Glasslike Behavior and Novel Pressure Effects in $KTa_{1-x}Nb_xO_3$

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High-pressure studies have shown that $KTa_{1-x}Nb_xO_3$ crystals with small x (≈ 0.02) exhibit relaxational glasslike behavior rather than a static ferroelectric structural phase transition as previously thought. The results show a pressure-induced transition from frozen to relaxing impurity behavior and evidence for an off-center to on-center transition of the Nb ion at the B site of the perovskite lattice.

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In this paper I present high-pressure results which shed new light on the nature of the "phase transition" in an important and much-studied material system, namely, $KTa_{1-x}Nb_xO_3$ in the limit of small x ($\lesssim 0.02$). Specifically, the following are shown: (1) This system exhibits a continuous pressure-induced transition from frozen "impurity" to relaxing "impurity" behavior; (2) the large peak in the dielectric susceptibility (or dielectric constant), long thought to be a static phenomenon associated with a ferroelectric structural phase transition, is a relaxational glasslike phenomenon; and (3) this peak vanishes above a certain pressure. I discuss these results in terms of the freezing of an Ising-type impurity (a Halperin-Varma center),[1,2] and, within the framework of this model, the vanishing of the susceptibility peak is interpreted as a pressure-induced off-center to on-center transition of the Nb^{5+} ion at the B site in the perovskite lattice. The results are important in relation to theories of the behavior of isolated impurities in crystals with soft phonon modes.[1-3] Additionally, I believe that this system represents a beautiful example of the tunability of an atomic potential in a crystal by the application of pressure.

Pure potassium tantalate, $KTaO_3$, which crystallizes in the cubic perovskite structure, exhibits a soft ferroelectric phonon mode and is a thoroughly investigated crystal.[4] At low temperatures the soft mode is stabilized by quantum fluctuations, and consequently the crystal does not undergo a phase transition. The substitution of Nb for Ta yields mixed crystals, $KTa_{1-x}Nb_xO_3$ (or KTN), which have become a classic system for the study of soft-mode transitions in mixed crystals. Much recent work has centered on samples with $x \leqslant 0.04$, as these samples exhibit on cooling large peaks in the dielectric susceptibility believed to be associated with paraelectric to ferroelectric structural phase transitions.[5,6] Decreasing x from 0.04 lowers the susceptibility peak from ~ 50 to 0 K; for this reason, KTN has been used to study the onset of quantum effects and the approach to the quantum displacive limit.[5,6] An alternative method to changing x for studying these quantum effects is to choose samples with fixed x and lower T_c to 0 K by the application of high pressure.[7] It was in the course of such a pressure study that we observed results which deviated from the expected quantum response for a ferroelectric phase transition. A close examination of these deviations led to the results and conclusions presented in this paper.

In the present work we investigated the temperature (4–50 K), hydrostatic pressure (0–10 kbar), and frequency (10^2–10^6 Hz) dependences of the dielectric susceptibility of KTN samples with $x \leqslant 0.02$. Single-crystal samples, kindly provided by Dr. D. Rytz, were cut in the form of thin plates ~ 5 mm^2 in area and ~ 0.7 mm thick. Vacuum-deposited gold films served as electrodes on the large (100) faces. The apparatus and techniques have been described elsewhere.[8] All the results were reversible and reproducible on temperature, pressure, and frequency cycling.

Figure 1 shows the temperature dependence of the real part of the dielectric constant ϵ' of the $x = 0.02$ sample at different frequencies and pressures. At atmospheric pressure ($P = 1$ bar) the peak in ϵ' occurs at 33.5 K, and the $\epsilon'(T)$ response is very nearly frequency independent. At higher pressures the peak shifts to lower T and a dramatic frequency dispersion is induced as seen in the 3.6- and 5.6-kbar isobars. At each of these pressures the peak shifts to higher T and the peak amplitude decreases with increasing frequency. The imaginary part of the dielectric constant ϵ'' exhibited qualitatively similar behavior; however, the peak in ϵ'' occurred at a lower T than that in ϵ' and the large dispersion occurred on the high-T side of the peak.[9]

