

Monte Carlo simulation of the dielectric susceptibility of Ginzburg-Landau mode relaxors

J.-M. Liu* and X. Wang

*Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China
and International Center for Materials Physics, Chinese Academy of Sciences, Shenyang, China*

H. L. W. Chan and C. L. Choy

Centre for Smart Materials, Hong Kong Polytechnic University, Kowloon, Hong Kong

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The electric dipole configuration and dielectric susceptibility of a Ginzburg-Landau model ferroelectric lattice with randomly distributed defects are simulated using the Monte Carlo method. The simulated characteristics of the lattice configuration and dielectric susceptibility indicate that the model lattice evolves from a normal ferroelectric state to a typical relaxor state with increasing defect concentration. Consequently, the energy and dielectric susceptibility characteristics associated with the ferroelectric phase transitions become smeared. The simulated results approve the applicability of the Ginzburg-Landau model in approaching relaxor ferroelectrics.

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Ferroelectric relaxors have been receiving attention from physicists and materials researchers for over 40 years, mainly because of their fascinating electric-dipole ordering and phase transition phenomena and the excellent dielectric and electromechanic properties for practical applications.¹⁻⁶ The well-established features for the dielectric response of relaxors include the diffusive ferroelectric phase transition, strong frequency dispersion, and sensitivity to external electric bias. Over the past 40 years, a number of theoretical models were proposed to explain these features that are quite different from normal ferroelectrics, and those well-documented models include the compositional inhomogeneous model,¹ spin(dipole)-glass-like model,³ superparaelectric model,² and defect model,^{2,4} etc. One essence of these models is the existence of internal random field as induced by either compositional inhomogeneity or defects. This concept is popular and well accepted.⁵ The major effect of the internal random field is characterized by the coexistence of nanosized electric dipole clusters embedded in the matrix of paraelectric phase. These nanoclusters hold their stability over a wide range of temperature T , leading to a weak hysteresis of polarization above the phase transition point and the frozen microregions of electric dipoles at low T . In fact, the system at low T may exhibit the same behaviors as the normal ferroelectrics.

While some of the models mentioned above consider relaxors as spinlike systems,⁷ the Hamiltonian includes a term accounting the randomly distributed internal field. In addition to the statistical mechanics approach, the Monte Carlo (MC) method represents a popular technique employed to investigate the static and dynamic dielectric behaviors of relaxors.⁸ The predicted behaviors are similar somehow to those identified for spin-glass systems. The simplest and representative dynamics is the multistate Potts model with a random Potts field,^{9,10} in which the random field is imposed by assigning a variable spin-interaction factor or a variable internal electrostatic energy obeying some assumed distribution function, such as the Gaussian distribution. In these models, the dielectric relaxation is dynamically modulated

by the randomly distributed field. Consequently, the dielectric behaviors under different internal and external conditions have been investigated.¹¹⁻¹³ However, for an electric-dipole ordered lattice, the involved interactions may be more complicated. One needs to consider the Landau potential f_L , the dipole-dipole interaction f_{dip} , the gradient energy f_G associated with the spatial distribution of dipoles and long-range elastic interaction f_E , in addition to the electric field induced electrostatic energy f_S .¹⁴⁻¹⁶ It can be argued that in these interactions, the latter four terms are the resultant terms upon the dipole moment and alignment in the lattice, and only the Landau free energy is the origin to generate an electric dipole. Therefore, one may argue that introduction of a defect into the lattice will mainly influence f_L , and consequently modulate the other free energy terms. In fact, this is the main argument of the Ginzburg-Landau (GL) model for relaxors recently developed by Semonovskaya *et al.*,¹⁷ which allows us to access the evolution of the dipole configuration and dielectric property in a ferroelectric lattice as function of the induced defects.

