Raman Study of Cluster Dynamics in Disordered Ferroelectrics

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We demonstrate for the first time that information on the dynamics of polar clusters in disordered ferroelectrics can be obtained from an analysis of the first order Raman scattering by hard phonon modes. The model developed allows one to separate the effect of the critical slowing down due to the divergence of the static dielectric susceptibility from that of the slowing down of the dynamics of local clusters. Raman results obtained on a $K_{1-x}TaNb_xO_3$ crystal with $x = 15.7\%$ have revealed such a dichotomy of the cluster dynamics. The experimental results are consistent with the picture that, in disordered ferroelectrics, the slowing down of local clusters presents similarities to that in glasses and spin glasses.

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The description of cluster dynamics in disordered systems is a challenging problem, and many attempts have been made to solve it in different systems. The short range character of clusters results in very similar behavior of their dynamics in glasses, spin glasses, and disordered ferromagnets and ferroelectrics showing long time relaxation with a logarithmic dependence, hysteresis phenomena, aging, etc. [1–3]. Moreover, in some cases extremely slow dynamics of clusters can suppress critical anomalies that one could expect at a thermodynamic phase transition with the appearance of long range order. As we argue below, such a suppression of critical anomalies does take place at low impurity concentrations in $KTa_{1-x}Nb_xO_3$ (KTN), where off-center Nb ions form a system of randomly relaxing dipoles.

KTN (together with its counterpart KLT—$K_{1-x}Li_xTaO_3$) has attracted much attention in the past because it presents the rare situation in which the degree of disorder can be controlled simply by changing the Nb concentration [4]. The very pronounced cluster dynamics in KTN [5–8], in contrast to KLT, originate in the fact that the reorientational frequency of isolated Nb ions in $KTaO_3$ is comparable to the soft mode frequency of the host lattice. In this situation the interaction between Nb ions within local clusters has a crucial effect on the slowing down of the Nb dynamics. The latter effect was originally observed by Samara [5], who found the dielectric dispersion for 0.9% KTN and concluded against a ferroelectric phase transition and in favor of the freezing of slow relaxing clusters. Based on their Raman results Lyons, Fleury, and Rytz [6] supported this conclusion and proposed the Vogel-Fulcher law as an adequate expression to fit the data for the Nb reorientation frequency. These authors also indicated that other fitting formulas could be used as well and described their observation as a dramatic increase of the relaxation times with a transition to a glassy state. This conclusion, however, fails to explain the fact that the dielectric susceptibility of 0.9% KTN reaches the same high value ($\sim 10^5$) as that of 1.2% KTN, which has been shown [9] to undergo a true structural transition. On the other hand, we will show below that a very similar dynamical behavior is observed for Nb concentration as high as 15.7%, where the existence of a structural transformation to long range order is beyond doubt.

In this Letter we demonstrate for the first time that first order Raman (FOR) scattering can be used as a powerful technique for the investigation of cluster dynamics in systems undergoing structural (ferroelectric) phase transition. The model developed allows one to separate the effect of the critical slowing down of the long-wavelength fluctuations connected with the divergence of the static susceptibility (which is the only effect in mean field theory) from that of more local noncritical contributions. The effect of the dynamical broadening of the Raman lines is most pronounced on the low frequency side of the line, which, as we show below, is not very sensitive to the critical slowing down connected with the ferroelectric transition and thus provides a measure of the dynamics of local fluctuations.

Although FOR scattering from hard optical phonons induced by polar fluctuations in KTN was observed long ago [10], the spectra were never completely analyzed with regard to the dynamical properties of the system. Bruce, Taylor, and Murray [11] suggested that FOR scattering provides information on the value of the local order parameter, but this is true only in the extreme case of the very short lifetime of the hard optical phonons when one can neglect the effect of inhomogeneous broadening (static contribution). The latter was initially considered by Uwe *et al.* [12] in the limit of very dilute impurity concentrations when a ferroelectric phase transition does not take place. Using FOR results, they manage to estimate the noncritical correlation length r_c in pure $KTaO_3$, which gives rise to impurity-induced isotropic local polar distortions of the lattice, predicted theoretically earlier [13].

