Multiple aging mechanisms in relaxor ferroelectrics

Eugene V. Colla, Lambert K. Chao, and M. B. Weissman
Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801-3080
(Received 16 October 2000; published 7 March 2001)

In three relaxor ferroelectrics strong low-field aging effects are found for the dielectric susceptibility. Different regimes, marked by different time dependence and by different stability under subsequent thermal cycles and field changes, are found in different materials and at different temperatures. One regime strongly resembles aging in spin glasses, but others do not.

DOI: 10.1103/PhysRevB.63.134107 PACS number(s): 77.84.Dy, 77.80.Bh, 75.10.Nr, 77.84.−s

I. INTRODUCTION

The ways in which underlying chemical disorder leads to a disordered frozen state in the low-temperature regime of relaxor ferroelectrics remain poorly understood.[1,2] Proposed models include simple freezing of small ferroelectric nanodomains in the presence of polar disorder,[3] spin-glass-like frozen disorder induced by random interactions among polar nanodomains,[4] spin-glass-like freezing with a small but significant amount of polar disorder,[5] and spin-glass-like freezing with strong random anisotropy and weak random vector fields.[6] Probes of the dynamics within the frozen state should be useful to distinguish among different models, or at least to test the extent to which a single picture applies to different materials. Since relaxors, like many other frozen disordered systems,[7–13] show significant ''aging'' of susceptibility within the frozen regime,[14–19] we have studied details of the aging for three different relaxor materials. We find substantial diversity in the detailed behavior, suggesting that the relaxor category may lump together materials with significantly different underlying physics.[20–22] In particular, the spin-glass-like aging we reported in one material[16] is not universal in materials called relaxors.

Generically, aging refers to the gradual change (usually loss) of ac susceptibility when a material sits at fixed temperature T and applied fields (E for dielectric systems, H for magnetic ones, and stress for mechanical ones). Aging, unlike simple slow response, cannot result from simple collections of independent two-state systems but rather requires coupling between processes occurring at different rates.[23,24] Aging can be a complicated function of sample history, so it is characterized by a large number of parameters. Systems that show similar susceptibility and similar aging under simple conditions can turn out to have very different aging patterns when more complicated histories are studied.

In a simple experiment, T is lowered to some T_A and the complex susceptibility $\chi(\omega)$ is measured as a function of the aging time t_W. In some cases (e.g., spin glasses[9]) the reduction in $\chi(\omega)$ depends almost entirely on the product ωt_W rather than on the separate factors ω and t_W. Such ωt_W scaling shows not only that there is a broad distribution of relaxation rates for both the response and its aging, but also that the time scales for these two types of processes are linked. That result can indicate that the aging and response come from the same sort of degrees of freedom, as in hierarchical kinetic schemes.[25–28] If, on the other hand, the aging time scale is distinct from the response function time scale, one is led to suspect that these are distinct processes, e.g., the aging might result from the growth of ordered domains, and the response from other degrees of freedom within the domains.[29,30]

The stability of the aging effects under subsequent changes in T or field can also vary widely. In many but not all cases, slight increases of T erase any effects of prior aging at lower T.[9] In some cases, aging at T_A reduces χ at all subsequent measurements at lower T, but in other cases the effect is confined to a narrow window near T_A.[9] Aging below the initial T_A can either erase the effects of the aging at T_A, add to them, or leave them untouched.[9] In the latter case, one can age at a sequence of decreasing T's, then measure a sequence of ''holes'' in χ around those T's upon reheating.[9,31] Ordinary mechanical aging in structural glasses does not show such effects—so long as T is kept below the glass transition temperature, aging is close enough to being cumulative and irreversible to invite modeling as a simple reduction of a scalar parameter, the free volume.[12]

Perhaps the most interesting aging effects are those exhibited by spin glasses, in which the aging is believed to be directly connected with equilibration on the free-energy landscape for spin configurations within the spin-glass phase.[28,31] Other types of aging can involve effects less intrinsic to the frozen disordered state. For example, in materials with mobile defects, diffusion of defects can stabilize any particular frozen state when the frozen order involves strain.

In this paper we describe detailed measurements of the time dependence of aging and the stability of aging holes in the dielectric susceptibility of three relaxor ferroelectrics: $PbMg_{1/3}Nb_{2/3}O_3$ (PMN), $(PMN)_{1-x}(PbTiO_3)_x$ (PMN-PT), and $(Pb_{1-x}La_x)(Zr_yTi_{1-y})_{1-x/4}O_3$ (PLZT). We find aging dynamics that are not at all universal, with multiple regimes as a function of temperature and with strong dissimilarities between the different materials. In PMN (as we reported earlier)[15] and deep in the relaxor regime of PLZT, we find aging strongly resembling spin-glass effects, but aging in PMN-PT and in other temperature ranges in PLZT is qualitatively different. The phenomena are ''rich,'' i.e., too complicated for us to explain fully. Some speculative comments on the origins of the distinct aging regimes will be included at the end of the paper.

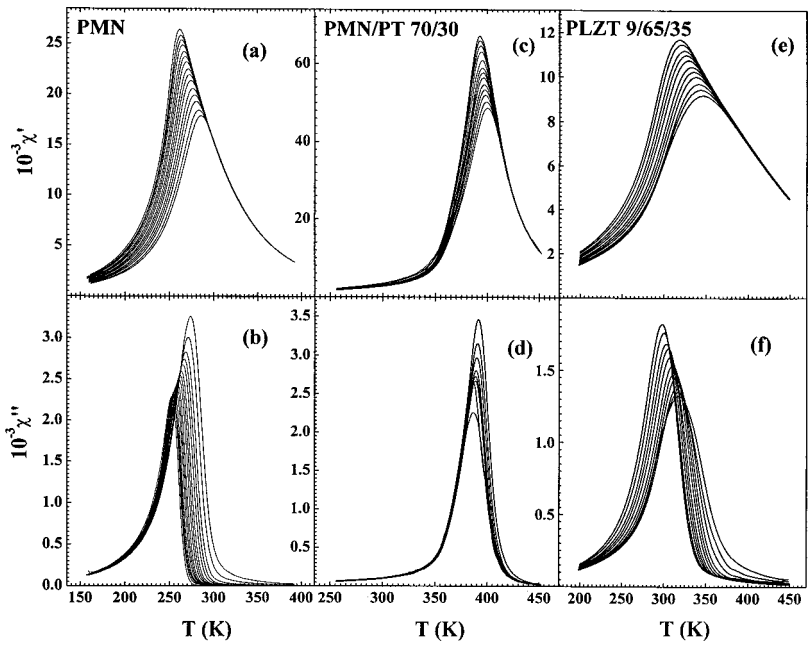

FIG. 1. $\chi'(T,f)$ and $\chi''(T,f)$ are shown for each sample at a range of f's from 20 to 200 kHz, in approximately equal log steps in f. The cooling rates were about 4 K/min, and the rms ac measuring field was 10 V/cm.