In this report, we would like to perform a Monte Carlo study on the dielectric relaxation behaviors of a GL-model relaxor. The MC simulation is performed on a two-dimensional (2D) $L \times L$ lattice with periodic boundary conditions applied. Four equivalent orientation states $\pm[0,1]$, $\pm[1,0]$ for each dipole are allowed. We note that a three-dimensional (3D) simulation would produce more reliable simulations than the 2D simulation. In the earlier simulations based on the random-field models, 3D $16 \times 16 \times 16$ lattice was often employed, however, the one-dimensional size (16 lattice units) is too small for the present simulation based on the GL model, since the dipole-cluster statistics seems to be quite bad if one notes that the intercluster separation is ~ 10 lattice units. A 3D lattice larger than $40 \times 40 \times 40$ makes the computational capability unavailable to us because we would simulate the lattice evolution over a wide temperature range. As for the 2D simulations, Semonovskaya *et al.*¹⁷ employed a lattice as large as 128×128 . In our presimulation, we did not find substantial difference when L is reduced to 64 in

terms of the system energy and dielectric susceptibility evaluation. Therefore, we take $L=64$ in our simulations.

The GL theory on normal ferroelectrics was proposed earlier.^{15–17} For each lattice site, a dipole vector $\mathbf{P}=[P_x(\mathbf{r}),P_y(\mathbf{r})]$ with its moment and orientation defined by the system energy minimization, where P_x and P_y are the two components along the x axis and y axis, respectively, is imposed. It is known that for ferroelectric crystals the ferroelastic effect cannot be ignored. However, this effect would be weak for relaxors where no long-range ordering structure exists. The Landau double-well potential f_L is written as¹⁶

$$f_L(P_i)=A_1(P_x^2+P_y^2)+A_{11}(P_x^4+P_y^4)+A_{12}P_x^2P_y^2+A_{111}(P_x^6+P_y^6), \quad (1)$$

where subscript i refers to lattice site i and A_1 , A_{11} , A_{12} , and A_{111} are the energy coefficients, respectively. For normal ferroelectrics, the first-order phase transitions occur if $A_1 < 0$. When a spatial distribution of the dipoles exists, the as-induced gradient energy is f_G :^{16,17}

$$f_G(P_{i,j})=\frac{1}{2}G_{11}(P_{x,x}^2+P_{y,y}^2)+G_{12}P_{x,x}P_{y,y}+\frac{1}{2}G_{44}(P_{x,y}+P_{y,x})^2+\frac{1}{2}G'_{44}(P_{x,y}-P_{y,x})^2, \quad (2)$$

where $P_{i,j}=\partial P_i/\partial x_j$. Since parameters G_{11} , G_{12} , G_{44} , and G'_{44} are all positive, $f_G > 0$ in general, which favors the homogeneous dipole alignment in the lattice. The dipole-dipole interaction f_{dip} is long-ranged. In the SI unit, this term at site i is written as¹⁶

$$f_{\text{dip}}(P_i)=\frac{1}{8\pi\epsilon_0\chi}\sum_{\langle j \rangle}\left[\frac{P(r_i)P(r_j)}{|r_i-r_j|^3}-\frac{3[P(r_i)(r_i-r_j)][P(r_j)(r_i-r_j)]}{|r_i-r_j|^5}\right], \quad (3)$$

where $\langle j \rangle$ represents a summation over all sites within a cycle of infinite radius ($R \Rightarrow \infty$) centered at site i , parameters r_i , r_j , $P(r_i)$, and $P(r_j)$ here should be vectors, r_i and r_j are the coordinates of sites i and j , respectively. However, in simulation, a finite cutoff is needed and we take $R=8$ in our simulation. A difference of $\sim 2\%$ is estimated as compared with the value obtained at $R=30$ because f_{dip} decays very rapidly with vector (r_i-r_j) . Therefore, taking $R=8$ will not produce substantial error in the simulation. A minimizing of f_{dip} over the lattice favors a head-to-tail alignment of dipoles. Finally, the external electric field E introduces the electrostatic energy

$$f_S(P_i)=-P_i \cdot E, \quad (4)$$

where P_i and E should be vectors. The total interaction energy counting these interactions is

$$H=\sum_{\langle i \rangle}[f_L+f_G+f_{\text{dip}}+f_S], \quad (5)$$

which serves as the Hamiltonian for the system used in our simulation, where $\langle i \rangle$ represents a summation over the whole lattice.

