# Study of the ferroelectric soft mode in solid solutions of $KTa_{1-x}Nb_xO_3$ by hyper-Raman scattering

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Hyper-Raman scattering from mixed crystals of $KTa_{1-x}Nb_xO_3$ is studied as a function of temperature ($15 \leq T \leq 300$ K) and Nb concentration ($0.008 \leq x \leq 0.21$). We determine accurate values of the soft-phonon frequency $\omega_0$ and linewidth $\Gamma$. In accordance with previous dielectric measurements, the temperature dependence of $\omega_0$ shows significant deviations from the mean-field behavior. As the ferroelectric phase transition is approached, we observe an increase of the relative damping $\Gamma/\omega_0$ for all Nb concentrations. Attention is paid especially to the transition from underdamping at $x=0$ to overdamping at $x=1$. Overdamping can be found at values of $x$ less than 0.2 in the vicinity of the phase transitions.

## I. INTRODUCTION

The oxidic ferroelectrics with perovskite structure are well known to be materials with large nonlinear optical and electro-optical coefficients, which make them particularly attractive for optical-device applications.[1] In recent years a growing effort has been made to understand the basic physics underlying these properties. $KTa_{1-x}Nb_xO_3$ (KTN) is a typical compound of this family. It shows large electro-optic effects at temperatures just above the ferroelectric Curie point $T_c$ which can be varied very easily by a suitable choice of the Nb concentration $x$. For integrated optics a value of $T_c$ near room temperature is desirable; this requires a Nb concentration of about 35 at. %. Owing to the difficulty in obtaining striation-free mixed solutions of KTN, pure crystals such as $KNbO_3$, $LiNbO_3$, or $KH_2PO_4$ are, at present, preferred in technological applications.

The interest in KTN has been recently renewed by studies on the role of impurities near phase transitions.[2–7] By varying the Nb concentration, the properties can be adjusted between extremes, displayed by $KNbO_3$ and $KTaO_3$, respectively. $KNbO_3$ behaves as a proper ferroelectric undergoing a sequence of three phase transitions:[8] With decreasing temperature, it transforms successively from the cubic to the tetragonal structure at 703 K, from the tetragonal to the orthorhombic structure at 490 K, and finally, from the orthorhombic to the rhombohedral structure at 210 K. All of these phase transitions are associated with a large increase of the static dielectric constant,[8] which can be only partly explained by the softening of a ferroelectric phonon mode. A large disagreement between the directly measured dielectric constant[8–11] and the value calculated from phonon frequencies by means of the Lyddane-Sachs-Teller relation has been found in the cubic[12] as well as tetragonal phase.[13] Furthermore, the soft mode is strongly overdamped in the cubic and tetragonal phases, while it becomes underdamped in the vicinity of the orthorhombic-rhombohedral phase transition.[14] The nature of these phase transitions turns out to be quite complicated and a simple soft-mode model seems to fail in describing the dynamical and dielectrical behavior through the hole sequence of phases. Recently, Fontana *et al.*[14] proposed a description involving a crossover from a displacive mechanism to an order-disorder one.

On the other hand, pure $KTaO_3$ is an incipient ferroelectric. Its dielectric constant increases rapidly as the temperature is reduced, but it does not undergo a ferroelectric phase transition. The increase of the dielectric constant is related to the softening of the ferroelectric phonon mode which has been extensively studied by ir, Raman, and neutron spectroscopy over a wide range of temperatures. An excellent review of this aspect can be found in Ref. 15. The soft mode displays very small damping as confirmed by recent hyper-Raman investigations of Vogt and Uwe.[16]

