Nature of copper in the new cuprate superconductors $Pb_2Sr_2Ca_{1-x}L_xCu_3O_{8+\delta}$

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(Received 17 January 1989)

Based on Cu K-edge absorption spectroscopy as well as Cu($2p_{3/2}$) and Cu(LVV) Auger spectroscopies it is shown that the recently discovered $Pb_2Sr_2Ca_{1-x}L_xCu_3O_{8+\delta}$ (L = Y or Lu) superconductors contain well-defined Cu^{1+} species in admixture with Cu^{2+}. The proportion of Cu^{1+} is small in the nonsuperconducting samples with $x=1$, a feature which is uniquely different from that in $YBa_2Cu_3O_{7-\delta}$.

Extensive studies on $YBa_2Cu_3O_{7-\delta}$ by employing x-ray-absorption spectroscopies (XAS), x-ray photoelectron spectroscopy, and related techniques have revealed that the proportion of the Cu^{3+} (d^8) species is essentially negligible in this doped cuprate.[1-4] Instead, holes are present on oxygen. Similar observations have been made with regard to $Bi_2CaSr_2Cu_2O_8$, $Tl_2CaBa_2Cu_2O_8$, and related cuprates.[5,6] Furthermore, these studies suggest an important role for Cu^{1+} (d^{10}) species. X-ray absorption spectroscopy at the Cu K edge[7] does not, however, provide direct evidence for the presence of Cu^{1+} in $YBa_2Cu_3O_{7-\delta}$ ($\delta < 0.4$); Cu^{1+} is present in nonsuperconducting $YBa_2Cu_3O_6$ and other compositions with large δ. The recent discovery[8] of high-T_c superconductivity in the $Pb_2Sr_2Ca_{1-x}L_xCu_3O_{8+\delta}$ (L = Y or Lu) system is of special interest since the chemical stoichiometry of these cuprates requires the presence of Cu^{1+} in them. We have investigated $Pb_2Sr_2Ca_{1-x}Y_xO_{8+\delta}$ and $Pb_2Sr_2Ca_{1-x}Lu_xCu_3O_{8+\delta}$ ($0.5 \leq x \leq 1.0$) by Cu K edge XAS, Cu $2p_{3/2}$ core-level spectroscopy, and Cu(LVV) Auger spectroscopy. The study has not only revealed the presence of distinct Cu^{1+} species, but also that Cu^{1+} is essential for superconductivity in these lead cuprates.[9]

Samples of $Pb_2Sr_2Ca_{1-x}L_xCu_3O_{8+\delta}$ were prepared by heating PbO with a previously prepared oxide matrix of the other constituent metals at 1170 K in an atmosphere of N_2 with 1% O_2 for 4–12 h. The samples were characterized by x-ray diffraction, magnetic susceptibility, and electrical resistivity measurements. Oxygen content of the samples was determined by thermogravimetric analysis in a current of hydrogen at 770 K. It was found that δ varied between 0.0 and 0.3 in the x range of 0.5 to 1.0. The $Pb_2Sr_2Ca_{1-x}Y_xCu_3O_{8+\delta}$ samples showed onset of superconductivity at 65 and 75 K, respectively, when x was 0.5 and 0.75; the $x=1.0$ sample was nonsuperconducting. The corresponding samples with Lu showed similar superconducting characteristics. X-ray-absorption measurements were carried out at the Cu K edge with a Rigaku spectrometer fitted with a bent crystal monochromator Si(440) and a rotating anode x-ray generator. A resolution better than 2 eV was obtained with a 100 μm slit and calibrated with respect to a Cu foil. X-ray-photoelectron spectra and Cu(LVV) Auger spectra were obtained with a VG ESCA-III Mark 2 spectrometer operating at a vacuum of 5×10^{-10} Torr with Mg $K\alpha$ radiation (1253.6 eV). The samples were scraped with a ceramic file in the preparation chamber before the measurements.

The absorption at the Cu K edge in copper oxides is predominantly a $1\underline{s} \rightarrow \underline{p}$ symmetry dipole transition. The intensity of this transition is extremely sensitive to the state of Cu and the nature of coordination. Thus, in Cu_2O with a twofold coordination of Cu^{1+}, we see a sharp feature at 8983 eV and the corresponding feature in CuO is around 8987 as shown in Fig. 1. A mixture of Cu_2O and CuO shows both these features. The feature due Cu^{1+} is hardly seen in $YBa_2Cu_3O_{6.9}$, but it is distinctly found in $YBa_2Cu_3O_{7-\delta}$ with $\delta > 0.5$ where twofold coordination of Cu is present due to oxygen deficiency. The main peak in the K-absorption edge of copper in CuO is found at 8997 eV. $YBa_2Cu_3O_{6.9}$ also shows this feature around the same energy. The main feature of Cu_2O appears at a lower energy. In the Cu K-edge spectrum of $Pb_2Sr_2Ca_{1-x}Y_xCu_3O_{8+\delta}$ ($0.5 \leq x < 1$), we clearly see the feature at 8983 eV due to Cu^{1+} (Fig. 1), but the feature becomes very weak in $Pb_2Sr_2YCu_3O_{8+\delta}$ ($x=1$). The main peak of $Pb_2Sr_2Ca_{1-x}Y_xCu_3O_{8+\delta}$ ($0.5 \leq x < 1$) is broad due to the presence of both Cu^{1+} and Cu^{2+}. It is really curious that the proportion of Cu^{1+} is higher in superconducting $Pb_2Sr_2Ca_{1-x}Y_xCu_3O_{8+\delta}$ ($0.5 \leq x < 1$),

