

Aging in a Relaxor Ferroelectric: Scaling and Memory Effects

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A crossover as a function of temperature is found in the zero-field aging properties of the relaxor ferroelectric $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$. Below a temperature near which nonlinear susceptibility has indicated a suspected phase transition, the time-frequency dependence shows simple scale-independent behavior resembling that for spin glasses. As in spin glasses, high temperature aging is stable as further aging occurs at lower temperature, but not vice versa, indicating hierarchical state arrangement. A more general interpretation of such effects is briefly discussed.

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The reasons why relaxor ferroelectrics freeze in states lacking long-range ferroelectric or antiferroelectric correlations remain uncertain [1,2]. Among the ways by which underlying chemical disorder might induce the disordered polarization state are random interactions between ferroelectric nanodomains (e.g., [3]), random anisotropy on nanodomains (e.g., [4]), and random polar fields on nanodomains (e.g., [5]). To the extent that random interactions and random anisotropy are important, the underlying Hamiltonian for the interacting nanodomain polarizations resembles the Hamiltonians for real spin glasses [6]. Since relaxors also show rough phenomenological resemblance to spin glasses in several regards, there has been substantial interest in the question of how far the analogy may extend [2,7,8].

The strong aging of the susceptibility of some relaxors [9,10] looks *prima facie* strongly similar to the corresponding phenomenon in spin glasses [11–13]. Both aging effects are much stronger than those found in typical dipolar glasses [14]. Most probes of the approach (as temperature is lowered) to a suspected glassy phase transition in relaxors are confounded by the very slow dynamics above the suspected transition temperature. This problem is more severe than in spin glasses because the nanodomains have inherently slower kinetics than do spins. Since aging is a probe of the energy landscape *within* the frozen regime it can provide a particularly important test of whether the frozen regime of relaxors actually has much in common with spin glasses, and a test of the generality of some aging features of disordered systems [13].

One of the most remarkable features of aging phenomena in spin glasses is that reductions in the ac magnetic susceptibility χ_M , which develop for a narrow range of temperatures close to an aging temperature T_A , can be stable after the temperature T is lowered, but not after it has been raised much above T_A . [The return of $\chi_M(T)$ to the nonaged curve for T a bit below T_A is called “rejuvenation.”] Most dramatically, sequential aging at several decreasing T ’s produces multiple such “holes” in $\chi_M(T)$, which can be measured (once) upon reheating [11].

A full interpretation is not yet established, but the general idea can be outlined [15–17]. On aging, the system approaches equilibrium, spending more time in low free-energy states. If the free energies of the transition states (mountain passes in a landscape picture) are not strongly correlated with the free energies of the occupied states (valley bottoms), the typical activation energies for transitions between occupied states will grow, reducing $\chi(f)$. Rejuvenation indicates that different degrees of freedom are involved in the aging at different T ’s. The $\chi(f, T)$ depends only on structure on a particular energy scale, set by an Arrhenius expression, and the free-energy differences among states separated by barriers on that scale are either too small or too dependent on T to age at much higher T . Aging at lower T involves equilibration among smaller valleys in the free-energy landscape, and all such aging is reset by transitions over larger features in the landscape at higher T [17].

Such hierarchically nested order requires that large numbers of degrees of freedom be coupled, because the key feature is that the detailed fine structures of different valleys differ; i.e., the state cannot be written as the product of a large number of independent few-degree-of-freedom modes [18]. Individual spins or nanodomains “freezing” independently in random fields, for example, could not produce such behavior [19].

In this paper we describe detailed measurements of such aging holes in the out-of-phase dielectric susceptibility χ'' of the relaxor ferroelectric: $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, PMN. PMN, probably the best-studied and most reproducible relaxor, is particularly suitable for studies of the aging of internanodomain order because various structural aging effects common in other relaxors are absent. (We have other data on $(\text{PMN})_{1-x}(\text{PbTiO}_3)_x$, called PMN-PT, and $(\text{Pb}_{1-x}\text{La}_x)(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3$ to be described in subsequent work, which show multiple messy aging regimes distinct from the phenomena described here.) A glassy phase transition at roughly 220 K has been suggested, based on extrapolations of nonlinear susceptibility, suggesting divergence at about $T = 230$ K [20,21] and based on thermal depolarization at about 210 K of the field-induced

moment [22]. There are no observed features in the susceptibility itself in this range, although a continuous change in the wave-vector dependence of the diffuse synchrotron x-ray scattering occurs for wavelengths of 5 to 50 lattice constants [2], with longer-wavelength correlations saturating at about 170 K [23].

