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Ferroelectric microregions and Raman scattering in $KTaO_3$

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Raman spectra of both nominally pure and deliberately doped $KTaO_3$ are presented which support the view that symmetry-breaking defects induce ferroelectric microregions even far above the bulk T_c which grow dramatically as temperature is lowered. A characteristic size of these regions is extracted from an analysis of the spectra. The value of R_0/a varies from nearly 4 at low temperatures to about 1.3 at 100 K, the highest temperature where it was determined. For a mixed crystal long-range order sets in when these regions become sufficiently large so as to occupy the major fraction of the sample's volume. We also find evidence of such regions even in nominally pure $KTaO_3$, thus implicating very dilute symmetry-breaking defects of unknown chemical composition, or intrinsic localized fluctuations.

The role of defects in the dynamics and the phase transitions of simple displacive ferroelectrics has received increased attention recently. The behaviors of the simple-cubic perovskite $KTaO_3$ and its relatives $KTa_{1-x}Nb_xO_3$ (KTN) have led to conflicting interpretations which range from a simple increase in ferroelectric T_c with x,[1] to there being no phase transition at all, but merely a "dipolar glass" at low temperatures.[2] Very recent refractive-index and linear-birefringence measurements on this system have even been interpreted in terms of a "cooperative dipole glass."[3] In this paper, we present Raman spectra of both nominally pure and deliberately doped $KTaO_3$ which support the view that symmetry-breaking defects induce ferroelectric microscopic regions (FMR's) (randomly oriented domains) even far above the bulk T_c which grow dramatically in size as temperature is lowered. For a mixed crystal, long-range order sets in when these FMR's become sufficiently large so as to occupy the major fraction of the sample's volume. We find evidence of such FMR's even in nominally pure $KTaO_3$, thus implicating very dilute symmetry-breaking defects of unknown chemical composition. While the presence of such FMR's has been hypothesized previously,[4–6] the present measurements represent the first quantitative determination of their size.

Pure $KTaO_3$ contains one formula unit per unit cell, belongs to space group O_h^1, and exhibits no first-order Raman effect since all long-wavelength phonons are of odd parity.[7] Defects may induce one-phonon scattering by relaxing the momentum-conservation selection rule so that single phonons from throughout the Brillouin zone may contribute to the spectrum of inelastically scattered light. The resulting disorder-induced Raman spectrum (DIRS) depends in shape and intensity upon the magnitude and spatial extent of the deformation associated with each defect and the defect concentration. Because the intrinsic allowed second-order Raman effect in $KTaO_3$ is so strong, quantitative studies of the disorder-induced scattering have not been reported. Nevertheless, as we demonstrate below, the DIRS spectrum associated with dilute defects in a host crystal whose lattice dynamics are well known permits quantitative measurement of the effects which the defects have on the host lattice. These effects are particularly striking in $KTaO_3$, which is an incipient ferroelectric and exhibits a classical soft-mode instability as temperature is lowered toward 0 K.[7]

We report here the temperature-dependent Raman spectra of both nominally pure and deliberately doped $KTaO_3$. The spectra were obtained using conventional 4880-Å argon laser excitation, a double-grating spectrometer, and photon-counting electronics. Typical spectra for the "pure" crystal and for a lightly Sr-doped ($n=1.8\times10^{18}$ cm^{-3} at 77 K) crystal are shown in Fig. 1. Previous studies have shown that substituting Sr^{2+} or Ca^{2+} for K^+ in-

