PHYSICAL REVIEW B        VOLUME 42, NUMBER 1        1 JULY 1990

# Electronic structure of the electron-doped superconductor $Nd_{2-x}Ce_xCuO_{4-y}$ studied by photoemission spectroscopy

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The electronic structure of the electron-doped superconductor $Nd_{2-x}Ce_xCuO_{4-y}$ has been studied by photoemission spectroscopy. The results indicate that the system is indeed doped with electrons supplied by the $Ce^{4+}$ ions substituting $Nd^{3+}$ sites. From the Cu core-level and the valence-band results, however, we find no evidence for the occupation of Cu $3d$ orbitals by the doped electrons at least for low doping concentrations $x \leq 0.15$.

The recent discovery of high-temperature superconductivity in the electron-doped system $Nd_{2-x}Ce_xCuO_{4-y}$ by Tokura *et al.*[1] has aroused considerable interest, since superconductivity in Cu-based oxides has previously been achieved only through hole doping. The new superconductor forms in the $T'$-$Nd_2CuO_4$ structure which has $CuO_2$ planes as in the hole-doped superconductors but has no oxygen atoms above and below the Cu sites, leading to a square-planar oxygen coordination of Cu. Superconductivity is observed for a narrow composition range, $0.14 \leq x \leq 0.18$.[2] A muon-spin-rotation study[3] has shown that the antiferromagnetic ordering of Cu persists up to $x$ as large as $\sim 0.1$.

In this work, we have studied the electronic structure of $Nd_{2-x}Ce_xCuO_{4-y}$ by photoemission spectroscopy. Of particular interest is the character of doped electrons: Whether or not the doped electrons go into the unoccupied $(x^2-y^2)$-symmetry Cu $3d$ orbitals has important consequences on the electronic and magnetic interactions in this system, and hence on the mechanism of superconductivity. This issue was already addressed by a Cu $K$-edge x-ray absorption study,[4] in which it was concluded that the doped electrons go into the Cu $3d$ orbitals. One of our purposes is therefore to check whether the same conclusion can be obtained from photoemission spectroscopy.

$Nd_{2-x}Ce_xCuO_{4-y}$ samples with $x=0$, 0.05, 0.1, 0.15, and 0.2 were prepared by sintering stoichiometric mixtures of CuO, $Nd_2O_3$, and $CeO_2$ at 1100 °C in air followed by quenching or furnace cooling them to room temperature. We have also studied samples which were subsequently reduced in a mixed $Ar+O_2$ atmosphere at 1050 °C or in $CO_2$ at 900 °C for $\sim 10$ h, which is necessary to obtain superconducting samples.[1] Spectra were taken using He I and He II resonance lines ($h\nu=21.2$ and 40.8 eV) for ultraviolet photoemission spectroscopy (UPS) and Mg $K\alpha$ radiation ($h\nu=1253.6$ eV) for x-ray photoemis-