It is well known that the range of stability in the polar phase is determined by the competition between the long-range ordering forces and the fluctuations in the dipolar system. In the majority of cases the fluctuations are of classical Boltzmann character, leading to a Curie-Weiss law for the static dielectric constant, i.e.,

$$\epsilon_0 = C(T-T_c)^{-\gamma} \text{ with } \gamma = 1 , \quad (1)$$

where $C$ and $T_c$ are the Curie constant and the Curie temperature, respectively. $KTaO_3$, as well as KTN crystals with low Nb concentrations, obey such a classical law for sufficiently high temperatures ($T > 60$ K). For those KTN crystals which have a very low $T_c$, the stability limit falls into a region of predominantly quantum-statistical fluctuations.[17] This displacive limit is defined by a new set of coupling parameters for which the critical temperature $T_c$ becomes equal to 0. As a consequence, the disordered phase extends below its classical limit and the critical temperature is lower than the classical one. The lead-

 

ing critical exponent $\gamma$ of the dielectric constant has a value $\gamma=2$ in contrast to $\gamma=1$ in the Curie-Weiss law.[7,17] In general, as confirmed by dielectric susceptibility and acoustic measurements,[3,6,7] various crossovers from the displacive to other regimes have been predicted and observed.

In this paper we report and discuss hyper-Raman studies of the concentration and temperature dependence of the soft mode in KTN. The hyper-Raman (HR) effect is a three-photon process by which two photons of the exciting light are simultaneously annihilated and one scattered photon is created. The parity selection rule is the same as for one-photon infrared absorption and all the infrared-active modes are also HR active. Therefore, HR scattering allows the direct observation of the ferroelectric $F_{1u}$ soft mode which is normally Raman forbidden and may be cumbersome to detect by infrared-reflectivity measurements in the low-frequency range. At low frequencies the ir reflectivity is high and displays broad bands so that any analysis yields mode parameters which are less precise than those obtained from direct HR measurements. Furthermore, in the case of oxidic perovskites all of the lines are sufficiently intense to be well resolved by HR scattering, yielding the mode frequencies and their damping with better accuracy than those obtained from neutron scattering and electric-field-induced Raman scattering.[16,18,19]

## II. EXPERIMENTAL DETAILS

Hyper-Raman measurements have been performed on five crystals of $KTa_{1-x}Nb_xO_3$ with $x=0.008$, 0.012, 0.02, 0.09, and 0.21. The samples used were rectangular-shaped plates of about $9\times1\times0.7$ mm$^3$ for the three lowest Nb concentrations, of $6\times1\times0.5$ mm$^3$ for $x=0.09$, and of $5\times5\times4$ mm$^3$ for $x=0.21$. The faces of the plates were parallel to the (100) planes. The samples were cut from larger crystals grown by a flow method described elsewhere.[20] They showed a gradient of concentration along the $z$ axis of about 0.002 mol/mm which may lead to a small distribution of $T_c$ across the sample. The values of $T_c$ had been determined by an ultrasonic method[21] to be 0 K for $x=0.008$, 17.6 K for $x=0.012$, 28 K for $x=0.02$, 93 K for $x=0.09$, and 175 K for $x=0.21$. As reported in the next section, the transition temperatures have been checked independently by second-harmonic generation.

The source of the exciting radiation was an acousto-optically $Q$-switched neodium: yttrium-aluminum-garnet (Nd:YAG) laser with $\lambda_L=1.06$ $\mu$m, a peak power of about 10 kW and a pulse-repetition rate of 5 kHz. The experimental arrangement has been described elsewhere.[21] The sample temperature was kept constant within 0.5 K and could be varied between 15 and 296 K. Significant changes of sample temperature by laser heating could be excluded by checking the anti-Stokes/Stokes intensity ratio of the soft mode with sufficient accuracy. HR scattering was observed in the backscattering configuration $Z(YY)\bar{Z}$ where $Z$ and $Y$ are taken along the cubic crystal axes and $Z$ corresponds to the direction of the concentration gradient. In order to evaluate the experimental background arising from the elastic second-harmonic peak at $2\omega_L$, we carefully measured the instrumental profile of the spectrometer as a function of the slit width. This was done with a $LiIO_3$ crystal under phase-matching conditions, which generates an unbroadened second harmonic at $2\omega_L$.

