Local Dynamic Deformation of the Superconducting CuO₂ Plane in the Nd_{2-x}Ce_xCuO_{4+δ} Compound

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Abstract—The local structure of the electron-doped high-temperature superconductor Nd_{2-x}Ce_xCuO_{4+δ} has been investigated by EXAFS spectroscopy using synchrotron radiation in the temperature range 5–300 K. The radii, coordination numbers, and Debye–Waller factors of the nearest coordination spheres of the copper, neodymium, and cerium local environment have been obtained. The Einstein temperatures, characterizing the strength of Cu–O, Nd–O, and Ce–O interatomic bonds have been determined. The dynamic local deformation of the superconducting CuO₂ plane in the form of vibrations of some part of oxygen ions in a double-well potential due to the difference in the electronic filling of neighboring CuO₄ complexes has been established.

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The Nd_{1.85}Ce_{0.15}CuO₄ (NCCO) compound is a high-temperature superconductor with *n*-type conductivity, with only one CuO₂ plane per unit cell and without apical oxygen ions above copper ions. At the same time, the presence of out-of-plane oxygen ions plays a very important role in its superconducting properties. Even with the optimal cerium content (*x* = 0.15), NCCO does not exhibit superconductivity without vacuum annealing. Removal of ~1% oxygen by vacuum annealing leads to an increase in conduction in the normal state and formation of the superconducting state with *T_C* > 23 K, which is indicative of a significant transformation of the electronic structure at a relatively small change in the local atomic structure. In this context, investigation of the features of local atomic structure of the superconducting CuO₂ plane and the local position of out-of-plane oxygen with respect to neodymium and cerium is of great interest. To this end, we investigated the *E*4-line extended X-ray absorption fine structure (EXAFS) spectra of NCCO compounds with *x* = 0, 0.15, and 0.2 above the Cu *K*, Nd *L*_{III}, and Ce *L*_{III} absorption edges in the temperature range 5–300 K. The EXAFS study was performed at the HASYLAB synchrotron center (DESY, Hamburg, Germany).

The EXAFS spectra measured above the Nd *L*_{III} and Ce *L*_{III} absorption edges were processed by the VIPER software [1], using the standard procedure of selection and Fourier analysis of the EXAFS function $\chi(k)$. The spectra were simulated according to the formula

$$\chi(k) = -S_0^2 \sum_j N_j \frac{|f_j(\pi, k)|}{kR_j^2} \times \sin(2kR_j + 2\phi_i(k) + \phi_j(k)) \exp(-2\sigma_j^2 k^2), \quad (1)$$

where summation is over all coordination spheres of the absorbing atom, *N_j* is the coordination number, *R_j* is the mean radius for the *j*th coordination sphere, σ_j^2 is the Debye–Waller factor (mean-square deviation of the interatomic distance), and *k* is the modulus of the photoelectron wave vector. The scale factor *S*₀² takes into account the many-electron effects. The backscattering amplitudes *f_j*(*π*, *k*) and phase shifts 2 $\phi_i(k)$ and $\phi_j(k)$ were calculated using the FEFF-8.20 program [2].

Figure 1 shows the backward Fourier transform (BFT) of the experimental EXAFS function $\chi(k)k^2$ of Nd_{1.85}Ce_{0.15}CuO₄, measured above the Ce *L*_{III} and Nd *L*_{III} absorption edges. EXAFS simulation gave the radii and Debye–Waller factors of the nearest coordination spheres of neodymium and cerium local environment. It is established that doping of Nd₂CuO₄ with cerium leads to deformation of the local structure of this compound: the interatomic distance between cerium and out-of-plane oxygen (Ce–O(2)) for Nd_{1.85}Ce_{0.15}CuO₄ and Nd_{1.8}Ce_{0.2}CuO₄ is smaller by 0.07 Å in comparison with Nd–O(2); this difference is in agreement with the results of [3]. The Nd–O(2) bond length remains the same. In addition, the Nd–O(2) bond strength increases: the Einstein temperature Θ increases from 474 to 522 K for Nd_{1.85}Ce_{0.15}CuO₄; for Nd_{1.8}Ce_{0.2}CuO₄, Θ = 634 K. The Einstein temperatures for the Ce–O(2) and Nd–O(2) bonds in Nd_{1.85}Ce_{0.15}CuO₄ are very close (508 and 522 K respectively); however, the Einstein temperature for the Ce–O(2) bond in Nd_{1.8}Ce_{0.2}CuO₄ decreases to 458 K.

