

Cluster Dynamics in a Dipolar Glass

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We have directly observed fluctuating dipolar clusters in the mixed crystal $\text{KTa}_{0.991}\text{Nb}_{0.009}\text{O}_3$ using inelastic-light-scattering techniques for temperatures between 1.8 and 25 K and for electric fields up to 2 kV/cm. Together with earlier dielectric-relaxation data, our data span over nine decades in frequency and obey a Vogel-Fulcher relaxation model over the temperature range 6–15 K with an extrapolated transition at 3.0 K to a glassy dipolar state.

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The competition between development of long-range order and the freezing in of disorder at low temperatures is currently a subject of high interest. Considerable theoretical progress has been made in magnetic systems¹ such as the random-field² and the spin-glass³ problems. In addition,⁴ much attention has been given to analogous systems involving electric dipoles or quadrupoles, rather than magnetic spins.

We report here a study of a material of the latter sort. By combining results of inelastic light scattering with earlier dielectric-relaxation data, we obtain a quantitative measure of the dipolar dynamics spanning more than nine decades in frequency. We find clear evidence for a cooperative dynamic regime, suggesting a transition at a finite transition temperature to a glassy dipolar state. Furthermore, we find a crossover to long-range order in fields $E > 400$ V/cm.

The system of interest here, $\text{KTa}_{0.991}\text{Nb}_{0.009}\text{O}_3$, is a simple cubic perovskite lattice (KTaO_3) containing a dilute concentration ($x=0.009$) of isoelectronic defects (Nb^{5+}). The host lattice is centrosymmetric at all temperatures, and hence should exhibit no first-order Raman scattering. It is, however, potentially unstable to a ferroelectric distortion and exhibits a soft zone-center infrared-active TO phonon. For $x > 0.05$, $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ exhibits a ferroelectric phase transition with $dT_c/dx > 0$. Hence,⁵ the Nb ion must be a relaxing symmetry-breaking defect, residing off the Ta site and able to hop among several equivalent positions. The direction of the spontaneous polarization, as well as NMR⁶ and extended x-ray-absorption fine-structure⁷ measurements and our own central-peak data reported below, indicates that the dominant Nb displacement is along [111].

However, the situation at low temperature and for $x \leq 0.02$ remains controversial. Dielectric relaxation,⁸ Raman scattering,⁹ optical birefringence,¹⁰ and refractive index measurements¹⁰ have led to interpretations ranging from a gradual freezing into a disordered dipolar state at zero temperature to a true long-range fer-

roelectric order with a finite T_c . Clearly as T decreases the Nb hopping slows down. Simultaneously the host lattice correlation length ξ increases as the lattice softens, thus increasing the size of the distorted regions as well as the Nb-Nb interaction. When the distorted regions overlap, the Nb motion becomes cooperative. The "dipolar clusters" discussed in this work refer to the polarization clouds surrounding one or more Nb moving cooperatively.

As the clusters grow, their relaxation slows precipitously. A delicate competition results between tendencies to long-range order and freezing in of a random-cluster, or glassy, state.¹¹ For $x=0.009$, the mean Nb-Nb distance is about 5 unit-cell diameters. Our earlier studies using defect-induced first-order Raman spectroscopy¹² show that the range of symmetry breaking which extends from each defected cell reaches this value at temperatures of order a few degrees Kelvin. Hence, the competition is very delicately balanced in this system.

Two samples were used for these studies, both 0.5 mm thick along [100] and [111], respectively, with gold electrodes deposited over a flash chromium coat by evaporation. The electrodes covered nearly the entire sample face. The other sides of the [100] sample were also [100] faces, while for the [111] sample, the incident direction was $[1\bar{1}0]$, and hence, the viewing direction was $[11\bar{2}]$. The samples were cut from neighboring portions of a single-crystal boule of $\text{KTa}_{0.991}\text{Nb}_{0.009}\text{O}_3$. The [100] sample was the same one used in the dielectric study.⁸