II. EXPERIMENTAL METHODS AND RESULTS

A. Techniques

The materials used were single crystals of PMN and of PMN-PT ($x=0.28$), and a transparent ceramic sample of PLZT ($x=0.09$, $y=0.035$). Each sample was about 0.2 mm thick with about 1 mm^2 surface area. Contacts were made via sputtered gold pads. The PMN sample was grown by the Chokhralsky method, with the main face perpendicular to the (111) direction. The PMN-PT sample, with the main face perpendicular to the (100) direction, was grown by the spontaneous crystallization method. These two samples were obtained from the Rostov-on-Don Institute of Physics. The PLZT sample was obtained from D. D. Viehland.

Susceptibility was measured by conventional frequency domain techniques using an ac bridge with a digital lock-in amplifier. Except as noted, all measurements employed ac measuring fields of approximately 4 V/cm on PMN and PMN-PT and 7 V/cm on PLZT, within the field range for which χ does not depend appreciably on field. Temperature T was maintained with a standard transfer-line cryostat, capable of changing T at rates up to about 20 K per minute. Because aging data are intrinsically slow to generate, we did not make as many different types of measurements on PMN-PT which seemed relatively uninteresting, as on PLZT and PMN.

B. Basic susceptibility and aging measurements

Figure 1 shows the real and imaginary dielectric susceptibilities (χ' and χ'') as a function of T for the three samples, measured in continuous T sweeps taken at cooling rates of about 4 K/min. All show the standard relaxor behavior found in these materials. A measure of the cooperativity of the freezing effects can be found in $d\ln T_P/d\ln(f)$, where $T_P(f)$ is the temperature of the peak in $\chi''(T,f)$. For simple Arrhenius processes with typical attempt rates, this log derivative is less than about 25, while in some spin-glass transitions it is as large as 700. For PMN and PLZT it is a little greater than 100, while for PMN-PT it is around 300, indicating some cooperative freezing effects, although not necessarily among separate nanodomains.

For PMN at these moderate cooling rates, there is very little hysteresis between the cooling and heating curves, giving a well-defined reference curve for comparison with aging results. For PLZT, aging effects near T_P are very large (as quantified below) even for moderate heating and cooling rates, making it difficult to obtain a standard $\chi(T)$ curve for comparison with aging results in that regime.

Figure 2 illustrates the basic aging and memory phenomenon in PMN. When T is held at a fixed value T_A (180 K here) $\chi''(T)$ steadily drops as a function of t_W. On subsequent cooling $\chi''(T)$ returns to the same curve that would have been reached on uninterrupted slow cooling. On slow reheating, there is a hole in $\chi''(T)$, i.e., a dip below the standard slow-cooling-slow-heating curve, centered around T_A with a width of about 5% in T. As one can see from $\chi''(T)$, slow dynamics are still present (including, as we shall see, aging) below 170 K, so the memory effect seen in Fig. 2 is nontrivial.

For PMN-PT, there is substantial hysteresis between the cooling and heating curves, shown in Fig. 3. As in spin glasses, $\chi''(T)$ does return to the reference curve when cooling after aging. However, most importantly, for PMN-PT $\chi''(T)$ on heating turns out to be independent of prior cooling history, including any pauses for aging during cooling, as shown. Thus although the initial aging in PMN-PT looks similar to that in PMN, PMN-PT completely lacks the key ''memory effect'' found in spin glasses, in PMN, and to some extent, in some other frozen disordered systems.[9]

Figure 4 shows a dimensionless model-independent aging magnitude, $d\ln\chi''(f,t_W)/d\ln(t_W)$ at $t_W=10^4$ s, in simple aging experiments (described above) as a function of T_A for

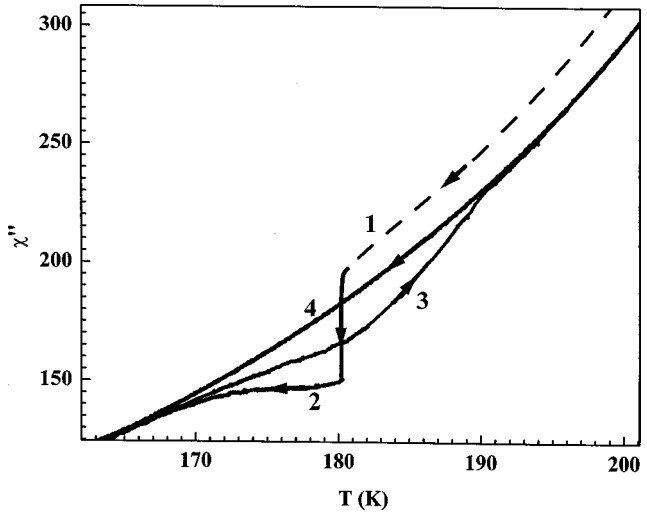

FIG. 2. A typical $\chi''(T)$ aging effect is shown. Dashed line 1 was taken during cooling at about -25 K/min from 350 to 180 K. T was then held at $T_A=180$ K for 64 h (vertical line), then cycled down to 140 K and back (lines 2 and 3), with about ± 1-K/min sweep rates. The reference curve (line 4) is taken on cooling from 350 K at 1 K/min.

each of the three materials. The magnitudes and temperature dependences of the aging effects are obviously quite different. For PMN, aging sets in near T_P and grows monotonically as T is lowered. For PMN-PT (for which we took sparser data), aging remains large near T_P. For PLZT, there is huge aging near and above T_P, but at low T the aging falls to a level very close to the low-T value for PMN.

Figure 5 shows examples of the decay of $\chi''(t_W)$ as a function of t_W for each of the materials, in several T regimes.

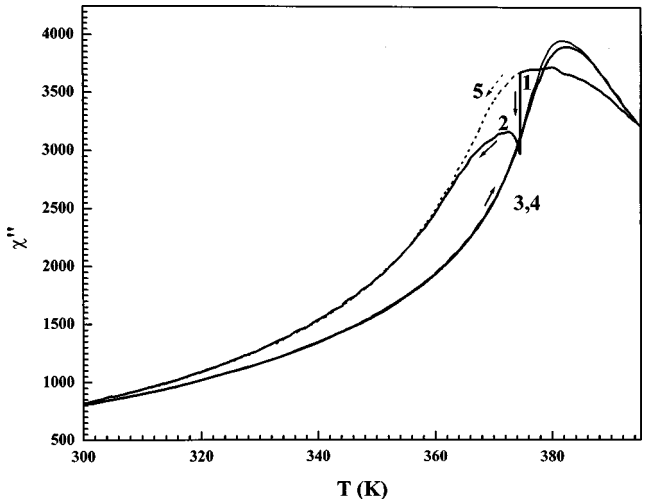

FIG. 3. $\chi''(T,10\,\text{Hz})$ on PMN-PT measured at 4 V/cm ac field. The numbers denote the order in which the data were taken, with all T sweeps at close to 2 K/min. Segment 1 includes cooling from 400 to 375 K and aging for 15 hr at 375 K. Segment 2 shows subsequent cooling to 300 K. Curve 3 shows reheating to 400 K. Curve 4 is a reference heating curve and curve 5 is a reference cooling curve, each taken without aging pauses.