sion spectroscopy (XPS). Satellites of the radiation sources have been numerically subtracted. The energy resolution was $\sim 1$ eV for XPS and $\sim 0.15$ eV for UPS. Since photoemission spectroscopy is a surface-sensitive technique, utmost care was taken to produce clean surfaces representative of the bulk electronic structure. The samples were introduced into the spectrometer having a base pressure of $\sim 1 \times 10^{10}$ Torr via an airlock entry and were scraped *in situ* with a diamond file. To avoid oxygen losses and/or surface degradation, the samples were cooled to liquid nitrogen temperature ($\sim 80$ K) while scraping and during the measurements. Even with these precautions, spectra of sintered samples may be contaminated by grain boundary phases. In order to minimize the grain boundary contribution, we have selected spectra only of those surfaces which satisfy the following conditions: (i) The O $1s$ XPS spectra shows a single peak at a binding energy $E_B \sim 529$ eV without an additional peak at $E_B \sim 532$ eV since the latter peak is an indication of contamination or surface degradation[5] (Fig. 1). (ii) The valence-band UPS spectra show a negligibly small hump at around 9–10 eV below the Fermi level ($E_F$). This hump is also a characteristic feature of degraded or contaminated surfaces[5] (Fig. 1). (iii) The atomic ratio as determined by core-level photoemission intensities agrees with the bulk chemical composition. Most of spectra from reduced samples were thus eliminated based on obvious signs of grain boundary contaminations, probably of $Cu_2O$, and therefore the experimental data presented here are those of quenched and furnace-cooled samples unless otherwise stated. Nevertheless, we expect that the effect of the reduction on the bulk electronic structure is small at least on the scale of the energy resolution and the sensitivity of photoemission spectroscopy because of the very small amount of oxygen deficiency.[6] Thus we assume that systematic changes in the spectra of the unreduced samples as a function of Ce concentration indeed
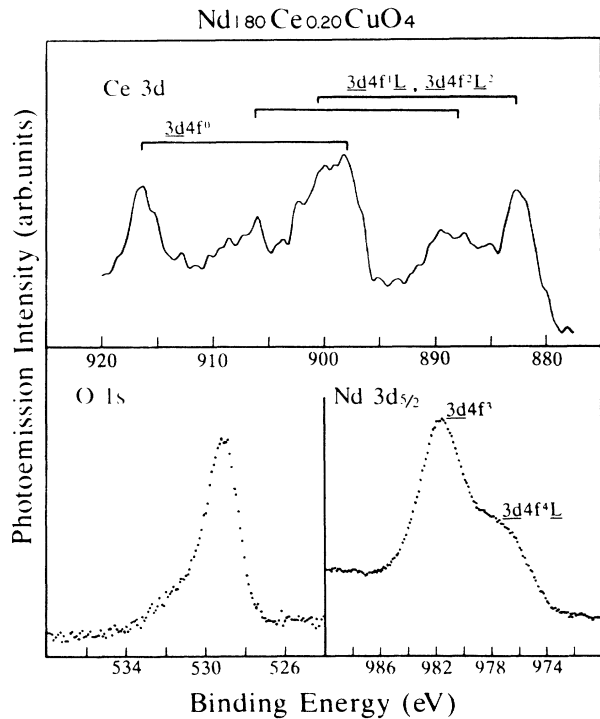
FIG. 1. Ce $3d$, Nd $3d_{5/2}$, and O $1s$ core-level XPS spectra of $Nd_{1.8}Ce_{0.2}CuO_{4-y}$. $\underline{3d}4f^0$, etc., denote final-state configurations with a Ce or a Nd $3d$ core hole. The weakness of the high binding energy shoulder at $E_B \sim 532$ eV in the O $1s$ spectrum guarantees that the quality of the sample surface is comparable to that of single crystals.

represent changes in the electronic structure associated with electron doping and the occurrence of superconductivity, even though the unreduced samples do not show metallic conductivity at low temperatures up to $x \sim 0.2$.

The Ce and Nd $3d$ core-level XPS spectra shown in Fig. 1 exhibit satellite structures characteristic of $Ce^{4+}$ (formally $4f^0$) and $Nd^{3+}$ ($4f^3$) valence states, respectively. The intensities of these core levels relative to that of Cu as functions of $x$ indicate that Nd is indeed replaced by Ce. The Nd core level shows a "shake-down" satellite on the low binding energy side due to a ligand-to-$4f$ charge transfer in the photoemission final state.[7] The complex satellite structure of the Ce core level arises from both $4f$-ligand hybridization in the ground state and the charge-transfer effect in the final state.[8] We may thus conclude that most ($> 95\%$) of the Ce atoms are in the tetravalent state and that each $Ce^{4+}$ ion substituting $Nd^{3+}$ supplies one electron carrier to the system. Here it should be remarked that the number of carriers supplied by the Ce substitution is *exactly one* per Ce in spite of the fact that the actual Ce $4f$ occupancy is as large as $\sim 0.5$.[8] This is because the $4f$ occupancy is a result of $4f$-ligand hybridization occurring across the large band gap, and should not be confused with ordinary valence mixing in metallic compounds in which the number of carriers is intermediate between those of $Ce^{3+}$ and $Ce^{4+}$.

