RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 33, NUMBER 3 1 FEBRUARY 1986

Local properties, long-range order, and quantum ferroelectricity in $KTa_{1-x}Nb_xO_3$

J. J. van der Klink, S. Rod, and A. Châtelain
Institut de Physique Expérimentale, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland
(Received 5 August 1985)

We present the first data (^{39}K, ^{93}Nb, and ^{181}Ta NMR) on local properties at the phase transition in slightly Nb-doped $KTaO_3$, where quantum effects have been thought to be important. The Nb ions go off center at low temperatures, but not all Ta do the same: The distortion of the host lattice has no long-range order. Each off-center Nb ion polarizes a cloud of some 100 $KTaO_3$ unit cells. We suggest that coupling with the soft mode creates orientational order among these clouds, but with varying magnitude of the dipole moment per $KTaO_3$ unit cell.

The possibility of suppressing a ferroelectric phase transition by quantum motion has been recognized long ago by Blinc, who suggested[1] that in the potassium dihydrogen phosphate (KDP) family members might exist where the ferroelectric transition takes place only for the deuterated, but not for the undeuterated compound. Similarly, the suppression of the phase transition in KDP under hydrostatic pressure[2] is now thought[3] to be due to an *increase* in tunnel frequency, which opposes ordering. The variation of T_c with composition in tris-sarcosine calcium chloride (bromide) has also been ascribed to the influence of quantum fluctuations.[4]

Among the perovskite (quasi-) ferroelectrics, the doped potassium tantalates have attracted much attention. Pure $KTaO_3$ is an incipient ferroelectric, but replacing potassium partly by Li or Na, or tantalum by Nb, induces a polar behavior below a concentration-dependent transition temperature T_c. We will be concerned here[5] with $KTa_{1-x}Nb_xO_3$ (KTN), $0 \leq x < 0.06$, $T_c < 60$ K. For a number of experiments in the critical region (e.g., acoustic resonance[6]), tuning T_c by the dopant concentration is (at least in principle) much more convenient than by application of external pressure. It has been argued[5] that the main effect of the Nb ions on a microscopic scale should be an enhancement of the dipolar interaction in $KTaO_3$, and that the randomness of this interaction should be negligible with respect to the average value. Starting from this consideration, the critical behavior in KTN has been compared[6,7] with theoretical predictions[8,9] concerning the effect of quantum motion on critical exponents in the limit $T_c \rightarrow 0$ K, for *uniform* (undoped) displacive systems with vanishing interaction parameter ("quantum ferroelectrics").

Up to now, due to a lack of data on local properties in KTN, no profound justification exists for the identification of the dopant concentration with the "interaction parameter" of the theoretical models. Such data also allow comparison with a class of models where the local properties of the impurity are considered explicitly: As we will show, a particularly interesting case is that[10] where impurities are on center at high temperatures, but freeze out at a local (but sharply defined) temperature T_c^{loc} above the critical temperature of the host (which is ≤ 0 K for $KTaO_3$) due to the interaction with the soft mode of the host in the temperature range of interest.

In two recent papers, the quantum ferroelectric picture for KTN has been criticized. Dielectric experiments[11(a)] have been explained by the hopping of single impurities that are off center at all temperatures of interest (at ambient pressure) without a real transition temperature. From refractive index and birefringence measurements it has been deduced[12] that diffuse local transitions within impurity clusters occur, followed by a strain-induced collective ordering of these clusters. A disadvantage of these experimental methods is that they are *global* and require a certain amount of modeling and interpretation to arrive at the mentioned local properties of the Nb impurities (clusters). We show that the "off-center" description probably is incorrect, and propose a more detailed description of "clusters" (in the limiting case, a single Nb ion surrounded by a finite cloud of polarization in the $KTaO_3$ lattice) and of "cluster ordering" (by the polarization field of the long-wavelength soft mode of the $KTaO_3$ lattice; in the limiting case no direct interaction between polarization clouds need exist).

Our experiments are on ^{39}K, ^{93}Nb, and ^{181}Ta nuclear magnetic resonance. The KTN crystals were grown by D. Rytz at the Swiss Federal Institute of Technology (Ecole Polytechnique Fédérale de Lausanne) using slow-cooling methods.[13] An excellent specimen of pure $KTaO_3$ was kindly provided by V. Belruss of the Massachusetts Institute of Technology. The labeling of the KTN samples follows that of Refs. 6 and 13.

