Diffuse Phase Transitions and Random-Field-Induced Domain States of the "Relaxor" Ferroelectric $PbMg_{1/3}Nb_{2/3}O_3$

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The diffuseness of the ferroelectric phase transition in $PbMg_{1/3}Nb_{2/3}O_3$ is proposed to be due to quenched random electric fields originating from charged compositional fluctuations. They are responsible for the extreme critical slowing down, the freezing into nanometric ferroelectric domains, and the slow relaxation of the polarization below $T_c \sim 212$ K. Barkhausen jumps during poling exclude glassiness, which was conjectured previously. At T_c a ferroelectric anomaly of the dielectric permittivity appears, if the random fields are overcome by an external electric field.

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Diffuse phase transitions (PT) in "relaxor" ferroelectrics, extending over a finite range of temperatures, ΔT, have been a challenging subject to both experimentalists and theorists ever since their detection nearly forty years ago [1]. As a rule [2], they occur in disordered ionic structures, in particular, in solid solutions. Within the Curie range ΔT, the dielectric permittivity achieves very high values and displays a large dispersion, which is reminiscent of that found for orientational glasses [3]. This is, in fact, the model which has recently [4] been applied to the best-known relaxor system, $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) [5], the structure of which is pseudocubic with vanishing spontaneous polarization P_s at all temperatures T [6]. It has to be stressed, however, that static freezing has not been evidenced yet, since the system continues to slow down beyond the laboratory time scale [7] in the vicinity of the decay temperature of the remanent polarization, $T_0 \sim 200$ K [4].

It has been argued [4] that the glassy behavior of PMN might be due to frustrated correlations between superparaelectric moments [8]. These are due to ferroelectric symmetry breaking on a nanometric scale, which was evidenced very recently by x-ray and neutron diffraction [9]. Profile analysis of the diffraction lines shows that correlated clusters with ⟨111⟩ distortions develop upon cooling from about 600 K to T_0. They are about 10 nm in diameter at low T. On the other hand, quenched compositional fluctuations extending over about 3 nm with one-by-one ordering of Mg^{2+} and Nb^{5+} cations on the perovskite B sites have been observed by transmission electron microscopical imaging [9]. These nanodomains carry negative charges and are thus intense sources of quenched random electric fields. These have to be taken into account together with compositional and, hence, space-charge fluctuations on smaller length scales in the interpretation of the observed diffuse PT.

In this Letter we propose that random fields (RF) are, indeed, at the origin of the observed tremendous slowing down of the dynamics of PMN and its eventual freezing into a domain state on a nanometric length scale. We refer to the original idea of Imry and Ma [10], pointing out the stability of domain states due to the local fluctuations of quenched microscopic fields in the case where the PT is driven by an order parameter with continuous symmetry. This situation seems approximately to apply to PMN despite its eightfold dipolar degeneracy, which reflects cubic anisotropy. It should be noted that only in the case of large cubic anisotropy is relaxation towards long-range order (LRO) expected [11], as in the case of Ising systems [10]. Very probably the PT of the low-anisotropy system PMN is destroyed by virtue of the RF. The observed "diffuse PT" merely signifies the rounding and the slow dynamics which is left. The ground state of PMN is, hence, disordered on macroscopic scales and therefore resembles a dipolar glass in many respects. There are, however, a number of arguments which are clearly in favor of the RF mechanism and the basic ferroelectric nature of PMN. In addition to the observation of ⟨111⟩ distorted nanodomains [9] we present new experimental data showing that (i) Barkhausen jumps of microdomains control the low-T poling process, and that (ii) a ferroelectric anomaly of the dielectric permittivity appears slightly above T_0 when applying a moderate poling field. The latter phenomenon, which was already observed previously [12,13], is explained in the spirit of Andelman and Joanny's idea [14] that the external field helps privileged domains to grow up to macroscopic size. The appearance of a sharp PT under similar conditions was recently evidenced on the ferroelectric RF Ising system $KTaO_3$:Li (KTL) with $x_{Li} = 0.063$ [15].

