

## Off-centre displacements and ferroelectric phase transition in dilute $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2001 J. Phys.: Condens. Matter 13 8817

(<http://iopscience.iop.org/0953-8984/13/39/309>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.226

The article was downloaded on 16/05/2010 at 14:55

Please note that [terms and conditions apply](#).

# Off-centre displacements and ferroelectric phase transition in dilute $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$

Yakov Girschberg and Yizhak Yacoby

Racah Institute of Physics, Hebrew University, Jerusalem, 91904, Israel

Received 22 March 2001, in final form 20 June 2001

Published 13 September 2001

Online at [stacks.iop.org/JPhysCM/13/8817](http://stacks.iop.org/JPhysCM/13/8817)

## Abstract

We present a theory of the Nb-ion off-centre displacements and ferroelectric phase transition in dilute  $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ . We believe that this theory is generally applicable to ferroelectric transitions in incipient ferroelectrics induced by impurities. We show that the non-uniform strong intraband electron–phonon interaction leads to the localization of virtual conduction band electrons around the Nb ions and to the off-centre displacements of these ions. We consider the off-centre displacements as pseudospins and show that their interaction with the soft phonon mode of the host lattice ( $\text{KTaO}_3$ ) plays a fundamental role in the phase transition dynamics.

The model quantitatively reproduces the basic experimental data in the quantum regime: the temperature dependence of the inverse dielectric function  $\epsilon^{-1}(T)$ , the impurity and temperature dependence of the renormalized soft-mode vibrational frequency  $\tilde{\omega}(x, T)$  and the impurity concentration dependence of the transition temperature  $T_C(x)$ . In particular we show that the critical concentration  $x^*$  is determined by the ion tunnelling frequency, the parameters for the bare soft mode and the pseudospin–phonon coupling constant.

## 1. Introduction

X-ray absorption fine-structure (XAFS) measurements on a number of oxygen perovskites (see [1] and references therein) have conclusively shown that the atoms in these systems do not occupy high-symmetry positions, even far above the temperature of the transition to the cubic nominally undistorted phase. These crystals display both displacive-like and order–disorder-like properties [2–5]. Recently [6–9], we have developed a phase transition model of pure ferroelectric perovskites, which takes into account the soft transverse optical mode (the phonon subsystem), the dynamical spontaneous off-centre displacements (the pseudospin subsystem) and the interaction between them. We have demonstrated that the existence of the spin subsystem and especially its interaction with the soft mode play a major role in the ferroelectric transition in these systems.

In this paper we address the mechanism of ferroelectric phase transition of incipient ferroelectric crystals, doped with ions that drive them into the ferroelectric phase, such as  $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$  (KTN). Pure  $\text{KTaO}_3$  is an incipient ferroelectric, which does not undergo any phase transition. But with temperature decreasing towards zero, it shows a strong increase in the dielectric constant, related to the softening of its ferroelectric mode [10]. Substituting Nb for Ta modifies the properties of  $\text{KTaO}_3$  and for  $x > 0.008$  KTN undergoes a ferroelectric phase transition with  $T_C = 0$  at the critical concentration  $x = x^* = 0.008$  [11].

The bulk of experimental investigations of KTN [11–16] were devoted to concentrations  $x \geq x^*$ , in the search for peculiar quantum effects in the phase transition near zero temperature. The theory of such a ‘quantum ferroelectric’ was developed in [17–19], showing the possibility of ‘pure’ displacive-like transition at  $T_C \rightarrow 0$  (the displacive or quantum limit). The theory predicted non-trivial relations for the transition temperature  $T_C(x)$ , the variation of the inverse dielectric constant  $\epsilon^{-1}(T)$  with temperature and the zero-point dielectric susceptibility  $\epsilon^{-1}(T = 0, x)$ :

$$\begin{aligned} T_C(x) &= A(x - x^*)^{0.5} \\ \epsilon^{-1}(T) &\propto (T - T_C)^2 \quad (\text{for } T_C = 0) \\ \epsilon^{-1}(T = 0, x) &\propto (x - x^*). \end{aligned} \quad (1)$$

The first and last relations agree satisfactorily with experiment [11, 12] in the quantum regime ( $x^* \leq x \leq 0.04$ ) with  $A = 276$  K. As for the temperature dependence of the inverse dielectric constant  $\epsilon^{-1}(T)$ , the experimental results [13] for  $x = 0.006$  ( $x < x^*$ ),  $x = 0.008$  ( $x = x^*$ ) and  $x = 0.012$  ( $x > x^*$ ) in the temperature range  $4 \text{ K} \leq (T - T_C) \leq 200 \text{ K}$  can be well described by the Barrett expression [20]

$$\epsilon(T) = \epsilon_\infty + B/[T_1 \coth(T_1/T) - T_0]$$

with  $x$ -dependent constants  $B$ ,  $T_1$  and  $T_0$ . Clearly, this expression is quite different from that predicted by the theory.

In the above-mentioned theory the quantum effects are simply a result of the transition from classical statistics, valid at sufficiently elevated temperatures, to quantum statistics, valid at very low temperatures. XAFS measurements on  $\text{KTaO}_3$  [21] and on  $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$  [22], performed after the publication of the above theoretical work, have conclusively shown that within experimental accuracy the Ta ions always occupy the centre of symmetry positions. However, the Nb ions occupy off-centre positions even at low Nb concentrations and at temperatures far above  $T_C$ . The presence of these spontaneous off-centre ionic displacements shows that the ions are subject to a multiwell potential and may display another quantum effect, namely tunnelling among equivalent potential minima. This effect has not been considered in the previous theory and is taken into account here.

Another ‘pure phonon’ theory of phase transition in KTN [23] takes the presence of Nb into account by introducing  $x$ -dependent linear and non-linear polarizabilities of the oxygen ions [24]. By refining these parameters this approach is able to reproduce some experimental results. This approach is however purely phenomenological; i.e. the nature of the  $x$ -dependence of the polarizabilities is not explained by this model.

An alternative semi-phenomenological model [25, 26] has discussed the interaction of the dipoles at the impurity sites with the host crystal soft mode. We believe that this model is basically correct. However, it does not explain the origin of the spontaneous off-centre displacements and does not consider Nb tunnelling and zero-point vibrations. Yacoby and Girshberg [27] pointed out the importance of these factors at low temperatures. Recently, Kleemann *et al* [28] have suggested a number of models including one that takes into account off-centre impurities, spin–phonon interactions, tunnelling, direct spin–spin interaction and

zero-point vibrations and calculates expressions for the zero-frequency dielectric function. However, the authors do not discuss which of the models actually applies to impurity-doped incipient ferroelectrics nor do they explain the origin of the off-centre displacements.

As discussed above, the results of the XAFS measurements on dilute  $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$  show that Nb ions and only Nb ions are at off-centre positions in the cubic phase. Furthermore, these local off-centre displacements are independent of Nb concentration, suggesting that the displacements are the result of a strong *local* interaction. This fundamental fact suggests that the origin of the Nb off-centre displacements is the same for both pure  $\text{KNbO}_3$  and KTN and that the phase transition in KTN is also related to the pseudospin interaction with the host lattice soft mode. Thus as in  $\text{KNbO}_3$ , we consider both interband and intraband electron–phonon interactions except that in this case the latter is site dependent.

