Dipolar-glass model for lead magnesium niobate

Dwight Viehland, J. F. Li, S. J. Jang, and L. Eric Cross*
Materials Research Laboratory, Pennsylvania State University, University Park, Pennsylvania 16802

Manfred Wuttig
Engineering Materials Program, University of Maryland, College Park, Maryland 20742
(Received 21 June 1990; revised manuscript received 30 October 1990)

The static polarization of lead magnesium niobate has been studied using a standard Sawyer-Tower circuit. The square-to-slim-loop hysteresis transition was phenomenologically modeled by modifying Néel's equation for the magnetization of a superparamagnet to a similar relationship for a superparaelectric. A temperature-dependent internal dipole field was included to account for cluster interactions. The slim-loop polarization curves were found to scale to $E/(T-T_f)$, where E is the electric field and T_f the freezing temperature. A glassy character was subsequently proposed to exist in the zero-field-cooled state with local dipole fields between superparaelectric moments controlling the kinetics of the polarization reversals and the freezing process. Recent quasielastic-neutron-scattering results have been interpreted to support this model.

I. INTRODUCTION

Lead magnesium niobate is a dispersive ferroelectric. It is characterized by a relaxation of the dielectric permittivity, and an inability to sustain a macroscopic polarization for temperatures significantly below the permittivity maximum (T_{max}). Burns and Darol[1,2] have shown that a local polarization exists for temperatures far above T_{max} indicating that the local symmetry is lower than the global. Randall *et al.*[3] and Chen, Chang, and Harmer[4] have shown in $Pb(Mg_{1/3}Nb_{2/3})O_3$ that there is a partitioning on the nanometer scale into clusters which are chemically ordered and disordered. Cross[5] suggested that the size of these clusters is such that the polarization may be thermally reversible, analogous to superparamagnetism.[6] He has recently proposed that a coupling between polar clusters controls the kinetics of the polarization fluctuations and the development of frustration near the freezing temperature (T_f), similar to spin glasses.[7] T_f was determined by analyzing the frequency dispersion of T_{max} with the Vogel-Fulcher relationship and was shown to agree with the temperature at which a stable remanent polarization collapsed. Similar phenomenological modeling has been used in spin glasses.[8,9]

In the zero-field-cooled (ZFC) state the structure of $Pb(Mg_{1/3}Nb_{2/3})O_3$ appears cubic indicating that the scale of the polar behavior is smaller than the coherence length of x-rays; however, in the field-cooled (FC) state the structure appears rhombohedral. Optical microscopy reveals no domain structure in the ZFC state, but normal micrometer-sized domains are observed in the FC state. Cross[10] has investigated the field dependence of the dielectric and elastic responses. He found the maximum nonlinearities near T_f. Bokov and Myl'nikova[11] and Smith[12] have previously investigated the static polarization. They found a large hysteresis at lower temperatures, but with increasing temperature it decreased; i.e., the so-called square-to-slim-loop transition.

Spin glasses are magnetic systems that cannot establish long-range magnetic ordering in the ZFC state due to some form of a chemical or structural inhomogeneity. The glassy behavior is believed to arise due to competing interactions between magnetic moments resulting in a freezing of the magnetization reversals below a characteristic temperature (T_f). Freezing has been shown to occur due to random fields between clusters[13,14] and a competition between ferromagnetic and antiferromagnetic exchanges.[15,16] The FC state exhibits behavior resembling a normal ferromagnet below T_f, i.e., irreversibility and hysteresis.[17]

II. EXPERIMENTAL PROCEDURE AND RESULTS

The samples used in this study were $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics with 10 at.% $PbTiO_3$. They were prepared as described by Pan, Jiang, and Cross.[18] The samples were free of aging,[18] were free of pyrochlore as described by Swartz and Shrout,[19] were of dimensions $1\times0.5\times0.03$ cm^3, and were electroded with gold. The hysteresis loops were measured as a function of temperature using a standard Sawyer and Tower circuit. Measurements were made between 150 and -50 °C on cooling. The samples were allowed to equilibrate for 30 minutes at each temperature. The cycling frequency was 50 Hz, and the maximum bias applied was 20 kV/cm. To decrease the low frequency impedance, a large capacitance (10 μF) was placed in series with the sample.