The spectra were excited by a single-mode argon-ion laser providing 100 mW at 5145 Å. Space-charge effects caused by carrier pumping and trapping in the laser beam can, under normal power and focusing conditions, distort and even dominate the results obtained in an external field.¹³ Therefore, the beam was defocused to a 300- μm diameter, and gated with an acousto-optic modulator. The light was collected with $f/5$ optics and focused either to the slit of a Spex dou-

ble monochromator or to the input of a tandem pressure-scanned Fabry-Perot interferometer (resolution 1.2 GHz FWHM). The iodine reabsorption technique¹⁴ was employed to remove elastically scattered light from the Fabry-Perot spectra reported here. The scattering plane was horizontal, parallel to the electroded faces of the crystal, with both incident and scattered polarizations vertical. Both the transmitted and scattered light exhibited little depolarization.

An alternating electric field was applied to the sample by use of the square-wave pattern shown in the inset of Fig. 1. The data for $E \neq 0$ discussed here were collected by use of 25-msec laser pulses during the "field-on" portions of the four-step cycle shown.

Raman spectra have been obtained previously in similar crystals.⁹ However, since crystal properties are a strong function of x in this region of concentration, we deem it important to report measurements on the same sample. Examples of our data are shown in Fig. 2. There is no evidence above 20 K for first-order scattering from the soft TO phonon greater than that observed in nominally pure material. An underdamped soft-mode peak appears below 14 K, which has been taken as evidence of a ferroelectric transition.⁹ However, this mode appears far above the temperature (6 K) where the χ' dielectric data⁸ indicate a maximum. Since the spectra were obtained on the same sample as used for the dielectric study, and they exhibit no apparent position dependence, we must attribute the dis-

crepancy to the different probe frequencies employed in the different experiments. Evidently, between 6 and 14 K, the Nb are hopping sufficiently rapidly that they exhibit an average on-site position on the time scale of the dielectric data ($> 10^{-6}$ sec), but exhibit clear symmetry breaking on the time scale of the soft-mode vibration ($\sim 10^{-12}$ sec). According to this picture any phase transition, if one occurs, must lie below 6 K. Moreover, at intermediate temperatures, the strong electric field dependence [Fig. 2(b)] of the soft-mode intensity indicates that only a fraction of the sample bulk is in fact distorted for $E=0$. As E is increased at 8 K, the intensity saturates after tripling for $E \sim 1$ kV/cm. This suggests that only $\sim \frac{1}{3}$ of the sample is distorted in zero field.

The Raman spectrum shows no rapid temperature dependence over the temperature range 4–12 K. The Brillouin data, however, reveal a strongly temperature-dependent quasielastic feature, which obviously couples to certain acoustic modes. A typical spectrum is shown, together with a fit, in Fig. 1. The fits to these data employed damped harmonic oscillator functions for the weak phonons evident in the 25–50 GHz range, plus a sum of two Lorentzian functions centered at zero frequency to fit the central feature, with the width of the narrower Lorentzian function held at the instrumental resolution. This treatment provides a high-quality fit to the main features of the spectra, as may be seen in Fig. 1. A full dynamical treatment, including a distribution of relaxation times, might be needed to account for the behavior of the coupled TA mode; however, such a treatment is unlikely to change our conclusions relative to the polarization dynamics and will be discussed in detail in a future publication.