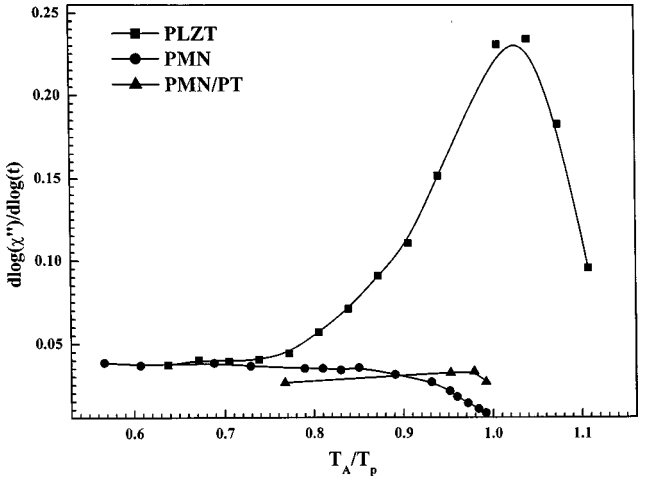

FIG. 4. The dimensionless aging rate at $t_W=10^4$ s is shown for PMN and PMN-PT (ac frequency 10 Hz) and PLZT (ac frequency 40 Hz).

PMN and PLZT each show a low-temperature regime for which the aging approximately follows a weak power-law decay in time,[15]

$$\chi''(\omega,t_W)=\chi_0''(\omega)\left(1+\frac{g(\omega)}{t_W^{\gamma}}\right). \tag{1}$$

PMN-PT aging does not fit this form as well, and instead shows simple logarithmic aging near T_P. Figure 6 gives the exponent γ for a range of T for PMN and PLZT. The data for $T>240$ K for PMN are very approximate, due to the small net aging rate in that regime.

C. Stability under perturbations

Figure 7 illustrates the stability of the aging memory in PMN and PLZT under the effects of rapid (roughly 5-K/min sweep rate) post-aging thermal cycles. In each case there is a strong asymmetry between the effects of heating and cooling. In all cases, slight heating (about 10% above T_A) erases most of the prior aging. In each case, slight cooling reduces the aging memory appreciably, but further cooling does not, leaving a substantial memory effect. Since the sweep rate was approximately constant here, the memory loss should be viewed as a *cumulative* effect over the entire range of T from T_A to the maximum excursion. Thus these data imply that memory is lost for T slightly below T_A, but much less so for T much below T_A.

The loss of memory in PMN and PLZT on rapid cooling cycles (at about 5 K/min) is shown as a function of T_A in Fig. 8. For PMN, the memory on these cycles grows monotonically as T is lowered below T_P. For PLZT, there is little memory loss on cooling near and above T_P, but there is a regime near 250 K with substantial memory loss, followed at lower T by a reentrant regime that exhibits increased memory on cooling cycles. The measured cooling rates in all the data were comparable, so the nonmonotonic dependence of memory loss on T_A is not an artifact of different times

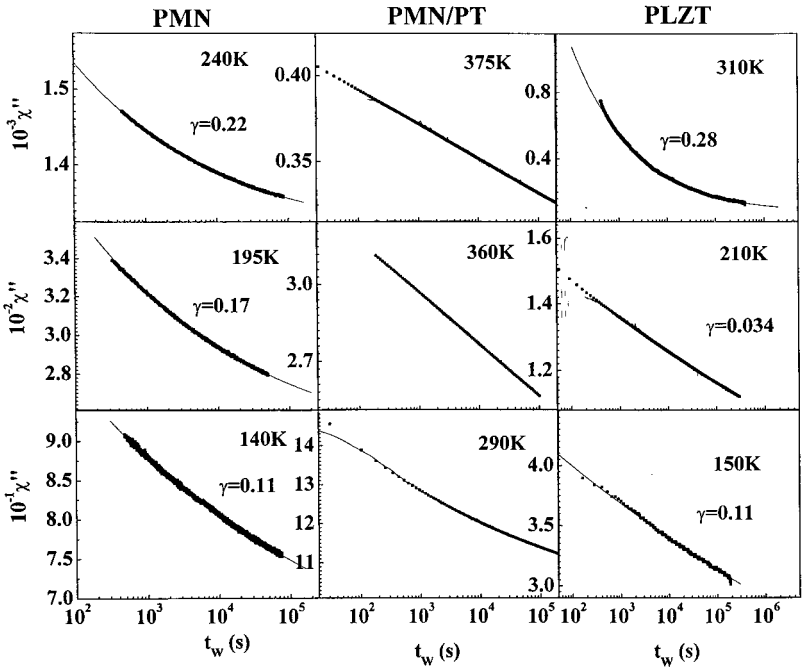

FIG. 5. $\chi''(t_W)$ is shown for a few representative cases. For the PMN data, the T drop preceding the aging was about 20 K. (Roughly similar results were found if the preaging T was 350 K.) For the other materials, T was dropped from 350 K before aging. t_W was calculated with an adjustable parameter, to allow for the delay before T reached T_A. The parameter was adjusted to obtain a good fit to either a power-law or logarithmic form, if either of these worked. In the cases shown, one form gave much smaller chi-squared than did the other. For these PMN data, the uncertainty in t_W is about 100 s, and for the other data a few hundred seconds, varying between data sets.

spent just below T_A. For the low-T points in PLZT, there was no change in memory if the cooling temperature was changed from 150 to 120 K.

Figures 9 and 10 illustrate the effect of prolonged second aging below T_A on the memory of the T_A aging. In PMN (Fig. 9), for reduction to 0.63 T_A, there is some loss of the aging effect during the temperature cycle. However no memory loss was found during the prolonged aging at 0.63 T_A, despite the substantial aging occurring at this lower T. For intermediate reductions (e.g., to 0.94 T_A) the hole at T_A is reduced as the new hole forms during prolonged aging at the lower T, as expected from the transient cooling data. For PLZT (Fig. 10), low-T aging coexisted with a persistent high-T hole in the regime $T_A < 200$ K and for T_A at (and presumably also near) 300 K. Figure 10 illustrates this persistence for $T_A = 180$ and 300 K, as well as the loss of memory found for $T_A = 270$ K.

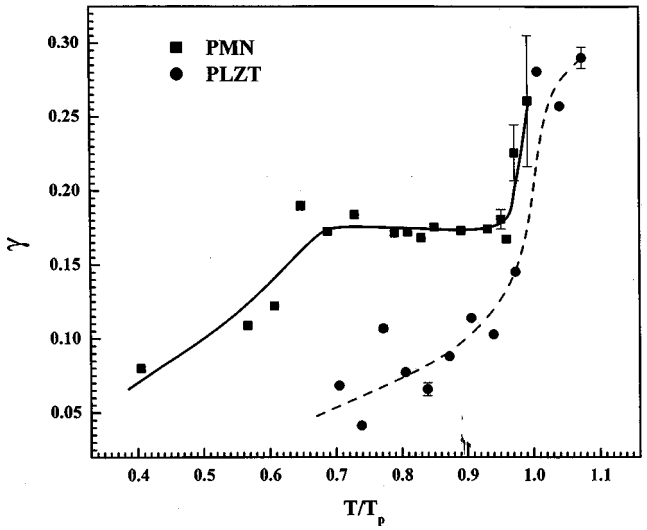

FIG. 6. The exponent γ is shown for those cases for which it could be calculated. Error bars are from standard chi-squared fittings including adjustable baselines and slightly adjustable starting times. Error bars are larger for data taken after large-T decrements than for data taken after smaller decrements, due to larger uncertainty in the $T(t)$ profile of the sample and hence larger error bars on the starting time.

