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Effect of defect-induced internal field on the aging of relaxors

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The effect of a defect-induced internal field on the dielectric response of relaxor ferroelectrics is investigated using a Monte Carlo simulation. It was observed that only at a small temperature range near the temperature of the dielectric maximum does the susceptibility decrease markedly due to the internal field. This temperature range increases with enhancing internal field. We found that the susceptibility is almost independent of the internal field width at low internal field width, and then decreases linearly with enhancing internal field width. This dependence of the susceptibility on the internal field width is very similar to the relation of the dielectric constant with logarithmic aging time, which probably suggests a linear dependence of the internal field on the logarithm of the aging time. The frequency dependence of the susceptibility aging is sensitive to the temperature. With increasing temperature, the curve of the susceptibility change against logarithmic frequency varies from concave to approximately linear, and then to convex, which is in agreement with the recent aging rate measurement.

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Relaxor ferroelectrics (relaxors) have special dielectric characteristics compared with normal ferroelectrics. A typical relaxor ferroelectric displays a diffuse phase transition, a strong frequency dispersion of the dielectric properties, and an absence of macroscopic polarization at zero electric field.[1] Although the origin of these dielectric features is still controversial, it has been suggested that the presence of polar microregions in nanoscale is crucial to the relaxor behaviors. 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.[2–6]

The relatively high dielectric constant and low-temperature coefficient has led to many successful applications of relaxors such as multilayered capacitors. Due to their influences on the actual applications and the comprehension of the dielectric mechanism, the dielectric aging behaviors of relaxor ferroelectrics have been extensively investigated in the last decade.[7–14] The experimental results have indicated the importance of the defect structure in the aging in this type of material. For example, very little dielectric aging was observed for a carefully prepared pure PMN. However, PMN with Mn and other acceptor dopants shows significant aging.[10] The main characteristic of acceptor dopants is the introduction of O^{2-} vacancies, which results in the formation of the oxygen-vacancy–metal-impurity defect dipoles.[7,8] The reorientation and alignment of the defect dipoles with the local nanoscale polar domains lead to the internal field, which provides a pinning to the polar microregion and results in a decrease of the switchable polarization.[15,16] It is widely accepted nowadays that the defect-induced internal field is responsible for the aging behavior in relaxor ferroelectrics, but how the internal field influences the aging behavior remains unclear.

The purpose of the present study is to investigate the correlation between the defect-induced internal field and the aging behaviors of relaxors. By regarding microregions as dipoles, a model Hamiltonian including the random interactions between the microregion was previously proposed[3] to describe the dielectric-response process in relaxor ferroelectrics. The model also described well the dc bias field dependence of the dielectric response of relaxor ferroelectrics.[17] In this paper, by generalizing the above model to include the pining effect of the internal field, the effect of the defect-induced internal field on dielectric aging in relaxors was investigated. In particular, the model Hamiltonian with the internal field is given as

$$H=-\sum_{i\neq j} J_{ij}\sigma_i\sigma_j-E_{\mathrm{ext}}\bar{\mu}\sum_i \frac{|\mu_i\cos\theta_i|}{\bar{\mu}}\sigma_i-\sum_i E_i\sigma_i, \tag{1}$$

where σ_i, $\sigma_j=\pm 1$ are dipole spins. When the projection of the ith dipole moment $\vec{\mu}_i$ on the direction of the external field $\vec{E}_{\mathrm{ext}}$ is positive, σ_i takes the value $+1$; otherwise, σ_i

takes the value -1. θ_i is the angle between $\vec{\mu}_i$ and $\vec{E}_{\rm ext}$, and $\overline{\mu}$ is the maximal magnitude of the dipole moments. J_{ij} is the effective interaction energy between the nearest-neighbor dipoles, which has a Gaussian distribution with a width ΔJ. J_{ij} reflects the correlation between polar microregions, which is essential to the glassy behaviors.[2,3,18] E_i is the internal field pinning the ith dipole. To minimize the system energy, the internal field, which originates from the reorientation and alignment of the defect dipoles, has a tendency to be parallel with the microregion polarization. Once the internal field comes into being, it can be regarded as unchanged upon application of a measuring field due to the very high active energy of defect dipoles. Considering the random distribution of the volumes and the polarization directions of polar microregions, we can reasonably assume that the internal field has a Gaussian distribution with a width σ_e, i.e.,

$$P(E_i)\propto \exp\left(-\frac{E_i^2}{2\sigma_e^2}\right). \qquad (2)$$

The internal field width can be determined from the differential ferroelectric hysteresis loop.[19] According to Takahashi's definition,[19] the measured value of the internal field with the Gaussian distribution can be expressed as follows:

$$E_0=\int_{-\infty}^{\infty}|E_i|P(E_i)dE_i=\frac{2}{\sqrt{\pi}}\sigma_e. \qquad (3)$$

Namely, what is measured in experiments is the internal field width. The experiment showed that the internal field width is almost proportional to the acceptor doping concentration in the system.[20] Therefore the dependence of the dielectric susceptibility on the internal field width will be helpful in understanding the aging and doping dependence of dielectric susceptibility.

