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The local structure of the CuO_2 plane in $Nd_{2-x}Ce_xCuO_{4-\delta}$: an X-ray absorption study

Alexander Ignatov, [a,b*] **Josef Feldhaus,** [c] **Vladimir Chernov** [d] **and Andrey Ivanov** [a]

[a] *Department of Quantum Electronics, Moscow Engineering Physics Institute, Kashirskoe sh. 31, 115409 Moscow, Russia,* [b] *Department of Physics Southern Illinois University, Carbondale, IL 62901-4401, USA,* [c] *Hamburger Synchrotronstrahlungslabor, HASYLAB at DESY, Notkestraße 85, D-22603 Hamburg, Germany,* [d] *Siberian Synchrotron Radiation Centre at Budker INP, Lavrentyev 11, 630090 Novosibirsk, Russia.*
E-mail: ignatov@physics.siu.edu

The local structure of the CuO_2 plane in $Nd_{2-x}Ce_xCuO_{4-\delta}$ (x=0,0.15;δ~0.01) has been examined by Cu K-edge EXAFS *vs* temperature. Three different Cu-O distances can be extracted up to at least 100K, indicating that the atomic structure of the CuO_2 plane deviates from the T ' structure much more than it was expected earlier. Furthermore, the magnitudes of O1 displacements are larger in a superconducting x=0.15 sample than in a nonsuperconducting x=0 one. Space location of displaced O1 atoms for superconducting sample were obtained from the comparative analyses of experimental and calculated XANES spectra.

Keywords: local structure, XAFS, domains, superconductors.

1. Introduction

The variation in the local structure of high-temperature superconductors (HTSCs) has a profound effect on their normal state and superconducting properties (Ginsberg, 1988-1996; Bar-Yam *et al.*, 1992). The short-range atomic structure of $Nd_{2-x}Ce_xCuO_4$ (x=0.165,0.2) was found to be significantly different from the crystallographic T ' structure (Billinge & Egami, 1993). Multiple scattering analysis of EXAFS data at the Cu K-edge of $Nd_{2-x}Ce_xCuO_4$ (x=0,0.15) showed a clear difference in the Nd-Cu distance distribution between the parent and doped samples (Sperandini *et al.*,1998).

In the present work we report the determination of the local structure of the CuO_2 plane in $Nd_{2-x}Ce_xCuO_{4-\delta}$ (δ~0.01) for x=0 and x=0.15 with the use of EXAFS and XANES analysis. The local structure of the CuO_2 plane may be understood as a mixture of modified 'displaced configurations' proposed by Bishop and his collaborators (Yonemitsu, Bishop & Lorenzana, 1992; 1993).

2. EXAFS study

Two polycrystalline samples with x=0 and x=0.15 were prepared by solid-state reaction. The Cu K-edge EXAFS measurements were performed on the EXAFS-II beamline of HASYLAB at DESY at Hamburg. The data were collected in the transmition mode as a function of temperature in the range T=5-300 K.

The Fourier-filtered contribution from the Cu-O1 bonds exhibits a beat at k=13-14 Å^{-1} at low temperature for both x=0 and x=0.15 samples. Neither a single-shell (1S) model, assuming a single Cu-O1 distance as expected from the T' structure, nor a model involving two different Cu-O1 distances can provide good fits at k>13 Å^{-1}. However, a three-shell (3S) model indicated by a dashed line in Fig. 1 gives much better agreement. The local structure parameters for the 1S and 3S models were derived from the non-linear least-squares fits over the range of k=3-16 Å^{-1}, using the curved wave EXAFS theory. According to our best 3S model, *three different Cu-O1 distances* may be extracted at 10 K: R_U =1.96±0.01 Å, R_{D1}=1.85±0.02 Å, and R_{D2}=2.07±0.02 Å for $Nd_2CuO_{4-\delta}$ and R_U =1.96±0.01 Å, R_{D1} =1.85±0.02 Å, and R_{D2}=2.10±0.02 Å for $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$. The fraction of strongly distorted Cu-O1 bonds for both samples is 40±10%. Thus, the atomic structure of the CuO_2 plane deviates from the T ' structure much more than it was expected earlier (Billinge & Egami, 1993; Sperandini *et al.*, 1998).

