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AGING AND BARKHAUSEN NOISE IN THE RELAXOR FERROELECTRICS

BY

LAMBERT KEY CHAO

B.S., Stanford University, 1998
M.S., University of Illinois at Urbana-Champaign, 1999

DISSERTATION

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Abstract

Relaxor ferroelectrics are disordered crystalline materials whose polar order is limited to mesoscopic-scaled nanodomains. There is no ferroelectric phase transition, but a faster than Arrhenius cooperative freezing into a glassy relaxor regime instead. It is not understood how the random fields and random interactions present in these dielectrics inhibit the formation of long-range ferroelectric order. This thesis presents two types of experiments aimed at shedding light on this issue: aging and Barkhausen noise. Aging shows low-temperature regimes with spin-glass-like behavior in relaxors with cubic perovskite crystalline structure that are not present in those with uniaxial tungsten-bronze crystalline structure. In particular, the cubic relaxor PMN/PT (90/10) \([(PbMn_{1/3}Nb_{2/3}O_3)_{1-x}(PbTiO_3)_x, \ x = 0.1]\) shows aging that directly parallels that in re-entrant spin-glasses, with “hole-like” aging at low-temperature, where the uniaxial relaxor SBN:La (60/40) \([Sr_{x-y}La_yBa_{1-x}Nb_2O_6, \ x = 0.6, \ y = 0.01]\) shows cumulative, not “hole-like” aging. The Barkhausen experiments measure the noise from the abrupt reorientation of polar clusters driven by an ac field, giving a measure of a typical dynamic dipole step size in PMN/PT (90/10) of about 100 nanodomains in the paraelectric regime, which then abruptly freezes out on cooling into the relaxor regime. This suggests an abrupt growth of barriers associated with the dipoles.

The presence of complicated spin-glass-like aging, requiring cooperativ-
ity between many aging units, combined with the relative insensitivity of aging effects to small field perturbations suggest that units much smaller than nanodomains are responsible for the aging. This points to a picture of the cubic relaxors where polar regions are coupled to canted moments orthogonal to the mean mid-scale polarization (Egami, 1999; Dkhil et al., 2001) which provide the glassy freezing, much like a re-entrant $xy$ spin-glass. These canted moments are the unit cell analogs to tweed domain-patterning seen in PMN/PT compositions with large ferroelectric doping (Viehland et al., 1995; Xunhu et al., 1994). We note the relevance of a theory mapping the pre-martensitic tweed Hamiltonian onto a spin-glass Hamiltonian (Kartha et al., 1991; Sethna et al., 1992).

We also present evidence of possible discrete polarization/depolarization steps in the pyroelectric current of SBN:La (60/40).
To my parents
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I found it difficult to give thanks to my advisor that did some justice without sounding embarrassingly gushing. Mike Weissman is a great, generous teacher: both by explanation and by example. Not just on how to do physics, but also how to be a person (the latter by example rather than didactic explanation). It was a privilege (and a challenge trying to manage some semblance of keeping up) to watch him come up with interpretations and models of new results in real time. His unique ingenuity and physical intuition and his inspiring enthusiasm for challenging problems scientific or otherwise is a well known given but still never ceases to amaze. But of course, all this is painfully obvious to any who know him. If I have managed to absorb a minute fraction of all that I could have learned from him, then my time as a graduate student would have been more than well spent. I am humbled to consider him a friend.

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Chapter 1

Introduction

Relaxor ferroelectrics encompass a diverse array of disordered dielectric materials grouped together by exhibited phenomena. The physics underlying the behavior of relaxor ferroelectrics is still poorly understood despite forty-plus years of research. These relaxors have crystalline structure, but with chemical disorder from ion substitution at crystallographically equivalent sites. They exhibit a diffuse cross-over into a relaxor regime where long range ferroelectric/antiferroelectric order is inhibited and some sort of glassy freezing occurs. Much of the interest in relaxors is driven by material applications (Uchino, 1994; Scott, 1996): the relaxors’ broad, weakly $T$-dependent, large dielectric maximum (as compared to regular ferroelectrics) is of particular interest for dielectric applications; thermal, electrostrictive, and electrooptics properties make them useful for applications such as micropositioners, motors, light valves, displays, deformable mirrors, and electrostrictive actuators. For physicists, the fundamental interest lies in understanding how the chemical disorder inhibits any long-range order leading to glassy behavior.

Relaxors have crystalline structure with chemical disorder from ion substitution at crystallographically equivalent sites. The prototypical relaxors have cubic perovskite structure (ABO$_3$) with cation substitution possible at the A and/or B sites ($A^{1-x}_1 A^2_{1-x} B^1 y B^2_{1-y} O_3$) (Fig. 1.1). Lead magnesium niobate PbMg$_{1/3}$Nb$_{2/3}$O$_3$ (PMN) is the archetypal representative of the cubic perovskites. Other examples include the PMN/PT family
Crystalline structure of the cubic perovskite relaxors. ABO$_3$ cubic perovskite structure is shown for PMN, which has B-site ion substitution. After Tkachuk and Chen (2001).

(PbMn$_{1/3}$Nb$_{2/3}$O$_3$)$_{1-x}$(PbTiO$_3$)$_x$, a solid solution of PMN with the ferroelectric PbTiO$_3$, lead lanthanum zirconate titanate PLZT (Pb$_{1-x}$La$_x$Zr$_{1-y}$Ti$_y$O$_3$), lead scandium niobate PST (PbSc$_{1/2}$Ta$_{1/2}$O$_3$), lead zinc niobate PZN (PbZn$_{1/2}$Nb$_{1/2}$O$_3$), and lead lanthanum titanate PLT (Pb$_{1-x}$La$_x$TiO$_3$). Also of interest to us is a family of relaxors with uniaxial tungsten bronze structure, which includes relaxors such as SBN (Sr$_x$Ba$_{1-x}$Nb$_2$O$_6$), SBN:La (SBN doped with La, Sr$_{x-y}$La$_y$Ba$_{1-x}$Nb$_2$O$_6$) and SBN:Ce (SBN doped with Ce, Sr$_{x-y}$Ce$_y$Ba$_{1-x}$Nb$_2$O$_6$). It turns out that the difference in crystal structure (cubic vs. uniaxial) gives rise to fundamentally different relaxor behavior and points to a possible explanation for relaxor behavior in the cubics.

Relaxor ferroelectric behavior is quite different from that of conventional ferroelectrics. The temperature dependence of the complex ac susceptibility $\chi^*$ shows a broad, diffuse peak [Fig. 1.2(a,b)] with frequency dispersion [Fig. 1.2(c)] and deviation from Curie-Weiss law (Viehland et al., 1992). The peak in $\chi(T, \omega)$ occurs at the temperature $T_P(\omega)$ where the dominant relaxation rate matches that of the measurement frequency. On cooling, unlike...
Figure 1.2: Typical dielectric behavior of relaxors. (a) In phase and (b) out of phase susceptibility vs. temperature is shown for frequencies from 20 Hz to 1 MHz in logarithmic steps for the relaxor PMN. Deviation of $\chi'$ from Curie-Weiss law is shown in panel (a), right axis. (c) shows frequency dispersion at several temperatures. Vogel-Fulcher freezing is evident in the frequency dependence of the peak temperature $T_P$ in (d). (a,b) after (Colla et al., 2001). (c,d) courtesy E. V. Colla, unpublished.

For a conventional ferroelectric, the material does not spontaneously polarize (hence the polarization cannot be an order parameter for a transition of the relaxor into a ferroelectric state). Instead there is some sort of faster-than-Arrhenius cooperative freezing which can be seen, e.g., in $T_P(\omega)$ which fits to a Vogel-Fulcher form [Fig. 1.2(d)]:

$$\omega = \omega_o \exp \left[ \frac{E_o}{k_B(T_P - T_{VF})} \right]$$  \hspace{1cm} (1.1)

Compare this to the behavior of a conventional ferroelectric such as the
cubic perovskite lead titanate (PbTiO$_3$) which undergoes a structural phase transition at the Curie temperature $T_C$ to a ferroelectric state with long range order ([Remeika and Glass, 1970]). Instead of a broad diffuse peak, the susceptibility follows the Curie-Weiss law

$$\chi = \frac{C}{T - T_C} \quad (1.2)$$

and diverges at $T_C$ [Fig. 1.3(a)]. The susceptibility doesn’t show frequency dispersion or an out-of-phase component except for a small region near $T_C$. At $T_C$, PbTiO$_3$ undergoes a displacive phase transition from cubic to tetragonal symmetry, where the B-site Ti cation along with the oxygen octahedra shifts with respect to the A-site Pb cation. This structural transition results in the appearance of a spontaneous polarization [Fig. 1.3(b)], which serves as an order parameter for the transition.

Unlike a conventional ferroelectric, relaxors do not show a structural transition at the susceptibility peak. Instead of forming long-range ferroelectric domains, relaxors show the formation of short-range order below the Burns temperature $T_d$ in the form of polar nanodomains (of dimension on order of 10 nm). Optical birefringence experiments on PLZT first suggested the formation of local polarizations on cooling ([Burns and Dacol, 1983]). Polar nanodomains were observed using TEM ([Randall et al., 1990]) and also neutron scattering ([Vakhrushev et al., 1989]). But while the nandomains grow somewhat on further cooling, ferroelectric order remains limited to mesoscopic scales and no macroscopic domains are formed.

One of the key issues regarding relaxors is understanding why the polar order starts to form but then quits before forming any long-range macroscopic order. Random fields, which arise from quenched static chemical disorder
Figure 1.3: Behavior of the conventional ferroelectric PbTiO$_3$. (a) shows the temperature dependence of the dielectric constant $\epsilon = 1 + \chi$, which follows the Curie-Weiss law (inset). (b) A spontaneous polarization is measured. (c) shows the specific heat $c_P(T)$. After (Remeika and Glass, 1970).
resulting in local charge imbalance, is likely a key factor in setting length scales for the polar cooperativity. For some relaxors, a correlation length may be associated with the chemical disorder, involving regions with non-stoichiometric 1:1 ordering of, e.g., the B-site cations (Hilton et al., 1990). These regions are referred to as chemical nanodomains.

At this point, it may seem that the rounded diffuse peak is just a smeared out ferroelectric phase transition where disorder from the mixed cations turns the relaxor into a inhomogeneous dirty ferroelectric which has a distribution of regions, each with it’s own \( T_C \) (Smolenskii and Agronovskaya, 1960). However, this is not a viable explanation, since there is no eventual spontaneous polarization or formation of long-range ferroelectric domains when the relaxor is cooled in zero field. And even while it is possible to induce long-range ferroelectric order by the application of a large enough field, this order is not always stable once the external field is removed.

The \( E − T \) phase diagram for PMN (Fig. 1.4) shows a paraelectric phase at high temperature, and below that, a glassy relaxor phase for low field and a ferroelectric phase at high field. A ferroelectric state can be induced by application of an external bias field greater than some threshold field \( E_{Th} \) [defined as the field required on field cooling\(^1\) to induce a stable FE phase at low \( T \) that remains even after the external bias field is removed (i.e., even after crossing from the FE to the GL-II regime across curve \( b \))]. This FE state remains on heating until it depolarizes abruptly at curve \( c \). In ZFC experiments crossing into the FE state from GL-II, Colla et al. (1995) observed a time delay before a transition into the induced FE state is evident.

\(^1\) In a field cooling experiment (FC), the relaxor is cooled under a bias field. The zero field cooling (ZFC) protocol involves cooling the relaxor in zero field to a fixed temperature, after which a field is applied. We also have zero field heating (ZFH), field cooling (FC), and field heating (FH).
It is interesting to note that this delay follows an Arrhenius dependence with temperature and an exponential dependence on the field. The glassy relaxor regime is non-ergodic, so the state at a particular $E - T$ point depends on the path taken to arrive at that point. E.g., if PMN is cooled in fields less than $E_{Th}$ past curve $c$ into the GL-II regime, PMN is in a glassy relaxor state. On the other hand, if we arrive at the same point by crossing over curve $b$ from the FE state, PMN would be in a stable ferroelectric state. The instability of polar order induced by fields below $E_{Th}$, as well as the abrupt depolarization of the thermoremanent polarization (for the case of FC above $E_{Th}$) all point to the the presence of something competing against the ferroelectric order that is beyond simple entropy, which should have minimal effect on order on the scale of nanodomains.