## III. EXPERIMENTAL RESULTS

### A. Second-harmonic generation

In order to determine the Curie temperature of the samples independently from the ultrasonic investigations, we measured the intensity of the second-harmonic generation (SHG) as a function of temperature. Normal SHG only occurs in crystals without inversion symmetry. Therefore, the elastic line at $2\omega_L$ is expected to be weaker by orders of magnitude in the centrosymmetric cubic phase than in the ferroelectric phase. In Fig. 1 we represent the intensity of the $2\omega_L$ line as a function of temperature for two samples with Nb concentrations of $x=0.012$ and $x=0.02$. A drastic increase is observed in both crystals within a temperature range of about 3 K showing the para- to ferro-electric phase transition. Nevertheless the precise determination of $T_c$ is spoiled by the relatively large width of the characteristic step of the SHG. We determined $T_c$ from the inflection points of the intensity curves which gives values in reasonably good agreement with the elastic compliance measurements.[22] Furthermore, we observe significant SHG intensity far above $T_c$. This can be due to inhomogeneities and concentration gradients in the crystals. Nevertheless, an increase of the SHG intensity with decreasing temperature is also detected in pure $KTaO_3$, which remains paraelectric[16] even at the lowest temperatures. Therefore, an explanation of the distribution in $T_c$ by inhomogeneities does not seem to be entirely sufficient. On the other hand, critical effects in the vicinity of the phase transition have to be considered. Thus, the violation of the inversion symmetry required for the SHG may be either static (local ferroelectric clusters)

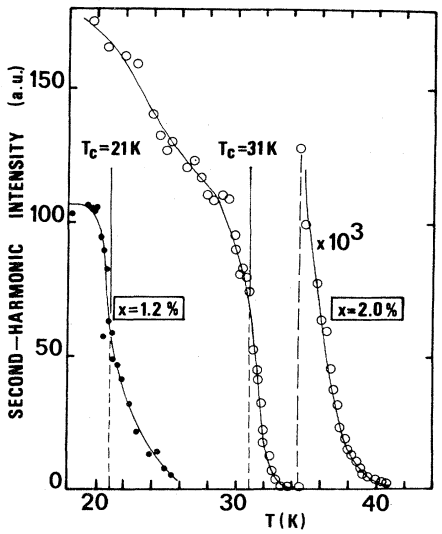


FIG. 1. Second-harmonic–generation intensity in $KTa_{1-x}Nb_xO_3$ ($x=0.01$ and 0.02) as a function of temperature.

or dynamical (polarization fluctuations). Such precursor-order effects have already been detected in the cubic phase of $BaTiO_3$ (Ref. 23) and $KNbO_3$ (Ref. 24).

The determination of $T_c$ by SHG in the crystals with higher Nb concentrations (9 and 21 at.%) shows still more ambiguous features. In addition to the previously mentioned effects above $T_c$, the signal rises drastically in a range of some degrees around a temperature which can be reasonably assigned to $T_c$, but then continues to increase strongly in a range of about 50 K below $T_c$. Currently, we have no definitive interpretation of this deviation from the expected sharp increase of the second-harmonic signal. For an interpretation we have to take into account the fact that there is not just a single phase transition, but an entire sequence of phase transitions (cubic-tetragonal-orthorhombic-rhombohedral) in these high-Nb-concentration crystals. Moreover, we have to consider the influence of ferroelectric domain structures on SHG (Ref. 25).

### B. Hyper-Raman results for crystals with low Nb concentration

Hyper-Raman spectra of crystals with $x=0.008$, 0.012, and 0.02 in the wave-number range from 0 to 100 $cm^{-1}$ are shown in Figs. 2, 3, and 4, respectively. The ferroelectric phonon mode is clearly detected and its softening with decreasing temperature is seen. Note that in Fig. 2 the HR intensities for the various temperatures are not drawn with the same intensity scale. However, the intensities of the spectra in Figs. 3 and 4 can be compared since the measurements have been recorded under the same experimental conditions. A strong enhancement of the HR intensity with decreasing temperature is observed.