Pair distribution functions (PDFs) of the Cu-O1 atoms for the samples with x=0 and x=0.15 at T=10 K are shown in Fig. 2. They were generated from the best 3S models as a superposition of three Gaussians. The main peaks 'U' at R_U =1.96 Å originate from the undistorted Cu-O1 bonds. The peaks 'D1' at R_{D1} =1.85 Å and peaks 'D2' at R_{D2} =2.07 Å for x=0 and R_{D2} =2.10 Å for x=0.15 correspond to the distorted Cu-O1 bonds. In $Nd_2CuO_{4-\delta}$, the 'D1' and 'D2' peaks are arranged symmetrically with respect to the 'U' peak, so that $R_{D1}+R_{D2}\approx 2R_U$. Both in-plane displacement perpendicular to the Cu-O1 bond, $\Delta O1_\perp$ and out-of-plane displacement, $\Delta O1_z$ seem to be rather small and the distortions of the CuO_4 plaquettes are of almost breathing type, $\Delta O1_{||}$. On the contrary, in superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, $R_{D1}+R_{D2}>2R_U$, so that the positions of the 'D1' and 'D2' peaks become asymmetrical, indicating clearly that along with breathing displacements there exist considerable $\Delta O1_\perp$ and $\Delta O1_z$ displasements. Therefore, the magnitudes of O1 displacements are larger in a superconducting x=0.15 sample than in a nonsuperconducting x=0 one at 10 K.

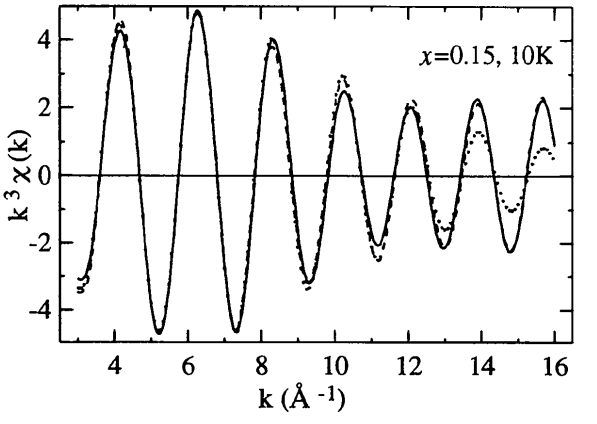

Figure 1
Comparison of the Fourier-filtered contribution from the Cu-O bonds, x=0.15, 10K data (solid line) with fitting curves corresponding to the 1S (dots), and 3S (dashed line) models. The Fourier-transform range is 2.1-17.2 Å^{-1}, square

window; the backtransform range is=1-2 Å.

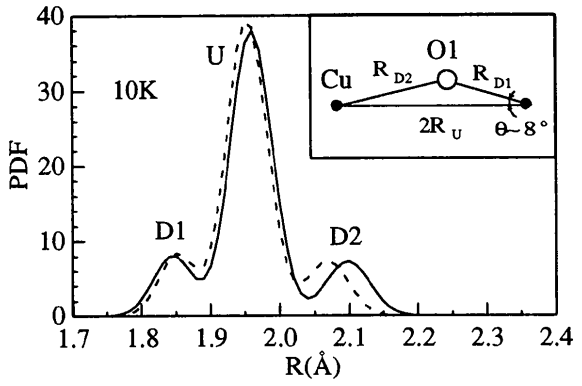

Figure 2
PDFs of the Cu-O1 atoms for the samples with x=0 and x=0.15 are shown by dashed and solid curves, respectively.

The temperature dependence of the Cu-O1 distances for the x=0 and x=0.15 samples is shown in Fig. 3. We found that the quality-of-fit parameter for the 1S model $R^{(1S)}$, is 2.3-1.2 times larger than for the 3S model at low temperature (T<100-120K).

