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# Copper K-Edge X-ray Absorption Studies of $La_{2-x}K_xCuO_4$ Superconductors, $Ba_4NaCuO_4(CO_3)_2$, and $NdCu_2O_4$

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X-ray near-edge absorption spectroscopy (XANES) measurements are reported at the Cu K-edge for $La_{2-x}K_xCuO_4$ superconductors with $x = 0.1$ and 0.2. Comparisons of the data were made with the absorption spectra of a Cu(II) standard ($La_2CuO_4$), a new Cu(III) standard ($Ba_4NaCuO_4(CO_3)_2$), and a new mixed-valent Cu(II)/Cu(III) phase ($NdCu_2O_4$). There is a consistent increase in the energy of the main Cu absorption edge in the following series: $La_2CuO_4 < La_{1.9}K_{0.1}CuO_4 < La_{1.8}K_{0.2}CuO_4 \sim NdCu_2O_4 < Ba_4NaCuO_4(CO_3)_2$. This trend can be attributed to an increase in the average Cu valence and to a decrease in bond length and an increase in covalency. The magnitude of the energy shift from Cu(II) to Cu(III) for the main absorption edge is ~3 eV. There is no measurable change in the energy of the pre-edge feature irrespective of Cu valence. Furthermore, no new features appear at the edge for samples with formal oxidation state between 2 and 3, even for $NdCu_2O_4$, which contains both Cu(II) and Cu(III) in crystallographically distinct sites.

## Introduction

There is a strong correlation in cuprate superconductors between average formal Cu oxidation state and the superconducting transition temperature, $T_c$.[1] While Cu(II) oxides are semiconductors, superconductivity is found for phases in which the Cu is in an average formal oxidation state distinct from and generally greater than Cu(II). This nonintegral formal oxidation state is achieved typically through modification of the stoichiometry of a Cu(II) oxide by metal doping, changing the oxygen stoichiometry, or introducing cation vacancies. In order to learn more about the Cu valence in these materials one can probe charge and geometry by X-ray near-edge absorption spectroscopy (XANES).[2] Here we report XANES measurements at the Cu K-edge for $La_{2-x}K_xCuO_4$ superconductors with $x = 0.1$ and 0.2. On the basis of comparisons of the data with the absorption spectra of a Cu(II) standard ($La_2CuO_4$), a new Cu(III) standard ($Ba_4NaCuO_4(CO_3)_2$),[3] and a new mixed-valent Cu(II)/Cu(III) phase ($NdCu_2O_4$),[4] the energy of the absorption edge was found to increase with increasing Cu valence.

The onset of the absorbance of X-rays for transition metal ions is due primarily to transitions from the 1s core level to the first empty d or p level.[5] Since the energies of these levels are affected by the oxidation state of the absorbing metal ion, valence can be probed by monitoring the energy of the transition.[5b,6] However, the coordination environment (i.e., ligand type, geometry, coordination number, bond lengths, and bond covalency) also will affect the binding energies of the various electrons[6,7] and, therefore, will also affect the energy of this transition. Unfortunately, there is no adequate theory to predict the interrelationship between the spectral characteristics and the valence and coordination environment. Instead, it is necessary to draw conclusions based on comparisons with model compounds. In order to probe the effects due to variations in band filling for $La_{2-x}K_xCuO_4$, where the Cu atoms are in a distorted octahedral environment of oxygen atoms, we chose model compounds with oxygen coordinated to Cu in either distorted octahedral or square planar geometry.