Based on what we know so far about the relaxors, what would a model describing them most likely look like? Since relaxors are loosely defined by a set of phenomenological characteristics, we should highlight those characteristics which we feel might indicate that a material could be an interesting relaxor: namely, that there be a kinetic freezing that is much faster than Arrhenius, along with the presence of some short range order that is somehow inhibited from forming macroscopic domains at low temperature. Given that, what are the ingredients that we need to incorporate into a model describing such a material? Clearly, random fields must play a key role in any viable model, as they most likely set the length scale for any polar order and strongly affect their dynamics. Random interactions between regions of polar order should also be a key ingredient: glassy behavior at low-temperatures has led some to postulate that relaxors are similar to spin-glasses, where random interactions play an important role (Viehland et al., 1991). But we also know that relaxors also have random fields, for which there is no ana-
Figure 1.4: $E$-$T$ phase diagram for the relaxor PMN. There are three regions in the $E$-$T$ plane for the nonergodic behavior of PMN. A high-$T$ paraelectric regime (PE), a glassy relaxor regime (GL-I and GL-II) for low $E$ and $T$, and a field-induced “ferroelectric” regime for low-$T$ and high $E$. Because of nonergodicity in the relaxor regime, the relaxor phase is separated into two parts: GL-I and GL-II. GL-I is always glassy irrespective of the path on the $E$-$T$ phase diagram taken to arrive at that phase. A point in GL-II is glassy if arrived at by cooling in a field less than $E_{th}$; if the point is arrived at by reducing the field from the field-induced FE phase, the relaxor is in a FE phase and remains so on heating until it passes curve $c$. Curve $a$ is obtained from positions of the second harmonic susceptibility maxima on cooling. Curve $b$ from third harmonic maxima. Curve $c$ from susceptibility maxima on depolarization. After Colla et al. (1996).
log in the magnetic spin-glass systems, so a direct analogy between relaxors and spin-glasses would not work. Unsurprisingly, models have been postulated where both random interactions and random fields play a role: e.g., some have claimed that uniaxial relaxors follow a random field Ising model (RFIM) \cite{Kleemann et al., 2002}. So could the relaxors be modeled as a group of polar regions randomly interacting with neighboring regions under a local random field? Are individual nanodomains analogous to individual spin in a spin-glass? Are there be cooperative clusters of nanodomains? Is it the polar regions that freeze and account for the glassy behavior?

The challenge in answering these questions is that it is difficult to discriminate between the various models - they can be adjusted to match macroscopic properties such as the temperature and frequency behavior of the susceptibility. Even though the crossover to low-temperature relaxor behavior cannot be described by a simple order-parameter such as the polarization, it is clear (e.g., from the Vogel-Fulcher dependence of $T_P(\omega)$ of the susceptibility) that there is some sort of cooperative freezing as the material is cooled into the relaxor regime. So it may be possible to describe the relaxors with some glassy order parameter. However, structural functions obtained from scattering probes are typically not sensitive to glassy order parameters.

In this thesis, I will describe aging and noise experiments performed on the glassy relaxor regime aimed at clarifying the nature of the cooperative freezing and answering some of the questions above. The primary focus will be on the cubic perovskite relaxors, but we will use results from the uniaxial relaxors for comparison. Two types of experiments were performed: dielectric aging experiments and noise experiments. Dielectric aging experiments study the slow approach to equilibrium of the frozen relaxors, and in comparison with behavior in other glassy systems (e.g., spin-glasses) shed
light on the nature of the glassy order present. Noise experiments were of
two types - Barkhausen and dielectric polarization noise experiments. In the
Barkhausen experiments, we drive the relaxor with ac electric fields and mea-
sure the Barkhausen noise as any cooperative polar regions are forced to flip
under the driving field. This gives us a measure of the size of the dynamic
cooperative polar units along with their temperature and field behavior. We
also found possible evidence of discrete steps in the polarization current of
several relaxors as they form an induced polarization under FC and as they
depolarize on subsequent ZFH. These results will be presented for SBN:La.
We will discuss the aging experiments in Chapter 2. In Chapter 3 we dis-
cuss the Barkhausen noise experiments, and Chapter 4, the polarization step
noise.

These experiments have given us a better idea of what is occurring in the
cubic perovskite relaxors. In particular, we now have a better idea of what
units are responsible for the glassy freezing, the role that the random fields
play, as well as the size scale and cooperative nature of the polar regions.
The results point to a picture of the relaxors where polar regions consisting
of cooperative clusters of nanodomains, already strongly affected by local
random fields, become coupled to much smaller frozen spin-glass-like degrees
of freedom which are responsible for the glassy aging. A possible candidate
for these glassy units are dipole moments orthogonal to the mid-scale mean
polarization which have been observed in PMN (Egami 1999; Dkhil et al.
2001). We will present this in detail in the concluding chapter.
Chapter 2
Aging

When disordered materials are rapidly cooled below a glassy freezing temperature, they become quenched in a metastable non-equilibrium state. As the material approaches equilibrium and slowly settles into lower free energy states, aging occurs, which is seen as a slow change (usually decrease) in the susceptibility over time while the material is held at fixed temperature $T$ and field (e.g., electric field $E$ for dielectrics). Among the many disordered materials which exhibit aging are the canonical dielectric glasses (such as fused silica SiO$_2$) (Salvino et al., 1994), orientational glasses (Alberici-Kious et al., 2000), supercooled liquids (Dixon et al., 1990), charge density waves (Beleznay and Mihály, 1993), superconductor vortices (Du et al., 2006), and spin-glasses (Fenimore and Weissman, 1994). Aging behavior can be complicated and diverse, especially when the material is subjected to complicated histories. Such complicated aging behavior (e.g., that showing frequency dependent behavior) cannot be explained by a collection of independent two-level systems (TLSs) but requires some kind of interaction between glassy units (Fenimore and Weissman, 1994). By studying the aging behavior of the relaxors under complicated histories, we can gain further understanding about the nature of the cooperativity between glassy units often by comparison with other aging systems such as spin-glasses. Aging experiments were performed on several relax-

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For a review of aging in disordered materials, see (Hammann et al., 2000).
ors, including PMN, PLZT (9/65/35), PMN/PT (72/28), PMN/PT (90/10), and PMN/PT (88/12) (Colla et al., 2000, 2001; Chao et al., 2006) which have cubic perovskite crystalline structure, as well as SBN (60/40) and SBN:La (60/40) (Chao et al., 2005), which have a uniaxial tungsten bronze structure. We have consistently found that while the cubic perovskites (which have canted moments orthogonal to the mid-scale mean polarization) show spin-glass-like low-temperature aging behavior, the uniaxial relaxors (with no canted moments), do not show such low-temperature spin-glass behavior. In this chapter, we will use PMN/PT (90/10) and SBN:La (60/40) to illustrate the aging behavior of these two types of relaxors.

2.1 Experimental Methods

The single crystal PMN/PT (90/10) sample under study was grown by the spontaneous crystallization method at the Institute of Physics, Rostov State University (Rostov-on-Don, Russia). It was configured as a capacitor with a thickness of 0.35 mm and electrodes with an area of $\approx 5 \text{ mm}^2$ on faces perpendicular to the (100) direction. The SBN:La (60/40) sample with 1% La doping was grown at Rockwell International Science Center, (Thousand Oaks, CA) using the Czochralski technique. (Neurgaonkar et al., 1988)

The complex ac susceptibility was measured with conventional frequency domain techniques using a current-to-voltage converter built around a high-impedance op-amp with low input bias current (Analog Devices AD549LH or Burr-Brown OPA111BM) and a lock-in amplifier (Signal Recovery 7265). Typically, ac fields of $\approx 3 \text{ V/cm}$ rms were applied (within the linear response regime). Experiments were conducted in a Janis continuous-flow cryostat.

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2 PMN/PT (78/28) with its strong ferroelectric content showed no SG-like aging, but little memory and large temperature hysteresis in the susceptibility. (Colla et al., 2001)
flowing liquid nitrogen (with a temperature range of roughly 80 K to 450 K and sweep rates of up to 20 K/min) and controlled by a Lakeshore DR-91C temperature controller allowing for a temperature stability of ±0.02 K over a period of days. Software written in HP-VEE™ was used to automate the experiment and handle data acquisition.

2.2 Basic Susceptibility and Aging Measurements

Figure 2.1 shows the complex ac dielectric susceptibility $\chi^*(\omega, T) = \chi'(\omega, T) - i\chi''(\omega, T)$ for PMN/PT and SBN:La, which both show the typical broad diffuse peak seen in PMN and other relaxors (Colla et al., 2001). Because of aging, susceptibility curves for relaxors are somewhat history dependent, and especially so in PMN/PT and SBN:La because both exhibit cumulative aging. We define $T_P = 297$ K, 299 K to be the $\chi''(T)$ peak at 50 Hz of PMN/PT (90/10), SBN:La, respectively.

In a typical aging memory experiment [see Fig. 2.2(a) inset for a temperature history profile], the sample is cooled to $T_A$ and held there while $\chi(T)$ steadily decreases. After aging, the sample is thermally cycled to a lower excursion temperature $T_{EX}$ and then immediately reheated past $T_A$. For comparison, reference curves are also taken at the same sweep rates without stopping at $T_A$.

Our PMN/PT (90/10) sample shows several regimes of aging behavior. Above about 330 K, there is little aging. Starting from about 330 K to 290 K, aging is cumulative: any reduction in $\chi$ remains during the subsequent thermal cycle [Fig. 2.2(a)]. Around 280-250 K [Fig. 2.2(b)], lowering $T$ returns $\chi(T)$ to the reference cooling curve as if there had been no aging, an effect
Figure 2.1: Dielectric susceptibility $\chi^*(T)$ for PMN/PT (90/10) and SBN:La (60/40). The susceptibility was measured with an ac field of 3 V/cm rms (0.7 V/cm rms) at 50 Hz and a $T$-sweep rate of 3 K/min (2 K/min) for PMN/PT (SBN:La). Hysteresis of $\chi$ on cooling/heating (solid/dashed lines) from aging is seen for both PMN/PT and SBN:La.

Known as rejuvenation. In this regime, when cooling excursions are within approximately 10 K of $T_A$, PMN/PT (90/10) shows weak memory of the aging hole (there is small dip around $T_A$ on reheating); but if cooled further below $T_A$, PMN/PT (90/10) shows no memory and the reheating curve coincides with the reference curve. Starting around 240 K, PMN/PT (90/10) gradually crosses over into another cumulative regime [Fig. 2.2(c)]: $\chi'$ does not rejuvenate at all on subsequent cooling after aging, while $\chi''$ does partially rejuvenate but does not return completely to the reference cooling curve. This
Figure 2.2: Aging behavior of $\chi''(T)$ for PMN/PT (90/10) for several $T_A$. Inset of panel (a) shows the temperature profile for a typical aging experiment. Curve 1 is taken as the relaxor is cooled from the initial annealing temperature $T_{AN}$ to aging temperature $T_A$ and held there for aging time $t_A$. Curve 2 is taken on subsequent cooling to $T_{EX}$ with immediate reheating back to the $T_{AN}$ along curve 3. Curves 4 and 5 are reference cooling and heating curves (respectively). Measurements were taken with an ac field of 2.9 V/cm rms at 50 Hz with $T$-sweep rates of about 3 K/min. $T_{AN} = (a,b)$ 400 K, (c) 340 K, (d) 330 K; $t_A = (a,c,d)$ 16 h, (b) 4 h; $T_{EX} = (a)$ 240 K, (b) 250 K (Curve 3a), 240 K (Curve 3b), (c,d) 130 K. For clarity, damped oscillations from 302-308 K lasting about 0.5 h arising from the initial temperature overshoot have not been shown in (a). (b) shows aging curves for two sets of experiments with different $T_{EX}$’s. Curves 1 and 3 overlay over each other for the two experiments and only the heating curve 3a of the first experiment is shown for clarity. Curve 3a in (d) is a polynomial fit of curve 3 with the “hole” from 165-200 K excised and is used to separate the aging memory into cumulative and hole-like components (see text).
reduction in $\chi''$ remains on reheating well past $T_A$, and the cumulative effect of aging in this regime can be seen in the hysteresis between cooling and heating $\chi(T)$ curves (taken without pause for aging at fixed $T$) (Fig. 2.1). Below 200 K [Fig. 2.2(d)], there is a gradual cross-over to spin-glass-like aging. On subsequent reheating from $T_{EX}$, $\chi(T)$ shows both cumulative memory (an offset between the reheating curve and reference heating curve) and hole-like memory [a dip in $\chi(T)$ in the vicinity of $T_A$ on reheating, reminiscent of memory in spin glasses (Hammann et al., 2000)]. We have used a polynomial fit of the reheating curve (with the dip around $T_A$ excised) to separate the cumulative and the hole-like components of the memory. We also found corresponding aging regimes in PMN/PT (88/12), except near $T_P$, where the aging is hole-like with strong memory effects (Chao et al., 2006). As in spin glasses, it is possible for multiple independent aging holes to coexist in the spin-glass-like regime of PMN/PT (90/10): after aging at $T_{A1}$ and $T_{A2}$ (less than $T_{A1}$), there is memory of both aging holes on reheating (Fig. 2.3).

