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## FAST TRACK COMMUNICATION

# Quantum paraelectricity coexisting with a ferroelectric metastable state in single crystals of $\text{NaNbO}_3$ : a new quantum effect

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## Abstract

We experimentally show that, in contrast to the data having been collected so far, some single crystals of  $\text{NaNbO}_3$  exhibit a dielectric permittivity of several thousand, at low  $T$ , and this value is saturated when approaching 0 K on cooling. Other sodium niobate crystals (having larger dielectric losses) present a first-order phase transition to a ferroelectric phase on cooling (at 80–200 K). The width of the thermal hysteresis in these crystals increases when the temperature of the phase transition obtained on heating decreases. The dielectric permittivity at the phase transition obtained on cooling shows a tendency to increase and saturate, when the thermal hysteresis increases. We identify the ground state of the sodium niobate crystal exhibiting the smallest dielectric losses (in the studied set of crystals) as a novel quantum paraelectric state coexisting with a metastable ferroelectric state. In principle, the crystal presenting the state of quantum paraelectricity can be considered as having the largest (among the crystals studied) thermal hysteresis, for which the low boundary is below 0 K.

Sodium niobate  $\text{NaNbO}_3$  (NN) is a model system exhibiting a series of antiferrodistortive phase transitions [1]. Comparatively low electric fields trigger in NN a ferroelectric phase, stable in a very wide temperature range, spreading from low temperatures up to 515–550 K [2–4]. At present, NN is considered as the basic element for environmentally friendly piezoelectrics [5].

The ground state of NN is usually identified as ferroelectric and is described by the  $R3c$  group (phase N according to Megaw notations [1]). The first phase transition, on heating, has been thought to happen from the  $R3c$  phase to an antiferroelectric orthorhombic  $Pbnm$  phase (phase P according to [1]). The majority of the studies of this transition report a step-like dielectric permittivity  $\epsilon'$  anomaly at 100–150 K, on cooling [2, 3, 6–9]. The P–N and N–P phase transitions are accompanied by anomalies of the lattice parameters [10, 11], specific heat [7], optical birefringence [12], and changes of the number of the lines in the Raman spectra [10, 13]. Similar anomalies have been

observed in NN with small additions of different ions, e.g. Li, K, V, and Mn [3, 6–9]. The phase transition temperatures reported by different laboratories are spread over a large temperature interval that, probably, reflects the dependence of the results on the quality of the crystals and their pureness. We will present dielectric data obtained for the crystals we grew, which show a possibility of the coexistence of the quantum paraelectricity and ferroelectricity in NN, resulting in a novel quantum state never reported so far.

The single crystals of NN studied in the present work were grown by the spontaneous crystallization method by using either  $\text{NaBO}_2$  or  $\text{NaVO}_3\text{--NaF}$  as a flux. Details of the growth process have been described elsewhere [14]. We usually used for our study only thin (30–100  $\mu\text{m}$ ) plates with edges of 1–3 mm. Optical studies in the polarized light showed that these plates were twinned, in accordance with earlier studies of other NN crystals [2, 3, 15, 16]. The large faces of these plates were electroded with Aquadag. Thin (0.05 mm) copper wires were used to attach the crystals to the sample holder