Static polarization curves are shown in Figs. 1(a)–1(d) at measurement temperatures of -50, 10, 50, and 110 °C, respectively. The experimental data are the closed circles, and the solid line is a phenomenological model, which will be presented. The square-to-slim-loop hysteresis transition is evident in the figures. The polarization behavior became hysteretic near and below T_{max}. The saturation polarization was approximately 20 C/m^2

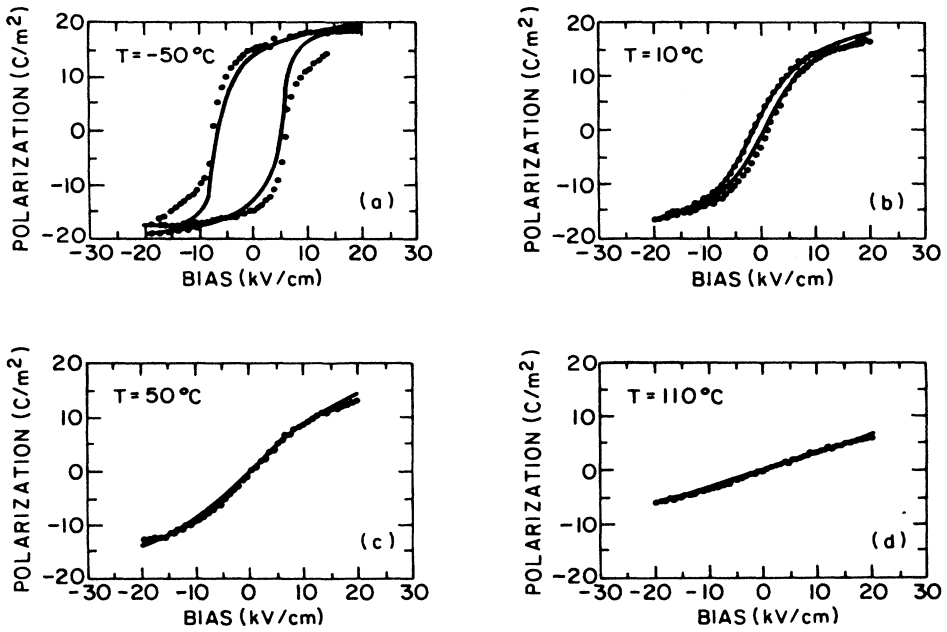

FIG. 1. Polarization curves at various temperatures. The solid points are the experimental data and the solid line is the curve fitting to Eq. (2). (a)–(d) are at measurement temperatures of −50, 10, 50, and 110 °C, respectively.

at lower temperatures. It was not possible to drive the sample into saturation at higher temperatures because breakdown occurred. Above 25 °C the remanence was so small that determination of the coercive field was difficult, but at lower temperatures it increased rapidly.

III. DISCUSSION

In systems consisting of nanometer-scale ferromagnetic or ferroelectric clusters the thermal energy of the particle can strongly influence the macroscopic magnetic or polar properties. These clusters are designated as superparamagnetic or superparaelectric, respectively. The magnetic behavior with no anisotropy can be described by a Langevian function, but real systems have an anisotropy that acts as an energy barrier for reorientation as originally proposed by Neel.[6] The polarization behavior of an ensemble of uniform noninteracting clusters having uniaxial symmetry can be described by