First we discuss the ^{93}Nb line shape. This nucleus has $I = \frac{9}{2}$, and in a noncubic environment $2I$ different resonance lines are observed. Its quadrupole moment is sufficiently important that small random deviations from cubic point symmetry (due to strains, defects) will visibly broaden the "satellite" transitions (all transitions except the "central" one $m = -\frac{1}{2} \leftrightarrow m = +\frac{1}{2}$), whose center, however, will coincide with the central transition. The resulting line shape as a function of temperature is shown in Fig. 1, for $KTa_{1-x}Nb_xO_3$ with $x = 0.012$. Here the broad base of the line is due to the satellite transitions; the sharp part of the line is the central transition. The ratio of the two contributions is considerably distorted by instrumental effects, the satellite transitions being shown too small. When the temperature is lowered below T_c, the average position of the $2I-1$ satellite transitions no longer coincides with the central transition, and the intensity of the base of the line is distributed over (for tetragonal symmetry) $3 \times (2I-1)$ different lines. We have not been able to detect these weak, broad lines, but Fig. 1 clearly shows that the base disappears below T_c. Additionally, we find no evidence for thermal

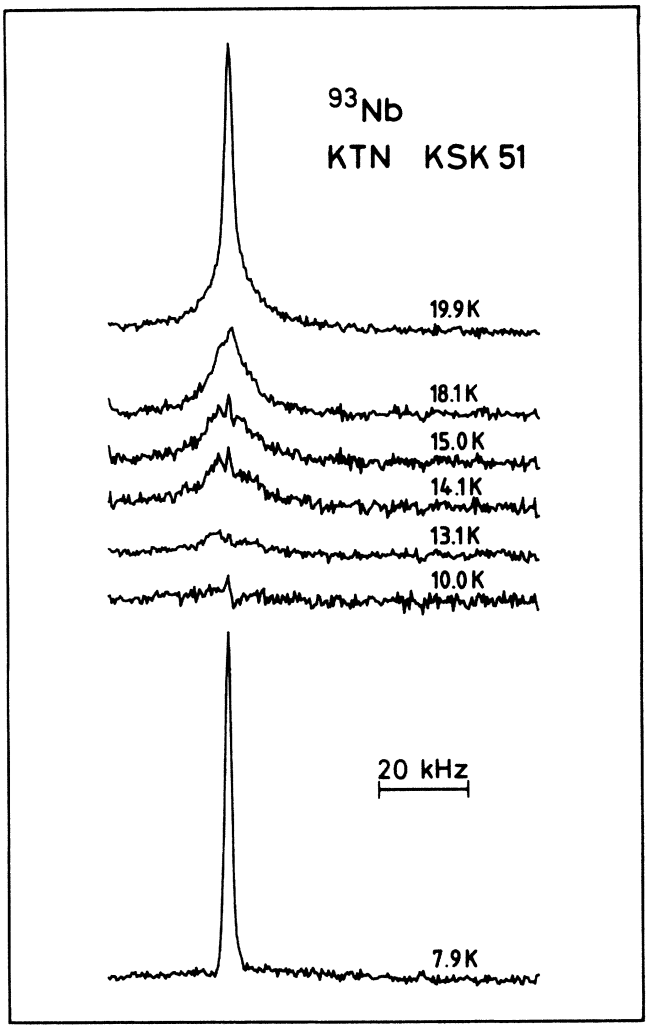

FIG. 1. Evolution of the satellite transitions in the ^{93}Nb NMR spectrum of KTN (sample No. KSK 51, x=0.012, in Ref. 6) as a function of temperature. The upper and lower traces are the full line shapes above and below T_c, respectively. The intermediate traces are differences between the observed line shapes and a suitable normalization of the lower trace. Above T_c the satellites show up as a broad base of the central line ($m=-\frac{1}{2}\leftrightarrow m=\frac{1}{2}$), showing that the ^{93}Nb ions are on center on the timescale of the experiment (in the μs–ms range). Below T_c they disappear, showing that the point symmetry of the ^{93}Nb site is lower than cubic. The central transition is not affected in first-order perturbation theory. Larmor frequency 75.3 MHz.

hopping in the ^{93}Nb spin-lattice relaxation times. Therefore, on the time scale of the inverse of a typical quadrupole frequency (say 10^4 Hz) the Nb ions are on center in the cubic phase (and off center in the low-temperature one). It follows that a model of off-center Nb ions, thermally hopping over a barrier whose height is reduced by pressure, cannot be correct, since it predicts[11(a),11(b)] that at ambient pressure the off-center Nb ion should be immobile on laboratory time scales at any temperature.

