Double-well potential for oxygen ion vibrations in $Nd_{2-x}Ce_xCuO_{4-\delta}$

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Abstract. X-ray absorption spectra of the oxide systems $Nd_{2-x}Ce_xCuO_{4-\delta}$ (NCCO) above the K-Cu absorption edge were investigated in temperature range $4 \div 300$ K. It is assumed that oxygen ions in superconductive CuO_2 plane move in a double-well potential similarly to abnormal oxygen vibrations uncovered earlier in superconductive systems $Ba_{1-x}K_xBiO_3$ and $La_{2-x}Sr_xCuO_4$. A model of relationship between electronic and local crystalline structures is proposed. Obtained results point to the direct connection of the observed local dynamic structure nonuniformity with local dynamic charge ordering. Role of dynamic charge ordering in superconductive CuO_2 plane in HTSC mechanism is discussed.

1. Introduction

Neodymium-cerium cuprate $Nd_{2-x}Ce_xCuO_{4-\delta}$ (NCCO) belongs to a class of electron-doped high temperature superconductors (HTSC) [1]. Parent insulator Nd_2CuO_4 upon substitution of Nd atoms with Ce gains extra electrons and becomes a conductor: measurements of the Hall coefficient R_{H} demonstrate negative values up to $x < 0.13$ [2]. Further doping with cerium leads to the appearance of superconductivity in a narrow interval of $0.13 < x < 0.18$ and to non-trivial change of conductivity to p-type at $x > 0.18$ [3]. Nd_2CuO_4 is characterized by a tetragonal I4/mmm symmetry also called as the T'-structure. The only difference from similar tetragonal La_2CuO_4 structure is the lack of apical oxygen. Cerium-doped $Nd_{2-x}Ce_xCuO_{4-\delta}$ keeps the same symmetry varying only lattice parameter and z-coordinate of Nd atoms.

The existence of local structure peculiarities in superconducting CuO_2 plane of hole-doped cuprate HTSC at low temperature was reported in a number of independent observations [4, 5, 6, 7]. First models tended to explain local peculiarities in CuO_2 plane as a structure of static stripes [4]. But recent models consider such peculiarities as a dynamic vibration of oxygen atom in a double-well potential [5, 6, 7]. In [8] it was reported about broadening of the Cu-O-Cu angle distribution, which is assigned to variations in the local vibrational modes involving the in-plane oxygens, induced by electron-doping in $Nd_{2-x}Ce_xCuO_{4-\delta}$. First the vibrations of oxygen atom in double-well potential were founded by us in the superconducting $Ba_{1-x}K_xBiO_3$ (BKBO) oxides [9, 10] that have similar to cuprate HTSC perovskite lattice but with three-dimensional structure instead of layer-type in cuprates. Later we have revealed the presence of double-well vibrations of oxygen in CuO_2 plane in superconducting $La_{2-x}Sr_xCuO_4$ (LSCO) system [11].

Here we report the results of EXAFS study of the NCCO system treated in the real space in an anharmonic approach similar to the one we have applied for BKBO analysis. We used "VIPER for Windows" software package [12] as it allows us to construct an arbitrary potential of atomic pair oscillations and to obtain the corresponding pair radial distribution function (PRDF). This approach gives an opportunity to investigate the character of oxygen atom vibrations, to understand the nature of the structural phase transitions in these systems and to establish the analogy between the local structure anomalies observed in BKBO, LSCO and NCCO systems.

2. Experimental

Polycrystalline ceramic samples of $\mathrm{Nd}_{2-x}\mathrm{Ce}_x\mathrm{CuO}_{4-\delta}$ (x=0, 0.15, 0.2) were synthesized by solid-state reaction technique. X-ray absorption spectra were collected at E4 beamline of the DORIS III (DESY, Hamburg, Germany) storage ring above K-Cu absorption edge (8995 eV). Energy resolution of the double-crystal Si (111) monochromator at 9 keV was $\sim$ 1.4 eV. Low-temperature measurements were carried out using a liquid-helium flow cryostat, temperature instability didnt exceed ±1K at 300K and 0.1K at 4K. EXAFS data reduction was performed according to the standard procedure described elsewhere [13]. Contribution from the first oxygen shell around copper atoms was filtered in a region of 0.8 - 2.0 Å. The model EXAFS function for atomic pair absorber-scatterer oscillations was constructed as follows. Suppose we know the potential of these oscillations as a parametric function of interatomic distance. Solving the stationary Schrödinger equation numerically for the particle with the reduced mass of atomic pair [10], one obtains a pair radial distribution function of atoms in the ith sphere:

$$g_i(r) = N_i \sum_n |\Psi_n(r)|^2 \exp\left(-E_n/kT\right) \Big/ \sum_n \exp(-E_n/kT) \quad (1)$$

where N_i is the coordination number, and E_n and Ψ_n are the nth energy level and its corresponding wave function. For known PRDF model EXAFS function is calculated as

$$\chi(k) = \frac{1}{k} \sum_i F_i(k) \int_{r_{\min}}^{r_{\max}} g_i(r) \sin\left[2kr + \phi_i(k)\right] \Big/ r^2 dr \quad (2)$$

where $k = \sqrt{2m_{\mathrm{e}}/\hbar^2\,(E - E_{\mathrm{th}})}$ is the photoelectron wavenumber relative to the ionization threshold E_{th}, and $r_{\min}$ and $r_{\max}$ are determined by the windowing function of the back-Fourier transform. The phase shift $\phi_i(k)$ and the scattering amplitude $F_i(k)$ were calculated using the FEFF code [14]. Parameters of the potential were extracted from the model-to-experimental EXAFS function fits.

3. Results

In figure 1 (upper) we show the experimental EXAFS functions $\chi(k)k^2$ for NCCO with x=0, 0.15, 0.2 measured above the K Cu absorption edge at 10 K. The good signal-to-noise ratio seen up to wavenumber values $k \approx 14\,\mathrm{Å}^{-1}$ indicates the high spectral quality. The absence of signal in the Fourier transform modulus the low-r range of figure 1 (lower) testifies to a correct backround-removal procedure.

From the inset to lower panel of figure 1 one can see that for insulator $\mathrm{Nd_2CuO_4}$ and for overdoped nonsupercoductive metal $\mathrm{Nd_{1.8}Ce_{0.2}CuO_4}$ the amplitude of Cu-O(1) peak normally decrease with temperature increasing from 10 K to 300 K. However for the superconductive $\mathrm{Nd_{1.85}Ce_{0.15}CuO_{4-\delta}}$ the peak amplitude at 90 K is higher that at 10 K. This differs from the results of [8], where the authors did not find any visible changes of peak amplitude with temperature increasing. However we should point out that the absence of peak amplitude changes in wide temperature range is also abnormal for harmonic vibrations.