$$p = \tanh\left[\frac{EP}{kT}\right], \tag{1}$$

where p is the reduced polarization, E the electric field, P the moment of the cluster, and kT the thermal energy. A consequence of Eq. (1) is that the polarization curves at different temperatures should superimpose when plotted against E/T, the analogous behavior has been observed for numerous superparamagnets.[20–22] The implication of the superposition is that at higher temperatures it takes more electrical energy to align the moments against the thermal energy. The slim-loop hysteresis curves of $Pb(Mg_{1/3}Nb_{2/3})O_3$ with 10 at. % $PbTiO_3$ did not superimpose when plotted against E/T as shown in Fig. 2; p is obviously more strongly temperature dependent. This may be a reflection of interactions between polar regions. Interactions might be accounted for by including a phenomenological freezing temperature. T_f has been previously estimated as 18 °C for $Pb(Mg_{1/3}Nb_{2/3})O_3$ with 10 at. % $PbTiO_3$.[7] The polarization curves plotted as a function of $E/(T-T_f)$ are shown in Fig. 3. It is obvious that the polarization curves nearly superimpose.

Interactions between superparamagnetic clusters have

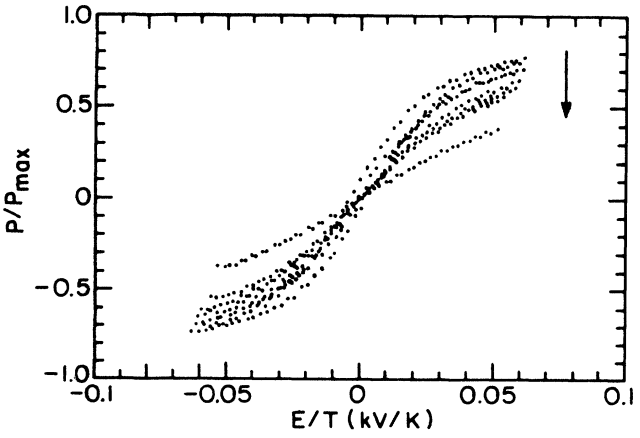

FIG. 2. Reduced polarization plotted as a function of the temperature normalized electric field at various temperatures. The arrow visually illustrates the direction of increasing temperature. The polarization curves shown are at temperatures of 38, 48, 54, 59, 69, 86, 110 °C.

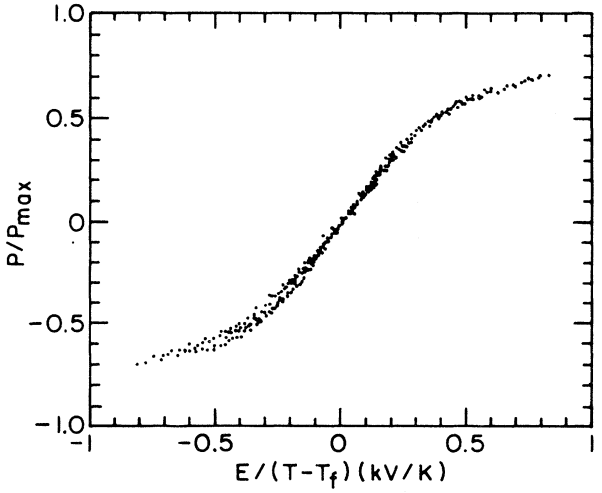

FIG. 3. Reduced polarization at various temperatures plotted as a function of $E/(T-T_f)$ where T_f is the freezing temperature. The polarization curves shown are at temperatures of 39, 48, 54, 59, 69, 86, 110 °C.

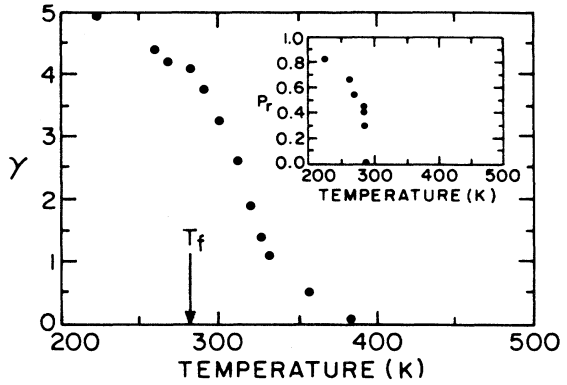

FIG. 4. Reduced internal field ($\gamma = P\alpha/kT$) as a function of temperature where T_f is the freezing temperature. The inset shows the reduced remanent polarization (ρ_r) as a function of temperature as calculated from Eq. (3).

