

Correlation of the local and the macroscopic properties of high-temperature superconductors: EXAFS data analysis†

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Based on temperature-dependent EXAFS studies of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ superconducting oxide, a model of the relationship between the local crystal and the local electronic structures has been proposed. Oxygen ions were found to vibrate in a double-well potential and their vibrations are correlated with the local electron pair transfer due to the dynamical exchange $\text{BiO}_6 \leftrightarrow \text{Bi}\underline{\text{L}}^2\text{O}_6$, where $\underline{\text{L}}^2$ denotes the hole pair in the antibonding Bi $6s$ $\text{O}2p_{\sigma^*}$ orbital of the octahedral complex. The similarity of the EXAFS spectra features of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ allowed us to propose a similar model for Cu-based superconducting oxides. The model, in a common approach, explains the antiferromagnetic state, metal-insulator phase transition and the appearance of superconductivity at Sr^{2+} doping of La_2CuO_4 , and eliminates discrepancy between the neutron-scattering and EXAFS data.

Keywords: EXAFS; superconducting oxides; local electronic structure; local crystal structure.

1. Introduction

During the last decade there has been mounting interest in explaining the mechanism of high- T_c superconductivity on the basis of electronic and structural inhomogeneities of the CuO_2 plane (see, for example, Egami & Billinge, 1994; McQueeney *et al.*, 1999; Ichikawa *et al.*, 2000). The most compelling evidence for these inhomogeneities comes from the discovery of a static stripe phase in non-superconducting $\text{La}_{1.48}\text{Nd}_{0.4}\text{Sr}_{0.12}\text{CuO}_4$ (Tranquada *et al.*, 1996). Later, Bianconi *et al.* (1996) claimed to have found the stripe-like feature for the superconducting composition of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ based on EXAFS experiments. However, the recent neutron-scattering analysis of the local structure in an $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ single crystal by Braden *et al.* (2001) refutes the existence of in-plane charge inhomogeneities related to static stripe correlation. Moreover, the inelastic neutron-scattering measurements of McQueeney *et al.* (1999) showed that the local charge ordering in the superconducting plane must be dynamic, not static. We suppose that this strong contradiction between EXAFS (Bianconi *et al.*, 1996) and neutron-scattering data (Braden *et al.*, 2001; McQueeney *et al.*, 1999) arises from the difficulties in interpretation of the EXAFS spectra due to the existence of several different Cu–O bonds and to short Cu–O distance in the CuO_2 planes of cuprates.

Meanwhile there exists the three-dimensional superconducting perovskite-like oxide $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ (BKBO), which is more favourable for extraction of the local structure inhomogeneities from the EXAFS spectra due to more simple structure and longer Bi–O distances.

In this paper we present a comparative analysis of our temperature-dependent EXAFS study of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ and experimental

data concerning $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ which elucidates the nature of the local crystal and charge inhomogeneities and connects the local features with the main macroscopic properties of both compounds.

2. Experiment and data analysis

Temperature-dependent X-ray absorption investigations were carried out for $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ (Bi L_3 -edge) with $x = 0.0, 0.25, 0.4, 0.5$ and for BaPbO_3 (Pb L_3 -edge). The EXAFS spectra were collected at beamline D-21 of the DCI (LURE, Orsay, France) synchrotron operated at an energy of 1.85 GeV and with an average current of ~ 250 mA in the positron beam. The energy resolution of the double-crystal Si(311) monochromator at 13 keV was about 2–3 eV. The low-temperature measurements were performed using a liquid-helium circulation-type cryostat with a temperature control of ~ 1 K. The background in the experimental spectra was removed as described by Newville *et al.* (1993) taking care to remove the low-frequency oscillations. The EXAFS functions $\chi(k)k^2$ obtained from absorption spectra were Fourier transformed in the wavenumber k range from 1.5 to 16.5 \AA^{-1} using the Kaiser–Bessel windowing function.

Since we found that the oxygen vibrations in the first Bi–O shell are strongly anharmonic (Menushenkov *et al.*, 1997) we used the EXAFS-treatment method applied by Mustre de Leon *et al.* (1992) for the analysis of apical oxygen oscillations in $\text{YBa}_2\text{Cu}_3\text{O}_7$. In this case we considered the potential of Bi–O vibrations to be a parametric function of interatomic distance, and the potential parameters were extracted from the model to experimental EXAFS-function fits according to (Menushenkov & Klementev, 2000)

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

where

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

is the pair radial distribution function of atoms in the j th sphere, N_j is the coordination number, E_n and ψ_n are the n th energy level and its corresponding wavefunction in a model potential, and r_{\min} and r_{\max} are determined by the windowing function of the back Fourier transform. The variable parameters in this case are N_j and the parameters of the model potential. The phase shift φ_j and scattering amplitude $F(k)$ were calculated using the *FEFF6* code (Rehr *et al.*, 1991). The above treatment procedure was performed using the new program *VIPER* (Klementev, 2001; Klementev, 2003).