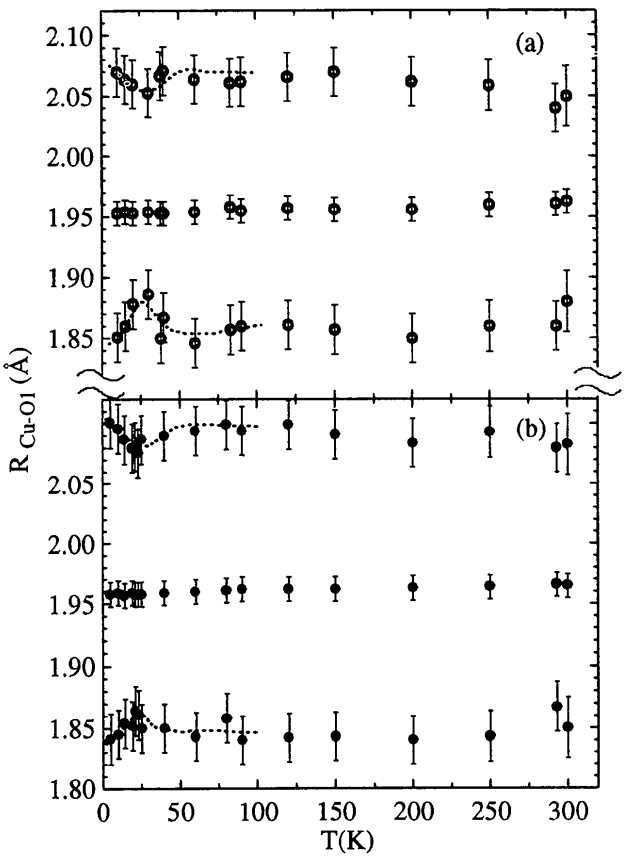

Figure 3
The temperature dependence of the Cu-O1 distances: (a) the sample with x=0 (,), (b) the sample with x=0.15 (•). All lines are guided by eye. Decreasing of the separation between the 'D1' and 'D2' peaks at the range T~15-40 K should be noted.

As the temperature rises, the ratio $R^{(1S)}/R^{(3S)}\rightarrow 1$, so that it turns to be impossible to reveal unequivocally which model should be preferred. Nevertheless, the large value of the Debye-Waller factor for the single-shell model argue in favor of the presence of multiple distances even at room temperature. It is interesting to mention that the 'D1' and 'D2' peaks approach in both compounds at T~15-40 K. Though this approaching is small (~0.04 Å) it is out of estimated uncertainty.

The EXAFS data give evidence for multi-domain picture of the CuO_2 plane where the localized and itinerant charges coexist. The similar results have been obtained earlier for the hole-doped superconductors: $Bi_2Sr_2CaCu_2O_8$ (Bianconi & Missori, 1994) and $La_2CuO_{4+\delta}$ (Bianconi *et al.*, 1996). In the temperature range near to the critical temperature (T_c~25 K for x=0.15), the local structure of the CuO_2 plane becomes more perfect, indicating that the local structure does play an important role in high T_c superconductivity.

3. XANES study

To determine a space location of the displaced O1 atoms, the polarized Cu K-edge spectrum of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ epitaxial film measured in a **E** || **ab** geometry has been analyzed. At this orientation of the x-ray polarization vector with respect to the **ab** axis the predominant contribution to the measured spectrum comes from the atoms forming the CuO_2 plane.

Film preparation and characterization were described elsewhere (Ignatov *et al.*, 1998). Polarized x-ray absorption measurements were performed on the EXAFS beamline of SSRC at Novosibirsk. The third-order reflection of a Si(111) double-crystal monochromator was extracted by pair of W/Si multilayers. Harmonic rejection was better than 10^{-4}. Data were collected in the FY mode at 80 K.

Calculated Cu K-edge XANES spectra was obtained as a convolution product of the single-electron transition from the Cu 1*s* core-level to the unoccupied electronics states, $I(\omega)$ and spectrum of many-body excitations in the electronic states of the CuO_2 plane in the presence of Cu 1*s* core-hole, $S(\varepsilon)$ (Mahan, 1974):

$$\sigma(\omega) = \int S(\varepsilon) I(\omega - \varepsilon) d\varepsilon \qquad (1)$$

$$S(\varepsilon) = \sum \left| \left\langle \Psi_f^i \middle| \Psi_0 \right\rangle \right|^2 \delta(\varepsilon - E_i + E_0) \qquad (2)$$

where Ψ_0 is the ground state with energy E_0 and Ψ_f is the i-th excited state with energy E_i referred to Hamiltonians in the initial H_0 and final states H_f respectively. H_0 has been taken as the two-dimensional Peierls-Emery Hamiltonian in the hole representation (Ignatov, 1999). In the final states $H_f = H_0 + H_c$, H_c is subjected to the 1*s*-3*d* inter-hole Coulomb repulsion.

The Lanczos technique was employed for numerical diagonalization and spectral calculation of the $S(\varepsilon)$ in the cluster of 12 atoms with periodic boundary conditions. Parameters (in eV) of the Hamiltonian employed for $S(\varepsilon)$ calculations are: $t_{pd}^0 = 1$, $t_{pp}^0 = 0.7$, $\Delta = 0.5U_d - 1$ (Yonemitsu, Bishop & Lorenzana, 1993), $U_d = 6(9)$ for the MCDW(AF) model, $U_p = 3$, $U_{pd} = 1$, $t_{pd}(r) \propto r^{-4}$, $t_{pp}(r) \propto r^{-3}$. The *1s-3d* Coulomb repulsion, $U_c = 6$. The energy to displace each oxygen

atom by $u_{\parallel}$ and $u_{\perp}$, $E_d = \frac{1}{2}K_{\parallel}u_{\parallel}^2 + \frac{1}{2}K_{\perp}u_{\perp}^2 + \xi u_{\perp}^4$. Here $K_{\parallel}$ = 7 eV Å^{-2}, $K_{\perp}$ = 0.17 eV Å^{-2}, ξ = 0.7 eV Å^{-4}. Three-hole wavefunctions corresponding to the 25% electron-doped material were used. $I(\omega)$ was calculated in real space with the use of the formalism of multiple scattering of the photoelectron in the cluster of 50 atoms and then convoluted with a Lorentzian to introduce the energy-dependent broadening.