The first attempt made to understand quantitatively the effect on the growth of polar nanoregions on the shape of the FOR line near T_c was reported by DiAntonio *et al.* [14]. In this study, a dramatic increase of the static FOR peak intensity was observed in the vicinity of T_c, and this fact, as well as the characteristic shape of the line, was quantitatively explained by a theory that takes into account the critical increase of the correlation length R_c in the doped crystals. However, the effect of dynamical fluctuations on the FOR line shape still remained unexplained. We shall show below that this effect can be explained in the framework of a model that separates explicitly the inhomogeneous broadening of FOR lines, caused by static disorder, from the homogeneous broadening due to the dynamics of polar clusters.

Here we have chosen to investigate a 15.7% KTN crystal on which dielectric measurements have previously shown three distinct peaks [15] corresponding to the three transitions expected in perovskite ferroelectrics. The first dielectric peak at 138.6 K, which marks the transition from a cubic to a tetragonal phase, coincides with a sharp increase in the magnitude of the nonpolar TO_3 mode in the FOR spectrum of this crystal.

Experimental TO_2 Raman spectra are presented in Fig. 1 for different temperatures above the transition. Two features are most noticeable: (1) the asymmetry of the line and (2) the rapid change in line shape upon approaching the transition from above. As was shown earlier [14], the asymmetry of the line originates in the presence of static or quasistatic polarization fluctuations $P^\mu(r,t)$ (polar nanoregions). As we show below, the change in the line shape visible on the low frequency side of the line is essentially connected with a change in the contribution of the dynamic clusters.

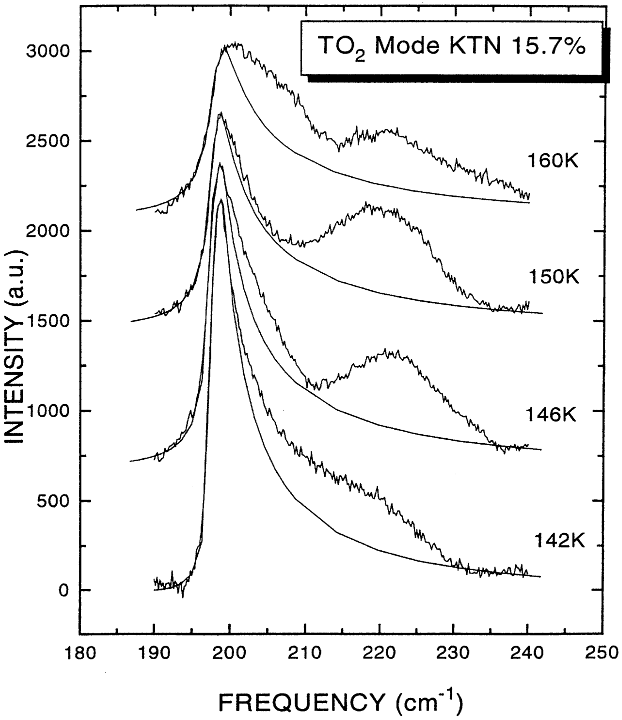

FIG. 1. Experimental FOR spectra with theoretical curves calculated from Eqs. (3) and (4), representing the best fit.

It is well known [16] that the origin of Raman scattering in perovskite ferroelectrics is a modulation of the oxygen electronic polarizability by optical vibrational modes of the lattice. Changes in the electronic polarizability $\delta\alpha(r,t)$ due to the presence of the slowly fluctuating polarization $P^\mu(r,t)$ can be written in the form

$$\delta\alpha(r,t) = P^\mu(r,t)\cdot\Lambda\cdot P^h(r,t), \qquad (1)$$

where $P^h(r,t)$ is a polarization associated with the hard optical phonons and Λ is a second rank tensor.

The scattering intensity is given by the spatial and temporal Fourier components of the polarizability correlation function

$$I^h(\omega) \sim \langle\delta\alpha(r,t)\delta\alpha(0,0)\rangle_{q\approx 0,\omega} \qquad (2)$$

or, using Eq. (1),

$$I^h(\omega) \sim \int dq\, q^2 \langle P^\mu(r)P^\mu(0)\rangle_q g_q(\omega - \Omega_q), \qquad (3)$$

where

$$g_q(\omega - \Omega_q) = \frac{1}{\pi}\frac{\Gamma + \nu_q}{(\Gamma + \nu_q)^2 + (\omega - \Omega_q)^2}, \qquad (4)$$

$$\nu_q = \nu\frac{R_c^{-2} + q^2}{r_c^{-2} + q^2}. \qquad (5)$$

R_c is the critical correlation length, which, in the doped crystal, should diverge at the impurity-induced ferroelectric phase transition.

$$R_c^2 = \frac{\epsilon}{\epsilon_0}r_c^2, \qquad (6)$$

where ϵ and ϵ_0 are the dielectric permittivities of doped and pure crystals, respectively.

