Valence state of copper in $Nd_{2-x}Ce_xCuO_4$

Y. Hwu, M. Marsi, A. Terrasi, D. Rioux, Y. Chang, J. T. McKinley,
M. Onellion, and G. Margaritondo

University of Wisconsin-Madison, Stoughton, Wisconsin 53589-3097

M. Capozi, C. Quaresima, A. Campo, C. Ottaviani, and P. Perfetti

Laboratorio di Struttura della Materia, Consiglio Nazionale delle Ricerche (CNR),
via Enrico Fermi 38, I-00044 Frascati, Italy

N. G. Stoffel and E. Wang

Bellcore, 331 Newman Springs Road, Red Bank, New Jersey 07701

(Received 27 March 1990; revised manuscript received 30 July 1990)

New photoemission data are presented for a series of Ce-doped or undoped, reduced or nonreduced, Nd cuprates. The data, taken with high signal-to-noise level in the constant-initial-state mode, demonstrate the presence of Cu^+, in contrast with previous photoemission and electron-energy-loss studies.

The discovery of high-temperature superconductivity in Ce-doped Nd cuprates has generated a great deal of controversy concerning the valence state of copper and, to some extent, the nature of the carriers.[1−4] The early experiments on these materials reported n-type conductivity based on Hall measurements;[1] this seemed consistent with the evidence for Cu^+ derived from core-level photoemission data.[2] Later, energy-loss experiments by Nücker et al. [3] raised questions about the presence of Cu^+ in Ce-doped samples. Earlier valence-band photoemission experiments by Fujimori et al., [4] as well as preliminary results of our study,[5] seemed to corroborate these questions, since they did not provide evidence for Cu^+. The controversy produced doubts about the mechanism of superconductivity in this class of materials, including, perhaps, questions about the revolutionary discovery of n-type high-temperature superconductivity.[1]

We recently completed a careful study of this issue using resonant photoemission, and our results eliminate the controversy by showing a weak, but clearly detectable, resonating Cu^+ signal in Ce-doped samples. This conclusion is based on a careful analysis of constant-initial-state photoemission spectra[6,7] taken on nine different $Nd_{2-x}Ce_xCuO_4$ samples. In this way, we have been able to observe the resonating Cu^+ signal that was not detected in earlier experiments.

The experiments were performed on a series of $Nd_{2-x}Ce_xCuO_4$ samples with $x=0$, 0.05, 0.10, 0.15, and 0.20. We examined samples that had or had not been reduced in a nitrogen atmosphere; specifically, reduced samples of all compositions were investigated and nonreduced samples with $x=0$, 0.10, 0.15, and 0.20. Of these, the nitrogen-reduced $x=0.15$ compound is a high-temperature superconductor. The procedure for growing and characterizing these materials has been described in Ref. 8. The samples were sintered pellets, and clean surfaces were obtained by scraping *in situ* under ultrahigh-vacuum conditions with a diamond grinder. The surfaces

were characterized by taking valence-band and core-level photoemission spectra; in particular, valence-band spectra (see Fig. 1) do not show evidence of contamination. The procedure used for the photoemission experiments is equivalent to that described in Ref. 5, except for the constant-initial-state technique[6,7] described later.

The technique used to detect the Cu^+ signal was resonant photoemission.[7] Under certain conditions, the intensity of features in the photoemission spectra resonates for a narrow range of photon energies. The resonance is due to the quantum interference between two different channels for photoelectron production, both with the same initial and final states. Resonances occur for photon energies near the optical absorption thresholds of the element that produces the resonating photoemission features. Thus, this phenomenon can be exploited to enhance the signal from a given element, and to extract information on its properties. In the present case, from
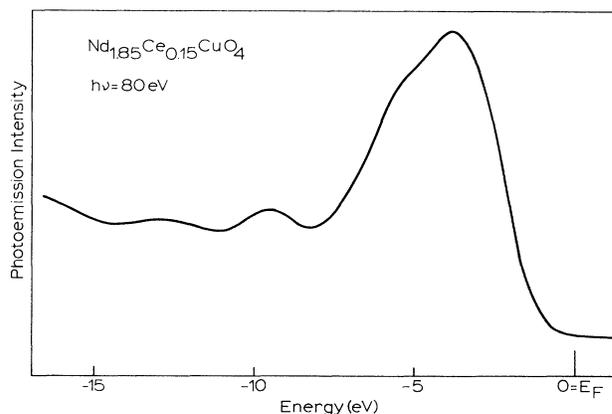

