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The regular approach for identifying the atomic displacements in ABO_3 crystals and its application to high-temperature phases of $KNbO_3$

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The approach for identifying the atomic displacements from the ideal positions in perovskite structure is proposed, based: on characteristic features in the Fourier Transforms (FT) for different models of atomic displacements and on the results of EXAFS calculations for alternative models of ideal structure distortions, generated using the value of averaged atomic displacement provided by diffraction methods. The approach is applied to study the local structure distortions in tetragonal and cubic phases of KNbO3. The effect of anharmonic motion of atoms on the obtained structure information is simulated through the cumulant expansion.

Keywords: EXAFS; local structure; ferroelectrics; $KNbO_3$; anharmonicity.

1. Introduction

The crystalline structure and phase transitions in perovskite type ABO_3-compounds are studied intensively. In spite of the simple enough crystalline structure, the presence of local structure distortions and disorder was revealed (Comes *et al*, 1968), especially in the high-temperature phases of ABO_3. However, the type of these distortions and the character of corresponding phase transitions often remain undetermined due to the controversy in different experimental data, obtained by diffraction methods, EPR and Raman spectroscopies and ambiguity in these data interpretation. The main difficulty is that the traditional diffraction methods give the averaged values of atomic displacements from the ideal sites in lattice. The most reliable information on local structure distortions can be obtained using EXAFS-spectroscopy. Recently this method was intensively applied to structure determination in ABO_3 compounds and the EXAFS analysis reveals the presence of atomic displacements from the ideal sites even in high-symmetry cubic phase of $PbTiO_3$, $BaTiO_3$, $KTa_{1-x}Nb_xO_3$ (Stern & Yacoby, 1996; Sircon *et al*, 1994). However, as shown by Bugaev *et al*, 1997 the traditional EXAFS analysis of crystalline phases with low symmetry can lead to ambiguity in experimental data interpretation and hence severe mistakes in determination of values and directions of atomic displacements. The correct values may be obtained by polarized XAFS (Shuvaeva *et al*, 1998), but this experimental technique is quite sophisticated and not widely used in practice. To overcome these difficulties, a regular approach is proposed, based 1) on the revealed qualitative differences in imaginary parts of Fourier transforms (FT) of EXAFS spectra for different models of atomic displacements, shown (Bugaev *et al*, 1997) to be a sensitive probe for identification of such displacements and 2) on the results of EXAFS calculations for alternative models of ideal perovskite structure distortions, generated under the fixed value (Δ) of B-atom displacement projection on the polar axis, taken from the diffraction data for the analyzed phase. Using this approach, the local structure distortions in high-temperature (tetragonal and cubic) phases of $KNbO_3$ were studied. The description of EXAFS measurements for these phases can be found in Bugaev *et al*, 1998; Shuvaeva and Antipin, 1995.

The local structure distortions in these phases were simulated through the splitting of the 1-st oxygen octahedron around the absorbing Nb-atom into a number of subshells with radii R_{1j} (j is the number of the subshell) and coordination numbers (CN) - N_{1j}, corresponding to the direction and the value of Nb displacement from the center of this octahedron. Within each displacement model the parameters R_{1j} and N_{1j} were fixed by the Δ value obtained from the diffraction data.

2. Method of calculation

Information on radial atomic distribution (RAD) function obtained by EXAFS is usually extracted from the FT of the experimental spectrum - F(r) functions. In the following the $|F(r)|$ and Im F(r) of experimental Nb K-EXAFS weighted function $k\chi^{exp}(k)$ and the theoretical contribution into Nb K-EXAFS from scattering processes on the split O_6-octahedron - $k\chi^{th}(k)$, calculated for different distortion models, are compared within the O_6-octahedron r-range: 1.4<r<2.5 Å. When the 3-rd (Nb) -shell contribution is included into the analysis, the comparison is carried out also within the 3-rd shell r-range: 3.5<r<4.1 Å. The FT is performed within the k-range from k_{min}=3.5 to k_{max}=13 $Å^{-1}$. All FT are uncorrected for the phase shifts.

