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Electronic Structure of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ Irradiated by He^+ Ions: An X-Ray Absorption Study on the Cu-L_{3} and $\text{Ce-M}_{4,5}$ Edges

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Abstract. Polarisation- dependent x-ray absorption spectroscopy at the Cu L_3 and $\text{Ce M}_{4,5}$ edges have been performed on the epitaxial films $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ vs. defect concentration induced by He^+ ion irradiation. The Cu L_3 edge exhibits increasing of integral intensity of both the white line in $\text{E}||\text{ab}$ and the first peak in $\text{E}||\text{c}$ by about 15% and 30% , respectively, after suppression of superconductivity. The partial filling of $\text{Ce } 4f$ orbitals ($\sim 15\%$) takes place although the Ce ions remain formally tetravalent, Ce^{+4} . Thus, XAS experiments give a clear evidence that the excess electrons leave $\text{Cu } 3d^{10}x^2y^2$ orbital and become simultaneously localised in the $\text{Ce-O}(2)$ chains. The symmetry of the free states and the mechanism of superconductivity suppression in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ under He^+ ion irradiation are discussed.

It is well known that high T_c superconductors are very sensitive to the non-magnetic impurities and crystal structure defects produced, for instance, by irradiation. Disorder leads to the superconductor to semiconductor transition, and critical temperature, T_c , drops to zero. Change of T_c under atomic disorder depends on coupling mechanism [1]. That is why the study of variation in electronic structure of NdCeCuO under the He^+ irradiation may be useful for clarifying the nature of the carriers supplied by Ce doping and the coupling mechanism.

In this paper we have reported the analysis of the Cu L_3 and $\text{Ce M}_{4,5}$ absorption edges of the superconducting and semiconducting (irradiated by He^+ ions, $E = 1.2 \text{ MeV}$, $\phi = 10^{16} \text{ cm}^{-2}$) $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$.

The $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ thin films (thickness $\sim 1000 \text{ \AA}$) were prepared by *in situ* laser deposition technique on YSZ (100) substrates. X-ray diffraction patterns of the superconducting and semiconducting films indicated a pure T' - phase.

The polarised x-ray absorption measurements were performed on ABS-2 station of Super-ACO storage ring at the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (Orsay, France), using a double crystal $10\bar{1}0$ beryl monochromator. The energy resolution was $\sim 0.3 \text{ eV}$ at 900 eV with a 1.0 mm slit. The energy scale was calibrated by assigning $E = 931.2 \text{ eV}$ to the maximum of the white line of the L_3 Cu absorption edge of CuO oxide. The drift of the energy scale through all experiments did not exceed 50 meV that was tested by repeated recording of the spectra. Polarised spectra were recorded for $\theta = (20, 30, 40, 60, 90)^\circ \pm 5^\circ$, here θ is the angle between the x-ray polarisation vector E and the c axis. All spectra were collected in the TEY mode at room temperature.

Polarisation- dependent Cu L_3 absorption edge of the superconducting and semiconducting (irradiated by He^+ ions) $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ films is shown in Fig. 1. The spectra in $\text{E}||\text{c}$ polarisation were obtained by numerical extrapolation from the spectra recorded at different angles to $\theta = 0^\circ$. The $\text{E}||\text{ab}$ Cu L_3 spectrum of superconducting $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ exhibits a strong absorption at about 931.8 eV . White line has a symmetric Lorentzian- like shape. Its full width at half maximum (FWHM) is $\sim 1.0 \text{ eV}$ that is comparable to the FWHM reported in previous EELS measurements [2]. There is energy shift of 0.3 eV between the white line in $\text{E}||\text{ab}$ and the first peak in $\text{E}||\text{c}$ spectrum. Under irradiation, the white line exhibits downward energy shift of 0.2 eV and increase of integral intensity of $\sim 15\%$. This line remains quite symmetric. It indicates that no hole states are formed in irradiated $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$, at least up to the fluence of 10^{16} cm^{-2} . No broadening of the white line was observed within an accuracy of 0.1 eV .