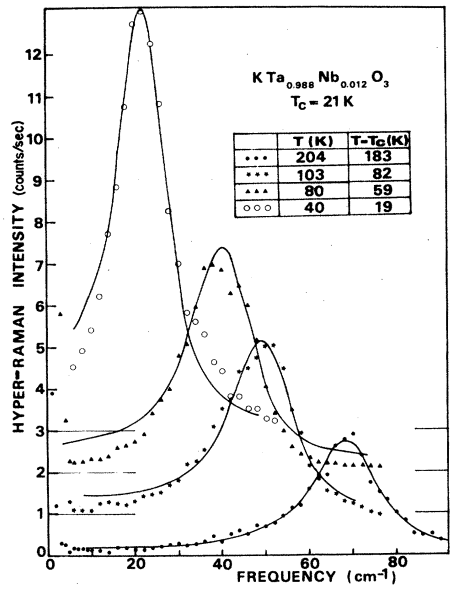


FIG. 3. Hyper-Raman spectra of $KTa_{0.988}Nb_{0.012}O_3$ at 240, 103, 80, and 40 K. The different spectra have been recorded under the same experimental conditions. Their intensities are given in the same scale. The solid lines represent Lorentzian fits.

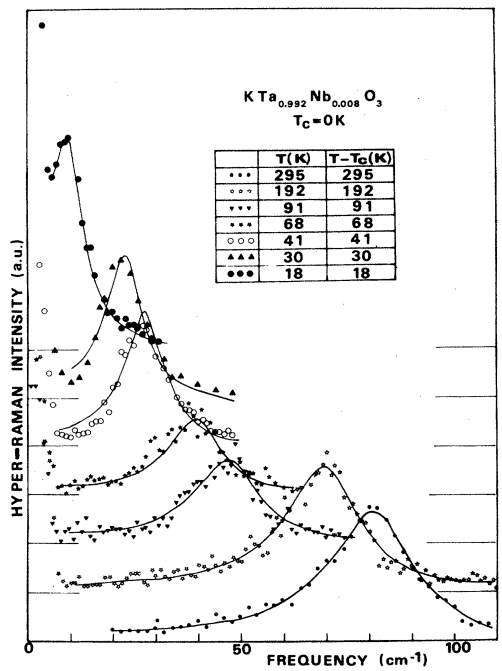


FIG. 2. Typical hyper-Raman spectra of $KTa_{0.992}Nb_{0.008}O_3$ for various temperatures. Note that the HR intensities for various temperatures are not drawn with the same intensity scale. The solid lines represent Lorentzian fits.

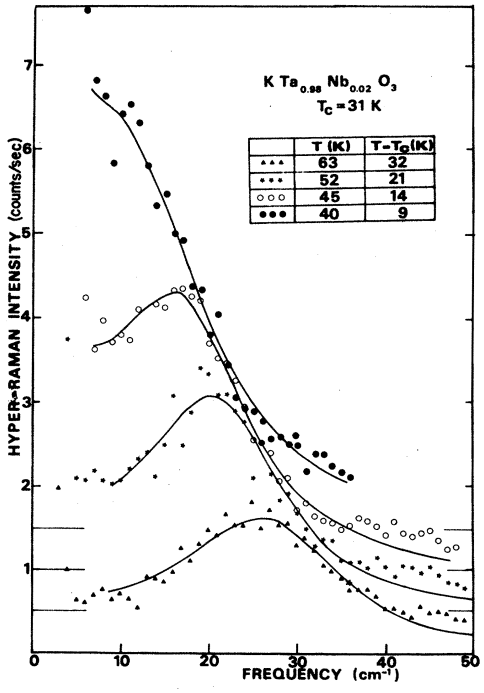


FIG. 4. Hyper-Raman spectra of $KTa_{0.98}Nb_{0.02}O_3$ between 63 and 40 K. The different spectra have been recorded under the same experimental conditions. Their intensities are given in the same scale. The solid lines represent Lorentzian fits.

We shall discuss this interesting aspect in a planned forthcoming paper.