Optical experiments have been carried out on a single-crystalline platelet-shaped sample of PMN with polished (001) face, edges parallel to [110] and [1$\bar{1}$0], respectively, and size 2×1 mm^2. Two lateral faces of size 2×1 mm^2 were aluminized in order to apply electric fields E along [110]. Linear birefringence (LB) was measured at $\lambda = 589$ mm by use of standard methods [16] including a polarizing microscope in order to select strain-free sample sections. The field-induced LB is due to the polarization preferentially aligned along two of the eight dipolar ⟨111⟩

directions, [111] and [11$\bar{1}$]. At sufficiently high fields parallel to [110] only these two dipolar states are occupied. The polarization affects the LB directly via second-order electro-optics and indirectly via electrostrictive strain. The (001)-plane LB then reads $\Delta n = g_{44} n_0^3 P_s^2/2$ [17], where n_0 and g_{44} are the cubic refractive index and the total polarization optic coefficient, respectively. At lower fields and in the paraelectric regime, P_s^2 has to be replaced by $\delta P^2 \propto 3(P_\parallel^2 - P_\perp^2)/2$, where $P_\parallel$ and $P_\perp$ are the polarization components along [110] and [1$\bar{1}$0], respectively. The dielectric permittivity, ϵ' and ϵ'', was measured at a frequency $f = 1$ kHz along the [110] direction of another sample with thickness 0.35 mm under electric fields up to $E = 4$ kV/cm with an automatic bridge, HP 4192 A.

Figure 1 shows the intraplanar LB observed upon (i) field heating after zero-field cooling (ZFC/FH) with $E = 3.3$ kV/cm between 5 and 300 K, followed by (ii) field-cooling (FC) down to 5 K with $E = 3.3$ kV/cm, and (iii) subsequent ZFH again up to 300 K. Using equal heating and cooling rates, $|dT/dt| \sim 25$ mK/s, the limit of ergodicity of the system appears at $T_f \sim 234$ K, where FC and ZFC/FH curves split apart. Because of the slow dynamics of PMN, however, T_f only signifies a dynamic freezing temperature at frequencies in the hertz regime.

At $T \leq 160$ K the system appears completely frozen. On the one hand, zero LB in the ZFC/FH curve indicates a random distribution of spontaneously polarized domains and their complete immobility. On the other hand, nearly perfect coincidence of the large induced LB upon FC *and* subsequent ZFH shows the thermal stability of the polarized state once frozen in. The wiggly shape of the LB curves is due to interference effects by multiple reflection at the sample surfaces [18]. Defreezing of the induced polarization starts above 180 K quite rapidly, such that $\Delta n \sim 0$ at $T_0 \sim 200$ K. Similar observations of the field-induced strain [6] hint at the existence of an equilibrium phase-transition temperature T_c in the absence of random fields, $T_0 < T_c < T_f$. Unlike KTL, $x_{Li} = 0.063$ [14], which is a random-field Ising system, the electret state of PMN does not persist up to T_c, owing to its lower anisotropy connected with eightfold orientational degeneracy.

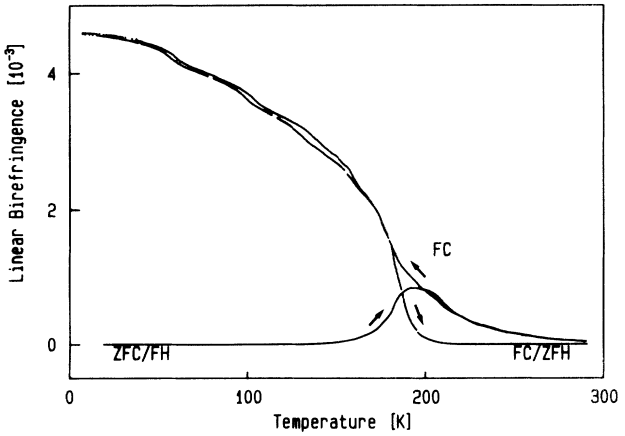

FIG. 1. Temperature dependence of the linear birefringence in the (001) plane of PMN induced by an electric field $E = 3.3$ kV/cm along [110].

