Ce-doping and reduction annealing effects on electronic states in Pr$_{2-x}$Ce$_x$CuO$_4$

studied by Cu $K$-edge X-ray absorption spectroscopy

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We investigated Ce-substitution and reduction annealing effects on the electronic states in copper sites by Cu $K$-edge x-ray absorption fine structure measurements in Pr$_{2-x}$Ce$_x$CuO$_{4+\alpha-\delta}$ (PCCO) with varying $x$ and $\delta$ values. Absorption near-edge spectra were transformed by Ce-substitution and reduction annealing in a qualitative similar manner with increasing $x$ and $\delta$. Considering electron doping by Ce-substitution, this similarity indicates an increase of electron number at the copper sites due to annealing $n_{AN}$. Thus, the total number of electrons is determined by the amount of Ce and oxygen ions. Furthermore, results from quantitative analysis of the spectra clarified that a number of Cu$^+$ sites, corresponding to the induced electron number by Ce-substitution $n_{Ce}$, increases linearly with $x$ in the as-sintered PCCO ($\delta = 0$), whereas $n_{AN}$ is not exactly equal to twice of $\delta$ (the amount of oxygen loss during annealing), which is expected from charge neutrality. For each $x$-fixed samples, $n_{AN}$ tends to exceed $2\delta$ with increasing $\delta$, suggesting the emergence of two types of carrier due to annealing.

I. INTRODUCTION

High transition temperature superconductivity occurs due to electron doping into $RE_{2-x}$CuO$_4$ ($RE = Pr, Nd, Sm, Eu$) with T'-type structure, where Cu ions have fourfold coplanar coordination. The undoped $RE_2$CuO$_4$ was reported to be an antiferromagnetic Mott insulator, as is the same ground state of La$_2$CuO$_4$, which is the parent compound of hole-doped superconducting La$_{2-x}$Sr$_x$CuO$_4$. As-sintered (AS) compounds of T'-$RE_{2-x}$Ce$_x$CuO$_4$ show insulating behavior, even in the heavily electron doped region, and a post-annealing procedure in a reducing atmosphere is required for the emergence of superconductivity [1]. Several models have been proposed to explain the emergence of superconductivity due to annealing. Excess oxygen atoms may occupy the apical sites [2] and/or Cu defects on the CuO$_2$ plane in the as-grown sample can be removed by annealing [3]. Although the local disorder is considered to be related to superconductivity, the microscopic mechanism of annealing-induced superconductivity and the variation in the electronic states due to annealing are not fully understood.

Recently, a superconducting transition in T'-$RE_2$CuO$_4$ without cation substitution was reported to occur in annealed (AN) thin films [4]. It is considered that the chemical disorder in the thin film can be adequately removed by annealing due to a large surface-to-volume ratio, whereas the removal of disorder in a homogeneous manner is difficult in a bulk sample. This means that the electronic states in T'-$RE_2$CuO$_4$ are sensitive to the chemical disorder, and undoped $RE_2$CuO$_4$ free from the disorder is not a Mott insulator. Subsequently, superconductivity in the parent T'-$RE_2$CuO$_4$ material was confirmed to occur in a low-temperature synthesized powder sample [5]. These results cast doubt on the fundamental recognition that parent compounds of the cuprate superconductors are antiferromagnetic Mott insulators. An important question then is regarding the influence of reduction annealing on the electronic states.

Angle-resolved photoemission spectroscopy (ARPES) studies [6-8] claimed that the electron number per Cu ion, which is estimated from the Fermi surface area, increases due to annealing and is larger than the concentration of Ce ($x$). This result suggests that the carrier concentration is influenced by non-stoichiometry of oxygen. However, the relationship between the concentration of oxygen vacancies and the carrier number variation caused by the annealing have not yet been investigated quantitatively. So far, the annealing effects were mostly studied in connection with the appearance of superconductivity, and no systematic measurement was reported for the undoped and lightly-doped bulk compounds, which do not show superconductivity even after annealing [9, 10]. In contrast to x-ray photoemission spectroscopy measurements, which are difficult to use for measuring the electronic states in insulating materials, x-ray absorption fine structure (XAFS) measurements are a suitable tool to measure electron-doping levels in compound types ranging from insulating to metallic [10, 12].

In this work, we performed Cu $K$-edge XAFS measurements on Pr$_{2-x}$Ce$_x$CuO$_{4+\alpha-\delta}$ (PCCO) with various
x and δ. This is the first systematic XAFS investigation on the evolution of the electronic states against oxygen contents at several x values. It was found that variations in the absorption near edge spectra induced by reduction annealing are qualitatively similar to the case of Ce-doping, indicating aspects of electron doping in the annealing effect. Furthermore, a detailed analysis of the spectra revealed that in as-sintered PCCO, the electron number increases linearly with x, whereas the number of additionally introduced electrons by annealing nAN deviate from the simple relation nAN = 2δ (the amount of oxygen loss) for each x value. Thus, the annealing effects exhibit another phenomenon beyond electron-doping.