The valence-band UPS spectra (Fig. 2) show no detectable emission between the Fermi level ($E_F$) and $\lesssim 1$ eV
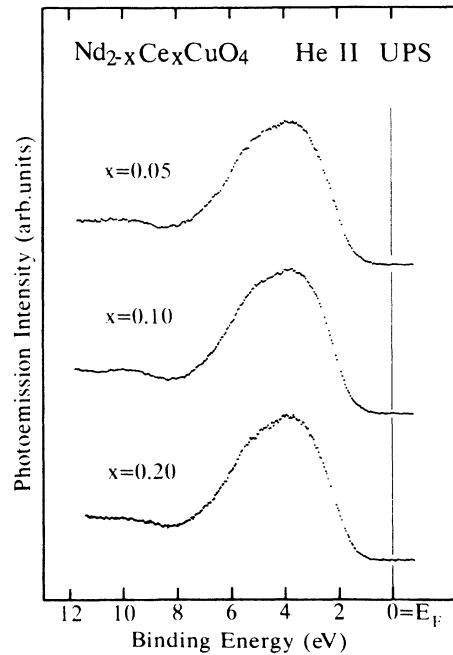


FIG. 2. Valence-band UPS spectra of $Nd_{2-x}Ce_xCuO_{4-y}$ taken with $h\nu = 40.8$ eV.

below it, i.e., the top of the main Cu $3d$–O $2p$ band. This observation is consistent with electron doping into an insulator and is contrasted with the case of hole doping, where $E_F$ is located within oxygen $p$-derived states just above the top of the Cu $3d$–O $2p$ band.[9] States occupied by doped electrons, however, are not observable in the UPS spectra at $E_F$ even for $x = 0.2$. It is not clear at this stage whether the absence of emission at $E_F$ is due to the low photoionization cross sections of these states (atomic-orbital photoionization cross sections are tabulated in Ref. 10) or due to surface degradation that did not significantly distort the O $1s$ line shape and the valence band around $E_B \sim 9$ eV but affected the emission at $E_F$.[11]

Shifts in $E_F$ with doping as observed in the valence-band UPS spectra are found to be negligibly small ($\ll 0.05$ eV relative to the Cu $3d$–O $2p$ band position between $x = 0.05$ and $0.2$). This observation, if it is intrinsic,[11] can be interpreted as due to the pinning of $E_F$ by localized or band states formed below the bottom of the conduction band in the doped materials. The formation of the new states may be ascribed to the electrostatic potential of the $Ce^{4+}$ ions substituting the $Nd^{3+}$ sites, or could possibly be due to many-body effects of unspecified origin. The energy of the optical absorption edge in $Nd_2CuO_4$ has been reported to be 1.5 eV,[12] which combined with the $E_F$ position would locate the pinning level at $\gtrsim 0.5$ eV below the bottom of the conduction band.

A direct measure of the occupancy of the Cu $3d$ orbitals can be obtained from the doping dependence of the Cu $2p$ core-level spectra. As shown in Fig. 3, the Cu $2p_{3/2}$ core-level peak of divalent Cu (formally $d^9$) is split into the main peak (corresponding to the charge-transfer-screened $\underline{2p}3d^{10}\underline{L}$ final state) and a satellite (corresponding to the unscreened $\underline{2p}3d^9$ final state), where $\underline{2p}$

