

**Zeitschrift:** Helvetica Physica Acta  
**Band:** 62 (1989)  
**Heft:** 6-7

**Artikel:** Phase transition and ionic displacements in doped potassium tantalates  
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**DOI:** <https://doi.org/10.5169/seals-116060>

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## PHASE TRANSITIONS AND IONIC DISPLACEMENTS IN DOPED POTASSIUM TANTALATES

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**Abstract :** When  $\text{KTaO}_3$ , that is structurally stable down to at least 1.6 K, has a few percent of K or Ta substituted by other ions, disordered and unstable crystals result. Here mainly NMR data on the local ionic motion accompanying the phase transitions in these systems without strict translational symmetry are reviewed. Some results from non-local (optical, dielectric) techniques are also mentioned.

### Introduction

Certain materials that we usually think of as crystals can occur in phases that lack translational periodicity : e.g. in incommensurate systems, a local atomic property is spatially modulated with a period that is not an integral multiple of the underlying unit cell dimension. Magnetic resonance methods have contributed much to the microscopic understanding of these phases [1].

During the last years, our groups and others have been working on phase transitions in disordered crystals, that lack translational symmetry due to ionic substitution. We have studied crystals of  $\text{KTaO}_3$  with percent-level substitution of Nb for Ta ( $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$  or KTN), of Li for K ( $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$  or KTLi), of Na for K ( $\text{K}_{1-x}\text{Na}_x\text{TaO}_3$  or KTNa). One should stress that the substitutional ions are not "dirt", even if we call them often impurities, but sources of collective effects without translational symmetry. Some experiments will see the substitution as "symmetry conserving", just modifying an effective, uniform crystal. Other

experiments will see "symmetry breaking", up to the point where the underlying crystal merely serves to transmit impurity-impurity (cluster-cluster) interactions. Clearly, in many experiments both aspects are present [2].

Here, we focus on a description of ionic displacements in KTLi, KTNa and KTN obtained mainly by nuclear magnetic resonance (NMR) of  $^7\text{Li}$ ,  $^{23}\text{Na}$ ,  $^{39}\text{K}$ ,  $^{93}\text{Nb}$  and  $^{181}\text{Ta}$ . These nuclei all have an electric quadrupole moment, and therefore their NMR frequencies (spectra) are sensitive to displacements away from sites of cubic symmetry. The timescale over which an NMR observation "integrates" is in the microseconds to milliseconds range : modulation of the electric quadrupole interaction at a rate faster than that will give a cubic spectrum; but at the same time it will become visible in the spin-lattice relaxation time  $T_1$ . This short review cannot be self-contained : for details the original papers cited should be consulted.

#### **$\text{K}_{1-x}\text{Li}_x\text{TaO}_3$ (KTLi)**

In optical depolarization experiments,  $T_c$ -values of 30 K and higher have been found for  $x \geq 0.015$ . An X-ray study [3] at 10 K found  $|c/a-1| < 2 \times 10^{-4}$  and  $\alpha = \beta = \gamma = 90^\circ \pm 0.01^\circ$  for  $x = 0.016$ ; but a tetragonal structure with  $c/a-1 = (13.8 \pm 0.5) \times 10^{-4}$  for  $x = 0.05$ . For the  $x = 0.016$  sample, the depolarization -  $T_c$  has been confirmed by a (very small) softening effect on the spin-lattice relaxation times of  $^7\text{Li}$  and  $^{181}\text{Ta}$  [4]. Such results indicate a "symmetry-conserving" character for the substitutional impurity, and an "effective crystal" description of the transition.

The  $^7\text{Li}$  NMR spectrum [5] on the other hand suggests a strongly symmetry-breaking character : below 50 K, a very nicely resolved seven-line spectrum shows that the Li ions are distributed over six equivalent off-center positions. From the observed line splittings, an off-center distance of 1.26 Å has been deduced. Above 50 K the spectrum disappears, not due to a phase transition, but because of increasingly fast thermal hopping, as shown by  $T_1$ . In NMR one says that "on the average" the ion is in a cubic position, although actually at no single moment

the ion is there. All NMR data are dominated by this single-particle hopping behaviour, and show little influence of collective dynamics in the impurity system. Dielectric data however show a glassy type of kinetics in addition to the single-particle jumping [6].

### **$K_{1-x}Na_xTaO_3$**

Optical depolarization has given values of  $T_c$  above 10 K for  $x \geq 0.12$ . For  $x = 0.18$ ,  $T_c \cong 18$  K. For  $x > 0.20$  it becomes increasingly difficult to prepare homogeneously substituted samples : it is thought that regions of pure  $NaTaO_3$  (cubic perovskite only above 930 K) might occur.