Let us now turn to the ^{39}K NMR data. From a lack of observable second-order quadrupolar shift, we conclude, as in the case of $K_{1-x}Li_xTaO_3$, that[14] an upper limit to the tetragonal distortion $c/a-1$ is $c/a-1<7\times10^{-3}$ at 10 K and for $x=0.029$. This is compatible with x-ray results[15] that give $c/a=(1\pm2)\times10^{-4}$ at 10 K and for $x=0.017$.

More interesting is the nuclear spin-lattice relaxation rate that shows an enhancement around T_c (see Fig. 2). Although a general theoretical description of this phenomenon is lacking, it is usually ascribed[16] to "direct" relaxation (emission or absorption of a phonon by the spin system) driven by low-frequency, long-wavelength fluctuations in the order parameter, and it has been observed in perovskites,[17] in many members of the KDP family,[18] and in other ferroelectric systems,[16] but not in $KTaO_3$:Li (Ref. 14) and $KTaO_3$:Na (Ref. 19), which are both thought to have glasslike properties. So apparently some degree of fluctuating long-range order is necessary to produce the enhanced relaxation, but the local character of the measurement does not tell whether a true divergence occurs. It is therefore possible that a local ordering[10] produces (locally) a similar enhancement. The ^{39}K relaxation data can therefore be interpreted as showing "critical" slowing down (as in a regular ferroelectric, but without proof of a diverging correlation length), rather than "gradual" slowing down (as in a glassy system).

Whereas the ^{93}Nb and ^{39}K NMR behavior discussed so far is not different from what would be expected in any perovskite ferroelectric (with small $c/a-1$), the ^{181}Ta NMR signal shows a very peculiar characteristic. This nucleus has a huge quadrupole moment, and even in a very good crystal, the signal in a free-induction-decay Fourier-transform experiment is only due to the central transition. We studied its intensity as a function of temperature. In a nominally pure crystal, it follows a simple Curie susceptibility. If a ferroelectric transition, even of extremely small

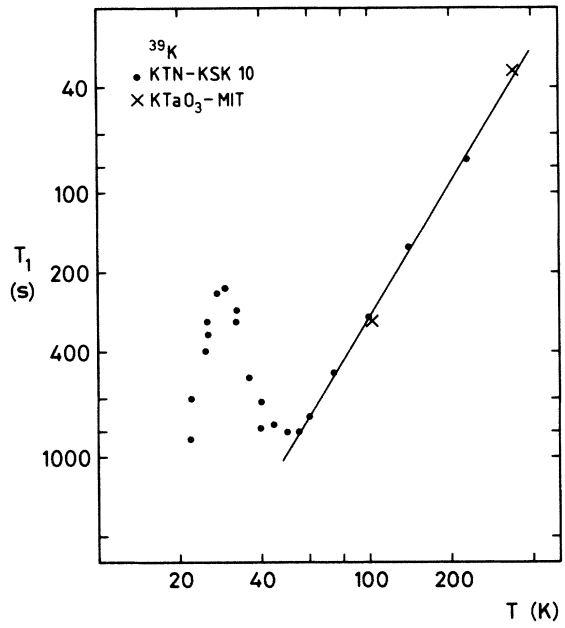

FIG. 2. Nuclear spin-lattice relaxation times of ^{39}K in KTN (sample No. KSK 10, $x=0.021$, $T_c=32.2$ K, in Ref. 6) as a function of temperature. Above 60 K the relaxation is due to phonon scattering ("Raman relaxation") as in pure $KTaO_3$ (crosses). Around T_c an enhancement of the relaxation rate occurs, that indicates the occurrence of slowly fluctuating (at the Larmor frequency, 15.9 MHz) polarization clusters.