Owing to the high scattering intensity, the measurements were able to be performed under optimal spectrometric conditions. The spectral slit width varied between 1 $cm^{-1}$ at low temperatures and 6 $cm^{-1}$ at room temperature. In almost all cases it was small compared to the phonon linewidth. Therefore we could neglect the convolution of the spectra with the resolution function of the spectrometer. Small errors due to the finite resolution of the spectrometer may be found in the high-temperature spectra.

We analyzed the experimental data by fitting the three parameters of a damped-harmonic-oscillator response function to the measured spectra,

$$I(\omega)=[n(\omega)+1]\frac{f\omega_0^2\omega\Gamma}{(\omega^2-\omega_0^2)^2+\Gamma^2\omega^2},$$

where $\omega$ is the HR shift, $\omega_0$ is the phonon frequency, $\Gamma$ is the phonon linewidth, $f$ is the oscillator strength, and $n(\omega)$ is the thermal occupation number. In the fitting procedure, the squares of the deviations have been weighted by $I^2(\omega)$; this enhances the weight in the region of the peak position relative to the tails. The calculated oscillator response functions are represented by solid lines in Figs. 2–4. In Fig. 5 we have plotted the soft-mode frequency $\omega_0$ and the damping $\Gamma$ as a function of temperature for the three crystals with Nb concentrations of $x=0.008$, 0.012, and 0.02. The damping constants at room temperature range from 20 to 24 $cm^{-1}$. These values are very similar to the damping constant measured in pure $KTaO_3$.[16] However, our phonon linewidths are smaller than the value $\Gamma=32$ $cm^{-1}$, which was obtained from infrared measurements of a KTN crystal with $x=0.018$.[22] The damping decreases with decreasing $T$ down to about 9 $cm^{-1}$ and then increases when the phase transition is approached. The relative damping $\Gamma/\omega$ rises continuously with decreasing $T$ and, near $T_c$, reaches values corresponding to an overdamped phonon. In the crystal with 2 at. % Nb the damping is higher than in the two crystals with lower Nb concentration and the phonon starts to become overdamped at about 20 K above $T_c$. The result found in the crystal with $x=0.008$ at 18 K ($\Gamma=11.5$ $cm^{-1}$) is consistent with electric-field-induced Raman scattering[4] giving $\Gamma=10$ $cm^{-1}$.

It is interesting to examine the frequency of the soft phonon as a function of both $x$ and $T$ especially at low temperatures. For comparison in Fig. 5 we include the soft-mode behavior of $KTaO_3$ as measured by Vogt and Uwe.[16] As already mentioned by Rytz,[22] the static dielectric constant, which can be also deduced from our results by means of the Lyddane-Sachs-Teller relation, does not follow a Curie-Weiss law for lower temperatures, but may be described by Barrett's formula.[26] The deviations from a Curie-Weiss law are particularly obvious for $KTaO_3$ and for KTN with Nb concentrations of $x=0.008$ and 0.012 near $T_c$. The case of the crystal with $x=0.02$ is more difficult to analyze since the increasing damping prevents us from following the mode frequency down to temperatures sufficiently close to $T_c$.

In order to deduce the critical exponent of the dielectric susceptibility, we present, in Fig. 6, $\omega_0^2$ as a function of $T-T_c$ in a double-logarithmic graph. For the crystal with a Nb concentration of $x=0.008$, we find that the measured frequency follows a classical Curie-Weiss law ($\gamma=1$) in the temperature range between 300 and 35 K. Below 35 K we observe a crossover to the quantum limit with $\gamma=2$. Near $T_c$ we find a slight indication of saturation. The critical exponents obtained from our investigations are in accordance with the results of dielectric measurements in the Kilohertz range.[7,22] For the crystal with a Nb concentration of $x=0.012$, the transition tempera-