Here we report a crossover, in the same T window indicated by other techniques, to a regime in which the time-dependent aging shows spin-glass-like scaling. (In this paper we do not address the question of whether there is a phase transition within this crossover.) Although some of the aging hole is lost on low- T thermal cycles, a large component of the hole remains stable as further aging occurs at lower T .

We used a single crystal of PMN grown by the Chokhralsky method, obtained from the Rostov-on-Don Institute of Physics. The sample had about 1 mm² surface area, with the main face perpendicular to the (111) direction, and was 0.22 mm thick. Contacts were made via sputtered gold pads. The complex $\chi(\omega)$ was measured by conventional frequency-domain techniques, using a bridge with a digital lock-in amplifier to detect current with a fixed applied ac voltage. Temperature was maintained with a standard transfer-line cryostat. Before each aging experiment the sample was heated about 20 K above T_A , then cooled to T_A at a rate of up to 20 K/min. [Other data taken using cooling directly from 350 K to T_A were similar but less reproducible due to uncertainties in the $T(t)$ profile.]

Figure 1 shows $\chi''(\omega)$ as a function of temperature T , illustrating the standard relaxor behavior. The inset shows an example of aging, including a hole aged into $\chi''(T)$ by holding the sample for a time at T_A . Such holes could always be erased by brief heating by about 10 K, but were partially stable under prolonged cooling, as discussed in more detail below.

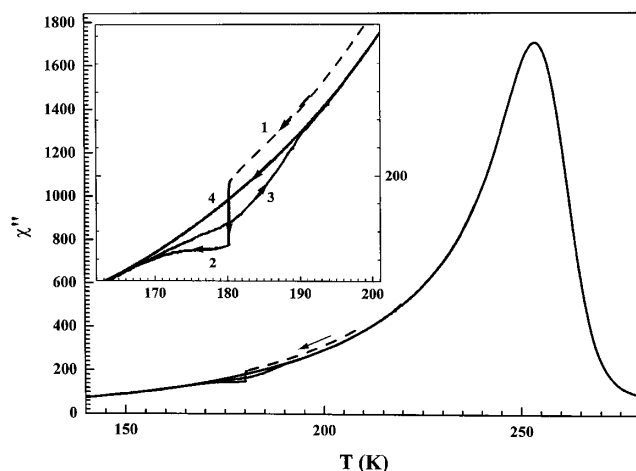


FIG. 1. χ'' (100 Hz, T) is shown, with data taken with a sweep rate of about 1 K/min. The inset shows aging after rapid cooling to 180 K (dashed line 1, taken at about -25 K/min) from 350 K. T was then held at $T_A = 180$ K for 64 hours (vertical line), then cycled down to 140 K and back (lines 2 and 3), with about ± 1 K/min sweep rates. The reference curve (line 4) is taken on cooling from 350 K at 1 K/min.

Figure 2 illustrates the dependence of the aging of χ'' (1 Hz) on the time t_w after T has been lowered to $T_A = 180$ K. A time-independent baseline plus a $t_w^{-\gamma}$ power-law decay fits these data very well. The starting time for the aging is kept as a slightly adjustable parameter, because the time required to cool to T_A depended on the thermal history of the cryostat. However, the range of adjustments for the cooling time is usually only from 100 to 300 s. The exponent γ and the time to reach T_A obtained from the fitting become essentially independent of the total aging time, so long as total aging times exceed about 10^4 s.

