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Polarized XAFS study of the atomic displacements and phase transitions in $KNbO_3$

Victoria A.Shuvaeva[a,b], Koichiro Yanagi[b], Kenichiro Yagi[b], Kiyoshi Sakaue[b] and Hikaru Terauchi[b]

[a]Institute of Physics, Rostov State University, Stachki 194, Rostov-on-Don, 344090, Russia, and [b]School of Science, Kwansei-Gakuin University, Uegahara, Nishinomiya 662, Japan. E-mail: vshuvaev@uic.rnd.runnet.ru

Polarized XAFS technique has been applied for the determination of the directions and the values of the Nb displacements relative to the centers of oxygen octahedra in $KNbO_3$. The temperature dependence of the both EXAFS and XANES spectra were analyzed in order to reveal the role of disorder in the phase transitions of this compound. The polarized XAFS appeared to be enough sensitive to detect the delicate balance between order-disorder and displacive mechanisms of the phase transitions in $KNbO_3$. The magnitude of the pre-edge peak on the Nb K-XAFS spectra was found to be highly correlated with the value of the Nb off-center displacement, obtained by fitting of the EXAFS spectra.

Keywords: polarized XAFS; local structure; ferroelectrics; KNbO3; phase transitions.

1. Introduction

The crystal structure of $KNbO_3$ is under discussion for several decades. Numerous evidences of existence of the structural disorder have been obtained via various experimental techniques (Comes et al., 1968; Kwei et al., 1995; Dougherty et al., 1995). On the other hand the displacive nature of the phase transitions in this compound also gained solid experimental support (Holma et al., 1995; Shuvaeva & Antipin, 1995, Shuvaeva et al., 1997). According to the displacive model of phase transitions, the Nb atoms should be displaced from the centers of oxygen octahedra along polar axes in orthorhombic and tetragonal ferroelectric phases and should be located at the centers of octahedra in the cubic phase. The disorder would result in the additional Nb shift orthogonal to the polar axis directions $\Delta_\perp$ and off-center displacement in cubic phase. The aim of this study is to refine the Nb positions in orthorhombic, tetragonal and cubic phases and to establish mechanisms of the phase transitions in this compound using the advantages of polarized XAFS. This technique allows to determine the Nb shifts along main perovskite axes independently and thus to avoid the ambiguity in the results of analysis of XAFS obtained from powder samples of perovskite compounds (Bell et al., 1991; de Mathan et al., 1993; Bugaev et al., 1997; Frenkel et al., 1997). Both EXAFS and near-edge structure were used for the determination of the atomic shifts.

2. Experimental

Spectra from $KNbO_3$ single crystals of about 1.5×1.5×0.015 mm in size were measured in a transmission mode at BL-10B and 7C Photon Factory of National Laboratory for High Energy Physics (Tsukuba), using a Si(111) crystal monochromator. Ring energy and current were 2.5 GeV and 300 mA, respectively. Spectra were obtained at about 20 temperature points in the range from 20 to 460 ° C. The crystal was aligned to coincide the vector of X-ray polarization e with one of the main perovskite directions which were parallel to the crystal faces. Polarization measurements were made with sample oriented in two different ways, so that orientation of the vector of ferroelectric polarization P relative to e was: in orthorhombic phase P⊥e and P^e=45°, in tetragonal phase P⊥e for the both sample orientations. More details on the experiment and data analysis can be found in (Shuvaeva et al., 1997, Shuvaeva et al., 1998) and in the XAFS-X experimental database.

3. EXAFS

According to both alternative order-disorder and displacive models of phase transitions in $KNbO_3$, Nb off-center shift orthogonal to the polar axis direction $\Delta_\perp$ should be constant in all phases. However the displacive model assumes that $\Delta_\perp$ is equal to 0, while order-disorder eight-site model, proposed by Comes et al., 1968, predicts that its value is quite essential.