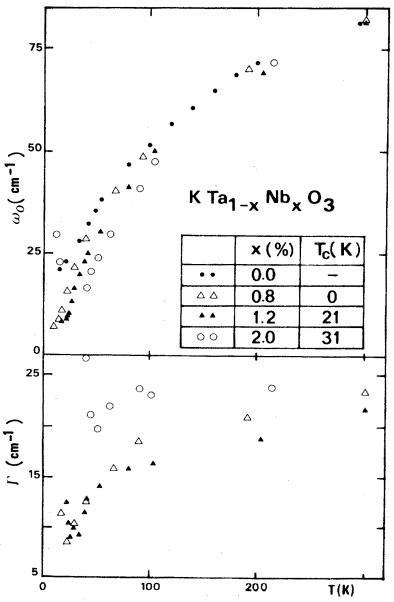


FIG. 5. Frequency $\omega_0$ and damping constant $\Gamma$ of the ferroelectric soft mode $F_{1u}$ in KTN as a function of temperature.

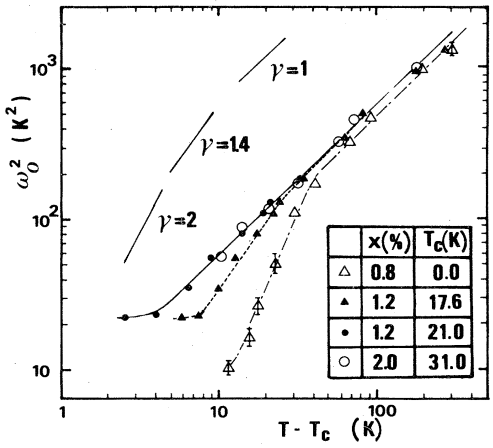


FIG. 6. Double-logarithmic representation of the square of the soft-mode frequency ($\omega_0^2$) as a function of $T-T_c$ in KTN ($x=0.008$, 0.012, and 0.02). The crystal with a Nb concentration of $x=0.012$ is represented with two different $T_c$ assumptions (solid circles, $T_c$ as determined from SHG measurements; solid triangles, $T_c$ as determined from acoustic measurements).

ture $T_c$ obtained from SHG on one hand, and by dielectric and acoustic measurements on the other, are slightly different (21 and 17.6 K, respectively). The solid line in Fig. 6 is obtained from our results taking a Curie temperature $T_c = 21$ K as being deduced from SHG. We find a mean-field regime ($\gamma = 1$) down to 5 K above $T_c$ and saturation below. If we take $T_c$ equal to 17.6 K, as determined from ultrasonic measurements and confirmed by dielectric experiments, we obtain the dashed line. In this case, a slight deviation from the Curie-Weiss law is found below 40 K. In the low-temperature range the critical exponent $\gamma$ is about 1.4, which corresponds to a mode-coupling regime.[27] Our analysis shows that the deduction of the critical exponents from experimental results is very sensitive to the $T_c$ values chosen. Before we can draw any further conclusion about the deviation of the critical exponent from a Curie-Weiss law, we have to understand the reason for the difference in the $T_c$ values obtained with various experimental methods. For the sample with a Nb concentration of $x = 0.02$, a Curie-Weiss law is found down to 10 K above $T_c$; at lower temperatures the mode becomes overdamped. It is therefore not possible to determine the critical exponent in the temperature range near $T_c$ from our experimental results.

### C. Hyper-Raman studies on crystals with Nb concentrations higher than 5 at. %

Hyper-Raman scattering measurements on crystals with $x = 0.09$ and 0.21 reveal essentially a large increase of the damping of the soft mode with increasing Nb concentration. Figure 7 shows two Raman spectra for $x = 0.09$ recorded at 263.5 and 112.5 K. The phonon linewidth of about 30 $cm^{-1}$ at 263.5 K increases rapidly with decreasing $T$ and becomes heavily overdamped at 112.5 K, a temperature which is still 20 K above $T_c$. At a Nb concentration of $x = 0.21$ the soft mode is overdamped even at room temperature. Figure 8 shows two room-temperature spectra taken with the direction of the incident and the scattered beam parallel and perpendicular to the direction of the possible Nb-concentration gradient. Comparison of the two spectra reveals that the crystal orientation has no sensitive influence. This clearly shows that the damping of the ferroelectric mode is an intrinsic property of the crystal and cannot be attributed to sample inhomogeneities. Such a conclusion is further supported by additional HR measurements of the high-frequency transverse optic mode at about 540 $cm^{-1}$, recorded at