In contrast to the cubic perovskite relaxors, the uniaxial system SBN:La [as well as pure SBN (Chao et al., 2005)] shows no SG-like aging regime at low temperature. While there is some hole-like aging near $T_P$ [Fig. 2.4(a)], the aging starts to exhibit a cumulative component at 250 K [Fig. 2.4(b)], and gradually crosses over to a purely cumulative behavior at low-temperature with no SG-like aging [Fig. 2.4(c)]. Note that we have plotted $\chi''/\chi'$ instead of $\chi''$ to make the hole-like nature of the aging near $T_P$ more apparent.

Figure 2.5 shows a dimensionless aging rate $d\ln \chi''(t_W)/d\ln(t_W)$ at $t_W = 10^4$ s plotted against a normalized aging temperature ($T_A/T_P$) for PMN/PT (90/10), SBN:La and several other relaxors. The cubic relaxors PMN, PLZT, and PMN/PT (90/10) all show similar aging rates in their SG-like regimes. SBN:La shows the fastest aging in the crossover region between the hole-like
Figure 2.3: Multi-hole SG-like aging memory in PMN/PT (90/10). The ability to create successive aging holes in $\chi''$ with independent memory is shown. PMN/PT (90/10) is aged at 175 K (1a) and subsequently 130 K (1b) for 8 h each, then cooled to 100 K (2) and immediately reheated (3). $T$-sweep rates were about 3 K/min and $\chi''$ was measured with an ac field of 2.9 V/cm rms at 50 Hz.

and cumulative regimes. The aging rate then levels off in the low-temperature cumulative regime to a rate similar to the other relaxors.

Figure 2.6 shows the decay of $\chi''(t_W)$ at several temperatures for PMN/PT (90/10). It follows different functional forms depending on the regime in which aging occurs. Near $T_P$ (330-290 K) (Fig. 2.6(a)), aging fits well to a stretched exponential form

$$\chi''(\omega, t_W) = \chi''_0(\omega) \cdot \left(1 + \alpha(\omega) \exp\left(-\gamma(\omega)t_W\right)\right)^{\beta}, \quad (2.1)$$

while aging in the cumulative regime (240-200 K) (Fig. 2.6(c)) fits better to a logarithmic form

$$\chi''(t_W) = \chi''_0 + g \ln(t_W) \quad (2.2)$$
Figure 2.4: Aging behavior of SBN:La (60/40). Aging of $\chi''/\chi'$ is shown for several $T_A$ following the aging protocol and curve numbering convention in Fig. 2.2. $T_{AN} = 350$K for panels (a-c) and 300 K for panel (d). $T_{EX} = 180$ K for panels (a-b), 140 K for (c) and 120 K for (d). The sample was aged at $T_A$ for (a-c) 16 h and (d) 17.6 h.
Figure 2.5: Aging rates for various relaxors. A dimensionless aging rate at $10^4$ s for PMN/PT (90/10), SBN:La (60/40) (ac frequency 50 Hz), PMN, PMN/PT(72/28) (10 Hz), and PLZT (40 Hz) is plotted against the reduced aging temperature.

A power law functional form

$$\chi''(t_W) = \chi''_0 + \frac{g}{t^\gamma_W}$$

(2.3)

better describes aging in the rejuvenating regime (280-240 K) and aging well into the spin glass regime (roughly below 150 K), where domain-growth effects from the cumulative regime have frozen out [Fig. 2.6(b,d), respectively]. SBN:La in the hole-like regime and the cumulative aging regime (Fig. 2.7) fits to a powerlaw form (Eq. 2.3 was used for the single frequency measurement at 190 K. The more constrained Eq. 2.4 was used for the multi-frequency measurement at 250 K).

We have previously reported clean $\omega t_W$-scaling of $\chi(\omega, t_W)$ in PMN and PLZT in the spin-glass-like regime, with very little frequency dependence of the long-time asymptotic $\chi''$ (Colla et al., 2000, 2001). In PMN/PT (90/10),
Figure 2.6: Representative $\chi''(t_W)$ is shown for each of the aging regimes of PMN/PT (90/10) along with best fits to various functional forms (chosen depending on which give physically reasonable parameters or a smaller chi-squared). (a) $\chi''$ at 300 K was fitted to a stretched exponential form ($\beta(\omega)$ ranged from 0.63 at 10 Hz to 0.50 at 1 kHz). (b) 280 K at 50 Hz fitted to power law ($\gamma = 0.19$), (c) 230 K fitted to logarithmic form, and (d) 150 K again to power law form ($\gamma = 0.14$). (c, d) were measured with the same set of frequencies as (a), with $\chi(\omega)$ decreasing monotonically as a function of frequency (only for early $t_W$ in (c)). Data for some frequencies have been omitted for clarity.

on the other hand, because the asymptotic $\chi''$ is more frequency dependent, only the time-dependent part of the susceptibility scales for temperatures up to 260 K (i.e. not just in the spin-glass-like regime). The aging is well described by

$$
\chi''(\omega, t_W, T) = \chi''_0(\omega, T) \cdot \left(1 + \frac{c(T)}{(\omega t_W)^\gamma(T)}\right) \tag{2.4}
$$

Figure 2.8 shows scaling for $\chi''(\omega t_W) - \chi''_0(\omega)$ for $T = 150$ K in the spin-
Figure 2.7: Representative $\chi''(t_W)$ for each aging regime in SBN:La (60/40). (a) 250 K in the hole-like regime (at several frequencies) and (b) 190 K (at 50 Hz) in the cumulative aging regime. Fits to a powerlaw functional form are also shown. Eq. 2.3 was used for the single frequency measurement at 190 K. The more constrained Eq. 2.4 was used for the multi-frequency measurement at 250 K.

We have previously reported the lack of scaling in $\chi''(\omega, t)$ for SBN (60/40) and SBN:La (60/40). The behavior of PMN/PT has led us to reanalyze our previous data, and we find that for SBN:La $\chi''(\omega)/\chi''_o(\omega)$, and not $\chi''(\omega) - \chi''_o(\omega)$, is the quantity that scales at 250 K (Fig. 2.8). Because at the time we thought there was no interesting scaling, we only have sparse multi-frequency aging data at low-$T$, where we find that $\chi''(\omega)/\chi''_o(\omega)$ also scales at 190 K, although we are not sure of the reliability of the phase calibration of the ac susceptibility measurement for that particular experiment.
Figure 2.8: $\omega t_W$-scaling for PMN/PT (90/10) and SBN:La (60/40). (a) PMN/PT: $\chi''(\omega, t_W) - \chi_o(\omega)$ is plotted against $\omega t_W$ for several frequencies at 300 K (right axis), 260 K and 150 K (left axis). Scaling is found in PMN/PT (90/10) at lower $T$. (b) SBN:La: $\chi''(\omega, t_W)/\chi_o(\omega)$ is seen to scale with $\omega t_W$ at 250 K.

2.3 Stability of Aging Effects Against Perturbations

Probing the stability of aging memory against perturbations can provide information about the detailed nature of the aging and glassy units involved. To test the stability against temperature perturbations, we use the aging protocol described above, cycling to a lower temperature $T_{EX}$ and back after initial aging. The total aging reduction in $\chi(T_A)$ is compared to the amount of memory of the aging, i.e., the remaining reduction in $\chi(T_A)$ on reheating after cooling to $T_{EX}$. Because of the small temperature range in which SBN:La exhibited hole-like memory, the following aging experiments testing memory stability against thermal cycles were performed only on PMN/PT (90/10).

Figure 2.9 shows the amount of aging memory for PMN/PT (90/10) after fixed-rate (3 K/min) cycling to $T_{EX}$ as a function of initial aging time $t_A$ for two aging temperatures. Clearly, any aging effects are more stable against
Figure 2.9: Aging memory for PMN/PT (90/10) is shown as a function of initial aging time after a cooling cycle to $T_{EX}$ at sweep rates of ±3 K/min. For $T_A = 175$ K (150 K), $T_{EX} = 120$ K (105 K).

thermal cycling the longer the initial aging time.

Figure 2.10 shows aging memory after small (positive and negative) thermal excursions of $\Delta T$ around $T_A$ for two aging temperatures in the spin glass regime. The behavior is similar to that in the spin glass regime of other cubic relaxors. (Colla et al., 2001) There is a strong asymmetry in the effect of heating and cooling cycles: heating erases much more memory than cooling. Most memory loss occurs for small temperature excursions within 10% of the aging temperature. While slight cooling erases a large amount of memory, further cooling does not, leaving some aging memory that is not erased until $T$ is heated above $T_A$.

We can probe the temperature dependence of this more persistent memory using aging experiments with large thermal excursions. Figure 2.11 shows memory (in percentage of the aging reduction remaining) after large thermal excursions as a function of $T_A$. The sample was aged at $T_A$ for 16 h, then cycled to a fixed $T_{EX}$ (much lower than any $T_A$) and back. While the
Figure 2.10: Aging memory after small thermal excursions of $\Delta T$ about $T_A$ for PMN/PT (90/10) at 175 K and 150 K. Sweep rates were about $\pm$3 K/min. The absolute magnitude of the aging decreases with decreasing temperature, the percentage of that aging retained increases. Since there is a cumulative as well as a hole-like part to the aging memory in this regime (Fig. 2.2(d)), we have separated the total memory into its cumulative and hole-like parts using a polynomial fit as before. The crossover from mostly cumulative to mostly hole-like aging is evident.

We also studied the effects of field perturbations on aging in the spin glass regime. This gives an estimate of the field scale necessary to disrupt any established aging order. In a typical experiment, PMN/PT (90/10) is cooled and aged for 3 h in zero field. A DC field is then applied for 1 h, and then turned off and the sample allowed to relax in zero field (Fig. 2.12(a) at 175 K with a field of 286 V/cm). We see that applying the field erases some of the aging done in zero field, but after the field is turned off, the sample returns asymptotically to the initial zero-field aging curve. The loss of memory on turning on $E$ is a monotonic function of $\Delta E$ reaching 50% loss at roughly 500 V/cm (Fig. 2.13). Assuming a saturation polarization
Figure 2.11: Aging memory after cooling cycles to $T_{EX}$ well below $T_A$ is shown. Memory has been separated into cumulative and hole-like components (see Fig. 2.2(d)). For $T_A$ of 175 K and above, $T_{EX} = 130$ K. For $T_A = 165$ K, $T_{EX} = 115$ K. $T_{EX}$ is below 95 K for the lowest $T_A$.

of roughly 30 $\mu$C/cm$^2$, the field scale for disturbing the aging corresponds to a coherent aging unit with polarization $\Delta P = \varepsilon_0 \chi' \Delta E$ of 0.2 $\mu$C/cm$^2$, or less than 1% of the total polarization. This is roughly comparable to other relaxors such as PMN (Colla et al., 2001) where aging is disturbed by a field of 400 V/cm at 160 K, corresponding to a polarization of 0.08 $\mu$C/cm$^2$ and pure SBN (60/40) (Chao et al., 2005) where 270 V/cm disrupts aging at 250 K (Fig. 2.12(b)) and corresponds to a polarization of 0.09 $\mu$C/cm$^2$. We did not perform corresponding experiments on SBN:La.

### 2.4 Discussion

#### 2.4.1 PMN/PT (90/10) Discussion

First off, it should be noted that previous work by Kircher et al. on a ceramic PMN/PT (90/10) sample concentrated near the susceptibility peak show results qualitatively different from those of our PMN/PT (90/10) sam-
Figure 2.12: Effect of dc field zero-field aging for PMN/PT (90/10) and SBN (60/40). (a) PMN/PT: $\chi''$ is plotted against aging time $t_W$. A DC field of 290 V/cm was applied for 1 h after aging in zero field for 6 h. (b) SBN: A temporary DC field of 270 V/cm was applied [SBN data after (Chao et al., 2005)].

Figure 2.13: A measure of the effect of a sudden application of an electric field (as in Fig. 2.12) on aging of $\chi''$ is shown as a function of applied field for PMN/PT. We define the amount of initial zero-field aging reduction of $\chi''$ remaining 30 s after the DC field application as a measure of aging recovery.
ple: hole-like aging with stronger memory effects near $T_P$, no $\omega t_W$-scaling, and a $\chi''$ peak nearly 20 K below ours (280 K compared to 296 K, measured at 20 Hz). While the difference in $T_P$’s suggest a substantial difference between the two 10% samples (one possibility being ceramic strain effects), it is unclear how they could explain such qualitatively different aging behavior near $T_P$, especially considering that we also have results on a PMN/PT (88/12) sample which show hole-like aging similar to the Kircher sample near $T_P$ (Chao et al., 2006).

