is zero and consequently no macroscopic polarization can appear spontaneously in a cooling process; the overheated temperature T_+ is a finite value, and thus the polar

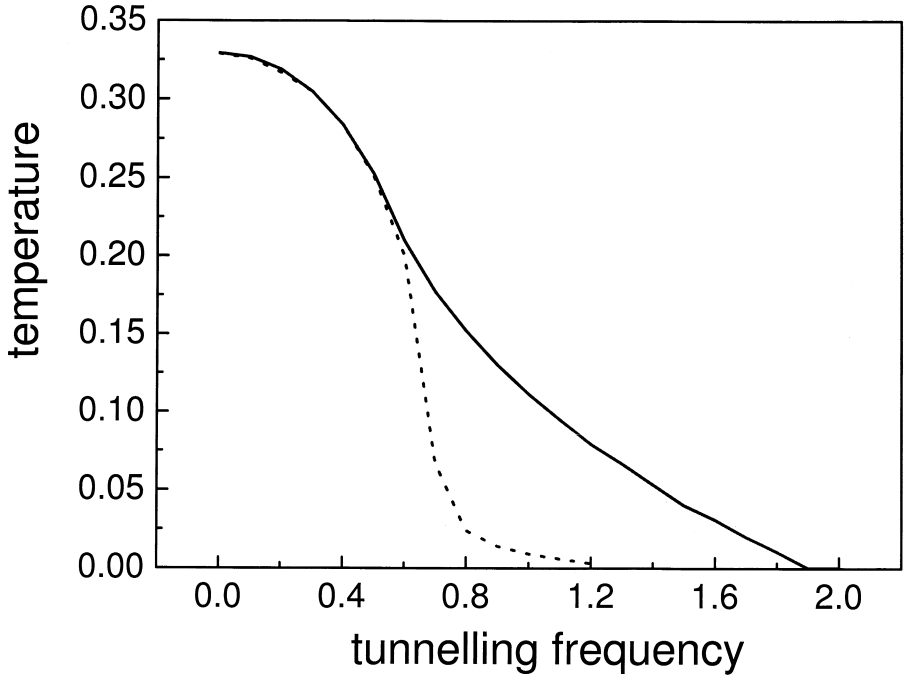

Fig. 2. Phase transition temperatures (in units of J/k_B) as functions of tunneling frequency when random field width $\sigma_e = 0.1J/p_0$. The solid and dotted lines represent the overheated and the overcooked temperatures, respectively.

state can be induced at low temperatures and will disappear at T_+ in the heating process. This is qualitatively consistent with the dielectric properties of PMN, for which the zero-field depoling of an induced state occurs at a certain temperature no matter what the induced polarization is [11].

The linear dependence of $\ln(1/\varepsilon - 1/\varepsilon_m)$ on $\ln(T - T_m)$ nearby T_m is clearly shown in Fig. 3. This shows that the dielectric constant can be well fitted with the modified Curie–Weiss formula. The slope of the line (i.e. the critical exponent γ) increases with increasing tunneling frequency Ω. The dependence of the critical exponent γ on the tunneling frequency Ω is shown in Fig. 4. When $\Omega < 0.5J$, the critical exponent $\gamma \simeq 1$, and the temperature dependence of the dielectric constant complies well with the Curie–Weiss law. This is consistent with the second-order phase transition in that tunneling frequency range. γ is always larger than 1.0 for the first-order phase transition, which has been observed in some ferroelectrics. For example, experimentally fitting value γ is equal to 1.08 for $BaTiO_3$ [3]. When $\Omega > 0.9J$, no macroscopic polarization can appear spontaneously in a cooling process, and the calculated critical exponent γ (> 1.6) is consistent with experimental results of typical relaxors such as PMN ($\gamma = 1.64$) and PZN ($\gamma = 1.76$), and exhibits a very strong dielectric diffuseness. For $0.5J < \Omega < 0.9J$, the critical exponent γ increases quickly with enhancing tunneling frequency Ω. The obvious dielectric diffuseness nearby T_+ and the spontaneous macroscopic polarization at T_- coexist at $\Omega \approx 0.7J$, which shows that a spontaneous relaxor-ferroelectric phase transition can occur during the temperature decreasing. The spontaneous relaxor-ferroelectric phase transition has been observed in $Pb(Sc_{1/2}Nb_{1/2})O_3$ and $Pb(Sc_{1/2}Ta_{1/2})O_3$ [14]. The fact that the ferroelectric phase transition is of first-order in these materials also supports our results. Now we