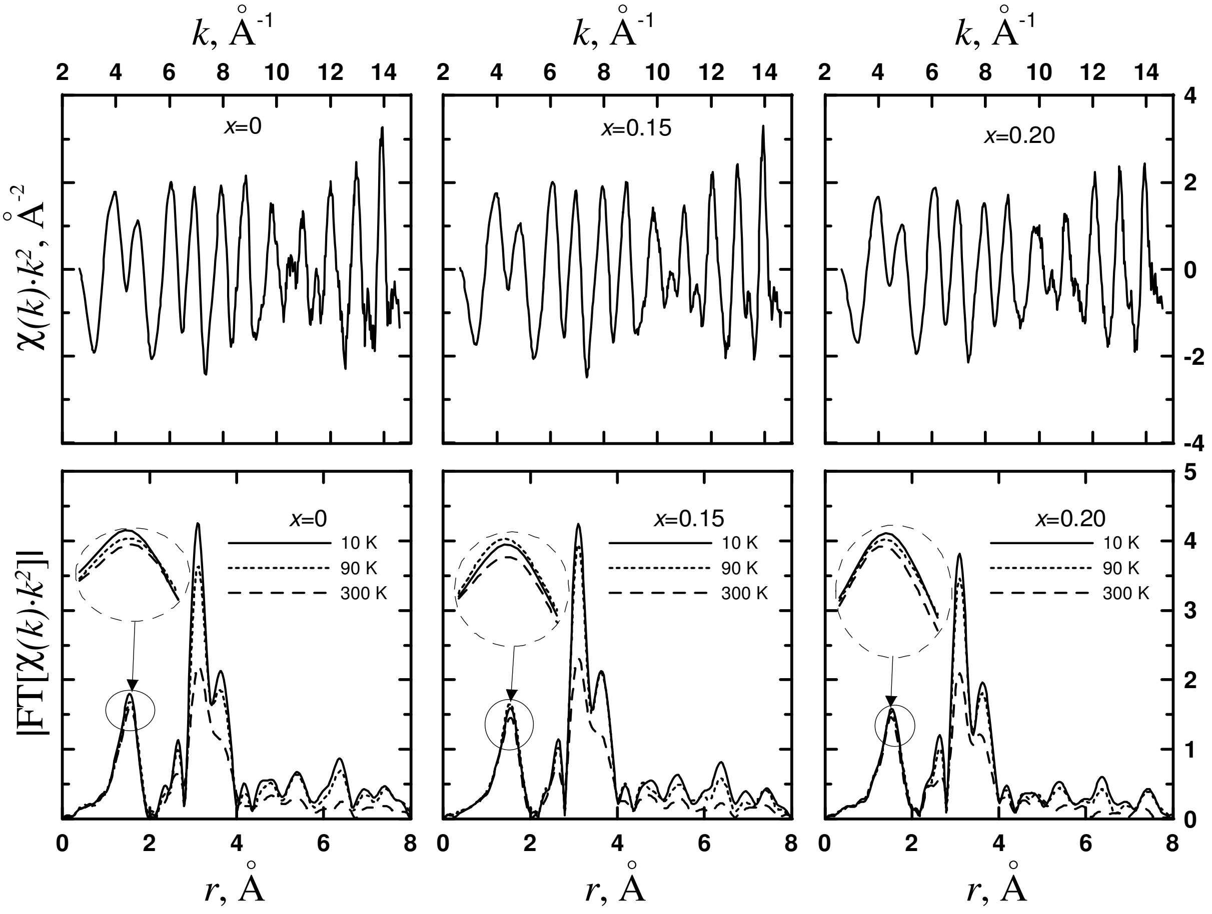

Figure 1. The experimental EXAFS $\chi(k)k^2$ (upper) measured at the K Cu absorption edge at 10 K and Fourier transform modulus for $Nd_{2-x}Ce_xCuO_{4-\delta}$ at 10, 90 and 300 K (lower). The inset shows the amplitudes of the first peak, corresponding to Cu-O(1) near-neighbouring shell, at different temperatures.

So the experimental $\chi(k)k^2$ EXAFS-functions for the first Cu-O(1) shell for x=0 and x= 0.2 fit very well in traditional harmonic approximation, they are shown at figure 2 and 3. This fact proves normal harmonic character of oxygen vibration in non-superconductive compounds.

At the same time an harmonic approximation does not give satisfactory fits of the experimental EXAFS function for the same Cu-O(1) shell of the superconductive $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, especially in the $k > 11$ Å^{-1} region (see figure 4). So we can conclude that in this case the pair Cu-O(1) radial distribution function cannot be described by Gaussian one and thus it is impossible to use the harmonic approach for EXAFS function description.

We had discovered similar anomaly in EXAFS - spectra of hole-doped BKBO and successfully described it by using the double-well potential for oxygen atoms vibrations [9, 10]. It was supposed that reason for appearance of such potential is the difference in electron filling of neighboring octahedral BiO_6 complexes. Later we observed the similar picture in hole-doped HTSC LSCO [11] and independently Bishop et al. [5] and Mustre de Leon et al. [7] have reported the existence of double-well potential oscillation of oxygen ions in superconductive $La_2CuO_{4.1}$.

So we supposed that oxygen vibrations occur in double-well potential in electron-doped $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ due to different electron filling of neighboring CuO_4 complexes. We

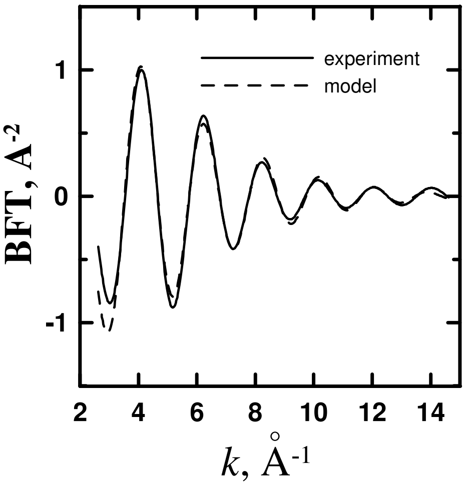

Figure 2. EXAFS-functions for Nd_2CuO_4 at 10 K for the first Cu-O(1) near-neighbouring shell.

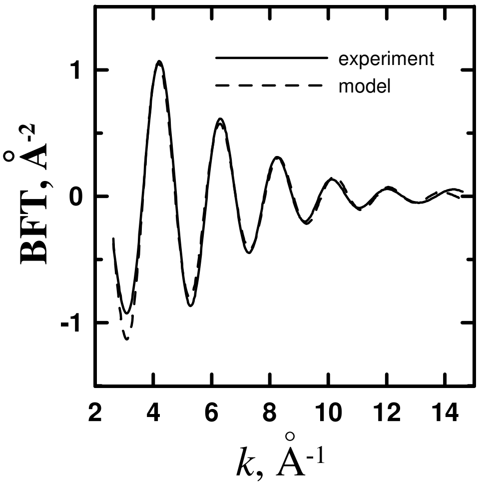

Figure 3. EXAFS-functions for $Nd_{1.8}Ce_{0.2}CuO_4$ at 10 K for the first Cu-O(1) near-neighbouring shell.