Two of the aging regimes of PMN/PT (90/10) (the rejuvenating regime just below $T_P$ showing little memory and the spin-glass-like regime at low temperature) directly parallel regimes in reentrant spin glasses, such as CdCr$_{2x}$In$_{2-2x}$S$_4$ ($x > 0.85$) (Vincent et al., 2000; Dupuis et al., 2002). For weak disorder, these materials cool from a paramagnetic phase into a “ferromagnetic” regime with short range order. On further cooling, they subsequently enter a low-temperature spin glass regime. The “ferromagnetic” phase shows aging like our rejuvenating regime: rejuvenation and weak memory easily erased by small cooling excursions. Similarly the reentrant spin glass regime shows typical spin glass behavior, as does ours. As in PMN/PT (90/10), both regimes show $\omega t_W$-scaling of the time-dependent part of the susceptibility. However, aging in the crossover between these two magnetic regimes was not reported in detail, so it is unknown whether there is a corresponding distinct cumulative aging regime in between the two, as seen in our PMN/PT (90/10) system. Cumulative aging is also seen in polymers (Bellon et al., 2000) and ferroelectrics (Mueller and Shchur, 2004; Alberici-Kious et al., 1998; Bouchaud et al., 2001).

We have found most of the relaxors to exhibit some form of $\omega t_W$-scaling. PMN and PLZT showed scaling of $\chi''$ (Colla et al., 2001) at low temperature,
while PMN/PT (90/10) showed scaling of the time-dependent part $\chi'' - \chi''_0$, and SBN:La for $\chi''/\chi''_0$. Scaling in PMN and PLZT is similar to that seen in spin-glasses (Hammann et al., 2000) and suggests that the ferro regions responsible for the response are tightly coupled to the glassy order responsible for aging. Hierarchical schemes are believed to explain dynamics of spin glasses as well as pinned domain walls (Balents et al., 1996; Dupuis et al., 2002). For PMN/PT (90/10) with stronger ferroelectric correlations, it is not surprising that the coupling between the ferro and glassy components has changed and $\omega t_w$-scaling is different from that of pure PMN. The field required to perturb established aging is also comparable to that of pure PMN (Colla et al., 2001), and Barkhausen noise experiments show a similar temperature dependence and dipole moment step size (Chao et al., 2003). In fact, it seems that for PMN/PT, increasing the PT concentration has the effect of tuning the strength of the ferroelectric correlations from that of pure PMN. Since $\omega t_w$ scaling need not arise exclusively from hierarchical schemes, scaling in other non-SG-like regimes such as the high temperature regime of SBN:La need not imply similar underlying physics.

### 2.4.2 Aging in Relaxors: Implications of Aging

**Stability Against Field Perturbations**

The take-away message from these aging results should be that while the cubic perovskite relaxors, which show canted dipole moments orthogonal to the mid-scale mean polarization, exhibit SG-like aging at low-temperature, the uniaxial relaxors, without the canted moments, do not. This is consistent with our picture (discussed below) of glassy behavior in the cubic relaxors as arising from the coupling of the frozen canted moments with local po-
larizations, much like the $xy$-spins in a reentrant spin-glass. The striking similarities of PMN/PT (90/10) aging to that in reentrant spin-glasses support this idea.

As we’ve said in Chapter 1, one of the key characteristics we would like to determine about the relaxors is the length scale of any cooperativity in the relaxor regime, whether glassy or polar (or both). The field perturbation experiments testing the stability of established aging holes can give us an idea of the size of cooperative aging units. Since the cubic relaxors show spin-glass-like aging behavior, it is useful to discuss analogous field-jump experiments on the spin-glasses (Fenimore and Weissman 1994). In order to get such complicated aging behavior, cooperativity between many aging units are necessary: in the spin-glasses, the magnetic clustering and the aging both came from the spins themselves, involving clusters of up to $10^5$ spins. It would be useful to do an analogous calculation for the relaxors, where we assume that the nanodomains, which are the units involved in the polar clustering, are also responsible for the aging as well.

Given the susceptibility $\chi$ and the change in the field $\Delta H$ (or $\Delta E$) needed to significantly perturb any established aging, we can calculate the resulting dipole moment change and estimate the size of a coherent cooperative cluster of dipole moments (whether spins for the spin-glasses or nanodomains for the relaxors). Now we can expect that we would have to change the energy scale by at least $k_B T$ to perturb the current aging state by any significant amount (otherwise, thermal fluctuations alone would be enough to erase any aging). Hence we can expect

$$\mu \Delta H \gtrsim k_B T,$$

where $\mu$ is the net change in dipole moment from flipping the coherent spin
cluster. In the spin-glass CuMn, hole burning experiments found that a magnetic field change of 300 Oe was needed to wipe out the aging hole at low temperature (6 - 14 K). Converting the difference in magnetic susceptibility of the aging hole to a change in dipole moment then gives

$$\mu \Delta H = 300 \mu_o \cdot \Delta H \approx k_B T,$$

(2.6)

where $\mu_o$ is the dipole moment of a single spin (which is 2 Bohr magnetons from the Mn ion in CuMn). For a spin-glass, where each individual spin is under the influence of only random interactions with its neighbors, a coherent cluster would consist of $N$ randomly oriented spins. Now, select any two random clusters in the ensemble, and the difference in net dipole moment between them would scale with the standard deviation, or $\mu = \sqrt{N} \mu_o$. Given Eq. (2.6) a typical cluster size for CuMn is on order of $N = 10^5$ spins for CuMn. This number agrees roughly with other measures of a typical coherent cluster size, e.g., from thermal fluctuation statistics (Israeloff et al., 1991), second spectra statistics (Weissman et al., 1992), and finite size effects of thin films (Gavrin et al., 1990).

If we do the same calculation for the relaxors and then try to make analogous interpretations assuming that the polar nanodomains are also the aging units, we start to get in trouble. For the various relaxors, we get that roughly

$$pE \approx p_{nano}E \approx k_B T,$$

(2.7)

where $p$ is the change in dipole moment from the field jump and $p_{nano}$ is a typical dipole moment of a nanodomain. So for the relaxors, a larger field jump produces a smaller dipole moment change compared to spin-glasses: E-
fields of about a $1/3$ of that needed to induce the relaxor into a ferroelectric state produce a roughly 0.6% change in polarization involving about a nanodomain, whereas for the spin-glasses, a magnetic field that is less than 1% of the field at the d’Almeida-Thouless line (Fenimore and Weissman, 1994; Kenning et al., 1991) produces a comparable magnetization change of 0.3% involving $10^5$ spins.

At first brush, one might run with this and infer that the cooperative clusters in relaxors consists of roughly a single nanodomain, but this is not likely the case. Simply put, independent nanodomains cannot account for the complicated spin-glass-like aging which require cooperativity between many units ($10^5$ units for spin-glasses). In fact, independent nanodomains, growing as they cool, are associated with cumulative aging (where, with the domains frozen, aging comes mostly from the domain walls, of which there are fewer as the domains grow). If there were many cooperative nanodomains responsible for the aging (in the next chapter we will see that there are large cooperative polar clusters of 100 nanodomains, albeit not the clusters of $10^5$ spins in spin-glasses), we would then expect the aging to be more sensitive to field changes (i.e., smaller field jumps should produce larger changes in $p$). So how do we reconcile the dynamic polar cluster size with the smaller dipole moment obtained from field perturbations of the aging?

These results point to a scenario where the glassy aging behavior doesn’t come from the nanodomains, but from a large number of units much smaller (so that they are less sensitive to field perturbations) and more concentrated than the nanodomains. If the small amount of anomalous heat capacity (whose origin is disputed) at lower temperatures in PMN (Hegenbarth, 1995; Gvasaliya et al., 2001) is associated with the same glassy units involved in the relaxor freezing, it is further indication that they are much smaller.
and larger in number than the nanodomains (of which there are too few for them to be the source of the extra heat capacity). Polar cooperativity involving the nanodomains would then exist in parallel to (and somehow couple to) the glassy cooperativity involving these glassy aging units. One such candidate could be moments canted with respect to the mean mid-scale \( \langle 111 \rangle \) polarization seen in PMN (Egami, 1999; Dkhil et al., 2001) that we’ve mentioned in Chapter 1. Given that a nanodomain is on order of 10 nm on a side and that the unit cell lattice spacing is 0.4 nm, a single nanodomain consists of several thousand unit cells which could have these orthogonal moments. These much smaller canted moments would be less sensitive to field jumps.

Now one may ask why the nanodomains themselves don’t respond to the field jump. It is simply that they are pinned and cannot be flipped by the applied field. In the spin-glass case, there can be no quenched magnetic fields because of time-reversal symmetry, so the spins inside a cluster are randomly oriented and only subject to random interactions with neighboring spins. However, the relaxors are dielectric systems with strong quenched random (electric) fields that set the preferred orientations of the nanodomains inside a coherent cluster and pin them there. In addition, we will see from the Barkhausen experiments that polar clusters of nanodomains will rapidly freeze out on cooling into the glassy regime possibly from rapid growth of associated barriers. This could arise from the strong coupling of the polar order to the glassy units which then freeze, causing the barriers to grow rapidly.

In other words, a direct analogy between nanodomains in relaxors and spins in a spin glass (which already needs adjustment given the strong random fields in relaxors) breaks down. But we still need many degrees of freedom
to account for the spin-glass-like aging. This suggests that there are smaller units responsible for the glassy aging which exists in parallel and couples to nanodomains involved in the polar order. While this argument doesn’t inevitably follow from the aging results, it is at least consistent with them. In the next chapter, we will describe in detail the above-mentioned Barkhausen experiments showing polar clusters of nanodomains abruptly freezing out on cooling. Then, in the concluding chapter, we will tie these aging and Barkhausen results together to suggest a picture of how the freezing of the canted moments affects the larger local polar moments.
Chapter 3

Barkhausen Noise Experiments

3.1 Introduction and Theory

As we have said before, at first glance, the relaxors would seem to be a ferroelectric, where the cubic perovskite crystal structure would seem to favor a long-range structural transition into a ferroelectric phase. It follows then that we want to understand how the long-range order is inhibited. To do that, we can ask what the correlation lengths are, and how they behave with temperature and electric field. As we have seen in the last chapter, there is glassy order present in the relaxors. The DC field jump aging experiments suggest that random fields pin most of the nanodomains and set their local orientations, so that the units responsible for glassy aging seem to be much smaller than nanodomains, but still somehow coupled to the ferroelectric order. It would be important to understand how the polar order behaved.

Of particular interest would be a measure of the coherence length of any polar cooperative units. We do know that nanodomains form at the Burns temperature on cooling from high-temperature annealing, and there is evidence that they grow somewhat \cite{Vakhrushev98}. But beyond that, are there coherent clusters of nanodomains, or are they so strongly pinned by their local random fields, as the aging field-jump experiments suggest, that there is not much cooperative order beyond the nanodomains? And if there are cooperative clusters of nanodomains, how do they behave?
with field and with temperature as they are cooled into the glassy relaxor regime?

While scattering techniques (such as neutron scattering) which provide static structure functions are well suited to probing ordered, crystalline materials, and indeed have provided copious information on the structural behavior of relaxors, they are ill-suited to disordered materials with glassy order parameters which show a distribution of characteristics. Nonequilibrium noise techniques, on the other hand, are particularly well-suited to probing glassy order (Weissman, 1996). In this chapter, we discuss Barkhausen noise experiments in the non-ferroelectric (paraelectric and relaxor) regimes of the relaxors which measure the size-scale of any dynamic cooperative glassy units.

Materials exhibit Barkhausen noise when coherent polar/magnetic units change their polarization/magnetization via domain reorientation or domain wall motion. The magnitude of the noise reflects the total dipole moment change as well as the dipole step size, so we can infer from the Barkhausen noise the size scale of any dynamic cooperativity beyond the conventional static order of nanodomains. In a cartoonish sense, one can think of Barkhausen experiments as trying to figure out what’s inside a closed box by roughly shaking it and listening for the rattling sounds. The difficulty is that what’s inside is usually very small, so in order to be sensitive to the statistics of these individual fluctuators, you have to fabricate a really small box (mesoscopic samples), or use other techniques to improve sensitivity for measuring the small Barkhausen noise.

Using the techniques described below, we have previously reported on Barkhausen experiments on PMN which show temperature and driving field dependence of the cooperative step size which suggest the sharp growth of
kinetic barriers to dipole reorientation upon cooling ([Colla et al., 2002]). Here we will focus on results for PMN/PT (10% and 32%), solid solutions of PMN with lead titanate (PbTiO$_3$), where, again similar to the aging behavior, the ferroelectric nature of PT serves to tune the relationship between the dipole moment step size and their kinetic barriers. These Barkhausen results together with the aging behavior point towards a reentrant spin-glass-like picture of the relaxors, which we discuss in the concluding chapter.

### 3.1.1 Barkhausen Theory

In our Barkhausen experiments, we drive the material with a sinusoidal field, measure a time series of the Barkhausen fluctuations, and Fourier transform that time series to get a power-spectrum in frequency space for analysis. In this section, we will present the mathematical formalism for interpreting the noise measurements using a simple basic model for the Barkhausen steps.