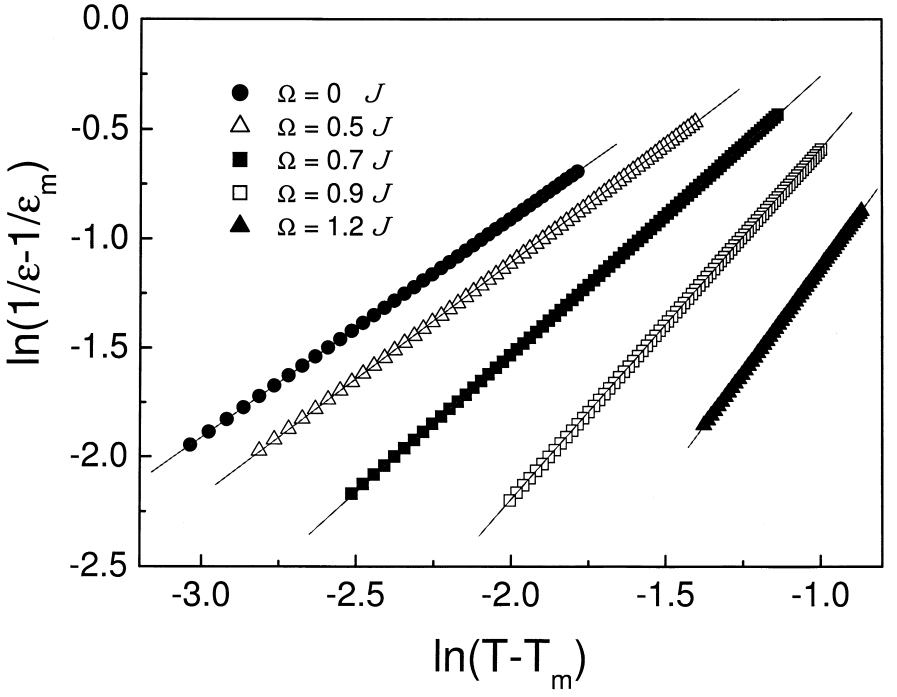

Fig. 3. The relation of $\ln(1/\varepsilon - 1/\varepsilon_{\mathrm{m}})$ with $\ln(T - T_{\mathrm{m}})$ at different tunneling frequency.