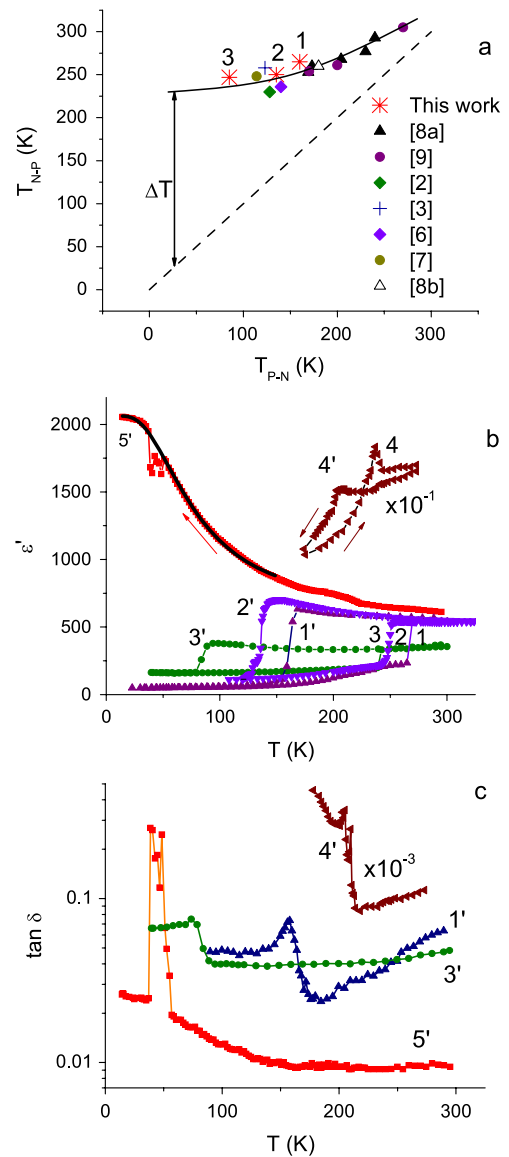
in order to carry out the measurements in the mechanically free mode. The sample holder was mounted inside the measuring cell of the closed-cycle helium cryostat-refrigerator Janis Ccs-850 operating in the 12–300 K range. For better heat exchange, the measuring cell was filled with gaseous helium. Dielectric measurements were performed at the  $2 \text{ K min}^{-1}$  heating/cooling rate using a computer-controlled impedance analyzer E7-20.

Figure 1(a) presents the dependence of the N–P phase transition temperature,  $T_{N-P}$ , on the P–N phase transition temperature,  $T_{P-N}$ , drawn on the basis of the data obtained for our crystals. For the sake of comparison, we add to this figure also some data obtained earlier for crystals grown in other laboratories as well as the data for V, Li, Mn, and K doped crystals [2, 3, 6–9]. The dashed line shows the trivial linear dependence of  $T_{P-N}$  on  $T_{P-N}$ . We need this latter line in order to show, in the same plot, the width,  $\Delta T = T_{N-P} - T_{P-N}$ , of the temperature hysteresis of the phase transition temperature between the P and N phases.

One can see from figure 1(a) that the data for all crystals lie in one line, which suggests the existence of a parameter that makes all these data so different. The data obtained on the Li, K, and Mn doped crystals shown in figure 1(a) also lie in the same line. This fact prompts us to think that just the concentration of the defects is the parameter scattering the experimental data.

Figure 1(b) shows the  $T$ -dependence of  $\varepsilon'$  for some of the crystals grown in our laboratory. It is worth noting that the  $\varepsilon'$  values of NN measured along different axes differ greatly, while the temperatures of the steps in  $\varepsilon'$  are insensitive to the twinning [2]. The  $T_{P-N}$  and  $T_{N-P}$  as well as  $\Delta T$  obtained for crystals 1 and 2 are similar to the majority of the published data for NN single crystals [2, 3, 6–10]. However, the  $T_{P-N}$  value for crystal 3 is substantially lower than the values ever reported for NN crystals. Both  $T_{N-P}$  and  $\Delta T$  values for this crystal match well the  $T_{N-P}(T_{P-N})$  dependence shown in figure 1(a). Curves 4 and 4' represent the oxygen vacancy mediated Maxwell–Wagner-kind apparent permittivity of a semiconducting (gray-colored) NN crystal. The temperature of the  $\varepsilon'(T)$  step on cooling, in these crystals, is much higher and the  $\Delta T$  value is much smaller than ever reported for the NN crystals. This opens up an intriguing possibility of considering the interaction between the electron and atomic-soft-mode degrees of freedom. The oxidation of such crystals by annealing in air at 800–1000 K makes them insulating, and the permittivity values as well as the  $T_{P-N}$  and  $\Delta T$  values become similar to those usually reported for the NN crystals. Note that the conducting samples possess a relatively large amount of ferroelectric phase  $Q$  [17]. Curve 5' in figure 1(b) exhibits most interesting features. In this crystal, the increase of  $\varepsilon'$  on cooling does not stop, down to approximately 30 K, where  $\varepsilon'$  saturates. This behavior reminds us of the well-known data for quantum paraelectrics [18]. However, the quantum paraelectrics never showed the *giant* thermal hysteresis presented in figures 1(a) and (b). Thus, we are dealing here with a new class of quantum paraelectrics. Below, we will discuss this situation in more detail.