FIG. 1. Conventional photoemission spectrum (energy distribution curve) taken for the valence band of the superconducting cuprate $Nd_{1.85}Ce_{0.15}CuO_4$ at a photon energy of 80 eV.

the enhanced copper signal, information is extracted on the valence state of copper.

The resonating photoemission features explored in our study were the so-called copper satellites.[9] Each one of these satellites is caused by a multielectron photoemission process from copper in a specific valence state.[10] Consider the ground configuration of a Cu atom in the $1+$ valence state (as, for instance, in Cu_2O): $3p^63d^{10}$. The excitation of a single photoelectron from the d band leaves the atom in the configuration $3p^63d^9$. The photoelectric process, however, can also involve the parallel excitation of a second electron to an empty state nl (in this case $4s,p$); the final configuration is $3p^63d^8nl$. The excitation of the second electron reduces the energy of the photoelectron. Thus, this process produces a low-kinetic-energy satellite of the main Cu $3d$ photoemission feature.[9]

Similarly, for Cu atoms in the $2+$ state, such as in CuO, the single-electron photoemission process is

$$3p^63d^9 + \text{photon} \rightarrow 3p^63d^8 + \text{photoelectron} .$$
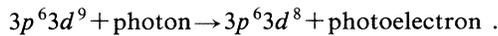
The corresponding satellite occurs when a second $3d$ electron is excited to an nl state (in this case, an empty $3d$ state). Because of the different states and configurations involved, the position in energy of this satellite is different with respect to that of Cu^+.

The presence or absence of a copper satellite is, therefore, a powerful test for the existence of the corresponding valence state.[9] This technique has been extensively applied to high-temperature superconductors.[11] The con-

troversy concerning the valence state of copper in Ce-doped Nd cuprates stimulated the use of resonant photoemission to explore this issue. Early experiments produced inconclusive data,[4,5] and were unable to detect a clear signal from Cu^+.

We have been able to reverse this situation primarily by taking constant-initial-state spectra with signal-to-noise ratio as high as possible. The constant-initial-state mode of photoemission is implemented[6,7] by measuring the number of photoelectrons detected per unit time in an energy window centered at E_f and with a photon energy $h\nu$; both E_f and $h\nu$ are scanned simultaneously, but their difference is kept constant. In this way, one observes the photon-energy dependence of the feature that appears E_f-$h\nu$ below the Fermi level in conventional photoemission spectra. This approach is quite effective in emphasizing resonating features.

The evidence for Cu^+ as well as for Cu^{2+} resonances is presented in Figs. 2 and 3. Figure 2 presents conventional photoemission spectra (energy distribution curves), i.e., the distribution as a function of E_f of the detected photoelectrons for a fixed photon energy. The spectra shown here were taken on three different specimens and with different photon energies; specifically, $h\nu = 74$ and 76.5 eV are photon energies near the resonances for Cu^{2+} and
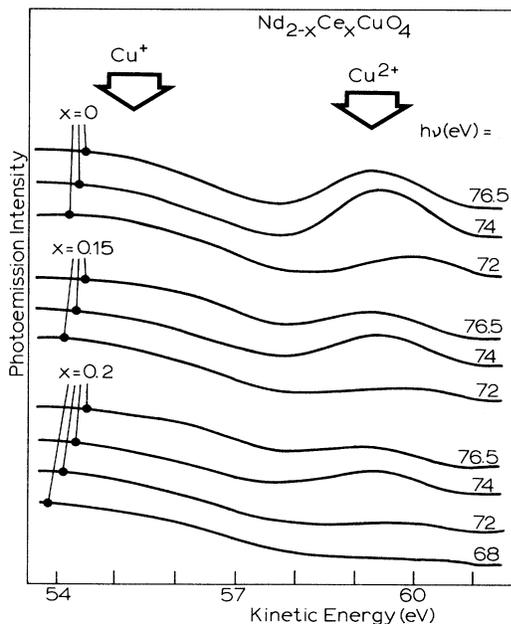