XAFS simulations were carried through the method of Hartree-Fock (HF) MT-potential generation (Bugaev et.al., 1991). The interstitial potential value E_{MT}=18965.0 eV, obtained within this method for $KNbO_3$, was fixed and used then as the beginning of the wave number $k=(0.262(E-E_{MT}))^{1/2}$. The HF scattering phase shifts and amplitudes permit to use the physically reasonable value of the reduction factor S_0^2=0.9. The electron inelastic losses were taken into account by the traditional form exp(-0.262 ΓR/k) and the thermal atomic motion - through the Debye-Waller (DW) factor with parameter σ^2. So within the proposed approach, the only variable parameters for each displacement model are σ^2 and Γ. They were varied in the wide physically reasonable regions and their final values were obtained from the best fitting of experimental F(r) by theoretical ones within each displacement model. To reduce the number of parameters in the fitting procedure, the reasonable assumption was used, taking the equal σ^2 values for all oxygen subshells, which simulate the splitting of the O_6-octahedron in the studied model. The experimental Nb K-EXAFS spectra for tetragonal and cubic phases were measured by lab XAFS-spectrometer (Bugaev *et al*, 1998).

3. Tetragonal phase of $KNbO_3$

The diffraction data on Nb displacement in this phase give the value Δ=0.15 Å along [100] direction (Darlington & Knight, 1994). Using this value, the following distortion models

were generated for Nb displacements : 1) along [100] direction (oxygen octahedron is split into 3 subshells with R_{1j}=1.88, 1.95, 2.03 Å); 2) along [211] direction (oxygen octahedron is split into 4 subshells with R_{1j}= 1.88, 1.93, 2.08, 2.18 Å); 3) along [111] direction (oxygen octahedron is split into 4 subshells with R_{1j} = 1.86, 1.89, 2.15, 2.19 Å).

The comparison of theoretical $|F(r)|$ and Im F(r) for these models with the experimental ones is presented in Fig.1. It can be seen that there are quite pronounced differences in the Im F(r) of spectra calculated for the studied displacement models. The

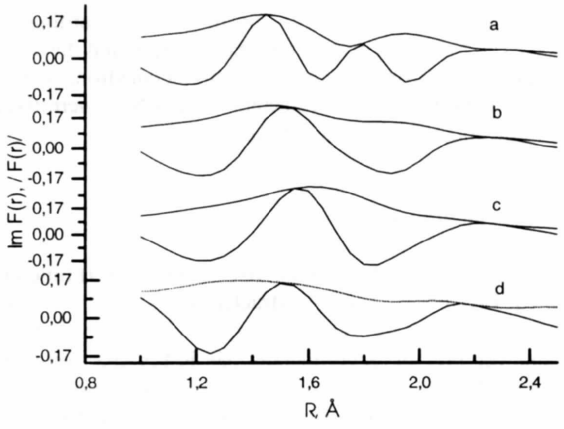

Figure 1. $|F(r)|$ and Im F(r) of experimental Nb K-EXAFS in tetragonal $KNbO_3$ (t=310 ^{0}C) - (d) and of $k\chi^{th}(k)$ for model 1 - (c), model 2 - (b), model 3 - (a).

variations of σ^2 and Γ in wide, physically reasonable regions, enable us to arrive at the conclusion: the successful fitting of experimental F(r) by theoretical ones, can be obtained only within one model of atomic displacement. Therefore the revealed strong differences in F(r) permits to choose the most appropriate model of atomic displacement (along [211] direction) through the qualitative comparison of the experimental and theoretical F(r) functions. At low r experimental F(r) contain an additional input, originated from the errors in μ_0(E) determination. However these inputs are known to appear at r ≤1 Å and do not affect the F(r) features within the r-range from 1.4 to 2.5 Å for the O_6-octahedron. As can be seen from Fig.1, the F(r) behavior in this r-range unambiguously indicates that in the tetragonal phase Nb is shifted closely to [211] direction from the center of the O_6-octahedron. The further refinement of the experimental data on the basis of this model gives the value of the shift to be equal to 0.19 Å. The results of the fitting procedure, carried out by variations of σ^2 and Γ, are reflected in the behavior of the discrepancy factor δ in diagram of Fig.2, taking its cross-section under the coefficient C_4 =0.

