Deviation from Curie-Weiss behavior in relaxor ferroelectrics

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The deviation from Cure-Weiss behavior has been investigated in lead magnesium niobate relaxor ferroelectrics. At high temperatures, the susceptibility was found to follow the Curie-Weiss relationship. A Curie constant and temperature of 1.2×10^5 and 398 K, respectively, were obtained. With decreasing temperature the deviation was found to increase. It is proposed that this deviation arises due to short-range correlations between polar regions, and that these correlations at high temperatures are the precursor to a freezing of the polarization fluctuations into a glassy state. A local (glassy) order parameter was calculated from the susceptibility by analogy to spin glasses [D. Sherrington and S. Kirkpatrick, Phys. Rev. Lett. **35**, 1972 (1975)]. These results are compared to the rms polarization [G. Burns and F. Dacol, Solid State Commun. **48**, 853 (1983)] and to the measured remanent polarization. The frequency and field dependence has also been investigated.

I. INTRODUCTION

Lead magnesium niobate (PMN) is a relaxor ferroelectric. Relaxors are characterized by a frequency dispersion of the complex susceptibility, where the temperature of the susceptibility maximum (T_{max}) shifts to higher temperatures with increasing frequency. Relaxors have an inability to sustain a macroscopic polarization until temperatures significantly below T_{max}, but a local (rms) polarization is known to exist at much higher temperatures.[1] Smolenski[2] proposed that the relaxor behavior was due to compositional heterogeneity. This heterogeneity was believed to arise due to a positional disorder on the B-site cation leading to locally varying ferroelectric transition temperatures. Microscopic (Kanzig) regions were hypothesized to exist, each with slightly different compositions. A semiquantitative treatment based on a Gaussian distribution of local Kanzig compositions evolved which tried to parametrize the relative broadness of the dielectric response.[3]

The inverse susceptibility of a relaxor is known to deviate strongly from Curie-Weiss behavior over a wide temperature interval.[4-7] The values for the Curie constant (C) and temperature (Θ) are strongly dependent on the temperature range modeled, and C is significantly larger than in a normal perovskite ferroelectric.[8] Smolenski modeled the deviation from Curie-Weiss behavior using the compositional heterogeneity model predicting a $(T-\Theta)^{\gamma}$ relationship, where γ was approximately two.[4,7] Experimentally, no single value of γ was found which uniquely described the dependence, but rather γ depended on the width of the temperature window analyzed and the measurement frequency.

Randall[9] and Harmer[10] have observed contrast on the nanometer scale in PMN using transmission electron microscopy (TEM). It is believed that a partitioning occurs into regions which are Mg rich. Randall has subsequently proposed that it is the scale of this process which underlies the relaxor behavior.[9] Cross has suggested that the scale of these regions is such that the orientation of the polarization is thermally activated,[11] analogous to superparamagnetism.[12] The density of polar regions as observed by TEM (Refs. 9 and 10) is large enough that collective effects may be important. Viehland[13] has recently shown that the polarization fluctuations have a freezing temperature (T_f) analogous to spin glasses. Interactions between polar regions were believed to control the kinetics of the fluctuations and the freezing process. The purpose of this work is to investigate the deviation from Curie-Weiss behavior and determine if it can be explained using a glass model.

II. PROCEDURE AND RESULTS

The samples used in this study were PMN ceramics. They were prepared as described by Pan and Cross.[14] The samples were free of pyrocholore as described by Shrout,[15] were electroded with gold, and were of dimensions $1\times0.5\times0.05$ cm^3. The 100-KHz dielectric response was measured as a function of temperature between 800 and 100 K at a cooling rate of 4 K/min. The measurements were made using a HP4275A *LCR* meter. The pyroelectric current was also measured as a function of temperature and the polarization calculated by integration for comparison.