Hysteretic effects are seen in field cycles of the induced LB as shown in Fig. 2 for three temperatures. In the paraelectric regime, at 285 K, the LB varies roughly as E^2, since $P \propto E$ in the low-field regime [Fig. 2(a)]. It is seen, however, that the cycles are not fully reversible despite their very low frequency, $f \sim 1$ cycle/h. At $T = 221$ K [Fig. 2(b)], under the same conditions, the hysteresis becomes substantially larger with a coercive field $E_c = 0.8$ kV/cm and a remanence of about $0.1\Delta n(E_{max})$, where $E_{max} = 2.7$ kV/cm. It should be noticed that Δn still increases after inverting the scanning direction at $E = \pm E_{max}$. This clearly indicates very sluggish relaxation in the submillihertz regime, which is even more pronounced in the ferroelectric temperature range at $T = 181$ K [Fig. 2(c)].

Time dependences of the field-induced LB as measured at $T = 221$ and 181 K are shown in Fig. 3. After ZFC, a field $E_0 = 3.3$ kV/cm was first applied in order to induce polar order and uniaxial strain. At both temperatures the LB rises sublinearly with time t, but apparently nonexponentially. This is seen from the finite slope, $|d\Delta n/dt|$, in the long-t limit. There is obviously *no* simple temporal dependence, e.g., according to a stretched exponential function. Occasionally, additional points of inflection do occur in both curves. Presumably they refer to subsequent different domain growth processes. Even steplike decreases of the LB are often observed. They can be traced back to the strong generation of intermediate "90°" domains (i.e., $P_s \parallel [1\bar{1}1],[1\bar{1}\bar{1}]$), which cause stripe domain patterns as observed recently under a polarizing microscope [12].

Figure 3(a) shows, after intermediate relaxation in zero field (see below), the poling process in a reversed field, $E = -E_0$. Under this condition, after initial monotonic sublinear increase of the LB, starting at $\Delta n \sim 0$, a

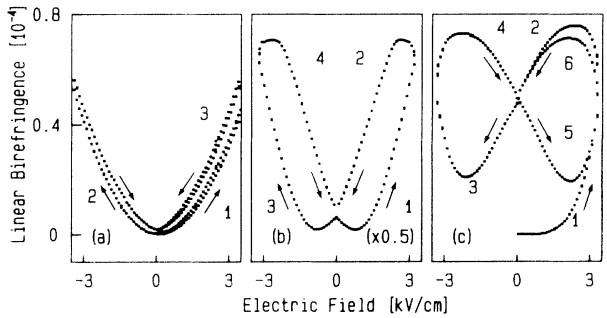

FIG. 2. Field dependences of the induced linear birefringence at (a) 285, (b) 221, and (c) 181 K, cycled as indicated by arrows and successive numbers.

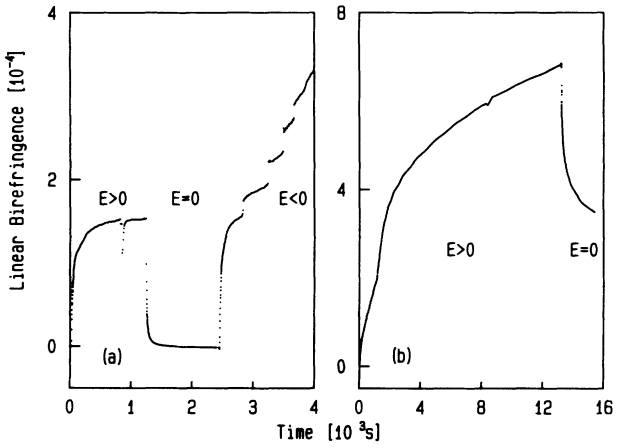

FIG. 3. Time dependence of the linear birefringence at (a) 221 and (b) 181 K measured successively under an applied ($E>0$), removed ($E=0$), and inverted electric field ($E<0$), where $|E|=3.3$ kV/cm for $E\neq 0$.