II. SAMPLE PREPARATION AND XAFS EXPERIMENT

Polycrystalline samples of PCCO were synthesized by a solid-state reaction method. Dried powders of Pr6O11, CeO2 and CuO were mixed. The mixture was pressed into pellets and sintered at 1030°C in air with intermediate grinding. The oxygen-reduced samples were prepared by annealing the AS samples in flowing Ar gas at 900°C or 940°C for 12 h. The phase purity of the samples was confirmed by laboratory-based x-ray diffraction measurements. The α and δ values represent the amount of excess oxygen in the AS samples and that of oxygen loss due to reduction annealing, respectively. Although we didn’t determine α for the present samples, α for the samples previously prepared under the same conditions was evaluated to be 0.02 – 0.04 by Iodometry method. The value of δ was evaluated from the weight lost of the sample due to annealing, and it tended to be larger in samples annealed at higher temperature when x is fixed. The value of δ and reduction annealing conditions are summarized in Table I. Among these samples, only PCCO with x = 0.16, annealed at 940°C, shows superconductivity with 18 K transition temperature (Tc). XAFS measurements were carried out at the BL01B1 and BL14B1 in SPring-8. Cu K-edge absorption spectra were measured in transmission mode using a Si(1 1 1) double-crystal monochromator. For the measurement of each sample, we prepared a small pellet (7 mm in diameter and 0.5 mm in thickness) mixed with boron nitride so that the pellet was self-supported. All measurements were performed at 300 K using the pressed pellets.

III. RESULTS

Figure 1(a) shows Cu K absorption near-edge spectra for AS PCCO with x = 0 – 0.20. The intensity of the spectra for AS PCCO is normalized by the value in the high-energy region, which is insensitive to the electronic states. The characteristic structure of the spectra shown in Fig. 1(a) were observed as in previous studies[10–12]. The shoulders at 8983 eV (labeled A) and 8991 eV (labeled B) correspond to dipole transitions from 1s to 4pπ of Cu2+, and the peaks at 8994 eV (labeled C) and 9000 eV (labeled D) correspond to dipole transitions from 1s to 4pσ of Cu2+. The final states for A and C are well-screened states, and those for B and D are poorly-screened states. The spectrum for Cu2O is also plotted as a reference of Cu+ configuration. When a core hole is created at the Cu+ site, corehole potential at the site is screened by the same number of electrons as the well-screened state. While cost of the charge transfer energy

| x  | δ     | Annealing condition         |
|----|-------|-----------------------------|
| 0  | 0.029(1) | 900 °C/12 hours              |
| 0  | 0.040(1) | 940 °C/12 hours              |
| 0.08 | 0.021(1) | 900 °C/12 hours              |
| 0.08 | 0.031(1) | 940 °C/12 hours              |
| 0.12 | 0.018(1) | 900 °C/12 hours              |
| 0.12 | 0.023(1) | 940 °C/12 hours              |
| 0.16 | 0.016(1) | 940 °C/12 hours              |

![Table I: Amount of oxygen lost δ and reduction annealing conditions for Pr2−xCexCuO4+δ−x](image-url)
is necessary for the well-screened state, it is not for the state at the Cu\(^{2+}\) site. Then, peak of the Cu\(^{2+}\) state is located at lower in energy than the well-screened state and we ascribe the peak at 8981 eV to the energy of 1s–4p\(\pi\) transition of Cu\(^{2+}\) in Cu\(_2\)O.

As seen in Fig. 1(a), the spectra around the near-edge region varies systematically upon Ce-substitution. Intensity around an energy corresponding to 1s–4p\(\pi\) transitions gradually increase, while that for 1s–4p\(\sigma\) transitions decrease with increasing Ce concentration. Fig. 1(b) shows the difference spectrum, which were obtained by subtracting the normalized spectra of AS PCCO with \(x = 0\) from that of AS PCCO with \(x = 0.04\) – 0.18. The difference spectra of AS PCCO shows a peak at an energy similar to the 1s–4p\(\pi\) transition in Cu\(^{2+}\) in Cu\(_2\)O, indicating the formation of Cu\(^{2+}\) sites by Ce-substitution. The intensity enhancement indicates increased electron density at the copper sites, which is consistent with the result from a Cu L-edge x-ray absorption spectroscopy study reporting the reduction of unoccupied states in Cu 3d\(_{x^2-y^2}\)–\(\gamma^2\) orbitals.

