RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 36, NUMBER 4 1 AUGUST 1987

Nonanalytic polarization response of a dipolar glass

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(Received 1 June 1987)

The polarization response of the dipolar glass $KTa_{1-x}Nb_xO_3$ ($x=0.009$) over a range of temperature ($1.8\ K < T < 15\ K$) near T_g is found to be a nonanalytic function of field, revealing the inadequacy of the usual nonlinear susceptibility description, as well as the incorrectness of even the linear response previously reported in such systems. A model based upon activated switching of two-level systems with a barrier distribution extending to zero energy adequately describes our data. Nonanalytic response may be a general feature of dipolar glasses, as well as other random systems, including magnetic spin glasses.

The behavior of systems in which long-range order competes with continuous random freezing has recently become a topic of considerable interest.[1-6] One such system[7-9] is $KTa_{1-x}Nb_xO_3$ (KTN). Although it exhibits a transition to a low-temperature state[10] of long-range ferroelectric order for sufficiently high x values, several experiments[9,11] suggest that $KTa_{1-x}Nb_xO_3$ is a dipolar glass for $x \sim 0.01$, exhibiting a random local polarization at low temperatures. Specifically, relaxation evident in measurements of the linear susceptibility[11] $\chi_1(\omega)$ is primary evidence for the existence of the dipolar glass. It has further been proposed that the dipolar glass state bears strong analogies with the well-studied spin glass.[1,8] Verification of the spin-glass analogy requires that the nonlinear susceptibilities, $\chi_n(\omega)$, exhibit singularities[12-14] at a well-defined "dipolar glass temperature." It is therefore clear that careful measurement of the nonlinear polarization response is a key to the study of the competition between long-range order and dipolar glass behavior.

We report here a detailed study of the nonlinear behavior in $KTa_{1-x}Nb_xO_3$ for $x=0.009$. Surprisingly, we find that there is no observable range of field over which χ_n may be defined without ambiguity. Instead, it is evident that the electric polarization P is a nonanalytic function of E even at the lowest fields amenable to study (on the order of 0.5 kV/m). Similar behavior has been found for concentrations of 0.006, 0.012, and 0.02. This constitutes the first direct experimental verification of the nonanalytic response of a dipolar glass, in analogy with that seen in spin glasses[15] and pinned charge-density-wave (CDW) systems.[16] In contrast to spin glasses, however, we find no region where the response is completely analytic, even well above the apparent T_g. This extreme nonlinearity has significant influence as well on measurements of the linear susceptibility, and has resulted in quantitative distortion of results previously reported. We find that a model invoking a set of activated two-level systems with a distribution of barrier heights extending to zero energy provides an adequate description of most aspects of our data.

Our experiments were carried out on a rectangular parallelepiped of $KTa_{1-x}Nb_xO_3$, $3.7\times0.9\times0.5\ mm^3$, with all faces polished and the two largest faces (normal to [111]) coated with a gold film deposited over a flash chromium coat by evaporation. The sample used for the previous dielectric measurements[11] was taken from an adjacent region of the same boule. The circuit employed for the measurements was adapted from the familiar Sawyer-Tower circuit usually employed for hysteresis measurements. The sample was connected in series with a standard capacitor (see Fig. 1), $C=4.31\ \mu F$. A pure sinusoidal waveform was applied across the combination. The voltage response V_{sig} at the junction, proportional to $D \sim P$ in the sample, was then recorded in real time with a digital-to-analog (D-A) converter, using a preamplifier

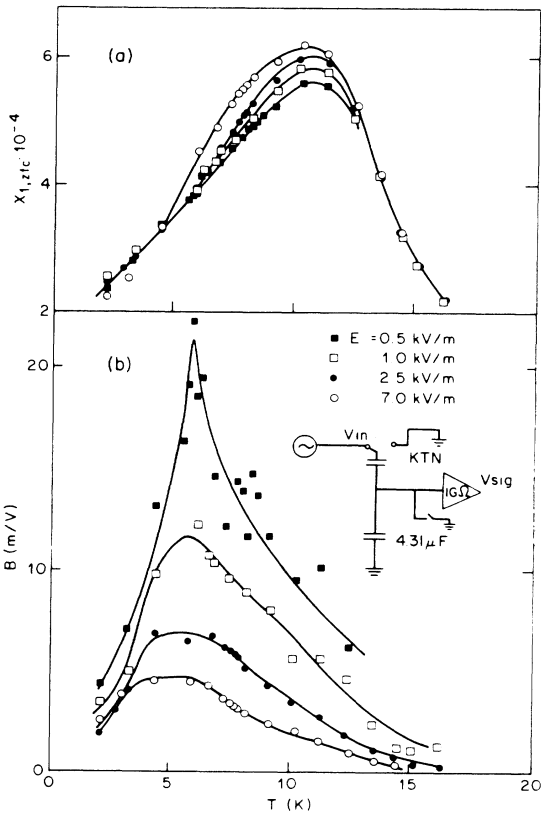

FIG. 1. Values of the coefficients (a) $\chi_{1,zfc}$ and (b) B in the Rayleigh relation (3) for $E \parallel [111]$. Legend shown applies to both (a) and (b).

with a 1-GΩ input impedance. During zero-field cooling of the sample, both electrodes were shorted to ground.