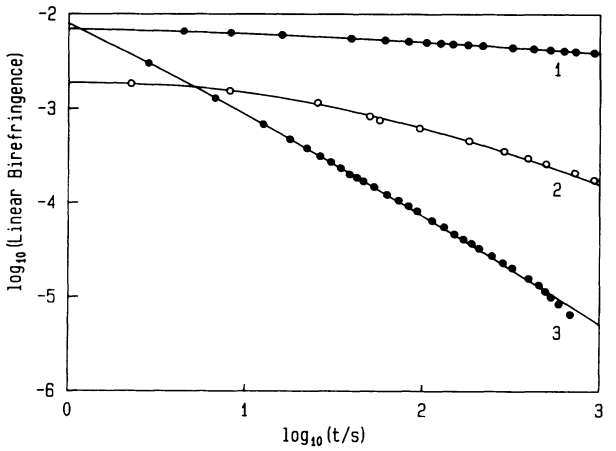

FIG. 4. Time dependence of the linear birefringence after isothermal poling with $E=3.3$ kV/cm at (1) 181, (2) 201, and (3) 221 K, respectively. Only part of the measured data (circles) is shown together with best-fit decay functions (see text).

number of discontinuities occur within a period of about 10^3 s. Obviously, avalanchelike depinning of microdomains takes place, thus giving rise to optically detected Barkhausen jumps. These are not compatible with glassy reorientation, which takes place on submicrometric length scales, hence, continuously and monotonically.

The decay curves of the polarization as measured after removing the poling field at 221 and 181 K (Fig. 3, curves "$E=0$") are monotonic and smooth. They are shown in a double logarithmic plot together with data taken in a similar way at $T=201$ K, in Fig. 4. It is seen that the decay slows down tremendously at decreasing temperature. In addition, the convexity of the functions increases significantly upon lowering T.

This impression is confirmed by testing the usual [19] set of decay functions applicable to random systems: logarithmic, stretched exponential, power, and generalized power laws. Best fits for the data at 181 and 201 K (solid lines in Fig. 4) are provided by the generalized power law

$$\Delta n(t)=\Delta n(\tau)\exp\{-b[\ln(t/\tau)]^{\beta}\},\quad t\geq\tau. \tag{1}$$

Whereas the parameter $\Delta n(\tau)$ merely describes the starting conditions, the exponents $b=0.02$ and 0.11 and the characteristic relaxation times $\tau=2.2$ and 0.3 s, respectively, reflect the acceleration of the decay with increasing T. Remarkably, however, we find an exponent $\beta=1.73$ in both cases, which indicates a substantial deviation from a simple power law, $\beta=1$. On the other hand, the 221-K data fitted by Eq. (1) yield $\beta=1.14$, hence, nearly power-law behavior (solid line in Fig. 4). A fit of the 221-K data by a power law is only slightly worse despite the use of only two fitting parameters.

Equation (1) describes the fluctuations of the order-parameter autocorrelation function $C_i(t)$ of droplets in a homogeneous surrounding with an inverted order parameter under the constraint of quenched RF [19]. This model is probably valid also in the present case, where the order parameter $\mathbf{P}$ is homogeneous at the beginning, $\mathbf{P}_{\parallel}$, and droplets with differently orientated polarization, $\mathbf{P}_{\perp}$, are thermally excited. The LB measures the spatial and temporal average of the quadrupolar order parameter, $\langle P_{\parallel}^2\rangle-\langle P_{\perp}^2\rangle$. Its variation is, hence, directly proportional to $C_i(t)\equiv\langle P_{\perp}^2(t)\rangle$. Contrary to the Ising case [19], however, the droplets in PMN tend to grow instead of decaying because of the low anisotropy and the high directional degeneracy of the order parameter in PMN. The validity of Eq. (1) in the case of droplet formation with thick domain walls [10] remains, hence, to be shown.

The situation at higher temperatures, $T=221$ K (curve 3), is qualitatively different, since a pure power law appears adequate. In fact, very probably an essentially paraelectric behavior is probed, since the Curie temperature of the system is $T_c\sim 212$ K (see below). Tentatively, we suppose that the temporal behavior of the LB describes the growth of a percolating paraelectric cluster within the homogeneously polarized single domain, which is stochastically pinned to the RF distribution. Very probably the paraelectric cluster is fractal. Its growth is hence described by a power law, e.g., as observed on fractal antiferromagnetic domains in diluted Ising antiferromagnets in zero field [20]. As a result of the considerable smearing of the ferroelectric transition, however, a transition regime between low-T generalized and high-T simple power-law behavior will be encountered. This might explain the slight departure of β from unity when fitting the 221-K data by Eq. (1).

