Coupled spherical pseudospin-phonon model and the pressure-temperature phase diagram of relaxor ferroelectrics

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A coupled spherical random bond-random field pseudospin-phonon model is presented, which explains the effects of pressure on the relative stability of the ferroelectric, relaxor-, and paraelectriclike phases and thus the temperature-pressure phase diagram of relaxor systems. Within this model we derived an expression for the dynamic susceptibility of relaxors, which describes the pressure and temperature dependence of the peak in the dynamic dielectric permittivity.

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I. INTRODUCTION

The relaxor phase in compositionally disordered perovskites is characterized by the appearance of nanosized polar clusters embedded in a nonpolar matrix.[1] In contrast to normal ferroelectrics, relaxors show a strong frequency dispersion of the dielectic properties in the radio frequency and microwave regions connected with a broad distribution of relaxation times.[2,3] The parent perovskite compounds of relaxor materials are typical monodispersive soft-mode ferroelectrics or antiferroelectrics. The disorder induced polar regions are formed far above the temperature region where the characteristic relaxor dispersion behavior is observed.[1] In a normal relaxor state the dipole moments of the polar clusters are randomly oriented and the crystal remains macroscopically cubic down to the lowest temperatures. However, depending on the composition, a ferroelectric phase may coexist with the relaxor state below a critical temperature T_c. Alternatively, the relaxor phase can be rather easily changed into a ferroelectric phase by the application of an electric field exceeding a critical value E_c. Hydrostatic pressure, on the other hand, induces a crossover from ferroelectric to relaxor behavior as recently shown in Ca-doped $KTa_{1-x}Nb_xO_3$,[4] as well as in $Pb_{1-x}La_x(Zr_yTi_{1-y})_{1-x/4}O_3$ (PLZT).[5] At high enough pressures it even produces a vanishing of the relaxor phase.[4]

In spite of many investigations, it is not yet definitely known whether the relaxor state in zero electric field is a ferroelectric phase broken up into nanodomains under the constraint of quenched random fields, or whether it is a kind of a dipolar glass state with randomly interacting polar microregions. Furthermore, none of the proposed models has so far been used to describe the pressure-temperature phase diagram of relaxors.

It has recently been demonstrated that many static properties of relaxors such as the linear and nonlinear dielectric permittivity and the NMR spectra can be described by the spherical random bond–random field (SRBRF) model.[6–8] This model is based on randomly competing ferroelectric (FE) and antiferroelectric (AFE) interactions between the reorientable polar clusters of different sizes in the presence of random fields.

Here we present a coupled SRBRF-phonon model which takes into account both the order-disorder as well as the displacive features of the relaxor behavior, and explains the effects of pressure on the relative stability of the ferroelectric, relaxor, and paraelectric phases. In particular, we show that hydrostatic pressure induces a crossover from the ferroelectric to the relaxor phase.[5] This is due to the fact that pressure increases the polar-phonon frequencies. Within the framework of a dynamic version of this model[9] we also present an expression for the dynamic susceptibility of relaxors, which explains the pressure dependence of the peak in the dielectric permittivity.

II. COUPLED SRBRF-PHONON MODEL

Since the polar clusters—which are the basic reorientable dipoles in the structure—vary not only in their orientation but also in their size, the system cannot be described by an ordering field of fixed length as in, say, Ising-type systems. The dimensionless continuous pseudospin order-parameter field $-\sqrt{N}\leqslant S_{i\mu}\leqslant+\sqrt{N}$, $(\mu=x,y,z)$, which is related to the dipole moment of the ith polar cluster, is subject to the spherical condition

$$\sum_{i=1}^{N}\vec{S}_i^2=3N, \tag{1}$$

where N is the total number of reorientable clusters.