The interband e–p coupling has been known to be strong and responsible for the existence of the soft mode [29–31]. Furthermore, this interaction is in essence equivalent to the 2p–3d orbital hybridization found in first-principles calculations [32]. Both  $\text{KNbO}_3$  [33, 34] and KTN [35, 36] have small polarons, thus showing that Nb induces strong intraband e–p coupling. The value of the coupling constant has been experimentally determined.

Site-dependent intraband electron–phonon (e–p) interaction has been considered in various mixed crystals and glasses (see review [37]), where the authors were concerned with such phenomena as the effect of small polarons on dc and ac conductivity, optical absorption, conductivity in strong electrical fields, the Hall mobility etc. Here we shall show that the presence of virtual electrons in the conduction band of KTN due to the interband electron–phonon coupling and the strong intraband electron–phonon coupling of Nb drives the Nb ions to off-centre positions in agreement with XAFS experiments. Furthermore, as a result of the interaction between the off-centre Nb displacements and the host lattice soft mode, KTN undergoes a ferroelectric phase transition. However, due to the fact that the Nb atoms tunnel among the equivalent potential minima, it is necessary to have a finite minimum Nb concentration for  $T_C = 0$ .

We shall show that using quantum statistics for both phonons and spins, this model leads, in the molecular field approximation, to the correct concentration dependence of  $T_C$  including a correct prediction of the critical concentration  $x^*$  and to the correct temperature and concentration dependence of the inverse dielectric function and the soft-mode frequency.

## 2. System Hamiltonian, off-centre displacements and dynamical disorder

We approach the model of KTN in the following way:

- (a) The electronic band structures of  $\text{KTaO}_3$  and  $\text{KNbO}_3$  are similar. We therefore assume that the bare electronic band structure (ignoring electron–phonon interaction) of KTN for small  $x \geq x^*$  is essentially equal to that of  $\text{KTaO}_3$ .
- (b) The soft mode of  $\text{KTaO}_3$  extrapolates to zero at  $T_0 \simeq -12$  K. Although  $\text{KNbO}_3$  undergoes a ferroelectric transition at 760 K, its soft mode extrapolates to zero at  $T_0 \simeq 100$  K. This has been shown experimentally [38] and is in agreement with our theoretical model [9]. Thus, we can assume that the bare-phonon system of KTN is approximately equal to that of  $\text{KTaO}_3$  with a small correction to the soft mode due to the presence of up to a few per cent of Nb. Notice that, due to the relatively small difference between the values of  $T_0$  of  $\text{KTaO}_3$  and  $\text{KNbO}_3$ , this alone cannot account for the fact that KTN undergoes a phase transition at  $T_C = 0$  for  $x$  less than 1%.
- (c) We propose that the main difference between KTN and  $\text{KTaO}_3$  is that the intraband electron–longitudinal phonon interaction constants at Ta and Nb sites are very different.

We know that this is the case in pure  $\text{KTaO}_3$  and pure  $\text{KNbO}_3$ . Here we assume that the interaction constants at the Ta and Nb sites are equal to their values in  $\text{KTaO}_3$  and  $\text{KNbO}_3$  respectively.

Ordinarily, impurities give rise to local or resonant modes and to changes in the phonon spectrum of the host. Due to the fact that the host lattice soft-mode branch overlaps in part the acoustic branches, the low-frequency impurity modes are by definition resonant modes. Since the Nb off-centre displacements are dynamic and much larger than the vibrational amplitudes and since the resonant mode frequencies are hardened as a result of the off-centre displacements, we believe that the effect of the resonant modes on the phase transition is negligible in comparison to the effect of the impurity off-centre displacements.

The Hamiltonian  $H$  of KTN is identical in structure to that of pure  $\text{KNbO}_3$  (see [9]) and includes a two-band electron Hamiltonian  $H_e$ , a free-phonon-field Hamiltonian  $H_{ph}$  and an electron–phonon interaction Hamiltonian  $H_{e-ph}$ .

We assume that replacing a small fraction of Ta ions with Nb does not significantly affect the bare electronic structure of the system—that is, that the electron energies  $\varepsilon_\alpha$  and all overlap integrals  $J_{\alpha\alpha}(\mathbf{m} - \mathbf{m}')$  do not depend on the site index. So, the electronic part of the Hamiltonian  $H$  remains unchanged and in a site representation is given by

$$H_e = \sum_{\mathbf{m}, \alpha} \varepsilon_\alpha a_{\alpha\mathbf{m}}^\dagger a_{\alpha\mathbf{m}} + \sum_{\mathbf{m}, \mathbf{m}', \alpha} J_{\alpha\alpha}(\mathbf{m} - \mathbf{m}') a_{\alpha\mathbf{m}}^\dagger a_{\alpha\mathbf{m}'} \quad (2)$$

where  $\alpha$  takes the values 1 and 2 for conduction and valence bands respectively,  $\mathbf{m}$  labels the site and  $a_{\alpha\mathbf{m}}^\dagger$  ( $a_{\alpha\mathbf{m}}$ ) is the ( $\alpha$ ,  $\mathbf{m}$ )-site creation (annihilation) electron operator.

The bare-phonon subsystem is also assumed to be unaffected by disorder: the phonon spectrum is described by the wave vectors and by the index of the vibrational branches. We include in the free-phonon Hamiltonian two terms:

$$H_{ph} = H_{ph}^l + H_{ph}^t = \sum_{\mathbf{q}} \omega_{q_l} b_{q_l}^\dagger b_{q_l} + \sum_{\mathbf{q}} \omega_{q_t} b_{q_t}^\dagger b_{q_t} \quad (3)$$

where  $s = l, t$  labels the longitudinal or transverse polar optical branch, respectively,  $\omega_{q,s}$  is the frequency of the phonon with wave vector  $\mathbf{q}$  and branch index  $s$ ,  $b_{q,s}^\dagger$  ( $b_{q,s}$ ) are the phonon creation (annihilation) operators.

