Resonant Photoemission Study of $Nd_{2-x}Ce_xCuO_{4-y}$: Nature of Electronic States near the Fermi Level

J. W. Allen,(1) C. G. Olson,(2) M. B. Maple,(3) J.-S. Kang,(1,3) L. Z. Liu,(1) J.-H. Park,(1) R. O. Anderson,(1) W. P. Ellis,(4) J. T. Markert,(3) Y. Dalichaouch,(3) and R. Liu(2)

(1)*Department of Physics, University of Michigan, Ann Arbor, Michigan 48109-1120*

(2)*Department of Physics and Ames Laboratory—U.S. DOE, Iowa State University, Ames, Iowa 50011*

(3)*Department of Physics and Institute for Pure and Applied Physical Sciences, University of California at San Diego, La Jolla, California 92093*

(4)*Los Alamos National Laboratory, Los Alamos, New Mexico 87545*

(Received 18 October 1989)

The electronic structures of single-crystal and ceramic samples of the electron-doped superconductor $Nd_{2-x}Ce_xCuO_{4-y}$ with $x=0$ and 0.15 have been studied using resonant photoemission spectroscopy. Comparing these spectra with previous results for $La_{2-x}Sr_xCuO_4$ shows that for both electron and hole doping the Fermi level lies at nearly the same energy, in states that fill in the $x=0$ insulator gap. We point out that this would occur if the states at the Fermi level obey a Luttinger-type sum rule, i.e., according to standard theory, if the metallic state is a normal Fermi liquid.

PACS numbers: 74.70.Vy, 71.28.+d, 79.60.−i

Negative Hall and Seebeck coefficients obtained from measurements on the $Nd_{2-x}Ce_xCuO_{4-y}$ system suggest that superconductivity in the $L_{2-x}M_xCuO_{4-y}$ systems (L =Pr,Nd,Sm,Eu; M=Ce,Th; $x=0.15$)[1-4] involves electron carriers produced by the doping. Ce $3d$ x-ray photoemission spectroscopy (XPS) shows[5] that this occurs because formally tetravalent Ce replaces formally trivalent Nd. Because the states at the Fermi energy E_F have been observed only in one XPS study,[6] and not in any resonant photoemission spectroscopy[7] (RPES) studies, detailed spectroscopic information about the E_F states has been lacking, and a unified description that includes the important comparison to the E_F states of the hole-doped material $La_{2-x}Sr_xCuO_{4-y}$ has not been given.

In this paper we report angle-integrated valence-band RPES results for both single-crystal and ceramic samples of $Nd_{2-x}Ce_xCuO_{4-y}$ with $x=0$ and 0.15. The E_F emission in the metallic $x=0.15$ sample is clearly observed. We use the well-known Fano-like resonances[8,9] which occur in the Cu $3d$ and Nd $4f$ photoemission cross sections for photon energies near the Cu $3p$ and Nd $4d$ absorption edges, respectively, to find that the E_F emission has Cu $3d$ but not Nd $4f$ character. Comparing our results to spectra[8] for hole-doped $La_{2-x}Sr_xCuO_4$ yields the important result that *for the metallic state produced by both hole and electron doping, E_F lies at nearly the same position, in new states that fill in the $x=0$ insulator gap.* As discussed below, we reason that these gap-filling states must be derived by transfer of weight from *both* the valence and conduction bands of the insulator.

This result leads us to suggest, with others,[10] that the E_F position and the Fermi surface of the metals are governed by a Luttinger-type[11] sum rule. This sum rule is central to the usual Fermi-liquid theory of metals, and states that the volume enclosed by the Fermi surface is unchanged as Coulomb interactions are turned on, so long as the symmetry of the ground state remains the same. Paraphrased for the present situation, its validity would mean that when the gap fills in for sufficiently large doping, the number of holes or electrons corresponds to the Fermi surface calculated in a band theory. The Fermi level of such a theory must have nearly the same energy for either hole or electron doping. Although not required by the sum rule, it is plausible that the band-theory E_F occurs in the energy range of the insulator's correlation gap, because the theory does not reproduce the gap.