The SRBRF Hamiltonian on a rigid lattice in the presence of an external field $\vec{E}$ is given by[6–8]

$$\mathcal{H}_S=-\frac{1}{2}\sum_{ij}J_{ij}^{(b)}\vec{S}_i\cdot\vec{S}_j-\sum_i\vec{h}_i\cdot\vec{S}_i-g\vec{E}\cdot\sum_i\vec{S}_i, \tag{2}$$

where g is an effective dipole moment corrected by the appropriate local-field factor. We assume that the bare interactions $J_{ij}^{(b)}$ are randomly frustrated and infinitely ranged in view of the long-range nature of the intercluster interactions and are described by a Gaussian distribution with mean value $J_0^{(b)}/N$ and variance $(J^{(b)})^2/N$. The random fields $h_{i\mu}$ are similarly normally distributed with zero mean and nonzero second cumulant,

$$[h_{i\mu}h_{j\nu}]_{av}^{c}=\delta_{ij}\delta_{\mu\nu}\Delta. \tag{3}$$

The total Hamiltonian of the coupled SRBRF-phonon system is now formally written as

$$\mathcal{H}=\mathcal{H}_S+\mathcal{H}_L+\mathcal{H}_{SL}, \tag{4}$$

where $\mathcal{H}_L$ represents the lattice Hamiltonian

$$\mathcal{H}_L=\frac{1}{2}\sum_{\vec{k}p}[\omega^2_{\vec{k}p}Q_{\vec{k}p}Q_{-\vec{k}p}+P_{\vec{k}p}P_{-\vec{k}p}], \tag{5}$$

and $\mathcal{H}_{SL}$ the pseudospin–polar-phonon coupling

$$\mathcal{H}_{SL}=\sum_{\vec{k}p} Q_{-\vec{k}p}\vec{\gamma}_{\vec{k}p}\cdot\vec{S}_{\vec{k}}. \tag{6}$$

Here we introduced the normal coordinates and momenta $Q_{\vec{k}p}$ and $P_{\vec{k}p}$, respectively, of polar optic phonons with branch index p, wave vector $\vec{k}$, and frequency $\omega_{\vec{k}p}$. Further, $\gamma_{\vec{k}p}$ represents the pseudospin–polar-phonon coupling constant and $\vec{S}_{\vec{k}}=N^{-1/2}\Sigma_i\vec{S}_i\exp(i\vec{k}\cdot\vec{R}_i)$ is the Fourier transform of the order-parameter field. The pseudospin–acoustic-phonon coupling does not contribute to the intercluster interactions in view of the presumed cubic symmetry of the nonpolar matrix.

As shown by Elliott *et al.*[10] one can derive an effective intercluster coupling by introducing displaced phonon coordinates, which are determined by the equilibrium condition $\partial\mathcal{H}/\partial Q_{-\vec{k}p}=0$. After this transformation the terms linear in the phonon coordinates in $\mathcal{H}$ disappear and $J^{(b)}_{ij}$ in Eq. (2) is replaced by an effective coupling $(J_{ij})_{\mu\nu}$. The random averaging makes the matrix of the effective coupling constants $\mathbf{J}_{ij}$ diagonal and isotropic, i.e.,

$$([\mathbf{J}_{ij}]_{av})_{\mu\nu}=\frac{J_0}{N}\delta_{\mu\nu};\quad ([\mathbf{J}^2_{ij}]^c_{av})_{\mu\nu}=\frac{J^2}{N}\delta_{\mu\nu}\ . \tag{7}$$

The parameters J_0 and J now represent the new effective parameters of the SRBRF model on a deformable lattice replacing $J^{(b)}_0$ and $J^{(b)}$, respectively. They are explicitly given by

$$J_0=J_0^{(b)}+\sum_p\frac{|\vec{\gamma}_{0p}|^2}{\omega^2_{0p}}-\frac{1}{N}\sum_{\vec{k}p}\frac{|\vec{\gamma}_{\vec{k}p}|^2}{\omega^2_{\vec{k}p}}, \tag{8}$$

and

$$J^2=(J^{(b)})^2+\frac{1}{N}\sum_{\vec{k}}\left[\sum_p\frac{|\vec{\gamma}_{\vec{k}p}|^2}{\omega^2_{\vec{k}p}}\right]^2-\left[\frac{1}{N}\sum_{\vec{k}p}\frac{|\vec{\gamma}_{\vec{k}p}|^2}{\omega^2_{\vec{k}p}}\right]^2. \tag{9}$$