To extract reliable structure information from FT of EXAFS spectra one must be sure that the effect of anharmonicity in atomic thermal motion does not change dramatically the typical behavior of FT for different displacement models. Therefore the effect of anharmonicity on FT was simulated through the cumulant expansion (Tranguada & Ingalls, 1983) by variations of the C_4-coefficient value - making asymmetry in RAD-function for O_6-octahedron. The model calculations were carried out on the basis of $KNbO_3$ distances and CN, under the fixed values of all other parameters for $KNbO_3$, mentioned above. For $KNbO_3$ the value of C_3-coefficient in cumulant expansion was not varied, since we didn't observe significant changes in the position of the 1-st oxygen peak in the FT of Nb K-EXAFS within the wide temperature range (Bugaev *et al*, 1998).

The stability of the results, obtained above for the Nb displacement in tetragonal $KNbO_3$, is justified under all possible values of C_4 by the diagram for the discrepancy factor (δ) shown in Fig.2. It must be noted that the minimum in δ - is a conditional minimum relative to parameters R and N, which are fixed within each studied model of structure distortion by the diffraction data on the displacement projection on the polar axis. We have revealed also that under two different C_4 values one can obtain similar $|F(r)|$-functions, which correspond to different directions

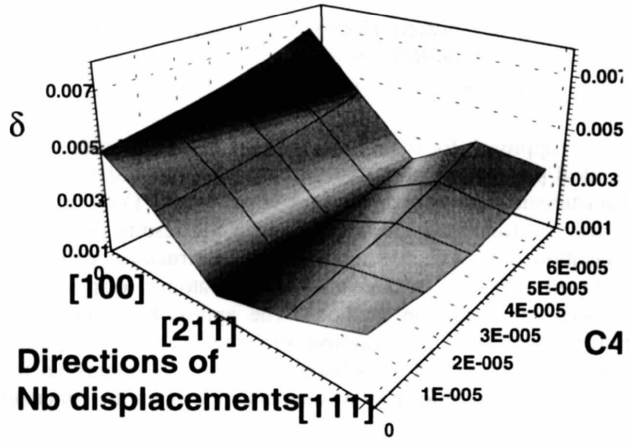

Figure 2. The diagram for discrepancy factor (δ) - averaged square deviation between theoretical and experimental F(r)-functions

of Nb-displacement. As a result the uncertainly in local structure determination takes place if the analysis is based on $|F(r)|$ only. However the strong difference in Im F(r) for these displacement directions remains under all possible C_4 values, which makes Im F(r) to be a reliable probe for B atom displacement identification, independent of radial distribution function asymmetry.

4. Cubic phase

According to the diffraction data, in cubic phase Nb is centered in the O_6-octahedron with Δ=0 Å (Darlington & Knight, 1994). Therefore the problem of identification of local distortions becomes more complicated and we can propose now only the most probable direction for B-atom displacement. To obtain more reliable results, the 3-rd Nb coordination shell has been also involved into the analysis, making the consistent description of the 1-st and 3-rd shells in $KNbO_3$ by fitting the values of distances and CN: R_{1j} , N_{1j} , R_{3j} , N_{3j} for these shells, within each displacement model analyzed. To study the local distortions in the cubic phase we have generated three alternative models for Nb displacements: 1) cubic model - Nb is centered in O_6-octahedron (oxygen shell is not split and R_1=2.02 Å); 2) tetragonal model - Nb is shifted along [100] direction (oxygen octahedron is split into 3 subshells with R_{1j}=1.83, 2.03, 2.21 Å); 3) rhombohedral model - Nb is shifted along [111] direction (oxygen shell is split into 2 subshells with R_{1j}=1.9, 2.15 Å).

