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Polarization x-ray-absorption near-edge structure study of $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ single crystals: The nature of Ce doping

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A polarization Cu K -edge x-ray-absorption near-edge structure study has been carried out on $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ single crystals. The spectra for x-ray polarization vector \mathbf{E} nearly parallel to the crystal c axis suggest that electrons contributed by Ce doping are initially localized at the Cu site. The spectra for \mathbf{E} perpendicular to the c axis exhibit an almost rigid edge shift to lower energies upon Ce doping. This suggests that the unoccupied in-plane Cu $4p$ states shift to lower energies. Therefore, the Ce doping donates electrons to the Cu site and also shifts the unoccupied $4p$ band. We propose that the upper unoccupied band consisting of predominantly Cu $3d$ states shifts downward and eventually joins the initially localized states near the Fermi level and thus, forms the conduction band in the n -type superconductor.

The observation of superconductivity in Ce- and Th-doped $L_2\text{CuO}_4$ ($L = \text{Pr, Nd, Sm, and Eu}$)¹⁻⁴ has attracted considerable attention to these materials. The negative Hall coefficient and Seebeck coefficient¹⁻⁴ of these materials indicate that conduction takes place through electrons which differs from the hole conduction observed in other high- T_c copper oxide superconductors. Ce L_3 x-ray absorption⁵⁻⁸ and Ce $3d$ emission⁹⁻¹² experiments show that the Ce valence in the superconductors is formally tetravalent, which supports electron doping. X-ray absorption experiments at the Cu K edge^{5-8,13} and L_3 edge⁹ all suggest that electrons are doped at the Cu site. The interpretation of the Cu K -edge x-ray absorption near-edge structure (XANES) data has been controversial regarding whether the electron doping creates Cu^{1+} or it is a bandlike effect. Photoemission^{8,10,11} and electron energy-loss¹² spectroscopy studies concerning the observation of a Cu $3d^{10}$ configuration have not reached general agreement. The existing experimental results seem to point to electron doping to the Cu site. Disagreement still exists regarding the importance of local effects versus bandlike effects and thus questioning the states of the doped electrons. Part of the disagreement among different spectroscopy studies may rise from a possible Cu_2O impurity phase difficult to detect in small particle form that can exist in the "reduced" superconductors.⁷ In addition, the interpretation of Cu XANES data on powdered samples suffers from the fact that the power spectrum consists of strongly varying contributions from different orientations with respect to the x-ray polarization.

In this paper, we report a study of polarization Cu K -edge XANES of $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ single crystals. We

found that the Ce doping donates electrons to the Cu site and also affects the upper unoccupied band. The spectra for polarization vector \mathbf{E} nearly parallel to the crystal c axis suggest that the doped electrons are initially localized at the Cu site. These doping-produced states may locate near the Fermi level and pile up to form a rather localized band as the Ce concentration increases. The spectra for \mathbf{E} perpendicular to the c axis exhibit an almost rigid edge shift to lower energies upon Ce doping. This is consistent with the interpretation that the upper unoccupied band consisting of in-plane states shifts to lower energies with Ce doping. We suggest that as the doping level increases, the unoccupied band shifts down and eventually joins the localized band near the Fermi level and thus forms the conduction band.

Single crystals of T' -phase $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ and $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ were grown from CuO flux in Pt crucibles. Rare-earth ($L = \text{Pr and Nd}$) oxide, CeO_2 , and CuO powders were mixed in a concentration of $L:\text{Ce}:\text{Cu} = (2-x):x:6$, then heated above the peritectic melting temperature ($\sim 1260^\circ\text{C}$ for Nd_2CuO_4), slowly cooled down to the eutectic temperature ($\sim 1030^\circ\text{C}$ for Nd_2CuO_4), and finally quenched to room temperature. Crystals as large as $3 \times 3 \times 0.1 \text{ mm}^3$ with flat and shiny surfaces were grown on the surface of the flux. The crystals were annealed at 875°C in flowing argon gas for 5 h and furnace cooled to room temperature. The Ce concentration in these crystals was determined by lattice parameter measurements by x-ray diffraction and are accurate to $\pm 5\%$.

