The double-well oscillating potential of oxygen atoms in perovskite system Ba(K)BiO$_3$: EXAFS – analysis results

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Abstract

Temperature-dependent X-ray absorption investigations were made on the Bi L$_3$-edge in Ba$_{1-x}$K$_x$BiO$_3$ with $x = 0.0$ h, 0.4 and 0.5. For the superconducting samples ($x = 0.4$ and 0.5) it has been found that the local structure differs from the ideal cubic in contrast to the neutron and X-ray diffraction data. The provided analysis of the EXAFS spectra indicates that the oxygen atoms move in double-well potential produced by the existence of two non-equivalent octahedral types of the oxygen environment of bismuth. The vibrations in such a potential lead to modulations of the Bi–O lengths with low frequency which is determined by the soft oxygen octahedron rotation mode frequency. This induces strong electron–phonon interaction and may be the reason for relatively high-temperature transition ($T_c \sim 30$ K) to the superconducting state. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Superconductivity in Ba$_{1-x}$K$_x$BiO$_3$ (BKB) system with $T_c = 30$ K is observed for K concentration $x > 0.37$ close to phase (metal–insulator) transition [1,2]. This transition corresponds to the structure changes leading to disappearance of static (frozen) distortions of breathing and rotational modes of oxygen octahedra, which are typical for parent compound BaBiO$_3$ with monoclinically distorted perovskite structure. The integral structure methods: X-ray diffraction and neutron diffraction show that BKB with $x > 0.37$ has simple cubic lattice with Pm3m symmetry [3]. However, EXAFS-spectroscopy, as a local sensitive method, reveals the presence of local tilting of oxygen octahedra around pseudocubic axes [1 1 0] or [1 1 1] on the angle 4–5° which may have static or dynamic character [4]. A number of experimental works argue in favour of dynamics (see Refs. [5–10]).

In current publication we report on the investigation of temperature-dependent EXAFS-spectra

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of BKB with $x = 0$; 0.4; 0.5 in the temperature range 5–300 K which points to the high anharmonicity of oxygen ion vibrations and their possible connection with superconductivity.

2. Experiment

The X-ray absorption measurements were performed on D21 beam line of DCI storage ring at Laboratoire pour l'Utilisation du Rayonnement Electromagnetique (LURE, Orsay, France) using Si [3 1 1] double-crystal monochromator. The storage ring was operated at positron beam energy 1.85 GeV and maximum current 300 mA. The energy resolution was estimated as 2 eV at 13 keV. Low-temperature measurements were carried out using liquid-helium circulation-type cryostat. The temperature was regulated by the helium flow and measured by carbon detector with an accuracy ~ 1 K.

3. Results and discussion

The experimental EXAFS-function of the first shell for superconducting $Ba_{0.6}K_{0.4}BiO_3$ obtained by back Fourier transform of Fourier-image of experimental spectrum using Hanning windows in the 1.0–2.1 Å range in real space is presented in Fig. 1(a). Comparison with harmonic model (see dashed curve) shows the presence of beating at 12–14 $Å^{-1}$ which specifies a highly anharmonic motion of oxygen atoms in the potential with complicated shape. To restore the form of potential we used the method of model EXAFS-function construction proposed in Ref. [11] to describe the strongly anharmonic vibrations of apical oxygen of $YBa_2Cu_3O_{7-\delta}$. As a basis for realising the potential, the model scheme of dynamic distortion of the BKB lattice was employed, taking into account the asymmetry of rotational mode (see Fig. 2), as suggested in Ref. [12].

EXAFS-studies revealed that Bi in $BaBiO_3$ is situated in two non-equivalent positions, characterized by both different lengths (static distortion of breathing type) and different strengths of Bi–O bonds. Different bond strengths in BiO_6 complexes
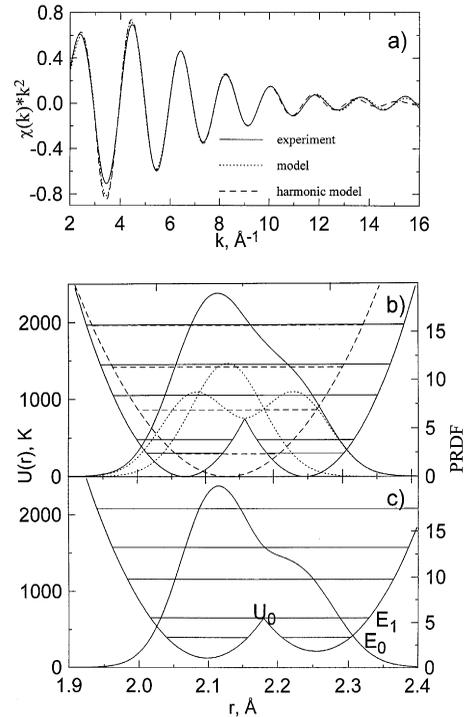