The simplest formula to fit to the experimental data in the quantum regime was suggested by Barrett [19]:



**Figure 1.** (a) Dependence of the temperature  $T_{N-P}$  of the N–P phase transition (heating mode) determined from the dielectric studies versus the temperature  $T_{P-N}$  of the P–N phase transition (cooling mode) for single crystals of NN as well as for (Na, Li)NbO<sub>3</sub> [8] and (Na, K)NbO<sub>3</sub> [9] solid solutions. The numbers in the legend give the citations. The numbers near the experimental points marked by asterisks numerate the crystals studied by us. The solid line is a guide for the eye. The dashed line marks the  $T_{P-N}$  boundary. The difference between solid and dashed lines represents the value  $\Delta T$  of the temperature hysteresis of the transition between P and N phases. (b) Temperature dependence of permittivity measured at 1 kHz in the heating (curves 1–4) and cooling (curves 1'–5') modes for some of the NN single crystals studied. Curves 4 and 4' represent the apparent permittivity values for highly conducting (gray-colored) crystal. Large difference in permittivity values of poorly conducting crystals (curves 1–3, 5') are due to the difference in twin pattern. The solid line in curve 5' shows the fit by formula (1). (c) Dependence of  $\tan \delta$  on  $T$  for selected samples. The numbers numerate the samples. (This figure is in colour only in the electronic version)

$1/\chi = A[T_s \coth(T_s/T) - T_0]$ , where  $T_s$  is the saturation temperature,  $T_0$  has the sense of the Curie temperature in the classical regime, and  $A$  is a material constant. Fitting of this

formula to our experimental data gave us  $T_s = 49$  K, and  $T_0 = -30$  K. The quality of this fit is no worse than the one obtained by Müller and Burkard for SrTiO<sub>3</sub> [18]. Above about 190 K, the experimental data deviate from the Barrett and Curie–Weiss dependence which can be, probably, explained by local phase transitions and the change of the antiferroelectric order parameter. The extrapolation of the linear portion of the inverse susceptibility provides a temperature  $-44$  K. These data correspond well to those obtained for quantum paraelectrics earlier [18]. Note that first principles computations [20, 21] have shown the possibility of a low-temperature ferroelectric phase transition in NN. However, it was mentioned that quantum effects may change the situation drastically.

A more sophisticated approach based on the self-consistent phonon approximation, which considers the fourth-order anharmonicity as a perturbation to the phonon frequency [22–25], generalizes the Barrett formula in the part connected with the soft mode dispersion (notice that the Barrett approach is based on the Einstein approximation to the phonon spectrum, which neglects the importance of ferroelectric mode dispersion). As a result, the inverse susceptibility is given by the following integral dependence on temperature [22]

$$\frac{1}{\chi - \chi_\infty} \sim \omega_c^2 = \omega_{c0}^2(T) + \frac{g_0 v_c}{8\pi^2} \int_0^Q q^2 dq \frac{1}{\omega(q)} \left( \coth \frac{\omega(q)}{2k_B T} - 1 \right) \quad (1)$$