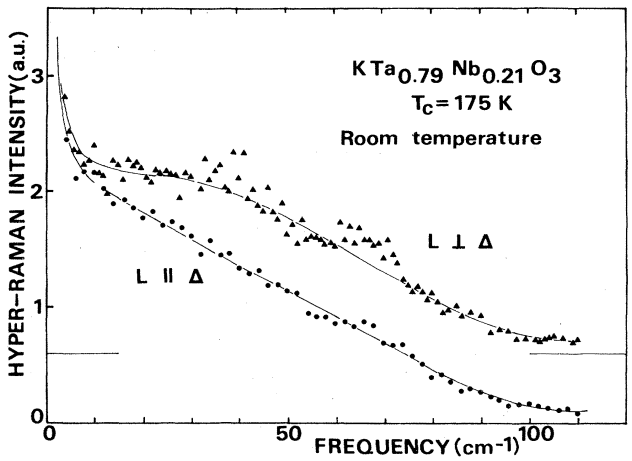


FIG. 8. Hyper-Raman spectra of the ferroelectric soft mode of $KTa_{0.79}Nb_{0.21}O_3$ at room temperature with the direction of the incident and scattered light parallel and perpendicular to the direction Δ of the concentration gradient.

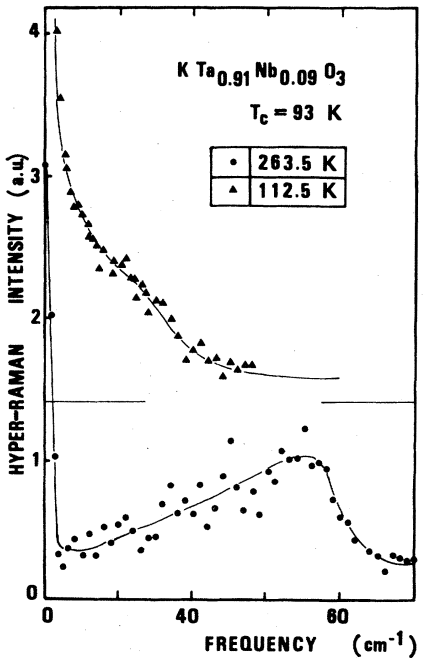


FIG. 7. Hyper-Raman spectra of the ferroelectric soft mode of $KTa_{0.91}Nb_{0.09}O_3$ at 265.5 and 112.5 K.

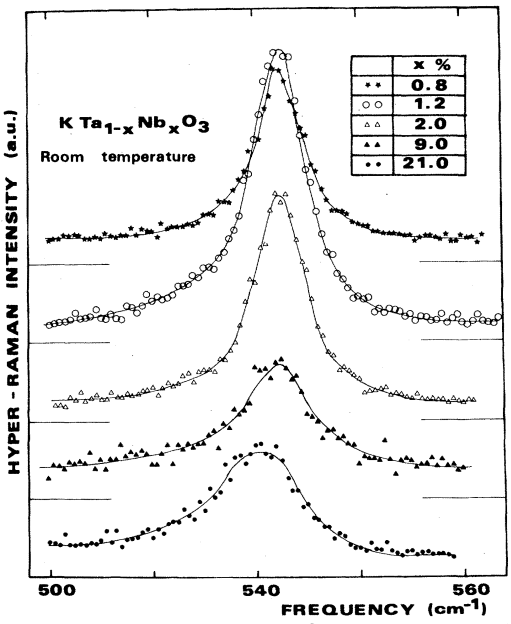


FIG. 9. Hyper-Raman spectra of the TO mode at about 540 $cm^{-1}$ at room temperature for the five crystals under investigation.