III. EFFECTS OF PRESSURE

It is well known that in perovskites the phonon frequencies depend on the temperature and the hydrostatic pressure P.[4,5,11] To estimate the variation of J_0 and J with pressure we consider Eqs. (8) and (9) in which $\omega_{\vec{k}p}=\omega_{\vec{k}p}(P)$. The main contribution to $J_0(P)$ is given by the $\vec{k}=0$ term in Eq. (8) involving the sum over all polar optic branches p. Since in perovskites the squares of the phonon frequencies at the at the zone center ω^2_{0p} linearly increase with pressure,[12] this term will result to leading order in a linear decrease of $J_0(P)$ with increasing pressure. The next term, which has a negative sign, involves the average over the entire phonon-dispersion branch and is thus less important. This is so since the phonon frequency $\omega_{\vec{k}p}$ at $\vec{k}\rightarrow 0$ is lower than the average over the pth branch, as is indeed observed in the case in $\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3}$ (PMN).[13] Thus we obtain

$$J_0(P)=J_0(0)-\alpha_1 P+\ \dots . \tag{10}$$

In contrast to J_0, the phonon contribution to J^2 is determined by the fluctuation of the averages over the optic-phonon branches. For a flat spectrum this contribution would be precisely zero. In general, the optic branches have some dispersion, but we may expect that the pressure dependence of $J(P)$ is weaker than that of $J_0(P)$.

For $J_0<\sqrt{J^2+\Delta}$ long-range order cannot exist and the system is in a spherical glass (SG) phase at all temperatures, with a nonzero value of the SG order parameter $q(T)$.[8] If $\Delta=0$ as in magnetic spin glasses, a transition from a high-temperature paraelectric to a SG phase occurs at $T_f=J/k$. For $\Delta\neq 0$ and $\Delta\ll J^2$ the sharp transition disappears, but the nonlinear susceptibility shows a maximum at $T_f\approx\sqrt{J^2+\Delta}$.

For $J_0>\sqrt{J^2+\Delta}$, however, long-range order is possible and a phase transition to an inhomogeneous ferroelectric (IFE) phase occurs below the critical temperature

$$T_c=J_0\left(1-\frac{\Delta}{J_0^2-J^2}\right)/k. \tag{11}$$

Since J_0 depends on pressure P according to Eq. (10), T_c is also a function of P. Thus the relative stability of the ferroelectric, relaxor, and paraelectric phases is strongly affected by the application of hydrostatic pressure. Experiments show[4,5] that at low values of pressure T_c is a linear function of P, i.e., $T_c(P)\simeq T_c(0)-\alpha P$. This suggests that the Δ term in Eq. (11) is negligible at low P—in relaxors usually $\Delta\ll J^2$[6,7,14]—and thus according to Eq. (10) we find $\alpha_1=k\alpha$ and $J_0(0)=kT_c(0)$.

In the IFE phase, ferroelectric long-range order and spontaneous polarization $P_\mu=N^{-1}\Sigma_i\langle S_{i\mu}\rangle$ coexist with the spherical glass (SG) order represented by the Edwards-Anderson-type order parameter $q(T)=N^{-1}\Sigma_i\langle S_{i\mu}\rangle^2$. If the system is an inhomogeneous ferroelectric at $P=0$, and $T_c(P)$ is given by Eq. (11) in which $J_0=J_0(P)$, then a critical pressure P_c may exist beyond which ferroelectric order is not possible at any temperature, and a ferroelectric-to-relaxor crossover occurs. The critical pressure is given by the condition $J_0(P_c)=\sqrt{J^2+\Delta}$. Assuming $\Delta\ll J^2$, we can thus estimate the value of J from the experimental values of $T_c(0)$, α, and P_c using the relation $J\simeq J_0(0)-k\alpha P_c$. The thus calculated pressure dependence of T_c in the entire range $0<P<P_c$ is shown as a solid line separating the ferroelectric from the ergodic relaxor phase on the $T-P$ phase diagram presented in Fig. 1. The solid triangles represent the experimental points obtained by Samara in PLZT 6/65/35,[5] whereas the asterisk denotes the critical pressure P_c.[5] The horizontal line corresponding to the relation $J_0(P=P_c)$