The samples studied in this work are ceramic samples of $Nd_{2-x}Ce_xCuO_{4-y}$ ($x=0$ and 0.15) and a single crystal of $Nd_{2-x}Ce_xCuO_{4-y}$ ($x=0.15$), prepared at the University of California at San Diego as described in Refs. 4 and 12. X-ray diffraction measurements show the so-called T'-phase structure for all samples. The $x=0.15$ samples are superconducting. The oxygen stoichiometry was verified using an iodometric-titration technique, with an uncertainty in the oxygen deficiency of less than $\Delta y=0.02$.

The photoemission measurements were performed at the Synchrotron Radiation Center (SRC) at Stoughton, Wisconsin, using monochromatized synchrotron radiation obtained from the grasshopper monochromator on beam line Mark II. A commercial double-pass cylindrical-mirror analyzer (CMA) was used to analyze the kinetic energies of the emitted photoelectrons. The ceramic samples and single crystals were cooled to, cleaved, and measured at ~100 and ~20 K, respectively, *in situ* in a vacuum better than 5×10^{-11} Torr. The overall instrumental resolution for spectra presented in this paper is about 0.35 eV. The beam flux was measured from the yield of a nickel mesh, which was first calibrated against a gold diode having a known photon energy response. The energy distribution curves (EDC's) for each sample were normalized to the incident photon flux in this way, and also to the transmission function of the CMA. This photon-flux normalization is approximate because the nickel mesh yield includes a small contribution from second-order light which is not completely removed by filters on the monochromator, and which excites, in the sample, photoelectrons that contribute to a second-order background in the spectra.

The procedure for quantitatively comparing EDC's for $x=0$ and $x=0.15$ is as follows: Each EDC is a sum of a primary photoelectron spectrum, a background of inelastically scattered electrons, and the second-order background. For a homogeneous photon flux, and two chemically identical samples, perfectly normalized EDC's at the same photon energy $h\nu$ should scale perfectly onto one another by a factor independent of $h\nu$. For our nonideal beam, imperfect normalization, and samples which are similar but not chemically identical, we scale to match EDC intensities above E_F in the second-order background, and find that the requisite scale factor varies by about 20% over the range 40 to 140 eV. Nonetheless, using this procedure, the spectra essentially overlay, as in the $h\nu=72$ eV example of Fig. 1, which is entirely typical.

The solid and dotted lines of Fig. 1 and its inset show normalized energy distribution curves for ceramic samples of $\mathrm{Nd_{2-x}Ce_xCuO_{4-y}}$ with $x=0$ and 0.15, respectively. The $h\nu$'s for the EDC's are near the Cu $3p \rightarrow 3d$, and Nd $4d \rightarrow 4f$ absorption edges, which occur, respectively, near $h\nu \sim 70$ and ~ 120 eV. The familiar[8] Cu $3d^8$ feature is seen at -12 eV. Its spectral shape and its resonance behavior around 74.5 eV are well predicted for $x=0$ by detailed calculations[13] based on a formal $\mathrm{Cu^{2+}}$ state. The Nd $4f$ emission between E_F and ~ -10 eV shows a Fano minimum for $h\nu \sim 121$ to 124 eV and Fano maxima at $h\nu \sim 128$ and 134 eV. RPES for the Ce $4f$ states is discussed further below. The largest features of the spectra for doped and undoped samples are identical. However, the presence of a Fermi edge for x nonzero is clearly seen in the 72-eV comparison and in the Fermi-edge detail of the inset. It is obvious that for $x=0$, a Fermi edge is not observed, and that for the doped sample, E_F does not lie in states already present in the insulator, but in new states produced by the doping.