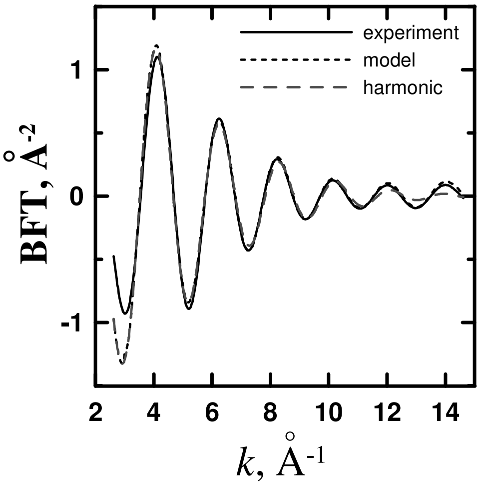

Figure 4. EXAFS-functions for $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ at 10 K for the first Cu-O(1) near-neighboring shell.

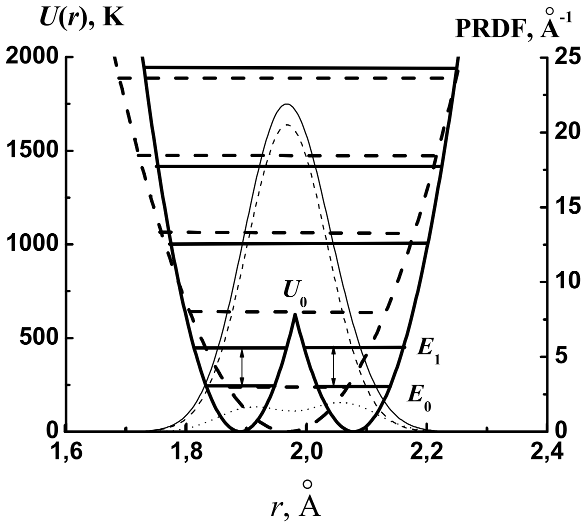

Figure 5. The model potentials (harmonic and double-well) with the corresponding PRDF's and energy levels. U_0 is the energy of the potential barrier, the total PRDF is shown by a solid line.

considered a parabolic form for each well, $U_1 = \kappa_1(r - r_1)^2/2$ and $U_2 = \kappa_2(r - r_2)^2/2$, joined continuously. In our model we assumed that part (15%) of oxygen ions which belong to the neighboring CuO_4 complexes with different electronic structure oscillate in double-well potential and rest oscillate in harmonic potential. Given the calculated $\chi(k)$ defined by equations 1 and 2 we performed a least-squares fit of the experimental $\chi(k)$ (see figure 4 and 5). One should note that used one-dimensional potential is only an empirical approach to describe the non Gaussian pair radial distribution function of Cu-O(1) bond along [100]-type axis in CuO_2 - plane. Since the system is actually three-dimensional, this potential can not describe the real three-dimensional oxygen vibrations. And although our model provided better fitting to experimental data than harmonic one we do not exclude other possible mechanisms, for example, weakly anharmonic models.

4. Discussion

In [10, 15] it was showed that oxygen ions in BKBO compounds move in considerably anharmonic double-well potential which appears due to existence of two different types of BiO_6 octahedra: some octahedra have a hole pair in the upper antibonding Bi6s-O2p_{σ^*} molecular orbital while others have an electron pair. Oxygen ions belonging to the neighboring complexes with identical electronic filling oscillate in harmonic potential, but those that belong to the neighboring complexes with different electronic filling move in the double-well potential due to the tunneling of the local electron pair from one complex to another in compliance with consecutive dynamic exchange $BiO_6 \longleftrightarrow Bi\underline{L}^2O_6$ ($\underline{L}^2$ denotes the hole pair). In the same manner as in BKBO case we have proposed a model of the relationship between local electronic and local crystalline structure of the hole-doped HTSC $La_{2-x}Sr_xCuO_4$, which has a structure of two types of octahedral complexes: $Cu\underline{L}^2O_6$ and $Cu\underline{L}^1O_6$ (here $\underline{L}^1$ denotes the presence of one hole in the upper Cu3$d_{\mathrm{x}^2-\mathrm{y}^2}$-O2$p_{\sigma^*}$ antibonding orbital) [11].