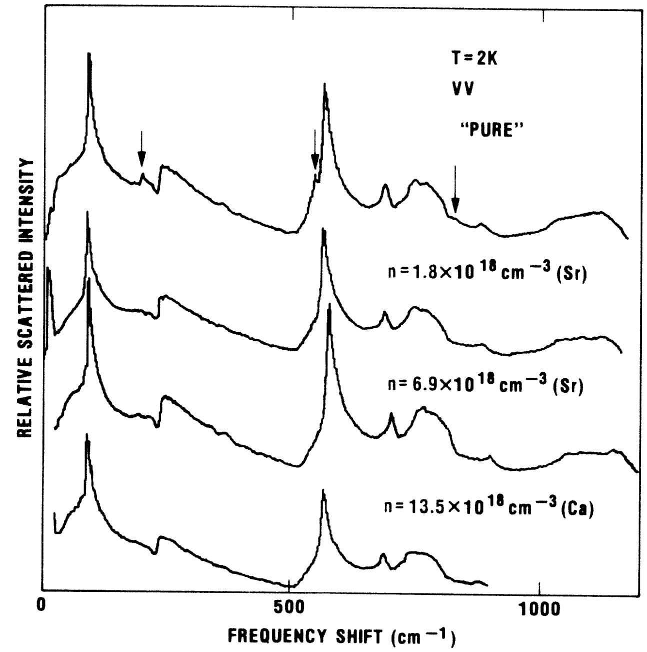

FIG. 1. Raman spectra of the several $KTaO_3$ samples, one nominally pure and the other three doped as indicated. All spectra are taken at a temperature of 2 K, with both the incident and scattered light polarized perpendicular to the scattering plane (vv geometry).

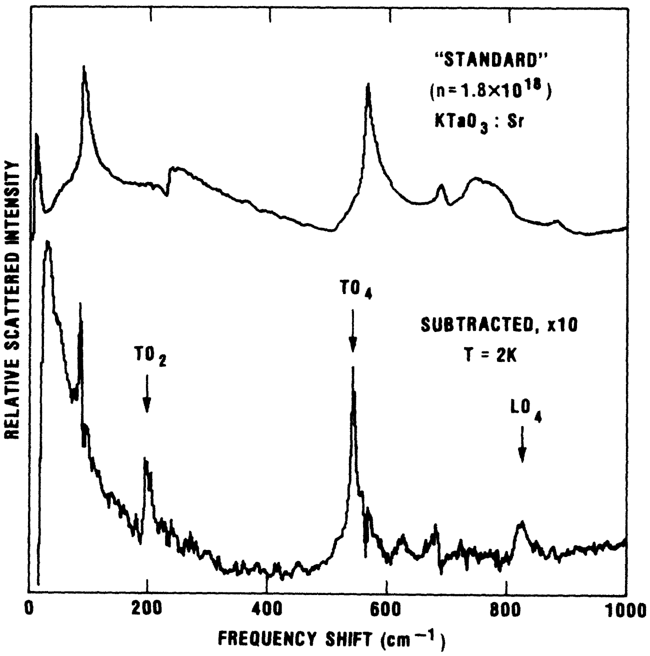

FIG. 2. Illustration of the result of the subtraction procedure described in the text. The bottom trace is that of a pure sample, with the standard spectrum (top) subtracted after appropriate adjustment of its intensity. Note the change of intensity scale.

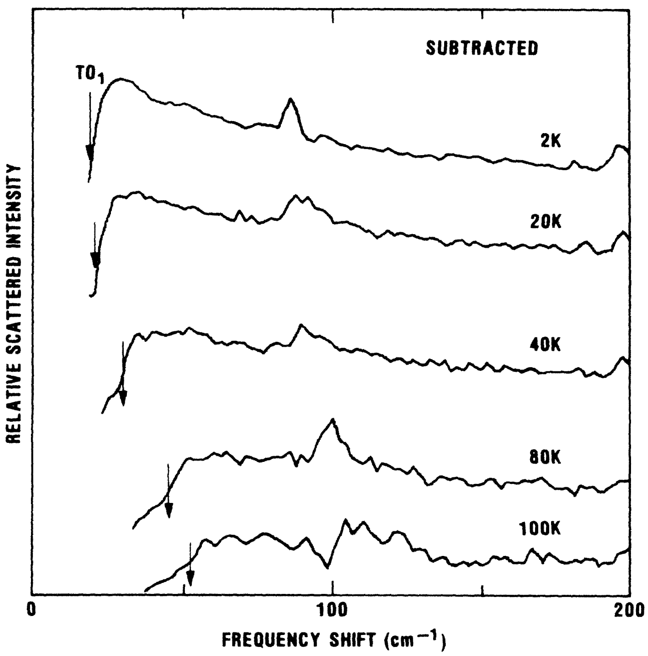

FIG. 3. Subtracted spectra, as in Fig. 2, displayed as a function of temperature. Only the low-frequency portion is shown. The arrows indicate the known positions of the zone center TO_1 mode at the temperatures indicated.