FIG. 2. Conventional photoemission spectra taken for three different Nd cuprates; the two Ce-doped samples were reduced in a nitrogen atmosphere. The horizontal scale is the kinetic energy for the $h\nu = 76.5$ spectra, the other spectra have been shifted to compensate for the change in $h\nu$. The vertical arrows mark the position of the Cu^+ and Cu^{2+} resonances.
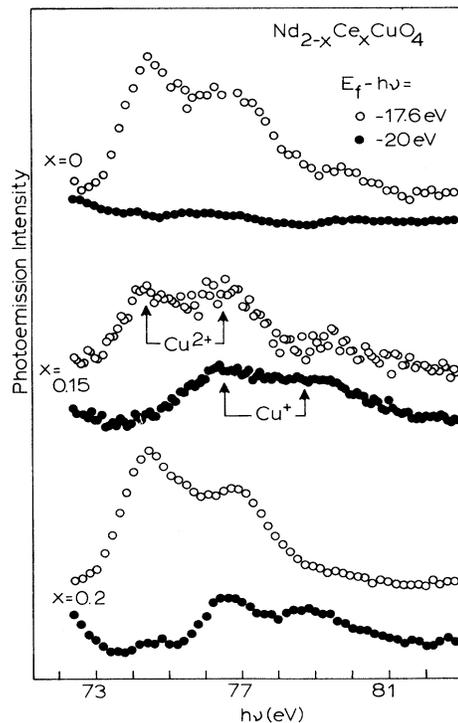

FIG. 3. Constant-initial-state photoemission spectra taken at (constant) E_f-$h\nu$ energies -17.6 (open circles) and -20 eV (solid circles), where E_f is the photoelectron kinetic energy. Data are presented for the same three specimens of Fig. 2. The positions of the two resonances are marked for the central spectra. The two curves for each concentration have been normalized to each other, but the scales for different concentrations are different and arbitrary.

for Cu^+. The spectral region of the figure corresponds to the copper satellites.[9] The resonating Cu^{2+} satellite is readily visible. On the contrary, the 1+ satellite is barely, if at all, visible.

The 1+ satellite, however, becomes much more evident by taking constant-initial-state spectra with high signal-to-noise ratio. Figure 3 shows typical data for the same specimens as Fig. 2. The Cu^+ resonance is clearly visible for the Ce-doped specimens, and the 2+ resonance is evident for all specimens. This result eliminates all questions about the presence of copper in the 1+ state for Ce-doped materials.[3-5]

We tried to quantitatively investigate the relative amounts of Cu^+ and Cu^{2+} in the different specimens. Unfortunately, this procedure is affected by two problems; first, we do not have an absolute normalization for the Cu^+/Cu^{2+} concentration ratio. Second, because of the weakness of the signal, the background correction procedure introduces rather large uncertainties. On a non-normalized scale, we found a Cu^+/Cu^{2+} ratio of 0, 0.5, 0.3, and 0.3 for the nonreduced $x=0$, 0.1, 0.15, and 0.2 samples. The uncertainty is at least 0.1–0.2 on this scale, so the differences between the last three specimens are not necessarily significant.[12] For the reduced sample, we found ratios of 0.2, 0.5, 0.4, 0.4, and 0.5 for $x=0$, 0.05, 0.1, 0.15, and 0.2 on the same scale. The nonzero ratio for the reduced $x=0$ sample is somewhat surprising. The absolute value of the ratio is at the borderline of uncertainty but some Cu^+ could be conceivably produced by the reduction process.