been reported to alter magnetization curves. Local internal Lorentz fields have been used to obtain an understanding of the magnetic behavior in these systems.[23,24] A relationship for a superparaelectric cluster having rhombohedral symmetry including an internal dipole field follows:

$$p = \frac{\sinh\left[\frac{P(E+\alpha p)}{kT}\right]}{\cosh\left[\frac{P(E+\alpha p)}{kT}\right] + 3\cosh\left[\frac{P\cos 70(E+\alpha p)}{kT}\right]}, \tag{2}$$

where p is the reduced polarization, and α the internal field. The hysteresis curves were modeled by a nonlinear least squares fitting to Eq. (2), shown as the solid lines in Figs. 1(a)–1(d). The fitting was done by allowing the temperature changes to be absorbed by α. P can be approximated as $P_S V$, where P_S is the saturation polarization and V the cluster volume. P_S is approximately 20 C/m^2, and the cluster diameter has been found to be between 20 and 50 Å.[3,4] Assuming an average diameter of 35 Å, P can be estimated as 5×10^{-25} C cm. A normalized internal bias ($\gamma = P\alpha/kT$) as a function of temperature is shown in Fig. 4. The reduced remanent polarization (p_r) can be approximated by setting $E=0$ in Eq. (2). Nonzero solutions for p_r will only exist when $\gamma > 4$, which occurred between 10 and 20 °C. p_r as a function of temperature is shown as the inset of Fig. 4. The temperature dependence of p_r was calculated by using the experimental values for γ, but close to T_f γ was determined by interpolation. These results are consistent with the experimental polarization.[7,11]

The magnetization and polarization of spin and dipole glasses are known to be irreversible below T_f.[17,25–27] The irreversibility is believed to arise due to the onset of nonergodicity. In particular if Sawyer-Tower measurements are made hystersis is observed.[17,27] This hystersis has been shown to decrease with temperature,[28] somewhat similar to $Pb(Mg_{1/3}Nb_{2/3})O_3$. The scaling of the polarization to $E/(T-T_f)$ in $Pb(Mg_{1/3}Nb_{2/3})O_3$ with 10 at. % $PbTiO_3$ is strongly suggestive of a glassy mechanism, whereas the polarization equation of state was derived for a rhombohedral superparaelectric moment. Binder and Young[16] have suggested that interacting superparamagnetic moments should be treated as spin glasses. It is proposed that the polarization of the relaxor is glassy due to interactions between superparaelectric moments. In the ZFC state, the lack of macroscopic polarization indicates that the moments freeze into random orientations devoid of long-range order. Local dipole fields may try to polarize neighboring moments over a distance of a correlation length, as illustrated in Fig. 5. But if the dispersion in the fields is larger than the average field, long-range ordering is impossible. In the FC state the moments freeze into ordered configurations, characteristic of a normal ferroelectric. A somewhat similar superparaelectric glassy model has been proposed for $K_{1-x}Li_xTaO_3$, for $x = 0.026$.[26]

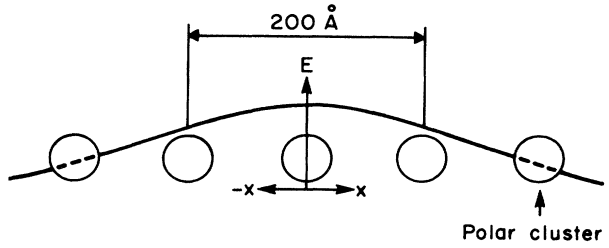

FIG. 5. Proposed model for freezing in $Pb(Mg_{1/3}Nb_{2/3})O_3$ where E is a local internal dipole field that acts to couple the polar clusters. The open circles represent the polar clusters.