Logarithmic curves did not fit the time dependence nearly as well, at least for $T < 240$ K, giving obvious systematic residuals and χ -squared values at least 3 times as large as for the power laws. (We should note that previous reports of logarithmic aging were based on results at nonzero electric field [24].) Stretched exponentials, used to fit some different types of relaxor aging [25], did not come close to fitting these results.

γ was T dependent, as illustrated in the inset in Fig. 2. Error bars include uncertainty in the starting time and long-time baseline. There appears to be a rapid transition near 240 K from $\gamma = 0.17$ to $\gamma = 0.29$. Also, we found that the high- T regime does not fit the $t_w^{-\gamma}$ scaling as well as the lower- T regime does.

In spin-glass aging, $\chi''(\omega, t_w)$ comes close to scaling as a function of ωt_w alone, rather than depending on ω and t_w separately [13]. (Such scaling contrasts sharply with the behavior of some other related systems—e.g., aging in an orientational dielectric glass [26].) Figure 3 shows aging data from PMN taken at several T at different ω as a

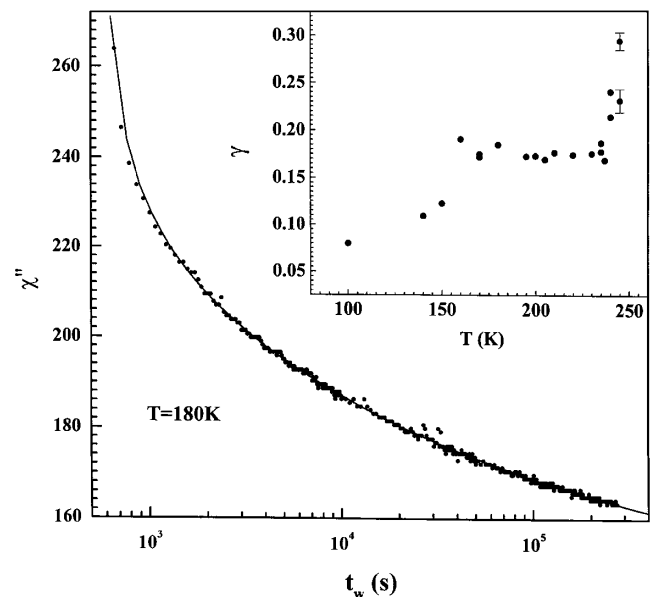


FIG. 2. The dependence of the aging of χ'' (1 Hz) on t_w at 180 K is shown, along with the fitting to a $t_w^{-\gamma}$ form. The inset shows γ as a function of T . Error bars are from standard χ -squared fittings including adjustable baselines and slightly adjustable starting times. Error bars from the fitting are shown when they are much bigger than the size of the filled circles.

function of ωt_W alone. At 235 K the aging does not scale well. (Above 240 K, the aging does not come remotely close to ωt_W scaling.) The aging at 225 K comes close to fitting ωt_W scaling. At 180 K the data collapse well onto a single curve. (Aging effects with ωt_W scaling have also been found in dynamical hole-burning experiments at a single T near the susceptibility peak in a related relaxor [25].)

Below 225 K, the form of the relaxation is well described by

$$\chi''(\omega, t_W, T) = \chi_0''(T) \left(1 + \frac{c}{(\omega t_W)^\gamma} \right), \quad (1)$$

where c is a monotonic decreasing function of T , falling from about 2.5 at 160 K to 2.2 at 210 K, before decreasing sharply between 210 and 245 K. $\chi_0''(T)$ increases monotonically and smoothly from about 100 at 150 K to about 800 at 230 K, showing no distinct features.

The qualitative features of the aging memory below 220 K (significant stability under low- T cycling, erasure under slight increases in T , power-law decay of χ'' , ωt_W scaling) resemble those found in spin glasses [13]. The ωt_W scaling is associated with the absence of any particular features in the distribution of characteristic rates near the experimental time scale but also requires that the interactions among modes at different frequencies be at most weakly dependent on the overall frequency scale. These features shared by PMN and spin glasses, along with

the nearly logarithmic decay of polarization (i.e., nearly frequency-independent χ'') [3], are typically expected for activated hierarchical dynamics [27], so long as the hierarchy has random free energies and thus can support aging. Such a model has been discussed at length in the context of the two-point and four-point correlations (corresponding to $\chi''(f)$ and to its time-dependent aging) in spin-glass fluctuation statistics [28].