troduces free carriers and reduces the extrapolated ferroelectric T_c, while doping with Nb^{5+} (which is isoelectronic with Ta) raises T_c. In fact, for ~1% Nb, ferroelectricity is thought to set in at ~20 K. As shown in Fig. 1, in addition to the strong second-order spectrum, the pure sample somewhat surprisingly shows several relatively sharp features which are absent in the Sr sample. This effect is more dramatically evident in Fig. 2, where we have plotted the difference spectrum after normalizing both spectra to equalize the two-phonon intensities between 680 and 800 cm^{-1} for these two samples. This reveals sharp but asymmetric peaks at the positions for the single-phonon frequencies at TO_2, TO_4, and LO_4. In addition, the position of the zone-center soft-mode frequency TO_1 (indicated by the arrow in Fig. 3) signals the onset of a very asymmetric feature which extends out to ~200 cm^{-1} (the maximum zone-boundary frequency for the soft-mode branch is 200 cm^{-1}). As shown in Fig. 3, both the shape and magnitude of this feature are markedly temperature dependent.

The observation that the DIRS is evidently more pronounced in the nominally pure sample than in the lightly doped Sr sample is at first surprising, but can be explained by the following picture. The primary effect lies in the different influences of symmetry-breaking (SB) and non-symmetry-breaking (NSB) defects.[8] While any defect will relax the k-conservation selection rule, SB defects will induce a local dipole moment (ferroelectric order parameter) within its unit cell which will polarize adjacent defect-free unit cells within a neighborhood whose extent depends upon the dielectric response of the host lattice. The resulting DIRS will thus be enhanced as the size of these induced ferroelectric microregions grows with increasing ϵ, and the weight with which phonons of various k vectors contribute will also evolve with FMR size. The absence of DIRS from the Sr-doped $KTaO_3$ can be attributed partly to Sr being a NSB defect, on the one hand, and partly to screening of any internal electric fields by the carriers introduced because Sr carries a different charge from the K for which it substitutes.

In the following analysis, we will use the line shape of the soft-mode DIRS to extract the size and temperature dependence of the FMR. The most likely explanation of our spectra is that SB defects are present in our nominally pure sample. We have been unable to determine the chemical identity of these defects despite a thorough search using the x-ray fluorescence microprobe technique. Common impurities like Nb, Ti, Ca, Sr, etc., if present, are well below the ~1% detection limit. Our recent experiments on 0.9% Nb-doped samples provide results virtually identical for $T > 20$ K to those in our nominally pure sample. While suggestive, this observation does not confirm the identity of defects in our pure sample as being Nb. Any SB point defect will have the same effect on the DIRS.

The scattered spectrum is proportional to $\langle \alpha(r,t)\alpha(0,0) \rangle_{q,\omega}$, where the subscripts denote a Fourier transform. Let $V(r)$ represent the static distortion induced around a symmetry-breaking defect and let $u(r,t)$ represent the vibrational or phonon displacement field, which is Raman inactive when $V=0$. Thus $\alpha(r,t)=V(r)u(r,t)$. The desired correlation function may be approximated:

$$\langle \alpha(r,t)\alpha(0,0)\rangle_{q,\omega} = (\langle V(r)V(0)\rangle \langle u(r,t)u(0,0)\rangle)_{q,\omega} \; . \tag{1}$$

This may be evaluated (in the limit $q \to 0$ and assuming an isotropic dispersion) by use of the convolution theorem. Ignoring phonon damping, we may approximate

$$\langle u(r,t)u(0,0)\rangle_{q,\omega} = \omega_q^{-1}\delta(\omega_q - \omega) \; , \tag{2}$$

where ω_q is the mode frequency for the branch u at wavelength q. The δ function permits easy evaluation of the convolution represented by Eq. (1); so the spectral intensity can be expressed in terms of the defect-induced correlation function $\langle V(r)V(0)\rangle_{q,\omega} = S(q)\delta(\omega)$ and the phonon density of states $[(d\omega_q/dq)_{q=q_\omega}]^{-1}$ as follows:

$$I(\omega) = \frac{(1-e^{-\beta\hbar\omega})^{-1}}{\omega} q_\omega^2 S(q_\omega) \left[\left(\frac{d\omega_q}{dq} \right)_{q=q_\omega} \right]^{-1} , \tag{3}$$

where we have included the Bose factor and have defined q_ω implicitly through $\omega = \omega_q(q_\omega)$. The simplest representation of the dispersion curve for the TO mode in $KTaO_3$ is $\omega_q^2 = \omega_0^2 + D^2 q^2$, where D and ω_0 are constants for a given temperature. The zone-center values of the mode frequency (ω_0) are known[7] as a function of temperature, but the value of D has been obtained with sufficient completeness only at room temperature.[9] Thus, we treat D as a constant independent of temperature as well.

The dispersion curve of the TO mode[9] is, of course, not isotropic. At room temperature, the values for D (expressing q in reduced units, equal to 0.5 at the zone boundary) are 68 meV (for [100]), 106 meV (for [110]), and 100 meV (for [111]). At 20 K, where only the value for [100] is known, D is 89 meV. Since we are ignoring the anisotropy in any event, and since the valley in the dispersion curve is quite localized along [100],[9] for the purposes of this paper we use simply $D = 100$ meV.

The final step in evaluating $I(\omega)$ requires specifying the defect-induced order-parameter correlation function $S(q) = \langle V(r)V(0)\rangle_q$. Physically $V(r)$ is proportional to the polarization field induced by a dipole located at $r=0$ in the background of a $KTaO_3$ host lattice. For uncorrelated, randomly located defects, the spatial average of the induced order parameter $\langle V\rangle$ must vanish. The important quantity for our purposes is the correlation function

$$S(q) = \langle V(r)V(0)\rangle_q = \langle V_q V_{-q}\rangle \; . \tag{4}$$

The form of $S(q)$ arising from the correlation function of the random defect-induced order parameter may be argued as follows. The Hamiltonian for the soft-mode system with a random field $h(r_i)$ which couples linearly to the order parameter u is

$$H = \sum_q \tfrac{1}{2} u_q u_{-q}(q^2+k^2) + \sum_q h_q u_q \; , \tag{5}$$

where $k = 2\pi/\zeta$, with ζ the correlation length for the order-parameter fluctuations. To minimize the energy in the presence of h_q, we take

$$\frac{\delta H}{\delta u_q} = 0, \quad u_{-1}(q^2+k^2) + h_q = 0 \; . \tag{6}$$

The static distortion $V(r)$ is the response to the static impurity field $h(r)$. Thus,

$$S(q) = \langle V_q V_{-q}\rangle = \langle u_q u_{-q}\rangle = \frac{\langle h_q h_{-q}\rangle}{(k^2+q^2)^2} \; , \tag{7}$$

where the subscript d denotes the "defect contribution" and we have ignored the dynamic contribution to $\langle u_q u_{-q}\rangle$ arising from thermal fluctuations. For random point defects $h(r) = h_0\delta(r-r_i)$ so that $\langle h_q h_{-q}\rangle = h_0^2 = \text{const}$. We then have

$$S(q) = \frac{h_0^2}{(k^2+q^2)^2} \; . \tag{8}$$

This form is expected to hold only so long as the correlation range of the random field itself is small compared to k^{-1}, that of the intrinsic order-parameter fluctuations. In general, both the intrinsic thermal contribution to $\langle u_q u_{-q}\rangle$ (which is Lorentzian) and the above random defect contribution (proportional to Lorentzian squared) appear in random field problems.[10] For the static field imposed by the defects, we thus expect a static distortion $V(r)$ with a correlation function

$$S(q) = \frac{S_0}{(1+q^2R_0^2)^2} \; . \tag{9}$$

Hence, from (3) we find

$$I(\omega) \sim (1-e^{-\beta\hbar\omega})^{-1} \frac{NKQ}{(K^2+Q^2)^2} \; , \tag{10}$$

where

$$K = \frac{a}{2\pi R_0}, \quad Q^2 = \frac{a^2 q_\omega^2}{(2\pi)^2} = \left(\frac{a}{2\pi} \right)^2 \frac{\omega^2 - \omega_0^2(T)}{D^2} \tag{11}$$

and a is the lattice constant.