X-ray absorption measurements were carried out at the National Synchrotron Light Source on beam line X-11A

using a Si(111) monochromator and a 0.25-mm entrance slit, and on beam line X-23A2 using a Si(220) monochromator and a 1.0-mm slit. The spectra were measured using fluorescence detection since the crystals were too thick for transmission measurements. A relatively small distortion in the fluorescence spectra due to self-absorption¹⁴ does not affect our comparative study between Ce-doped and undoped Pr_2CuO_4 . Energy calibration was achieved by simultaneously measuring the absorption spectrum of a copper foil. The first inflection point in the spectrum of copper metal was chosen as the zero energy.

A particular effort was made to detect any Cu_2O , CuO , or copper metal impurity phases in the Ce-doped samples. This was done by comparing the Fourier transforms of the Cu extended x-ray absorption fine structure (EXAFS) of doped samples with the undoped compound.^{7,15} The presence of Cu_2O affects the Cu *K* edge XANES significantly. We will discuss only XANES data obtained on samples that have no impurity detectable in the EXAFS analysis. Figure 1 presents the Cu XANES spectra for $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ polycrystalline samples which were discussed earlier.⁷ The main result from these XANES data is that Ce doping indeed donates electrons and the doped electrons are associated with Cu states.

Before discussing the spectral features in detail, we examine the origin of certain features which are better resolved in polarization XANES spectra of the Nd_2CuO_4 signal crystal as shown in Fig. 2. First of all, the XANES spectrum for polarization vector *E* nearly parallel to the crystal *c* axis contrasts strongly with that for *E* perpendicular to the *c* axis. Features *A* and *B* are solely associated with the $\text{E}||c$ axis and correspond to transitions to the out-of-plane $4p_\pi$ states of a Cu $3d^9$ ground-state configuration. The lower energy of feature *A* is due to a better screened core hole by an electron transferred from the oxygen ligand, in which the final state can be described as $3d^{10}L^-$, where L^- stands for a hole on the ligand. Feature *B* corresponds to a poorly screened Cu

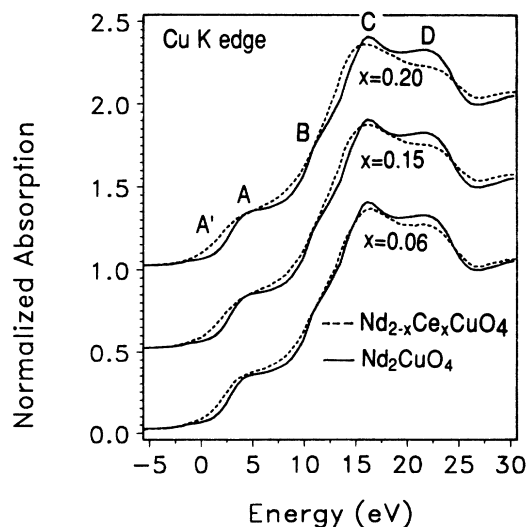


FIG. 1. Cu XANES spectra for polycrystalline vacuum-annealed $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ comparing Ce-doped samples with the undoped sample (from Ref. 7).

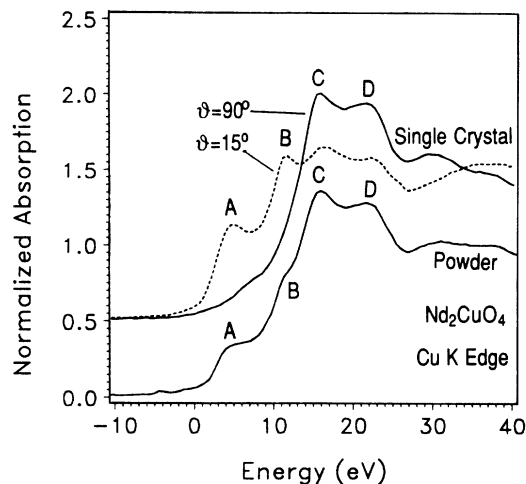


FIG. 2. Cu XANES spectra for polycrystalline and single-crystal Nd_2CuO_4 . θ is the angle between the x-ray polarization vector *E* and the crystal *c* axis.