No single-particle symmetry breaking (as in  $KTaLi$ ) is found from  $^{23}Na$  NMR spectra [7]. Below 150 K, but far above  $T_c$ , spin-lattice relaxation times  $T_1$  for NMR frequencies  $\omega_0/2\pi$  between 10 and 20 MHz are  $x$ - and  $\omega_0$ -dependent, due to the correlated motion of pretransitional clusters. In terms of the local potential seen by the Na-ions, the clusters cause strong anharmonicity, but the amplitude of thermal motion remains larger than the separation of the off-center minima of the potential. This temperature- and frequency region has not yet been studied by dielectric relaxation spectroscopy.

At 4.2 K, and for  $x \cong 0.18$  but not for  $x = 0.05$ , a resonant spin-lattice relaxation process occurs at  $\omega_0/2\pi = 14$  MHz. The phenomenon disappears rapidly with increasing temperature [8]. Among several possible explanations, coherent lattice motion, such as tunnelling, seems the most likely. Dielectric relaxation spectroscopy has not yet been performed with sufficient spectral resolution; but very recent ultrasound experiments below 1 K give support to this idea [9].

Dielectric experiments [2] and NMR recovery laws [7] have indicated metastability and history-dependent effects.

### **$KTa_{1-x}Nb_xO_3$**

For  $x > 0.008$ , optical depolarization experiments have given  $T_c$  values of 18 K and above. A softening of the lattice at these

$T_c$ 's has been found from NMR  $T_1$  measurements on  $^{39}\text{K}$ ,  $^{93}\text{Nb}$  and  $^{181}\text{Ta}$  [10,11]. Soft modes have been determined from neutron [12] and hyper-Raman [13] scattering. All these data can be interpreted in a symmetry-conserving, "effective crystal" approach, and lattice-dynamical models thus based can be fitted very well to the optical data.

Static NMR data do show, however, that the situation in the low-T phase is more complicated. While the lineshape of the  $^{93}\text{Nb}$  NMR can be understood as caused by all Nb-ions going off-center at  $T_c$  (similar to what happens e.g. in  $\text{KNbO}_3$ ), the behaviour of the  $^{181}\text{Ta}$  resonance is more peculiar : at  $T_c$ , most Ta-ions go off-center, but an x-dependent T-independent fraction of them does not. Otherwise stated : certain regions of the crystal yield a visible  $^{181}\text{Ta}$  NMR signal whereas others do not. The visible regions have a (nearly) vanishing deviation from (local) cubic symmetry : the Ta ions stay centered in their unit cells. From the x-dependence, it is found that about 100 unit cells are distorted around each Nb ion. It is suggestive that the reciprocal of this number is about equal to the fractional substitution required to obtain a non-zero  $T_c$ . These data show that the local order parameter in KTN is non-uniform.

Certainly the distortions of the lattice (believed to be rhombohedral [14]) are very small : at 10 K, X-ray experiments [3] for  $x = 0.017$  give  $a = b = c = 3.984 \pm 0.0008 \text{ \AA}$  and  $\alpha = \beta = \gamma = 90 \pm 0.001^\circ$ . In comparison, rhombohedral  $\text{KNbO}_3$  [15] has  $a = b = c = 4.016 \text{ \AA}$  and  $\alpha = \beta = \gamma = 89.817^\circ$ . In all phases of  $\text{KNbO}_3$  the off-centering of Nb with respect to the K-cage stays below  $0.1 \text{ \AA}$ .

## Conclusion

In phase transitions in disordered crystals, even more than in incommensurate systems, the local information, available from NMR, is an important complement to the "global" (optical, dielectric) data. The best example treated here is the inhomogeneous order parameter (Ta displacement) in KTN (qualitatively the same phenomenon has been observed in  $\text{KTLi}$  and  $\text{KTNa}$  : in these cases we have been unable to quantify, however); but also the only direct

observation of the Li-off-centering in KTLi is by NMR. The disordering dynamics and a coherent motion (tunnelling ?) indicated by  $^{23}\text{Na}$  NMR in KTNa, although requiring confirmation by other techniques, are further examples of unusual dynamics that can be detected by NMR.

### Acknowledgments

Collaboration by D. Rytz, S. Rod, S. Torre and M. Maglione in one or more phases of work reviewed here is gratefully acknowledged. M. Corti, J. Savoie and A. Vonnez are thanked for their experimental assistance.

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