The 100-KHz dielectric response of PMN is shown in Fig. 1 as the solid line. Also shown in this figure as dashed lines are hypothetical Curie (C/T) and Curie-Weiss [$C/(T-\Theta)$] behaviors, calculated from the values of C and Θ obtained by extrapolation from temperatures

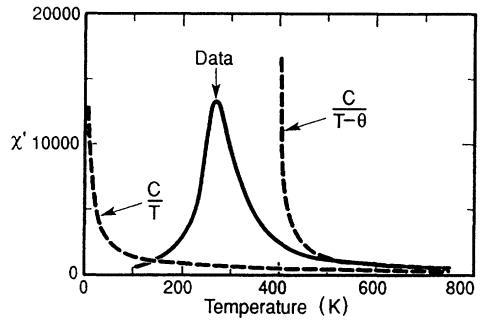

FIG. 1. The 100-KHz dielectric susceptibility (χ') as a function of temperature, where the points are the data and the solid line is the fitting to Eq. (1). C/T and $C/(T/\Theta)$ are hypothetical Curie and Curie-Weiss behaviors, respectively.

above that of the onset of local polarization. The dielectric susceptibility maximum (χ_{max}) and temperature of the susceptibility maximum (T_{max}) were approximately 20 000 and 273 K, respectively.

III. DISCUSSION

The Curie-Weiss law has been found to be obeyed in spin glasses at temperatures much greater than T_F ($T > 5T_f$), but at lower temperatures strong deviations occur.[16,17] A plot of the inverse susceptibility of PMN over a wide range of temperatures is illustrated in Fig. 2. At higher temperatures Curie-Weiss behavior was observed as illustrated by the dashed line. A Curie constant (C) and temperature (Θ) of 1.25×10^5 and 398 K were obtained, respectively. These values are consistent with those of other perovskites, and more realistic than those obtained from fitting the data near the susceptibility maximum ($C=4\times10^5$).[8] The deviation from Curie-Weiss behavior started approximately near 600 K, which is close to the temperature of the onset of local polarization (T_{Burns}).[1] The deviation from Curie-Weiss behavior in relaxors might be modeled by allowing C and Θ to be temperature dependent, reflecting the onset of local polarization.

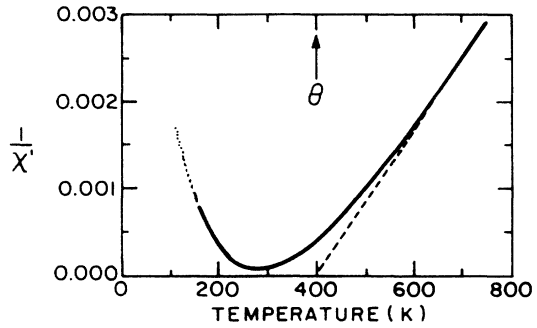

FIG. 2. The inverse of the 100-KHz susceptibility ($1/\chi'$) as a function of temperature. The dashed line is the Curie-Weiss behavior determined from high temperature and Θ is the determined Curie temperature.

Sherrington and Kirkpatrick[18] developed an infinite range model for a spin glass which related the temperature dependence of the susceptibility below T_f to the onset of a local (spin-glass) order parameter as given in Eq. (1):

$$\chi = \frac{C[1-q(T)]}{T-\Theta[1-q(T)]}\ , \tag{1}$$

where q is the local order parameter and χ the susceptibility. This relationship has previously been used to extract a spin-glass order parameter from the static susceptibility in CuMn,[19] where C and Θ were determined by Curie-Weiss analysis from high temperatures. Deviation from Curie-Weiss behavior was not observed in these measurements, and q extrapolated to zero near T_f. Subsequent work[16] has revealed strong deviations. Calculations by Binder,[20] using an Ising model with a Gaussian distribution of correlation strengths between neighboring moments, has indicated that q does not go to zero at T_f but tails to zero at much higher temperatures suggestive of Curie-Weiss deviation about T_f. The 100-KHz susceptibility data of PMN was modeled phenomenologically with Eq. (1) using the values of C and Θ determined from high temperatures, solving for q at various temperatures. The 100-KHz q is shown in Fig. 3 as a function of temperature, q decreased linearly with increasing temperature between 300 and 100 K, at higher temperatures q seemingly tailed to zero near 590 K.

The deviation from Curie-Weiss behavior in spin glasses has been interpreted to mean that, on a local scale, strong magnetic correlations develop far above T_f.[16,17] The ideal (noninteracting) superparamagnet is known to exhibit Curie-Weiss behavior for finite measurement frequencies. The local polar regions in PMN are believed to be homogeneous and of nanometer size, i.e., superparaelectric.[11] This cluster model is substantiated by TEM which reveals compositionally homogeneous regions on the scale of approximately 2–5 nm.[9,10] It is proposed that the deviation from Curie-Weiss behavior in PMN is due to correlations between polar (superparaelectric) regions, i.e., $q \equiv \langle P_i P_j \rangle^{1/2}$, where P_i and P_j denote neighboring cluster-sized moments. The correlation may have contributions from both local dipolar and electrostrictive strain fields. At T_{Burns}, local ferroelectric

