RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 40, NUMBER 4 1 AUGUST 1989

Effect of Ce doping on the Cu charge in the electron superconductor $Nd_{2-x}Ce_xCuO_4$

E. E. Alp, S. M. Mini, M. Ramanathan, B. Dabrowski, D. R. Richards, and D. G. Hinks
Argonne National Laboratory, Argonne, Illinois 60439

(Received 3 April 1989)

We have investigated the effect of Ce doping on the net Cu charge via x-ray absorption spectroscopy at the Cu K and the Ce L_3 edges. We conclude that Ce ions add electrons to the CuO_2 planes. It is most likely that this additional electron is injected into a band and rather than being localized on each Cu site leading to Cu^+. We observe that the amount of electron doping is larger than Ce concentration.

The observation of superconductivity in Ce-doped Nd_2CuO_4 (Ref. 1) suggested that electron doping of the CuO_2 planes may lead to a superconducting state in this material. We have prepared the compounds $Nd_{2-x}Ce_xCuO_4$ with $x=0.0$, 0.1, 0.15, 0.17, and 0.25 by prefiring stoichiometric mixtures of Nd_2O_3, CeO_2, and CuO powders at 1100 °C for 4 h in air, followed by quenching to room temperature on cold Cu plates. No superconductivity was found in these materials. After subsequent annealing at 950 °C for 24 h under the reducing conditions of flowing nitrogen gas, the $x=0.17$ sample showed bulk superconductivity with $T_c=24$ K, and the materials with compositions $x=0.1$, 0.15, and 0.25 displayed traces of superconductivity with the same T_c. All compositions above $x=0.17$ were not single phase. The following x-ray absorption study was performed only on nitrogen-annealed single-phase materials.

We have measured x-ray absorption near-edge structure of the Ce L_3 edge (5723 eV) and the Cu K edge (8980 eV) at beamline II-3 at Stanford Synchrotron Radiation Laboratory (SSRL), and at beamlines X18-B and X11-A at National Synchrotron Light Source, using Si(111) and Si(220) crystals, respectively, to monochromatize the beam. The reference spectra of CeO_2 and Cu metal are measured simultaneously at the respective absorption edges for calibration purposes.

In Fig. 1, the Ce L_3 edge absorption spectra of CeO_2 and that of $Nd_{1.83}Ce_{0.17}CuO_4$ are presented. The valence state of Ce in CeO_2 has been very controversial.[2] However, the recent pressure-dependent Ce L_3 edge measurements[3] indicate that the valence state of Ce in CeO_2 [as observed by L_3 edge x-ray absorption spectroscopy (XAS) method] can be taken as $+4$. It is clear that the valence of Ce is greater than $+3$ in the $x=0.17$ sample, and therefore the argument of donating electrons via substituting Ce for Nd is plausible.

The location of the absorption edge at the Cu K-edge transition, as in many other transition-metal elements, is very sensitive to the net charge on Cu $3d$ orbitals. As the net charge on Cu increases from $+1$ to $+3$ the absorption edge shifts to higher energies by as much as 8 eV (Refs. 4 and 5). In Fig. 2(a) we present the absorption spectra at the Cu K edge for $Nd_{2-x}Ce_xCuO_4$ for $x=0.0$, 0.10, 0.15, and 0.17, and the spectrum of Cu_2O for comparison. Figure 2(b) shows the difference spectra obtained by subtracting the normalized Nd_2CuO_4 spectrum from the spectra of the Ce-doped samples, as well as that of Cu_2O. Following a similar procedure, Tranquada *et al.*[6] concluded that the effect of Ce doping is to reduce some of the Cu atoms to stable Cu^+. This assertion was based on the location of the difference peaks at 2, 8, 16, and 22 eV. On the other hand, the feature at 13 eV, which results from an overall shift of the edge position, was not accounted for. The energy scale in our study is referenced to the first inflection point in a Ce metal spectrum measured simultaneously, and therefore may be shifted slightly from that of Ref. 6.