Additional results not presented in Fig. 1 show that the ϵ' and ϵ'' peaks vanish at all frequencies employed at pressures > 8.0 kbar, and for these pressures the response becomes frequency independent. This is, for example, the case for the 9.2-kbar

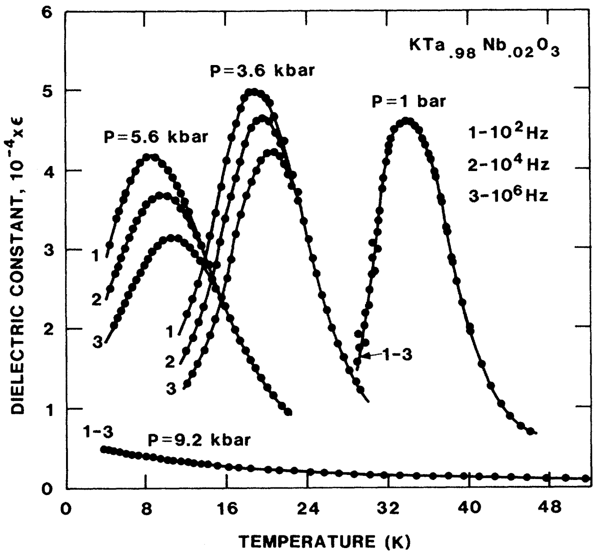

FIG. 1. Temperature dependence of the real part of the dielectric constant of a KTN sample at different pressures and frequencies showing the strong pressure-induced dispersion.

data in Fig. 1. Additionally, at a given pressure these peaks and the dispersion vanish with the application of modest ($\sim 10^3$ V/cm) dc biasing fields. Results on two other crystals with different x values show behavior qualitatively similar to that in Fig. 1.

The above results clearly show that the $\epsilon(T)$ responses in these crystals are not associated with a static phenomenon but rather are due to a relaxational process. In fact, the shapes of the frequency dispersions observed at high pressures are qualitatively very similar to those observed on freezing at 1 bar in the magnetic susceptibility of spin glasses[10] and in the dielectric susceptibilities of the dipolar glass systems $KBr_{1-x}CN_x$[11] and $KTaO_3$:Li.[12] I believe that we are dealing with a glasslike phenomenon associated with the freezing of random dipoles or local order (or short-range clusters of these) in the present case as well. Two additional factors support this view. (1) The Nb concentration in the samples of interest is $\leq 2\%$ ($x \leq 0.02$) This means that less than one in every fifty unit cells has a Nb ion. It is felt that at these concentrations the system is sufficiently dilute making it unlikely to have the long-range dipolar correlations needed for a ferroelectric phase transition. (2) KTN samples with low Nb concentrations are known to exhibit a first-order Raman scattering in the high-temperature phase. There has been some controversy about the origin of this scattering,[13,14] but one interpretation could be that the Nb occupies an off-center position as discussed below.

The above evidence is consistent with the following physical picture. At 1 bar the Nb occupies an off-center position at the B site, and, being pentavalent, it has a large associated dipole moment. There are several equivalent such off-center positions in the cubic perovskite structure, and the Nb can hop among these positions with a frequency ν. The motion can be described in terms of a double-minimum potential with an energy barrier E and a separation d between the two minima which is proportional to the off-center distance of the Nb ion. An impurity moving in such a potential is referred to as an Ising-type impurity.[1]

For an impurity which can move between two positions $Q_i = \pm\rho_i$ ($\rho \propto d$) with relaxation (Debye) dynamics, the low-field real and imaginary parts of the susceptibility are given by[1]

$$4\pi\chi'(\omega) = \frac{\rho^2}{kT}\frac{1}{1+\omega^2\tau^2} \simeq \epsilon'(\omega), \tag{1}$$

$$4\pi\chi''(\omega) = \frac{\rho^2}{kT}\frac{\omega\tau}{1+\omega^2\tau^2} \simeq \epsilon''(\omega), \tag{2}$$

where ρ is proportional to the effective dipole moment, ω is the angular measuring frequency, and τ ($=1/\nu$) is the single-particle relaxation time. Note that ϵ' and ϵ'' are proportional to $1/T$, i.e., they obey a Curie law.