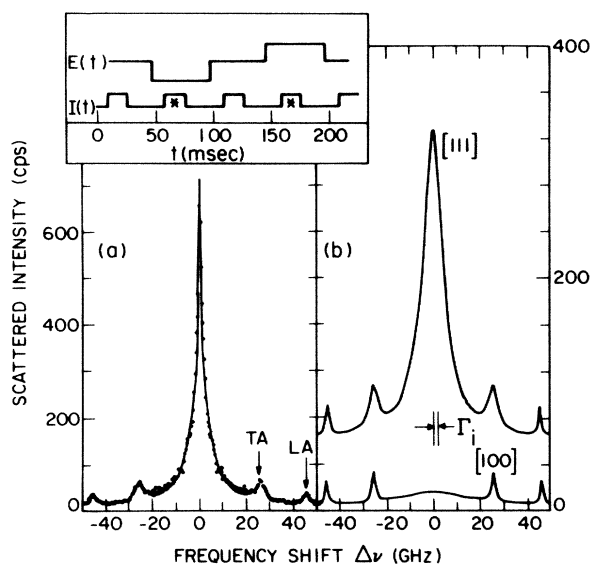


FIG. 1. (a) Central-peak spectral data (points) and the fit (line) described in the text, for the [111] sample; $E=0.4$ kV/cm and $T=12$ K. (b) Fits to the spectra, as displayed in (a) minus the instrumentally narrow central-peak component for [111] (top) and [100] (bottom) orientations; E and T as in (a). Inset: time sequence of field $E(t)$ and laser $I(t)$ pulses used. The spectra shown were obtained during the pulses indicated by asterisks.

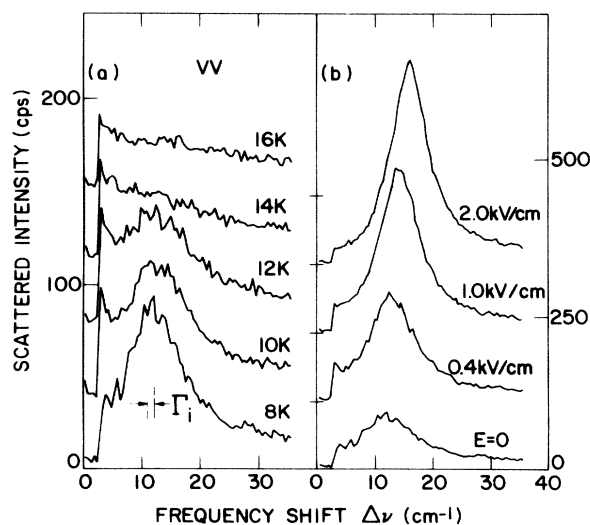


FIG. 2. Raman spectra obtained in $KTa_{0.991}Nb_{0.009}O_3$ (left-hand side) in zero field at various temperatures and (right-hand side) at $T=8$ K in various fields.

All the elastically scattered light is removed by the I_2 absorption cell. Hence, the narrow component, although instrumentally narrow, is indeed inelastic, containing frequency components between 0.5 and 1 GHz.

Since the main feature under discussion here is the broad central-peak component, we plot the remainder of the data as in Fig. 1(b), where we show the fits to the data with the instrumentally narrow component removed. Additional central-peak spectra are shown in Fig. 3 as functions of temperature and field. The central-peak width changes very rapidly above about 10 K. This temperature is intermediate between that where the soft mode appears in the Raman spectrum (14 K) and where χ' has its peak (6–7 K). This behavior is consistent with the picture given above, since the central-peak frequency ($\sim 10^{10}$ Hz) is intermediate between those probed in the other two experiments. Since the Nb ions break the local symmetry, the fluctuations in the polarizability and in the polarization are linearly related. Thus, light scattering and dielectric measurements probe the same physical quantity in this case.

Clearly, there is an average characteristic relaxation time which increases dramatically as temperature is lowered from 14 to 6 K. A simple activated relaxation would obey an Arrhenius behavior: $\tau_c^{-1} = \nu_0$

$\times \exp(-E_a/kT)$. In the left-hand inset of Fig. 3, we show an Arrhenius plot of our data together with the dielectric relaxation.⁸ Not only is there a clear disagreement over a broad frequency range, but the attempt frequency $\nu_0 \approx 10^{21}$ Hz extrapolated from the low-frequency data is physically unreasonable. The breakdown is due to the interactions of the clusters. In essence, the slowing down is accelerated as the clusters communicate via the diverging susceptibility of the host lattice. An alternative, often used, empirical description of glassy relaxation is the Vogel-Fulcher equation¹⁵

$$\tau_c^{-1} = \nu_0 \exp[-E_a/(T - T_0)], \quad (1)$$

where τ_c is the average relaxation time, E_a an activation energy, ν_0 an attempt frequency, and T_0 the temperature where all relaxation times diverge. Figure 3(d) shows good agreement with Eq. (1) over nine decades in frequency, where the fit shown yields the physically reasonable parameters $\nu_0 = 300 \text{ cm}^{-1}$, $E_a/k = 70 \text{ K}$, and $T_0 = 3.0 \text{ K}$. In this plot we have shown only the central-peak data above 10 K, since at lower temperature the 0.5-GHz width of the iodine absorption may result in a significant distortion of the spectral profile. While expressions other than (1) may fit the same data¹⁶ over nine decades, they usually yield higher values for T_0 . Hence, the essential point is that the data extrapolate to a divergence of relaxation times, and hence a transition to a glassy state, at a finite temperature.