At the Fig 1 absolute parts of Fourier transforms of EXAFS for orthorhombic, tetragonal and cubic phases are shown. Strong difference of the FT peaks in the range between 1 and 2 A is clearly seen. These peaks are due to the oxygen atoms and strongly depends on the Nb off-center displacement Δ in the corresponding direction. Fitting of the spectra provided the following values of Δ:

orthorhombic phase	(T=20 C),	P^e=45°	$\Delta_{\angle O}$=0.15Å
orthorhombic phase	(T=20 C),	P⊥e	$\Delta_{\perp O}\leq$0.055Å
tetragonal phase	(T=260 C),	P⊥e	$\Delta_{\perp T}$=0.085Å
cubic phase	(T=430 C),		$\Delta_{\perp C}$=0.11Å

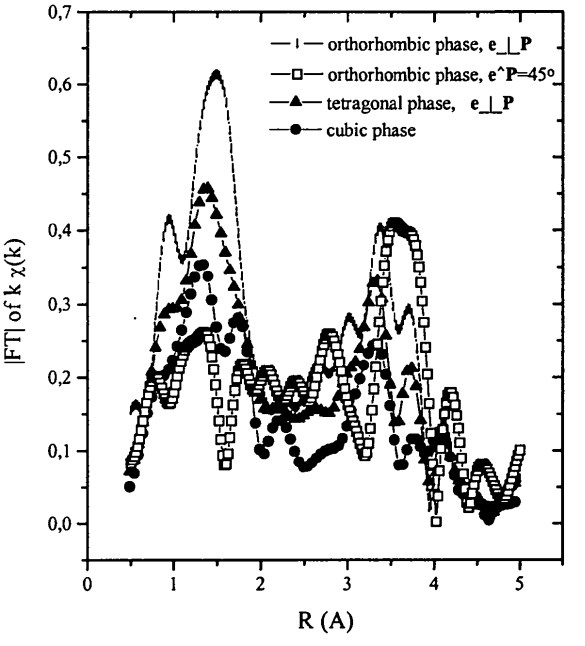

Figure 1
Absolute values of k-weighted Fourier transforms of the Nb K XAFS for the orthorhombic, tetragonal and cubic phases of $KNbO_3$

It can be seen that in the orthorhombic phase the displacement along the polar axis is much larger than in the orthogonal direction, and spectra can be successfully fitted in the frame of the displacive model, which assumes that $\Delta_\perp$ is equal to zero in all phases. In tetragonal and cubic phase the «disorder» component $\Delta_\perp$ of the Nb shift is much more essential. Strong difference of $\Delta_\perp$ in different phases is in contradiction with the both models of phase transitions in $KNbO_3$ and indicate quite complicated crossover of order-disorder and displacive behavior.

4. The near edge structure

Recently the new probe for atomic displacements from symmetrical positions has been proposed (Vedrinskii et al., 1997; Skeath et al., 1987). It has been shown that the pre-edge peak at the K-XAFS of transition metal atoms, originated from 1s electron transition to the unoccupied d bands of crystals, strongly depends on the symmetry of the atoms position. If the atoms are situated at the inverse symmetry center then the transition is dipole forbidden and the amplitude of the peak is equal to 0. The off-center displacement causes the increase of the amplitude of the peak. This approach has been successfully applied to the investigation of the displacement of Ti in $PbTiO_3$ and $BaTiO_3$ (Skeath et al., 1987; Ravel et al., 1998). Nb is 4d transition metal, so we attempted to apply the same approach in order to study its displacements in $KNbO_3$.

At the Fig. 2 uniformly scaled $KNbO_3$ XANES spectra for orthorhombic, tetragonal and cubic phases are shown. It can be seen that the pre-edge peak is not resolved, but the difference between the spectra on the slope of the edge is seen clearly. It can be seen, that the higher curves correspond to the higher values of the Nb displacement.

We chose the spectra for room temperature and e⊥P which appeared to have the lowest values in the pre-edge region to be a baseline and calculated the difference curves between other spectra and this one. The difference curves had quite pronounced peak in the pre-edge region. The temperature dependence of the integral intensity of this peak for two orientation of the crystal is shown at the Fig.3. It can be seen that the values of these intensities and hence the corresponding Nb displacements change abruptly at the phase transition points. The significant difference of these values for two orthogonal orientations of the crystal in orthorhombic phase is in agreement with the displacive model. On the other hand the abrupt strong increase of the «disorder component» of the displacements during the phase transitions to the high temperature phases shows that the disorder play quite important role at high temperatures. Cubic phase appears to be essentially disordered. The last result is in agreement with earlier XAFS studies of $KNbO_3$ (Bell et al., 1991). It should be noted that polarized XAFS study of tetragonal and cubic phases of $BaTiO_3$ led to similar conclusions (Ravel et al., 1998).