Calculated XANES were assumed to be a function of the cluster geometry. Only O1 displacements that are compatible to the PDF function obtained from EXAFS were allowed to refine. The best agreement between the calculated and the experimental XANES spectra depicted in Fig. 4 was achieved for a model that is the mixture of a antiferromagnetic (AF) (Fig. 5a) and a modified charge density wave (MCDW) (Fig. 5b) domains taken in ratio 60:40. The local structure of the MCDW domains can be characterized by the following *correlated displacements*: $\Delta O1_{\parallel}$ = ±0.12 Å, $\Delta O1_{\perp}$ = ±0.25 Å, $\Delta O1_z$ = ±0.12 Å.

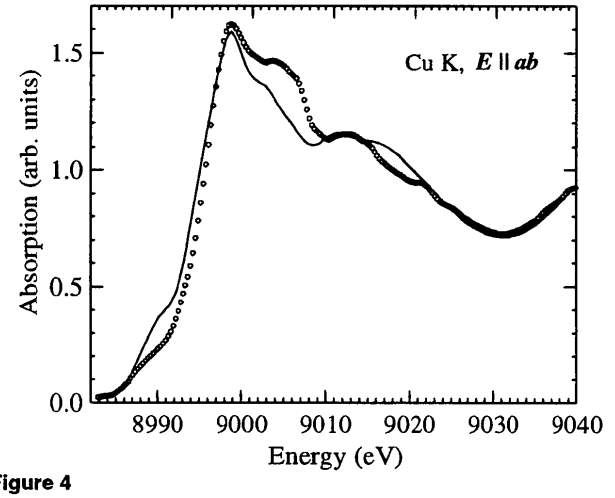

Figure 4
Comparison of experimental (dots) and calculated (solid line) XANES spectra. An agreement factor over the range of the figure is 6.3 %.

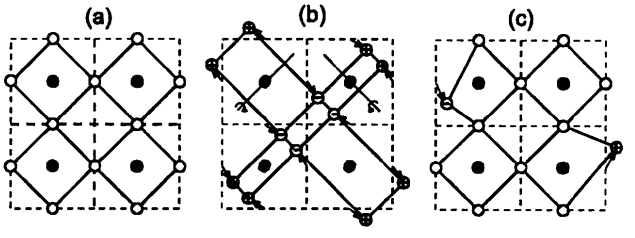

Figure 5
Sketch of some displacement configurations (domains) in the CuO_2 plane of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ used for XANES calculations. Open (closed) circles denote the positions of the O1(Cu) atoms. The in-plane displacements are marked by arrows. The out-of-plane displacements are illustrated by '+' and '-'. (a) AF, (b) MCDW, (c) MSP+AF.

It is interesting to notice that the MCDW and AF configurations *cannot be connected directly*. It is necessary to assume the presence of intermediate (I) domains, where the local structure relaxes from the MCDW to AF. We have found that a modified spin-Peierls (MSP)+AF state (Fig. 5c) is quite appropriate for description of the I-domains. It is most likely that the displaced O1 atoms within the I-domains are locally uncorrelated.

4. Conclusion

Three different Cu-O1 distances observed from EXAFS analysis indicate that the structure of the CuO_2 plane in $Nd_{2-x}Ce_xCuO_{4-\delta}$ (x=0,0.15;δ~0.01) differs locally from the average T' structure up to at least T<100 K. We have seen an evidence of an increase in the magnitudes of the O1 displacements in the superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ compared to the nonsuperconducting $Nd_2CuO_{4-\delta}$. Along with the breathing displacements $\Delta O1_{\parallel}$~ 0.12 Å, which are compatible for both samples, the superconducting sample characterized by substantial in-plane $\Delta O1_{\perp}$~ 0.25 Å, and out-of-plane $\Delta O1_z$~ 0.12 Å displacements that are perpendicular to the Cu-O1 bond. The local structure of the CuO_2 plane in x=0.15 is best explained if three types of domains, namely, (i) the undistorted AF, (ii) the locally tetragonal, heavily distorted MCDW, and (iii) the intermediate, MSP+AF are superimposed.

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