$3d^9$ final state. Features *C* and *D* are most pronounced for *E* in the CuO_2 plane. The much weaker *C* and *D* in the $\theta = 15^\circ$ spectra may be due to the small in-plane component of *E*. Feature *C* corresponds to a transition to the in-plane $4p_\sigma$ states.^{5,6,13} Feature *D* has been attributed to the $4p_\sigma$ state.¹³ Judging from the fact that features *C* and *D* behave differently upon Ce doping [Fig. 3(b)], feature *D* may be better attributed to a low-energy tail of the EXAFS contribution in the CuO_2 plane.¹⁶

Figure 3 compares Cu XANES spectra for Ce-doped and undoped Pr_2CuO_4 crystals. For polarization nearly parallel to the *c* axis [$\theta = 20^\circ$, Fig. 3(a)], the intensities of features *A* (4.4 eV) and *B* (12 eV) are both reduced by Ce doping. This indicates that the number of Cu in the $3d^9$ ground state decreases upon Ce doping. In the meantime new intensities (feature *A'*) are observed at 1.2 eV. *A'* is a well-defined peak as shown in the difference spectra between Ce-doped and undoped samples (see also Refs. 5, 6, and 13). *A'* is present only for the $\text{E}||c$ axis, suggesting that it is due to a transition to the $4p_\pi$ state. In the XANES data of Cu_2O the $4p_\pi$ feature of the Cu $3d^{10}$ configuration is at 2.7 eV. For Cu metal the $4p_\pi$ feature of the Cu $3d^{10}4s^1$ configuration, with the *s* electrons in the conduction band, is at 1.6 eV. Feature *A'* is at an energy close to, but lower than, those of the $4p_\pi$ features in both Cu_2O and copper metal. The low energy of 1.2 eV indicates that feature *A'* arises from Cu in a $3d^{10}$ ground-state configuration. The lower energy of *A'* than that of the $4p_\pi$ feature in Cu_2O may be due to a better screening of the core hole for the fourfold oxygen-coordinated Cu in the $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$. However, even with a better screened Cu by oxygen neighbors, a $3d^{9+\delta}$ (for a δ significantly less than one) ground-state configuration is not likely to lead to such a low energy for *A'*. Thus, in a qualitative picture, one electron is added to some of the Cu atoms by Ce doping. A $3d^{10}4s^1$ configuration for Cu in the Ce-doped samples is unlikely since this requires two electrons to be added to a single Cu. To summarize our $\theta = 20^\circ$ data, we conclude that Ce

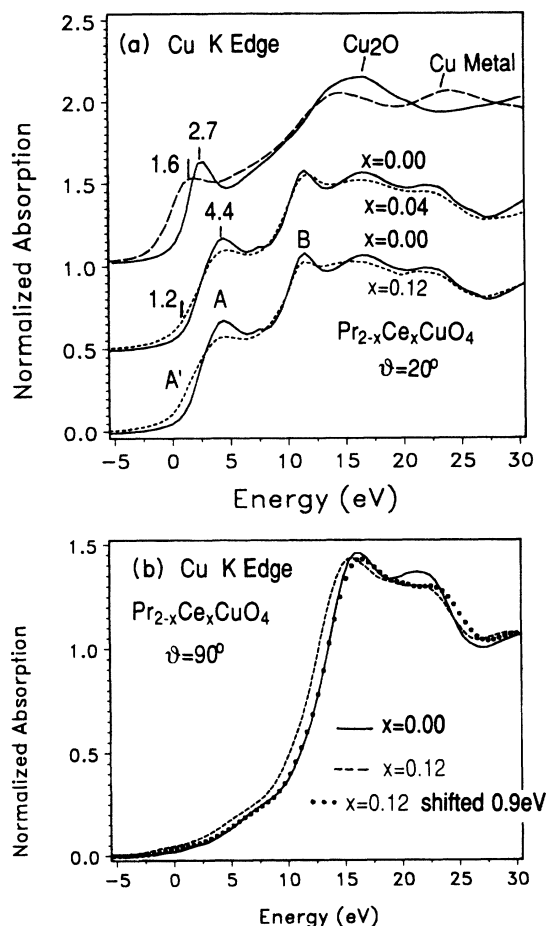


FIG. 3. Polarization Cu XANES spectra for $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ single crystals comparing Ce-doped and undoped samples. θ is the angle between polarization vector \mathbf{E} and c axis. (a) $\theta = 20^\circ$. Intensities of features A and B are reduced while new intensities appear at feature A' . The spectra on polycrystalline Cu_2O and copper metal are included for reference purposes. (b) $\theta = 90^\circ$. The main edge of the $x = 0.12$ sample shifts down by about 0.9 eV.

doping adds one electron to the Cu $3d$ states which remain localized, at least for low Ce concentrations.