The $\text{Ce M}_{4,5}$ absorption edges of the normal and irradiated $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ are shown in Fig. 2. We could not find any noticeable polarisation- dependence of $\text{Ce M}_{4,5}$ edges. This result is in agreement with the fact that the Ce site in the T' structure has rather symmetric eightfold oxygen coordination. The 15% decrease of the integral intensity of the $\text{M}_{4,5}$ edges was observed upon He^+ irradiation. The shape of $\text{Ce M}_{4,5}$ edges did not change. No shoulder at the low energy side of the main peaks, which is usually assigned to the Ce^{+3} , could be distinguished. The Ce ions remain formally tetravalent, although the $4f$ count $\langle n_{4f} \rangle$ of the Ce ions estimated as ~ 0.5 in superconducting $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ increases to ~ 0.6 upon irradiation.

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Figure 1: Cu L_3 edge of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ before (solid) and after (dashed) irradiation.

Figure 2: Ce $M_{4,5}$ edges of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ before (solid) and after (dashed) irradiation.

Figure 3: The structure of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ upon He^+ irradiation, [4].

The Cu L_3 edge of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ changes under irradiation as if Ce concentration decreased [2]. Variation of Ce concentration is completely excluded. Therefore, the experiments on the Cu L_3 and Ce $M_{4,5}$ edges give a clear evidence that the excess electrons leave Cu $3d^{10}$ orbitals and become simultaneously localised in the Ce-O(2) chains under irradiation. Nevertheless, there are differences between the final states in pure Nd_2CuO_4 and those in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ irradiated by He^+ ions. (i) No energy splitting between the $2p \rightarrow 3d_{x^2-y^2}$ and $2p \rightarrow 3d_{3z^2-y^2}$ transitions was observed in Nd_2CuO_4 [2], while in irradiated $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ this value is as large as 0.5 eV. (ii) The first peak in $E||c$ spectrum of irradiated $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ increases in integral intensity by about 30% with respect to that of Nd_2CuO_4 .

To clear up the mechanism of superconductivity suppression in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ upon He^+ irradiation, let us compare the Cu L_3 and Ce $M_{4,5}$ data with polarised Cu K-edge XANES [3] and EXAFS [4] studies. XANES on Cu K edge pointed out that radiative defects bring the distinctive variations of Cu $4p_\pi$ states, while variations of Cu $4p_\sigma$ states were not found [3]. Such a behaviour of electronic structure of CuO_2 plane looks puzzling, since the resistivity measurements indicated the suppression of superconductivity after irradiation. Hence, some changes of the electronic structure in CuO_2 plane should take place. These changes were observed by present Cu L_3 edge measurements. In contrast to Cu-K measurements, they provide direct information on Cu $3d$ orbitals which along with O $2p$ ones are responsible for superconductivity in cuprates.

EXAFS study showed [4] that O(2) atoms are displaced from their primary site up to 0.1 Å upon irradiation (see Fig. 3). It should give rise to additional hybridisation between Nd(Ce) $5d(4f)$ and O(2) $2p$ orbitals and partial localisation of the charges due to contraction of Nd(Ce)-O(2) interatomic distances. Localisation of the charges in the Ce-O(2) chains is clearly observed from present Ce $M_{4,5}$ measurements. The excess electrons, occupying dominantly Cu $3d^{10}_{x^2-y^2}$ orbital [2] in superconducting $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$, localise in the Ce-O(2) chains under irradiation and dope no longer CuO_2 planes. Thus, at least two channels for superconductivity suppression in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ upon He^+ irradiation are assumed. Both (1) the localization of excess carriers in the chains accompanied by the simultaneous releasing of Cu $3d^{10}_{x^2-y^2}$ orbital and (2) the random space fluctuation of charge density in the chains suppress the coupling. It should be mentioned that existence of the mechanism- (1) is a necessary condition for that of the mechanism- (2), since there was not observed any broadening of Cu $3d_{x^2-y^2}$ states upon irradiation from Cu L_3 edge experiment.

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