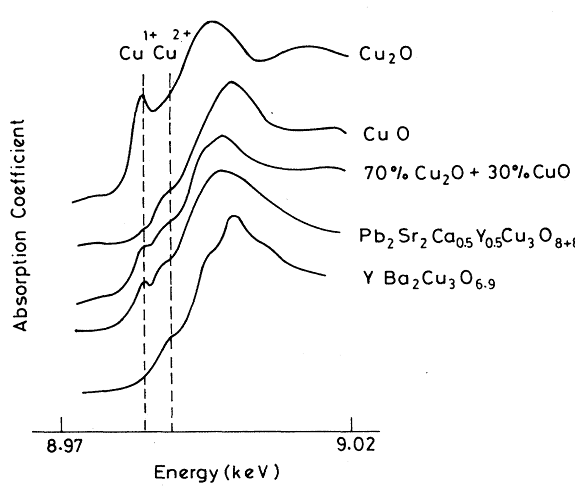

FIG. 1. Cu K-edge absorption near-edge structure of $Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$ and other copper oxides.

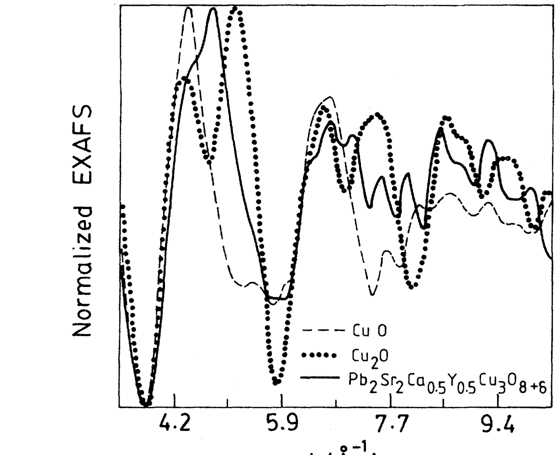

FIG. 2. Cu K-edge normalized EXAFS of Cu_2O, CuO, and $Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$.

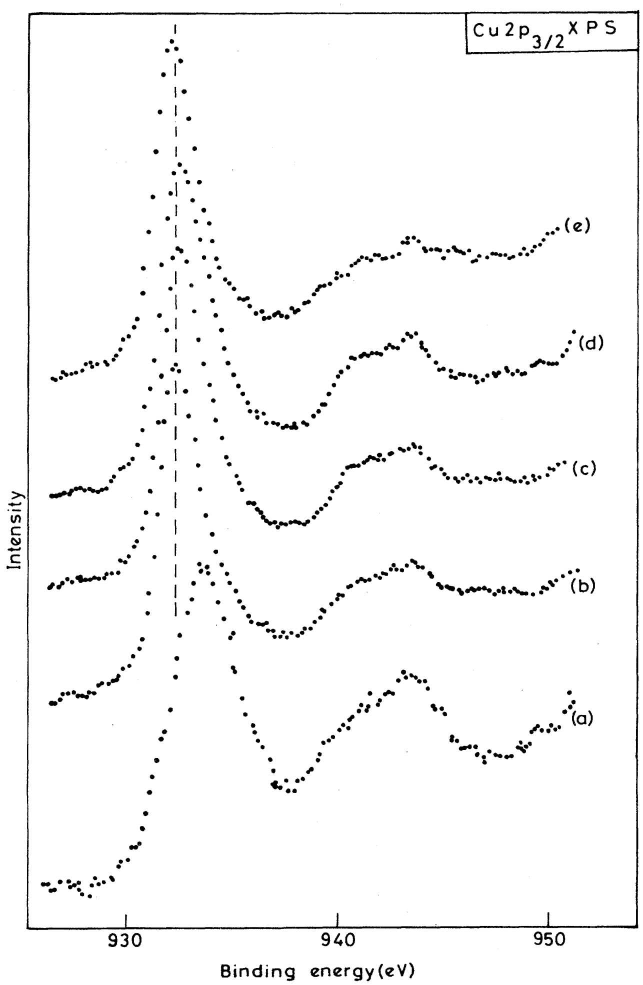

FIG. 3. Cu $2p_{3/2}$ spectra of (a), $YBa_2Cu_3O_{6.9}$; (b), $Pb_2Sr_2Ca_{0.5}Lu_{0.5}Cu_3O_{8+\delta}$; (c), $Pb_2Sr_2Ca_{0.25}Lu_{0.75}Cu_3O_{8+\delta}$; (d), $Pb_2Sr_2LuCu_3O_{8+\delta}$; and (e), $Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$.

becoming negligible in the nonsuperconducting sample with $x \simeq 1.0$.[9] This situation is exactly opposite to that found in the $YBa_2Cu_3O_{7-\delta}$ system.