In summary, by carefully exploring many different specimens of Ce-doped or undoped Nd cuprates with the constant-initial-state technique, we have been able to remove the puzzling controversy[1-5] concerning the presence or absence of Cu^+. This also removes questions about the nature of the carriers in these specimens; our own oxygen resonance data fully support n-type conductivity.[5] The clarification of this issue should make it easier to exploit the existence of n-type high-temperature superconductivity for a simplification of the theoretical picture of this exciting phenomenon.

[1]H. Tagaki, S. Uchida, and Y. Tokura, Phys. Rev. Lett. **62**, 1197 (1989).

[2]J. M. Tranquada, S. M. Heald, A. R. Moodenbaugh, G. Liang, and M. Croft, Nature **337**, 720 (1989); Y. Tokura, H. Takagi and S. Uchida, *ibid.* **337**, 345 (1989); Y. Fukuda, T. Suzuki, M. Nagoshi, Y. Syono, K. Oh-ishi, and M. Tachiki, *ibid.* (to be published).

[3]N. Nücker, P. Adelmann, M. Alexander, H. Romberg, S. Nakai, J. Fink, H. Rietschel, G. Roth, H. Schmidt, and H. Spille, Z. Phys. B **75**, 421 (1989).

[4]H. Namatame, A. Fujimori, Y. Tokura, N. Nakamura, K. Yamaguchi, A. Misu, H. Matsubara, S. Suga, H. Eisaki, T. Ito, H. Takagi, and S. Uchida, Phys. Rev. B **41**, 7205 (1990); F. Fujimori, Y. Tokura, H. Eisaki, H. Takagi, S. Uchida, and E. Takayama-Muromachi, *ibid.* **42**, 325 (1990).

[5]T. Terrasi, Y. Hwu, D. Rioux, M. Marsi, Y. Chang, J. T. McKinley, M. Onellion, G. Margaritondo, M. Capozi, C. Quaresima, A. Campo, C. Ottaviani, P. Perfetti, N. G. Stoffel, and E. Wang (unpublished).

[6]G. J. Lapeyre, A. D. Baer, J. Hermanson, J. Anderson, J. A. Knapp, and P. L. Gobby, Solid State Commun. **15**, 1601 (1974); G. J. Lapeyre, J. Anderson, P. L. Gobby, and J. A. Knapp, Phys. Rev. Lett. **33**, 1290 (1977).

[7]G. Margaritondo *Introduction to Synchrotron Radiation* (Ox-

ford, New York, 1988), and references therein.

[8]J. -M. Tarascon, E. Wang, L. H. Greene, B. G. Bagley, G. W. Hull, S. M. D'Egidio, P. F. Miceli, Z. Z. Wang, T. W. Jing, J. Clayhold, D. Brawner, and N. P. Ong, Phys. Rev. B **40**, 4494 (1989).

[9]M. R. Thuler, R. L. Benbow, and Z. Hurych, Phys. Rev. B **26**, 669 (1982).

[10]For simplicity, we adopt here a quasiatomic picture for the resonant satellites of copper. An alternate model is based on the "ligand-to-metal charge transfer" described, for example, in A. Fujimori, E. Takayama-Muromachi, and Y. Uchida, Solid State Commun. **63**, 857 (1987), and references therein.

[11]*Thin Film Processing and Characterization of High-Temperature Superconductors,* edited by J. A. Harper, R. J. Colton, and L. C. Feldman (American Institute of Physics, New York, 1988); *High T_c Superconducting Thin Films, Devices and Characterization,* edited by G. Margaritondo, Robert Joynt, and M. Onellion (American Institute of Physics, New York, 1989).

[12]Keeping in mind our experimental uncertainty, the ratios we found for nonreduced specimens are qualitatively consistent with those estimated by S. Uji, M. Shimoda and H. Aoki, Jpn. J. Appl. Phys. **28**, L804 (1989).