For polarization perpendicular to the c axis [$\theta = 90^\circ$, Fig. 3(b)], the main absorption edge due to $1s \rightarrow 4p_\sigma$ transitions of the $x = 0.12$ sample shifts almost rigidly to a lower energy. This edge shift is demonstrated by shifting the $x = 0.12$ spectrum to higher energy by 0.9 eV. The shifted spectrum is almost identical to that of the undoped Pr_2CuO_4 sample in the 0–18 eV region including feature C. The XANES spectra at energies above 20 eV cannot be described as an energy shift since the EXAFS contribution becomes important. This edge shift has to be associated with the majority of Cu atoms in the sample. Since the doped electrons remain localized at the Cu site at least for low Ce-doping levels, the screening effect on the majority of Cu atoms due to the doped electrons is negligibly small, as evidenced by the fact that the main edge in the $\theta = 20^\circ$ spectra [Fig. 3(a)] is not shifted to lower energies. The variation in the Cu XANES spectra upon doping observed on the powdered $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ samples (Fig. 1)

can be well reproduced by combinations of the $\theta = 20^\circ$ and 90° polarization XANES data. This gives us full confidence that the polarization XANES data measured on the limited number of crystals are representative of the general behavior upon doping. We interpret the edge shift as due to a shift of the upper unoccupied band to a lower energy. The upper unoccupied band that consists of the in-plane $4p$ states shifts to a lower energy upon doping, and therefore the transition to the unoccupied in-plane $4p$ states takes place at lower energies. This band shift does not occur for the out-of-plane states since no edge shift is observed for polarization perpendicular to the CuO_2 plane [Fig. 3(a)]. This lowering of the band of in-plane states may be related to the expansion of the crystal a axis upon Ce doping.^{2,17,18} However, the c -axis contraction^{2,17,18} due to the smaller Ce^{4+} ion, as compared to the Pr^{3+} , may not be related to the electronic structure. We conclude from our polarization XANES study that Ce doping donates electrons to the initially localized Cu $3d$ states and also shifts the unoccupied band consisting of in-plane Cu $4p$ states to lower energies.

The controversy over the interpretation of Cu XANES data of polycrystalline $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ may be resolved in light of our polarization XANES data on single crystals. Tranquada *et al.*⁵ identified the filling of Cu $3d$ holes upon Ce doping, which is supported by the present polarization XANES data. However, the intensity increase at 13 eV (Fig. 1) mainly due to an edge shift was left unexplained. Alp *et al.*⁶ suggested that electrons are doped to a band based on an edge shift argument. But the intensity increase at 1.2 eV cannot be accounted for. Recently, Kosugi *et al.*¹³ suggested that each Ce dopant affects four to five Cu atoms based on a weighted subtraction between the spectra of doped samples and the undoped sample. Physically, an electron shared by four to five Cu atoms is not likely to screen the core hole well enough to give rise to the observed intensity at 1.2 eV. In addition,

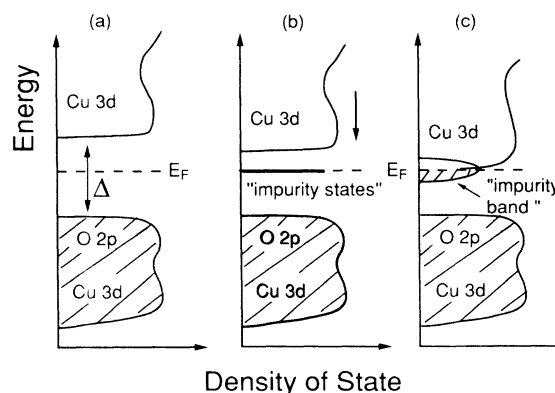


FIG. 4. A schematic diagram for the electronic structure and its evolution with Ce doping in Pr_2CuO_4 . (a) Charge-transfer insulator Pr_2CuO_4 . (b) Ce doping introduces localized impurity states near the Fermi level, and also shifts the upper unoccupied band toward lower energies. (c) As the doping level increases, the impurity states pile up to form an "impurity band" which is joined near the Fermi level by the upper unoccupied band. (See Ref. 21 for a diagram for hole-doped superconductor.)

the overall edge shift upon doping observed in our $\theta=90^\circ$ XANES data [Fig. 3(b)] indicates that the weighted subtraction between the spectra of doped samples and the undoped sample cannot be justified.