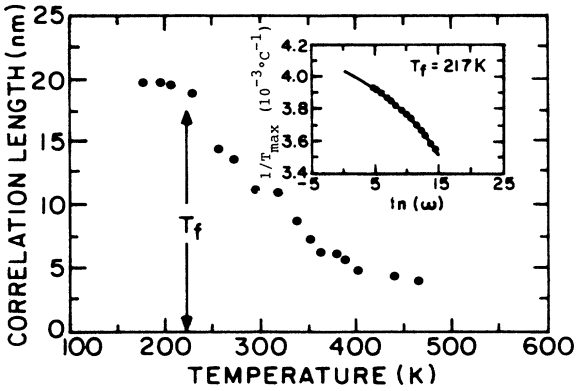

FIG. 6. The correlation length as determined by quasielastic neutron scattering as a function of temperature where T_f is the freezing temperature. This data is taken from Vakrushev.[2] The inset shows the modeling of the frequency dependence of the temperature of the dielectric relaxation with the Vogel-Fulcher relationship where the solid points are the experimental data and the solid line is the curve fitting.

Recent quasielastic neutron scattering (QES) results[29] on $Pb(Mg_{1/3}Nb_{2/3})O_3$ revealed a temperature dependent correlation length (λ) similar to spin glasses,[30] shown in Fig. 6. Near 400 K, λ was 50 Å, which is approximately equal to the cluster size observed by TEM.[4,5] In the temperature interval below 225 K, λ was nearly temperature independent with a maximum value of 200 Å. This data can be interpreted to support the hypothesis that relaxors are interacting superparaelectric moments. The scale of λ supports the argument that the glassy character arises due to random fields between moments on the mesoscopic level. The agreement of λ with the average size of the clusters at higher temperatures supports the argument that the moments are decoupled from each other behaving as ideal superparaelectrics. On cooling λ increased supporting the model of a temperature-dependent internal field that couples the moments more strongly. For comparison T_f has been estimated to be 217 K by analyzing the dispersion of T_{max} using the Vogel-Fulcher relationship, shown as the solid line in the inset of Fig. 6. This is close in temperature to the saturation of λ, a strong broadening of the relaxation time distribution,[31] and the collapse of the remanent polarization. This indicates that the saturation of λ at 200 Å may occur by the system freezing into local configurations of moment orientations, possibly by balancing the average orientation of nearest and next-nearest neighbors effectively compensating the local polarization.

Various reasons have been proposed to explain the existence of short-range order in dipolar glasses. The glassy behavior in $K_{1-x}Li_xTaO_x$ is believed to arise by a coupling of the Li defect structure to a soft mode lowering the local symmetry and stabilizing ferroelectric clusters.[32,33] In KCl:OH^-, OH^- dipoles are believed to exist that have six orientations; local dipole fields are believed to couple the moments resulting in glassy behavior.[34] The low-temperature phases of RbH_2PO_4 and $(NH_4)H_2PO_4$ are ferroelectric and antiferroelectric, respectively; frustrated interactions are believed to lead to glassy behavior in their solid solution.[35] $Pb(Mg_{1/3}Nb_{2/3})O_3$ is probably a normal ferroelectric that cannot establish long-range polar order due to gross inhomogeneities, i.e., the partioning (phase separation) on the nanometer scale.[5,6] Local polarization may form where allowed by this "fossil chemistry" via local ferroelectric transitions; dipole fields between moments then subsequently lead to glassy behavior.

IV. CONCLUSION

Static polarization curves for $Pb(Mg_{1/3}Nb_{2/3})O_3$ were parametrized using a superparaelectric model that included an internal dipole field. Local randomly orientated dipole fields between superparaelectric moments are believed to exist in the zero-field-cooled state leading to a freezing of the polarization fluctuations. A dipole glass model for relaxors was subsequently proposed.

ACKNOWLEDGMENTS

This work has been supported in full by contracts administered through the Office of Naval Research. Acknowledgement must also be expressed to Dr. S. Vakhrushev *et al.* for the use of their published data.

*Also in the Electrical Engineering Department.