There are two possible effects on the absorption spectrum of Cu in $La_{2-x}K_xCuO_4$ as $x$ increases: a shift in the energy at which the absorption occurs and (or) a new feature due to Cu(III). A

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shift in energy could reflect a change in the charge on Cu, changes in the Cu−O bond lengths, and/or a change in degree of covalency of the Cu−O bond altered by the presence of the electropositive ion. Reports conflict over whether there is a shift in energy for $La_{2-x}M_xCuO_4$, where M = Sr and Ba; for example, Tranquada *et al* reported no shift of the leading edge relative to CuO,[2a,b] while Alp *et al* report a shift of 2−3 eV.[2c,d] The second possibility, the appearance of a new feature due to Cu(III), would indicate two distinct charge states. Although this is not observed typically for transition metal compounds, even for localized mixed-valent systems,[7b] a feature due to Cu(III) has been claimed by Alp *et al*[r2c] and by Lytle *et al*[2e] for $La_{2-x}M_xCuO_4$. Choy *et al*[2f] have also claimed two distinct charge states in $La_2CuO_{4-x}$ on the basis of splitting of the pre-edge feature.

Our approach in interpreting the absorption spectra for the $La_{2-x}K_xCuO_4$ was to find suitable standards for Cu(II) and Cu(III). Finding a Cu(III) standard is challenging because so few Cu(III) phases are known. The XANES spectra have been measured previously for only eight Cu(III) compounds:[2c,8,9] $Cu(glycine)_4^-$, $K_2Cu(H_2NCONHCONH_2)_2$, $Cu(IO_4)_3$, $Cu_2O_3$, $NaCuO_2$, $KCuO_2$, $LaCuO_3$, and $La_2Li_{0.5}Cu_{0.5}O_4$. The first four compounds were reported to have essentially no shift in absorption edge compared with Cu(II) standards such as CuO.[8] This result is curious since there is a shift in the absorption edge for Cu(II) compared with Cu(I) of 3−4 eV [6] and a further shift to higher energies for Cu(III) is expected.[5b] Despite the structural similarities between the next two phases, $NaCuO_2$ and $KCuO_2$, the absorption edge was reported to be 0.5 eV higher than CuO for $NaCuO_2$[9] and 3.8 eV for $KCuO_2$.[2c,d] For the last two phases, $LaCuO_3$ and $La_2Li_{0.5}Cu_{0.5}O_4$, the absorption edge is approximately 2.7 eV higher than that of $La_2CuO_4$.[10]

We chose $Ba_4NaCuO_4(CO_3)_2$ as a Cu(III) standard for several reasons.[3] This phase consists of isolated $Cu^{III}O_4$ square planes. The diamagnetism (low spin, $d^8$) and the short Cu−O bonds of 1.85 Å are consistent with the assignment of the Cu valence as Cu(III). Large quantities of $Ba_4NaCuO_4(CO_3)_2$ are readily prepared as transparent, red crystals (up to 1 cm × 1 cm plates) under ambient conditions, and the phase is handled easily in a moisture-free atmosphere. Although $LaCuO_3$ and $La_2Li_{0.5}Cu_{0.5}O_4$ are perhaps better model compounds with respect to the coordination environment because the Cu is in a distorted octahedral environment as in $La_{2-x}K_xCuO_4$, we chose not to use these phases because they tend to be oxygen deficient such that the average Cu valence is below Cu(III). In contrast, $Ba_4NaCuO_4(CO_3)_2$ is stoichiometric with all the Cu present as Cu(III) on the basis of structural, spectroscopic, and magnetic data.

Although many Cu(II) phases are known, choosing a good standard is not trivial. We chose $La_2CuO_4$ because we wanted to determine changes that occur upon K-doping on the lanthanum site. We acknowledge that a small number of oxygen vacancies may be present in $La_2CuO_4$, as well as in the K-doped phases. Our measurements of the XANES spectrum of $La_2CuO_4$ compare well with those reported previously.[2c,e]

In order to determine whether two distinct features attributable to Cu(II) and Cu(III) are observable, we measured the XANES spectra of $NdCu_2O_4$, a mixed-valent Cu(II)/Cu(III) phase for comparison.[4] $NdCu_2O_4$ contains two crytallographically distinct Cu atoms, one with Cu−O bonds of 1.85 Å and another with Cu− O bonds of 1.94 Å. The copper−oxygen network consists of a three-dimensional array of $CuO_4$ distorted square planes that are corner-shared; the Cu−O−Cu bond angle is ~115°. The bond lengths, the stoichiometry, and the magnetic moment are all consistent with one Cu(II) and one Cu(III) per unit cell.