room temperature. Figure 9 shows the spectra of this mode for the five crystals investigated. No important changes in linewidth are observed. The frequency, however, decreases slightly with increasing Nb concentration, as expected from the values of 512 $cm^{-1}$ (Ref. 14) and 546 $cm^{-1}$ (Ref. 16) in pure $KNbO_3$ and $KTaO_3$, respectively. A gradient of Nb concentration in the crystal would therefore lead to a distribution of the mode frequencies and consequently result in pronounced broadening of the scattered intensity, which has evidently not been observed. We should mention that the transverse-optic phonon at about 200 $cm^{-1}$ would be a better candidate for supporting our arguments, because, in this mode, the central ion (Ta or Nb) is displaced, whereas it remains nearly at rest in the mode at about 540 $cm^{-1}$. However, the HR line at 200 $cm^{-1}$ is quite weak and has an almost unresolvably small linewidth. Moreover, it nearly coincides with a longitudinal-optic phonon.[16]

## IV. DISCUSSION

Our measurements of the temperature dependence of the soft-mode frequency for various Nb concentrations show significant deviations of the critical exponent $\gamma$ from the classical mean-field value ($\gamma=1$) in the temperature region close to the phase transition. For the crystal with a Nb concentration of $x=0.008$ a crossover from $\gamma=1$ to $\gamma=2$ is found near 35 K. The critical exponent $\gamma=2$ is characteristic of quantum behavior.[5,6,17,22] In this case, the phase transition is suppressed by the quantum-mechanical fluctuations, which become dominant in the low-temperature range and lead to a deviation of the critical exponent from its mean-field value. For the crystal with a Nb concentration of $x=0.012$ we find, in the low-temperature range, a mode coupling with $\gamma\approx1.4$, if we assume that the phase-transition temperature is 17.6 K.[22] For higher Nb concentrations we see only a mean-field regime down to the region where the soft mode becomes strongly overdamped. This heavy damping prevents the observation of a critical behavior close to $T_c$ by HR scattering. In this range, Kind and Müller[3] found a critical exponent of $\gamma=1.7$ for a crystal with a Nb concentration of $x=0.1$. They state that this is due to long-range dipolar interactions.

The results of our measurements can be understood within the framework of a model which takes into account the electronic polarizability of the $O^{2-}$ ion. It is well known that the $O^{2-}$ ion is not stable in a free state. In the crystal, the $O^{2-}$ ion is stabilized by the Coulomb field of the surrounding ions. The oxygen polarizability is strongly dependent on the boundary conditions in the investigated crystal. With increasing Nb concentration the polarizability increases, which leads to a strengthening of the dipolar interactions; consequently, $T_c$ is raised. The dynamical behavior of the investigated crystals can be described within a shell model which takes into account harmonic and fourth-order anharmonic intraionic core-shell coupling constants of the oxygen ion.[27,28] A recent renormalization-group study,[29] which is based essentially on the same model, predicts a continuous change of the critical exponent $\gamma$ from 1 to 2 in the low-temperature range.

Another interesting point is the concentration and temperature dependence of the phonon linewidth. In order to explain the observed behavior, the above-mentioned model has to be extended to include interionic anharmonicities. The contribution of such a supplementary term must become particularly important when $x$ rises. As a consequence, the increase of $T_c$ must induce an increase of the thermally weighted multiphonon densities of states in the frequency range of the soft mode. The high multiphonon density of states may allow a "plunging mechanism" which renormalizes the frequency of the soft phonon and yields an easy decay of the mode.

In summary, this work confirms the special feature (value of the critical exponent $\gamma=2$) of the quantum limit in KTN (for $x=0.008$): Previous dielectric susceptibility data[22] and our HR determination of the soft mode are in excellent agreement. At concentrations lower than $x=0.2$, however, the soft mode is already overdamped. This shows that overdamping exists for so-called second-order phase transitions, since the order of the ferroelectric phase transition in KTN changes from first (above $x=0.30$) to second order (below $x=0.30$)[30,31] and the full sequence of transitions (cubic-tetragonal-orthorhombic-trigonal) occurring in $KNbO_3$ takes place[32] when $x$ exceeds 0.04. It may be interesting to interrelate the concentration dependence of the damping and the critical point at $x=0.04$.

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