[1]G. Burns and F. Dacol, Solid State Commun. **48**, 10 (1983); **48**, 853 (1983).
[2]G. Burns and F. Dacol, Solid State Commun. **58**, 9 (1986); **58**, 567 (1986).
[3]C. Randall, A. Bhalla, T. Shrout, and L. E. Cross, J. Mat. Sci. **29**, 5 (1990).
[4]J. Chen, H. Chan, and M. Harmer, J. Am. Ceram. Soc. **72**, 593 (1989).
[5]L. E. Cross, Ferroelectrics **76**, 241 (1987).
[6]L. Neel, C. R. Acad. Sci. **228**, 664 (1949).
[7]D. Viehland, S. Jang, M. Wuttig, and L. Cross, J. Appl. Phys. **68**, 2916 (1990).
[8]J. Tholence, J. Appl. Phys. **50**, 7369 (1979).
[9]J. Tholence, Solid State Commun. **35**, 113 (1980).
[10]D. Viehland, S. Jang, M. Wuttig, and L. Cross, J. Appl. Phys. (to be published).
[11]V. Bokov and I. Myl'nikova, Fiz. Tverd. Tela (Leningrad) **3**, 3 (1961) [Sov. Phys. Solid State **3**, 1 (1961)].
[12]James W. Smith, Ph.D. dissertation, The Pennsylvania State University, 1967.
[13]P. Nozav, V. Sechovsky, and V. Kambersky, J. Magn. Magn. Mater. **69**, 71 (1987).
[14]A. Morgownik and J. Mydosh, Phys. Rev. B **24**, 5277 (1981).
[15]S. Kirkpatrick and D. Sherrington, Phys. Rev. B **17**, 4384 (1978).
[16]S. Edwards and P. W. Anderson, J. Phys. F **5**, 765 (1975).
[17]K. Binder and A. Young, Rev. Mod. Phys. **58**, 4, 860 (1986).
[18]W. Pan, Q. Jiang, and L. E. Cross, J. Am. Ceram. Soc. **71**, C-17 (1988).

[19]S. Swart and T. Shrout, Mater. Res. Bull. **17**, 1245 (1982).
[20]W. Henkelom, J. Brodeder, and L. Van Reijen, J. Chim. Phys. **32**, 3 (1958).
[21]M. Mayer and E. Vogt, Z. Naturforsch. **79**, 334 (1952).
[22]C. Bean and I. Jacobs, J. Appl. Phys. **27**, 1448 (1950).
[23]E. Vogt, W. Henning, and A. Hahn, *Berichte Arbeitsgemeinschaft Ferromagnetismus 1958* (Riederer Verlag, Stuttgart, 1959), p. 43.
[24]F. Luborsky and P. Lawrence, J. Appl. Phys. **32**, Suppl. 231S (1961).
[25]K. Lyons, Pl Fleury, T. Negran, and H. Carter, Phys. Rev. B **36**, 2465 (1987).
[26]U. Hochli, P. Kofel, and M. Maglione, Phys. Rev. B **32**, 4546 (1985).
[27]J. Prejan, M. Joliclerc, and P. Monad, J. Phys. **41**, 427 (1980).
[28]S. Senoussi, J. Phys. **45**, 315 (1984).
[29]S. Vakhrushev, B. Kvyatkovsky, A. Naberezhnov, N. Okuneva, and B. Topervers, Ferroelectrics **90**, 173 (1989).
[30]G. Aeppli, S. Shapiro, H. Maletta, R. Birgeneau, and H. Chen, J. Appl. Phys. **55**, 1629 (1984).
[31]N. Yushin (unpublished).
[32]G. Samara, Jpn. J. Appl. Phys. **24**, Suppl. 24-2, 80 (1985).
[33]B. Vugmeister and M. Glinchuck, Zh. Eksp. Teor. Fiz. **79**, 8 (1980) [Sov. Phys. JETP **52**, 3 (1980)]; **79**, 947 (1980) [**52**, 482 (1980)].
[34]M. Klein, C. Held, and E. Zuroff, Phys. Rev. B **13**, 8 (1976); **13**, 3576 (1976).
[35]E. Courtens, T. Rosenbaum, S. Nagler, and P. Horn, Phys. Rev. B **29**, 515 (1984).