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To cite this version:
O. Hanskepetipierre, E. Stern, Y. Yacoby. EXAFS MEASUREMENTS ON POTASSIUM TANTALATE NIOBATE. Journal de Physique Colloques, 1986, 47 (C8), pp.C8-675-C8-680. <10.1051/jphyscol:19868127>. <jpa-00226026>

HAL Id: jpa-00226026
https://hal.archives-ouvertes.fr/jpa-00226026
Submitted on 1 Jan 1986

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EXAFS MEASUREMENTS ON POTASSIUM TANTALATE NIOBATE

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Introduction

In this paper we discuss the application of EXAFS for the investigation of the fundamental nature of ferroelectric phase transitions in oxygen perovskite crystals. For many years oxygen perovskites were thought to be displacive ferroelectrics. However, in recent years different experiments cast serious doubts on this description [1-5]. Diffuse X-ray experiments on several oxygen perovskite materials [1] show that some sort of disorder exists in all but the rhombohedral phase. To explain their experimental results Comes et al [1] suggest that the cations (for example Nb in KNbO₃) are displaced in the [111] type directions in all phases including the cubic phase and the different phases are obtained as a result of correlation in the directions in which these ions are displaced.

The first experiments to show that some constituents in mixed perovskites are off-center in the paraelectric phase were Raman experiments [2]. In particular in KTaO₃:Nb [3] it was shown that in the paraelectric phase despite the selection rule, which forbids first order Raman scattering, first order Raman lines are observed. Moreover, the intensity of these lines is temperature dependent and it is consistent with the theory of Halperin and Varma [7]. These experiments show that the Nb ions are displaced already in the paraelectric phase, the displacement being dynamical namely the ions move from one equivalent position to another in a time which is short compared to laboratory time, but long compared to Raman interaction times, namely \( \tau > 10^{-11} \) sec. The object of the EXAFS experiments discussed here was to measure the temperature dependence of the magnitude and the direction of the displacement of the Nb in KTaO₃:Nb.
Experimental Results

Simultaneous transmission and fluorescence measurements were made on a powdered sample of \((\text{K-Ta}_0 \cdot 91\text{Nb}_0 \cdot 09)\text{O}_3\) at the Nb K-edge, at the temperatures of 70K, 78K, 90K, 130K, 200K and 300K. The lowest three temperatures are each in one of the three ferroelectric phases of KTN [7] namely the rhombohedral, orthorhombic and tetragonal, respectively. The upper three are in the paraelectric phase. The choice of temperatures permits a separation of the temperature dependence between phase transition effects and ordinary thermal vibration effects. Measurements were also made on the Ta L3-edge of KTaO3 and on the Nb K-edge of NbO to be used as standards in the interpretation of KTN.

![Fourier transform of \(k^2\chi(k)\) as a function of \(k\). Also shown is the window function used in order to filter out the first shell.]

The fluorescence data was of higher quality than the transmission data, so the final analysis was concentrated on the fluorescence data. Standard analysis techniques [8] were applied to obtain the normalized EXAFS absorption \(\chi(k)\) of the Nb K-edge over the k-range 1.8-15.3 \(\AA^{-1}\). The zero was set at the middle of the edge. The magnitude of the \(r\) space Fourier transform of \(k^2\chi(k)\) is shown in Fig. 1. The various peaks are well above the noise even out to 8 \(\AA\). The first peak is due to the Nb probe nearest neighbour oxygen atoms. This peak is the only well separated one and is the one we discuss here. It was isolated by the window function shown in Fig. 1 and back transformed into \(k\)-space. The back transform is given by the equation:

\[
X_1(k) = B(k) \cdot \frac{g(r)}{r^2} \cdot \exp[-2(r-\Delta)/\lambda] \cdot \sin(2kr+\delta(k)) \cdot dr \quad (1)
\]

Here \(B(k)\) is the back scattering amplitude for the oxygen shell and \(\delta(k)\) is the phase shift. \(g(r)\) is the distribution function of Nb-O pair distances and \(\lambda\) is the mean free path. To eliminate \(B(k)\), \(\delta(k)\) and \(\exp[-2(r-\Delta)/\lambda]\) from eq. (1) we have used the standards. The KTaO3...
standard was used to obtain $B(k) \exp[-2(r-A)/\lambda]$ while the NbO standard 
was used to determine $\delta(k)$. After eliminating these functions we 
obtained:

$$\chi_1^2(k) = \int \frac{g(r)}{r^2} \sin(2kr)dr = A(k) e^{i\phi(k)} \tag{2}$$

The NbO standard was not suitable for obtaining $B(k)$ because it had an 
unknown stoichiometry so the average coordination number of oxygens 
around the Nb is unknown. However, the lattice constant is still known 
and thus so is the average Nb-O distance permitting a determination of 
$\delta(k)$. Figures 2 and 3 plot the determined $A(k)$ and $\phi(k)$ in Eq.2 
respectively. The solid line is the average and the dashed lines display the 
range of error as a function of $k$. If $g(r)$ were $\delta(r-r_0)$, $A(k)$ 
and $\phi(k)$ would be constant. Actually, $A(k)$ displays a strong minimum 
characteristic of a beat between two or more nearly equal distances 
and $\phi(k)$ displays a rather fast change of phase also characteristic of 
such beat.

The measurements at all the temperatures mentioned above were ana-
yzed in the same manner. The results were found to be the same as at 
70 K within the experimental errors shown in Figs. 2 and 3.