The electron–phonon interaction is described by a Fröhlich-like Hamiltonian  $H_{e-ph}$  and includes two types of electron–phonon coupling: the strong interband interaction  $H_{e-ph}^t$  with transverse phonons and a coupling constant  $\Gamma_{\alpha\beta}(\mathbf{q})$  accounts for the soft mode, and the strong intraband interaction  $H_{e-ph}^l$  with longitudinal phonons and coupling constant  $\gamma_\alpha(\mathbf{q})$  causes the electron localization:

$$H_{e-ph} = H_{e-ph}^l + H_{e-ph}^t \quad (4)$$

To take the presence of the impurities into account we consider both coupling constants as functions of the site index  $\mathbf{m}$  and the phonon wave vector  $\mathbf{q}$ :

$$\Gamma_{\mathbf{m}\alpha\beta}(\mathbf{q}) = \sum_{i=1}^2 \Gamma_{i,\alpha\beta}(\mathbf{q}) \eta_{\mathbf{m}}^i \quad \gamma_{\mathbf{m},\alpha}(\mathbf{q}) = \sum_{i=1}^2 \gamma_{i,\alpha}(\mathbf{q}) \eta_{\mathbf{m}}^i \quad (5)$$

Here  $\eta_{\mathbf{m}}^i$  are the random occupation numbers [39]:  $\eta_{\mathbf{m}}^i = 1$  if site  $\mathbf{m}$  is occupied by an atom of type ‘ $i$ ’, otherwise  $\eta_{\mathbf{m}}^i = 0$ ; where  $i = 1, 2$  and  $i = 1$  corresponds to Ta,  $i = 2$  to Nb. Evidently,  $\sum_i \eta_{\mathbf{m}}^i = 1$ ,  $\eta_{\mathbf{m}}^i \eta_{\mathbf{m}}^j = \delta_{i,j} \eta_{\mathbf{m}}^i$ . The configurational averages for a fully disordered mix are

$$\langle \eta_{\mathbf{m}}^i \rangle = x_i \quad \langle \eta_{\mathbf{m}}^i \eta_{\mathbf{m}'}^j \rangle = x_i x_j \quad (6)$$

where  $x_i$  is the concentration of atoms of the  $i$ th type.

Since in the perovskites the conduction band is formed mainly by d states of metals (Ti, Nb, Ta) and the valence band is formed mainly by oxygen 2p states, we assume that the substitution of Nb for Ta modifies the electron–phonon interaction in the conduction band only: the occupation numbers  $\eta_m^i$  are meaningful only for the conduction band; for the valence band  $\eta_m^i \equiv 1$  and the indices  $i, j$  can be omitted. In addition, we shall deal below with intraband electron–phonon interaction in the conduction band ( $\alpha = 1$ ) only. Since the valence band is broad, hole polarons cannot form. So,

$$H_{e-ph}^l = \frac{1}{\sqrt{2N}} \sum_{q,m,j} \omega_{ql} [\gamma_{j,1}^*(\mathbf{q}) \eta_m^j \exp(-i\mathbf{q} \cdot \mathbf{m}) b_{qt}^+ + \gamma_{j,1}(\mathbf{q}) \eta_m^j \exp(i\mathbf{q} \cdot \mathbf{m}) b_{qt}] a_{1m}^+ a_{1m} \quad (7)$$

$$H_{e-ph}^t = \frac{1}{\sqrt{N}} \sum_{q,m,\alpha,\beta,\alpha \neq \beta,j} \Gamma_{\alpha\beta,j} \eta_m^j \sqrt{\frac{\omega_{qt}}{2}} \exp(i\mathbf{q} \cdot \mathbf{m}) [b_{qt} + b_{-qt}^+] a_{\alpha m}^+ a_{\beta m}. \quad (8)$$

The intraband coupling constants of the Ta sites,  $j = 1$ , taken from  $\text{KTaO}_3$ , are small [40,41], namely  $\gamma_{1,1}(\mathbf{q}) \simeq 0$ . In contrast the constants of Nb,  $j = 2$ , taken from  $\text{KNbO}_3$  are large [9,33]:

$$\bar{\gamma} \equiv \frac{1}{N} \sum_{\mathbf{q}} |\gamma_{2,1}(\mathbf{q})|^2 \simeq 4.5 \gg 1 \quad \Gamma_{2,\alpha\beta} > \Gamma_{1,\alpha\beta}. \quad (9)$$

As in the case of pure  $\text{KNbO}_3$  [9], the first inequality necessitates the application of the small-polaron canonical transformation [42,43]:

$$\tilde{H} = \exp(-S) H \exp(S) \equiv \tilde{H}_e + \tilde{H}_{ph} + \tilde{H}_{e-ph}^l + \tilde{H}_{e-ph}^t \quad (10)$$

where

$$S = \sum_m S_{1m} a_{1m}^+ a_{1m} \quad (11)$$

and

$$S_{1m} = \frac{1}{\sqrt{2N}} \sum_{q,j} [(b_{-qt}^+ \gamma_{j,1}^*(\mathbf{q}) - b_{qt} \gamma_{j,1}(\mathbf{q})) \eta_m^j \exp(i\mathbf{q} \cdot \mathbf{m})] \quad (12)$$

yielding a set of new electron and phonon operators:

$$a_{1m}^+ = \tilde{a}_{1m}^+ \exp \left[ -\frac{1}{\sqrt{2N}} \sum_{q,j} (b_{-qt}^+ \gamma_{j,1}^*(\mathbf{q}) - b_{qt} \gamma_{j,1}(\mathbf{q})) \eta_m^j e^{i\mathbf{q} \cdot \mathbf{m}} \right] \quad (13)$$

$$b_{qt}^+ = \tilde{b}_{qt}^+ - \frac{1}{\sqrt{2N}} \sum_{m,j} a_{1m}^+ a_{1m} \gamma_{j,1}(\mathbf{q}) \eta_m^j \exp(i\mathbf{q} \cdot \mathbf{m}). \quad (14)$$

After some transformations we are led to three significant results:

- (a) The overlap integrals for impurity and matrix ions are strongly renormalized, whereas the overlap integrals of the host atoms remain unchanged:

$$\tilde{J}_{11}^{1,2} = \tilde{J}_{11}^{2,1} = J_{11} \exp(-\bar{\gamma}) \ll J_{11} \quad \tilde{J}_{11}^{1,1} = J_{11}. \quad (15)$$

Here  $\tilde{J}_{\alpha\alpha}^{i,i'}$  is the renormalized overlap integral.

- (b) The impurity electronic energy level is strongly renormalized while that of the host level is not:

$$\tilde{\varepsilon}_{1,1} = \varepsilon_1 \quad \tilde{\varepsilon}_{2,1} = \varepsilon_1 - \frac{1}{2N} \sum_{\mathbf{q}} \omega_{ql} |\gamma_{2,1}(\mathbf{q})|^2 \equiv \varepsilon_1 - E_p \quad (16)$$

where  $\tilde{\varepsilon}_{i,\alpha}$  is the renormalized site energy and  $E_p$  is the polaron energy shift.

(c) As shown below, the polaron canonical transformation leads to an off-centre displacement of the impurity (Nb) ions that tunnel among the equivalent off-centre positions.

Notice that within our approximations, neglecting the e–p interactions leaves the system completely ordered. The introduction of these interactions introduces the disorder. In addition, the polaron transformation gives rise to two new terms: a direct residual interaction between two polarons at different sites ( $m \neq m'$ ), and a residual intraband polaron–longitudinal phonon interaction  $\tilde{H}_{e-ph}^l$ . In our problem of ferroelectric phase transition, the corrections associated with these terms are small relative to the background of interband interaction  $\tilde{H}_{e-ph}^l$  even for pure KNbO<sub>3</sub> (see [9]). This is especially so in our case of small Nb concentration ( $x_2 \ll x_1, x_2 \equiv x$ ), and the corrections may therefore be left out.