We report below the near-edge absorption spectra for $La_2CuO_4$, $La_{1.9}K_{0.1}CuO_4$, $La_{1.8}K_{0.2}CuO_4$, $NdCu_2O_4$, and $Ba_4NaCuO_4(CO_3)_2$. Careful attention was paid to the preparation of superconducting samples, as well as model compounds, to obtain the highest purity; elimination of impurity phases is key because the leading absorption edge is obscured by absorption due to impurity phases, such as CuO. Our samples were crystallized from molten hydroxides ($Ba(OH)_2$ or KOH) as described previously.[3,4,11] In addition, the energy scale for each spectrum was calibrated carefully by measuring a Cu reference foil simultaneously.

## Experimental Section

**Synthesis.** For preparation of $La_2CuO_4$, $La_{2-x}K_xCuO_4$, $Ba_4NaCuO_4(CO_3)_2$, and $NdCu_2O_4$, the following reagents were used: CuO (reagent grade, Aldrich), $La_2O_3$ (99.99%, Aldrich), $Nd_2O_3$ (99.9%, Alfa Products), $Na_2CO_3$ (reagent grade, Fisher Scientific), $BaCO_3$ (reagent grade, Fisher Scientific), NaOH (reagent grade, Fisher Scientific), KOH (reagent grade, Fisher Scientific), anhydrous $Ba(OH)_2$ (reagent grade, Fisher Scientific), and $BaCl_2{\cdot}2H_2O$ (reagent grade, Fisher Scientific). These reagents were used as purchased, except for the following: $BaCl_2{\cdot}2H_2O$ was dried in air at 110 °C for several hours before use, and the $La_2O_3$ was heated in air to 800 °C for 30 h to remove $H_2O$ and $CO_2$.

$La_2CuO_4$ was prepared by solid-state reactions of CuO and $La_2O_3$. Stoichiometric ratios were ground together with an agate mortar and pestle, pressed into a pellet, and placed in an alumina crucible. The reactants were heated in air to 1000 °C in 4 h, held at 1000 °C for 24 h, and, subsequently, cooled to room temperature in approximately 2 h.

The K-doped samples were prepared by direct precipitation from molten alkali metal hydroxides as described previously.[11] The reactants, 0.1 g of CuO and 0.41 g of $La_2O_3$, were added to 20 g of KOH in an open Ag crucible. $La_{1.8}K_{0.2}CuO_4$ and $La_{1.9}K_{0.1}CuO_4$ were prepared by raising the temperature to 430 and 470 °C in 2 h, respectively, holding the temperature for 20 h, and finally cooling by removing the crucible from the furnace. The black crystals were isolated by dissolving the hydroxide in water, filtering, and drying the material at room temperature.

$Ba_4NaCuO_4(CO_3)_2$ was synthesized in a $Ba(OH)_2$−$BaCl_2$ flux as described by VerNooy and Stacy.[3] The reactants, 0.5 g of CuO, 0.33 g of $Na_2CO_3$, and 1.9 g of $BaCO_3$, were added to 14.0 g of $Ba(OH)_2$ and 2.5 g of $BaCl_2$. The powders were mixed and placed in a 20 mL Ag crucible with a tightly fitting alumina lid and placed in the furnace. The furnace was heated from room temperature to 750 °C over 2.5 h, held at 750 °C for 5 h, and cooled gradually to 600 °C over 36 h. The crucible was then removed from the furnace and placed in a dry nitrogen atmosphere, in which all further manipulations took place. The crystals were isolated mechanically and cleaned in absolute methanol in an ultrasonic cleaner for 1 h.