As mentioned above, in the GL model,¹⁷ introduction of a defect into the lattice is thought to change the stability of a local dipole. For example, in $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) with acceptor dopants, where O^{-2} vacancies are introduced. Each vacancy may be combined with a metal impurity ion to form a defect dipole which may be imposed onto the local lattice dipole. Therefore, the moment of dipoles at these sites attached with defects can be enhanced or suppressed. In other words, the stability of these sites for a local dipole becomes site dependent. Because the stability of a dipole (its moment) is mainly determined by coefficient A_1 of the Landau potential Eq. (1), the randomly distributed defects in fact impose the spatial-dependent coefficients A_1 , A_{11} , A_{12} , and A_{111} in Eq. (1). Following the argument of Semenovskaya *et al.*, it is assumed that only A_1 is affected by the defects¹⁷

$$A_1(r_i)=A_{10}+b_m c, \quad A_{10}=\alpha(T-T^0), \quad \alpha > 0, \quad (6)$$

where $\alpha > 0$ is a materials constant, T^0 is a critical temperature for a normal ferroelectric crystal of the first-order phase transitions, parameter $c(=0,1)$ labels the defect state of a site. $c=1$ means that site i is imposed with a defect and it remains perfect if $c=0$. Parameter b_m is the coefficient characterizing the influence of defects on the dipole stability. In this model, coefficient b_m can be positive or negative in our simulation in order to model a suppression or enhancement of the dipole stability.

The MC simulation is performed via the following procedure. For a lattice, each site is imposed a dipole with its moment P and orientation randomly chosen within $(0-1.0)$ and the four equivalent states. Also, on each site is probably imposed a defect, with the probability determined by C_0 , the defect concentration of the lattice. A random number R_1 is generated and this site is attached with a defect ($c=1$) if $R_1 < C_0$, and not ($c=0$) otherwise. The defect type to this site is measured by a random number R_2 within $(-0.5, 0.5)$ associated with a choice of b_m within $(-b_M, b_M)$, where b_M is the maximal of b_m . The simulation begins at an extremely high temperature $T=8.0$ at which no freezing effect remains ($T^0=3.0$). The simulation follows the standard kinetic METROPOLIS algorithm for dipole flip among the all candidate states. For a site chosen randomly, all those energy terms defined in Eqs. (1)–(4) are calculated for the whole lattice to obtain $H=H_0$ from Eq. (5) and then this site is imposed with a new dipole chosen randomly to simulate the dipole flip. Those energy terms are calculated again and we obtain $H=H_1$. Consequently, a third random number R_3 is generated to compare with probability p defined below:

$$p=\exp[-(H_2-H_1)/T] \text{ if } H_2 > H_1, \quad p=1 \text{ if } H_2 \leq H_1, \quad (7)$$

where T is the temperature scaled by energy (kT) and the Boltzmann constant k is omitted. If $R_3 < p$, the dipole flip is approved and rejected otherwise. Then one cycle is completed. This cycle is repeated until a given number of cycles is reached.

The time of simulation is scaled by the Monte Carlo step (MCS) and one MCS represents $L \times L$ chosen flip events. In our simulation, at each temperature, the initial 600 MCS runs are discarded and then the configuration averaging is performed over the subsequent 2500 MCS. Here it should be pointed out that such a short time for configuration averaging is not long enough for simulating many statistical mechanical phenomena. However, it was verified that for spin-glass-like systems such as relaxors studied here, the short-time Monte Carlo simulation gave excellent agreement with experiments.¹⁸ In fact, we performed one averaging sampling over a time series as long as 40 000 MCS and no substantial difference of the data from our short-time data was found. In addition, the data presented below represent an averaging over four runs with different seeds for random number generator of both the initial lattice and defect distribution. Under an ac-electric field of frequency ω , the lattice dielectric susceptibility χ is written as¹⁹

$$\chi' = \frac{K}{N} \left\langle \sum_i^N \frac{1}{1 + (\omega\tau)^2} \right\rangle,$$

$$\chi'' = \frac{K}{N} \left\langle \sum_i^N \frac{\omega\tau}{1 + (\omega\tau)^2} \right\rangle, \quad (8)$$