3. Results and discussion

The EXAFS study of the nearest oxygen environment of Bi in BKBO showed that oxygen ions vibrate in the double-well potential due to the different electronic structure of the neighbouring octahedral complexes BiO_6 and $\text{Bi}\underline{\text{L}}^2\text{O}_6$, where $\underline{\text{L}}^2$ denotes the hole pair in the antibonding Bi $6s$ $\text{O}2p_{\sigma^*}$ orbital of the octahedral complex (see Menushenkov & Klementev, 2000). We found that these two different types of complexes exist in the full range of the K-doping of BaBiO_3 including the superconducting compositions and are observed in EXAFS spectra as the dynamical local lattice distortions. It allowed us to propose a model of the relationship between the local crystal and the local electronic structures and to establish the correlation between the local and the macroscopic properties of the BKBO system (Menushenkov & Klementev, 2000; Menushenkov *et al.*, 2001). It was shown that oxygen ion vibrations in the double-well potential are correlated with the local electronic pair tunneling between the neighbouring octahedral complexes in accordance with the dynamical

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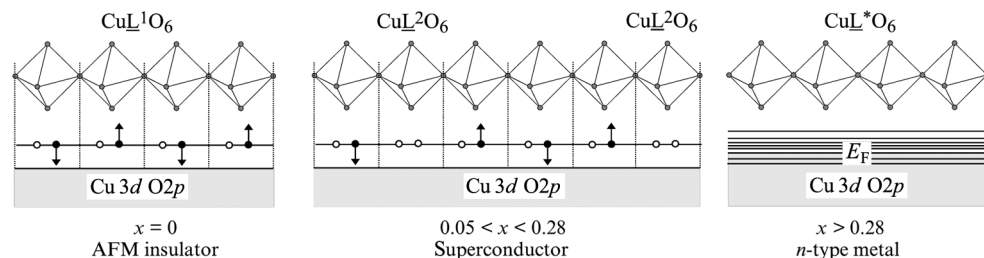


Figure 1

Scheme of the insulator–metal phase transition in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. The local crystal structure of the octahedral complexes (at the top) and the local electronic structure (at the bottom) are shown. The occupied states of the $\text{Cu } 3d \text{ O}2p$ valence band are marked in grey. Black and white circles denote electrons and holes, respectively. Arrows show the spin orientation in the neighbouring complexes. The antiferromagnetic phase of the parent insulator La_2CuO_4 is shown on the left. In the middle the superconducting phase of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with $0.05 < x < 0.28$ is presented. The metal non-superconducting phase at $x > 0.28$ (Fermi liquid state with Fermi level E_F) is shown on the right.

exchange: $\text{BiO}_6 \leftrightarrow \text{BiL}^2\text{O}_6$. At low temperature the local pair transfer becomes coherent due to the phase coherence between the oxygen ion vibrations in the double-well potential and the breathing-type vibrations along [100]-type axes at the Brillouin zone boundary. It explains the appearance of superconductivity in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$. The increase in temperature excites longitudinal stretching phonons other than the breathing type, which destroys the phase coherence in the local pair transfer and leads to superconductivity destruction at $T > T_c$ (Menushenkov *et al.*, 2001, 2002).

Observing the abnormal increase of the Cu–O-bond Debye–Waller factor with temperature decreasing below 100 K for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, the authors (Bianconi *et al.*, 1996) assigned it to the static stripe structure which consists of two types of CuO_6 octahedra with a 0.12 Å difference of in-plane Cu–O bond lengths. It contradicts not only the neutron-diffraction data (Braden *et al.*, 2001) but also the EXAFS study of Niemöller *et al.* (1998) who found the maximum splitting of the Cu–O bonds to be smaller than 0.06 Å.

We suppose that these contradictions are connected to the dynamic rather than static character of Cu–O bond splitting. The anomalous behaviour of the Cu–O-bond Debye–Waller factor means that it is incorrect to use the harmonic approximation treatment of EXAFS spectra for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. This situation is identical to what we observed for the Bi–O bond in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ which suggests that the oxygen ions in the CuO_2 plane vibrate in a double-well potential.

From this point of view we can propose a model of the relationship between the local crystal and the local electronic structures of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ in analogy with the $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ case, presented in Fig. 1.

In the parent La_2CuO_4 compound the upper $\text{Cu } 3d_{x^2-y^2} \text{ O}2p_{\sigma^*}$ antibonding orbital of every octahedral complex CuL^1O_6 is half filled, which leads to the antiferromagnetic order (see Fig. 1, left). Such a system should behave as a Mott-type insulator since the transfer of an electron from one complex to the neighbouring one changes the electronic structure of both complexes and requires an activation energy $E_a \simeq 2$ eV.

Doping of La_2CuO_4 by Sr^{2+} leads to the appearance of the octahedral complexes CuL^2O_6 with two holes in the antibonding orbital (see Fig. 1, middle), resulting in local hole pairs \underline{L}^2 , similar to the case of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$. These pairs can tunnel freely between the neighbouring complexes in accordance with the dynamical exchange $\text{CuL}^1\text{O}_6 \leftrightarrow \text{CuL}^2\text{O}_6$, producing the oxygen ion vibrations in the double-well potential. At low temperature the local pair transfer is coherent as in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$, which explains the superconducting

state of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ in the doping region $0.05 < x < 0.28$. At $T > T_c$ the coherency is destroyed and local pairs provide the normal conductivity of so-called ‘strange metal’. In addition, at $x > 0.05$ the antiferromagnetic order of the alternating CuL^1O_6 complexes with antiparallel local spins is suppressed (see Fig. 1).

In the overdoping case ($x > 0.28$) the concentration of the hole pairs becomes too large for the pair wavefunctions to be localized and free electronic levels of CuL^2O_6 complexes become extended. These \underline{L}^2 levels split and overlap with half-filled \underline{L}^1 levels of CuL^1O_6 complexes, and the partially filled conduction band of the Fermi liquid metal is formed as a result. Thus the hole (Sr^{2+}) doping of the p -type parent semiconductor La_2CuO_4 transforms it into n -type metal in the overdoping regime. Since local pairs disappear, this metal becomes non-superconducting.

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