For starters, dissipation in the relaxors (there is a lossy out-of-phase component to the susceptibility) means there will be equilibrium noise given by the fluctuation dissipation theorem:

\[ S_V(f) = 4k_B T \text{Re}(Z), \]

where \( S_V(f) \) is the voltage noise power spectral density, \( k_B \) is the Boltzmann constant, and \( Z \) is the complex impedance of the sample. The complex capacitance of the material is defined as \( C(f) = C'(f) - iC''(f) \), and is related to the complex susceptibility \( \chi(f) = \chi'(f) - i\chi''(f) \) and the geometric capacitance \( C_o = \epsilon_o A/d \) (\( A \) is the area, \( d \) the thickness of the capacitor) by \( C(f) = (1 + \chi(f))C_o \). So the equilibrium noise of a dissipative dielectric

36
material has a $1/f$ spectral form given by

$$S_V(f) = \frac{2}{\pi} k_B T \frac{C''}{|C|^2} \frac{1}{f} \quad (3.2)$$

Figure 3.1(a) shows an exaggerated cartoon of the individual polarization steps that occur as we traverse the hysteresis loop. We want a measure of a typical step size from the Barkhausen noise. What is the spectral form we would expect from a collection of such steps? Since each polar region has a random local environment with a local random field and a barrier to flipping, as the field $E(t)$ is swept, the polarization of the relaxor will follow a biased random walk about its mean driven response. It follows that the power spectrum is $1/f^2$ with noise power only at harmonics of the driving
Now let’s derive the power spectrum we expect to measure. The derivation is presented here in more detail than usual for future reference. We use a simple Preisach model \(^{1}\) to derive expected power spectral forms for interpreting the Barkhausen noise results. In this model, polarization steps occur at fixed fields distributed with uniform probability over the driving field sweep range. (Or equivalently, we assume a uniform distribution of random fields.)

Let’s consider one such coherent polar cluster, with dipole moment \(\delta p\), which we model as a two-level system with a double-well potential (Fig 3.1(b)). As the driving field \(E(t) = E_D \sin(\omega D t)\) is swept, the field will be large enough at some point to flip the cluster and \(p(t)\), the dipole moment as a function of time, shows an abrupt jump of size \(\delta p\) [Fig. 3.2(a)(i)]. Since this is a random walk, \(p(t)\) consists of a random sequence of such steps, so the derivative \(\dot{p}(t)\) consists of a random train of delta function pulses \(\delta p \cdot \delta(t)\) [Fig. 3.2(a)(ii)]. This is analogous to shot noise, which has a power spectrum

\[
S_I = 2Ie, \quad (3.3)
\]

where \(I\) is the average current and \(e\) is the current pulse size. Therefore, we can write the power spectrum for the derivative of the dipole moment as:

\[
S_p = 2\langle \dot{p} \rangle \delta p, \quad (3.4)
\]

---

\(^{1}\)For the calculation here, we consider only one half of the sinusoid with the field \(E(t)\) increasing monotonically from \(-E_D\) to \(E_D\). We will often be taking the linear approximation of the sinusoidal field as well.
Figure 3.2: Barkhausen power spectra derivations plots. We show here plots of (i) dipole moment $p(t)$ and (ii) its time derivative $\dot{p}(t)$ vs. time as well as (iii) the voltage power spectra vs. frequency on a log-log plot for each of three cases. (a) An independent abrupt step at some field $E$, (b) for fast, thermally jittered polar clusters in quasi-equilibrium smoothly following the driving field, and (c) thermally jittered clusters with large barriers that switch abruptly (for which the power spectrum is numerically calculated). See text for derivation and formulae.
where $\langle \dot{p} \rangle$, the average time derivative of the dipole moment, is given by

$$
\langle \dot{p} \rangle = \left( \frac{\# \text{ steps}}{\text{unit time}} \right) \delta p = \frac{\Delta p_{\text{tot}}}{2E_D} \frac{dE}{dt}
$$

(3.5)

Here we have calculated the number of steps based on the total change in dipole moment $p_{\text{tot}}$ when the field is swept from $-E_D$ to $E_D$, using a linear approximation of the electric field as $E(t) = dE/dt \cdot t$. Using Eqs. (3.4, 3.5) and the relationship between the Fourier transform of a function $f$, $\text{FT}\{f(t); \omega\}$, and that of its derivative ($\text{FT}\{\dot{f}(t); \omega\} = -i\omega \text{FT}\{f(t); \omega\}$) gives the dipole moment power spectrum:

$$
S_p = \frac{1}{\omega^2} \frac{\Delta p_{\text{tot}}}{E_D} \frac{dE}{dt} \cdot \delta p
$$

(3.6)

Since we measure voltage fluctuations and capacitances in our experiments, it is worthwhile to rewrite this as a voltage power spectrum using standard relationships between electric field, capacitance, voltage, and dipole moments:

$$
S_V = \frac{1}{2\pi^2 f^2} \frac{dV}{dt} \frac{1}{Cd} \cdot \delta p,
$$

(3.7)

where $C$ is the capacitance and $d$ is the thickness of the capacitor. As expected, the power spectrum goes as $1/f^2$, with power only at the harmonics of the driving frequency $f_D$, since dipole moment step pattern is periodically repeated.

Thermal fluctuations will jitter the timing of the steps, so that they do not occur at exactly the same point in the field cycle every time. This will reduce the harmonic component of the noise. Let’s consider the case of a fast polar cluster with a small barrier in quasi-equilibrium with the driving field $E(t)$. As $E(t)$ approaches the field where the cluster is on average likely to flip, the
cluster will rapidly switch back and forth between the two orientations. The probability \( \rho(t) \) that the cluster is in the switched state is then given by the canonical distribution

\[
\rho(t) = \frac{e^{-x}}{1 + e^{-x}}, \quad x \equiv -\frac{(E(t) + E_{rf})\delta p}{k_BT},
\]

(3.8)

where \( E_{rf} \) is the local random field and \( k_B \) is the Boltzmann constant. The sign convention of \( x \) is such that the switched state with dipole moment \( \delta p \) is more favored as \( E(t) \) increases with time. \( \rho(t) \) and hence the dipole moment will look like Fig. 3.2(b)(i), and \( \dot{\rho}(t) \) like Fig. 3.2(b)(ii). For mathematical convenience, and without (too much) loss of generality, let \( E_{rf} = 0 \). So the abrupt step now occurs smoothly over a time scale

\[
\tau = \frac{1}{2\pi f_D \delta p \cdot E_D} k_BT,
\]

(3.9)

where we have taken a linear approximation of the driving field \( E(t) \approx E_D \omega_D t \). And instead of random train of delta function pulses from abrupt square steps, \( \dot{p}(t) \) is now a convolution of \( \dot{\rho}(t) \) with the random train of delta functions from before [Fig. 3.2(b)(ii)].

\[
\dot{\rho}(t) = \frac{1}{4\tau} \text{sech}^2\left(\frac{t}{2\tau}\right)
\]

(3.10)

Following the same steps to calculate \( S_V \), we get:

\[
S_{p-\text{fast}} = |\text{FT}\{\dot{\rho}(t); \omega]\|^2 S_{p-SQ}
\]

(3.11)
Again the power spectrum of \( p(t) \) is related to that of \( \dot{p}(t) \) by

\[
S_p = \frac{1}{\omega^2} S_{\dot{p}}, \tag{3.12}
\]

So, the dipole moment power spectrum for fast quasi-equilibrium clusters is given by

\[
S_{p_{\text{fast}}} = \frac{1}{4\pi f_C^2 \text{csch}^2(\pi \frac{f}{f_C})} \delta p \frac{C d V}{d t} \tag{3.13}
\]

where the characteristic rolloff frequency

\[
f_C \equiv \frac{1}{2\pi \tau} = \frac{f_D \delta p \cdot E_D}{k_B T}. \tag{3.14}
\]

Or written in terms of the voltage power spectrum

\[
S_V = \frac{1}{4\pi f_C^2 \text{csch}^2(\pi \frac{f}{f_C})} \frac{d V}{d t} \frac{\delta p}{C d}. \tag{3.15}
\]

So we see that thermal jitter from fast domains smooths out the polar step over a characteristic time \( \tau \), so that the power spectrum falls off faster than \( 1/f^2 \) with a dramatic rolloff for \( f > f_C \) [Fig. 3.2(b)(iii)].

Now let’s consider the other extreme, when thermal jitter is changing the timing of the polar step, but there is a large barrier to flipping. Then the polar cluster is not in quasi-equilibrium with the driving field, and switches abruptly instead, much like Fig. 3.2(a)(i), but with jitter in the timing of the step with a characteristic width of \( \tau \). To calculate the power spectra, we treat this as an activated process in a double well potential with a barrier halfway in between the two wells (Fig. 3.1). The characteristic rate \( \Omega \) for crossing the barrier and flipping the polar state is then given by an Arrhenius
law:

\[ \Omega = \omega_o e^{-U_A/(k_BT)} \quad (3.16) \]

where \( U_A \) is the activation energy and \( \omega_o \) is the attempt rate (typically \( 10^{12} \) Hz). Since we are sweeping the field and changing the barrier height and the barrier is halfway in between the two dipole states, we can write the activation energy as

\[ U_A = U_{A0} - \frac{\delta p}{2} \frac{dE}{dt} t \quad (3.17) \]

where \( U_{A0} \) is the barrier height in zero electric field and we have taken a linear approximation of the field \( E(t) \). We can take \( U_{A0} = 0 \) without loss of generality. The minus sign is such that as we sweep the field (and increase \( E \)), the double well is tilted and the barrier lowered so that the switched state is more favored. We can define a characteristic time \( \tau \) as

\[ \tau \equiv \frac{k_B T}{\delta p \frac{dE}{dt}} \quad (3.18) \]

so that we can rewrite Eq. 3.16 as

\[ \Omega = \omega_o e^{t/(2\tau)} \quad (3.19) \]

The probability \( \rho_{\text{Not}}(t) \) that the cluster has not switched is then given by this characteristic rate \( f_C \) at which it is leaving the unswitched state

\[ \dot{\rho}_{\text{Not}}(t) = -\rho_{\text{Not}} \Omega = -\rho_{\text{Not}} \omega_o e^{t/(2\tau)} \quad (3.20) \]

Solving the differential equation gives

\[ \rho_{\text{Not}} = \exp \left( -2\omega_o \tau \exp \frac{t}{2\tau} \right) \quad (3.21) \]
Of course it then follows that the probability the cluster is in the switched state $\rho(t)$ (which is proportional to $p(t)$ as before) is given by

$$\rho(t) = 1 - \rho_{\text{Noa}}(t) = 1 - \exp \left( -2\omega_o \tau \exp \frac{t}{2\tau} \right)$$  \hspace{1cm} (3.22)\]

Fig. 3.2(c)(i) shows $p(t)$. We can follow the same method to calculate $S_V$ for this case. The derivative Fig. 3.2(c)(ii) is given by

$$\dot{\rho}(t) = \omega_o \exp \left( \frac{t}{2\tau} - \omega_o \tau \exp \frac{t}{2\tau} \right)$$  \hspace{1cm} (3.23)\]

While this does not have an analytical Fourier transform, Fig. 3.2(c)(iii) shows a numerically calculated power spectrum following the same steps as for the other two cases. For the calculation, we have used $f_o = 10^{12}$ Hz (a typical attempt rate) and $\tau \approx 1$ ms (we’re sweeping the field on order of $10k_B T$ or less at a rate of $f_D = 50$ Hz, or 10 ms to sweep from $-E_D$ to $+E_D$).

So jitter in timing of the steps for both cases reduces the periodic component from the original $1/f^2$ spectrum. This reduced harmonic power is instead found in broadband aperiodic noise. Taking the difference between the unjittered abrupt step, and the jittered abrupt $p(t)$, gives pulses of various widths on order less than $\tau$ and broadband aperiodic noise of roughly Lorentzian in shape with a roughly $1/f^2$ envelope.

A couple of things we should note. The quantity $\epsilon' \cdot \langle (\delta V)^2 \rangle$, where $\langle (\delta V)^2 \rangle$ is the voltage variance [integral of $S_V(f)$] and $\epsilon'$ is the in-phase dielectric permittivity, is proportional to the dipole moment of the polar cluster, $\delta p$. This can be seen by integrating $S_V$ and multiplying by $C$ (which is roughly proportional to $\epsilon'$) in Eq. 3.7.

Also, based on this simple Preisach model of independent steps, the
noise power grows linearly with the driving field amplitude. Integrate $S_V(f)$ (Eq. 3.7) from $f_D$ to infinity and take a linear approximation of $dE/dt \approx 2\pi E_D f_D$. This gives

$$\langle (\delta V)^2 \rangle \approx \frac{1}{\pi} \frac{\delta p E_D}{\epsilon C_o},$$

(3.24)

where $C = \epsilon C_o$, with $C_o$ being the geometrical capacitance of the sample.