Let us now consider the changes in the phonon spectra in more detail. The polaron canonical transformation does not affect the free-transverse-phonon Hamiltonian  $H_{ph}^t$ , but renormalizes the interband electron–phonon interaction:

$$\tilde{H}_{e-ph}^t = \sum_{m,q,\alpha \neq \beta,i} \Gamma_{\alpha\beta,i} \eta_m^i \sqrt{\frac{\omega_{qt}}{2N}} F_{\alpha\beta}(\mathbf{m}) e^{iq \cdot \mathbf{m}} (b_{qt} + b_{-qt}) \tilde{a}_{\alpha m}^+ \tilde{a}_{\beta m} \quad (17)$$

leading to the existence of the soft mode. The operator  $F_{\alpha\beta}(\mathbf{m})$ :

$$F_{\alpha\beta}(\mathbf{m})|_{(\alpha \neq \beta)} = \exp \left\{ \frac{1}{\sqrt{2N}} \sum_{q,i} [b_{qt}^+ \gamma_{i,1}^*(\mathbf{q}) \eta_m^i e^{-iq \cdot \mathbf{m}} - b_{qt} \gamma_{i,1}(\mathbf{q}) \eta_m^i e^{iq \cdot \mathbf{m}}] \right\} \quad (18)$$

describes multiphonon processes associated with the local deformation of the lattice, due to the electronic transition from state to state ( $\alpha \neq \beta$ ) on the same site in the presence of the strong intraband electron–phonon coupling [9]. Notice, however, that the intraband electron–phonon coupling is strong only for Nb ions.

The renormalized phonon spectrum defined by the Hamiltonian, equation (17), is given by the poles of the full phonon Green's function  $D(\mathbf{q}, \omega_n)$ . The technique for evaluating the diagrams, including the operator  $F_{\alpha\beta}(\mathbf{m})$ , was developed in [9] for pure ferroelectrics (for uniform coupling constants). In our case, the diagrams of the total polarization operator  $\Pi(x, T)$  of the system can be obtained in just the same way. The only difference is the impurity consideration in the diagrams, i.e. the production in the diagrams of two types of vertex (two types of coupling constant  $\Gamma_{\alpha\beta,i}$ ). It can be shown that the corrections to  $\Pi(x, T)$  associated with intraband interactions are proportional to  $x^2 (E_p/\bar{E})^2 \ll 1$ , and can therefore be neglected.

After some transformations, we obtain the soft-mode frequency ( $\Gamma_{\alpha\beta,i} \equiv \Gamma_i$ ):

$$\tilde{\omega}_0^2(x, T) = \omega_{0t}^2 [1 + \Pi(x, T)] = \omega_{0t}^2 \left[ -\tilde{\Delta} + \frac{3}{2} \left( \frac{\omega_{0t}}{\bar{\omega}} \right)^2 \left( \frac{\bar{\omega}}{2\bar{E}} \right) \coth \left( \frac{\bar{\omega}}{2T} \right) \right] \quad (19)$$

$$\tilde{\Delta}(x) = \Delta + 2x \left( \frac{\Gamma_2}{\Gamma_1} - 1 \right) \quad (20)$$

where  $\bar{E}$  is the average interband energy difference,  $\bar{\omega}$  is the average of the soft-phonon-branch frequency and  $\Delta \equiv 4(\Gamma_1)^2/\bar{E} - 1 \ll 1$ . The phonon subsystem is (ferroelectrically) unstable if, at  $T = 0$ ,

$$(1 + \Pi)_{q \rightarrow 0} < 0. \quad (21)$$

If condition (21) is satisfied, the transition temperature  $T_0$  is the temperature at which  $\tilde{\omega}_0^2$  tends to zero. Since the second term of equation (19) is always positive, it is necessary for  $T_0 \geq 0$  that  $\tilde{\Delta}_0 > 0$ . This is the threshold inequality [29–31], which bounds the coupling constant  $\Gamma_{\alpha\beta}$  from below.

Pure  $\text{KTaO}_3$  does not undergo any phase transition, i.e.

$$0 < \tilde{\Delta}(0) \equiv \Delta < \frac{3}{2} \left( \frac{\omega_{0f}}{\bar{\omega}} \right)^2 \left( \frac{\bar{\omega}}{2E} \right).$$

However, for  $x \geq \tilde{x}$  it is possible that

$$\tilde{\Delta}(x) \geq \frac{3}{2} \left( \frac{\omega_{0f}}{\bar{\omega}} \right)^2 \left( \frac{\bar{\omega}}{2E} \right)$$

and the system may undergo a phase transition. Here,  $\tilde{x}$  is the critical concentration (for  $x = \tilde{x}$ ,  $T_0 = 0$ ).

So, the presence of Nb-related vertices in the polarization operator of  $\text{KTaO}_3$  leads to an increase in interband polarizability that causes further softening of the renormalized soft mode and a possible phase transition. This effect explains on the micro-level the starting assumption of references [23], about the niobium-concentration-dependent polarizability in KTN. Although reference [23] discusses the changes in the oxygen ion polarizability, while in our model both bands make a contribution to interband polarizability, we deal with the same effect (recall that the valence band is formed mainly by oxygen 2p states). In principle, for sufficiently strong interband coupling constant this polarizability leads to a lattice instability and to phase transition. However, as already indicated, this mechanism fails in our case. Using the interband e–p coupling constants of Ta [41] and Nb [9], we find that  $\tilde{x} = 0.2$ , i.e.  $\tilde{x} \gg x^*$  (the experimental critical concentration  $x^* = 0.008$ ). Thus for  $x^* \leq x \leq \tilde{x}$ , this mechanism can be ignored. The temperature of the phase transition, induced by spin–phonon interaction, is always higher than the transition temperature of the associated displacive-like transition (see below). Therefore, the ‘spin–phonon’-induced transition must be dominant at smaller Nb concentration. So, the presence of impurities, at least for small ( $x \geq x^*$ ) concentrations, actually leaves the transverse optical phonon branch and, in particular, the soft mode  $\tilde{\omega}_0^2(T)$  remains approximately unchanged.

The transformations in equation (13) and equation (14) leave the frequency of the longitudinal branch  $\omega_{ql}$  unchanged, and in terms of the new operators  $\tilde{b}_{ql}, \tilde{b}_{ql}^+$  the Hamiltonian  $\tilde{H}_{ph}^l$  has the same form as  $H_{ph}^l$ . However, for the impurity ( $j = 2$ ), the second term in equation (14) describes an ionic displacement and the longitudinal vibrations with frequency  $\omega_{ql}$  are about the new equilibrium position. Substituting  $\tilde{b}_{ql}^+$  from equation (14) in the usual expression for the ionic displacement and using the homopolar approximation ( $\sum_{\alpha} \tilde{a}_{\alpha m}^+ \tilde{a}_{\alpha m} = 1$ ) we obtain a renormalized displacement operator of the central (Nb or Ta) ion in the  $m$ th unit cell:

$$\tilde{r}_m = \frac{1}{\sqrt{N}} \sum_{q,s} \sqrt{\frac{1}{2M^* \omega_{qs}}} [e_{qs} \exp(i\mathbf{q} \cdot \mathbf{m}) b_{qs} + e_{qs} \exp(-i\mathbf{q} \cdot \mathbf{m}) b_{qs}^+] + \mathbf{b}_m \quad (22)$$