The main absorption peak at 16 eV results from direct transition from the $1s$ level to the $4p_\sigma$ (in-plane) orbitals, whereas the shoulder at 5 eV is the transition to $4p_\pi$ (out-of-plane) orbitals. This tentative assignment is based on the experience gained by polarized XAS measurements on La_2CuO_4 (Refs. 7 and 8) as well as the results of theoretical calculations.[9] The shoulder at 5 eV is sometimes attributed to the so-called "shakedown" transition, resulting from a charge transfer from the ligand oxygen $2p$ orbitals into Cu $3d$ orbitals. It is not universally observed in Cu compounds and its intensity varies in copper oxides. We observe a shift in the position of the main peak at 16 eV by as much as 1.5 eV to lower values as the Ce content is increased. This shift is the origin of the peak at 13 eV in

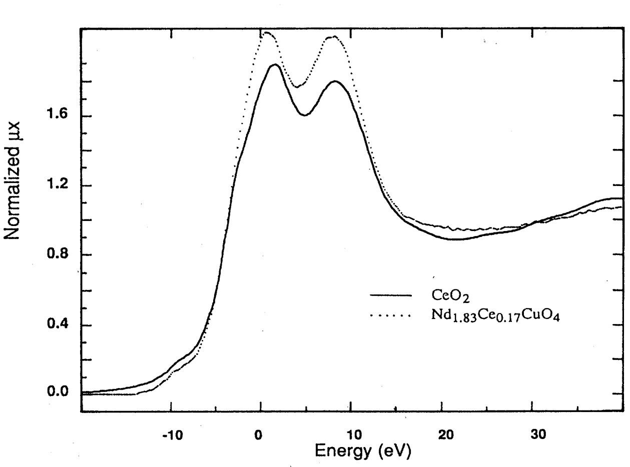

FIG. 1. The L_3 edge x-ray absorption spectra of CeO_2 and $Nd_{1.83}Ce_{0.17}CuO_4$ samples.

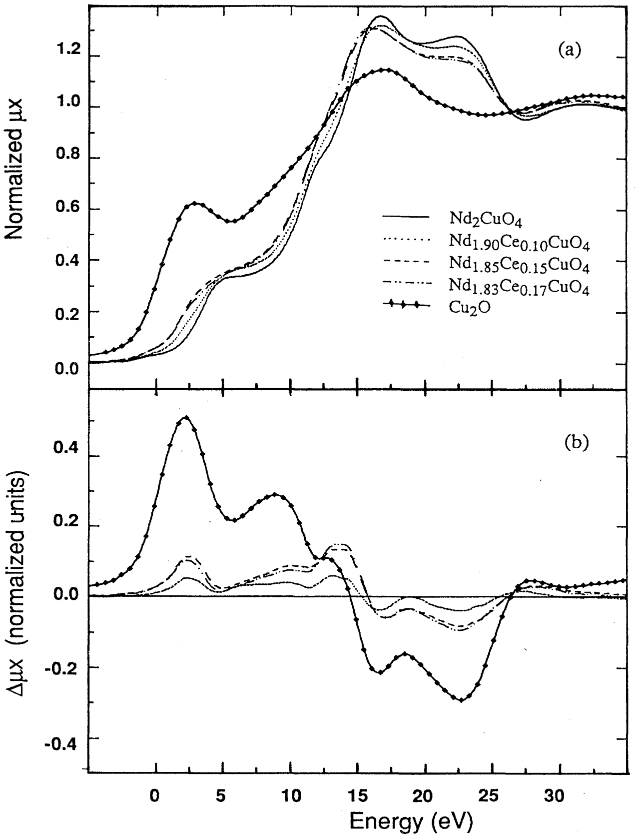

FIG. 2. (a) The normalized x-ray absorption spectra of $Nd_{2-x}Ce_xCuO_4$ for $x = 0.0$, 0.1, 0.15, and 0.17, and Cu_2O measured at the Cu K edge; (b) the difference spectra relative to pure Nd_2CuO_4. The peak at 13 eV cannot be accounted for by assuming conversion of Cu^{2+} into Cu^+.

the difference spectra given in Fig. 1(b). Such a shift can be accounted for by assuming that the extra electrons donated by the Ce^{4+} atoms are transferred into a band, reducing the charge on all Cu atoms effectively, rather than being localized at particular Cu atoms (at least for the time scale of the core hole lifetimes of 1s levels of Cu). Also, it should be noted that Cu^+ in oxides is only observed in structures where Cu is coordinated by two "dumbbell" oxygens as in Cu_2O. There is, so far, no structural evidence for such a copper environment in this material.[1]