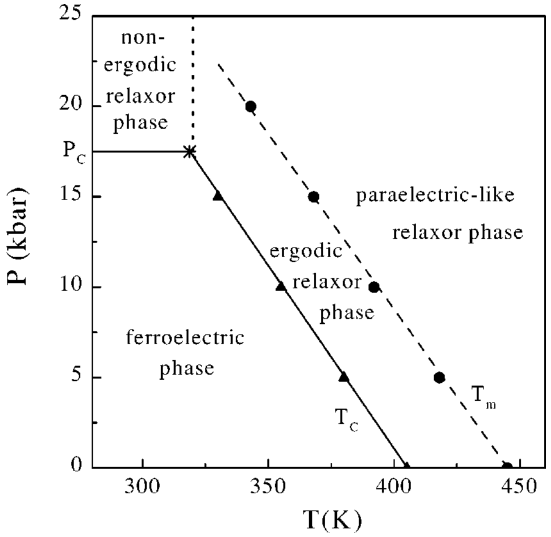

FIG. 1. Temperature-pressure phase diagram of the relaxor ferroelectric PLZT 6/65/35. The solid and dashed lines are evaluated from the static and dynamic coupled SRBRF-phonon models, respectively, whereas the solid triangles and solid circles are experimental points obtained by Samara (Ref. 5). The vertical dotted line corresponds to the freezing temperature T_f, where the static nonlinear permittivity has a peak.

$=\sqrt{J^2+\Delta}$ separates the ferroelectric phase from the nonergodic relaxor phase where the longest relaxation time diverges. The vertical dotted line corresponding to $T=T_f$ is determined by the peak in the static nonlinear dielectric permittivity.[8]

IV. DYNAMICS

Pressure strongly affects not only the static but also the dynamic properties of relaxors. At a fixed frequency ω the temperature dependence of the real part of the dielectric susceptibility $\chi'(\omega)$ shows a broad pressure dependent maximum at $T=T_m$. For $T>T_m$ the system is characterized by a weak dispersion corresponding to a paraelectriclike relaxor phase. For $T_f<T<T_m$ the system shows a strong frequency dispersion corresponding to an ergodic relaxor phase. For $T<T_f$ and $J_0<J$, however, the system is in a nonergodic relaxor phase, where the longest relaxation time diverges. With increasing ω, the maximum value of $\chi'(\omega)$ decreases, while T_m moves toward higher temperatures. Actually, in PLZT 6/65/35 it has been found that under hydrostatic pressure P the maximum temperature $T_m(P)$ moves towards lower values with increasing P^5 in a manner similar to $T_c(P)$.

To discuss the pressure and frequency dependence of T_m and to determine the boundary between the paraelectriclike and ergodic relaxor phases we adopt the concept of reorienting polar clusters[15] within the dynamic SRBRF-phonon model. Following the theory of spherical spin-glass models[16] we assume that the time dependence of the pseudospin field $\vec{S}_i$ is governed by the Langevin equation

$$\tau\frac{\partial}{\partial t}S_{i\mu}(t)=-\frac{\partial(\beta\mathcal{H}_S)}{\partial S_{i\mu}}-2z(t)S_{i\mu}(t)+\xi_{i\mu}(t). \qquad (12)$$

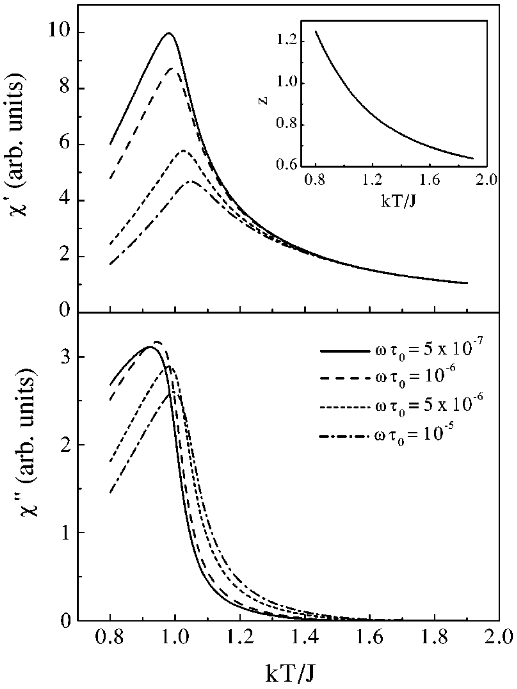

FIG. 2. Calculated temperature dependence of the real (top) and imaginary (bottom) part of the dielectric susceptibility $\chi(\omega)$ as given by Eq. (16). The inset shows the temperature dependence of the parameter $z(T)$ obtained from Eq. (14). The model parameters are $J_0/J=0.9$ and $\Delta/J^2=0.001$.