**Fig. 2:** The amplitude function obtained by the back Fourier transforma-
tion and the first shell. In this the curve the back reflection function 
b(k) and the attenuation of the electron wave function $\exp[-2(r-A)/\lambda]$ have 
already been divided out. The amplitude function - solid line; the error 
brackets - dashed lines; the fit corresponding to [110] type displacements 
(eq.6) - crosses; The fit corresponding to [111] type displacements (eq.7) 
- circles.

**Fig. 3:** The phase function after removal of the NbO-phase function - solid line. The 
error brackets - dashed lines.
Discussion

We consider first the qualitative effect that a displacement of the Nb ion would have on the amplitude and phase functions. We assume that the displacement is in one of the main crystalographic directions. If the displacement is in the [111] direction, three of the oxygens will have a shorter distance while the other three will be at a longer distance. In this case:

\[ g(r) = 3\delta(r - r_0 + \Delta R) + 3\delta(r - r_0 - \Delta R) \]  

Eq. [2] can then be represented by the sum of two phasors rotating in opposite directions, as shown in Fig. 4. The amplitude function will have a beat at \( k \Delta R = \pi / a \). Similarly the phase function will have a jump of \( \pi \) radians at \( k \Delta R = \pi / a \). If the displacement is in the [110] direction:

\[ g(r) = 2\delta(r - r_0) + 2\delta(r - r_0 + \Delta R) + 2\delta(r - r_0 - \Delta R) \]  

The amplitude function has a beat at \( \pi / 3 \) and the phase function a jump of \( \pi \) radians at \( k \Delta R = \pi / 3 \). On the other hand if the displacement is in the [100] direction:

\[ g(r) = 4\delta(r - r_0) + \delta(r - r_0 + \Delta R) + \delta(r - r_0 - \Delta R) \]  

In this case there is no beat in the amplitude function and no change in the phase.

We have fitted the amplitude function in Fig. 2 with two distribution functions. The first corresponds to a displacement in the [111] type directions:

\[ g_1(r) = \exp\left[-(r-r_0)^2/2\sigma_1^2\right] \left[ 3\delta(r - r_0 + \Delta R_1) + 3\delta(r - r_0 - \Delta R_1) \right] \]  

Here we represent the zero point and thermal vibrations by a Gaussian. Strictly speaking, this representation is not really adequate in these materials. The fit is represented by the circles in Fig. 2. In this case \( \Delta R_1 = 0.086 \text{ Å} \) and \( \sigma_1^2 = 3.68 \times 10^{-3} \text{Å}^2 \). Here \( \Delta R \) is the projection of the actual displacement onto the [100] type direction. Thus the actual displacement \( \Delta R_{[11]} = \Delta R_1 \times \sqrt{3} = 0.15 \text{Å} \). The second distribution function assumes that the displacements are in the [110] type directions:

\[ g_2(r) = \exp\left[-(r-r_0)^2/2\sigma_2^2\right] \left[ 2\delta(r - r_0) + 2\delta(r - r_0 - \Delta R_2) + 2\delta(r - r_0 + \Delta R_2) \right] \]  

(7)
The fit in this case is represented by the crosses in Fig. 2. The fit yields $\Delta R_s = 0.115 \text{ Å}$ and $\sigma_s^2 = 2.18 \cdot 10^{-3} \text{ Å}^2$. The actual displacement in the [110] type directions would then be $R_{[110]} = \Delta R_s / \sqrt{2} = 0.16 \text{ Å}$.

As seen from Fig. 2, the two possibilities cannot be distinguished from each other. The fact that within experimental accuracy the experimental results are temperature independent all the way up to room temperature, leading to two conclusions: a) The Nb ions are displaced off-center in the paraelectric phase. b) That the potential well walls are rather steep.

Combining the experimental results of X-ray diffraction, Raman spectroscopy and EXAFS, we arrive at the following conclusions. At 70° K the structure of $\text{K}Ta_{0.91}\text{Nb}_{0.09}\text{O}_3$ is rhombohedral [7]. Therefore, at this temperature we know from X-ray diffraction that the Nb ions are displaced in the [111] direction. The magnitude of this displacement as measured from EXAFS is 0.15 Å. This value is slightly smaller than the displacement of 0.18 Å measured by neutron scattering from pure $\text{KNbO}_3$ [9]. The displacement of the Nb ions does not change at least up to room temperature, thus it is quite likely that the ions are displaced in the [111] type directions also in the paraelectric phase. The fact that first order Raman lines are observed in the paraelectric phase means that the hopping time of the Nb ions among equivalent positions is longer than $10^{-11}$ sec. This is inspite of the fact that $\sigma$ is such that the Nb ions have a significant probability of being in the center position. Apparently when the ion is off-center the potential function is slightly distorted, so that the other equivalent positions have a slightly higher energy. The intensity of these
Raman lines decreases with temperature not because the Nb ions go on center, but because the polarization of the intermediate matrix material, namely the KTaO$_3$ becomes less polarizable as described by the Halperin and Varma theory. It is also possible that at high temperatures much higher than the P.T. temperature the hopping time becomes shorter. In this case the Raman scattering would disappear because the position will be effectively centrosymmetric.

At the phase transition the average displacement of the Nb ions becomes non zero together with a non zero polarization of the host lattice. Therefore, this system is neither a pure displacive nor a pure order disorder system.

In conclusion, EXAFS seems to be a vary powerful tool in providing quantitative microscopic structural information in oxygen perovskite type mixed crystals. Thus together with other techniques it would be an important means in understanding the fundamental nature of phase transitions in these systems.

Acknowledgement

This work has been partially supported by the U.S. Israel Binational Science Foundation and by US DOE contract DE ASOS-ER/0742.

References