$$\mathbf{b}_m = \frac{1}{N} \sum_{q,i} \sqrt{\frac{2}{M^* \omega_{ql}}} e_{ql} \exp(i\mathbf{q} \cdot \mathbf{m}) \gamma_{i,1}^*(\mathbf{q}) \eta_m^i \sum_{m'} \exp(-i\mathbf{q} \cdot \mathbf{m}') \tilde{a}_{1m'}^+ \tilde{a}_{1m'} \quad (23)$$

where  $s$  is the branch number,  $M^*$  is the reduced unit-cell mass and  $e_{qs}$  is the polarization unit vector of the corresponding mode. The first term in equation (22) contains only phonon operators, representing the usual vibrations about the equilibrium position, whereas the second term  $\mathbf{b}_m$  contains only electronic operators and represents a new position, the local off-centre displacement, which is proportional to the intraband electron–phonon coupling constant. This result is highly non-trivial, because in spite of the fact that the electrons and phonons involved in the e–p interaction extend throughout the crystal, the off-centre displacements



of the host lattice ions ( $i = 1$ ,  $\gamma_{1,1}(\mathbf{q}) \simeq 0$ ) are negligible, while those of Nb ( $i = 2$  with  $\bar{\gamma} \equiv (1/N) \sum_{\mathbf{q}} |\gamma_{2,1}(\mathbf{q})|^2 \gg 1$ ) are large.

Due to symmetry, the average of the vector  $\mathbf{b}_m$  is zero in the cubic phase, but the average of  $|\mathbf{b}_m|^2$  is not zero and may be rewritten as

$$|\mathbf{b}_m|^2 = \frac{1}{N} \sum_{q,i} \frac{2\omega_{qs}}{M^* \omega_{ql}^2} |e_{ql}^j|^2 |\gamma_{i,1}(\mathbf{q})|^2 \eta_m^i \left( \frac{N_e}{N} \right) \quad (24)$$

where  $N_e/N$  is the electron density in the conduction band.

It is clear that due to the large band gap  $E_g$ , there are no free electrons in the conduction band. The fact that  $N_e/N$  is not zero is entirely due to the virtual excitation of electrons by the strong interband electron–phonon coupling  $\hat{H}_{e-ph}^i$  (equation (17)). For non-ferroelectric crystals, where  $4\Gamma_{\alpha\beta}^2/\bar{E} \ll 1$ , this correction may be negligible. However, in our case, the threshold inequality requires  $4\Gamma_1^2/\bar{E} \geq 1$  (equation (21)). We know that this relation is satisfied because  $\text{KTaO}_3$  is an incipient ferroelectric. Thus  $N_e/N$  obeys the formula obtained in reference [9] and is valid for  $\text{KTaO}_3$ ,  $\text{KNbO}_3$  and  $\text{KTN}$ :

$$N_e/N = \left( \frac{4\Gamma_1^2}{\bar{E}} \right) \frac{\omega_{0r}^2}{2\bar{\omega}\bar{E}} \coth\left(\frac{\bar{\omega}}{2T}\right) \simeq \frac{\omega_{0r}^2}{2\bar{\omega}\bar{E}} \coth\left(\frac{\bar{\omega}}{2T}\right). \quad (25)$$

Substituting equation (25) in equation (24) we finally obtain

$$|b_0/a|^2 \simeq (E_p/E_{al}) \frac{\omega_{0r}^2}{2\bar{\omega}\bar{E}} \coth\left(\frac{\bar{\omega}}{2T}\right) \quad (26)$$

where  $b_0$  is the magnitude of the spontaneous local off-centre displacement,  $a$  is the lattice parameter  $E_{al} \equiv M^* \omega_l^2 a^2/2$  and  $E_p$  is the polaron shift of the Nb ion defined in equation (16).

The interaction Hamiltonian, equation (7), does not determine the direction of displacement  $\mathbf{b}_m$ —only its value. From symmetry considerations it is clear that the off-centre displaced ions may occupy several equivalent positions of equilibrium in the unit cell, with tunnelling (or, at high temperature, hopping) transitions among them. The position and the motion of the host lattice ions can be further described as before; however, the impurity ions perform small oscillations about each equilibrium position and occasionally jump or tunnel through the potential barrier to a neighbouring position of equilibrium. Thus, the expansion of the energy in terms of small displacements, commonly used for ordinary phonons, describing the motion in the vicinity of one equilibrium position is not applicable to the impurity ions. The basic idea of our model is to rewrite the complicated Nb non-linear oscillations in a different way, representing its tunnelling (or hopping) in an explicit form.

The small-polaron canonical transformation, equation (13) and equation (14), does not describe the ionic tunnelling or hopping among equivalent positions in the unit cell. We therefore approximate the operator of the off-centre displacement  $\mathbf{b}_m$  by a spin operator  $\sum_i b_i \eta_m^i \sigma_m^z$ , where  $\sigma_m^z$  is the Pauli matrix,  $b_2 = b_0$  and  $b_1 \equiv 0$ . Thus, the new displacement operator now takes the form

$$\mathbf{R}_m = \sum_i b_i \eta_m^i \sigma_m^z + \sum_{q,s} \sqrt{\frac{1}{2M^* \omega_{qs} N}} e_{qs} \exp(i\mathbf{q} \cdot \mathbf{m}) [b_{qs} + b_{-qs}^+]. \quad (27)$$

It should be noted that in the case of  $\text{KTN}$  there are eight symmetry-equivalent off-centre positions in the cubic cell ([111]-type off-centre displacements). However, the tunnelling probability is significant only between nearest-neighbour pairs, justifying the spin representation.

### 3. Ising-like model with a transverse field and ferroelectric phase transition in dilute crystals

Substituting  $R_m$  in the Hamiltonian  $\tilde{H}$ , we obtain the new effective Hamiltonian  $\hat{H}$ , in which two types of motion of the impurity ions—the tunnelling and the vibrations near the one equilibrium position—are separated. Including the term describing tunnelling in an explicit form, we arrive after some transformations (for more detail see [9]) at the Ising-like spin-phonon Hamiltonian in a transverse field:

$$\hat{H} = - \sum_{m,i} \Omega_m \sigma_m^x \eta_m^i + \sum_{m,m',i} f(\mathbf{m} - \mathbf{m}') \eta_m^i \sigma_m^z Q_{m'} + (1/2) \sum_q [P_q P_{-q} + \tilde{\omega}_{qt}^2(x, T) Q_{qt} Q_{-qt}] \quad (28)$$

where  $\Omega_m$  is the tunnelling frequency,  $Q_{qt}$  and  $P_{qt}$  are the critical phonon branch normal coordinate and the canonical conjugate of  $Q_{qt}$  respectively and

$$f(\mathbf{q}) = \sqrt{M^* \omega_{qt}^4 a^2} \left( \frac{b_0}{a} \right)$$

is the Fourier transform of the spin-phonon coupling constant  $f$ .

In ordinary order-disorder phase transitions the tunnelling term in  $\hat{H}$  plays a decisive role [44]. It determines the lowest spin-phonon coupling constant that still yields a phase transition. In our case it defines the critical (threshold) concentration  $x^*$  at which a ferroelectric phase transition takes place at  $T_C = 0$ .