D. Detailed scaling properties

We reported previously[15] that below 220 K, PMN aging exhibits clean ωt_W scaling, with increasingly prominent deviations at higher T, as illustrated in Fig. 11(b). In the scaling

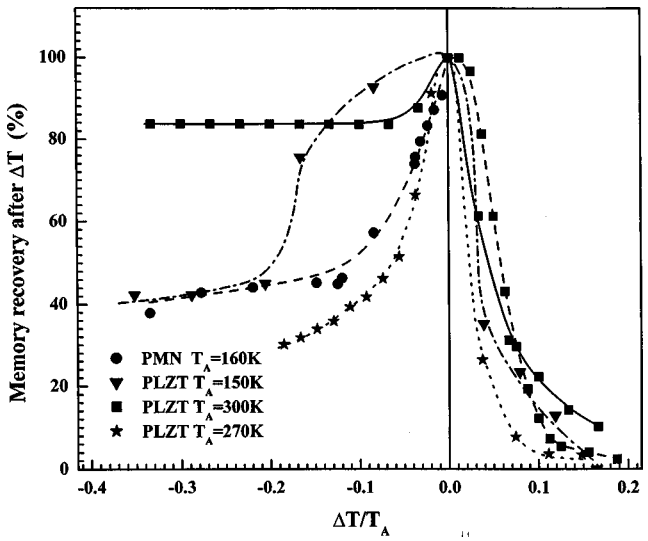

FIG. 7. The aging memory (remaining hole size) is shown as a function of temperature excursion from T_A for PMN and PLZT at a few different T_A. All data were taken with sweep rates of about 10 K/min.

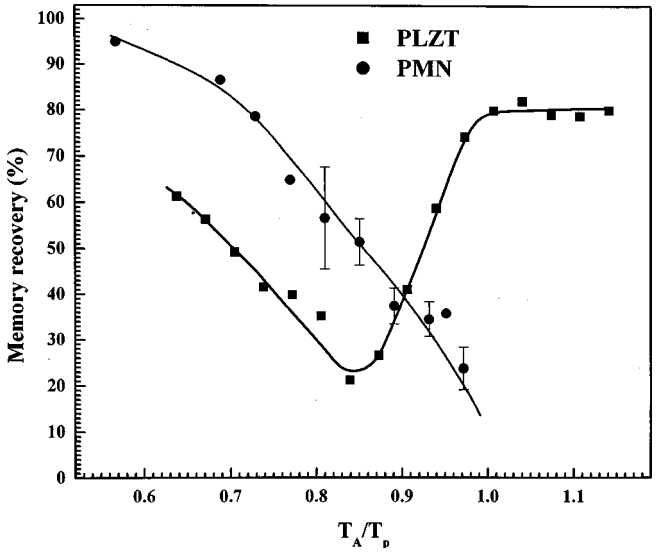

FIG. 8. The aging memory after cooling cycles, at about 5 K/min, down to 100 K for PMN and down to 150 K for PLZT is shown as a function of T_A/T_P.

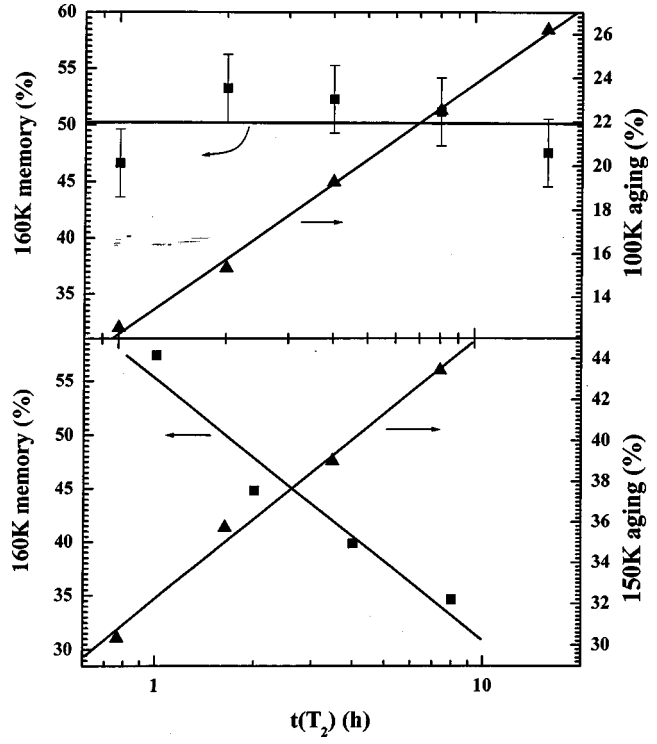

FIG. 9. The effect of aging in PMN at $T_2<T_A$ on the aging memory at T_A is illustrated. After aging 2 hr at T_A (the temperature referred to on the left-side axis), T was lowered to T_2 (the temperature referred to on the right-side axis) and held for a fixed length of time, before measuring $\chi''(T)$ on a heating sweep through T_A. After heating enough above T_A to reset the memory, the process was repeated with a different duration at T_2. The aging at T_2 is shown as a percent of the long-time asymptotic aging, estimated from the extrapolated power-law fit to $\chi''(T_2,t_W)$ and the initial $\chi''(T)$ curve. For some T_A, T_2 pairs, the manifest effects of aging at T_2 have no effect on the memory at T_A.

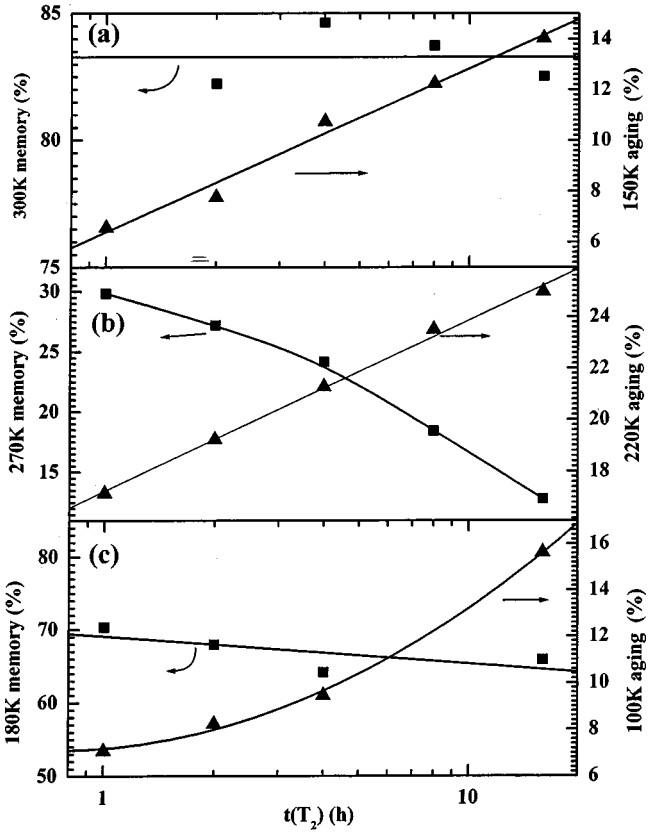

FIG. 10. These PLZT data were taken by the same procedure as the PMN data of Fig. 8.

regime, the long-term asymptotic χ'' has very little frequency dependence, and the aging data can be described by

$$\chi''(\omega,t_W,T)=\chi_0''(T)\left[1+\frac{c}{(\omega t_W)^{\gamma}}\right], \tag{2}$$

where c is a dimensionless number about equal to 2.