### 3.2 Experimental Methods

The difficulty with measuring Barkhausen noise in the relaxors is that there are no macroscopic domains, so the signal from any Barkhausen events from clusters of nanodomains will be very small. Previous experiments by O’Brien et al. (1997) did not find Barkhausen events in mesoscopic samples of the relaxor PLZT. In designing a measurement circuit, we must have sensitivity to such small Barkhausen events, as well as avoid introducing any spurious signals.

In our driven Barkhausen experiment, we apply a sinusoidal ac electric field on the sample, and then would like to measure the Barkhausen response. However, as can be expected from the large dielectric susceptibility for the relaxors, there is a large systematic response from the relaxor, most likely from smooth domain wall motions, which will provide a signal that would swamp out any Barkhausen events. Another competing signal is the nonlinear harmonic response from the relaxors - they have strong components at harmonics of the driving frequency $f_D$. Our solution to this problem is using a bridge setup (Fig. 3.3). Here two of the arms on one side of the bridge are identical relaxor samples so that systematic response at the fundamental frequency and higher harmonics would cancel each other out. The other side of the bridge consisted of resistors and decade capacitors in
parallel for balancing the bridge. The bridge was driven by two sinusoidal signals from op-amps 180° out of phase with each other, serving to “float” the bridge. The signal across the bridge is then amplified by a Stanford Research Systems SR550 preamp and a PAR113 broadband amplifier, passed through a Stanford SR650 serving as an anti-alias filter, and digitized by a 16-bit ADC on the Signal Recovery 7265 lock-in. By adjusting the impedances on the left side of the bridge, it is possible to balance the signal across the bridge to better than 80 dBC (compared to the original applied signal) at the fundamental frequency, leaving the random Barkhausen noise response of the system to be amplified and digitized. The impedances on the left arm served to balance out any uncompensated signal at the fundamental frequency from imbalance of the samples on the right side of the bridge. The matching of the samples serve to provide balancing of higher harmonic signal. A single crystal of the relaxor was configured as two capacitors in series with two small electrodes on one side and a single large electrode on the other. Thicknesses were typically 0.5 mm with electrode areas of roughly 1 mm² area.

Since we expect there to be periodic noise at the harmonics $f_D$, as well as aperiodic noise if there is any thermal jitter in the timing of the noise or slow drift in the detailed distribution of the steps with field (e.g., from aging),

---

Note that because the bridge is configured with the two samples on the same side of the bridge, any mismatching of the sample capacitances would result in unequal ac fields being applied on each sample. (The two samples on the right side of the bridge form a voltage divider.) Since the fields are unequal, the harmonics won’t cancel completely. This configuration was chosen so the balancing impedances on the other side of bridge did not have to be high-impedance components and could be mostly resistive. High-quality, stable potentiometers which are easily obtained.

One way to ensure that equal fields are applied to both samples (even if their capacitances did not match) is to turn the bridge on its side and apply the ac field at the points where the Barkhausen signal is currently measured. But then the balancing components on the bottom half of the bridge would need to match the high impedances of the samples in order to null the common mode signal across the bridge. Large variable capacitors (the relaxors have a very large dielectric permittivity) would be needed to balance the in phase signal along with large variable resistors in parallel with the capacitors to balance the out of phase signal. These electronic components are more difficult to obtain.

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2 Note that because the bridge is configured with the two samples on the same side of the bridge, any mismatching of the sample capacitances would result in unequal ac fields being applied on each sample. (The two samples on the right side of the bridge form a voltage divider.) Since the fields are unequal, the harmonics won’t cancel completely. This configuration was chosen so the balancing impedances on the other side of bridge did not have to be high-impedance components and could be mostly resistive. High-quality, stable potentiometers which are easily obtained.

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Figure 3.3: Bridge circuit for Barkhausen noise experiments. A sinusoidal voltage from the 7265 is filtered and amplified through two op-amps 180° out of phase with each other and applied across the bridge. Two matched capacitors S1 and S2 on the same relaxor single crystal are on one side of the bridge, and adjustable capacitive and resistive impedances are on the other side for nulling the voltage across the bridge. The Barkhausen off-balance signal of the bridge is then amplified, anti-alias filtered, and digitized.

It is important that we minimize any non-Barkhausen contribution to the noise. By matching samples on one side of the bridge, we help to eliminate the nonlinear systematic response. We also need to minimize the presence of higher harmonics as much as possible - we have used an oscillator with high spectral purity (the oscillator on the 7265 lock-in with -80dB total harmonic distortion at 1 kHz) which we then passed through a passive low-pass filter and an active notch filter. Now if there were some phase jitter in a periodic signal, this would show in frequency space as wings about the harmonics of the driving frequency. To minimize this, we need to make sure the data taking sweep stays synchronized with the driving signal - this is accomplished using the 7265 oscillator as well as the 7265 ADC, which run off the same master clock (EG&G, 2001).
Figure 3.4: Barkhausen spectra for PMN/PT (90/10). Typical power spectra for PMN/PT (10%) with $E_D = 121$ V/cm and $f_D = 50$ Hz at 280 K (spectrum 2) is shown above a background (spectrum 1) of equilibrium dissipative noise and amplifier noise. The harmonics of 60 Hz have been removed.

There are some practical considerations for the choice of driving field waveform and driving rate. A sinusoidal field is used instead of a triangular wave to avoid the high-frequency harmonics that arise from the non-analytic corners of a triangular wave. We also need to drive the clusters at a fast enough rate so that they are responding to the driving field rather than just thermal fluctuations (if the rate is too slow, all the clusters will just be in quasi-equilibrium and FDT noise would dominate), but not so fast as to make the bridge difficult to balance. We found a driving frequency $f_D$ of 50 Hz to be suitable. It also is commensurate with our sampling rate of 10 kHz, so that an integral number of periods are included in a 30,000 point digitization sweep, eliminating the need for windowing. Typically, 16 consecutive time series are measured, and the power spectra are then averaged.
3.3 Results

The PMN/PT (10%) Barkhausen results show qualitatively similar behavior to PMN [Colla et al., 2002] with some interesting differences given their stronger ferroelectric content. Figure 3.4 shows typical $S(f)$ measured for PMN/PT (90/10) with $E_D = 0$ and 121 V/cm at 280 K, where indeed there is periodic and aperiodic noise. The Barkhausen spectra do indeed show both periodic and aperiodic components, and are in reasonable agreement with spectral forms derived based on the Preisach independent step model, allowing us to use those derivations to extract an estimate for the typical dipole moment of a coherent polar cluster $\delta p$.

In one type of Barkhausen experiment, we measure $\delta p$ as a function of temperature. The relaxor is cooled from a high-temperature anneal to a series of temperatures $T$, where after the temperature has stabilized, noise spectra are taken. We then cooled to the next lower $T$, and repeated the
measurement, all with the same driving field $E_D$. Background spectra with zero driving field were also taken so that the equilibrium and amplifier noise power can be subtracted from the Barkhausen noise power. For consistency in the case of PMN/PT (90/10), we established the protocol of cooling in zero ac field, and taking zero ac field background spectra at $T$ before applying an ac field to measure the Barkhausen spectra. Similar to PMN, $\varepsilon' \cdot (\delta V)^2$ (and hence the dynamic dipole moment step size) shrinks abruptly as $T$ is lowered into the relaxor regime (Fig. 3.5).

Since the spectral form for the Barkhausen noise is close to that derived from a simple Preisach model, we can use Eq. 3.24 to calculate a typical dipole moment for PMN/PT (90/10). Using the aperiodic power at 310 K and 162 V/cm, we get a typical $\delta p \approx 1.5 \times 10^{-21}$ C-cm. Because we suspect that there may be additional noise power from artifacts in the measurement and sample mismatching (especially for drive fields larger than 162 V/cm), this number should be taken as an upper limit. The rolloff frequency $f_C$ of the envelope to periodic power (Eq. 3.14) gives another estimate of $\delta p$ of roughly $6 \times 10^{-22}$ C-cm.

It is interesting to note that PMN at smaller fields showed larger dipole moments than PMN/PT (90/10) with the added ferroelectric PT doping. We have previously calculated a rough estimate of a nanodomain dipole moment for PMN using static correlation lengths (Vakhrushev et al., 1996; You, 2000; Yoshida et al., 1998) and a saturation polarization of about $3 \times 10^{-23}$ C-cm, which should roughly be valid for PMN/PT (90/10). This corresponds to an order of 100 nanodomains in a coherent cluster (assuming random arrangement of the dipole moment, so that the cluster dipole moment scales as the square root of the number of nanodomains). We have previously reported (Colla et al., 2002) a dynamic dipole moment of $2 \times 10^{-22}$ C-cm at
250 K with a driving field amplitude of 110 V/cm, but PMN/PT (90/10) at
160 V/cm and 310 K has a step size of only $5 \times 10^{-23}$ C·cm, a slightly smaller step size for a slightly larger field. We performed the PMN Barkhausen experiments at lower fields than for PMN/PT (90/10), but extrapolating the PMN/PT (90/10) to lower fields (using the noise vs. field results) gave consistently smaller step sizes for PMN/PT. But of course this is from an extrapolation so the calculated PMN/PT values may be within error bars of the PMN measurements.

Now, one might suspect that the noise, like the dielectric aging behavior, would be very history dependent. However, the PMN Barkhausen noise showed no prominent dependence on history. We could take the noise temperature dependence under a fixed driving field on two separate runs that did not have an identical field and temperature history, and still have reproducible noise power between the two runs. Figure 3.6 shows one such example where two separate runs with different temperature histories gave quantitatively similar noise results. In fact, the background noise spectra for the PMN experiments were taken on separate runs from the driven Barkhausen experiments. The effect of aging only showed up to an extent as a slow drift in the balance of the bridge, but this was not significant enough on the time scale of a noise measurement. (As we’ve mentioned, typically 16 spectra, each 3 s long, are averaged. With the added time in between each spectra for downloading the data curve to the computer, about 15 min is spent per noise measurement, after which we would manually rebalance the bridge for the next measurement).

The most striking difference with PMN/PT (90/10), compared to PMN, is the hysteresis and history dependence of the noise. The protocol mentioned above for the noise vs. $T$ experiments was an effort to minimize differences
Figure 3.6: Insensitivity of Barkhausen noise in PMN to history. The dipole moment step size (arbitrary units) of PMN on two separate runs with different times spent at each measurement temperature is shown. A driving field of 150 V/cm rms was applied along the $\langle 100 \rangle$ direction. Noise power at overlapping temperatures in the two runs agree.

between runs arising from different histories of temperature and field application. Even so, without exactly identical histories, the noise measurements, while they showed qualitatively similar behavior, could differ by a factor of 2 in magnitude. In particular, the noise power is sensitive to the ac field application history. In one such experiment testing the field history dependence of PMN/PT (90/10), it was found that cooling in an ac field (acFC, ac-field-cooling) of 240 V/cm resulted in noise power ten times larger than cooling in zero ac field, then applying 240 V/cm ac field at 250K to perform the Barkhausen measurement (ZacFC, zero-ac-field-cooling). The effect of the ac field was only on the dynamic step size $\delta p$ and not the size of the equilibrium fluctuators: turning off the ac field gave background noise power similar to that in for ZacFC case. (At this temperature, the zero field background noise power is dominated by fluctuation dissipation noise and not
Figure 3.7: Noise power in the octave from 512 to 1024 Hz illustrating the dramatic history dependence seen in the noise for PMN/PT (68/32). Solid circles show the typical step size on cooling at $E_D = 28$ V/cm to $375$ K in the ferroelectric regime. $E_D$ was then set to $170$ V/cm and left overnight. On reheating at $28$ V/cm the next day, the noise has increased by an order of magnitude. Note the extreme sensitivity of the step size to incipient ferroelectricity.

background amplifier noise.)

This history dependence of the noise is even more dramatic in PMN/PT (68/32), which is near the morphotropic phase boundary (on cooling it enters a ferroelectric, then a relaxor regime). Figure 3.7 shows $(\delta V)^2$ taken with $E_D = 28$ V/cm on cooling to $375$ K (in the ferroelectric regime), where the ac drive was increased to $170$ V/cm and left overnight; the next morning, on reheating at $28$ V/cm, we see that the step size has increased by an order of magnitude, and follows a completely different curve on reheating. Such effects are likely attributable to the growth of large-scale ferroelectric correlations.

We also looked at the noise power vs. driving field amplitude at fixed temperature. In such an experiment, we again cool from a high-temperature anneal to the experimental temperature $T$, where at fixed $T$ we measure spectra for a particular ac drive amplitude $E_D$, then increase the field, re-
Figure 3.8: Noise Power vs. Driving Field Magnitude for PMN/PT (90/10). Noise power above the relevant backgrounds for PMN/PT (10%) in the octave from 512 to 1024 Hz as a function of $E_D$ for (a) aperiodic and (b) periodic components. Data points are compiled from experiments where $T$ is changed at fixed $E_D$. Compare the nonlinearity of the noise with (c) the linearity of the in-phase permittivity (normalized by the extrapolated ac permittivity at 0 V/cm) at 230 K.
balance the bridge, and repeat the noise measurement, all while sitting at $T$. Again, we see that as in PMN, the noise in PMN/PT (90/10) increases nonlinearly with $E_D$ in a region where the susceptibility response is close to linear (Fig. 3.8).