where $\langle \rangle$ represents the configuration averaging, χ' and χ'' are the real and imaginary parts of χ , τ is the time for the dipole at site i flipping from one state to another, $N = L^2$ and K is a temperature-dependent constant. Because the lattice is inhomogeneous once $C_0 > 0$, time τ becomes site dependent and it can be expressed in the Arrhenius form¹⁹

$$\tau = \tau_0 \exp(\Delta H/T) = \tau_{00} \exp(-f_0/T) \exp(\Delta H/T), \quad (9)$$

where τ_{00} is the preexponential factor scaling the characteristic time for lattice vibration, τ_0 is the typical flip time for a noninteracting system which should be dependent of the defect concentration C_0 , f_0 is the Landau potential for a defective system of no dipole-interaction, and ΔH is the difference in Hamiltonian after and before the dipole flip. Under the assumption of nondipole interaction, f_0 is actually the Landau potential f_L in the mean-field approximation. Excluding the higher-order terms (fourth order and above), one has $f_0 \sim A_1 P_0^2 \sim [\alpha(T - T^0) + b_m C_0] P_0^2$, where P_0 is the averaged dipole moment (magnitude). Here, $\tau_{00} = 1.0$ and $\tau = \tau_0/n$ is obtained from the statistics of the MC sequences where n is the number of dipole flips at site i per MCS.

In the simulation, b_M is given and C_0 is treated as variables to investigate. The other lattice parameters are chosen and the dimensionless normalization of them is done following the works by Hu *et al.* on the dynamics of domain switching in BaTiO₃.¹⁶ These parameters are given in Table I. In addition, the external electric field takes the form E

TABLE I. System parameters used in the simulation.

Parameter	Value	Parameter	Value	Parameter	Value
T^0	3.0	α	1.0	A_{11}	-0.5
A_{12}	9.0	A_{111}	0.8	G_{11}	1.0
G_{14}	0.2	G_{44}	1.0	L	64
b_M	10	C_0	0-1.0		

$= E_0 + E_m \sin(2\pi\omega t)$, where E_0 is the dc bias, E_m is the ac-signal amplitude, and t is time.

Figure 1 presents the simulated dipole configurations at $T/T^0 = 0.3$ for three lattices of various defect concentration C_0 . As $C_0 = 0.0$ [Fig. 1(a)], a normal ferroelectric configuration with multidomained structure is shown. The parallel dipole alignment within each domain and the 90° head-to-tail domain walls can be identified. All dipoles within the domains have similar moment while those at the walls are smaller in moment. As $C_0 > 0$ [$C_0 = 0.4$, Fig. 1(b)], one sees clearly the lattice inhomogeneity and the moment of those dipoles near the walls begins to shrink, while it is interesting to note that the defects are randomly distributed in the lattice.

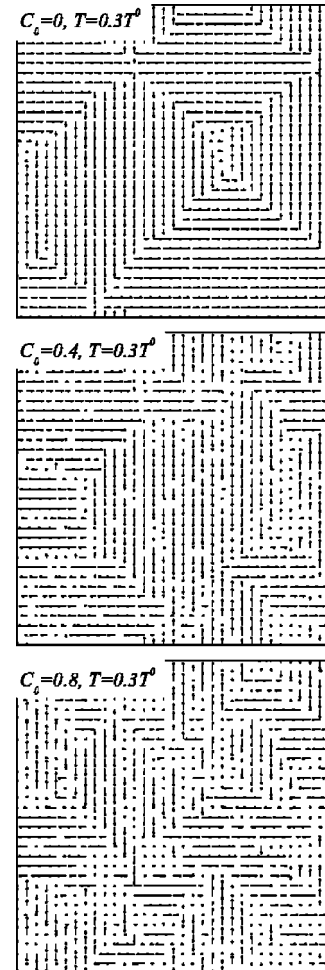


FIG. 1. Snapshot dipole configuration of mode ferroelectric lattice with different defects concentration C_0 at $T/T^0 = 0.3$. $E_0 = 0.0$, $E_m = 0.2$, and $\omega = 0.01$.