Hamiltonians of this type are well understood and commonly used to describe order-disorder-like phase transitions (the Kobayashi model [44, 45]). In our case, however, there are two essential differences. First, the spins interact with a soft mode and, as noted in reference [9], it leads to a strong temperature dependence of the effective spin-spin coupling constant. Second, we shall consider the transverse (tunnelling) field on the sites as a random field. For given ionic mass, oscillation frequency near the equilibrium position and off-centre displacement  $|b_m|$ , the tunnelling frequency  $\Omega_m$  in a multiwell potential can be calculated exactly [46]. In this case, for  $\beta b_0^2 > 1$ ,  $\beta \equiv (M\omega/\hbar)$ , the tunnelling frequency  $\Omega \propto e^{-\beta b_0^2}$ . Hence, a slight variation in the off-centre displacement from site to site changes strongly the site tunnelling frequency. We shall consider the site off-centre displacement  $|b_m|$  as a random variable with a Gauss-like distribution function

$$\rho(b) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(b-b_0)^2}{2\sigma^2}\right) \quad (29)$$

where  $\sigma$  is an experimentally determined distribution width.

Using the Hamiltonian equation (28) we have calculated in the mean-field approximation the temperature- and frequency-dependent dielectric function  $\epsilon(T, \omega)$ :

$$\epsilon(T, \omega) = C / [\tilde{\omega}_{0t}^2(T) - \omega^2 - x F(\omega, T)] \quad (30)$$

where

$$F(\omega, T) \equiv |f(\mathbf{0})|^2 \int \rho(b) \frac{\Omega(b) \tanh[\Omega(b)/T]}{\Omega^2(b) - \omega^2 - ig\Omega} db \quad (31)$$

and  $g$  is the damping factor of the host lattice soft mode.  $\epsilon(T, \omega)$  has peaks at  $\omega = \hat{\omega}(x, T)$  where the real part of the denominator in equation (30) vanishes:

$$\tilde{\omega}_{0t}^2(x, T) - \hat{\omega}^2 = x |f(\mathbf{0})|^2 \int \rho(b) \frac{\Omega(b)(\Omega^2(b) - \hat{\omega}_{qt}^2(x, T)) \tanh[\Omega(b)/T]}{(\Omega^2(b) - \hat{\omega}_{qt}^2(x, T))^2 + g^2\Omega^2} db. \quad (32)$$

If  $\sigma$  is small there is a range of temperatures for which this equation has three solutions. In the limit of  $\sigma \rightarrow 0$  the lowest- and highest-frequency solutions correspond to the two split branches while the intermediate-frequency solution yields  $\epsilon = 0$ . On the other hand, if  $\sigma$  is large enough, equation (32) has a single solution giving rise to a single peak in the dielectric function. Notice that even if  $g \rightarrow 0$  the imaginary part of  $F(\omega, T)$  does not vanish. This represents the broadening introduced by the interaction of the soft mode with the distribution of tunnelling frequencies.

The transition temperature  $T_C$  is the solution of the equation  $\widehat{\omega}_{0r}(x, T_C) = 0$ , or

$$\tilde{\omega}_{0r}^2(x, T_C) = x |f(\mathbf{0})|^2 \int \rho(b) \frac{\tanh[\Omega(b)/T_C]}{\Omega(b)} db. \quad (33)$$

This equation determines the function  $T_C(x)$ . Finally, the equation  $T_C(x^*) = 0$  yields the critical concentration  $x = x^*$ :

$$\tilde{\omega}_{0r}^2(x^*, 0) = x^* |f(\mathbf{0})|^2 \int \rho(b) \frac{db}{\Omega(b)}. \quad (34)$$

Equations (32)–(34) provide the three most important parameters related to the ferroelectric phase transition of KTN.

#### 4. Comparison with experiment

The basic assumption of our model is that the intraband e–p coupling constant is very non-uniform: it is large at the Nb ions and very small at the Ta ions. This leads to the creation of ground-state polarons and their localization on the Nb ions. This process, by itself, is not related to the phase transition and can be investigated independently. Experimentally, the most obvious manifestations of the small-polaron production in such (disordered) materials are the characteristic intraband light absorption by free carriers and the variation of the carrier mobility with increasing concentration of localization sites or, in our case, with increasing Nb concentration.

The theory of optical intraband absorption in disordered systems with strong electron–phonon interaction [43] predicts, just as in the case of pure (ordered) crystals [47], a Gaussian-shaped peak, with a temperature-independent peak energy, proportional to the polaron shift. The peak intensity depends strongly on temperature and on the concentration of ions with strong electron–phonon interaction. The peak width increases with increasing temperature.

This peak has indeed been observed in single reduced semiconducting KTN crystals (for  $x = 0.35$  [35] and  $x = 0.13$  [36]), and was not observed in reduced  $\text{KTaO}_3$  crystals [48]. Its energy ( $\simeq 0.6$  eV) is indeed independent of Nb concentration and coincides with the position of a similar peak in semiconducting  $\text{KNbO}_3$ . Its energy is equal to  $2E_p$ , where  $E_p$  is the polaron shift found in  $\text{KNbO}_3$  [33].

The carrier mobility  $\mu$  in  $\text{KTaO}_3$  [48] and in KTN was investigated for  $0 \leq x \leq 1$  [33,40]. Pure  $\text{KTaO}_3$  manifests normal electronic mobility ( $30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at room temperature), which sharply decreases to  $8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for  $x = 0.1$  and to ‘pure’ polaronic mobility in  $\text{KNbO}_3$  ( $0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ). Neither fact can be explained by standard (non-polaron) theory of conductivity and optical absorption.

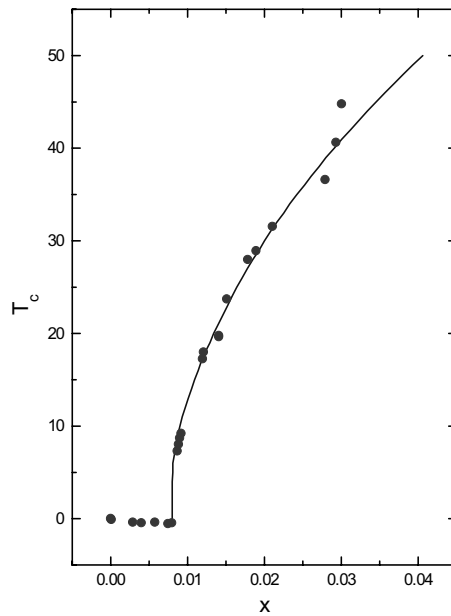
Let us now consider the experimental results related to ferroelectricity in KTN. As noted above, the tunnelling frequency  $\Omega$  is determined by the mass of the tunnelling ion  $M$ , the small vibration frequency near the equilibrium position  $\omega$  and the ion off-centre displacement  $b$ . Assuming that the parameters  $M$  and  $\omega$  for KTN are the same as for  $\text{KNbO}_3$  [49], we find that the tunnelling frequency  $\Omega(b) = A \exp(-b^2/B)$ , where  $A = 0.066$  eV and  $B = 6.5 \times 10^{-3} \text{ \AA}^2$ .