### 3.4 Discussion

Give that the Barkhausen noise is particularly sensitive to ferroelectric clustering, the progression of increased sensitivity of the noise to the ac field history in the PMN/PT family as we move towards the morphotropic phase boundary reflects a fundamental shift in nature of the underlying equilibrium state of the relaxor as PT doping is added. At one extreme, PMN is insensitive to ac field history. It is firmly frozen in a glassy state so that the application of small ac fields had no noticeable effect on the polar ordering. At the other extreme, the ac field history dependence of the noise is especially dramatic for PMN/PT (68/32) near the morphotropic phase boundary. The relaxor is far out of equilibrium and shows strong cumulative aging, so whether or not it forms large polar clusters is strongly dependent on the field history. In the middle is PMN/PT (90/10), where the polar cluster shows a significant dependence on ac field history: acFC in fields comparable to that used in the PMN noise experiments increases the polar cluster dipole moment by a factor of 10, but had no effect on the PMN polar clusters. Together with the zero-field cumulative aging behavior, this strongly suggests that PMN/PT (90/10) is not merely PMN with more ferroelectric content, but that it is really trying to form long-range ferroelectric order and that the ultimate equilibrium state may be ferroelectric.

The nonlinear dependence of the noise in a regime where the response
is close to linear does not agree with a simple Preisach-like picture of independent steps, which we expect to have a linear dependence on the driving field amplitude (Eq. 3.24). This suggests a broad distribution of \( \delta p \)'s, with a calculated \( \delta p \) at some \( E_D \) giving only a typical step size under the particular drive conditions. The distribution would likely include a large number of very small \( \delta p \)'s with small kinetic barriers that follow the drive field in quasi-equilibrium and provide most of the in-phase response. Noise response would be dominated by medium-sized \( p \)'s, while large \( p \)'s with large kinetic barriers would remain frozen until \( E_D \) was large enough to overcome local random fields as well as the large barrier. However, the barriers must grow faster with cluster size than do the dipole moments, or else large clusters would flip in small fields. In other words, as a cluster grows in size, whether it is likely to flip under the applied field depends on the competition between the increased driving force felt by the larger dipole moment under \( E_D \) and the coercive force (from the kinetic barrier, which is also growing with cluster size) against flipping. We do not yet have a good understanding of how the barrier depends on the size of the reorienting cluster, but in simple simulations (Attari et al., 2002), a power-law dependence of the barriers on \( p \) did give nonlinear noise dependence while keeping the response close to linear.

The abrupt drop in noise power as a function of temperature (by as much as two to three orders of magnitude in a temperature range of roughly 0.1 \( T_P \)) seen in PMN as well as PMN/PT is a surprising result with strong ramifications on possible models of the relaxors. To think about what kind of scenario is needed for such an abrupt shrinkage of \( \delta p \), let’s first take stock of what we do know. Since we know from neutron scattering that the static nanodomain size grows as \( T \) is lowered, and it is intuitive to expect that the nanodomains form cooperative coherent clusters, we might suspect that
the Vogel-Fulcher glassy freezing arises from growing polar clusters which eventually freeze out. It turns out that these scenarios cannot account for the abrupt drop in $\delta p$. The cluster and barrier distribution must also allow for a linear response but nonlinear noise dependence on the driving field amplitude.

Now we know from the nonlinear field amplitude dependence of the noise that we are measuring a $\delta p$ that reflects a typical size of the polar clusters that we are able to flip for the given field and temperature conditions. There is some distribution of polar clusters with dipole moment $p$ that is some function of cluster size in the relaxor. Associated with each cluster is a kinetic barrier $U_A$ which we expect to be a function of $p$. So for a particular
And $E_D$, we are able to flip clusters up to some cutoff dipole moment $p_{\text{cutoff}}$ set by the dipole moment of the cluster and the activation energy needed to flip the cluster. See Fig. 3.9 for an illustration of these concepts.

The abrupt drop in noise power tells us what models of the relaxor freezing are not likely to be true. A fixed temperature independent, unimodal distribution of polar clusters with associated barriers will show noise decreasing weakly on cooling just from simple activated kinetics. Simple growth of independent nanodomains on cooling is also not a likely explanation of the glassy freezing, since the dipoles will grow comparable with its associated anisotropy barriers, so $\delta p$ would continue to grow as the relaxor is cooled. Similarly, growing clusters of cooperative nanodomains would have a dipole moment that grew as the square root of the number of nanodomains (if the nanodomains were randomly aligned), but the associated barrier would grow slightly faster with the cluster size than the dipole moment, so in our Barkhausen experiments, for a particular drive field and temperature, we would be able to flip clusters up to some $p_{\text{cutoff}}$. As the clusters grow on cooling, the distribution of $p$'s in Fig. 3.9 would shift to the right and $\delta p$, a mean, typical dipole moment measured, would saturate near $p_{\text{cutoff}}$. As we cool, simple activated kinetics would mean $p_{\text{cutoff}}$ would start to shrink (since thermal activation is reduced) and move to the left, resulting in a drop in $\delta p$, but only as $T$ to some power less than one.

One way for these scenarios to work would be for the relaxors to have some bimodal distribution of $p$'s, so that as the distribution grows and the dominant larger mode of the distribution grows past $p_{\text{cutoff}}$, the mean would abruptly drop and reflect the mean of the smaller mode of the distribution. What we think is a more likely explanation is that the barriers grow dramatically for lower $T$. In this case, the barrier height is not simply a
function of cluster dipole moment $p$, but also has a temperature component that abruptly increases for lower $T$, e.g., possibly something of the form

$$U_A(p, T) = f(T)p^n, n > 1$$  \hspace{1cm} (3.25)

So in summary, our Barkhausen noise experiments give us a measure of a coherent dynamic polar step size for the particular driving field and temperature conditions. While a simple Preisach model of independent steps provided a useful method to derive spectral forms for interpreting the noise measurements, nonlinear noise power dependence on the driving field amplitude indicate that a distribution of dipole moments is present. The most striking result is the abrupt drop in $\delta p$ on cooling into the relaxor regime in both PMN and PMN/PT relaxors. Because of the large abrupt drop, we do not think that the glassy Vogel-Fulcher freezing in the relaxors can be explained by simple growing independent nanodomains (which we already suspected because of the presence of complicated aging behavior) or growing cooperative clusters of nanodomains. Instead of growing polar units, we think it is an abrupt growth in activation barriers which accounts for the glassy freezing. In discussing the aging behavior, we have already alluded to the idea that we think there are degrees of freedom separate from the nanodomains which provide the glassy freezing which then couple into a huge barrier growth for the polar clusters. We will pull results from these two probes of the relaxors into what we think is a likely picture in the concluding chapter. For the next chapter, we discuss another type of noise results which we believe are the first measurements of polarization noise in the relaxors.
Chapter 4

Polarization Current Noise in the Relaxors

As we have discussed in the previous chapter, there is a large systematic component to the polarization in our sinusoidally driven Barkhausen noise experiments that reflects the mean polarization. With the ac driven Barkhausen experiments, we were able to measure a typical dipole moment step size (for the particular field and temperature conditions) on top of this mean polarization. Another type of Barkhausen experiment would be to measure the field-induced polarization/depolarization Barkhausen events that occur after abruptly changing the applied DC bias field (e.g., from depolarization events after removing a DC bias field) and sweeping the temperature. A measure of any abrupt polarization steps would give an upper limit on the amount of polarization change occurring via such discrete polarization units compared to that from smooth domain wall motion. However, as we’ve already said, such discrete units in the relaxors are very small, and directly detecting these steps by measuring the pyroelectric current is difficult: e.g., any extraneous noise from vibrations (relaxors are very piezoelectric) or from pickup of 60 Hz power line noise could easily obscure the steps. In fact, early attempts to look for such steps in the pyroelectric current of SBN:La were plagued by noise problems and unsuccessful. However, while measuring polarization curves for SBN:La, we started observing steppy events on the oscilloscope which at first seemed like random pickup - but then showed promising correlations with field conditions (e.g., lack of steps without any history of field bias).
In this chapter, we will present results from measurements of these pyroelectric current steps. Small, individual pyroelectric steps along the polarization direction were measured for three relaxors [SBN:La (60/40), SBN (60/40), and PMN/PT (90/10)] when cooled in a dc field and along the depolarization direction when zero-field heated. We will present representative distributions of discrete polarization steps in SBN:La (60/40) for cooling under several fields and subsequent zero-field heating. These steps are not observed in the relaxors when cooled and heated in zero field, except for the occasional random step. Similar steps were observed in SBN (60/40) and PMN/PT (90/10), with results to be presented in a later publication. From the distribution of such steps vs. temperature we calculate an upper limit on the fraction of the polarization occurring as discrete steps (as opposed to, e.g., smooth domain wall motion) in these relaxors.

However, we cannot be certain that these results might not arise from artifacts (e.g., from surface contamination coupling to the intrinsic relaxor polarization and generating currents) for two reasons. We have prior data on SBN (60/40) (Chao et al., 2005) which did not show these large discrete steps and for which we extracted an upper limit to the size of discrete steps based on the excess noise in the polarization current. Later experiments on the same sample found discrete steps larger than previously given upper limit. Further, an initial cleaning of the sample surface produced a qualitative change in the shape of the steps observed, and also reduced the amount of step noise. The behavior after cleaning was more consistent with what would be expected from individual polarization/depolarization steps. A second cleaning of the samples produced no noticeable change in the results, so we believe that while the initial data (not presented) included artifacts from contamination, the results presented below may likely be from individual pyroelectric steps.
4.1 Experimental Methods

Experiments were performed on the same samples with electrode configurations as described in previous chapters. In these experiments, a DC bias field (supplied by everyday alkaline batteries) is applied to the sample on cooling (FC) to a low temperature (typically 200 K). The field is then turned off and the relaxor heated in zero field (ZFH). As the field is swept, the pyroelectric current is measured and digitized. Figure 4.1 shows the measurement circuit, using the same op-amp based current-to-voltage converter (with resistive feedback, typically 100 MΩ) as for the aging experiments. The voltage at the output of the CVC would then be further amplified as necessary,
anti-aliased filtered, and digitized by an ADC on the 7265 lock-in. Typically, 30000 point time-series were taken at a sampling rate of 1 kHz. These sweeps were taken continuously as the temperature was swept, with 14 s dead time in between the 30 s sweeps during which the curve is dumped over the GPIB bus from the lock-in to the computer. The signal to the ADC is ac-coupled to remove the dc component of the polarization current and allow for maximum digitization resolution for the small polarization steps. This DC component is instead measured by a second ADC immediately after the CVC at the beginning of every sweep. The intrinsic noise of the op-amp was not significant enough to affect the measurement for these experiments. The experiments were performed in the same flow-through cryostat and temperatures were typically swept at about 5 K/min or less for cooling and 5-10 K/min for heating.

The steps are small and relatively sparse in time. In order to build a distribution of step sizes, we must be able to extract only those points in the 30000 point time series that are actually steps for individual integration. To do this for a large amount of sweeps is harder than it sounds, especially when there is low-frequency drifts in the signal (on order of 10 s) combined with the small size of the steps above the background noise. We are currently using a program in Matlab for identifying the steps. The algorithm is as follows. Any baseline drift is first subtracted from the signal using a polynomial fit. Then a threshold is set for determining the start and end of a step. The thresholds are Schmidt-triggered, i.e., there are different thresholds for determining the start and the end of a step. For the start of the step, there are two independent thresholds (positive and negative) to better accomodate the uni-directional nature of the steps. Note that the assymmetric starting thresholds do not bias the results in favor of detecting unidirectional steps:
in practice, the two starting thresholds chosen are actually biased against
the direction of the step (i.e., the threshold in the direction of the steps is
larger than that of the opposite sign). Any time the voltage crosses beyond
the thresholds marks the beginning of a step. These thresholds are manually
set for each sweep, typically around 5 standard deviations from 0. A second
set of (symmetric) thresholds (smaller than the starting thresholds) is used
to detect the end of the current pulse, so that after \(x\) number of points are
encountered with voltages within the ending thresholds, the step is said to
end. Typical ending thresholds are about 0.5 standard deviations from 0.

4.2 Results

In this section we present representative results for SBN:La. Figure 4.2 shows
typical digitization sweeps for the pyroelectric current in SBN:La for (a) FC
at 190 V/cm and (b) subsequent ZFH. Current pulses from the discrete po-
larization steps are seen for both cooling and heating only for runs where a dc
bias field was applied on cooling. While the occasional small step is seen for
background ZFC/ZFH runs, the noise is gaussian. Background fluctuations
are from fluctuation dissipation and amplifier noise, and are comparable for
both the FC/ZFH and ZFC/ZFH cases.