$NdCu_2O_4$ was synthesized by precipitation as described previously by Keller *et al.*[4] First, 20 g of NaOH was melted in a silver crucible at 400 °C for 12−24 h in air in order to remove water. The reactants, 0.115 g of $Nd_2O_3$ and 0.109 g of CuO, were added to the hot melt. The reaction was allowed to proceed for 48 h at 400 °C. Upon completion of the reaction, a black precipitate was visible at the bottom and on the sides of the crucible, and the molten hydroxide flux had turned pale green. The flux was decanted, and the crucible was quenched into cold water. The remaining hydroxide was dissolved in flowing distilled water. The shiny, black crystallites were collected by vacuum filtration, washed with distilled water followed by acetone, and finally dried in air at 130 °C for several hours.

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**Table 1.** Lattice Parameters and Superconducting Properties of the Doped Lanthanum Copper Oxides

| composn | *a* param (Å) | *c* param (Å) | $T_c$ (onset) (K) | Meissner fraction (%) |
|---|---|---|---|---|
| $La_{1.9}K_{0.1}CuO_4$ | 3.777(1) | 13.289(1) | 20 | 15 |
| $La_{1.8}K_{0.2}CuO_4$ | 3.770(1) | 13.309(5) | 20 | 3 |

**Characterization.** All samples were characterized by powder X-ray diffraction on a Siemens D500 diffractometer, with Si as an internal standard. The lattice parameters were fit by using a least-squares refinement program. The composition of the alkali metal-doped lanthanum copper oxides was determined by wavelength dispersive X-ray fluorescence spectroscopy with an ARL SEMQ electron beam microprobe, by iodometric titrations, and by determination of the structure by single-crystal X-ray diffraction methods as reported previously.[11] The superconducting properties of the lanthanum copper oxides were determined by field cooled susceptibility measurements with a Quantum Design SQUID magnetometer; the field was calibrated with a superconducting tin sphere of known magnetization. A summary of the results of these measurements is given in Table 1.

**Cu K-Edge X-ray Absorption Near-Edge Spectroscopy**. Transmission spectra were taken at room temperature at beamline 4-3 of the Stanford Synchrotron Radiation Laboratory (SSRL). A Si(220) double-crystal monochromator was used, and the resulting energy resolution was 1−2 eV at 8.8 keV.[6] The absorption spectra were measured in transmission mode, with incident and transmitted beam intensities measured by using $N_2$-filled ionization chambers as a fluorescence detector. A Cu reference foil was measured simultaneously as an internal energy calibration,[12] and the relative energies were corrected to ±0.2 eV.[6] To ensure consistency in the relative energies, the Cu reference spectra were superimposed and found to be identical in energy for each of the samples that were measured.

Samples were ground and diluted with boron nitride (20 mg sample with 35 mg of boron nitride). The boron nitride is nonabsorbing at the photon energies used. The sample holders were constructed from Al, with 2 mm by 14 mm slits, and held in place with Mylar tape.

A linear fit to the pre-edge data was subtracted from each spectrum. The absorption in the post-edge region of each spectrum was normalized to 1. Finally, a linear fit to the post-edge data was subtracted from the spectrum.[8] Further quantitative analysis of the data was not done because the peak shape is highly dependent on the coordination geometry around the Cu atoms and the formal Cu oxidation state. Instead, shifts in energy and changes in shape are compared qualitatively with standards containing Cu(II) and Cu(III).

## Results and Discussion

**$Ba_4NaCuO_4(CO_3)_2$, $NdCu_2O_4$, and $La_2CuO_4$.** The XANES spectra for the Cu(III) standard, $Ba_4NaCuO_4(CO_3)_2$, and the Cu(II)/Cu(III) standard, $NdCu_2O_4$, are shown in Figure 1 along with the spectrum of the Cu(II) standard, $La_2CuO_4$, for comparison; the spectrum of the latter is similar to those reported previously.[2c,e] In the spectra of these three materials, there is an initial rise at the threshhold of absorption (pre-edge absorption) followed by a shoulder on a rising absorption curve (absorption edge) culminating in a relatively strong peak.