Next, the soft-mode frequency of  $\text{KTaO}_3$ ,  $\tilde{\omega}_{0t}^2(T)$  (equation (19)), can be expressed in a more convenient form:

$$\tilde{\omega}_{0t}^2(T) = A_0 \left[ \frac{\bar{\omega}}{2} \coth\left(\frac{\bar{\omega}}{2T}\right) - T_0 \right].$$

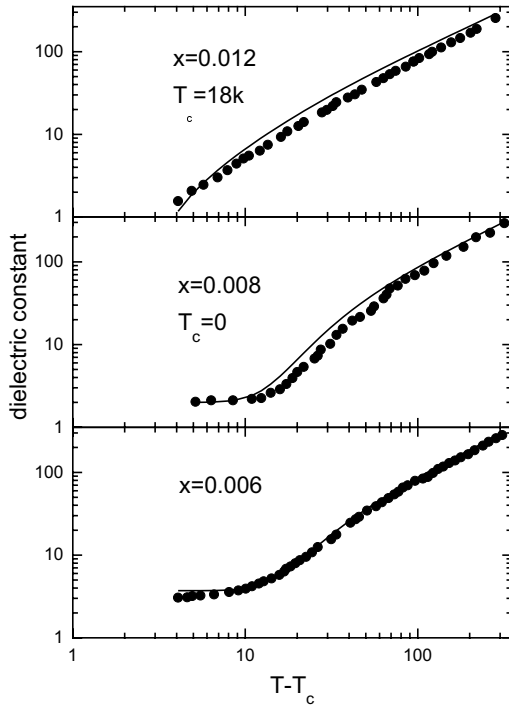
Its parameters have been obtained from references [40, 41]:  $A_0 = 0.0052$  eV,  $\bar{\omega} = 0.0046$  eV,  $T_0 = 0.0011$  eV. The spin-phonon coupling constant  $f(\mathbf{0})$  is practically the same as for  $\text{KNbO}_3$  [9].

Even in the absence of the off-centre displacement variance, i.e. for  $\rho(b) \sim \delta(b - b_0)$ , equations (30), (33), (34) provide a good description of the experimental results. In this case, using  $b = b_0 = 0.15$  Å found in XAFS measurements [22], we have calculated the tunnelling frequency and found  $\Omega(b_0) \equiv \Omega_0 = 15\text{--}17$  K. The corresponding critical concentration obtained from equation (34) is  $x_{th}^* = 0.0068$  which is in good agreement with the experimental value  $x^* = 0.008$  [11]. The concentration dependence of  $T_C(x)$  obtained from equation (33) and the corresponding experimental values [11, 12] are shown in figure 1. Notice that in spite of the fact that the functional form obtained from equation (33) is quite different from the square-root dependence, theory and experiment agree very well. Finally, the inverse dielectric susceptibility as a function of temperature for a number of concentrations ( $x = 0.006, 0.008$  and  $0.012$ ) has been calculated using equation (30). The theoretical values and the corresponding experimental results [13] are shown in figure 2. As can be seen, all theoretical curves are in good agreement with experiment.



**Figure 1.** The Nb concentration dependence of the ferroelectric transition temperature. Dots: experimental results; solid line: theory.

The temperature dependence of the renormalized soft-mode frequency is given by equation (32). In the limit that  $\sigma \rightarrow 0$ , namely when  $\rho(b) \sim \delta(b - b_0)$ , this equation reduces to the well studied equation of the Kobayashi model [44, 45], describing two renormalized spin-phonon branches, separated by a gap. The splitting is largest at the crossing point of the  $\Omega_0$  and  $\tilde{\omega}_{0t}^2(T)$  curves. The gap between the branches is proportional to the spin-phonon

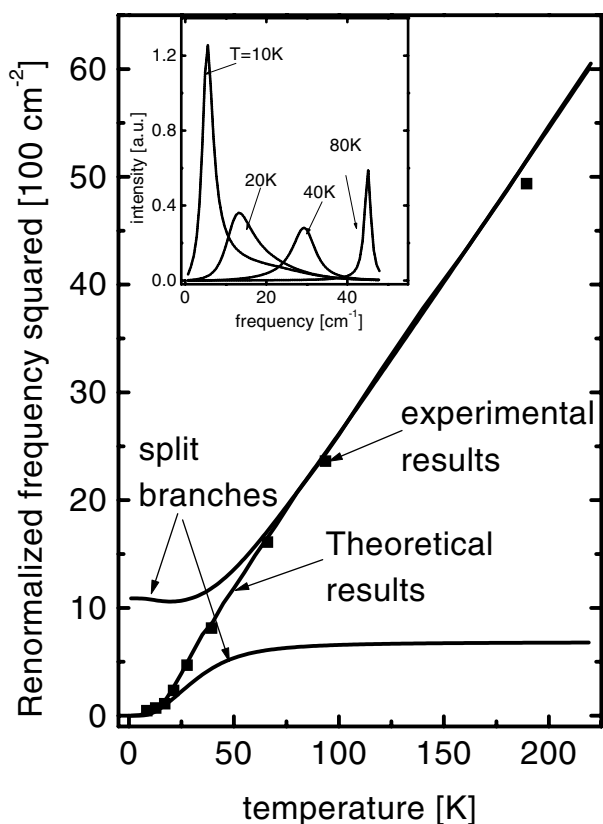


**Figure 2.** Temperature dependences of the inverse dielectric constant. Dots: experimental results; solid lines: theory.

coupling. However, Raman experiments [16] show that the soft-mode Raman line does not split and its frequency continuously decreases as the transition temperature is approached. We therefore conclude that the off-centre displacements have a slight spread causing a spread in the tunnelling frequencies.

We found that for  $\sigma^2 \geq 0.0017 \text{ \AA}^2$  equation (32) has only one solution; that is, the splitting disappears. This value is much smaller than the average displacement  $b_0$  and is consistent with the static disorder value found in XAFS measurements. Hence, we have found all of the parameters of our model and can now more precisely compare our results with the experimental data. The curves in figure 1 and figure 2 remain practically as before. The renormalized value of the soft-mode frequency (equation (32)) for  $x = x^*$  and the Raman measured peak frequencies (dots) [16] are shown in figure 3 and are in very good agreement with each other. The imaginary part of the dielectric function contributes to the broadening of the Raman lines. The theoretical Raman lines ignoring other broadening contributions are shown in the inset of figure 3.

In this work we identified the transition temperature  $T_C$  as the temperature at which the renormalized soft-mode frequency  $\tilde{\omega}_{0r}^2(T)$  tends to zero. We have recently calculated the spin-spin correlation function for small  $(T - T_C)$  beyond the mean-field approximation. These calculations are not presented here and will be published separately. The main result is that a central peak develops and becomes critical as  $T$  approaches  $T_C$ , while the soft-mode frequency saturates at a value of a few  $\text{cm}^{-1}$ . This central peak is different from the one for pure  $\text{KNbO}_3$ . The central peak for pure  $\text{KNbO}_3$  [6] is due to a relaxor associated with the correlated hopping of the Nb ions, while the central peak for  $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$  for small Nb concentrations is associated with the correlated tunnelling of the Nb ions. These results are in good agreement with the experimental results [14, 15] on the central peak of  $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$  (for  $x = 0.009, 0.1, 0.28$ ).