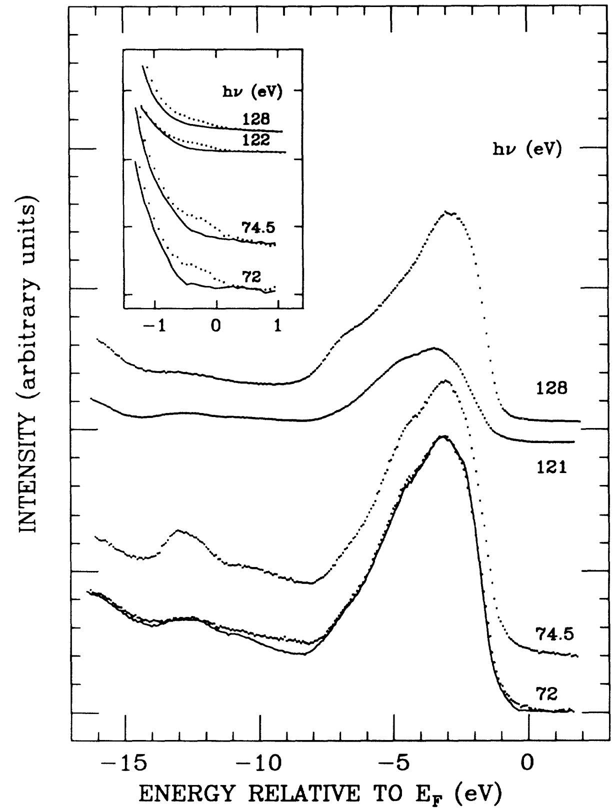

FIG. 1. Valence-band EDC's for ceramic samples of $\mathrm{Nd_{2-x}Ce_xCuO_{4-y}}$ with $x=0$ (solid) and $x=0.15$ (dotted). The curves have a common vertical scale, but are offset for clarity. Normalized spectra for the two x values are placed on a common intensity scale by an algorithm described in the text.

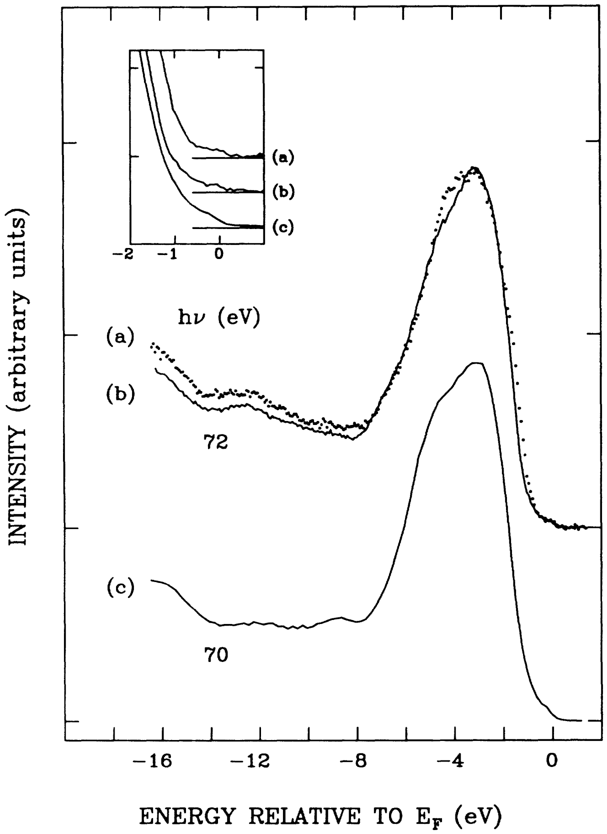

FIG. 2. Valence-band spectra at $h\nu=72$ eV for (curve a) a ceramic sample, and for (curve b) a single crystal of $\mathrm{Nd_{1.85}Ce_{0.15}CuO_{4-y}}$, and at $h\nu=70$ eV for (curve c) a ceramic sample of $\mathrm{La_{1.8}Sr_{0.2}CuO_{4-y}}$ (from Ref. 8).