Given the many shared features of PMN and spin-glass aging, we checked PMN for the most striking spin-glass result—the formation of low- T aging holes without significant loss of simultaneous high- T holes. Some of the aging hole is always lost on thermal cycling to lower T . (Spin-glass aging can also be lost at $T < T_A$, so long as the lower T is close to the original T_A [16], so our PMN results are not qualitatively different in this regard.) However, *a large component of the 160 K hole is completely stable as a second hole is aged in at 100 K*, as shown in Fig. 4. The key point is that the aging proceeds at 100 K without in any way disrupting (or increasing) the order responsible for the 160 K aging effect. (This result contrasts with the memory loss at T_A due to aging at about $0.6T_A$ in a disordered ferroelectric [29].)

The partial loss of memory on low- T cycles allows some experiments on the heterogeneous aging kinetics. As shown in Fig. 5, when the sample is returned to the original (higher) T_A , χ'' gradually relaxes back to the curve it would have been on had the time spent at that T_A not been interrupted, with the time coordinate remaining as the total time at T_A , as also found in spin glasses [16]. This result indicates that the same modes which reset quickly at lower T also reage quickly at the original T_A . If these two time scales were uncorrelated the reaging curve would instead be a reduced-amplitude version of the original aging curve, with the time origin reset to the time of the return to T_A . Similar results taken with small electric field perturbations

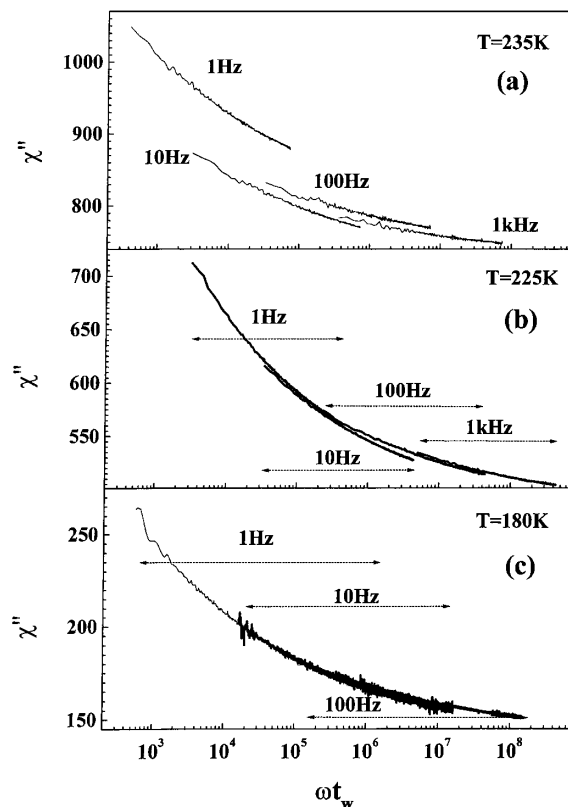


FIG. 3. $\chi''(\omega t_W)$ is shown at different T 's in (a)–(c).

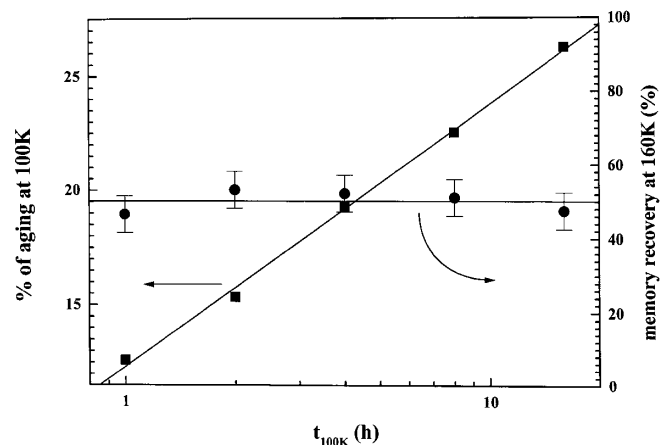


FIG. 4. How the hole in χ'' (40 Hz) at 160 K (formed by initially aging 120 min) and the 100 K hole change as a function of aging time at 100 K. The size of the 160 K hole is given as a fraction of its size before the low- T cycle. The size of the 100 K hole is given as a fraction of its extrapolated infinite-time limiting value.