**Figure 3.** The temperature dependence of the renormalized soft-mode frequency. The split branches and the theoretical results are obtained with and without spread in the Nb off-centre displacements, respectively. Inset: theoretical Raman line shapes.

In conclusion, the theory presented here accounts quantitatively for the off-centre displacements of the Nb ions in the paraelectric phase, the Nb concentration dependence of the transition temperature, the critical Nb concentration for  $T_C = 0$ , The temperature and Nb concentration dependence of the dielectric constant and the Nb concentration and temperature dependence of the renormalized soft-mode frequency. Notice that in these calculations we used only parameters that were previously determined for pure  $\text{KTaO}_3$  and  $\text{KNbO}_3$ . No additional adjustable parameters were used.

### Acknowledgments

The authors gratefully acknowledge very interesting discussions with Professor B Laihtman, Professor E Sonin and Professor M Klinger.

### References

- [1] Yacoby Y and Stern E A 1996 *Commun. Condens. Matter Phys.* **18** 1
- [2] Comes R, Currat R, Denoyer F, Lambert M and Quittet A M 1976 *Ferroelectrics* **12** 3
- [3] Yacoby Y 1978 *Z. Phys. B* **31** 275

- [4] Fontana M D, Metrat G, Servoin J L and Gervais F 1984 *J. Phys. C: Solid State Phys.* **16** 483
- [5] Fontana M D, Idrissi H and Wojcik K 1990 *Europhys. Lett.* **11** 419
- [6] Girshberg Ya and Yacoby Y 1997 *Solid State Commun.* **103** 425
- [7] Yacoby Y, Girshberg Ya and Stern E A 1997 *Z. Phys. B* **104** 725
- [8] Girshberg Ya and Yacoby Y 1999 *J. Supercond.* **12** 217
- [9] Girshberg Ya and Yacoby Y 1999 *J. Phys.: Condens. Matter* **11** 9807
- [10] Lines M and Glass A 1977 *Principles and Applications of Ferroelectrics and Related Materials* (Oxford: Clarendon)
- [11] Hochli U, Weibel H and Boatner L 1977 *Phys. Rev. Lett.* **39** 1158
- [12] Rytz D, Chatelain A and Hochli U T 1983 *Phys. Rev. B* **27** 6830
- [13] Rytz D, Hochli U T and Bilz H 1980 *Phys. Rev. B* **22** 6830
- [14] Lyons K B, Fleury P A and Rytz D 1986 *Phys. Rev. Lett.* **57** 2207
- [15] Chase L L, Sokoloff J and Boatner L A 1986 *Phys. Rev. Lett.* **55** 451
- [16] Kugel G, Vogt H, Kress W and Rytz D 1984 *Phys. Rev. B* **30** 985
- [17] Oppermann R and Thomas H 1975 *Z. Phys. B* **22** 387
- [18] Schneider T, Beck H and Stoll E 1976 *Phys. Rev. B* **13** 1123
- [19] Morf R, Schneider T and Stoll E 1977 *Phys. Rev. B* **16** 462
- [20] Barrett J H 1952 *Phys. Rev.* **86** 118
- [21] Nishihata Y, Kamishima O, Ojima K, Sawada A, Maeda H and Terauchi H 1994 *J. Phys.: Condens. Matter* **6** 9317
- [22] Hanske-Petitierre O, Yacoby Y, Mustre-de Leon J, Stern E A and Rehr J 1991 *Phys. Rev. B* **44** 6700
- [23] Kugel G E, Fontana M D and Kress W 1987 *Phys. Rev. B* **35** 813
- [24] Migoni R, Bilz H and Bauerle D 1976 *Phys. Rev. Lett.* **37** 1155
- [25] Halperin B and Varma C 1976 *Phys. Rev. B* **14** 4030
- [26] Vugmeister B and Glinchuk M D 1990 *Rev. Mod. Phys.* **62** 993
- [27] Yacoby Y and Girshberg Ya 2000 *Fundamental Physics of Ferroelectrics 2000 (AIP Proc. vol 535)* ed R E Cohen (New York: American Institute of Physics Press) p 56
- [28] Kleemann W, Dec J, Wang Y G, Lehnen P and Prosandeev S A 2000 *J. Phys. Chem. Solids* **61** 167
- [29] Bersuker I B 1989 *Vibronic Interaction in Molecules and Crystals (Springer Series in Chemical Physics)* (Berlin: Springer)
- [30] Kristoffel N N and Konsin P 1988 *Phys. Status Solidi b* **149** 11 and references therein
- [31] Girshberg Ya G and Tamarchenko V I 1976 *Fiz. Tverd. Tela* **18** 1066 (Engl. Transl. 1976 *Sov. Phys.—Solid State* **18** 609)
- Girshberg Ya G and Tamarchenko V I 1976 *Fiz. Tverd. Tela* **18** 3340 (Engl. Transl. 1976 *Sov. Phys.—Solid State* **18** 1946)
- [32] Cohen R E 1992 *Nature* **358** 136
- [33] Bursian E V, Girshberg Ya G and Starov E N 1971 *Phys. Status Solidi b* **46** 529
- [34] Bernasconi P, Biaggio I, Zgonik M and Gunter P 1997 *Phys. Rev. Lett.* **78** 106
- [35] DiDomenico M Jr and Wemple S H 1968 *Phys. Rev.* **166** 565
- [36] Tsukioka M, Nagata E, Ehara S and Tanaka J 1986 *Japan. J. Appl. Phys.* **25** 918
- [37] Bottger H and Bryksin V V 1966 *Phys. Status Solidi* **78** 9
- Bottger H and Bryksin V V 1966 *Phys. Status Solidi* **78** 415
- [38] Fontana M D, Metrat G, Servoin J L and Gervais F 1984 *J. Phys.: Condens. Matter* **16** 483
- [39] Streitwolf H W and Mertsching J 1973 *Phys. Status Solidi b* **55** 225
- [40] Wemple S, DiDomenico M Jr and Jayaraman A 1969 *Phys. Rev.* **80** 547
- [41] Vogt H and Uwe H 1984 *Phys. Rev. B* **29** 1030
- [42] Lang I and Firsov Yu 1963 *Sov. Phys.—JETP* **16** 1301
- [43] Bottger H and Bryksin V V 1974 *Phys. Status Solidi b* **64** 449
- [44] Vaks V G 1973 *Introduction to the Microscopic Theory of Ferroelectricity* (Moscow: Nauka) (in Russian)
- [45] Kobayashi K K 1968 *J. Phys. Soc. Japan* **24** 497
- [46] Gomez M, Bowen S R and Krumhansl J A 1967 *Phys. Rev.* **153** 1009
- [47] Firsov Yu A (ed) 1975 *Polarons* (Moscow: Nauka)
- [48] Wemple S H 1965 *Phys. Rev.* **137** A1575
- [49] Sokoloff J P, Chase L L and Rytz D 1988 *Phys. Rev. B* **38** 597