The nonlinear susceptibility is ordinarily measured by relating the harmonics observed in the polarization response (V_{sig}) to the nonlinear susceptibilities, with a sinusoidal field $E_0 \sin\omega t$ applied to the crystal. It is usually a trivial procedure to relate the harmonic amplitudes to the values of χ_n in the expansion

$$P/\varepsilon_0 = \sum_n \chi_n E^n \tag{1}$$

(here $\varepsilon_0 = 8.85 \times 10^{-12}$ for mks units). Our data obtained in this manner are similar to that reported recently[6] for $KTaO_3$:Na. However, since $\{\chi_n\}$ are material parameters, they should be independent of the field amplitude employed in the measurement. This requires that for low fields the amplitude of the nth harmonic be proportional to E^n. Our detailed measurements have demonstrated that this is *not* the case. In fact, the amplitude of all the harmonics goes roughly as E^2, even for field amplitudes as low as a few V/cm. Thus, the values obtained for χ_n are never independent of the applied field amplitude. The inescapable conclusion is that the expansion (1) fails to remain valid, even for very small fields. In other words, we observe a *nonanalytic* response at the lowest fields employed. This discovery has led us to a complete reevaluation of the customary treatment of susceptibility measurements in this system. As we shall see, the effects of this anomalous behavior extend even to the analysis of supposedly *linear* susceptibility measurements.[11]

Another manifestation of the invalidity of the expansion (1) lies in the behavior of the complex linear susceptibility. If the polarization is analytic in E, then we should expect any nonzero imaginary component of χ_1 to vary as ω. The relative size of the component should also be independent of the field amplitude. In our KTN samples, neither of these behaviors is observed. First, the measured value of χ_1'' depends significantly on field, increasing strongly with E_0. Second, at a fixed E_0, the observed value of χ_1'' is essentially independent of ω over the range from 10 Hz to 10 kHz, where we have measured it. This is true even for temperatures far in excess of that (6–8 K) at which χ_1' peaks. In fact, the behavior persists, albeit as a weak component, as high as 45 K. No simple relaxation mechanism can account for such a weak frequency dependence.

Such behavior is instead characteristic of switching among a set of discrete hysteretic states, as in a ferroelectric. However, in contrast to a ferroelectric, in the present case this behavior is observed for arbitrarily small fields, indicating the presence of a distribution of coercive fields which extends all the way to zero. A useful model for such behavior was first developed by Néel[17] to describe the phenomenon of rock magnetism. A useful review of this work which emphasizes its connection with spin glasses has been given by Rammal and Souletie.[14] The essential assumption of this approach is that the system contains switchable units, which need not be specified as to their details, but which exhibit hysteresis with a broad distribution of barrier heights, which extends to zero energy. These units may be viewed as two-level systems, but in this case the focus is not on tunneling behavior but rather on activated barrier crossing. One of the model's most interesting predictions is that the *initial* polarization response to a field imposed on the system after zero-field cooling will contain a component *quadratic* in the field. Further, $P(E)$ is, within this model, not an analytic function as E is cycled, and hence cannot be expanded as in (1). We have extended these arguments to show that the odd harmonics, with an ac applied field, will exhibit quadrature components which all increase as E_0^2. The exact result, assuming a uniform distribution of barrier heights, of unit density, is

$$G_n = -\frac{(-1)^{(n+1)/2}}{n}\frac{n^2+4}{n^2-4}E_0^2 \tag{2}$$

for n odd and $n \geq 1$, where G_n is the quadrature amplitude of the nth harmonic. The in-phase responses are identically zero for $n > 1$ within this model. This would not remain true if the distribution were nonuniform.

Disregarding for the moment the detailed nature of the switchable units (see below), we first consider the adequacy of the description this model provides for our data. Despite the simplicity of the model, the predicted behavior agrees qualitatively with that found: (i) the higher harmonics are all proportional to E_0^2, in reasonable agreement with the exponent we observe, ~ 1.6–1.8, and (ii) the quadrature components depend only very slowly on frequency, if at all. Thus, the model reproduces the most surprising features of our data.