On the basis of conclusions drawn for transition metal compounds in previous work,[5,6] the pre-edge absorption can be assigned as the 1s to 3d transition, the strong peak as the 1s to 4p transition, and the shoulder at lower energy as the 1s to 4p shakedown. The latter has also been assigned as the 1s to 4s transition,[8] but it has been shown by band structure calculations that the intensity for this transition is too low to be detectable.[5c] An alternative assignment of these peaks has been provided by Tolentino *et al.*[2g,h] On the basis of detailed work on single crystals of copper oxides, they describe the peaks as a mixture of charge-transfer configurations for copper, $3d^9$ and $3d^{10}L$ for Cu(II) and $3d^9L$ for Cu(III), where L refers to a hole on the oxygen ligands. The features beyond the 1s to 4p transition are due to a combination of effects such as transitions to higher np states and multiple scattering; these have been considered previously by Lytle *et al.*[2e] and are not considered further here.

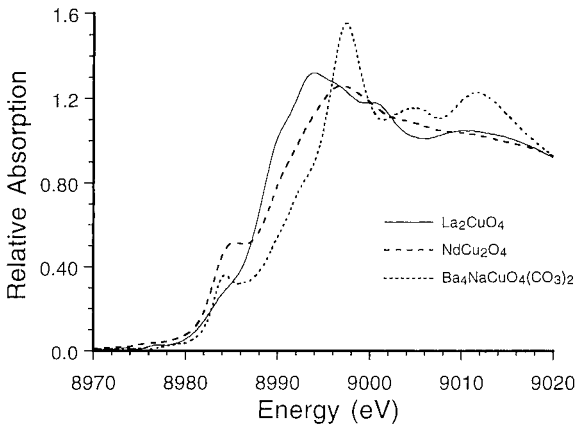

**Figure 1.** XANES spectra of $La_2CuO_4$, $NdCu_2O_4$, and $Ba_4NaCuO_4(CO_3)_2$. There is a shift of the main absorption edge to higher energies as the average formal copper oxidation state increases from 2+ to 2.5+ to 3+, respectively. The energy of the pre-edge does not change with Cu valence. No new features are observed at the absorption edge in the spectrum of $NdCu_2O_4$ despite Cu(II)/Cu(III) mixed-valence.

It has been shown previously that the intensity of the pre-edge absorption decreases as the site symmetry of the transition metal is increased from noncentrosymmetric to centrosymmetric, as the number of d vacancies decreases, and as the covalency of the metal−ligand bond decreases.[2e,5a] Here we find that the intensity of the pre-edge absorption decreases in the series $NdCu_2O_4 > Ba_4NaCuO_4(CO_3)_2 > La_2CuO_4$; for $La_2CuO_4$, the pre-edge feature is very subtle. Considering first geometric effects, the coordination changes from copper coordinated to oxygen atoms in distorted square planar geometry in $NdCu_2O_4$[4] to undistorted square planar geometry in $Ba_4NaCuO_4(CO_3)_2$[3] to distorted octahedral geometry in $La_2CuO_4$.[13] Thus, the intensity of the pre-edge absorption for $NdCu_2O_4$ is the largest because it is the only compound in the series in which the coordination environment is noncentrosymmetric. One might expect $Ba_4NaCuO_4(CO_3)_2$ to have the least intensity for geometric reasons alone, but it is second in the series because it has the largest number of d vacancies and the shortest Cu−O bonds (presumably the most covalent).