denotes a Cu $2p_{3/2}$ core hole. The $2p_{3/2}$ core level of monovalent Cu ($d^{10}$) for $Cu_2O$ shown in Fig. 3 has a single peak corresponding to the $\underline{2p}3d^{10}$ final state. If every doped electron occupies a Cu $3d$ orbital (and if the line shape of the $Cu^{2+}$ component does not change with $x$), the satellite intensity would decrease with $x$ as shown in Fig. 3(b). Experimental results show less pronounced changes with $x$ as shown in Fig. 3(a) or in the inset of Fig. 3. In the latter figure, where the satellite-to-main peak intensity ratio $I_s/I_m$ is plotted as a function of $x$, one
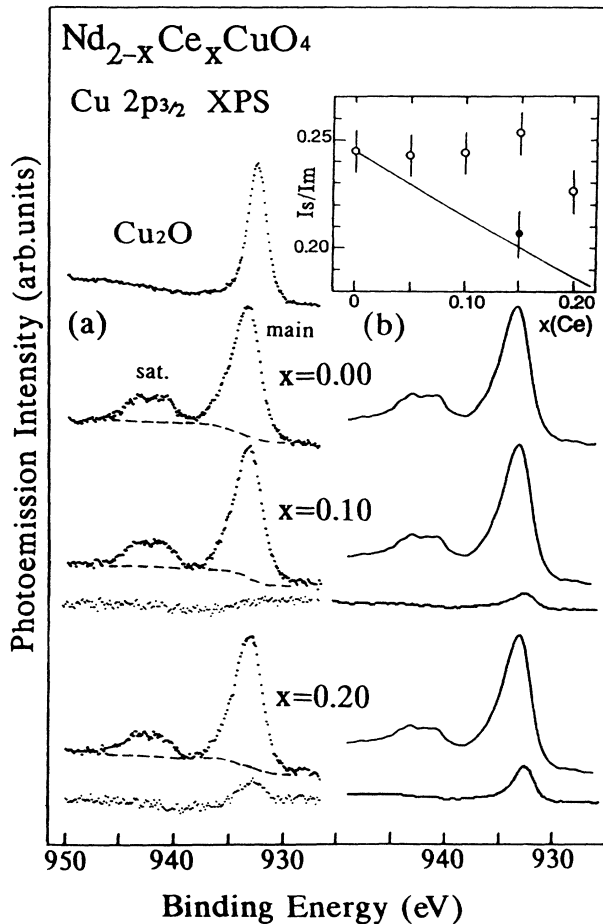
finds a fairly constant $I_s/I_m$ compared to what would be expected for the occupation of the Cu $3d$ orbitals by all doped electrons as represented by the solid line. Also, the difference spectrum between $x=0.0$ and $x=0.1$ [Fig. 3(a)] shows no appreciable $Cu^+$ contribution at $E_B \sim 932$ eV, whereas significant $Cu^+$ contribution would be expected in the difference spectrum as in Fig. 3(b). The satellite intensity of a reduced (superconducting) $x=0.15$ sample was found to be exceptionally small, as indicated by a filled circle in the $I_s/I_m$ plot, even though the O $1s$ and valence-band spectra suggest a clean surface. However, this small $I_s/I_m$ is likely to be due to extrinsic $Cu^+$ contamination since a prolonged reduction of the sample sample in $CO_2$ resulted in detectable impurity phases. As for the $x=0.2$ sample, it is not clear at present whether the small but appreciable decrease in $I_s/I_m$ and the small difference signal at the $Cu^+$ position ($\sim 10\%$ of the total Cu $2p_{3/2}$ intensity compared to 20% expected for the occupation of the Cu $3d$ orbitals) are intrinsic or not.

The above conclusion will not be altered even if the effect of itinerancy of the extra Cu $3d$ electrons is taken into account. Such itinerancy opens up a new channel for the core-hole screening through the filling of screening orbitals, i.e., unoccupied $d$ or ligand orbitals in the $d^9$ or $d^{10}\underline{L}$ configuration, via "intercluster" transfer of the itinerant electrons. We expect such a screening probability to be negligibly small and, if it exists, it would rather shift spectral weight from the $\underline{2p}3d^9$ or $\underline{2p}3d^{10}\underline{L}$ final states to the $\underline{2p}3d^{10}$ states thereby decreasing $I_s/I_m$ further.[7]