The difference of Nd_2CuO_4 structure from similar La_2CuO_4 one is the lack of apical oxygen and formation of $Cu\underline{L}^1O_4$ complexes instead of $Cu\underline{L}^1O_6$. The upper antibonding orbital of each $Cu\underline{L}^1O_4$ complexes of the parent compound Nd_2CuO_4 is half-filled and provides ordering of spin subsystem in ground antiferromagnetic state (figure 6, left). Nd_2CuO_4 is a Mott-type insulator because electronic transfer from one complex to the neighbouring one changes their energetic structure and thus entails energy expenses.

Doping of Nd_2CuO_4 with cerium leads to appearance of the CuO_4 complexes with two electrons at the upper antibonding orbital. Appearance of the local electronic pairs in NCCO due to electron doping occurs similarly to the local hole pairs appearance in LSCO due to hole doping (see figure 6, center). These pairs can tunnel between neighbouring complexes in compliance with the dynamic exchange $Cu\underline{L}^1O_4 \longleftrightarrow CuO_4$ producing oxygen ions vibrations in the double-well potential. At low temperature local pair movement is coherent that explains the existence of the superconductive state of NCCO in the range of cerium concentration $0.14 < x < 0.18$. At $T > T_c$ pairs movement is no longer coherent but conductivity in normal state is caused by local electron pairs providing the n-type metal state.

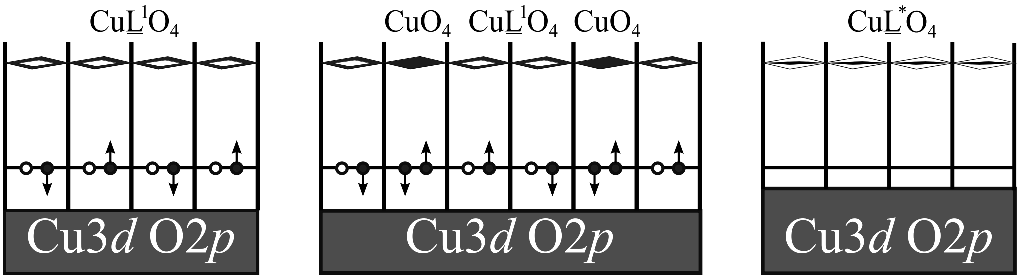

Figure 6. A schematic diagram of the relationship between the local crystalline and local electronic structures of $Nd_{2-x}Ce_xCuO_{4-\delta}$. Nd_2CuO_4 semiconductive state - left. $Nd_{2-x}Ce_xCuO_{4-\delta}$ supercondutive state ($0.14 < x < 0.18$) - center. $Nd_{2-x}Ce_xCuO_{4-\delta}$ p-type metal state ($x > 0.18$) - right.

In overdoped regime ($x > 0.18$) electron levels of CuO_4 complexes delocalize and complete the system of levels at the top of valency band together with half-filled levels of $Cu\underline{L}^1O_4$ complexes. Delocalized holes $\underline{L}^1$ of $Cu\underline{L}^1O_4$ complexes at the top of valency band provide hole-type conductivity in such a system (see figure 6, right). So the electron doping of n-type parent semiconductor Nd_2CuO_4 converts it to p-type metal in overdoped regime and this fact is proved by the Hall coefficient measurements giving the positive values of R_H at $x > 0.14$ [3].

5. Conclusions

We have performed an EXAFS study of local structure peculiarities in $Nd_{2-x}Ce_xCuO_{4-\delta}$. It was found that vibrations of the part of oxygen atoms along [100]-type axis in CuO_2 - plane can be described using the double-well potential, which arises from the charge carrier pair tunneling correlated with oxygen atom oscillations. The underlying relationship between local crystalline and local electronic structures was established. Proposed model explains insulator-to-metal phase transition with Ce doping of parent insulator Nd_2CuO_4 and appearance of the superconductive state. Similar results found independently in other copper-oxide superconductors allow to assume that anomalous oxygen vibrations in double-well potential are an inherent and general property of superconductive oxides with perovskite-like structure irrespective of the type of doping. Meanwhile the authors of [5, 7] explain the appearance of the double-well potential in superconducting $LaCuO_{4.1}$ in terms of Jahn-Teller polaron model. Their model is inapplicable for $Nd_{2-x}Ce_xCuO_{4-\delta}$ because of lack of apical oxygen atoms in the NCCO structure. So we suppose that our model of the relationship between local electronic and local crystalline structures is more suitable for explaining the observed these local dynamic distortions in the superconductive CuO_2 plane of HTSC.

Acknowledgments

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