

**Cu K-EDGE STUDIES OF THE CHARGE
CARRIERS IN Th-DOPED CUPRATE SYSTEM
 $R_{2-x}Th_xCuO_{4-\delta}$ (R = Nd, Sm and Gd)**

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To further study the charge carrier concentration in electron doped cuprate superconductors, a systematic x-ray absorption near edge structure (XANES) measurement has been carried out on Th-doped superconductor system $R_{2-x}Th_xCuO_{4-\delta}$ (R = Nd, Sm, and Gd). The XANES results show that, similar to the Ce-doped compounds, while the intensity of the $Cu^{1+} 4p_\pi$ feature increase with the increase of the Th doping level x , the intensities of the $Cu^{2+} 4p_\pi$ and $4p_\sigma$ features decreases. This clearly indicates that the electrons doped by the Th atoms are injected into the local Cu 3d-orbitals. The normalized $Cu^{1+} 4p_\pi$ intensity data show that the Cu^{1+} concentration in the Th-doped compound series with different R-elements is linearly proportional to the Th doping-level x . The data suggest that both Ce and Th donate the same fraction of electrons into the Cu sites.

1. Introduction

Considerable x-ray absorption near edge structure (XANES) studies¹⁻⁸ have been made to investigate the charge carriers in the Ce-doped n-type superconductor system $R_{2-x}Ce_xCuO_{4-\delta}$ with R to be rare-earth elements from Pr to Gd. Some of these studies indicated that the electrons doped by Ce atoms were injected into the Cu 3d orbitals converting Cu from Cu^{2+} to Cu^{1+} . The superconducting properties of the Th-doped compounds $R_{2-x}Th_xCuO_{4-\delta}$ are very similar to the Ce-doped compounds and thus they are excellent materials for further studying the charge carriers and the Cu valence in these n-type oxide superconductors. So far, for Th-doped compounds, only the $R_{2-x}Th_xCuO_{4-\delta}$ with R = Nd have been studied by XANES measurements⁷. However, the average fraction of electrons doped into Cu 3d orbitals from each Th atom has never been accurately estimated yet. In this paper, we present such estimate from Cu K-edge results for Th-doped compound

series $R_{2-x}Th_xCuO_{4-\delta}$ with $R = Nd, Sm$ and Gd .

2. Experimental

Polycrystalline samples of $R_{2-x}Th_xCuO_{4-\delta}$ ($R = Nd, Sm,$ and Gd) with $x = 0.0, 0.05, 0.10, 0.15,$ and 0.18 were prepared by solid-state reaction from a mixture of starting materials $R_2O_3, ThO_2,$ and CuO . The mixed powder was calcined in air at $900^\circ C$ for 50 h, $1000^\circ C$ for 60 h, and $1030^\circ C$ for 30 h (with intermediate grindings) and pressed into pellets. The pellets were sintered at $1080^\circ C$ for 60 h in air and slowly cooled to room temperature at a rate of about $2^\circ C/h$. The pellets were then divided into two groups: one group was annealed at $950^\circ C$ for 20 h in a pure oxygen atmosphere (oxidized samples), another group was annealed at $950^\circ C$ for 20 h in a pure helium atmosphere (reduced samples). All of the samples were checked to be single phase by x-ray diffraction measurements. The XANES measurements at Cu K-edge were carried out at the National Synchrotron Light Source (NSLS) on beam line X-11A using a Si(111) monochromator and 0.5-mm entrance slit. The spectra were measured using transmission mode detection. Energy calibration was made by simultaneously measuring the Cu K-edge spectrum of a reference compound Cu_2O . All of the spectra presented in this paper have been linear-background subtracted and normalized to unit in the continuum region.

3. Results and Discussions

Shown in Fig 1. are the Cu K-edge spectra for selected $R_{2-x}Th_xCuO_{4-\delta}$ compounds with $0 \leq x \leq 0.18$. The samples for the $R = Sm$ series were reduced in helium. The spectral features A, B and C, D can be interpreted in a similar way to those previously used for the polarized spectra of single crystals^{5,8} $R_{2-x}Th_xCuO_{4-\delta}$, i.e., the double features labeled by A and B can be assigned to the transitions from Cu $1s$ to the out-of-plane $4p_\pi$ states whereas the double features labeled by C and D are due to the transitions from Cu $1s$ to the in-plane $4p_\sigma$ states. The lower energy A and C features involve "shakedown" Cu final state $3d^{10}\underline{L}$ (where \underline{L} denotes a hole in the O-ligand shell) whereas the B and D features are related to Cu final state $3d^9$. The feature A' (or C') located about 3 eV below the feature A (or C) for the $x \neq 0$ samples can be attributed to the $1s \rightarrow 4p_\pi$ (or $1s \rightarrow 4p_\sigma$) transition with Cu in a $3d^{10}$ configuration^{5,8}. The intensity of the feature A' has been used for the estimate of Cu^{1+} concentration⁵. It can be observed from Fig. 1 that with Th doping to R_2CuO_4 ($R = Nd, Sm,$ and Gd), the spectral features vary in the same manner as that caused by Ce doping. That is, with the increase of doping level x , (1) the intensity of the Cu^{1+} features A' (or C') increases along with the