The high-T regime of PLZT is, as in PMN, very far from showing ωt_W scaling, but in the low-T regime the deviations become less pronounced, as shown in Fig. 11. These remaining low-T deviations from scaling were not fully reproducible, and may be due to some artifacts that are hard to avoid because χ'' is small in this regime. Figure 12 shows that at high T_A aging in PLZT *increases* the frequency dependence of $\chi''(T,f)$, in contrast to the reduction in frequency dependence found in PMN at low T. The relatively small size of the aging near T_P in PMN makes a direct comparison of matching regimes difficult.

E. Recovery from perturbations

As we have seen, cooling cycles substantially perturb the aging. On returning to T_A, the aging in PMN resumes, asymptotically approaching the same $\chi''(t_W)$ curve expected for simple aging at the initial T_A, as shown in Fig. 13. The recovery time is short compared to the time spent at lower T, not surprisingly since we have already seen that the aging memory loss during the prolonged time at the lower T is negligible, with the memory loss only occurring as T is

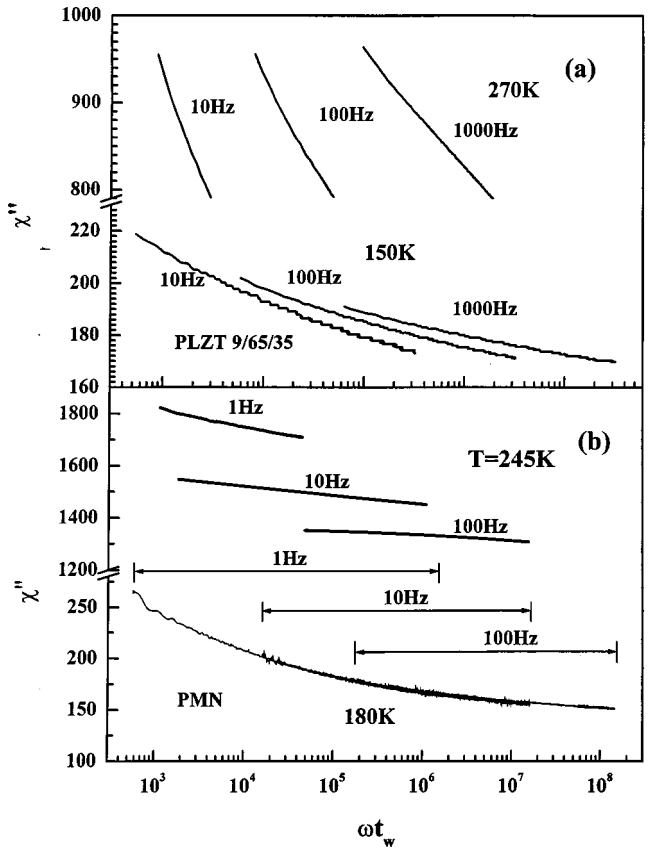

FIG. 11. $\chi''(f,t_W)$ is illustrated for a discrete set of f, as a function of ωt_W for both PMN and PLZT at several T. Scaling, i.e., collapse onto a single curve, is found at lower T in PMN.

swept just below T_A. It is important that here t_W is only the time spent at T_A, not including time spent at lower T.

The time required to forget an aging effect can be correlated with the time required for it to occur. Figure 14 shows that memory recovery at $T_A = 180$ K, after fixed-rate cycles

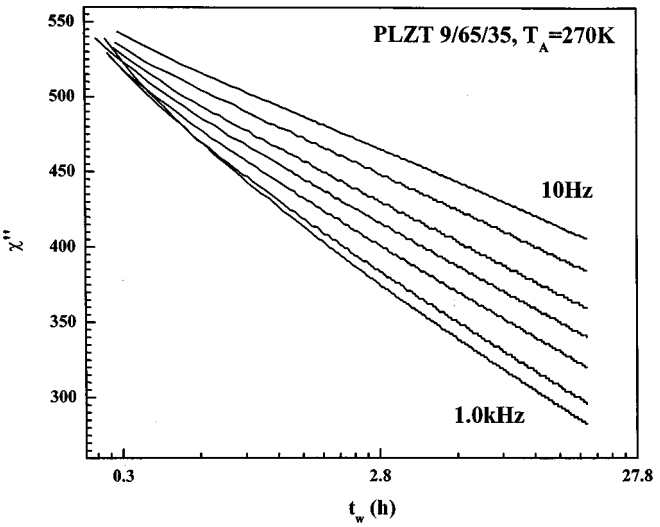

FIG. 12. Aging of $\chi''(f,t_W)$ in PLZT is shown for a range of f. Unlike PMN and PLZT at lower T, aging increases the frequency dependence of χ''.

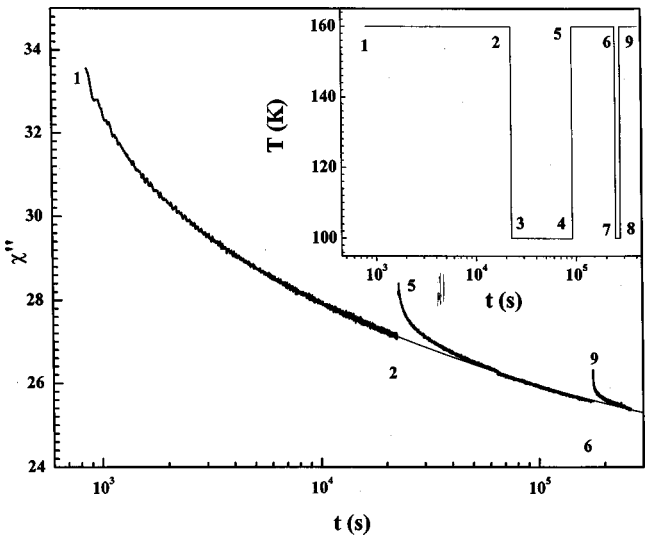

FIG. 13. Aging of $\chi''(10\,\text{Hz})$ for PMN at 160 K (after cooling from 350 K at about 15 K/min) interrupted by two excursions down to 100 K, as shown in the inset. The horizontal axis includes only time spent at 160 K. The origin of the small glitch near 60 000 s is unknown.

to lower T, as a function of the initial aging time. Clearly those aging effects that form after longer initial aging are more persistent during these low-T cycles.