The Cu extended x-ray-absorption fine-structure spectroscopy (EXAFS) of $Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$ also provides evidence for the presence of Cu^{1+} along with Cu^{2+}. In Fig. 2 we show the normalized EXAFS of this cuprate along with that of Cu_2O and CuO. The features in the superconducting cuprate are intermediate between those of Cu_2O and CuO. The Fourier transform of the normalized EXAFS of $Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$ shows the main peak due Cu-O scattering composed of two Cu-O distances arising from Cu^{1+} (1.82 Å) and Cu^{2+} (1.97 Å). The Cu K-edge absorption study thus clearly establishes the presence of Cu^{1+} as a distinct species with twofold oxygen coordination, and not as a product arising from other electronic effects.

X-ray photoelectron spectra of a few members of the $Pb_2Sr_2Ca_{1-x}L_xCu_3O_{8+\delta}$ series in the Cu $2p_{3/2}$ region are compared with the spectrum of $YBa_2Cu_3O_{6.9}$ in Fig. 3. All the cuprates exhibit a main peak at $\sim$932.5 eV and a weaker and broader feature (satellite) around 942 eV. The intensity of the satellite in the spectra of the Pb cuprates is generally weak. Since the relative intensity of the satellite (with respect to the main peak) is a measure of the proportion of the Cu^{2+} (d^9) configuration in the

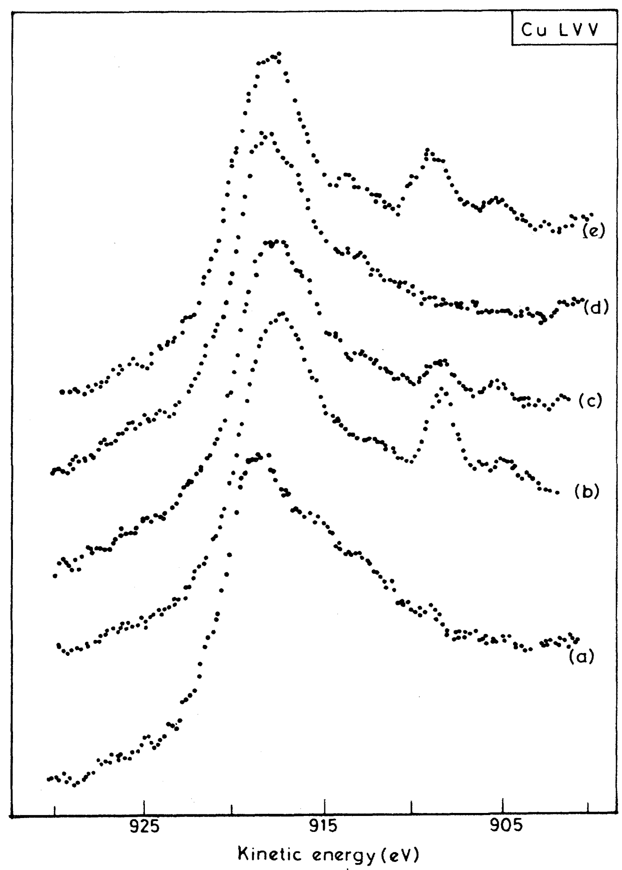

FIG. 4. Cu(LVV) spectra of the cuprates as in Fig. 3.

ground state, it appears that the Pb cuprates have a much smaller proportion of Cu^{2+} than $YBa_2Cu_3O_{6.9}$. Furthermore, we observe a shift of the main peak to a lower binding energy in $Pb_2Sr_2Ca_{1-x}L_xCu_3O_{8+\delta}$ compared to $YBa_2Cu_3O_{6.9}$, as expected in the presence of Cu^{1+} (note that the binding energy in Cu_2O is lower than that in CuO). In Fig. 4 we show the x-ray-induced Cu(LVV) Auger spectra of $Pb_2Sr_2Ca_{1-x}L_xCu_3O_{8+\delta}$ along with the spectrum of $YBa_2Cu_3O_{6.9}$. We notice the intensity around 917 eV to be considerably higher in the spectra of the Pb cuprates, again lending support for the presence of the Cu^{1+} species.

We have investigated $Pb_2Sr_2Ca_{1-x}Lu_xCu_3O_{8+\delta}$ for possible systematics. In this system, the oxygen content varied with x, the values being around 0.1, 0.0, and 0.3 when $x=0.5$, 0.75, and 1.0, respectively. The onset temperature for superconductivity was 65 and 73 K when $x=0.5$ and $x=0.75$, the sample being nonsuperconducting when $x=1.0$. This suggests that T_c is high only when the proportion of Cu^{1+} is high. Interestingly, the relative intensity of the Cu $2p_{3/2}$ satellite feature is highest in the $x=1.0$ sample.

The authors thank the Department of Science and Technology and the National Science Foundation for support of this research.

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[9]Pb L_3 edge measurements in this laboratory have shown Pb in these cuprates to be in the +2 state for all values of x.