In Fig. 3(a) we have tested the hypothesis that each added Ce forms one monovalent Cu atom by synthesizing a spectrum by mixing normalized spectra of Nd_2CuO_4, and Cu_2O at 85% and 15% ratios, respectively. In Fig. 3(b), we present the difference spectrum where pure Nd_2CuO_4 is subtracted from the synthesized spectrum. Clearly, the peak at 13 eV observed in the difference spectrum presented in Fig. 1(b) does not occur. Hence, we conclude that the measured spectra of $Nd_{2-x}Ce_xCuO_4$ cannot be accounted for by assuming a simple conversion of Cu^{2+} to Cu^+. If each Ce ion reduces one Cu^{2+} to Cu^+ as in Cu_2O, the spectra for doped and undoped compounds should have a common point at about 14 eV, where x-ray-absorption near-edge structure spectra for pure Nd_2CuO_4 and Cu_2O cross each other. Instead, we see a gradual shift to lower energies with increasing Ce content.

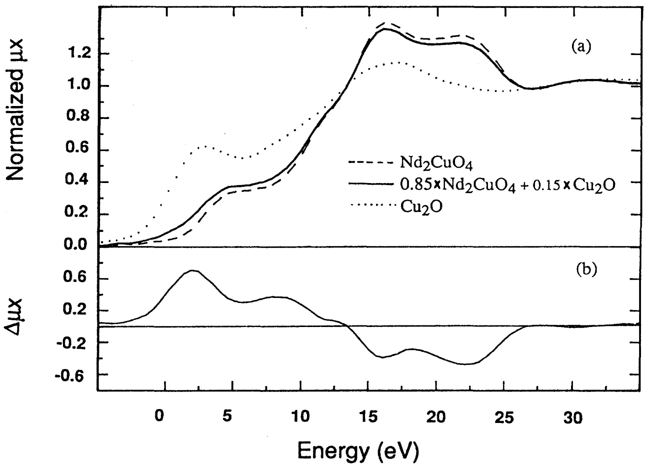

FIG. 3. (a) A synthesized spectrum composed of 85% Nd_2CuO_4 and 15% Cu_2O and the two pure components; (b) the difference spectrum in which the pure Nd_2CuO_4 is subtracted from the synthesized one. No shift is observed around 14 eV, indicating the difficulty to interpret the effect of Ce doping by formation of monovalent copper.

The magnitude of this charge removal, and a comparison of this with respect to $La_{2-x}Sr_xCuO_4$ can be done according to a procedure recently developed by us.[4] In this procedure, we use the integrated area under the absorption spectrum in an energy window of −10 to +40 eV range, to determine the "average" position of the absorption edge, which we call the "characteristic energy."[10] The numerical values for characteristic energies of Cu^+ compounds range from 1.5 to 3.6 eV. For formally Cu^{2+} compounds, this range is from 6.5 to 8 eV and for Cu^{3+} compounds from 8 to 10 eV. The exact values for several copper compounds are given in Table I. We have shown that for Cu_2O, CuO, $KCuO_2$, and for La_2CuO_4 the value of characteristic energy is proportional to the effective charges on Cu, which are theoretically calculated using a

TABLE I. The mean characteristic energies for several standard copper compounds and for the $Nd_{2-x}Ce_xCuO_4$ materials.

Compound	Characteristic energy (eV, ±0.2)
Cu_2O	3.58
CuO	6.49
$Nd_{2-x}Ce_xCuO_4$	
$x = 0.17$	6.34
$x = 0.15$	6.27
$x = 0.10$	6.81
$x = 0.0$	7.30
La_2CuO_4	7.72
$La_{1.85}Sr_{0.15}CuO_4$	8.00
$KCuO_2$	8.25

discrete variational method of a molecular cluster in the local-density approximation.[5] Therefore, we believe that there is physical significance in the characteristic energies given in Table I. We estimate that there is a shift by 3.3 eV to higher energies for each electron removed from a Cu atom. Based on this relative scale, we estimate that the net charge on Cu in Nd_2CuO_4 is less than that of Cu in La_2CuO_4 by about 0.13 electron. This is the first measurement of the difference in the oxidation state of Cu in a T and T' phase of cuprates, in which Cu is surrounded with six or four oxygens, respectively. Thus the two compounds do not start electron exchange upon doping at the same level. Upon 0.1 Ce doping into Nd_2CuO_4, based on shifts in the characteristic energies, we estimate that the net charge on Cu will be reduced by $0.15 \pm 0.05\ e^-$. This value for 0.17 Ce doping is $0.28 \pm 0.05\ e^-$. This estimate indicates that the effect of Ce doping is not simply and mechanically to donate one electron per each Ce added. Indeed, the change in the band structure should be such that Ce doping facilites charge transfer from ligands to Cu. In this respect, concentration-dependent O K-edge measurements for this series of compounds will be very useful.