The distribution of the steps vs. temperature is shown for FC (at several
fields) and subsequent ZFH for SBN:La (60/40) (Fig. 4.3). The pyroelectric
current and the integrated dc polarization is plotted vs. temperature in
Fig. 4.4. It is clear that there is hysteresis in the steps that coincide with the
pyroelectric current peaks. It also appears that there aren’t many discrete
steps in SBN:La until the bias field is above 100 V/cm. A histogram of
polarization steps at all temperatures is shown for the FC(190 V/cm)-ZFH
Figure 4.2: Example of steps in the pyroelectric current. Time series of the pyroelectric current are shown for SBN:La (60/40) for (a) FC at 190 V/cm and (b) subsequent ZFH. The dc component of the pyroelectric current has been removed by the ac coupling of the amplifier. The FC time series shown was taken at 275 K, where the formation of polarization is well under way. The ZFH time series is at 312 K, right after the depolarization current peak. Corresponding background time series from a separate run under zero field are shown in grey (and offset vertically for clarity). The insets are expanded views of selected steps.
Figure 4.3: Distribution of polarization steps vs. temperature for SBN:La (60/40). The dipole moment of discrete steps observed in the polarization current plotted against temperature is shown for SBN:La on field cooling (black dots) and zero field heating (red plus signs) for several FC bias field: (a) 65 V/cm, (b) 95 V/cm, (c) 130 V/cm and (d) 190 V/cm. The insets show enlarged views of the distribution.
Figure 4.4: Pyroelectric current and polarization vs. temperature for SBN:La (60/40). Pyroelectric current (right y-axis) and dc polarization (left y-axis) is plotted against temperature for FC (191 V/cm) and subsequent ZFH. The polarization curve (obtained from integrating the dc pyroelectric current) is approximate since the current is measured at the beginning of every digitization sweep (45 s apart). A current was measured near 400 K (not shown) is most likely a leakage current from the applied field and has been ignored in calculating the polarization.

experiment (Fig. 4.5).

4.3 Discussion

Not surprisingly, the individual discrete steps observed on field cooling are smaller in size and fewer in number as the polarization is slowly formed, with many of the steps occurring well below $T_P$ and after the peak in the dc component of the pyroelectric current. However, after spending time at low temperature, the polar clusters have grown, and on reheating in zero field, discrete depolarization steps are larger in size (often by a factor of 20) and number (about twice as much as during FC). Sometimes one large step is seen to cause a second one immediately after it. More of the depolarization is seen to occur in larger, discrete steps than the polarization steps, with a significant tail of steps at higher temperatures where much of the polarization formed
Figure 4.5: Histogram of dipole moment steps at all temperatures for SBN:La (60/40). SBN:La is FC at 190 V/cm and subsequently ZFH. The bin size is 5 fC·cm for FC, and 0.5 pC·cm for ZFH. Note that the y-axis scale is logarithmic.

has melted. That the depolarization steps are larger makes sense, since we expect the clusters to grow larger and correlations to become stronger after time spent at lower temperatures, although the difference in step size is probably enhanced by the larger temperature sweep rate on heating (5-10 K/min compared to less than 5 K/min).

For the 190 V/cm SBN:La run, there are roughly twice as many steps on ZFH compared to FC, with the mean step size of 63 fC·cm (14 pC/cm², 0.45 pC) compared to 5.2 fC·cm (1.2 pC/cm², 0.037 pC), and a total 42 pC·cm (9.6 nC/cm², 300 pC) of the depolarization occurs in these discrete steps, compared to 1.9 pC·cm (42 pC/cm², 13 pC) as discrete steps on FC. As we have mentioned, we are able to take data roughly two-thirds of the time (30 s sweeps with 14 s in between sweeps). So if we assume that the steps are evenly distributed in time, we measure about two-thirds of them. This means that roughly 0.0015% (0.03%) of the total polarization change of 40 μC/cm² occurs in these discrete steps on FC (ZFH). Using a rough estimate of the
saturation polarization as about 60 $\mu$C/cm$^2$, the largest discrete polarization [depolarization] steps of 0.26 pC·cm (60 pC/cm$^2$, 1.9 pC) [9.3 pC·cm (2 nC/cm$^2$, 66 pC)] corresponds roughly to units of dimension 16 $\mu$m [50 $\mu$m] on a side. The smallest steps we are capable of detecting is set by the amplitude of the background current fluctuations (1 pA rms amplitude at the susceptibility peak, where the background noise is largest) and the digitization time resolution (1 ms). Hence, we are sensitive to steps of roughly 1 fC in size, or a dipole moment of about 0.15 fC·cm.

So for SBN:La we have an upper limit on the size of polar clusters reorienting in discrete steps for a particular field bias, and the fraction of the total polarization that occurs in these steps. The rest of the polarization change would then come either from steps smaller than 0.15 fC·cm (below the background noise, so that we are insensitive to them), or from a very large, slow component such as domain wall creep. In fact, this must account for a large part of the polarization change, since we measure a large, smooth low-frequency component of the depolarization current along with individual discrete steps as we pass through the pyroelectric current peak. (Fig. 4.6).

When we first noticed these steps in the pyroelectric current, it was clear that they only occurred after the application of a dc bias field, but because there were such huge steps at 400 K (well above $T_P$ inside the paraelectric regime) as well as at temperatures away from the pyroelectric current peak, we were concerned that the steps were possibly from some artifact of surface contamination. Hence after taking enough data to characterize the steps, we removed the samples from the cryostat and cleaned them with ethanol and acetone by swabbing the surfaces and placing them in a solvent solution in an ultrasonic cleaner. Afterwards, the results were significantly different. While steps (now qualitatively different) still occurred on FC near 400 K (where
there is a large leakage current from loss in the sample), steps otherwise only occurred once the pyroelectric current peak was reached (and afterwards as well). This made much more sense as the steps occur where we expect the polarization to be forming. The steps were also 1000 times smaller in magnitude, and fundamentally different in shape - the ones before cleaning were very switchy, with a discontinuous drop in amplitude at the end of a step, compared to the steps after cleaning, which were of a smoother pulse shape with a slow decay back to the equilibrium fluctuation amplitude. After a thorough set of experiments, we again cleaned the samples a second time, and this time there was no noticeable effect on the polarization step behavior.

So we are now fairly certain that the pulses in the pyroelectric current we measure reflect actual polarization steps in the relaxors. In particular, the behavior of these steps is as we expect. They occur at temperatures which coincide with the formation/melting of the polarization: both for polariza-
tion and depolarization, we do not observe steps until slightly before the pyroelectric current peak. This is followed by a tail of steps for a significant temperature range after the current peak. The steps also point along the direction of the larger dc polarization current, and change sign along with the current on reheating. There is temperature hysteresis in the occurrence of the steps that corresponds with the temperature hysteresis of the polarization. The steps also have a logical dependence on the field: larger field, gives more steps and larger steps. All in all, the behavior fits with a sensible picture of individual clusters re-orienting as the polarization forms or melts. For those wanting to compare the $dp$ we measure here with the $\delta p$ from the Barkhausen experiments, keep in mind the experimental conditions under which they were measured. The Barkhausen experiment $\delta p$ was a dynamic step size for a given driving field and temperature that we were able to flip. In the pyroelectric current experiments, the $dp$ measured is polar cluster formed under a particular field-cooling condition, which then reorients abruptly as the temperature is swept.

In a prior publication (Chao et al. 2005)\textsuperscript{1}, we gave an upper limit on discrete polarization steps in SBN of $4 \times 10^{-22}$ C·cm, but this number is not directly comparable to our current results on the doped SBN:La sample, or later data showing steps in SBN (to be published). The analysis for SBN was done in the frequency domain, assuming that all of the polarization change occurred in discrete steps of a certain size (Preisach model), so that any $1/f^2$ noise power above the $1/f$ background spectrum was integrated to calculate a typical step size. However, we now know that less than 0.0015-0.03% of the polarization change occurs in these discrete steps (for SBN:La). So

\textsuperscript{1}This paper had multiple authors. The SBN pyroelectric current noise measurements published were taken by E. V. Colla.
assuming that 0.001% of the steps are discrete in SBN, this gives an estimated maximum step size from our published SBN data of $10^{-19} \text{C}\cdot\text{cm}$, compared to our current SBN:La mean step size on order of $10^{-15} \text{C}\cdot\text{cm}$. While the newer data presented is for SBN:La, we also have later data on the same SBN sample which also showed discrete steps not seen before. It remains a logical possibility that the samples could have changed with time. Also, a small ac field (used for simultaneous measurement of the susceptibility) was applied in the published but not the later experiments. It is possible that the ac field may have changed the polarization behavior, unpinning clusters so that more of the polarization change may occur smoothly. It is also possible that in the analysis for the published results that while looking for “typical” behavior, the quietest runs may have been favored and intermittent events ignored as glitches. The difference in behavior with prior results, as well as the large effect that an initial surface cleaning had on the polarization behavior (although, as has been stated, a second cleaning did not produce further changes) is cause for concern. Both results do agree to the extent that the majority of the polarization are occurring in very small steps which we are not sensitive to (i.e., in both sets of data, no steps are seen for a majority of the time), and the upper limit published for SBN may be low due to exclusion of actual excess polarization noise as glitches. Further analysis of the newer SBN data and detailed re-examination of older SBN data in light of the newer results is needed.
The aging and Barkhausen noise results point towards a likely picture of the glassy freezing in the cubic relaxors. Cubic relaxors PMN, PLZT, and PMN/PT with low PT content show spin-glass-like aging at low temperature. We have discussed in detail aging behavior in PMN/PT (90/10) which is analogous to the magnetic re-entrant spin-glass system CdCr$_{2x}$In$_{2-2x}$S$_4$ ($x > 0.85$) (Vincent et al., 2000; Dupuis et al., 2002). The complicated spin-glass aging requires cooperativity between many aging units; however, the insensitivity of the aging to small field perturbations suggest that the aging does not come from large cooperative clusters of nanodomains, but from a large number of much smaller units. One candidate for these aging units would be moments canted with respect to the mid-scale mean (111) polarization (along ⟨100⟩) which have been observed by neutron scattering (Egami, 1999; Dkhil et al., 2001). Glassy freezing of these canted moments would then couple to the local ferroelectric order, as in a re-entrant xy spin-glass. The temperature dependence of the dynamic polar step size, which shows an abrupt drop in the Barkhausen noise power, suggests a rapid growth of barriers much faster than any growth in the cluster size, is consistent with this. Then it follows that polar clusters of nanodomains would not be able to respond to dc field jumps as they are pinned by strong random fields as well as subject to a rapid growth of associated barriers from the glassy freezing. That the uniaxial relaxors SBN and SBN:La, which do not have the canted
moments, do not show SG-like aging at low-temperature strongly supports this argument.

In fact, it has recently come to our attention that this idea has been suggested before (Viehland et al., 1995). In PLZT and PMN/PT cross-hatched tweed-like domains have been observed optically and by TEM for compositions with large ferroelectric doping (Viehland et al., 1995; Xunhu et al., 1994). These premartensitic tweed precursors do not go away as the ferroelectric doping is lowered, remaining on the unit-cell scale as the above-mentioned canted moments. Viehland et al. (1995) has previously noted the relevance of a theory by Sethna and company (Kartha et al., 1991; Sethna et al., 1992), where the tweed precursors of the martensitic phase transition have been shown to be analogous to the spin-glass phase in disordered magnetic systems. In this two-dimensional model, diagonals between unit cells are shown to be analogous to frustrated spins in a 2D spin-glass, so that the tweed Hamiltonian can be mapped onto a 2-D Ising spin-glass Hamiltonian with random fields. The tweed precursor phase between the high temperature austenitic and the low-temperature martensitic phases is analogous to the spin-glass phase being an intermediate between the ferromagnetic and anti-ferromagnetic phases in disordered magnetic systems. The authors suspect that a generalization to 3-D would show a true spin-glass analog for the tweed phase.

In a sentence, our aging and Barkhausen results in the cubic relaxors, the lack of low-T SG-like aging in the uniaxial relaxors, along with Sethna’s theory of the tweed precursors, provide compelling evidence that the glassy freezing does indeed come from the canted moments. Further similations of the aging behavior of tweed precursors would be particularly interesting for comparison with experimental results.
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Author’s Biography

Lambert Chao graduated from Whitney M. Young Magnet High School (Chicago, Illinois) in 1994. He went on to study at Stanford University, receiving his B.S. in Physics and Mathematics with Honors in 1998. After entering the Ph.D. program in the Department of Physics at the University of Illinois at Urbana-Champaign, he joined the lab of Michael Weissman in 1999, earning his Ph.D. in 2006. In the meantime, he is staying on for the Fall 2006 semester at UIUC as a visiting lecturer and lab instructor, teaching and designing labs for Physics 598OS Optical Spectroscopy.