The Monte Carlo simulation was performed on a $N=16\times16\times16$ simple cubic lattice with periodic boundary conditions. The details of the simulation process can be found in Ref. 12. The dielectric susceptibility is defined as

$$\chi=\frac{C}{NT}\left\langle \sum_i^N \frac{1}{1+(\omega\tau_i)^2}\right\rangle, \qquad (4)$$

where C is a temperature-independent constant, $1/\tau_i$ is the number of flips of the ith dipole during the observation time $t_{\rm obs}$, ω is the measured frequency, and $\langle\cdots\rangle$ denotes the configurational averaging.

During the simulation, the attempt to flip was made for every dipole on the lattice sites in sequence.[3] The time was measured in units of Monte Carlo steps per dipole (MCS/dipole), which consists of $16\times16\times16$ attempted flips. For relaxors, what is observed at low temperatures is the quasiequilibrium properties of a certain component in the phase space due to the ergodicity broken. As proved in spin glass, the short-time Monte Carlo simulation gave excellent agreement with experiments.[21] Therefore we choose $t_0=1200$ MCS/dipole to eliminate the influence of the initial state and $t_{\rm obs}=2000$ MCS/dipole to be the observation time. The simulation was performed in many runs with various initial conditions so that the configurational averaging can be done.

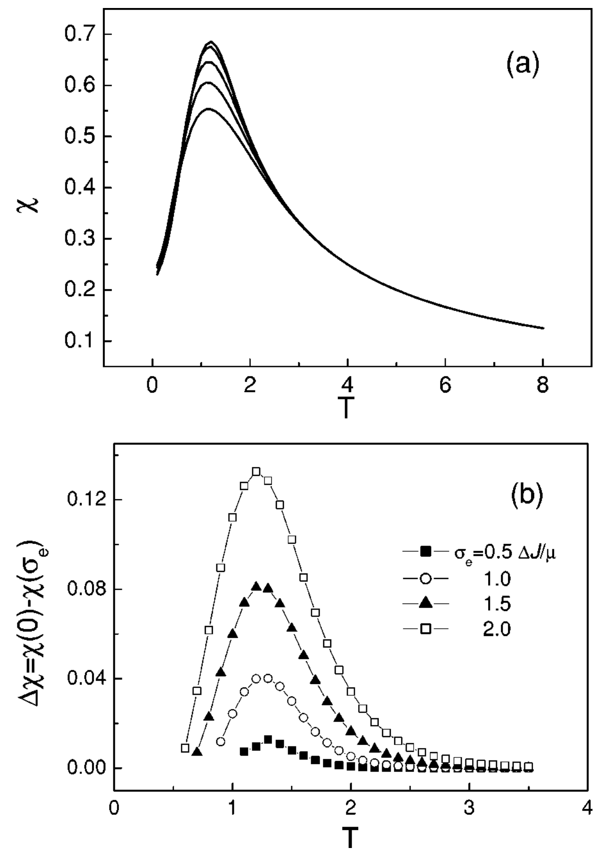

FIG. 1. (a) The susceptibility χ as a function of temperature T (in units of $\Delta J/k_{\rm B}$). The internal field widths are, from top to bottom, 0, 0.5, 1.0, 1.5, and 2.0 (in units of $\Delta J/\mu$). (b) $\Delta\chi=\chi(0)-\chi(\sigma_e)$ as a function of temperature T. The measuring frequency is 30/(2000 MCS/dipole).