In conclusion, we have shown that the effect of Ce doping in $Nd_{2-x}Ce_xCuO_4$ is to donate about 0.15 ± 0.05 electron per 0.1 Ce atom on all Cu atoms, rather than forming localized monovalent Cu atoms. The lack of monovalent Cu formation has also been confirmed recently by electron energy-loss spectroscopy measurements on Ce-doped Nd by Nücker *et al.*[11] This observation is consistent with the change in the lattice parameters a and c, as determined by x-ray diffraction. There is a decrease in the c lattice parameter from 12.15 to 12.07 Å as the Ce content is increased from 0 to 0.17. The a lattice parameter increases from about 3.943 to 3.948 Å over the same concentration change. Otherwise, there is no evidence of formation of Cu-O linear chains, as in Cu_2O. When the relation between oxygen stoichiometry and the lattice parameters becomes clear it will be easier to understand the possible source of these extra electrons, since oxygen deficiency can be another source of electrons.

We would like to acknowledge the help of the SSRL staff during the experiments. This work is supported by the U.S. Department of Energy, Basic Energy Science, Materials Sciences under Contract No. W-31-109-ENG-38. D.R.R. would like to thank America Air Liquide, and S.M.M. and B.D. would like to thank the Science and Technology Center for Superconductivity funded by the National Science Foundation under Contract No. STC-8809854 for support.

---

[1] H. Takagi, S. Uchida, and Y. Tokura, Phys. Rev. Lett. **62**, 1197 (1989); Y. Tokura, H. Takagi, and S. Uchida, Nature (London) **337**, 345 (1989).

[2] For a general discussion of Ce L_3 edges in trivalent and tetravalent compounds, see J. Röhler, in *Handbook on Physics and Chemistry of Rare-Earths,* edited by K. A. Gschneider, Jr., L. Eyring, and S. Hüfner (North-Holland, Amsterdam, 1987), Vol. 10, Chap. 71.

[3] G. Kaindl, G. Schmiester, and E. V. Sampathkumaran, Phys. Rev. B **38**, 10174 (1988).

[4] E. E. Alp, G. L. Goodman, L. Soderholm, S. M. Mini, M. Ramanathan, G. K. Shenoy, and A. S. Bommannavar, J. Phys. Condens. Matter (to be published).

[5] G. L. Goodman, D. E. Ellis, E. E. Alp, and L. Soderholm, J. Chem. Phys. (to be published).

[6] J. M. Tranquada, S. M. Heald, A. R. Moodenbaugh, G. Liang, and M. Croft, Nature (London) **337**, 720 (1989).

[7] E. E. Alp, S. M. Mini, M. Ramanathan, B. W. Veal, L. Soderholm, G. L. Goodman, B. Dabrowski, J. Guo, D. E. Ellis, and A. S. Bommannaver, in *Synchrotron Radiation in Materials Research, 1988,* edited by R. Clark, J. Gland, and J. H. Weaver, Materials Research Symposia Proceedings, Vol. 143 (Materials Research Society, Pittsburgh, 1989), p. 97.

[8] S. M. Heald, J. M. Tranquada, A. R. Moodenbaugh, and Y. Xu, Phys. Rev. B **38**, 761 (1988).

[9] E. E. Alp, G. K. Shenoy, D. G. Hinks, D. W. Capone, L. Soderholm, H.-B. Schüttler, J. Guo, D. E. Ellis, P. A. Montano, and M. Ramanathan, Phys. Rev. B **35**, 7199 (1987).

[10] In this procedure, the characteristic energy for an absorption edge is defined as follows. Let $M^{(n)}$ be the nth moment of the energy with respect to the absorption cross section $\mu(E)$ in the region between L_0 and L_1: $M^{(n)} = \int_{L_0}^{L_1} E^n \mu(E)\, dE$, $\langle E\rangle = M^{(1)}/M^{(0)}$, where L_0 and L_1 are the lower and upper limits of integration. Assuming a step-function model for the absorption edge with the unit height, located at position S, one can then show that $S = 2\langle E\rangle - L_1$ as the characteristic energy. This is further demonstrated on several Cu compounds in Ref. 4.

[11] N. Nücker, P. Adelmann, M. Alexander, H. Romberg, S. Nakai, J. Fink, H. Rietschel, G. Roth, H. Scmidt, and H. Spille (unpublished).