The multiple-scattering (MS) paths: Nb - O (1-st oxygen octahedron) - Nb (3-rd shell) were revealed within every studied model of atomic displacement and calculations of corresponding MS-terms: double (DS) and triple (TS) photoelectron scattering processes were carried out using the spherical wave formalism (Vedrinskii. & Bugaev, 1988) Different DW-factors were taken

for single-scattering (SS) term and MS -terms for the 3-rd Nb shell and their values were found through the best fitting of experimental F(r) by calculated ones within each studied model, in the 3-rd shell r-region: 3.5<r<4.1 Å. To simplify the analysis, the following approximation was made, taking the same DW-factors for DS and TS-terms. The value of parameter Γ was taken to be the same as for the 1-st oxygen shell and then the photoelectron extrinsic losses were included by the factor exp(-0.262 ΓR/k), where R is SS, DS or TS pathway length respectively. The similarity of theoretical and experimental spectra was treated to be only a qualitative probe for choosing the best model of local distortions, within which the further fitting was performed.

Nb K-EXAFS calculations at high temperatures and comparison with the experiment have shown that the contribution of the 2-nd K-shell is small due to the strong amplitudes of

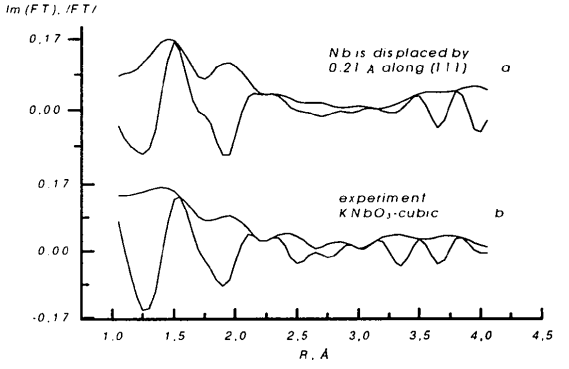

Figure 3. |F(r)| and Im F(r) of experimental Nb K-EXAFS in cubic $KNbO_3$ (t=440 ^{0}C) -(b) and of $k\chi^{th}(k)$ for rhombohedral model - (a)

thermal vibrations. This 2-nd shell is known to be split under the Nb atom displacement into a big number of subshells, with low signals into EXAFS, and their accurate description and analysis is a complicated problem, which needs an additional number of fitting parameters. However, calculations, carried out both including the SS-processes on the 2-nd shell and without them, show the quite similar F(r) behaviour in the r-region for the 3-rd Nb shell (3.5<r<4.1 Å). Therefore the theoretical kχ(k), used for FT-analysis, was calculated considering SS for theO_6-octahedron and SS and MS (Nb-O-Nb atomic chains) for the 3-rd Nb-shell. So, while performing the analysis of F(r) behaviour one must consider only the r-ranges for the 1-st shell (1.4<r<2.4 Å) and for the 3-rd Nb shell (3.5<r<4.1 Å).

The best agreement of theoretical |F(r)| and Im F(r) functions with the experimental ones was obtained within the model of rhombohedral local distortion in cubic phase. This comparison is presented in Fig. 3. As can be seen the agreement in ImF(r) is obtained both for the 1-st oxygen shell and for the 3-rd Nb-shell r-ranges. At the same time calculations show that the origin of disagreements in the intermediate r-region (2.5<r<3.5 Å.) - for example, peak in the experimental |F(r)| at r=3.25 Å. (see Fig.3), not observed in theoretical one, obtained without the 2-nd shell contribution, arises from the overlapping of the 2-nd (K) and the 3-rd (Nb) shells RAD functions.

According to the results of (Bugaev et al, 1997), the Im F(r) characteristic behaviour is a more sensitive probe than |F(r)| for B atom displacements identification. Therefore the agreement of Im F(r) oscillations in the 1-st and the 3-rd shells r-ranges, obtained only within the model of rhombohedral local distortions in cubic phase of$KNbO_3$, enables to choose this model as the most probable one for Nb displacement.

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