where  $g_0$  is an anharmonicity constant,  $v_c$  is the unit cell volume,  $Q$  is the cut-off wavevector,  $k_B$  is the Boltzmann constant,  $\chi_\infty$  is the high-frequency susceptibility, and  $\omega(q)$  is the soft mode phonon dispersion, which can be found from the following approximation,  $\omega^2(q) = \omega_{c0}^2(0) + S_1 q^2$ , where  $S_1$  is the constant responsible for the phonon dispersion,  $\omega_{c0}(T)$  is the bare phonon frequency, which depends on  $T$  over the dependence on  $T$  of the polarization  $P$  and antiferroelectric order parameter  $S$ , and  $\omega_{c0}^2(T) = \omega_0^2 + 3\beta P^2 + 5\gamma P^4 + \lambda S^2$ . Here  $\omega_0$  is a constant determining the extrapolated classical phase transition temperature, and the other coefficients correspond to the Landau expansion  $F = \frac{1}{2}\alpha\omega_c^2 P^2 + \frac{1}{4}\beta P^4 + \frac{1}{6}\gamma P^6 + \frac{1}{2}aS^2 + \frac{1}{4}bS^4 + \frac{1}{6}cS^6 + \frac{1}{2}\lambda S^2 P^2$  (for the sake of simplicity, we do not show the other terms appearing due to the cubic anisotropy). The polarization can be found from the equilibrium condition (the first derivative of the free energy with respect to the polarization should vanish, at equilibrium)  $\alpha\omega_c^2 P + \beta P^3 + \gamma P^5 + \lambda S^2 P = 0$ . A good fit was obtained for SrTiO<sub>3</sub> using formula (1) in [24]. Figure 1(b) presents the fit for the NN sample 5 in the temperature interval where the change of the antiferroelectric parameter is small (below 150 K). The parameters of the fit are:  $g = g_0 v_c / 8\pi^2 S_1^{3/2} \omega_{c0} \simeq 0.56$ ,  $y_m = S_1^{1/2} Q / \omega_{c0} \simeq 10.0$ , and  $T_s = \hbar \omega_{c0}^2 / 2k_B \simeq 35.3$  K (this saturation temperature corresponds to the phonon frequency at zero  $T$  of about  $40 \text{ cm}^{-1}$ ). This fit is better than the Barrett fit (not shown here), which emphasizes the importance of the soft ferroelectric mode dispersion.

It follows from the equilibrium condition that  $P^2 = [-\beta \pm \sqrt{\beta^2 - 4(\alpha\omega_c^2 + \lambda S^2)\gamma}] / 2\gamma$ . The boundaries of the existence of the metastable states can be found under the

condition that both these solutions (the former corresponds to ‘+’, in this formula, and the latter to ‘−’) can exist. As we are considering first-order phase transitions,  $\beta < 0$  and  $\gamma > 0$ . Limited by these inequalities, the upper boundary of the existence of the metastable ferroelectric states can be found from the equation  $\beta^2 - 4(\alpha\omega_c^2 + \lambda S^2)\gamma = 0$  (at this point the argument of the square root vanishes). The lower boundary can be obtained from  $\alpha\omega_c^2 + \lambda S^2 = 0$  ( $P^2$  vanishes at this point). When the bare frequency increases (this can, for example, correspond to a decreasing impurity and defect concentration), there is a point where the solution corresponding to the low-temperature boundary disappears owing to the quantum effects (the saturation of  $\omega_c$ ) and because the temperatures are confined by only positive values. However, this equation can still have a solution for the upper boundary. The accomplishment of this situation would imply the coexistence of the quantum paraelectricity and metastable ferroelectricity (which, in principle, can be stabilized by external fields). The coexistence of the quantum paraelectric and metastable ferroelectric states can result in unusual quantum phenomena such as quantum coherence, with the help of local tunneling between different phases of a crystal, quantum glass phenomena, owing to the local nucleation of the new phase with subsequent freezing the polar regions up, at lower temperatures, quantum percolation of the new phase over the polar fluctuations (stuck to defects) etc. This finding can also shed some light onto the properties of some other quantum paraelectrics. It is possible that the structure seen in curve 5’ of figure 1(b) at 50 K partly reflects the domain’s rearrangements owing to the instability of twins [26] or the nucleation of quantum ferroelectric polar regions or slow local quantum beatings. However, the jumps in  $\varepsilon'$  and  $\tan \delta$ , at 50 K, can also be due to contact phenomena. So, we have a pocket of extremely unusual and fundamentally important properties of the crystal, in this case.