We next investigated the effects of reduction annealing on the near-edge structure of Cu K-edge absorption spectra. In Fig. 2(a), the spectra from PCCO with \(x = 0\) reduced at 900\(^\circ\)C (RE900) and at 940\(^\circ\)C (RE940) are shown together with that for AS PCCO with \(x = 0\). The absorption spectra vary with reduction annealing temperature. The intensity at A and B (C and D) corresponding to 1s–4p\(\pi\) (1s–4p\(\sigma\)) transitions is stronger (weaker) in the sample with larger \(\delta\). The difference spectra between the AN and AS samples are shown in Fig. 2(c). The structure of the difference spectra is quite similar to that induced by Ce-substitution. (See Fig. 1(b).) Thus, the electrons could be introduced at the copper sites by reduction annealing. As seen in Figs. 2(b) – (d) and (f) – (g), PCCO with \(x = 0.08\), 0.12, and 0.16 show quantitatively the same trend against \(\delta\), suggesting a common aspect of electron doping in the reduction annealing for PCCO.

A relative variation of the electron number is evaluated by an integration of the absorption spectra between 8976 eV and 8983 eV, which corresponds to the intensity of Cu\(^{2+}\) 1s–4p\(\pi\) dipole transitions, \(I_{\text{Cu}^{2+}}\). We note that \(I_{\text{Cu}^{2+}}\) should be proportional to the number of Cu\(^{2+}\) sites. The increased number of \(I_{\text{Cu}^{2+}}\) by Ce-substitution for AS PCCO is shown in Fig. 3 as a function of Ce content \(x\). As one of the results in this study, we found that \(I_{\text{Ce}}\) increases linearly with increasing Ce-substitution. Considering the results for previous optical conductivity studies, which show a clear energy gap (charge transfer gap) in the optical spectrum for the AS Pr\(_2\)Ce\(_{0.16}\)Cu\(_{0.84}\)O\(_{4}\) sample, there are no or negligible carriers in the AS samples. Furthermore, a neutron scattering experiment reported that the evolution of magnetism by Ce-substitution in the AS sample can be well understood by a simple model, indicating an identical relationship between the proportion of Cu\(^{2+}\) sites induced by Ce-substitution and the Ce content \(x\). Based on these experimental results, we determined the conversion factor for \(n_{\text{Ce}}\) and \(I_{\text{Ce}}\) from a linear fit for the \(x-I_{\text{Ce}}\) relation of AS PCCO under the assumption that \(n_{\text{Ce}}\) is equal to \(x\). The right vertical axis in Fig. 3 represents \(n_{\text{Ce}}\), and the relationship between \(n_{\text{Ce}}\) and \(I_{\text{Ce}}\) can be written as \(n_{\text{Ce}} = I_{\text{Ce}}/1.16\).

Figure 4 shows the increased intensity for the Cu\(^{2+}\) 1s–4p\(\pi\) dipole transitions due to annealing in the sample with fixed \(x\), \(I_{\text{AN}}\) (the left vertical axis). The figure also shows the electron number \(n_{\text{AN}}\) (right vertical axis) as a function of the oxygen loss, \(\delta\), for RE900 and RE940 PCCO. The \(n_{\text{AN}}\) value is evaluated from the above relationship between \(n_{\text{Ce}}\) and \(I_{\text{Ce}}\). The \(I_{\text{AN}}\) (\(n_{\text{AN}}\)) tends to increase as \(\delta\) increases. The gray solid line in the
The figure represents a relationship of $n_{AN} = 2\delta$, which is expected from charge neutrality of the sample with the assumption that all electron carriers are doped into the CuO$_2$ plane. The present data roughly obeys this relation, meaning that the introduction of electrons through annealing comes from the removal of oxygen. However, when we look at the $\delta$-dependence of the $I_{AN}$ ($n_{AN}$) for each $x$, a characteristic tendency becomes visible. In Fig. 4, solid curved lines are drawn to guide the eye and illustrate the relationship between $\delta$ and $n_{AN}$ for samples with fixed $x$. Here, $n_{AN}$ should be zero at $\delta = 0$. In a sample with larger $x$, the variation of $n_{AN}$ is more sensitive to $\delta$; $n_{AN}$ for $x = 0$ approximately corresponds to $2\delta$, while that for $x = 0.12$ increases with increasing $\delta$, including a marked change around $\delta = 0.02$. The slope coefficient seems to be larger for the sample with larger $x$. These results are difficult to understand within a simple spin dilution model, as is not the case for Ce-substitution.