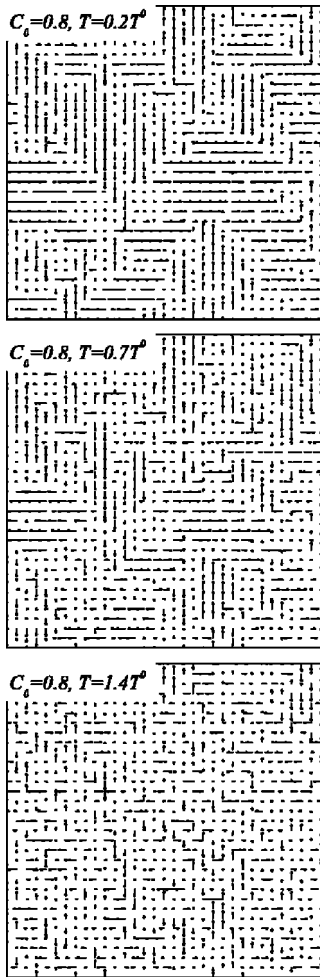


FIG. 2. Snapshot dipole configuration of mode ferroelectric lattice at different normalized temperatures T/T^0 as $C_0=0.8$. $E_0=0.0$, $E_m=0.2$, and $\omega=0.01$. The cycles label the dipole clusters.

As $C_0=0.8$ [Fig. 1(c)], the two-phase coexistence picture in the lattice becomes quite clear. The lattice consists of local ferroelectric regions embedded in the matrix of paraelectric phase, a typical pattern for relaxor ferroelectrics. We also observe the temperature dependence of this two-phase coexisted structure, as shown in Fig. 2, where $C_0=0.8$. While the ferroelectric phase dominates over the lattice as $T/T^0=0.2$, at $T/T^0=0.7$ the ferroelectric phase becomes minor and its size is much smaller than that at $T/T^0=0.2$. As $T/T^0=1.4$, the ordered dipole clusters become too small to be easily identified. Anyhow, one is shown that some small-sized dipole clusters remain stable at a temperature much higher than the stability point T^0 . Therefore, the present model produces a lattice configuration of dipoles consistent with our comprehensive understanding of relaxors.

The evaluated dielectric susceptibility as a function of T for several lattices of different defect concentrations as indicated is presented in Fig. 3(a) for real part and Fig. 3(b) for imaginary part. These curves are shifted for a clear illustration, and in fact the value of these curves at $T=6.0$ are very close to each other. The bigger C_0 is, the slightly higher the value is. As $C_0=0$, a typical ferroelectric phase transition

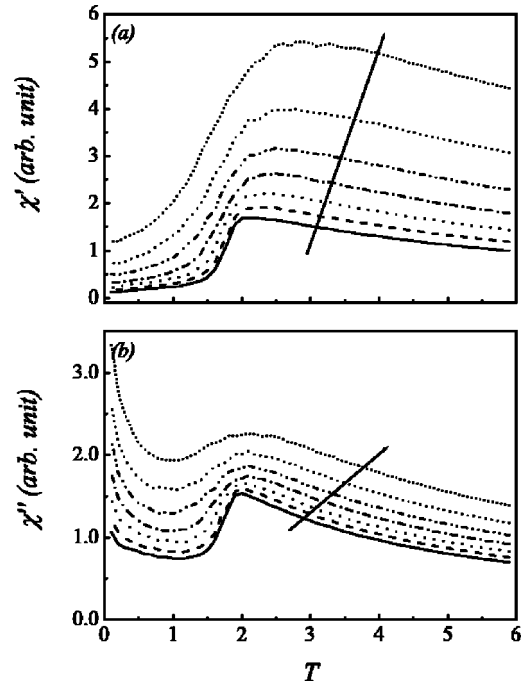


FIG. 3. Simulated dielectric susceptibilities χ' (a) and χ'' (b) as a function of temperature kT for different defect concentration C_0 (from bottom to top, $C_0=0.0, 0.1, 0.2, 0.4, 0.6, 0.8$, and 1.0). $E_0=0.0$, $E_m=0.2$, and $\omega=0.01$. The curves are shifted for eye guidance (see text).