The extreme field sensitivity of the soft-mode intensity and the absence of the second TA mode (Fig. 3) in the Brillouin spectra obtained at zero field are strong evidence for the absence of uniform distortion. Apparently, in zero field, cluster sizes remain small so that an acoustic phonon averages over all possible distortions, resulting in cubic dispersion curves. As E increases, the ordered clusters eventually become large enough to result in the observed TA splitting. Together with the above dynamic information from Raman and central-peak spectra, this picture gives a unifying basis for understanding all the relevant experimental results, and leads to the conclusion that no uniform distortion with long-range order is present in our sample for fields below 400 V/cm over the temperature range studied.

In summary, we have observed the soft mode of the host lattice, made Raman active by symmetry-breaking distortions imposed by growing clusters around Nb ions. We also observe a broad central-peak feature due to direct scattering from fluctuating dipolar clusters. At high temperatures, the lack of enhanced scattering from ferroelectric microregions indicates that the Nb are on site when probed at $\sim 25 \text{ cm}^{-1}$. At lower temperatures, their residence time at off-site positions increases, as does their interaction, until dipolar

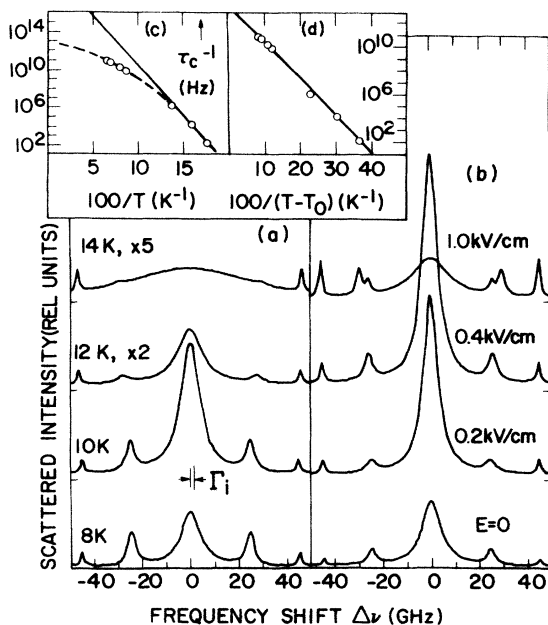


FIG. 3. (a) Central-peak spectra in zero field for various temperatures, and (b) similar spectra obtained at 10 K in various fields. All spectra are corrected for absorptions in the molecular-iodine filter employed. Insets: central-peak widths plotted with the dielectric-relaxation data (c) on an Arrhenius plot, and (d) with a Vogel-Fulcher law, assuming $T_0 = 3.0 \text{ K}$.

clusters form. The intensity difference seen for the cluster scattering in the [100] and [111] samples [Fig. 1(b)] verifies that the Nb reside predominantly at [111] positions in this temperature range. As temperature is lowered still further from 15 to 6 K, the average cluster relaxation time increases dramatically, apparently diverging toward a transition at 3.0 K to a dipolar glass state. In addition, the data show that no uniform distortion with long-range order (thousands of angstroms) exists in our samples at any temperature studied in fields below 400 V/cm.

Further work is necessary to determine the effect of the Nb-Nb interaction on the behavior below 6 K. Given the ability in $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ to tune that interaction conveniently by application of pressure, stress, or electric field, it should prove possible to delineate its glassy properties more easily than in systems where the only accessible experimental parameter is concentration. This tunability opens the possibility of quantitative study of the crossover between the glassy and the long-range-ordered states without having to vary concentration.

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