Here τ is a characteristic relaxation time for the reorientation of polar clusters and $\mathcal{H}_S$ is the SRBRF Hamiltonian (2) in which $J_{ij}^{(b)}$ has been replaced by the effective interaction J_{ij}. The function $z(t)$ plays the role of a Lagrange multiplier, which enforces the spherical condition (1) at all times.

The stochastic Langevin forces $\xi_{i\mu}(t)$ are specified by their ensemble average

$$\langle\xi_{i\mu}(t)\xi_{j\nu}(t')\rangle_{av}=2\tau\delta_{ij}\delta_{\mu\nu}\delta(t-t'), \qquad (13)$$

which ensures the proper equilibrium distribution.

Equations (12) can be solved exactly by introducing a representation of eigenstates and eigenvectors of the random matrix J_{ij}.[16] The details of this calculation will be presented in a separate publication.[9] In the asymptotic limit $t\gg t_c\approx 2J\tau/\Delta$,[16,9] the system reaches a steady state and the function $z(t)$ tends towards its static value z, which is determined by the equation

$$z-r+\frac{\beta^2\Delta}{2}\frac{z}{r}=\beta^2(J^2+\Delta), \qquad (14)$$

where $r\equiv\sqrt{z^2-\beta^2J^2}$. The calculated value of $z(T)$ is shown in the inset of Fig. 2. The result for the complex dielectric susceptibility is given by the following expression (for simplicity we set $g=1$):

$$\chi(\omega)=\frac{z-i\omega\tau/2-\sqrt{(z-i\omega\tau/2)^2-\beta^2J^2}-\beta J_0}{\beta(J_0^2+J^2)-2J_0(z-i\omega\tau/2)}. \qquad (15)$$

This result is valid in the phase without long-range order. The $\omega \rightarrow 0$ limit of Eq. (15) reproduces exactly the static susceptibility obtained earlier by the replica method.[8]

V. COMPARISON WITH EXPERIMENTS

Empirically, it has been found that the relaxation time in relaxors obeys the Vogel-Fulcher (VF) law $\tau = \tau_0 \exp [U/k(T-T_0)]$,[5,15] where the VF temperature T_0 has been identified with the freezing temperature T_f. In addition, relaxors are characterized by a heterogeneous dynamics[17] and a broad distribution of relaxation times.[18,19] To describe this we introduce a distribution of VF temperatures $w(T_0)$ in the interval $0 < T_0 < T_f$. Thus the observable dynamic susceptibility becomes

$$\overline{\chi(\omega)} = \int_0^{T_f} dT_0 \, w(T_0) \chi(\omega). \tag{16}$$

Assuming $T_0^{max} = T_f \simeq J$ and choosing a linear distribution $w(T_0) = 2(1 - T_0/J)/J$, we have evaluated numerically the integral in Eq. (16). In Fig. 2 the calculated real and imaginary parts of $\chi(\omega)$ are plotted as functions of temperature in the relaxor phase without long-range order for several values of frequency. The values of the parameters, which correspond to the system PLZT 6/65/35 are: $J/k = 318$ K, $J_0 = 0.9J$, and $\Delta/J^2 = 0.001$.

Since in PLZT 6/65/35 one has $T_m > T_c$, we can apply Eqs. (15) and (16) to determine the pressure dependence of T_m using the experimental values of $T_c(P)$, P_c, and the value of J derived from these as explained above. The maximum of the real part of $\chi(\omega)$ as a function of temperature has been found numerically from Eq. (16). Assuming a linear decrease of U with pressure[5] $U(P)/J = 6.5 - 0.13P/\mathrm{kbar}$, we obtain the pressure dependence $T_m(P)$ at $\omega\tau_0 = 10^{-5}$, which is shown as the dashed line in Fig. 1. The agreement with experiment[5] is rather good.