The essential quantitative result is that we expect the initial response to a field E, during the first half-cycle after zero-field cooling, to obey the Rayleigh relation[18]

$$P/\varepsilon_0 = \chi_{1,zfc}E + \mathrm{sgn}(E)BE^2 , \tag{3}$$

where the term $\chi_{1,zfc}$ accounts for the linear response of the lattice and of those switchable units for which the barrier W is sufficiently small, $W \lesssim k_B T$. Measurements of the parameters $\chi_{1,zfc}$ and B are shown in Fig. 1, obtained as the field is first applied to a sample cooled in zero field. These values were obtained by applying a single unipolar half-cycle to the crystal under computer control, for a total of 64 points, with each reading averaged 3 sec ($\omega/2\pi \sim 2.5$ mHz). Similar, albeit less accurate, results were obtained at 10 Hz. The quadratic form above (together with the more complicated expression[14] which is found as E decreases) was fit to the measured data, and was found to describe the response accurately for the first half-cycle. The fact that (3) describes the response even for fields as low as a few V/cm indicates that the barrier distribution for the switchable states extends effectively to zero energy.

If we use instead the form $P = E^\alpha$, and adjust α, we find values somewhat below 2.0. This fact is reflected in the slow increase of B as the field amplitude is decreased (Fig. 1). However, the data analysis suggests that the accuracy is insufficient to warrant such a procedure. (We note that the value of χ_5 extracted by the usual analysis varies by a factor of nearly 10^3 over the same field range.) In any case, the measurements of $\chi_{1,zfc}$ in Fig. 1 show that most of the field dependence observed for χ_1 is removed. In fact, on the basis of these measurements, we may easily

understand and evaluate the effect of the essential nonlinearity on previously reported measurements of χ_1. Note that there is a substantial offset between the peaks in $\chi_{1,zfc}$ and B as functions of temperature. Thus, in any finite field, the observed "linear" (first harmonic) response will show a broad peak at an intermediate temperature. The exact position and shape will depend on the field amplitude employed. Moreover, since the frequency dependences of the two components are no doubt different, a spurious frequency dependence may be observed as well. We note, in this context, that even at the lowest fields employed here, which are substantially below those normally employed for *linear* dielectric measurements, the value of χ_1 extracted by the usual analysis is some 50% higher than that found by the analysis based on Eq. (3).

Since we have now shown that the Néel-Preisach model, and the Rayleigh relation (3), provide an accurate phenomenological description of the KTN response, we now must consider the microscopic nature of the switchable states. A natural model results from consideration of a host lattice decorated randomly with dipolar impurities with an interaction length which is in turn determined by the incipient ferroelectric instability of the host. As the temperature is reduced, the effective interaction length increases. As it does so, the Nb ions will begin to interact in clusters, determined by their random positions in the lattice. The interaction of any pair of dipoles may be ferroelectric or antiferroelectric, depending upon their relative position and orientation. Thus, within such a cluster, the ions are not necessarily aligned parallel, but are certainly strongly correlated in orientation. The average relaxation time for clusters of size L is a function of L, since the energy barrier for flipping a cluster of size L must go as L^{θ}, where θ is some small power.[19] Thus, the distribution of cluster sizes results in a broad distribution of relaxation times, extending all the way to individual ions which may tunnel at GHz frequencies through their individual barriers. On the high side, the maximum relaxation time must diverge as the interacting cluster percolates to infinite size. This percolation is properly regarded as the glass transition. The energy landscape seen by the crystal is an n-dimensional phase space, if n is the number of dipolar impurities. At a temperature T, the range of this landscape, which may be sampled by the system in a time t, will be determined by the size of the barrier which may be scaled, roughly $k_B T \ln(t/t_0)$, where t_0 is some microscopic time. Thus, the "valleys within valleys" of the energy landscape correspond to "clusters within clusters" in real space. As t and/or T are increased, the size of the clusters which may equilibrate increases as well. The switchable units of the Néel-Preisach theory, then, correspond to these clusters, which in turn correspond to *local* double-well potentials in the n-dimensional energy landscape.

Support for this picture is drawn from diverse experiments, including, of course, the present ones. The very great sensitivity of the Raman soft-mode intensity to small fields[9] suggests a random-cluster interaction among the Nb dipoles. Further, at the temperature of the apparent freezing the volume fraction occupied by the interaction volumes of the individual ions, calculated using the microdomain size of the host crystal,[20] is in the neighborhood of 0.5, appropriate to a percolation process.

Our picture, then, is one of activated hopping among local minima in the energy surface, created by random clustering of the Nb ions. In order to verify this mechanism, we measured the relaxation of the polarization after application of a dc step voltage on a sample freshly cooled in zero field. The resulting polarization was recorded from the shortest times available (10^{-3} sec) out to a time of 200 sec, the latter limited by the input bias current of the preamp. Over this range an accurate straight line was obtained on a semilog plot, with a slope which could be determined to better than 0.2%. In Fig. 2 we show the results of these measurements, where we have chosen the parametrization $P/\varepsilon_0 = P_0 + P_1 \ln(t/\tau_0)$, with $\tau_0 = 10^{-3}$ sec. The relative size of the two contributions does not change much with E, but we note that the displacement between the two peaks is reminiscent of that found for the parameters B and $\chi_{1,zfc}$ in Fig. 1.