The aging can also be reset by changing the field E, as shown for PMN at 160 K in Fig. 15. When the initial field is restored, the aging asymptotically recovers to the $\chi''(t_W)$ curve expected for simple aging at a single E, on a time scale about equal to the time over which E was perturbed. Here t_W includes time spent at *each* E field, in contrast to the cooling cycle data, for which the time spent at the lower T must be omitted. The magnitude of the loss of memory on changing E was a monotonic function of ΔE, reaching about 50% loss in the vicinity of 500 V/cm.

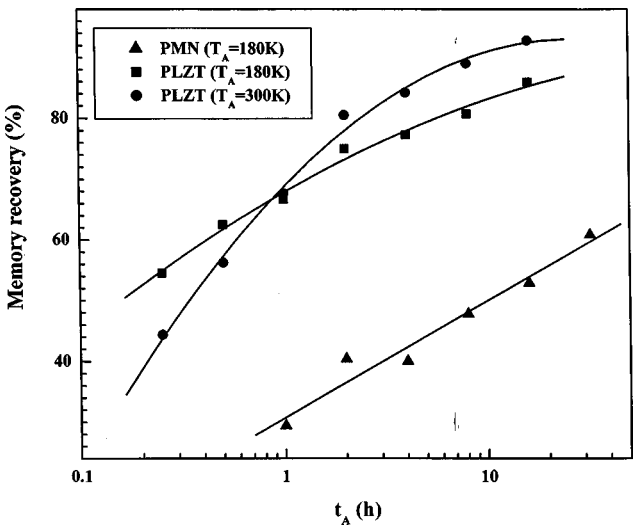

FIG. 14. The memory of holes in $\chi''(T_A)$ is shown as a function of the initial aging time after cycles at sweep rates of ± 4 K/min down to $T_2 < T_A$. For $T_A = 180$ K, $T_2 = 100$ K, and for $T_A = 300$ K, $T_2 = 150$ K.

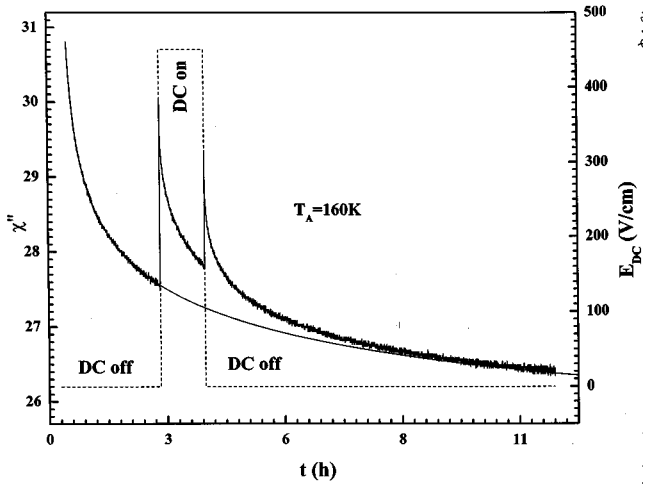

FIG. 15. Aging of $\chi''(10\,\mathrm{Hz})$ for PMN at 160 K (after cooling from 350 K at about 15 K/min) interrupted twice by applications of $E=400$ V/cm. The horizontal axis includes total time spent at 160 K.

Figure 16 shows aging in PLZT interrupted by changes in E at $T_A=160$ and 300 K. The low-T data are similar to those found in PMN. At 300 K, in contrast, the aging curve does not asymptotically approach the initial curve, at least on the time scale of these experiments.

Figure 17 shows peculiar effects in the initial data taken from a PLZT sample after aging for about a year in storage

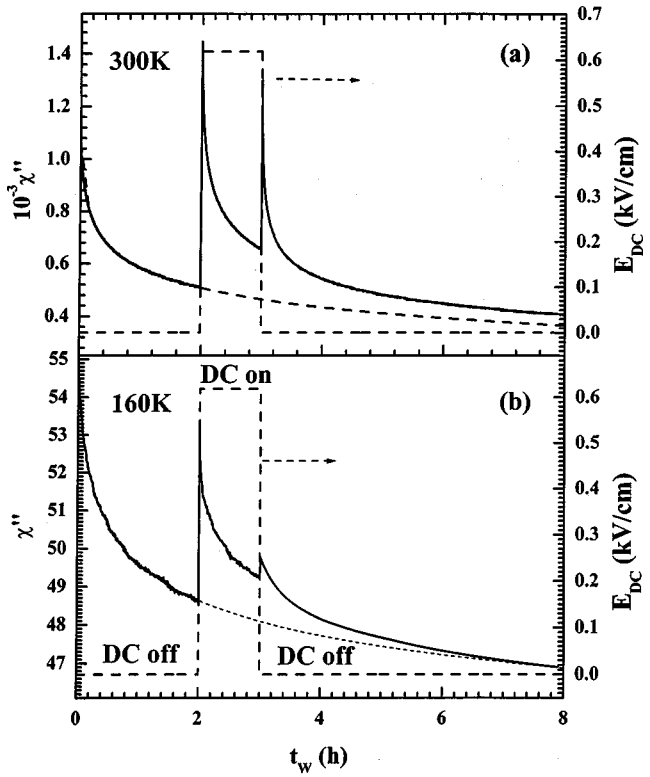

FIG. 16. Aging of $\chi''(10\,\mathrm{Hz})$ for PLZT at 300 K (part a) and 160 K (part b) (after cooling from 350 K at about 17 K/min) interrupted by applications of $E=600$ V/cm. The horizontal axis includes total time spent at T_A, regardless of E.

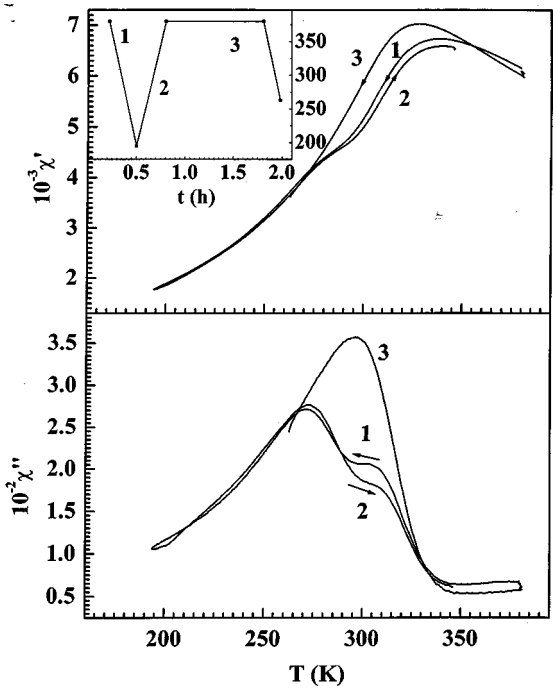

FIG. 17. Initial data from the PLZT sample, after aging near 295 K for about a year in storage. Sweep 1 was taken on continuous cooling after heating to 380 K for a few minutes. Sweep 2 was then taken on heating to 350 K. Sweep 3 started with aging for an hour at 380 K, followed by a continuous cooling sweep.

near 300 K. Heating for a few minutes to 380 K did not fully reset the sample. Subsequent aging for an hour at 380 K reduced $\chi''(T)$ rather uniformly over the range from 345 to 380 K, above the range in which the relaxor effects appear. This behavior is unlike the holes that develop within the relaxor regime, indicating the presence of a second aging mechanism. One remarkable effect appeared after the first cool down to below 200 K—$\chi''(T)$ measured on the subsequent heating *increased* in a window about 20 K wide around 300 K, the previous long-time aging temperature. The apparent implication is that a component of the aging whose effect on $\chi''(T)$ is positive rather than negative is forgotten in this cool down. Subsequent aging at 380 K erases a huge hole (actually a missing peak) spread over a much broader range in T, as well as changing $\chi''(T)$ at lower T. There thus appear to be at least two aging mechanisms present in this regime.