Curves *a* and *b* of Fig. 2 show, respectively, the EDC's from a ceramic and a single-crystal sample of $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ at 72 eV. It is important that the data from the two samples, while not perfectly identical, are sufficiently similar, especially in the important region near E_F, to give us confidence in the data from the ceramic samples. These were studied much more extensively in the E_F region than was the single crystal, because their areas are ~20 times greater than that of the single crystal and hence produce data with much better signal-to-noise ratio. Curve *c* shows an EDC at 70 eV, published previously,[8] for $La_{1.85}Sr_{0.15}CuO_{4-y}$. Relative to the energy of the largest-valence band peak, E_F is essentially the same in both materials.

Figure 3 shows the $h\nu$ dependence of the emission produced by Ce doping. It is a plot of the intensity 0.3 eV below E_F in the spectra obtained by subtracting normalized, scaled EDC's for $x=0$ from those for $x=0.15$. The difference spectra, shown in the inset, are free of the second-order background and show the E_F step very clearly. The error bars represent statistical uncertainty due to noise in the difference spectra, and do not include systematic errors of the analysis procedure. The small maximum around 50 eV and the generally decreasing shape of the $h\nu$ dependence is consistent with Cu 3*d* and O 2*p* character, based on atomic photoionization cross sections.[14] The presence of Cu 3*d* states is shown by the clear resonance dip[8] in the region of the Cu 3*p* edge, also observable in the inset spectra. Around the Nd 4*d* edge the E_F emission does not resonate, showing that it lacks a Nd 4*f* component. For states away from E_F, the Nd resonance is nearly identical to that[9] for Nd metal, so we conclude that the Nd valence is close to 3+. The Nd 4*f* spectrum obtained as the difference of the two upper normalized spectra of Fig. 1 changes only slightly with *x*. As found in other studies,[7] there is a main peak around −2.4 eV, and a shoulder at −7 eV, very different from the 4*f* spectrum[9] for Nd metal.

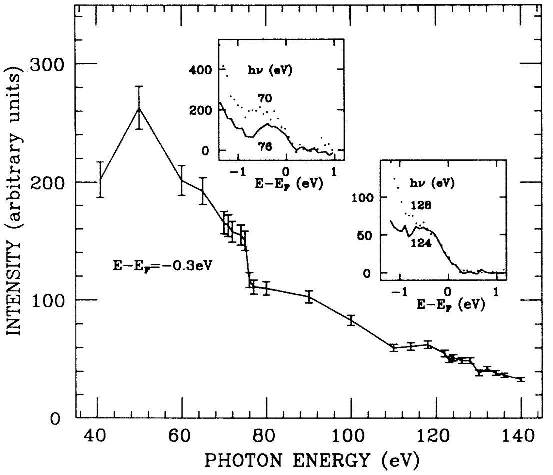

FIG. 3. $h\nu$ dependence of the emission induced by Ce doping, 0.3 eV below E_F for a ceramic sample of $Nd_{1.85}Ce_{0.15}CuO_{4-y}$. Insets: Spectra of states induced by doping for $h\nu$ near the Cu and Nd resonance energies.

It is not possible to use RPES to extract the Ce 4*f* states hybridized into the valence band. The known energies[15] of resonance for the 4*f* emission of Ce_2O_3 and CeO_2 overlap the Nd resonance spectrum. The Ce 3*d* x-ray photoemission spectrum[5] implies about 0.5 Ce 4*f* electron/(Ce ion), so the ratio of Ce to Nd 4*f* electrons in our sample is approximately 0.014. Although the $4d \rightarrow 4f$ absorption for Ce is larger than for Nd by the ratio of the number of 4*f* holes, $\frac{14}{11}$, this is not a large enough effect to offset the small number of Ce electrons, even for *x* as great as 0.20. Thus, in this energy range, the $h\nu$ dependences of the valence bands for $x=0$ and $x=0.15$ are perfectly identical.