We now discuss more generally the effect of Ce doping on the electronic structure of Pr_2CuO_4 . Similar to other insulating end members of the high- T_c cuprates like La_2CuO_4 and $\text{YBa}_2\text{Cu}_3\text{O}_6$, the undoped Pr_2CuO_4 can be described as a charge-transfer insulator with a gap of $\Delta \sim 1.5$ eV.¹⁹ The lower occupied band originates from hybridized O $2p$ and Cu $3d$ states and the upper unoccupied band consists of predominantly Cu $3d$ states with small amounts of O $2p$ admixtures. The Fermi level lies in the gap and there is no density of states in the gap^{19,20} for the undoped Nd_2CuO_4 and Pr_2CuO_4 . Resonant photoemission experiments indicate²⁰ that new states are introduced near the Fermi level which remains at about the same position as in the undoped sample. Thus, our XANES data for $\theta=20^\circ$ combined with the resonant photoemission results suggest that the Ce-doping produced electrons are initially localized near the Fermi level in the band gap [Fig. 4(b)]. Within our interpretation of the XANES data, the Cu $4p$ band of a width up to 15 eV as probed in the $\theta=90^\circ$ XANES spectra [Fig. 3(b)] shifts down rigidly upon Ce doping. Even though the $\theta=90^\circ$ Cu K -edge XANES probes the unoccupied in-plane $4p$ states at energies above the lowest unoccupied band, which consists of predominantly in-plane Cu $3d$

states, it seems reasonable to propose that the lowest unoccupied band also shifts down upon doping. We indicate this possibility in Fig. 4(b) by an arrow pointing downward. Within such a picture, the upper unoccupied band will shift down and eventually join the states that pile up near the Fermi level as the Ce doping level increases [Fig. 4(c)]. We caution that the unoccupied Cu $3d$ band does not necessarily shift rigidly nor will the shift be necessarily of the same size as the shift of the Cu $4p$ bands. Optical conductivity results¹⁹ (obtained on the same batch of $x=0.04, 0.12$ crystals used in the present XANES experiments) suggest that additional density of states other than the states contributed directly by the doped electrons is transferred to the gap, which appears to be consistent with our results. The d states near the Fermi level ("impurity states") are rather localized. We speculate that metallic conductivity and superconductivity can occur only when these impurity states join the upper unoccupied $3d$ band.

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

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

³J. T. Markert *et al.*, *Physica C* **158**, 178 (1989).

⁴J. T. Markert and M. B. Maple, *Solid State Commun.* **70**, 145 (1989).

⁵J. M. Tranquada *et al.*, *Nature (London)* **337**, 720 (1989).

⁶E. E. Alp *et al.*, *Phys. Rev. B* **40**, 2617 (1989).

⁷Z. Tan *et al.*, *Physica B* (to be published).

⁸G. Liang *et al.*, *Phys. Rev. B* **40**, 2646 (1989).

⁹C. L. Lin *et al.* (unpublished).

¹⁰A. Grassmann *et al.*, *Europhys. Lett.* **9**, 827 (1989); *Physica B* (to be published).

¹¹A. Fujimori *et al.*, *Physica B* (to be published).

¹²N. Nücker *et al.*, *Z. Phys. B* **75**, 421 (1989); J. Fink *et al.*,

Physica C **162-164**, 1415 (1989).

¹³N. Kosugi, Y. Tokura, H. Takagi, and S. Uchida, *Phys. Rev. B* **41**, 131 (1990).

¹⁴Z. Tan, J. I. Budnick, and S. M. Heald, *Rev. Sci. Instrum.* **60**, 1021 (1989).

¹⁵Z. Tan *et al.*, *Physica C* **160**, 571 (1989).

¹⁶S. M. Heald, J. M. Tranquada, A. Moodenbaugh, and Y. Xu, *Phys. Rev. B* **38**, 761 (1988); M. Qian *et al.*, *ibid.* **39**, 9192 (1989).

¹⁷J. M. Tarascon *et al.*, *Phys. Rev. B* **40**, 4494 (1989).

¹⁸J. L. Peng, R. N. Shelton, and H. B. Radousky, *Phys. Rev. B* **41**, 187 (1990).

¹⁹S. L. Cooper *et al.*, *Phys. Rev. B* **41**, 11605 (1990).

²⁰J. W. Allen *et al.*, *Phys. Rev. Lett.* **64**, 595 (1990).

²¹H. Matsuyama *et al.*, *Physica C* **160**, 567 (1989).