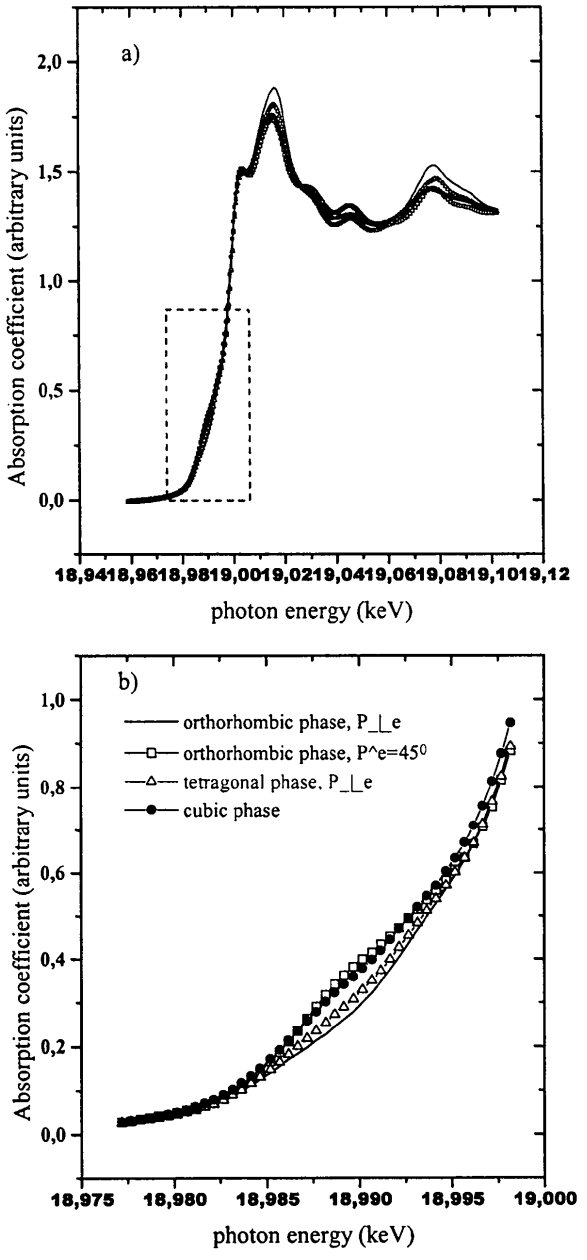

Figure 2
a) Nb K XANES and b) the pre-edge region for the orthorhombic, tetragonal and cubic phases of $KNbO_3$

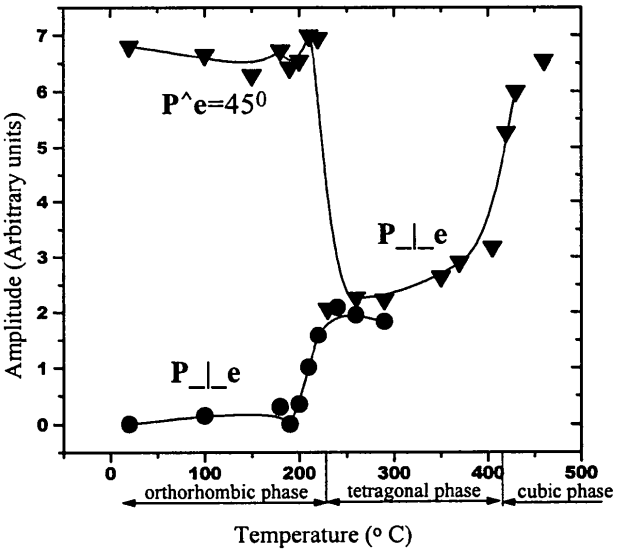

Figure 3
Temperature dependence of the integral intensity of the pre-edge peak

5. Conclusions

Both EXAFS and near edge structure analysis enable us to make the following conclusions on the structure and the phase transitions in $KNbO_3$:

1. At high temperatures the disorder play much more important role than at low temperatures. In the orthorhombic phase the «disorder component» of the Nb displacement is not essential and even hardly can be clearly detected. In the tetragonal and especially in the cubic phase the Nb positions are essentially disordered. The «disorder component» increases abruptly at the phase transition points.
2. The phase transitions have both order-disorder and displacive components. Both number of the Nb sites and their location within oxygen octahedra change in the phase transitions points.

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