$c/a-1$, were to occur, the signal would be completely shifted out of our observation window by quadrupolar effects, and thus have effectively zero amplitude. (The signal has to be *somewhere* on the frequency axis, but probably so much broadened that a search for it would be fruitless.) After an initial increase with decreasing temperature, the experimental data for the ^{181}Ta central-line amplitude show a drop in the vicinity of T_c. This is in agreement with the standard behavior sketched above, but upon further decreasing the temperature the signal does not disappear completely, but instead again follows Curie's law, with a smaller constant. This remaining signal is bigger, the smaller the concentration of Nb. It follows immediately that some of the ^{181}Ta are in unpolarized regions of the crystal, even at liquid-helium temperatures. We performed birefringence experiments on these same crystals to look for macroscopic regions of the cubic phase without finding any.

A quantitative analysis of the diminishing line intensity can be made in the same way as was used long ago for metal alloys.[20] It considers an "all or nothing" model based on the idea that the field gradient caused by a defect some distance away is a very rapidly varying function of the distance. It says that if the nearest p neighbor sites to a ^{181}Ta nucleus are free of defects, the signal of that nucleus will be observed at the unshifted resonance position, and that otherwise it will not be observed at all. If a fraction x of the total sites is occupied by defects in a random manner, the total signal S will be $S \propto (1-x)^p$ and the value of p can be found from a log-log plot, as in Fig. 3; it comes out to be around 100.

So, whereas we know from the ^{93}Nb line shape that these ions go off center below T_c, not all the Ta do the same. In the model used in the data analysis, those Ta nuclei that are outside a sphere of some three lattice spacings around any Nb stay on center (and perhaps even more of them: It is not necessary to go off center to sense a field gradient in a structure that is noncubic). A general ellipsoid rather than a sphere might be used in the data analysis, but this would introduce additional parameters. Anyway, the ^{181}Ta NMR data indicate that the distortion of the $KTaO_3$ lattice is not uniform, and certainly in that sense long-range order does not exist. It is implicit in the data analysis we used that the value of p should be independent of the niobium concentration x. Over the range investigated this seems to hold reasonably well, and might be interpreted as evidence for little interaction between the niobium impurities. That the interaction is not completely negligible is suggested by the fact that the critical value of x, below which no transition occurs,[5] is approximately equal to p^{-1}.

Each niobium ion, once it is off center, thus polarizes a cloud containing some 100 $KTaO_3$ unit cells. Why do these polarization clouds interact (if at all) to give a state that is more like a ferroelectric than like a glass? This would happen if the coupling occurs through the soft mode of the host lattice, rather than through direct dipolar interaction. Under influence of the soft mode (essentially a vibration of the central ion against a rigid oxygen cage) the Nb ions execute forced vibrations at the host's soft-mode frequency, but, being a smaller ion, the amplitude of its vibrations is larger. Therefore the mean-square polarization induced in the surroundings is larger for Nb than for Ta. Finally, the field due to this excess polarization destabilizes the Nb position

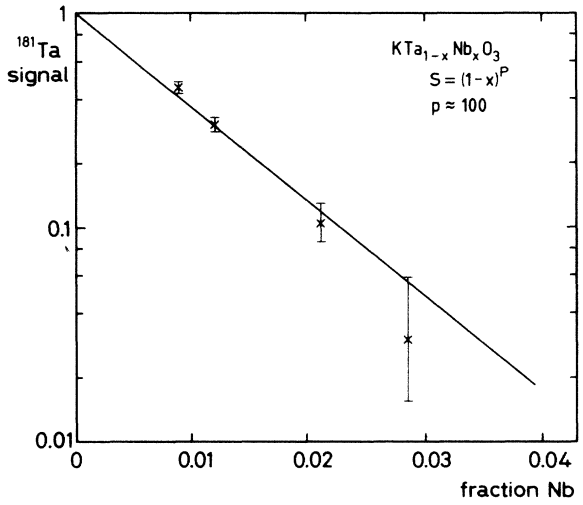

FIG. 3. In a normal ferroelectric, the ^{181}Ta NMR signal intensity as a function of temperature should follow Curie's law above T_c, and drop to zero below T_c, as explained in the text. In KTN the signal does not go to zero below T_c, but instead follows again Curie's law, but with a smaller Curie constant. In this log-log plot we show the ratio of the low- and high-temperature Curie constants (the normalized ^{181}Ta signal in the low-temperature phase) as a function of Nb concentration x. Pure $KTaO_3$ has $x=0$ and a relative signal amplitude 1. The straight line can be interpreted as showing that a ^{181}Ta nucleus does contribute to the low-temperature signal if the 100 next-neighbor Ta sites are not occupied by Nb, and gives zero signal otherwise. This hints at the existence of polarization clouds of $KTaO_3$ around each Nb ion, with relatively little direct interaction between them.