Probably the most convincing piece of evidence for the ferroelectric nature of PMN is the observation of an extra peak in the dielectric permeability when applying an ordering field to the domain state. This is shown in Fig. 5 by comparing the ZFC and FH curves, ϵ' and ϵ'' vs T, between 120 and 300 K. Very clearly, the field, $E=4$

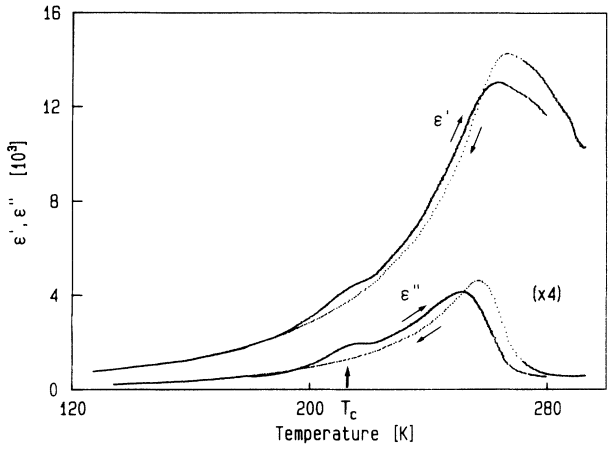

FIG. 5. Dielectric permittivity (ϵ',ϵ'') measured at 10^3 Hz upon zero-field cooling and successive field heating with $E=4$ kV/cm as indicated by arrows.

kV/cm, induces net, albeit broadened, peaks at $T_c \sim 212$ K. They are superimposed on the usual broad background, which is slightly decreased and shifted towards lower T as observed previously [12,21]. This is a consequence of partial poling of the network of *nonpercolating* ferroelectric clusters, which start to grow below $T=600$ K [9,22]. The extra peak at T_c, however, is attributed to the *percolating* cluster due to the Andelman-Joanny-type [14] suppression of the RF nanodomain structure. Sharper peaks of ϵ' vs T at T_c are induced by using higher fields, $E=20$ kV/cm [12,13]. PMN, hence, behaves similarly to KTL with $x_{\mathrm{Li}}=0.063$, whose ferroelectric ϵ anomaly, however, is observable even in zero field after FC. This signifies a basic difference between both systems, KTL being much closer than PMN to the RF Ising universality class, which has a long-range ordered ground state in three dimensions [10].

Summarizing, the RF field interaction is very probably at the heart of the extremely smeared ferroelectric phase transition of PMN. Our arguments *against* an orientational glass interpretation are (i) remanence curves $\langle P^2\rangle$ vs T, which mark lower limits of the transition temperature T_c; (ii) Barkhausen jumps indicating discontinuous domain rearrangements; (iii) field-induced peaks of ϵ' and ϵ'', which designate unsmearing by virtue of RF compensation; and (iv) generalized temporal power-law decay of the isothermal remanent polarization, which characterizes the reconstitution of a nanodomain state in zero field.

Clearly, the relaxational behavior of PMN and its connection with nonergodicity requires more attention, which has so far not been devoted to near-Heisenberg RF systems. Here we notice that the recently [4] reported de Almeida-Thouless-type line in the E-vs-T phase diagram of PMN does *not* prove dipolar glassy behavior. A similar phase line is also observed in the three-dimensional RF Ising model without frustration [20]. Moreover, the observed [4] Vogel-Fulcher-type divergence of the leading relaxation time at $T_f=217$ K does not unambiguously signify glassy freezing. An identical expression, $\tau=\tau_0\exp[a(T-T_c)^{-\theta\nu}]$ with $\theta\nu\sim 1$, is found within the activated dynamic scaling concept of the RF Ising model [19].

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