In order to verify the validity of our model and method, the dielectric susceptibility without the internal field is first calculated. The calculated susceptibility χ reaches its maximum at a certain temperature T_m and varies gradually around T_m, which is known as the diffuse phase transition in relaxors. A strong frequency dispersion has also been observed: χ decreases with increasing field frequency at low temperature, and T_m moves to higher temperature. The frequency dependence of T_m can be well fitted with the Vogel-Fulcher relation. All these characteristics are consistent with the experiments[1] and the previous theoretical results.[3,22]

The calculated susceptibility curves under different internal field widths σ_e are depicted in Fig. 1(a). We can see that only at a small temperature region nearby T_m does the susceptibility decrease markedly due to the internal field. The region expands with enhancing internal field, as shown in Fig. 1(b). The result is consistent with the temperature dependence of the aging rate and the fact that the strongest aging is found to appear near T_m.[9] The concepts of "slow dipole" and "fast dipole"[3] can help us to understand the variation of the susceptibility with the temperature and the internal field width. Fast dipoles are those dipoles that flip fast enough to keep up with the changing of the measuring

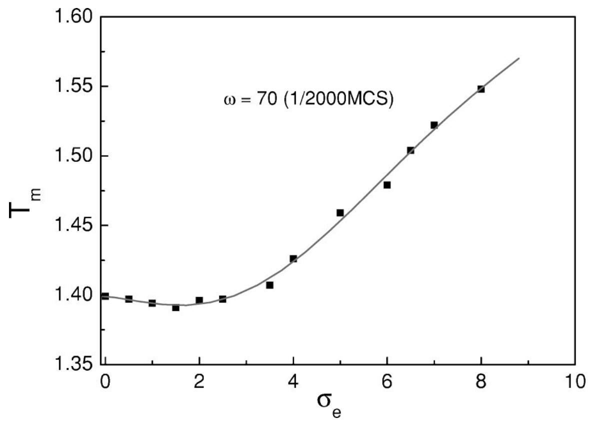

FIG. 2. The dependence of T_m on the internal field width σ_e. The measuring frequency is 70/(2000 MCS/dipole).

field and contribute to the dielectric susceptibility. But the slow dipoles do not contribute to the dielectric susceptibility due to their flipping too slow. When the temperature is near T_m, the proportion of fast dipoles varies rapidly with the temperature.[3,23] This means that some fast dipoles can be easily transformed into slow dipoles by the internal field. So the aging effect is more significant in this temperature region. At temperatures far higher than T_m, the dipoles flip quickly due to the thermal effect, and almost all dipoles can be regarded as fast dipoles.[3] In this case, it is very difficult to transform the fast dipole into the slow dipole by the pinning of the internal field. At low temperatures (far lower than T_m), due to a very low proportion of fast dipoles, the effect of the internal field is not obvious. The smaller the internal field width is, the more unlikely it is that the transformation occurs, and consequently, the narrower the temperature region is where the susceptibility decreases markedly

The dependence of T_m on the internal field width is shown in Fig. 2. It can be seen that the internal field increases T_m. The curve has a plateau at a small internal field width where T_m remains at about $1.4\Delta J/k_{\mathrm{B}}$ until σ_e is larger than $3\Delta J/\mu$. The shape of the curve is similar to the dependence of T_m on dc external bias fields.[3,24] In terms of the relation of the acceptor doping concentration and the internal field width, we can conclude that T_m will increase with enhancing acceptor doping concentration, which is in good agreement with the acceptor doping experiments.[10,25]

Figure 3 shows the susceptibility as a function of the internal field width in several temperature regimes. The susceptibility curves at different temperatures exhibit a common characteristic: the susceptibility is almost independent of the internal field width at low internal field width, and then decreases linearly with enhancing internal field width. The plot is very similar to the curve of the dielectric constant against logarithmic aging time (Ref. 6, Fig. 1), which reflects a near-linear relationship between the internal field width and the logarithm of the aging time when the internal field width is not too large. The linear dependence has been observed in normal ferroelectric $BaTiO_3$.[26] For relaxor ferroelectrics, there is hardly any report on the time dependence of internal field during aging because of the technical difficulty. Since the reorientation and alignment of the defect dipoles between

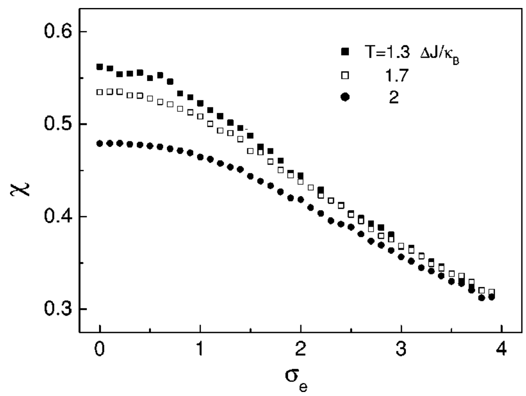

FIG. 3. The susceptibility χ as a function of the internal field width σ_e (in units of $\Delta J/\mu$) at different temperatures. The temperatures are, from top to bottom, 1.3, 1.7, and 2.0 (in units of $\Delta J/k_{\mathrm{B}}$). Herein, T_m without the internal field is taken as $1.4(\Delta J/k_{\mathrm{B}})$ and the measuring frequency is 70/(2000 MCS/dipole).