IV. DISCUSSION

In the present study, we clarify the similarity and differences between Ce-substitution and annealing effects on the electronic states at the copper sites by Cu K-edge XAFS measurements. Both Ce-substitution and annealing effects exhibit an aspect of electron-doping. Although the results for the AS sample are understood under the spin dilution model, the intensity enhancement due to annealing $I_{AN}$ is rather complicated. Here, we discuss how annealing may affect the electronic states.

We first mention that Cu K-edge XAFS measurements were used to collect information on the doped electrons through the creation of a Cu$^+$ site. No or less information about the holes, which would be predominantly doped in oxygen sites, was detected. Indeed, the effects of hole-doping on the Cu K absorption near-edge spectra in La$_2$-Sr$_x$CuO$_4$ is reported to be much smaller than the electron-doping effects in Nd$_{2-x}$Ce$_x$CuO$_4$. Considering this fact and charge neutrality, the present results located in the $n_{AN} > 2\delta$ region (the region above the straight line) in Fig. 4 indicates the existence of holes which compensate a number of induced electrons in excess of $n_{AN} = 2\delta$ in the sample. Thus, the deviation from $n_{AN} = 2\delta$ toward the upper side suggests an additional aspect in reduction annealing beyond the simple picture of electron-doping by Ce-substitution. On the other hand, in the $n_{AN} < 2\delta$ region (the region below the straight line), some of the electrons induced by annealing are not introduced into the Cu site. Then, the results show increases in $\delta$-$n_{AN}$. This indicates that as $\delta$ increases, the carrier characteristics change from the region where electrons do not effectively enter the CuO$_2$ plane to the region where two kinds of carriers are considered to exist. The variation tends to take place at smaller $\delta$ values in a sample with larger $x$, suggesting the existence of a critical electron number required to induce the two kinds of carriers. The two types of carrier in T'
$RE_{2-x}Ce_xCuO_4$ was suggested from the Hall coefficient and Hall resistivity measurements on thin films\cite{20, 21}. From the present systematic study, we showed experimental evidence that reduction annealing plays an essential role in the emergence of hole carriers, and that holes can appear with smaller $\delta$ for a sample with larger $x$. We speculate that such a change originates from a band structure transformation via heavy electron doping.

We now focus attention on the electronic states in the AS and AN samples with large and comparable electron numbers. Compared to AS PCCO with $x = 0.20$ and RE940-PCCO with $x = 0.16$, the integrated absorption spectra between 8976 eV and 8983 eV, i.e., the total value of $I_{Ce+IA_N}$, is almost equivalent. Thus, the total electron number in these compounds is comparable, although the former sample is an insulator and the latter one is a superconductor with $T_C$ of 18 K. The difference between the ground state in the SC(AN) and non-SC(AS) samples is mostly discussed in connection with the presence/absence of chemical disorder. The random potential in the CuO$_2$ plane suppress superconductivity. As for other differences, as mentioned above, the AN sample with larger $\delta$ would contain both electron and hole carriers, whereas the results for the AS sample is explained by the spin dilution model, which considers only electrons with $n_{Ce} = x$. Therefore, the electronic states relating to the hole carriers in these two compounds might be different.

From this point of view, distinct ground states in between the SC thin film and non-SC bulk samples of parent $T'_{-}RE_{2-x}CuO_4$ are possibly related with the existence or amount of hole carriers, although a considerable number of electrons can be doped in both film\cite{22, 23} and bulk samples by annealing. In the present PCCO with $x = 0$ and $\delta = 0.040$, in which the total electron number of $n_{Ce} + n_{AN}$ is 0.094, the deviation of $n_{AN}$ from the relation $n_{AN} = 2\delta$ yields the hole number $n_h$ of 0.014. In order to clarify the necessary conditions for superconductivity in $T'_{-}RE_{2-x}Ce_xCuO_4$, the electron and hole numbers for both SC thin film and a bulk sample with various $x$ and $\delta$ values must be determined.

V. SUMMARY

In summary, Ce-substitution and reduction annealing effects on the electronic states at copper sites were investigated by Cu K-edge x-ray absorption fine structure measurements for $T'$-type Pr$_{2-x}Ce_xCuO_{4+\delta}$. For the as-sintered PCCO, the absorption near-edge spectra systematically changed with Cu$^+$ content, and the electron number increased linearly with Ce-substitution. The spectra were changed by reduction annealing, similar to the case for Ce-substitution over the entire $x$ range in the present study. This result indicates the aspect of electron doping in reduction annealing. However, the electron number increased due to annealing $n_{AN}$ does not exactly follow the relation of $n_{AN} = 2\delta$, where $\delta$ is the amount of oxygen lost during annealing. Considering the charge neutrality, the upper deviation of $n_{AN}$ from $n_{AN} = 2\delta$ suggests the emergence of two types of carrier due to annealing.

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