The validity of Eqs. (4) and (5) implies the random-phase approximation and a relaxational character of the dynamics of the impurity-induced polar fluctuations [17]. ν_q is the relaxation frequency of the qth Fourier components of $P^\mu(r,t)$. Γ^{-1} is the lifetime of the hard phonons. $\langle P^\mu(r)P^\mu(0)\rangle_q$ in Eq. (3) is the polar Fourier component of the static correlation function of polar nanoregions, given by [17]

$$\langle P^\mu(r)P^\mu(0)\rangle \sim \frac{1}{(R_c^{-2} + q^2)(r_c^{-2} + q^2)}, \qquad T \geq T_c. \qquad (7)$$

We also assume a quadratic q dependence for the hard phonon frequency Ω_q:

$$\Omega_q^2 = \Omega_0^2 + \nu_h^2 q^2. \qquad (8)$$

In Eq. (3) the function $g_q(\omega - \Omega_q)$ represents the dynamical contribution, which is responsible for the homogeneous broadening of the FOR line, while the inhomogeneous broadening stems from the contribution of the static polar correlations given in Eq. (7). As can be seen by replacing the Lorentzian form of $g_q(\omega - \Omega_q)$ with the delta function $\delta(\omega - \Omega_q)$ in Eq. (3), the inhomogeneous broadening does not contribute to the low frequency part of the line ($\omega < \Omega_0$). This makes it possible to observe the effect of homogeneous dynamical broadening caused by the finite value of the Nb reorientation frequency, even if it is smaller than the inhomogeneous linewidth. (We will show below that $\Gamma \ll \nu$, meaning that the effect of a finite phonon lifetime is not very significant in KTN.)

The essential point of this Letter is the realization that, due to the particular q dependence of ν_q given in Eq. (5), different q values contribute differently to different parts of the FOR line. In particular, the contribution of long-wavelength fluctuations ($q \sim 1/R_c$) will dominate near the center of the line (for $\omega \approx \Omega_0$). As the temperature approaches T_c ($R_c \gg r_c$), Eq. (5) shows that ν_q will decrease dramatically for $q \sim 1/R_c$. This will result in a suppression of the dynamical contribution to the center part of the FOR line while the relative weight of the static contribution is fast growing in this part. On the other hand, the FOR intensity on the low frequency part of the line is dominated by short-wavelength fluctuations ($q \sim 1/r_c$), which are not affected by the critical slowing down. Thus this part is more sensitive to changes in the dynamics not associated with critical slowing down.

The sensitivity of the spectrum to changes in the dynamics, as one approaches the transition temperature, is illustrated in Fig. 2, where we present the theoretical spectra for 160 and 142 K and different values of the reorientation frequency ν. By comparing Figs. 2(a) and 2(b) one can clearly see that, as the temperature approaches T_c, the effect of dynamical broadening becomes less significant.

We have used the above model to fit the Raman line, focusing particularly on the low frequency side, in order to obtain estimates for the noncritical relaxation frequency ν. The ratio R_c^2/r_c^2 has been found from Eq. (6) using the experimental data [18] for dielectric permittivity in the same sample. This allowed us to take exactly into account the static critical anomalies associated with the ferroelectric phase transition.

Figure 1 shows the TO_2 Raman line measured on the 15.7% KTN crystal for different temperatures, 160, 150, 146, and 142 K. It is important to note that another spectral feature contributes to the line between 210 and 220 cm^{-1}. It is most likely connected with a (TO_2 + TA) overtone that becomes apparent due to a flattening in the TA branch near the transition [19]. It does not, in any case, affect the low frequency part of the line, which is the part most sensitive to dynamical changes, for reasons stated previously. Calculated line shapes representing the best fit are superposed on each experimental spectrum.

All calculated curves in Fig. 1 have been obtained with the same value of the parameter $A = v_h^2/2\Omega_0 r_c^2 = 11\ cm^{-1}$ and $\Gamma = 0.6\ cm^{-1}$, in good agreement with $\Gamma = 0.4\ cm^{-1}$ obtained earlier from the 1.2% KTN spectra [14]. The values of ν obtained from the fit are presented in Table I. At 142 K, where the effect of the critical slowing down dominates, we can only determine an upper bound value for ν, which is found to be very small (see Table I). At that temperature the linewidth can then be regarded as the static linewidth.