Representative fits to our data using Eq. (10) are displayed in Fig. 4. The values of $\omega_0(T)$ and D were determined from independent experiments,[7,9] so the only adjustable parameter is the region size R_0. The temperature dependence of R_0 is shown in Fig. 5. It is clear that the volume of the FMR's increase dramatically as the temperature is lowered.

Other forms for $S(q)$ may also be contemplated, but those we have considered either result in unphysical values for R_0 (e.g., R_0's $< a$) or in requiring additional adjustable parameters (e.g., FMR ellipticity) to fit the data.[11] We have chosen here to use the simplest form for the $S(q)$ which results from a random field, since it provides an adequate fit to the data.

In our opinion, analysis of the data on the basis of a more detailed model (e.g., taking into account the anisotropy of $\omega_q(\mathbf{q})$ or the deviation from a simple quadratic dispersion curve, or attempting other functions for the order-parameter correlation) is not called for. While such procedures could no doubt improve the fit, the physical significance of the improvement would be doubtful. Certainly, the useful physics is contained in the above treatment, namely, that the spectra are easily described as the result of "first-order" scattering induced by the structure factor of microscopic ferroelectric regions which exist in the sample.

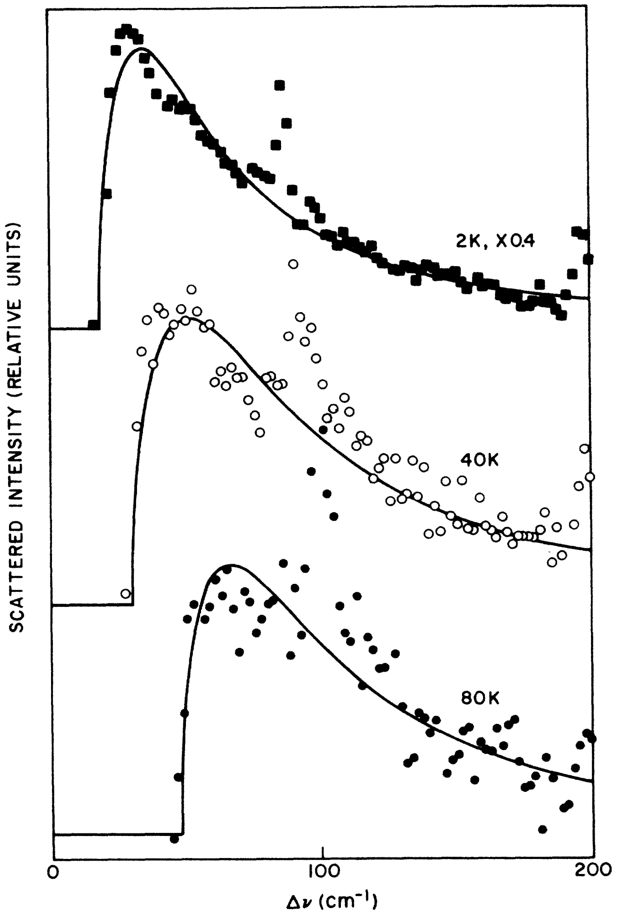

FIG. 4. Comparison of the text Eq. (10) (solid curves) with the experimental data (points) for various temperatures. The size parameters R_0 for the ferroelectric region are shown in Fig. 5. The feature in the vicinity of 100 cm^{-1} is related to the 2TA scattering and is not completely removed in the subtraction process.

It is most instructive to compare the values of R_0 obtained above to those which can be inferred from the *KTN* phase diagram.[1] For a given temperature, we can define an interaction radius for the Nb^{5+} ions to be $\xi = An^{-1/3}$, where n is the Nb^{5+} number density at which the ferroelectric phase transition occurs and A is close to unity. Thus, we easily convert the phase diagram into the dashed curve shown in Fig. 5 for the value of ξ as a function of temperature, with $A = 1$. We take this qualitative agreement to be a strong indication of the validity of the basic physics. It should be emphasized, though, that this agreement does not by itself indicate that the unknown impurities in our sample are Nb, since the region size R_0 could very well be a property of the host lattice, independent of the type of impurity which induces it. Indeed, nothing in our measurements precludes an explanation based upon localized intrinsic fluctuations, so long as their lifetimes exceed the inverse soft-mode frequency and their spatial extent is no longer than ξ.