suppression of the intensities of the Cu^{2+} features A through D (the reasons

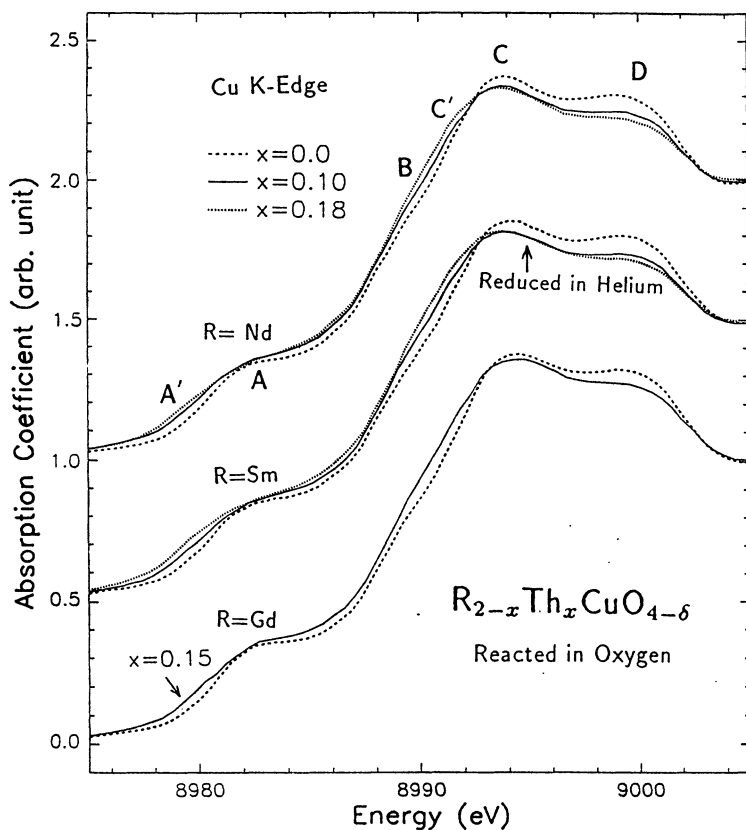


Fig. 1. Cu K-edge spectra for polycrystalline $\text{R}_{2-x}\text{Th}_x\text{CuO}_{4-\delta}$ compounds with $\text{R} = \text{Nd}, \text{Sm},$ and Gd . The $\text{R} = \text{Sm}$ series was helium-annealed and the other two series were oxygen-annealed.

that why the decrease of intensities for features A and B is not as obvious as for features C and D have been discussed previously⁵; (2) the edge is shifted to the lower energy side; (3) the intensities of feature C decreases relatively less than that of feature D. The observation (1) clearly indicates that Th atoms donate electrons into the Cu 3d orbitals to convert Cu from Cu^{2+} (with $3d^{10}\underline{L}$ or $3d^9$ configurations) to Cu^{1+} state (with $3d^{10}$ configuration). As discussed in Ref. 5 for polycrystalline $\text{R}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$ system, the observation (2) can be explained as being primarily due to the intensity increase of the electron-doping-induced $3d^{10}$ feature C' and the observation (3) can be attributed to the reduction of the charge transfer gap^{5,8}.

In previous XANES study on $\text{R}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$ system⁵, the Cu^{1+} concentration as a function of the Ce-doping level x was estimated from the $\text{Cu}^{1+} 4p_{\pi}3d_{10}$ feature A'. Here we will use the same method to estimate the Cu^{1+} concentration as a function of the Th-doping level x for the $\text{R}_{2-x}\text{Th}_x\text{CuO}_{4-\delta}$ system. The intensity values of the feature A' can be estimated approximately by the heights of the peaks

in the difference spectra which were obtained from subtracting the spectra of the undoped ($x = 0$) samples from those of the Th-doped (the $x \neq 0$) samples in each series. Fig. 2 shows, for example, such difference spectra for the R = Sm series. Also plotted in Fig. 2 is the difference spectrum of the Cu^{1+} reference compound Cu_2O , which was obtained by subtracting the spectrum of the undoped compound Nd_2CuO_4 from the spectrum of Cu_2O . In Fig. 2, all peak heights are normalized to the peak height of the Cu^{1+} (or $4p_\pi 3d^{10}$) peak in the difference spectrum of Cu_2O .