with sharp dielectric peak χ'_m at $T \sim T_m$ is observed. With increasing defect concentration, the temperature dependence of both χ' and χ'' becomes diffusive and the transition peak shifts upward and T_m is slightly up to a higher value, indicating the typical dielectric characteristics for relaxors. As $C_0 > 0.6$, the temperature range covered by the ferroelectric transition is already very broad. It is well known that for a relaxor the dielectric susceptibility above T_m can be described by the following equation:^{20,21}

$$\frac{1}{\chi'} - \frac{1}{\chi'_m} = C^{-1}(T - T_m)^\gamma, \quad (10)$$

where C is a material constant similar to the Curie-Weiss constant and γ is the transition exponent characterizing the diffusivity of the phase transition. The bigger γ is, the more diffusive the transition is. A best fitting of the data shown in Fig. 3(a) by Eq. (10) produces the fitted parameters χ'_m , C , T_m , and γ as a function of defect concentration C_0 , as shown in Figs. 4(a) and 4(b), respectively. While χ'_m remains roughly unchanged, constant C drops down slowly and γ and T_m increases with C_0 , until $\gamma \sim 1.8$ at $C_0=0.6$ and above. This exponent is quite close to the experimentally evaluated values for several relaxors, such as $\gamma=1.64$ for PMN and 1.76 for PZN [$\text{Pb}(\text{Zr}_{1/3}\text{Nb}_{2/3})\text{O}_3$].²⁰ This is a positive evidence to support the present GL model.

Our simulation reveals a stronger frequency dispersion of the dielectric susceptibility for a lattice of higher C_0 . A lower χ'_m value and a higher T_m value are observed when frequency ω increases. We also simulate the effect of ac-field

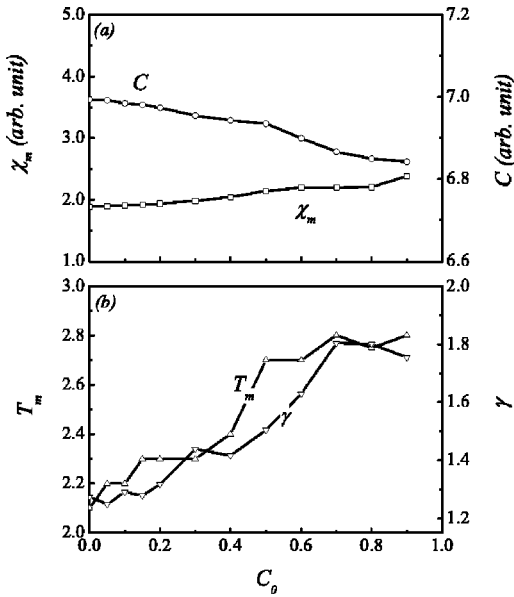


FIG. 4. (a) Evaluated maximal value of χ' , χ_m and constant C , and (b) evaluated temperature T_m for χ_m and transition exponent γ as a function of defect concentration C_0 . $E_0=0.0$, $E_m=0.2$, and $\omega=0.01$.

amplitude and dc-electric bias on the dielectric susceptibility. It is revealed that the value of χ'_m drops down and T_m shifts toward the higher value with increasing dc-electric bias. The effect of the ac-field amplitude is opposite to that of the dc-electric bias. With enhancing ac-field amplitude, the transition peak shifts upward and T_m approaches a lower value in the same time. All of these features are reflected in typical relaxors.

To understand this broadening behavior of the phase transition as reflected by the dielectric susceptibility as a function of T in a defective lattice, one may look at the evolution of the Landau potential and interaction terms f_L , f_{dip} , and f_G with defect concentration. In Fig. 5 are shown these terms as a function of T , respectively. As $C_0=0$, each of these terms as a function of T can be divided into two temperature regions: the paraelectric region and ferroelectric region, separated by a clean boundary around which the phase transition occurs. A prominent feature as reflected upon increasing C_0 is the obvious smearing of the boundary region. For f_L , the slope jump of the linear relation is disappearing with increasing C_0 . The rapid change of both f_{dip} and f_G over the low- T range is weakened as the lattice contains more defects. It is noted that in the low- T range, the dipole-dipole interaction and the gradient energy are lifted, and as a compensation a big drop of the Landau free energy is observed.