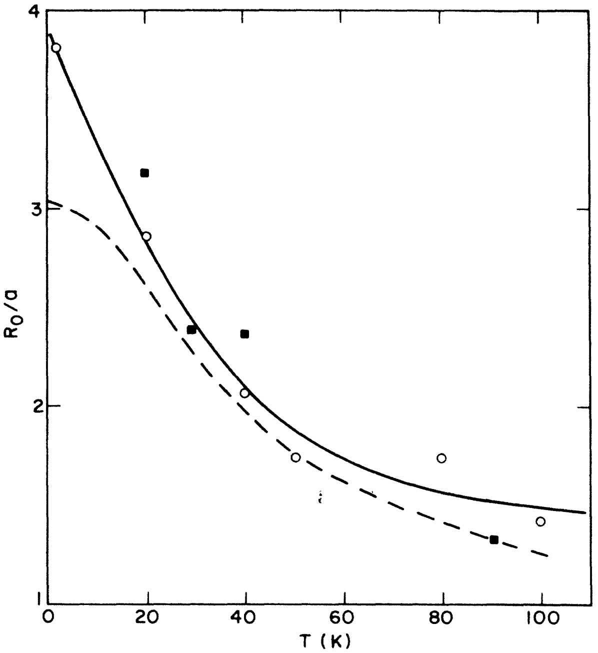

FIG. 5. Size of the microscopic ferroelectric regions as a function of temperature, determined by a fit of Eq. (10) to the experimental spectra, as in Fig. 4. The open circles refer to nominally pure $KTaO_3$, for which the solid curve is a guide to the eye. The solid squares are determined by the same procedure for the 0.9% Nb-doped sample. The dashed curve is the result of the analysis of the *KTN* phase diagram described in the text.

In fact, a calculation based on a point-charge model for $KTaO_3$:Li has been presented recently.[12] This calculation, which ignored thermal effects and thus is appropriate to the zero-temperature limit, yielded a linear dimension $(2R_0)$ of 5 unit cells for the distorted region. This is also in close agreement with our experimentally observed value of about 6. Some anisotropy was predicted by this calculation, but, as mentioned above, we view it as unnecessary to include this anisotropy in our present model.

There is, moreover, previous evidence for the presence of such microscopic ordered regions in $KTaO_3$, although it has not previously been possible to extract size parameters with any degree of accuracy. For example, in a study[6] of the thermal conductivity of doped $KTaO_3$ crystals, the suggestion was made that the pure material contains Nb or Na impurities and, furthermore, that the phonon scattering evident in those results was not correlated with several other common impurities. On the basis of their analysis, those authors conclude that the Nb concentration is around 10 ppm and that the perturbed volume of the crystal is about 8 unit cells (i.e., $R_0 \cong 2$ in our notation). This numerical discrepancy with our results is no doubt model dependent; hence, we do not consider it significant. We view the interpretation of Salce *et al.*[6] as substantially in support of our model.

An early report by Yacoby[4] discussed (and rejected) the possibility of impurity-induced scattering as the cause of the first-order Raman lines in Nb-doped $KTaO_3$. No numerical analysis of the data was attempted in this case. In the present work, we have observed and analyzed the contributions due to phonons at finite q, which Yacoby found to be unobservable.

Prater *et al.*,[5] on the other hand, concluded from a Raman scattering study of KTN that disorder-induced scattering was responsible for the first-order features observed, but that "Nb impurity is not a major contributor to the mechanism which breaks the lattice symmetry," since the intensity of the low-frequency scattering did not scale with Nb concentration. As we noted above, however, there is no need to identify Nb as the source of the microscopic regions, since their properties (especially their size) may be characteristic of the lattice and independent of the mechanism which nucleates them.

The experiments and analysis presented here demonstrate that $KTaO_3$ exhibits distorted regions encompassing dozens of unit cells, that this distortion volume increases markedly with lowered temperature, and that its size can be measured from the line shape of the DIRS from the soft optic-phonon branch. Furthermore, the x dependence observed for T_c in $KTa_{1-x}Nb_xO_3$ is just that expected from associating T_c with the point at which the volume accepted by the FMR's occupies the full sample volume.

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