(and part of its surroundings). Since the wavelength of the soft mode is long compared to the Nb-Nb spacing, the destabilization of neighboring Nb ions occurs in phase rather than randomly, thus building up an *orientational* long-range order, while the magnitude of the polarization per $KTaO_3$ unit cell is not constant (and zero in some places). For rigorously noninteracting polarization clouds, the transition temperature should be sharp, as in the local-mode models.[10] Actually, the interaction will locally shift the transition temperature by amounts that vary with the locally random concentration of Nb ions.

It seems that the description by Kleemann, Schäfer, and Rytz of their optical experiments[12] and of the pressure-dependent dielectric experiments,[11(a)] can be recast in terms of the polarization clusters and interaction with the soft mode we introduced here, without inconsistencies. Coupling of an "unknown" defect to the soft mode has been assumed in the analysis[6] of the singularity in the elastic compliance s_{11}, and a disorder in unit-cell polarizabilities has been suggested to explain features of critical quasielastic light scattering.[21] Theoretically, a local description of impurity quantum ferroelectricity should be possible, and the collective behavior (induced by the $KTaO_3$ soft mode) of the Nb-impurity system might be analyzed with such a model. At least at the theoretical level problems will arise concerning the truly divergent nature of this transition; on the experimental level the masking of divergences by the unavoidable spread in T_c due to concentration fluctuations[6] will probably be the most important.

[1]R. Blinc, J. Phys. Chem. Solids **13**, 204 (1960).
[2]G. A. Samara, Phys. Rev. Lett. **27**, 103 (1971).
[3]R. Blinc and B. Žekš, *Soft Modes in Ferroelectrics and Antiferroelectrics* (North-Holland, Amsterdam, 1974).
[4]W. Windsch, H. Braeter, U. Gutteck, B. Malige, and B. Milsch, Solid State Commun. **42**, 839 (1982).
[5]U. T. Höchli, H. E. Weibel, and L. A. Boatner, Phys. Rev. Lett. **39**, 1158 (1977).
[6]D. Rytz, A. Châtelain, and U. T. Höchli, Phys. Rev. B **27**, 6830 (1983).
[7]D. Rytz, U. T. Höchli, and H. Bilz, Phys. Rev. B **22**, 359 (1980).
[8]T. Schneider, H. Beck, and E. Stoll, Phys. Rev. B **13**, 1123 (1976).
[9]R. Oppermann and H. Thomas, Z. Phys. B **22**, 387 (1975).
[10]K. H. Höck. R. Schäfer, and H. Thomas, Z. Phys. B **36**, 151 (1979).
[11](a) G. A. Samara, Phys. Rev. Lett. **53**, 298 (1984). (b) This assertion in based on Eq. (3) and Fig. 2 of (a). In a more recent paper [G. A. Samara, Jpn. J. Appl. Phys. (to be published)] the author cautions against overinterpreting the values cited in (a), especially those at low pressures.
[12]W. Kleemann, F. J. Schäfer, and D. Rytz, Phys. Rev. Lett. **54**, 2038 (1985).
[13]D. Rytz and H. J. Scheel, J. Cryst. Growth **59**, 468 (1982).
[14]J. J. van der Klink and F. Borsa, Phys. Rev. B **30**, 52 (1984).
[15]S. R. Andrews, J. Phys. C **18**, 1357 (1985).
[16]G. Bonera, F. Borsa, and A. Rigamonti, Phys. Rev. B **2**, 2784 (1970).
[17]G. Bonera, F. Borsa, and A. Rigamonti, in *Magnetic Resonance and Related Phenomena,* Proceedings of the XVII Congress Ampère, Turku, 1972, edited by V. Hovi (North-Holland, Amsterdam, 1973).
[18]R. Blinc, in *Magnetic Resonance of Phase Transitions,* edited by F. J. Owens, C. P. Poole, and H. A. Farach (Academic, New York, 1979).
[19]J. J. van der Klink and D. Rytz, Phys. Rev. B **27**, 4471 (1983).
[20]N. Bloembergen and T. J. Rowland, Acta Metall. **1**, 731 (1953).
[21]Edward Lee, L. L. Chase, and L. A. Boatner, Phys. Rev. B **31**, 1438 (1985).