the polar microregion and normal ferroelectric domain are similar, the local internal field should obey the same familiar aging law as in normal ferroelectrics, namely, increase linearly with the logarithm of the aging time. From Eq. (3), this increase will lead to the linear increase of internal field width (or measured total internal field) with the logarithm of the aging time. According to the relation of acceptor doping concentration and the internal field width, our simulation results suggest that the aging phenomena is not obvious at low acceptor doping concentration.

The frequency dependence of the internal-field-induced susceptibility change $\Delta\chi=\chi(0)-\chi(\sigma_e)$ is shown in Fig. 4 when $\sigma_e=2.0\Delta J/\mu$ for various temperatures. Although $\Delta\chi$ decreases with increasing frequency at all temperatures, the shapes of the curves are different. From low temperature to high temperature, the shape of the $\Delta\chi\sim\ln(\omega)$ curve changes from concave to approximately linear, and then to convex. The aging of the susceptibility of relaxor ferroelectrics can be well fitted with the stretched exponential function:[27,28]

$$\chi_t=\chi_\infty+K\exp[-(t/\tau)^\nu], \tag{5}$$

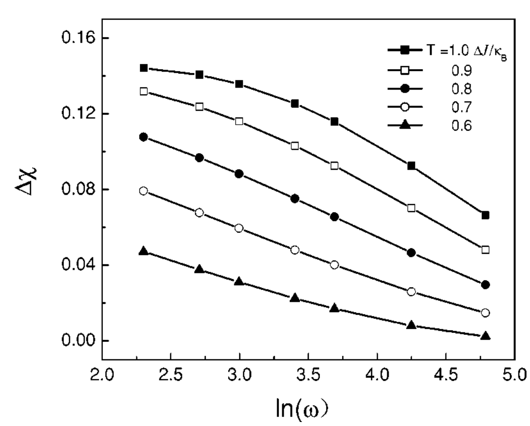

FIG. 4. The frequency dependence of $\Delta\chi=\chi(0)-\chi(\sigma_e=2.0\Delta J/\mu)$. The temperatures are, from top to bottom, 1.0, 0.9, 0.8, 0.7, and 0.6 (in units of $\Delta J/k_{\mathrm{B}}$).

where χ_t is the susceptibility at time t. Because the internal field width is zero when $t=0$ and reaches a fixed value when $t\rightarrow\infty$, $K=\chi_0-\chi_\infty=\chi(0)-\chi(\sigma_e)=\Delta\chi$. For many relaxors, the aging time constant τ is large and the distribution factor ν is small, and thus $\exp[-(t/\tau)^\nu]$ can be approximately expressed as $c(\tau,\nu)(\ln t+b)$ at large times. Therefore the aging of susceptibility is often written as

$$\chi_t=\chi_s-A\ln t, \tag{6}$$

where A is the aging rate.[9,12,13] Then we have $A \simeq c(\tau,\nu)\Delta\chi$. It is reasonable to assume that the aging time constant τ and the distribution factor ν are frequency independent. Therefore the curve shape of the aging rate A vs $\ln(\omega)$ is similar to the $\Delta\chi$ vs $\ln(\omega)$ curve shape shown in Fig. 4, which has indeed been observed by Wang *et al.*[9]

In summary, by introducing the pinning term of the internal field in the dipole glass model, we investigated the effect of the internal field on the aging of relaxors with the Monte Carlo method. The main results are as follows.

(1) Only at a small temperature region near T_m does the susceptibility decrease markedly due to the internal field. That temperature region expands with increasing internal field.

(2) The susceptibility is almost independent of the internal field width at low internal field width, and then decreases linearly with enhancing internal field width. This dependence of the susceptibility on the internal field width is very similar to the relation of the dielectric constant with logarithmic aging time, which suggests a linear dependence of the internal field on the logarithm of the aging time when the internal field width is not too large.

(3) The characteristic of the frequency dependence of the susceptibility change induced by the internal field is dependent on the temperature. From low temperature to high temperature, the shape of the $\Delta\chi$ vs $\ln\omega$ curve changes from concave to approximately linear, and then to convex.

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