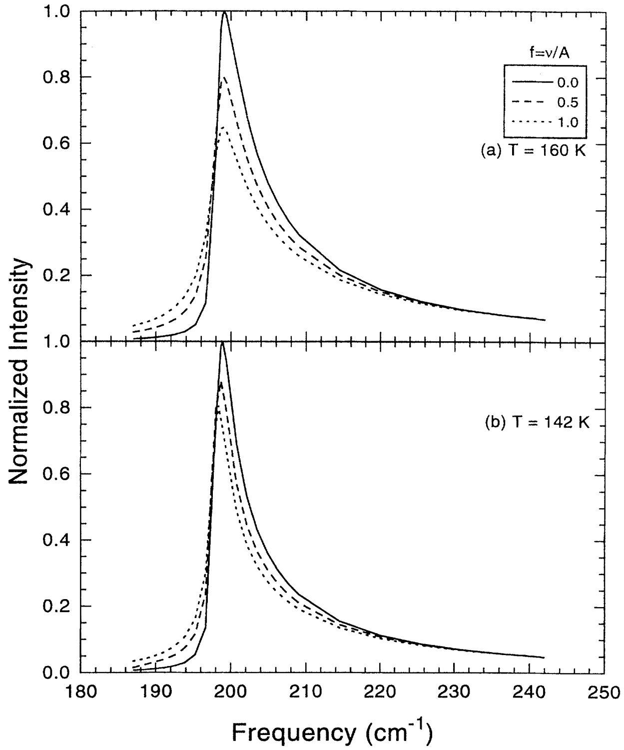

FIG. 2. Comparison of the theoretical spectra normalized to their peak intensity for (a) 160 K and (b) 142 K for 3 different values of the reduced reorientational frequency $f = \nu/A$.

It may be useful to note that a similar analysis of the line shape was also successfully applied to the FOR spectrum of KLT, far above the transition [20]. In that case, the off-center Li ions are not interacting and the frequency ν was found to obey the Arrhenius law with an activation energy approximately equal to 850 K, in good agreement with values obtained from dielectric measurements [21]. This confirms the validity of the model used here for KTN. The large difference between the reorientation frequency of Li and Nb clearly illustrate their different dynamical behavior in $KTaO_3$.

TABLE I. Reorientation frequency ν, corresponding to the best fit of theoretical to experimental spectra. Error bars for the values of ν listed do not exceed 20%.

T (K)	ν (cm^{-1})
142	≤ 1
146	4.5
150	6.5
160	9

Based on the data obtained for the reorientation frequency ν (see Table I) we can propose the following picture of the dynamics of polar fluctuations in KTN near T_c. Interactions between Nb ions in the highly polarizable $KTaO_3$ host lattice lead to the formation of short range polar clusters far above T_c. This cluster formation slows down significantly the dynamics of polar fluctuations. In fact, data of Samara [5] and Lyons, Fleury, and Rytz [6] suggested that the reorientation frequency ν_{Nb} of isolated Nb ions should obey the Arrhenius law $\nu_{\mathrm{Nb}} = (300\ \mathrm{cm}^{-1}) \times \exp(-70/T)$ implying $\nu_{\mathrm{Nb}} \approx 200\ \mathrm{cm}^{-1}$ at $T = 160$ K. However, in our experiment on KTN with 15.7% Nb also at $T = 160$ K, a well resolved FOR line is clearly seen, with the shape of its low frequency side corresponding to $\nu \approx 10\ \mathrm{cm}^{-1}$. Such a difference in reorientation frequency implies the formation of clusters due to Nb interactions at a temperature much higher than T_c.

When the temperature approaches T_c, the interaction between different clusters manifests itself in two different dynamical processes. One of them is the critical slowing down of the long-wavelength modes associated with a critical increase of the polar correlation length R_c and results eventually in the bulk ferroelectric phase transition. At the same time an additional dynamical process takes place, which leads to the slowing down of local short range fluctuations. We emphasize that the values of ν presented in Table I have been extracted from the low frequency wing of the FOR line, which is sensitive only to the short wavelength fluctuations.

Although our approach does not allow us to follow the peculiarities of cluster dynamics in the close vicinity of T_c ($T - T_c \leq 3$ K), the experimental results are consistent with the picture that the slowing down of local clusters in disordered ferroelectrics presents similarities to that in glasses and spin glasses, as was suggested earlier [3] for disordered ferromagnets.

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