Fig. 1. Analysis of the first (oxygen) shell from Bi L_3 edge for $Ba_{0.6}K_{0.4}BiO_3$ at 7 K: experimental EXAFS function (solid line), model function (dotted line), model function in one sphere harmonic approximation (dashed line) — "a"; model potentials, PRDF and energy levels for the cases of independent — "b" and co-operative — "c" oxygen atom vibrations, correspondingly.

is caused by different electronic structure: $Bi(I)L^2O_6$ and $Bi(II)O_6$ where L^2 denotes the pair of holes in O 2p-orbital of octahedral oxygen neighbouring to Bi as proposed in Ref. [13] disproportionation model of Bi valence. (More accurately L^2 must denote pair of holes in strongly hybridized antibonding $6s(Bi)O2p_\sigma$-orbitals of octahedral complex.)

The substitution of every two Ba^{2+} ions by two K^+ ions creates complementary pair of holes in $6s(Bi)O2p_\sigma$ orbitals. The amount of small rigid octahedra (with hole pairs) increases according to the ratio between small and big octahedra in $Ba_{1-x}K_xBiO_3$ $(1 + x)/(1 - x)$. As a result, static distortions of breathing and rotational modes disappear, mean lengths of Bi–O bonds equalize, but, since Bi–O bond strengths remain different, bismuth positions will remain non-equivalent [12].
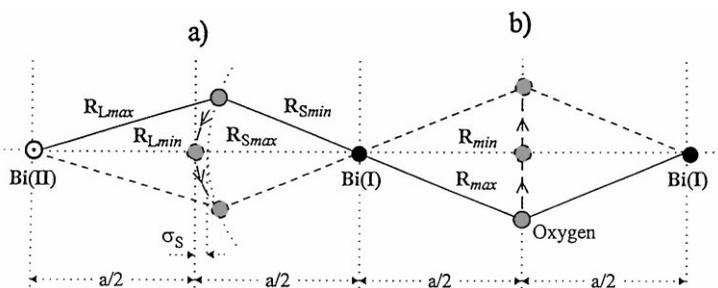
Fig. 2. Scheme of the local lattice dynamic distortions in $Ba_{0.6}K_{0.4}BiO_3$.

Dynamics of rotational oxygen vibrations is asymmetric relative to Bi atoms in the case of different types of $Bi(I)O_6$–$Bi(II)O_6$ octahedra contiguity (region "a" in Fig. 2) and symmetric in the case of two identical neighbouring $Bi(I)O_6$ octahedra (region "b" in Fig. 2).

In order to describe EXAFS-function in approximation of single scattering it is enough to consider the system of two atoms absorber–scatterer, expressing their mutual vibrations by vibration of particle with reduced mass in the potential which depends on the distance between them. For atom O in the region "b" this potential is harmonic due to equivalence of neighbouring octahedra complexes: $U_b(r) = A(r - x)^2/2$. For region "a" from Fig. 2: if the absorber is Bi(I), then the distance Bi–O is less than half of lattice parameter, if the absorber is Bi(II), Bi–O distance is greater than half of lattice parameter. As a result there are two maxima in the oxygen atoms distribution function relative to Bi atom for the first co-ordinate sphere, and potential has two minima, equidistant to the middle of Bi(I)–Bi(II) bond and can be described as double-parabolic: $U_a(r) = B(r - y)^2/2$ at $r < r_0$, $B(r - z)^2/2$ at $r > r_0$ where r_0 is defined from continuity conditions [11]. Then, finding eigenvalues of energy E_n and corresponding wave functions Ψ_n, we obtain pair radial distribution function (PRDF) of Bi–O atoms:

$$g(r) = N\sum|\psi_n(r)|^2\exp(-E_n/kT)/\sum\exp(-E_n/kT)$$

where N is the co-ordination number and estimate EXAFS-function as

$$\chi(k) = \frac{1}{k}\sum_{\text{"a","b"}}|F(k,\pi)|\int_{r_{min}}^{r_{max}} g(r)\sin(2kr + \phi_j(k))/r^2\,dr$$

where $\varphi(k)$ is the phase shift and $F(k)$ the scattering amplitude.