For the perfect lattice of no any defect, the ferroelectric phase transitions are mainly determined by coefficient A_1 in Eq. (1). As $T < T^0$, the paraelectric phase loses its stability. The introduction of defects into the lattice generates an inhomogeneity over the lattice where the stability for paraelectric phase varies from site to site. Some sites favor ferroelectric phase as $T \gg T^0$, while some others favor paraelectric phase as $T \ll T^0$. Therefore, the essence of the GL model for relaxors is to broaden the temperature range at which the

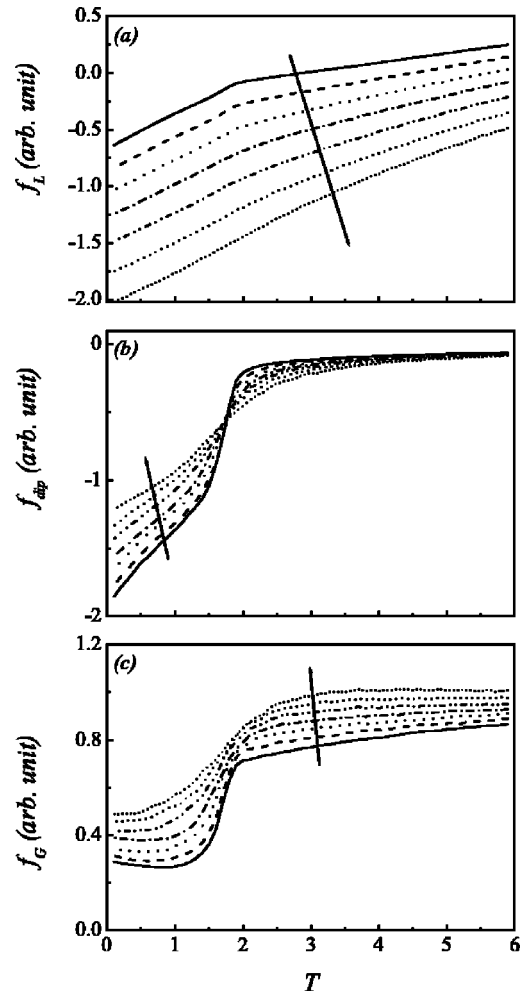


FIG. 5. Simulated Landau potential f_L , dipole-dipole interaction f_{dip} , and gradient energy f_G (per site) as a function of temperature kT , respectively, for different defect concentration C_0 (from bottom to top, $C_0=0.0, 0.1, 0.2, 0.4, 0.6, 0.8$, and 1.0). $E_0=0.0$, $E_m=0.2$, and $\omega=0.01$.

ferroelectric phase transitions proceed and the recorded transition region extends towards both the low- T range and high- T range in the same time.

Unfortunately, to the best knowledge of the authors, there has never been an experimental system reported in which the defect concentration can be modulated to cover the whole composition range, so that a direct checking of the present model becomes possible. It has been reported recently that an irradiation of some ferroelectric copolymers by electrons, ions, or protons introduces defects into the systems and results in an evolution of the dielectric behaviors from a normal ferroelectric state to a relaxorlike state.²² However, such an irradiation basically suppresses the ferroelectric phase transitions, probably by amorphization, while no dipole cluster can be stably retained at a temperature above the Curie point for the nonirradiated sample. Thus, such a defective system seems not compatible with the present model.

In conclusion, we have performed a Monte Carlo simulation on the electric-dipole configuration and dielectric behav-

ior of a Ginzburg-Landau ferroelectric lattice with randomly distributed defects. It has been revealed that introduction of the defects results in a gradual evolution of the system from a normal ferroelectric state to a typical relaxor state, characterized by the diffusive phase transitions, strong frequency dispersion, and enhancement of the dielectric susceptibility. A smearing effect of the Landau potential, the dipole-dipole interaction, and the gradient energy over the phase transition region has been observed. It is suggested that the present

Ginzburg-Landau model represents a realistic approach to the phase transition and dielectric property of relaxor ferroelectrics.

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*Author to whom correspondence should be addressed. Electronic address: liujm@nju.edu.cn

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