The results reported here clearly show that for the metallic state of electron-doped $Nd_{2-x}Ce_xCuO_{4-y}$ E_F lies in new states created in the insulator gap above the $x=0$ valence band. Exactly the same is true[8] for the hole-doped material $La_{2-x}Sr_xCuO_{4-y}$. Further, E_F has essentially the same position in the gap for both hole and electron doping. These experimental facts contrast sharply with the expectation in many models that for hole or electron doping, respectively, E_F would lie in the insulator's valence-band or conduction-band states, which are separated by a gap of about 2 eV.

Because (1) the dopant's bonding orbitals are isoelectronic to those of the replaced atoms and (2) the stoichiometry is unaltered with doping, it follows that the new E_F states must arise by a transfer of weight from the states of the insulator. Further, to accomodate both electron and hole doping, both the conduction-band and valence-band states of the insulator must be involved in the transfer. From the spectra of Fig. 2, and x-ray-absorption and electron-energy-loss spectra,[16] we conclude that for either hole or electron doping, in the metallic state the entire gap of the insulating $x=0$ compound is filled in. The fundamental breakdown is probably in the larger Cu 3*d* correlation gap, because the smaller charge-transfer gap[17] has essentially one-electron character. Many-body calculations with some aspects of this gap-filling character have recently been given.[18-20]

We now go beyond direct conclusions from the data and point out that one scenario in which E_F has a common value for both types of doping is that the gap-filling states of the metal obey at E_F a Luttinger-type[11] sum rule, i.e., that in the metal, although these states may have considerably increased masses and reduced spectral weights due to Coulomb interactions, they nonetheless "remember" the Fermi surface that would obtain in an independent-particle picture. This scenario has been suggested previously,[10] and is consistent with the result that high-resolution angle-resolved photoemission spectra[21,22] for the metallic states of other high-T_c materials show Fermi-level crossings at k values that are in substantial agreement with the predictions of band theory, although the dispersion of the experimental bands is considerably smaller than the theoretical dispersion. For the metallic state this picture is similar to that which has developed for many heavy-fermion materials, but there is the added richness and difficulty here that for small or zero doping, the material is an insulator for which the Luttinger theorem is violated.

In summary, the electronic structure of single-crystal and ceramic samples of electron-doped $Nd_{2-x}Ce_xCuO_{4-y}$ with $x=0$ and 0.15 have been studied using RPES. We learn from these spectra, and previous results for $La_{2-x}Sr_xCuO_4$, that the insulator-metal transition for both hole and electron doping occurs by the growth of states that fill in the charge-transfer gap, and that E_F is substantially the same for both hole or electron doping. We point out that this would occur if the states at the Fermi level obey a Luttinger-type sum rule.

It is a pleasure to acknowledge discussions with W. C. Herring and J. W. Rasul. Research support by the U.S. National Science Foundation (NSF)-Low Temperature Physics Program, Grants No. DMR-87-21654 (J.W.A., J.-S.K., and L.Z.L.) and No. DMR-87-21455 (M.B.M. and Y.D.), by the University of Michigan Presidential Initiatives Fund (R.O.A.), and by the U.S. Department of Energy (DOE) under Grant No. DE-FG03-86ER45230 (M.B.M. and J.T.M.) is gratefully acknowledged. The Synchrotron Radiation Center is supported by the NSF. The Ames Laboratory is operated for the U.S. DOE by Iowa State University under Contract No. W-7405-ENG-82. The work at Los Alamos National Laboratory is supported by the U.S. DOE.

---

[1] Y. Tokura, H. Takagi, and S. Uchida, Nature (London) **337**, 345 (1989).

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

[3] J. T. Markert and M. B. Maple, Solid State Commun. **70**, 145 (1989).