Thus, as we do not see any low-temperature phase transition in the NN crystal presented by curve 5’ in figure 1(b), the ground state of this NN crystal is not ferroelectric, but it is instead quantum paraelectric. In agreement with this finding, in [6], no dielectric anomalies have been observed in NN below room temperature down to 20 K. It is worth noting that in the pioneering work by Cross and Nicholson [2], the P–N phase transition was observed on zero-field cooling only in a few of the crystals studied. In the majority of the crystals,  $\varepsilon'$  increased on cooling down to 63 K (the lowest studied temperature in their report). These authors applied to their crystals high ac and dc electric fields at low temperatures and found an electric-field-induced ferroelectric phase transition accompanied by a dramatic decrease of  $\varepsilon'$  (see also a thorough study of the polarization loops and the  $E$ ,  $T$ -phase diagram for NN in [3, 15]). On subsequent heating, the field-induced ferroelectric phase transformed into the antiferroelectric phase, at 230 K, as evidenced by a step-like increase of the dielectric permittivity. This is in quite good correspondence with our data showing the dramatic increase of the thermal hysteresis width in NN in the sequence from crystal 1 to crystal 3. Another support of our observation was recently found in heat capacity measurements [27], which did not reveal any sharp anomalies

for an NN single crystal in the 4–300 K temperature range (in contradiction with the results obtained in [7] for an Mn doped single crystal of NN).

In principle, one could assume that the observed low-temperature saturation of the dielectric permittivity of sample 5 is due to defects or glassy disorder. Another possibility is the coexistence of the ferroelectric and antiferroelectric phases locally which means that some part of the volume is occupied by the first phase and some part is filled with the other phase. In the former case, one should observe huge dielectric losses in a wide frequency range. In the second case, one may expect (i) the appearance of the  $\varepsilon'(T)$  thermal hysteresis loops and (ii) dependence of the width of these loops on the turning point [28]. In order to check the first possibility, we have measured  $\tan \delta(T)$  characterizing the dielectric losses. The results are shown in figure 1(c) for crystals 1, 3–5 (crystal 2 exhibits a behavior similar to crystal (1)). One can see that the dielectric losses for sample 5 are minimal among the studied crystals, which implies that this sample is the most perfect (in the sense that the dielectric losses are minimal). We also found that the real part of the dielectric permittivity of this crystal changes by less than a few per cent when varying the frequency from  $10^2$  to  $10^5$  Hz. The absence of the dielectric dispersion means that the low-temperature state of this crystal is not glassy. Finally, the inverse susceptibility of sample 5 is well described by a straight line, at high  $T$  values, and the extrapolation of this straight line intersects the temperature axis in the negative region. For comparison, the behavior of the dielectric susceptibility in the textbook dipolar-glass-oxide lead-magnesium-niobate case is very different, i.e. the extrapolation of the inverse susceptibility intersects the temperature axis well above the temperature of the susceptibility maximum. All these data reliably show that sample 5 does not possess any glass behavior. In order to check the second possibility, we compared the dielectric permittivity values in sample 5 obtained on cooling and heating. We have not found any valuable difference of these two curves. This implies that the coexistence of the phases at the same time and in the same volume is not the case for the considered sample. Concluding our checking, we should state that the only plausible explanation of our experimental data is the influence of the quantum vibrations on the dielectric permittivity. Such influence is expected, as is seen from our theory and previous developments in the field [18]. The examples include  $\text{SrTiO}_3$ ,  $\text{KTaO}_3$ , and  $\text{CaTiO}_3$ . In these perovskite crystals, the value of the dielectric permittivity saturates and largely increases when the extrapolated (classical)  $T_c$  becomes closer to zero. The same tendency is seen in our set of the NN crystals—the dielectric permittivity at 0 K in sample 5 is intermediate between those of  $\text{KTaO}_3$  and  $\text{CaTiO}_3$  and the same relation is observed for the extrapolated  $T_c$  values of these three compounds. Thus, NN matches the correlation between the value of the dielectric permittivity of quantum paraelectrics measured at 0 K and the value of the extrapolated (classical)  $T_c$  [29]. This fact gives additional support for the idea that the ground state of the NN sample 5 is quantum paraelectric.

Finally, we conjecture that crystal 5 is not ferroelectric, but it is quantum paraelectric instead. Our theory explains

this as a result of vanishing of the lower boundary of stability of the ferroelectric metastable states, in this sample. This implies that this quantum paraelectric state can coexist with metastable ferroelectric states, which are well presented in the (1–3) crystals by the super-wide thermal hysteresis.

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