The energy of the pre-edge absorption does not appear to correlate with the formal copper oxidation state. The inflection points for the onset of absorption are the same (8983.0 eV) within experimental error, despite the change in formal oxidation state. This is consistent with previous reports that the energy of the pre-edge absorption feature is essentially invariant for a particular transition metal.[5a] Therefore, we take the invariance of the energy of this feature in our experiments as an indication of accurate energy calibration.

In contrast to the pre-edge absorption feature, the energy of the main edge is quite sensitive to formal oxidation state, degree of covalency, and point symmetry of the transition metal site.[2e,6,14] For the three materials studied here, the energy of the absorption edge is correlated with the formal oxidation state. There is a shift in energy of the absorption edge for

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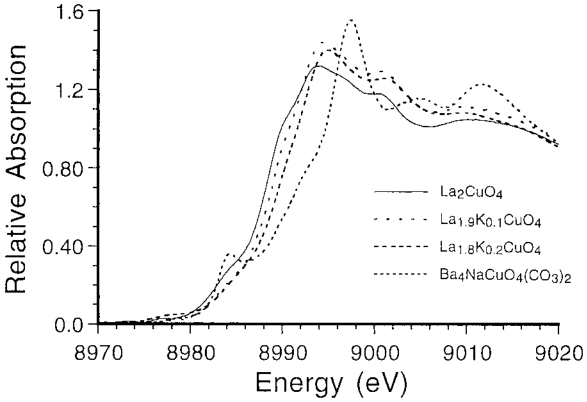

**Figure 2.** XANES spectra of $La_2CuO_4$, $La_{1.9}K_{0.1}CuO_4$, $La_{1.8}K_{0.2}CuO_4$, and $Ba_4NaCuO_4(CO_3)_2$. There is a systematic shift of the main absorption edge to higher energy with increasing Cu valence.

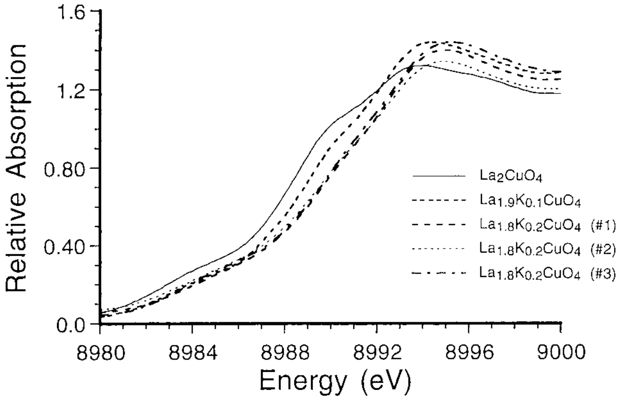

**Figure 3.** XANES spectra of $La_2CuO_4$, $La_{1.9}K_{0.1}CuO_4$, and three samples of $La_{1.8}K_{0.2}CuO_4$ from different preparations. The results for the three samples of $La_{1.8}K_{0.2}CuO_4$ show excellent reproducibility.

$Ba_4NaCuO_4(CO_3)_2$ compared with $La_2CuO_4$ by approximately 3 eV as determined by comparing the inflection points. The edge for $NdCu_2O_4$ is roughly in between.

The magnitude of the shift of 3 eV is similar to that reported for the Cu(III)-containing material $KCuO_2$ (approximately 4 eV higher in energy than CuO)[2c,d] but larger than that reported for $NaCuO_2$ (approximately 0.5 eV higher in energy than CuO).[9] $LaCuO_3$ and $LaLi_{0.5}Cu_{0.5}O_4$ also gave results similar to that reported here (approximately 2.7 eV higher in energy than $La_2CuO_4$).[10] In an earlier report on the XANES spectra for several Cu(III) model compounds (including $Cu_2O_3$, the existence of which has never been proven), it was claimed that the spectra were indistinguishable from Cu(II) compounds.[8] We propose that the smaller values reported previously are likely due to the presence of Cu(II) impurity phases or oxygen vacancies.