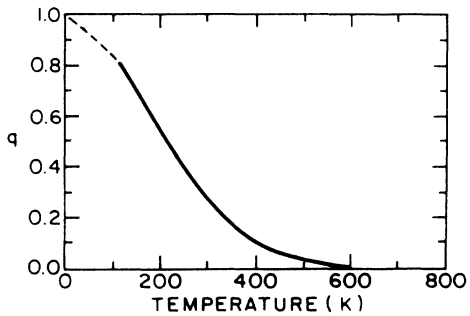

FIG. 3. The spin-glass order parameter (q) as determined from the deviation from 100-KHz Curie-Weiss behavior using Eq. (1).

transitions start to occur. In the temperature interval between 400 and 600 K, the disordering effect of temperature will be large enough to prevent most polar regions from coupling, i.e., $\langle P_i P_j \rangle^{1/2}=0$. As the temperature decreases, correlations develop as the volume fraction of polar regions increases and the thermal disordering effect decreases. At a lower characteristic temperature, a critical coupling will start to lead to a freezing of the polarization fluctuations; consequently, the field-cooled state develops characteristics of a normal ferroelectric. The implication is that the frustration of the glassy state is incipient from high temperatures. As the temperature is further decreased, a larger volume fraction of polar regions will freeze.

Plots of hypothetical Curie (C/T) and Curie-Weiss behaviors [$C/(T-\Theta)$] for PMN are shown in Fig. 1 alongside the 100-KHz susceptibility; the calculations were done using the values of C and Θ determined from high temperature. The susceptibility was enhanced over C/T. This undoubtedly is a reflection of the correlations between polar regions. The susceptibility was suppressed relative to a normal ferroelectric [$C/(T-\Theta)$], which is probably a reflection of the respective scales of the correlation lengths. Below Θ correlations between polar regions increase; consequently, the susceptibility increases approaching the value for the normal ferroelectric transition at lower temperatures. Below the susceptibility maximum, the correlation strengths are strong enough that the moments cannot respond to the measurement bias within the time scale of the measurement. A maximum in the susceptibility does not occur at any frequency due to a macroscopic phase transition. A normal transition is prevented near Θ. The reason for this is not presently known, but probably relates to the chemical clustering.[9,10]

Schmidt[6] has previously modeled the deviation from Curie-Weiss behavior using a modified Landau-Devonshire approach given in Eq. (2):

$$\frac{1}{\varepsilon}=\frac{T-\Theta}{C}+3b\langle P_{\text{local}}\rangle^2 , \tag{2}$$

where b is the dielectric nonlinearity. The temperature dependence of $3b\langle P_{\text{local}}\rangle^2$ was qualitatively similar to the work presented here, but the temperature effects of b and $\langle P_{\text{local}}\rangle^2$ could not be separated. Expanding $(1-q)$ in Eq. (1), a relationship similar to Eq. (2) could be derived but would involve even and odd powers of P_{local} and $3b$ would be equal to T/Θ. Schmidt's approach assumed that the deviation from Curie-Weiss behavior can be accounted for by a summation of individual second-order transitions with homogeneous polarizations. The model presented here assumes that the deviation arises due to correlations between these individual regions.

The deviation from Curie-Weiss behavior is known to increase with measurement frequency,[21] analogous to spin glasses. The 10^{10}-Hz dielectric response of PMN was obtained from the literature,[22] digitized, and modeled with Eq. (1). The 10^{10}-Hz q as a function of temperature is shown in Fig. 4 alongside the 10^5-Hz q; the reduced remanent (P_r) and rms polarizations (P_{rms}) are also shown for comparison. Significant differences between

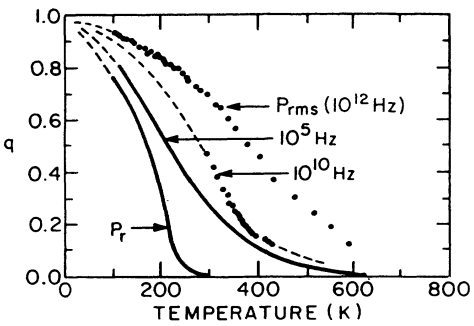

FIG. 4. The spin-glass order parameter (q) for various measurement frequencies. The 10^5- and 10^{10}-Hz values of q were determined from the deviation from Curie-Weiss behavior at the respective frequencies. The values of the reduced rms polarization [$P_{\text{rms}}(10^{12}$ Hz)] as determined from birefringence measurements and the reduced remanent polarization (P_r) as determined from pyroelectric measurements are shown in this figure for comparison.