Simulation of the EXAFS function measured above the Cu *K* edge was performed with allowance for the multiple-scattering contribution, which must be taken

Fig. 1. BFT of the EXAFS function $\chi(k)k^2$ of Nd_{1.85}Ce_{0.15}CuO₄ for the (a) Ce L_{III} and (b) Nd L_{III} absorptions edges.

Fig. 2. BFT of the EXAFS function $\chi(k)k^2$ of the Cu–O(1) bond in the CuO₂ plane for (a) Nd₂CuO₄ and (b) Nd_{1.85}Ce_{0.15}CuO₄.

into account due to the focusing effect on the ions aligned in a row in the CuO₂ plane (see, for example, [4]). It is found that introduction of cerium into Nd₂CuO₄ up to $x = 0.15$ leads to a decrease in the interatomic distance Cu–O(2) between copper and out-of-plane oxygen by 0.06 Å, whereas the other interatomic distances remain the same. When the cerium content increases to $x = 0.20$, this distance decreases even more by 0.04 Å. It was established that, in the case of Nd_{1.85}Ce_{0.15}CuO₄, the Einstein temperature for the copper–oxygen bond Cu–O(1) in the CuO₂-plane is shorter than those for Nd₂CuO₄ and Nd_{1.8}Ce_{0.2}CuO₄ ($\Theta = 476$ K against 513 and 554 K, respectively).

At the same time, for the superconducting compound Nd_{1.85}Ce_{0.15}CuO₄, simulation of the EXAFS function of the first coordination sphere Cu–O(1) in the CuO₂ plane within the harmonic approximation does not make it possible to adequately describe the amplitude and phase of the experimental EXAFS function at large moduli of the wave vector $k > 11$ Å⁻¹, in contrast to the initial insulating compound Nd₂CuO₄ (Fig. 2). This fact suggests strong deviation of vibrations of oxy-

gen ions in the superconducting CuO₂ plane from the harmonic law. A similar effect was previously found by us in the Ba_{1-x}K_xBiO₃ superconducting system [5, 6]. Later, deviation of oxygen vibrations in the CuO₂ plane from the harmonic law was observed in [7, 8] in analysis of local structural fluctuations in the superconductor La₂CuO_{4.1}.

Since the pair atomic radial distribution function cannot be described by a Gaussian function in this case, the experimental EXAFS function was simulated, as in [6], by constructing the vibration potential, specified by the parametric function of interatomic distances:

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

where $g(r) = N \sum |\Psi_n(r)|^2 \exp(-E_n/kT) / \sum \exp(-E_n/kT)$ is the pair atomic radial distribution function in the j th sphere; N is the coordination number; E_n and Ψ_n are,

Fig. 3. (a) BFT of the EXAFS function of the Cu–O(1) sphere of the $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ compound at $T = 5$ K; (b) two-well and single-well potentials of oxygen vibrations in the superconducting CuO_2 plane along with pair radial distribution functions (PRDFs). The arrows indicate the tunneling frequency in the double-well potential.

respectively, the n th energy level and its wave function in the model potential; $r_{\min}$ and $r_{\max}$ are the parameters of the BFT window. The variables are N and the model potential parameters. The backscattering phase shift $2\phi_i(k) + \phi_j(k)$ and amplitude $F(k)$ were calculated using the FEFF-8.2 program [2].

For $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$, the EXAFS function of the Cu–O(1) sphere was simulated using the VIPER software [1] using a double-well potential, according to the procedure described in [6]. It was assumed in the simulation that the contribution of vibrations to the double-well potential in the experimental EXAFS function is 15%, whereas the majority (85%) of oxygen ions oscillate in a single-well parabolic potential. As a result, we could not only completely reconstruct the experimental EXAFS function using this model but also obtain the

parameters of the double-well potential, describing oxygen vibrations in the superconducting CuO_2 plane (Fig. 3). The same conclusions about the existence of dynamic local deformations of the superconducting CuO_2 plane in high-temperature superconductors in the form of the double-well potential of oxygen vibrations were drawn in [7–9]. We believe that the formation of the double-well potential in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ is due to the difference in the electron filling of neighboring CuO_4 complexes, which occurs in the case of electron doping of the initial Nd_2CuO_4 cerium, by analogy with the hole-doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ compound [10, 11].

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