III. DISCUSSION

A. Possible sources of aging

There are several reasons why aging in relaxor ferroelectrics is likely to be more complicated than in spin glasses. One is the large coupling of the ferroelectric order to strain (evident in the huge piezoelectric coefficients[1,2,31]) which means that any mobile defect will couple strongly to the ferroelectric arrangement. Diffusion of defects will slowly stabilize any order. The polar nanodomains themselves, unlike the spins in simple spin glasses, are entities that form as

T is lowered, so their size can be T dependent and also t_W dependent. For example, it is believed that below 230 K in PMN the polar nanodomain size is T dependent.[21,32] Thus the effective interactions among these domains depend on T and t_W. Such effects are likely to be least prominent in PMN, for which at least the chemical disorder appears to be highly stable,[6,33] unlike in PLZT.[18,34]

B. PMN, low-temperature PLZT, and spin glasses

As we have discussed before,[15] most features of the PMN aging are very close to those found in spin glasses. Here we discuss briefly some similarities and differences.

As in spin glasses, no loss of the effects of the T_A aging is found to result from subsequent prolonged aging at much smaller T. However, the T_A aging effects do gradually go away during aging at T just below T_A. The most apparent difference is that this aging loss just below T_A is quicker in PMN and PLZT than in spin glasses,[30] so that it is difficult to thermally cycle the relaxors to lower T without partially losing aging effects at T_A. The relatively rapid memory loss in the relaxors allows a demonstration that shows the characteristic time for forgetting an aging effect is correlated with the time for its formation.

The window within which such memory loss occurs should be determined by two effects. One is ''thermal chaos''—i.e., the lowest free-energy configurations at different T can be very different if there are many nearly degenerate configurations, and if they are sufficiently complex to have different entropies.[35,36] Thus for a small change in T, aging leads to a different equilibrium configuration, erasing previous aging. The second effect is a strong dependence of characteristic rates on T, so that if T is lowered sufficiently, many of the effects of higher-T aging are simply frozen in kinetically, and subsequent low-T aging affects only fine structure within the previously frozen order. Apparently the ratios of these two effects are not the same in PMN, PLZT, and spin glasses. Thermal chaos appears to be more prominent in PMN and PLZT than in the spin glasses for which it was first proposed,[35] perhaps because the T dependence of the internal structure of the interacting entities in the relaxors can be more important than the entropic differences among different collective configurations of a fixed set of such entities.

The magnitude of the E field required to erase most of the aging memory in the relaxor regime of PMN provides some evidence concerning the basic physics of the cooperative units involved in the aging. The fields required to substantially perturb aging are of the order of several hundred volts per centimeter, similar to findings on other relaxors.[17,37] The product of this field scale and the approximate dipole moment of an individual polar nanodomain is roughly k_BT, where k_B is Boltzmann's constant. In spin glasses the product of the perturbing field and the magnetic moment of an individual spin is on the order of $3\times10^{-3}k_BT$.[22] Although the single-site perturbation-field energy scale calculated for PMN and other relaxors is uncertain to about an order of magnitude, it is still significantly greater than that for spin glasses.

The difference in dimensionless sensitivity to field perturbation between relaxors and spin glasses suggests that the cooperative units involved in aging in PMN and PLZT involve a smaller number of nanodomains than the roughly 10^5 spins in the cooperative units in spin glasses.[22,38] One likely reason is that single nanodomain kinetics are slower than single spin kinetics, so that all relaxation phenomena on the experimental time scale involve smaller numbers of nanodomains. However, another relevant basic difference is that time-reversal symmetry does not allow there to be any quenched random magnetic fields in a simple spin glass (other than those from the spin-glass state itself), while compositional disorder gives quenched random electric fields (that do not break time-reversal symmetry) in a relaxor. The existence of prior quenched random electric fields may reduce the sensitivity of the relaxor state to field perturbations.

C. Other regimes of PLZT

In PLZT, there are several distinct aging regimes. The high-T regime includes the neighborhood of T_P. A low-T regime appears below about 230 K. In between, there is a regime from about 230 to 280 K in which low-T cycles erase most of the aging memory. The crossover between these regimes is gradual, as seen in Fig. 8.

The low-T PLZT aging resembles PMN aging in several respects. The absolute magnitude and the time dependence are similar, and so is stability to low-T cycles. There also is at least an approach to ωt_W scaling that may be partially obscured by remnants of distinct aging effects. The behavior under field perturbations closely resembles that of PMN. This low-T aging is likely due to the slow approach of the collective nanodomain configuration to equilibrium.

The huge aging found near T_P in PLZT appears to have some other explanation. Its recovery from field perturbations looks qualitatively different from that found in PMN and in PLZT at lower T_A. Since there is significant aging even above the range in which relaxor effects appear, the high-T regime may be dominated by some effects associated with the growth of nanodomains, perhaps coupled to slow chemical diffusion of Pb vacancies,[18] rather than by the formation of order among fixed nanodomains with fixed interactions.

There is some intriguing complications in the PLZT high-T aging, however. One would expect that above T_P defect positions and other slowly relaxing degrees of freedom would reach thermal equilibrium with the paraelectric state. On cooling, as nanodomains form, defect positions would gradually reequilibrate to enhance the stability of the nanodomains. If some configurations of nanodomain orientation are favored by the interactions among them, these configurations, too, should gradually stabilize as defects reequilibrate. The net effect would be, roughly speaking, for both the ferroelectric and relaxor energy scales, an increase in aging time. Since it is the ratio of these scales to kT that is important in determining the Boltzmann factors, aging should be approximately equivalent to lowering T. Slightly above T_P, however, lowering T *increases* χ'', in contrast to the effects of aging. Therefore the simplest generic pictures of aging would not correctly capture the qualitative behavior

in this regime. Presumably some subtlety—e.g., different effects of defect reequilibration on ferroelectric and antiferroelectric interactions—is required, but we cannot propose a good model. We certainly have no coherent explanation for the peculiar behavior shown in Fig. 17.