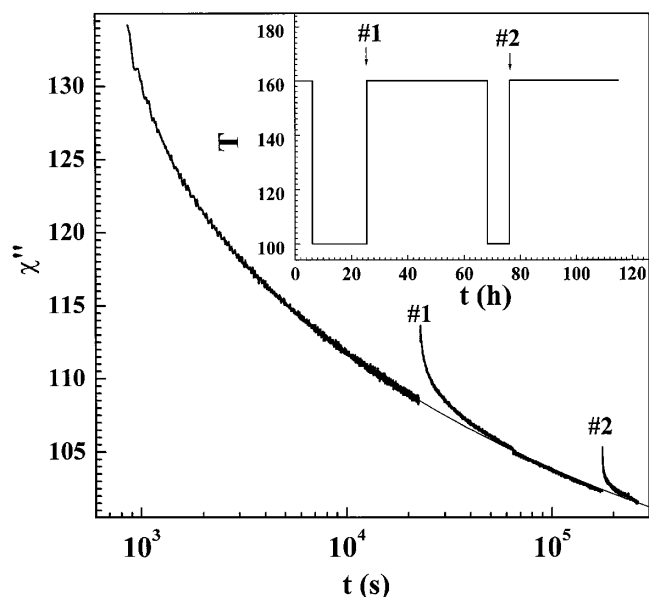


FIG. 5. χ'' (10 Hz) aging at 160 K interrupted twice by excursions of 69 000 and 27 000 s down to 100 K at the marked points, with the $T(t)$ profile shown in the inset. The horizontal axis includes only time spent at 160 K. The origin of the small glitch near 60 000 s is unknown.

during aging also show that when the field is returned to the original value, the aging curve asymptotically approaches the original curve, on the same time scale as the duration of the perturbing field, also similar to spin-glass results [16].

Our aging results show that one relaxor, PMN, has a low- T regime which exhibits not only the generic and nearly ubiquitous “ $1/f$ ” distribution of long relaxation times, but also a specific $(\omega t_A)^{-\gamma}$ scaling relation found for aging in spin glasses and expected for some hierarchical glassy kinetics models. Multi- T results show that the different detailed correlations which form as different energy scales equilibrate are at least substantially nested, as in spin glasses. Although in both cases full equilibration at $T < T_A$ destroys some of the correlations formed at T_A , in each case the normal aging effect can occur for T well below T_A without any further disruption of the correlations formed at T_A . Thus the free-energy landscape and its T dependence in the low- T regime of PMN are qualitatively similar to those found in spin glasses. There is a clear contrast with aging in disordered ferromagnets [13,17], which show much-reduced memory after low- T cycles, a result more similar to our findings in PMN-PT.

Some intriguing issues remain. The loss of aging at T_A on cooling to temperatures a bit below T_A , but not too far below it [16], is presumed to be due to “thermal chaos”—i.e., the T dependence of the relative depths of different minima in the free-energy landscape [30]. However, if T is lowered enough (see Fig. 4 again) further equilibration occurs only within the larger valley already chosen at the initial T_A , for purely kinetic reasons. Thus there are several different measurable T scales: the width around T_A of the holes, the T increase required to erase a hole, the

amount T can be reduced below T_A without stopping the reduction of $\chi(T_A)$, and the amount T must be reduced below T_A in order to stop further changes of either sign of $\chi(T_A)$. There is no well-established interpretation of the meaning of any of these scales, since translations of the hierarchical free-energy landscape into real-space pictures of metastable states remain speculative [15]. Careful comparisons of such temperature scales in different materials may help to clarify issues such as whether the rejuvenation effect arises from thermal chaos or just from hierarchical state arrangements.

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