the various measurement frequencies and techniques are observable. Similar behavior was observed for the 10^{10}-Hz q as for 10^5 Hz, but the values of q increased more rapidly with decreasing temperature below 400 K. The reduced remanent polarization approached the values for the other measurements at lower temperatures, but was much smaller above 100 K and extrapolated to zero near T_f. Tailing was observed above 220 K but was hard to distinguish due to leakage currents. The reduced P_{rms} was much larger than the 10^5- and 10^{10}-Hz q between 200 and 600 K, and did not tail to zero. These differences are undoubtedly a reflection of the various measurement techniques. P_{rms} was determined from the temperature dependence of the refractive indices[1] and thermal expansion.[11] These techniques pick up any polarization fluctuations below the phonon frequency of the lattice ($\tau_{\text{Debye}}\sim 10^{12}$), whereas the dielectric response can only pick up fluctuations below the measurement frequency, and the remanent polarization is the static response.

The difference between P_{rms} calculated from the birefringence and the deviation from Curie-Weiss behavior is that P_{rms} is the total response, i.e., both correlated and noncorrelated moments. The strong frequency dispersion in q indicates that there is a broad spectrum of coupling strengths and relaxation times. With increasing measurement frequency, the oscillating field is changing too fast for most of the relaxation modes to respond. At lower frequency more modes can keep up with the field, so the deviation from Curie-Weiss behavior seems smaller. The reduced remanent polorization may reflect the number of modes frozen. At 200 K, P_r is approximately 0.2, whereas the reduced P_{rms} is 0.8. At 150 K, P_r is approximately 0.6, whereas the P_{rms} is 0.9. This indicates that, on cooling below T_f, an increasing fraction of the relaxation time distribution lies at macroscopic time periods. Although, some polar regions are small enough that the thermal energy prevents them from establishing correlations until much lower temperatures. The susceptibility has been found to be nondispersive at low temper-

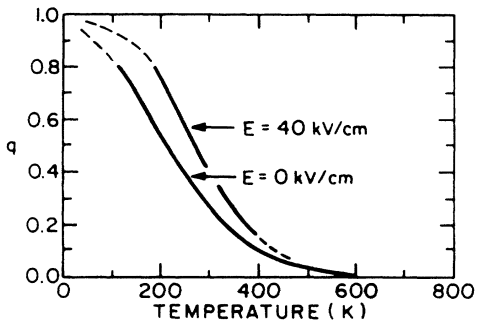

FIG. 5. The spin-glass order parameter (q) as determined from Curie-Weiss behavior under bias levels of 0 and 40 kV/cm.

atures;[22] other low-temperature effects have also been reported.[23] It is probable that, at a low finite temperature, all of the moments have frozen into the ground-state configuration of the glassy phase.

The deviation from Curie-Weiss behavior is also known to increase with bias.[21] The 100-KHz q as a function of temperature under 0 and 40 kV/cm is shown in Fig. 5. The field increased the value of q. At 300 K q was approximately 0.3 under 0 kV/cm, but was 0.5 under 40 kV/cm. It is proposed that the correlations between the various regions increase with bias. This is not a simple dipole alignment process, but rather the development of longer-range correlations typical of a normal ferroelectric. Further evidence for such behavior has been found previously. In the zero-field-cooled (ZFC) state, the structure appears cubic to x rays, however, in the field-cooled (FC) state the structure appears rhombohedral. This means that the scale of the polar regions in the ZFC state is too small to produce additional diffraction lines which are narrow enough in width to be observed. Optical microscopy reveals no domain structure in the ZFC state, but normal macrodomains are found in the FC state on the scale of 1–10 μm.

IV. CONCLUSION

The deviation from the Curie-Weiss relationship in relaxor ferroelectrics has been shown to be similar to that for spin glasses. The Curie-Weiss relationship was followed at temperatures much greater than the susceptibility maximum, but strong deviations developed with decreasing temperature. The deviation is believed to occur due to correlations between polar (superparaelectric) regions. The frequency and field dependence of the deviation have also been investigated.

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