The present results can be qualitatively described by Eqs. (1) and (2) with a thermally activated τ, i.e.,

$$\tau = \tau_0 \exp(E/kT), \tag{3}$$

where we take the activation energy to be the barrier height E. In doing so it should be noted that the measured ϵ ($=\epsilon' + i\epsilon''$) represents the response of the impurity [Eqs. (1)-(3)] superimposed on that of the highly polarizable (soft mode) $KTaO_3$ host. The latter response is similar to that of the 9.2-kbar isobar in Fig. 1.

Figure 2 shows that the τ's deduced from the $\epsilon''(\omega,T)$ data at high pressure are well described by Eq. (3) over four orders of magnitude change in τ. In Fig. 2 I have plotted, for the 5.6-kbar data, $\log\tau$ ($\tau = 1/\omega$) vs $1/T_{\max}$, where $T_{\max}$ is the T corresponding to the peak value of ϵ'' at the frequency ω. The E's deduced from such plots (inset Fig. 2) exhibit a remarkably strong pressure dependence decreasing from ~ 100 meV at 3 kbar to < 5 meV at 7 kbar.

In terms of the present model, at high T the Nb surmounts the energy barrier E and moves essentially freely between minima. Being localized and having a large dipole moment, it has a strong influence on the properties of the highly polarizable

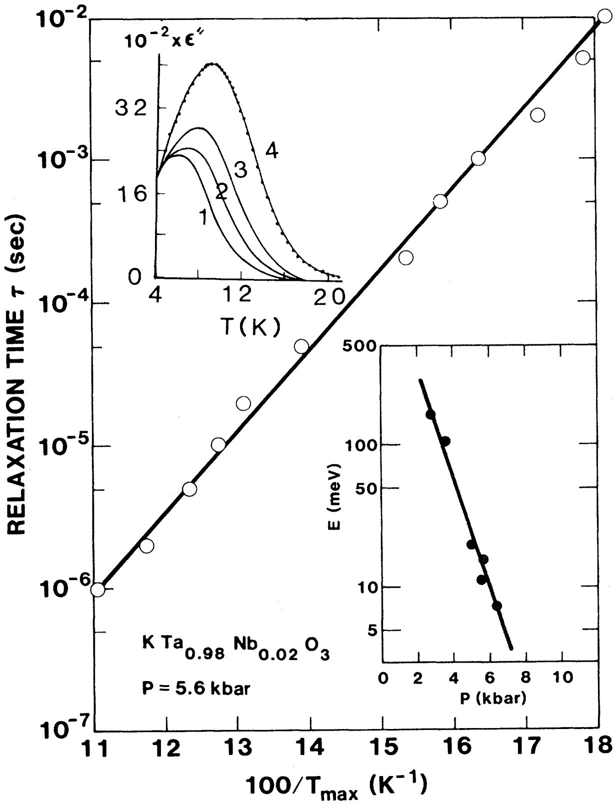

FIG. 2. Temperature dependence of the dipolar relaxation time of a KTN sample at 5.6 kbar. The lower inset shows the pressure dependence of the activation energy deduced from such Arrhenius plots. The upper inset shows some of the ϵ'' vs T results at different frequencies (1–4 correspond to 10^2, 10^4, 10^5, and 10^6 Hz, respectively) from which the logτ vs $1/T_{\mathrm{max}}$ data were obtained.

$KTaO_3$ host, and vice versa—hence the large enhancement of ϵ of the crystal by the Nb. The situation is akin to the giant local moments in magnetic systems. On cooling, the dipoles freeze in the potential minima at some characteristic T (T_{max}) and the polarizability decreases on further cooling. At 1 bar E is large (see Fig. 2), and at low T's there is practically no relaxation of the Nb from one potential minimum to the other in the frequency range of the present experiments; i.e., the hopping time is very long and the dispersion is weak, and one has essentially a frozen dipolar impurity.