In the intermediate regime around 250 K, low-T cycles eliminate most of the aging memory, in contrast to effects found at either higher or lower T_A. We may offer some sheer speculation by way of explanation. If the aging in this regime is partly due to defect equilibration and partly due to relaxor configuration equilibration, the defect effects will create a T-dependent Hamiltonian for the relaxor degrees of freedom. The result would be a very strongly T-dependent equilibrium relaxor configuration, causing the component of the aging due to the relaxor degrees of freedom to be erased by aging at lower T. At still lower T, the defect diffusion may be slow enough for the aging to be dominated by pure relaxor effects more similar to those in PMN.

D. PMN-PT

In PMN-PT a sharp hole in $\chi''(T)$ still appears just below T_A on first cooling below T_A. However, there is no memory of that hole on subsequent reheating. This result is qualitatively unlike those in spin glasses but similar to aging in disordered ferromagnets.[9] Given the proximity of the true ferroelectric phase in this material,[39,40] it is likely that the aging is dominated by the slow growth of ferroelectric order in at least some parts of the sample. The same relatively simple ferroelectric order parameter applies at different temperatures, i.e., thermal chaos should be absent.

IV. SUMMARY

In summary, there are a variety of aging regimes in different relaxor ferroelectrics, with aging properties showing much more diversity than the dielectric susceptibility. The relaxor phenomenon is thus likely to include a variety of disordered dielectrics, between which distinctions have not usually been made as sharply as in the magnetic analogs (e.g., spin glasses, wandering-axis ferromagnets, superparamagnets, etc.) Of the materials we studied, the classic relaxor PMN came closest to behaving as a spin-glass analog. Both PMN and PLZT show evidence of strong thermal chaos effects. PMN-PT (near the ferroelectric regime) aged more like a disordered ferromagnetic.

ACKNOWLEDGMENTS

This work was funded by Grant No. NSF DMR 99-81869. We thank D. D. Viehland for help in the early stages of this project, and H. Chen for helpful conversations.

[1] L. E. Cross, Ferroelectrics **151**, 305 (1994).
[2] L. E. Cross, Ferroelectrics **76**, 241 (1987).
[3] V. Westphal, W. Kleeman, and M. D. Glinchuk, Phys. Rev. Lett. **68**, 847 (1992).
[4] D. Viehland, S. Jang, L. E. Cross, and M. Wuttig, Philos. Mag. B **64**, 335 (1991).
[5] R. Blinc *et al.*, Phys. Rev. Lett. **83**, 424 (1999).
[6] T. Egami *et al.*, J. Korean Phys. Soc. **32**, S935 (1998).
[7] K. Jonason, E. Vincent, J. Hammann, J. Bouchaud, and P. Nordblad, Phys. Rev. Lett. **81**, 3243 (1998).
[8] I. A. Campbell *et al.*, J. Magn. Magn. Mater. **177-181**, 63 (1998).
[9] J. Hammann, E. Vincent, V. Dupuis, M. O. M. Alba, and J.-P. Bouchaud, J. Phys. Soc. Jpn., Suppl. A **69**, 206 (2000).
[10] D. J. Salvino, S. Rogge, B. Tigner, and D. D. Osheroff, Phys. Rev. Lett. **73**, 268 (1994).
[11] F. Alberici-Kous, J. P. Bouchaud, L. F. Cugliandolo, P. Doussineau, and A. Levulut, Phys. Rev. Lett. **81**, 4987 (1998).
[12] L. C. E. Struik, *Physical Aging in Amorphous Polymers and Other Materials* (Elsevier, Amsterdam, 1978).
[13] M. Cloitre, R. Borrega, and L. Leibler, Phys. Rev. Lett. **85**, 4819 (2000).
[14] W. A. Schulze, J. V. Biggers, and L. E. Cross, J. Am. Ceram. Soc. **61**, 46 (1978).
[15] W. Y. Gu, W. Y. Pan, and L. E. Cross, Ferroelectrics **89**, 47 (1989).
[16] E. V. Colla, L. K. Chao, M. B. Weissman, and D. D. Viehland, Phys. Rev. Lett. **85**, 3033 (2000).
[17] A. Shilnikov, A. Burkhanov, A. Sternberg, and E. Birks, Ferroelectrics **81**, 317 (1988).
[18] G. Borchhardt, J. V. Cieminski, and G. Schmidt, Phys. Status Solidi A **59**, 749 (1980).
[19] A. Burkhanov, A. Shilnikov, and A. Sternberg, Ferroelectrics **90**, 39 (1989).
[20] D. Viehland, J. F. Li, S. J. Jang, L. E. Cross, and M. Wuttig, Phys. Rev. B **46**, 8013 (1992).
[21] S. B. Dorogovtsev and N. K. Yushin, Ferroelectrics **112**, 27 (1990).
[22] S. Vakhrushev, B. Kryatkovsky, A. Naberezhov, N. Okuneva, and B. Toperverg, Ferroelectrics **90**, 173 (1989).
[23] P. W. Fenimore and M. B. Weissman, J. Appl. Phys. **76**, 6192 (1994).
[24] H. M. Carruzzo, E. R. Grannan, and C. C. Yu, Phys. Rev. B **50**, 6685 (1994).
[25] A. T. Ogielski and D. L. Stein, Phys. Rev. Lett. **55**, 1634 (1985).
[26] E. Vincent, J. Bouchaud, J. Hammann, and F. Lefloch, Philos. Mag. B **71**, 489 (1995).
[27] F. Lefloch, J. Hammann, M. Ocio, and E. Vincent, Europhys. Lett. **18**, 647 (1992).
[28] J. P. Bouchaud and D. S. Dean, J. Phys. I **5**, 265 (1995).
[29] C. Djurberg, P. Granberg, J. Mattson, and P. Norblad, Phys. Rev. B **50**, 15 775 (1994).
[30] Y. Joh, R. Orbach, G. Wood, J. Hammann, and E. Vincent, Phys. Rev. Lett. **82**, 438 (1999).
[31] K. Jonason, P. Nordblad, E. Vincent, J. Hammann, and J.-P. Bouchaud, Eur. Phys. J. B **13**, 99 (2000).
[32] W. Pan, W. Gu, D. Taylor, and L. E. Cross, Jpn. J. Appl. Phys., Part 1 **28**, 653 (1989).
[33] E. V. Colla, E. Y. Koroleva, N. M. Okuneva, and S. B. Vakhru-

shev, J. Phys.: Condens. Matter **4**, 3671 (1992).
[34] N. de Mathan *et al.*, J. Phys.: Condens. Matter **3**, 8159 (1991).
[35] W. Y. Gu, E. Furman, A. Bhalla, and L. E. Cross, Ferroelectrics **89**, 221 (1989).
[36] A. J. Bray and M. A. Moore, Phys. Rev. Lett. **58**, 57 (1987).
[37] D. S. Fisher and D. A. Huse, Phys. Rev. B **38**, 386 (1988).
[38] Z.-Y. Cheng, R. S. Katiyar, and X. Yao, J. Korean Phys. Soc. **32**, S1042 (1998).
[39] M. B. Weissman, N. E. Israeloff, and G. B. Alers, J. Magn. Magn. Mater. **114**, 87 (1992).
[40] S. W. Choi, J. M. Jung, and A. S. Bhalla, Ferroelectrics **189**, 27 (1996).