It is now clear that the dielectric relaxation measurements reported previously[11] for $KTa_{1-x}Nb_xO_3$ are quantitatively questionable. The nonanalytic response (B) makes a contribution to the first harmonic in an ac susceptibility experiment which will scale as E^2. The relative size of this effect is readily assessed from the data in Fig. 1. A field of 1 kV/m would yield a 50% effect at a temperature near 6 K. Such a field is typical of linear susceptibility measurements.

It is not possible, however, to assess with any certainty the effect that the nonanalyticity has on the *frequency* dependence of χ_1, It appears reasonable, though, from a comparison of the curves in Fig. 1 and Fig. 2, to attribute all the frequency dependence to the switchable states responsible for B. Our own measurements, at very low field,

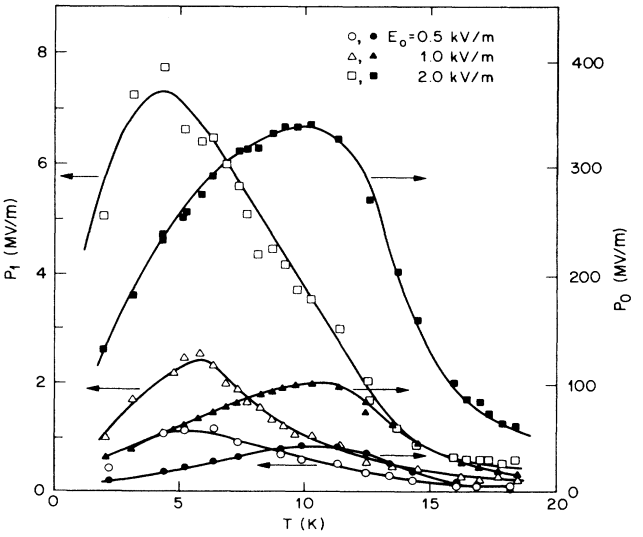

FIG. 2. Polarization relaxation results $P(t) = P_0 + P_1 \ln(t/\tau_0)$ with $E \parallel [111]$ and $x = 0.009$ and $\tau_0 \equiv 1$ msec. The closed symbols show values of P_0 (right scale) while the open symbols show values of P_1 (left scale), both the functions of temperature for the nominal field amplitudes shown. Lines are guides to the eye.

indicate that the frequency dependence of $\chi_{1,zfc}$ is in fact quite small, but it has thus far been difficult to obtain accurate data on this point. Thus, the qualitative picture drawn by Samara[11] remains valid, as does the polarization fluctuation analysis presented by Lyons, Fleury, and Rytz,[9] but we now identify the fluctuations with the clusters responsible for the nonanalytic response of the sample to a field.

The simple model used here fails to reproduce one important detail of our data. Namely, the decrease in B for $T < 6$ K suggests a *nonuniform* density of states as a function of E_c, while the polarization relaxation results suggest a *uniform* distribution as a function of W. Since we expect $W \sim \mu E_c$, where μ is the dipole of the cluster, this is simply a reflection of the fact that all three of these quantities depend on the cluster size L. Further discussion of this point will be given in a future report.

In summary, we have shown that in a dipolar glass (i) an analytical representation of $P(E)$, and the concomitant definition of χ_n, are inapplicable; (ii) fields as low as a fraction of a kV/m are sufficient to distort presumably linear dielectric measurements; (iii) a model based on activated two-level systems describes our data with a barrier distribution which extends to zero energy; and (iv) the polarization response after application of a step dc voltage is logarithmic in time over a wide range of time, temperature, and field. Certain details of the observed behavior remain unexplained, most notably the decrease in B at very low T. We speculate that similar effects may also be observed in magnetic spin glasses, and suggest that such measurements should be undertaken. The reasons for the deviation from spin-glass behavior above T_g may be related to the long-range nature of the dipolar interaction, but a definitive evaluation of those reasons must await further experiments. Finally, we suggest that further theoretical efforts should be directed at elucidating the connections and distinctions between the Néel-Preisach model and modern spin-glass theory.

We thank D. Rytz for providing the [111] sample used for these studied. We wish to acknowledge helpful discussions of our results with R. Bhatt, H. Bouchiat, D. Huse, L. Levy, P. Littlewood, A. Ogielski, and R. Rammal. We are especially indebted to R. Rammal for the suggestion of the applicability of the Néel-Preisach model. We thank G. A. Samara for furnishing us with the [100] sample used for his previous measurements.

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