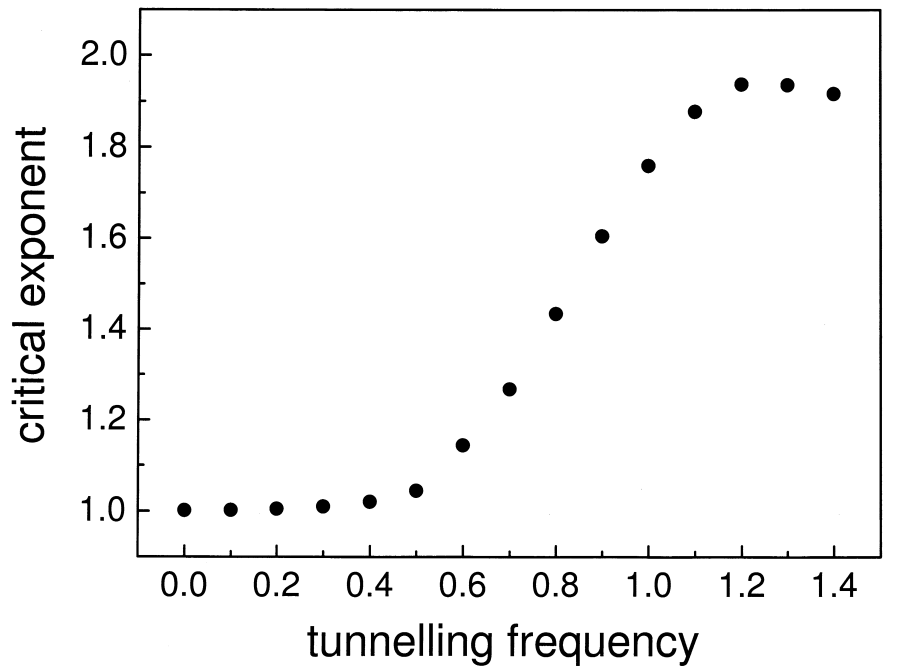

Fig. 4. The dependence of the critical exponent γ on the tunneling frequency when the random field width $\sigma_e = 0.1J/p_0$.

know that, with increasing tunneling frequency Ω, the system shows in sequence, the second-order normal ferroelectric behavior, the first-order normal ferroelectric behavior, the coexistence of the first-order ferroelectric behavior with relaxor behavior, and typical relaxor behavior. The tunneling frequency Ω depends on the distance between the opposite directional potential well. Under hydrostatic pressure, the distance will decrease, which leads to the increase of the tunneling frequency Ω. Therefore, our results indicate a pressure-induced crossover from normal ferroelectric to relaxor, which has been observed in some normal ferroelectrics [7,15,16].

The effect of random field on the critical exponent γ is shown in Fig. 5 for $\Omega = 0.35J$. γ decreases monotonously with increasing random field. From the inset of Fig. 5, we can see that the overheated and overcooled temperature curves do not intersect at any random fields width, which means that the first-order phase transition could not transform into a second-order phase transition with increasing random field width [9]. This is also supported by the curve of the critical exponent γ: there is no region where the critical exponent γ is unity.

In conclusion, the tunneling frequency significantly influences the ferroelectric behavior. For low tunneling frequency, the ferroelectric phase transition is of second-order and the system conforms to the Curie–Weiss law. With increasing tunneling frequency, the critical exponent γ departs significantly from the Curie–Weiss value of unity and increases monotonously, which is a typical diffuse phase transition behavior. Our work would be useful for understanding the phenomena that some normal ferroelectrics show pressure-induced crossover from normal ferroelectric to relaxor since the tunneling frequency increases with increasing pressure.

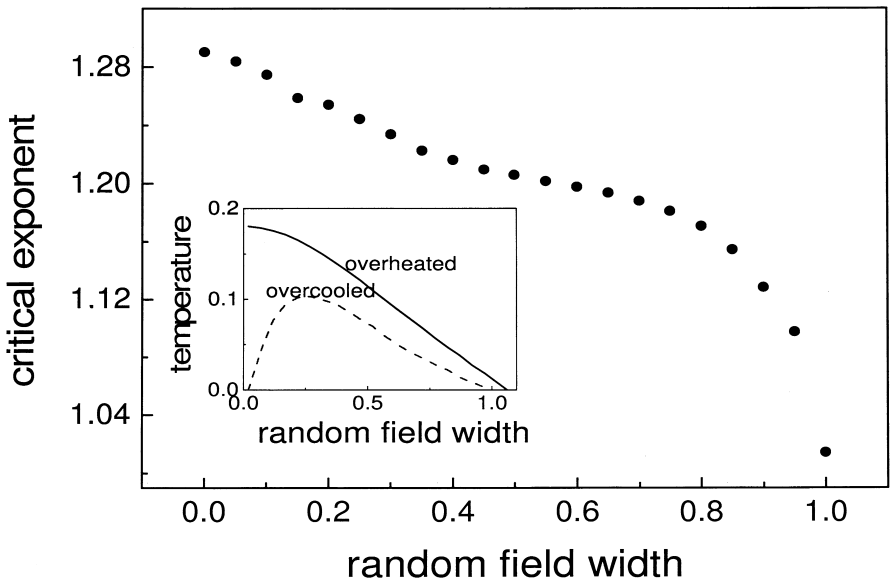

Fig. 5. The critical exponent γ as functions of random field width when the tunneling frequency $\Omega = 0.7J$. Inset shows the dependence of the overheated and the overcooked temperatures on random field width. The solid and dished lines represent the overheated and the overcooked temperatures, respectively.

Acknowledgements

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