If the Cu $d^{10}$ states remain largely unoccupied in the doped materials, the doped electrons will enter the lower conduction band states whose atomic-orbital origins are Nd $5d$, Ce $5d$, and Cu $4s$. According to band-structure calculations,[13] the conduction band minimum in $Nd_2CuO_4$ is located at the $\Gamma$ point of the Brillouin zone, where a considerable mixture of Cu $s$ character is expected from symmetry consideration. This is not the case for the $K_2NiF_4$-type $La_2CuO_4$, in which the conduction band minimum of La $5d$ character is located at the $Z$ point.[14] In the undoped material, the Madelung potential for electrons at the Cu site is low compared to that in $La_2CuO_4$ favoring the occupation of Cu sites.[15] [In this context, we note that the ligand-to-Cu charge-transfer energy is found to be smaller ($\Delta=0-0.5$ eV) than that of the related hole-doped system $Nd_{2-x-y}Sr_xCe_yCuO_4$ ($\Delta=0.5-1$ eV), consistent with the Madelung energies.] In the doped materials, however, the electrostatic potential due to the substitutional Ce ions may have to be taken into account in considering the electron doping process. The fact that similarly high $T_c$'s have been observed for $Pr_{2-x}Ce_xCuO_{4-y}$ and $Sm_{2-x}Ce_xCuO_{4-y}$ indicates that the magnetic moment at the Nd sites has virtually no effect on superconductivity,[1] which in turn suggests that the $5d$ orbitals at the Nd sites would not be much involved in the superconducting state. If carriers are not Cu $3d$ electrons, magnetic interaction with the Cu $d^9$ local moments would be much weaker than for Cu $3d$ carriers or for hole carriers at the oxygen sites in the $CuO_2$ planes.



FIG. 3. Cu $2p_{3/2}$ core-level XPS spectra of $Nd_{2-x}Ce_xCuO_{4-y}$ and $Cu_2O$. (a) Measured spectra; for $x=0.1$ and 0.2, the difference from the $x=0.0$ spectrum is shown on the bottom of each spectrum. (b) Superpositions of the $Nd_2CuO_4$ and $Cu_2O$ spectra, which simulate the case where all doped electrons enter the Cu $3d$ orbitals; for $x=0.1$ and 0.2, the difference from the $x=0.0$ spectrum is shown on the bottom of each spectrum. The subtractions have been made so that the satellites are canceled out; in some cases, the spectra were shifted (by $\sim 0.1$ eV) relative to each other prior to subtraction. The insert shows the relative intensity $I_s/I_m$ of the satellite ($\underline{2p}3d^9$) to the main peak ($\underline{2p}3d^{10}\underline{L}$) as a function of $x$ (open circles—quenched or furnace-cooled samples; filled circle—reduced sample, see the text). The solid curve in the insert shows the behavior expected when all doped electrons occupy the Cu $3d$ orbitals. Integral backgrounds have been assumed as shown by dashed curves.

Finally, we would like to comment briefly on the Cu $K$-edge x-ray absorption study by Tranquada *et al.*,[4] who have claimed that the Cu $d^{10}$ configuration is indeed created by electron doping. Their argument heavily relies on the assumption that the $1s \rightarrow 4p\pi$ absorption peak near the threshold of $Cu_2O$ is characteristic of the $Cu^+$ valence state. However, the high intensity of this peak in $Cu_2O$ is due to the linear oxygen coordination of Cu, hence strong $4p\pi$ character in this material, and its relevance to the valence of Cu has not been firmly established.[16] Further systematic studies on the Cu $K$-edge spectra of reference materials is necessary to settle this point.

In summary, while the results are consistent with electron doping realized by $Ce^{4+}$ substitution for $Nd^{3+}$, no evidence is found for the existence of Cu $d^{10}$ configurations for low doping concentrations $x \leq 0.15$. While the doping appears to induce new states below the bottom of the conduction band, the orbital origin of these states is not clear at present.

## ACKNOWLEDGMENTS

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