Previous workers report a correlation between the energy of the absorption edge and a quantity called "coordination charge", which takes into account the number of ligands and the degree of covalence of the bonds.[7b,14a] We predict a higher coordination charge for the compounds with a higher formal oxidation state and, therefore, an absorption edge at higher energy. The shift in the energy of the absorption edge has been shown to be linear with oxidation state for a variety of transition metal compounds.[5b] Accordingly, the shift in energy from Cu(II) to Cu(III) of approximately 3 eV is consistent with the shift of similar magnitude reported previously for Cu(I) to Cu(II).[6] However, a shift of 10−13 eV was predicted on the basis of calculations of the difference in energy between the ground and final state of an electron transferred from the 1s to the 4p state.[2a,b] Our results show that this prediction overestimates the magnitude of the shift in energy between Cu(II) and Cu(III) by more than a factor of 2.

We also note that there are no new features in the XANES spectrum of $NdCu_2O_4$ despite the presence of both Cu(II) and Cu(III). This is consistent with extensive work on Mn compounds which shows that the Mn K-edge inflection energy correlates with average valence, even for static mixed-valent systems.[5b] On the basis of these results, new features should not appear in the spectra for $La_{2-x}M_xCuO_4$; the main effect of raising the average Cu formal oxidation state through doping is to change the energy of the main absorption edge, rather than to add a new feature due to Cu(III).

**Doped Lanthanum Copper Oxides.** The spectra for the samples of $La_{2-x}K_xCuO_4$ superconductors displayed in Figure 2 show that there is a measurable difference in the absorption edge as the doping level changes from $x = 0.1$ to $x = 0.2$. The edges of $La_{1.9}K_{0.1}CuO_4$ and $La_{1.8}K_{0.2}CuO_4$ are approximately 0.5 and 1.0 eV higher than that of $La_2CuO_4$, respectively, as measured at the inflection points of the curves.

One way to derive information from these data is to assume a linear change in absorption energy between Cu(II) and Cu(III). Since a shift in absorption edge of approximately 3 eV was observed between Cu(II) and Cu(III) for the $La_2CuO_4$ and $Ba_4NaCuO_4(CO_3)_2$ standards, by interpolation a shift of 0.5 eV for $La_{1.9}K_{0.1}CuO_4$ yields a formal oxidation state of approximately $Cu^{2.17+}$, which is in reasonable agreement with the oxidation state of $Cu^{2.2+}$ on the basis of stoichiometry. Likewise the shift of 1.0 eV for $La_{1.8}K_{0.2}CuO_4$ yields a formal oxidation state of $Cu^{2.33+}$, which corresponds well with the oxidation state of $Cu^{2.4+}$ on the basis of stoichiometry.

The consistency of these measurements was checked with two additional samples of $La_{2-x}K_xCuO_4$ with x near 0.2, prepared by similar methods. As shown in Figure 3, the three spectra of $La_{1.8}K_{0.2}CuO_4$ are nearly identical. Any shifts in the absorption edge are below the resolution of the experiment. These results give us confidence in our ability to measure small shifts in the absorption edges and correlate the energies with the formal Cu oxidation state.

## Conclusions

The oxidation of copper beyond a formal value of Cu(II) causes a shift in the X-ray absorption edge to higher energies. There is a consistent increase in the energy of the main absorption edge in the following series: $La_2CuO_4 < La_{1.9}K_{0.1}CuO_4 < La_{1.8}K_{0.2}CuO_4 \sim NdCu_2O_4 < Ba_4NaCuO_4(CO_3)_2$. The magnitude of the shift from Cu(II) to Cu(III) for the 1s to 4p absorption edge is approximately 3 eV. This trend can be attributed to an increase in the average Cu valence and to a decrease in bond length and an increase in covalency. Furthermore, no new features appear at the edge for samples with formal oxidation state between 2 and 3, even for $NdCu_2O_4$, which contains both Cu(II) and Cu(III) in crystallographically distinct sites.

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