With increasing pressure E decreases dramatically (Fig. 2), the hopping time decreases, and the low-T relaxation (or dispersion) increases markedly (Fig. 1). I attribute the decrease in E to a decrease in the off-center distance of the Nb. At sufficiently high pressure we expect the Nb to move to the centrosymmetric position, and for such a circumstance $E \rightarrow 0$ and the associated dipole moment and dipolar relaxation should vanish. This appears to be the case for $P > 8$ kbar for the $x = 0.02$ crystal. The $\epsilon(T)$ response at 9.2 kbar in Fig. 1 shows no frequency dependence between 10^2 and 10^6 Hz and no evidence for a peak in ϵ. It resembles closely that of pure $KTaO_3$[4] as expected in the model. Strictly speaking, it is not necessary for E to vanish precisely for the above condition to obtain. All that is required is for E to become sufficiently small to allow the Nb to move (or tunnel) freely between the two potential minima at all temperatures.

The model also explains the vanishing of the dielectric anomalies and the dispersion with dc biasing field. The field simply freezes the Nb ion in one of the potential minima.

The above description is based on a single-ion, single-relaxation-time model. Closer examination of the frequency dependences of ϵ' and ϵ'' and of the concentration dependences of E and τ_0 in the data shows that there is clear evidence for the existence of a distribution of τ's. I attribute this primarily to collective effects due to the presence of some Nb clusters. These effects can be expected to become more evident the higher the Nb concentration, and the bigger the cluster, the stronger the correlation effects, and the larger the potential barrier E. The present experimental results are consistent with these observations.

One consequence of not having considered a distribution of τ's in the above analysis is that the deduced model parameters E and τ_0 may not have physically realistic values. In fact, we have evidence that this is the case for τ_0 where, for certain of the experimental conditions (e.g., for $P < 4$ kbar in the $x = 0.02$ crystal), τ_0's $< 10^{-17}$ s were obtained. A detailed analysis of the data based on the choice of suitable distribution functions is needed in order to determine the most probable values of E and τ_0. It should be emphasized, however, that such an analysis is not expected to alter the qualitative features of the model. Additionally, work is needed to confirm the microscopic nature of the proposed local freezing using x-ray diffraction, diffuse scattering, and spectroscopic tools. It is hoped that the present results will stimulate such work.

The present model for KTN with low Nb concentration provides a possible explanation for puzzling results in the literature. High-resolution specific-heat and thermal-conductivity data on a sample with $x = 0.012$ showed no evidence for anomalies at the presumed transition temperature $T_c = 18$ K.[15] This is quite surprising for a "transition" from a paraelectric phase to a polar ferroelectric phase. The absence of anomalies led the authors[15] to conclude that the properties of this sample are dominated by quantum fluctuations which quench the anomalies usually associated with a ferroelectric transition. In terms of the model here, the absence of these anomalies is a consequence of the view that there is no phase transition in this crystal.

Finally, we note that the behavior of isolated impurities in crystals with soft phonon modes has been the subject of much theoretical interest in relation to the existence of local modes and of central peaks in the dynamic structure factor as well as in other contexts.[1-3] Detailed experimental confirmations of these theories are still lacking. I believe that KTN with low Nb concentration represents an excellent system for testing these theories. As a specific example, Halperin and Varma[2] considered a defect in a double-well potential which couples linearly to the soft-mode coordinate—a situation similar to that in the present work. They consider the cases of both frozen and relaxing impurities, and it is the relaxing impurity which in their model gives rise to the dynamic central peak. The width of the peak is determined by the hopping time of the defect. By the proper choice of pressure and composition of KTN (and related systems) it may be possible to delicately tune the double-well potential and thereby induce transitions from frozen to relaxing impurity behavior and thus accurately control the hopping time. Thus, by such means one should have a unique method for study of the evolution of the central peak.

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