[4] J. T. Markert, E. A. Early, T. Bjømholm, G. Ghamatry, B. W. Lee, J. J. Neumeier, R. D. Price, C. L. Seaman, and M. B. Maple, Physica (Amsterdam) **158C**, 178 (1989); E. A. Early, N. Y. Ayoub, J. Beille, J. T. Market, and M. B. Maple, Physica (Amsterdam) C (to be published).

[5] S. Uji, M. Shimoda, and H. Aoki, Jpn. J. Appl. Phys. Part 2, **28**, L804 (1989); M. K. Rajumon, D. D. Sarma, R. Vijayaraghavan, and C. N. R. Rao, Solid State Commun. **70**, 875 (1989); A. Fujimori, Y. Tokura, H. Eisaki, H. Takagi, S. Uchida, and E. Takayama-Muromachi (to be published).

[6] Y. Fukuda, T. Suzuki, M. Nagoshi, Y. Syono, K. Oh-ishi, and M. Tachiki, Solid State Commun. **72**, 1183 (1989).

[7] A. Grassmann, J. Schlötterer, J. Ströbel, M. Klauda, R. L. Johnson, and G. Saemann-Oschenko, Europhys. Lett. **9**, 827 (1989); H. Namatame, A. Fujimori, Y. Tokura, M. Nakamura, K. Yamaguchi, A. Misu, H. Matsubara, S. Suga, H. Eisake, T. Ido, H. J. Takago, and S. Uchida (to be published).

[8] Z.-X. Shen, J. W. Allen, J.-J. Yeh, J.-S. Kang, W. Ellis, W. E. Spicer, I. Lindau, M. B. Maple, Y. D. Dalichaouch, M. S. Torikachvili, J. Z. Sun, and T. H. Geballe, Phys. Rev. B **36**, 8414 (1987).

[9] F. Gerken, Ph.D. thesis, University of Hamburg, 1982 (unpublished).

[10] S. Massida, N. Hamada, J. J. Yu, and A. J. Freeman, Physica (Amsterdam) **157C**, 571 (1989).

[11] J. M. Luttinger, Phys. Rev. **119**, 1153 (1960).

[12] Y. Dalichaouch, B. W. Lee, C. L. Seaman, J. T. Market, and M. B. Maple (to be published).

[13] O. Gunnarsson, J. W. Allen, O. Jepsen, T. Fujiwara, O. K. Anderson, C. G. Olson, M. B. Maple, J.-S. Kang, L. Z. Liu, J.-H. Park, R. O. Anderson, W. P. Ellis, R. Liu, J. T. Markert, Y. Dalichaouch, Z.-X. Shen, P. A. P. Lindberg, B. O. Wells, D. S. Dessau, A. Borg, I. Lindau, and W. E. Spicer, Phys. Rev. B (to be published).

[14] J. J. Yeh and I. Lindau, At. Data Nucl. Tables **32**, 1 (1985).

[15] J. W. Allen, J. Magn. Magn. Mater. **47 & 48**, 168 (1985).

[16] J. M. Tranquada, S. M. Heald, A. R. Moodenbaugh, G. Liang, and M. Croft, Nature (London) **337**, 720 (1989); 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); N. Kosugi, Y. Tokura, H. Takagi, and S. Uchida (to be published).

[17] J. Zaanen, G. A. Sawatzky, and J. W. Allen, Phys. Rev. Lett. **55**, 418 (1985).

[18] P. Horsch, W. H. Stephan, K. v. Szczepanski, M. Ziegler, and W. von der Linden, Physica (Amsterdam) (to be published).

[19] C. A. R. Sá de Melo and S. Doniach (to be published).

[20] M. Tachiki (private communication).

[21] C. G. Olson, R. Liu, A.-B. Yang, D. W. Lynch, A. J. Arko, R. S. List, B. W. Veal, Y. C. Chang, P. Z. Jiang, and A. P. Paulikas, Science **245**, 731 (1989).

[22] R. Manzke, T. Buslaps, R. Claessen, M. Skibowksi, and J. Fink, Physica (Amsterdam) C (to be published).