It should be noted that similar ideas were used earlier in discussing the impurity induced ferroelectricity in Li-doped $\mathrm{KTaO_3}$. As suggested by Vugmeister and Glinchuk,[20] the interaction of Li impurities with soft optical phonons of the highly polarizable $\mathrm{KTaO_3}$ lattice leads to a modification of the interaction between the off-center Li dipoles. The modified interaction is characterized by the correlation length r_c and a dimensionless parameter nr_c^3, where n is the Li concentration. The value of nr_c^3 controls the crossover from the glass like (relaxor) state to a true ferroelectric state. Based on this picture, Samara[21] proposed to use external pressure in order to change the value of r_c thus inducing the above crossover.

In conclusion, we have presented a coupled SRBRF-phonon model of relaxors, which explains the effects of hydrostatic pressure on the relative stability of the ferroelectric, relaxor, and paraelectric phases by a hardening of the phonon frequencies. This leads to a decrease of the mean intercluster coupling J_0 (favoring the ferroelectric state) while leaving its rms variance J (favoring the relaxor state) practically unchanged. Within the framework of this model we have derived an expression for the dynamic susceptibilty of relaxors, which describes the observed temperature and frequency dependence of the linear dielectric properties.

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[1] G. Burns, and F.H. Dacol, Ferroelectrics **104**, 25 (1990).

[2] G.A. Smolenskii and V.A. Isupov, Dokl. Akad. Nauk SSSR **97**, 653 (1954).

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

[4] G.A. Samara and L.A. Boatner, Phys. Rev. B **61**, 3889 (2000); G.A. Samara, J. Phys. Soc. Jpn. **28**, 399 (1970).

[5] G.A. Samara, Phys. Rev. Lett. **77**, 314 (1996).

[6] R. Blinc, J. Dolinšek, A. Gregorovič, B. Zalar, C. Filipič, Z. Kutnjak, A. Levstik, and R. Pirc, Phys. Rev. Lett. **83**, 424 (1999).

[7] R. Blinc, J. Dolinšek, A. Gregorovič, B. Zalar, C. Filipič, Z. Kutnjak, A. Levstik, and R. Pirc, J. Phys. Chem. Solids **61**, 177 (2000).

[8] R. Pirc and R. Blinc, Phys. Rev. B **60**, 13 470 (1999).

[9] R. Pirc, R. Blinc, and V. Bobnar, Phys. Rev. B **63**, 054203 (2001).

[10] R.J. Elliott, A.P. Malozemoff, S.R.P. Smith, W.S. Staude, and R.N. Tyte, J. Phys. C **4**, L183 (1971).

[11] G.A. Samara, *Fundamental Physics of Ferroelectrics 2000*, AIP Conf. Proc. No. 535, edited by R.E. Cohen (AIP, Melville, NY, 2000.)

[12] A.G. Beattie and G.A. Samara, J. Appl. Phys. **42**, 2376 (1971); G.A. Samara, *ibid.* **84**, 2538 (1998).

[13] B. Dorner, Ferroelectrics (to be published).

[14] V. Bobnar, Z. Kutnjak, R. Pirc, and A. Levstik, Phys. Rev. B **60**, 6420 (1999).

[15] B.E. Vugmeister and H. Rabitz, Phys. Rev. B **57**, 7581 (1998); **61**, 14 448 (2000).

[16] L.F. Cugliandolo and D.S. Dean, J. Phys. A **28**, 4213 (1995); **28**, L453 (1995).

[17] O. Kircher, B. Schiener, and R. Böhmer, Phys. Rev. Lett. **81**, 4520 (1998).

[18] D. Viehland, S.J. Jang, L.E. Cross, and M. Wuttig, Phys. Rev. B **46**, 8003 (1992).

[19] A. Levstik, Z. Kutnjak, C. Filipič, and R. Pirc, Phys. Rev. B **57**, 11 204 (1998).

[20] B.E. Vugmeister and M.D. Glinchuk, Zh. Éksp. Teor. Phys. **79**, 947 (1980) [Sov. Phys. JETP **52**, 482 (1980)]; Rev. Mod. Phys. **62**, 993 (1990).

[21] G.A. Samara, Jpn. J. Appl. Phys., Suppl. **24**, 80 (1985).