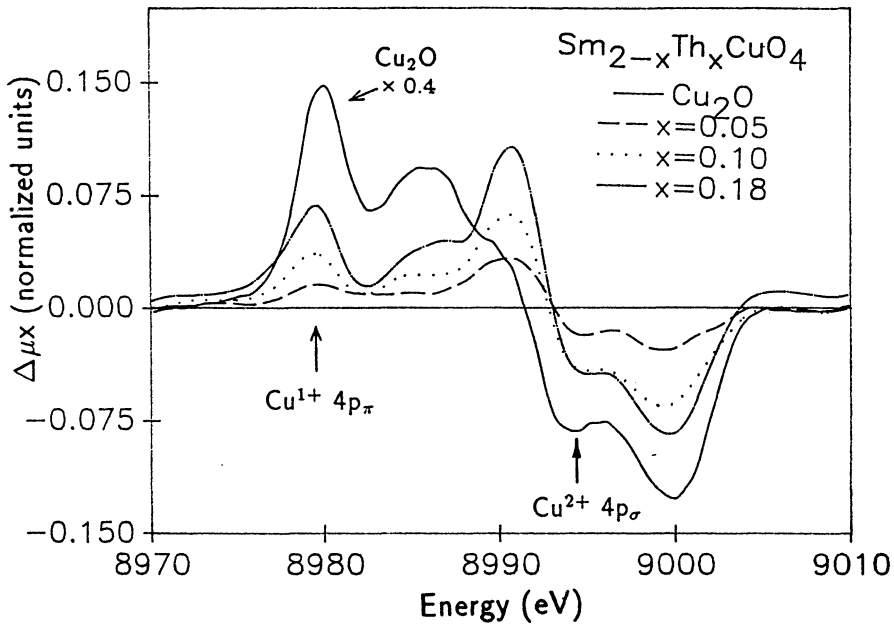


Fig. 2. The difference spectra at the Cu K -edge for the $\text{Sm}_{2-x}\text{Th}_x\text{CuO}_{4-\delta}$ series and Cu_2O .

In Fig. 3, we plot the intensity values of the $\text{Cu}^{1+}4p_\pi 3d^{10}$ peaks against Th-doping level x for all of the $\text{R}_{2-x}\text{Th}_x\text{CuO}_{4-\delta}$ series with R = Nd, Sm, and Gd. The linear relationship between the Cu^{1+} intensity and the Th-doping level x , observed also previously in the Ce-doped series⁵ (also plotted in Fig. 3 by the open squares and dashed fitting lines), is seen here for all of the three series. The values of the slopes of the fitted straight lines (the solid lines) in Fig. 3 are about 1.00 ± 0.05 for R = Nd series and 0.90 ± 0.05 for R = Sm and Gd series, which are almost the same as for the Ce-doped series $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$ (see Fig. 3)⁵. This means that the average fraction of the electrons, or the charge carriers, doped into Cu $3d$

orbitals from each Ce or Th atom is close to (but slightly smaller than) unity.

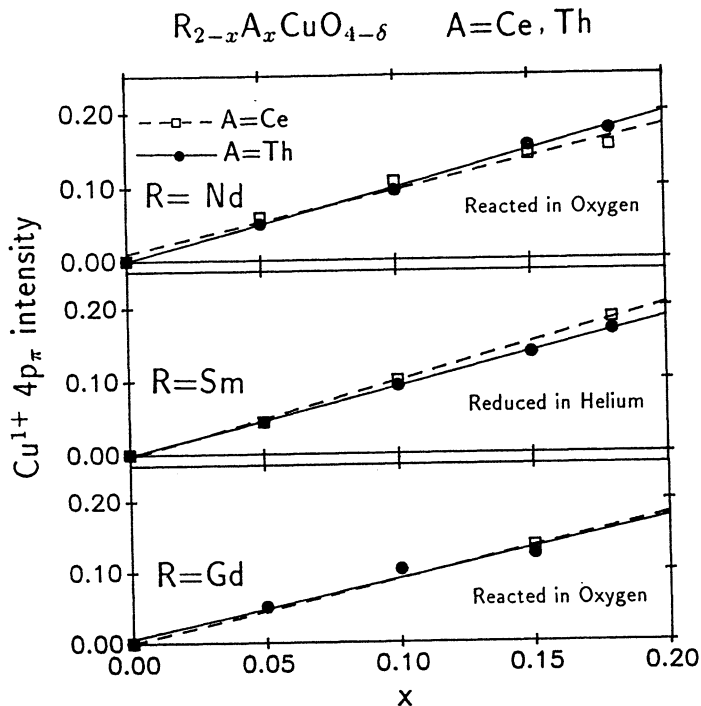


Fig. 3. The peak height of $Cu^{1+}4p_{\pi}$ spectral feature in the difference spectra (see Fig. 2 for example) as a function of x for the $R_{2-x}Th_xCuO_{4-\delta}$ system.

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