Model potentials with their self-energies and PRDF functions for BKB $x = 0.4$ at $T = 7$ K are shown in Fig. 1b in the case of independent motion of atoms in the region "a" and "b" from Fig. 2. However, rotational mode in the rigid octahedra model [12] causes coherent vibration of neighbouring oxygen atoms and, therefore, the system oscillates in the potential, obtained from the sum of potentials at the regions "a" and "b" with appropriate weights $(1 - x)$ and x correspondingly (see Fig. 1c). Model XAFS-function, constructed for such summarized potential (potential parameters were found fitting to experimental data) is illustrated in Fig. 1a as dotted line and almost coincides with the experimental one. In Fig. 1c PRDF function and the two lowest energy levels of the resulting double-well potential are also shown. It is worth to notice that considerably non-zero value of PRDF function at the barrier region points to the high tunnelling probability of oxygen atom, i.e. dynamic swapping of $Bi(I)O_6$–$Bi(II)O_6$ positions (herewith regions "a" and "b" are also mutually swapping and charge carrier pair is tunnelling from one octahedron to another). At low temperatures tunnelling between states $Bi(I)O_6 \leftrightarrow Bi(II)O_6$ has the highest probability at the moment of passing oxygen atom through Bi(I)–Bi(II) direction (the motion is due to rotational mode) because the distance between potentials minima is the smallest at this moment. Hence, the tunnelling frequency must be defined by the frequency of rotational mode. The estimation of tunnelling frequency gives the value $\omega_t = E_1 - E_0 = 251$ K (174 cm^{-1}), that is in good agreement with the rotational mode frequency

$\omega_s = 170$–180 cm^{-1}, obtained from Raman scattering spectra [8,9].

The employment of this method of EXAFS-spectra analysis allows us to improve considerably the quality of fitting the model spectra to the experimental function $\chi(k)$ for undoped BaBiO$_3$ (see Fig. 3). The results indicate that at low temperatures oxygen atoms in BaBiO$_3$ vibrate in considerably deeper (comparing with $x = 0.4$, 0.5) potential wells with a potential barrier energy U_0 which is essentially greater than the ground state energy level. This suggests that the probability of tunnelling of oxygen atoms between Bi(I)O$_6$–Bi(II)O$_6$ octahedra is negligibly small. With temperature increasing from 5 to 90 K the distance between potential wells abnormally increases. It can be explained, for instance, by negative linear thermal coefficient of expansion found in Ref. [14]. This fact results in a reduction of vibration amplitude of oxygen atoms in double-well potential, observed by us as an abnormal decrease of Debye–Waller factor values with increasing of temperature if EXAFS-spectra were treated in harmonic approach [15].

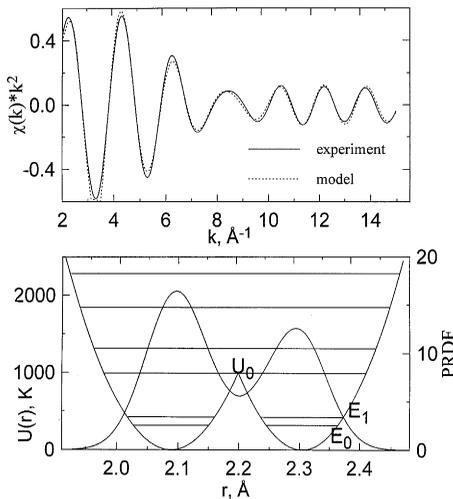Essentially, anharmonic character of oxygen ion vibrations in the soft rotational mode, which can be described by motion in the double-well potential, is the basis of anharmonic model of HTSC [16]. According to this model anharmonic coupling constant λ_s is greater than the one obtained in the harmonic approximation λ_{ph}, that can explain the high critical temperatures both for copper HTSC and BPB-BKB systems. Our results point out that due to non-equivalency of BiO$_6$ complexes the asymmetric rotational vibration at the region "a" (Fig. 2) promotes dynamic swapping of Bi(I)O$_6 \leftrightarrow$ Bi(II)O$_6$, that causes supplementary modulation of Bi–O bond lengths. It seems to be the main reason for strong electron–phonon interaction in the BKB system and must lead to a high value of coupling constant $\lambda_s (\lambda_s \sim 1/\omega_s^2$ [16]). Our estimations give $\lambda_s \approx 2.6$ at $\omega_s = 170$ cm^{-1} which according to the expression for moderate-coupling limit $T_c \approx 0.05\omega_s(\lambda_s - 0.25)$ [17] brings about to the value of critical temperature $T_c \approx 30$ K in Ba$_{0.6}$K$_{0.4}$BiO$_3$ which is in a good agreement with experiment.

Acknowledgements

Fig. 3. Analysis of the first oxygen shell from Bi L$_3$ edge for BaBiO$_3$: "a" — experimental (solid line) and model (dotted line) EXAFS-functions; "b" — model potential with PRDF and energy levels.

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