EXAFS Study of the Local Environment around the Rare Earth Site in $R_{1-x}Ca_xBa_2Cu_3O_{7-y}(R = \text{Gd and Ho})$

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The substitution of Ca for rare earth in $RBa_2Cu_3O_{7-\delta}(R = \text{rare earth})$ generates excess holes in the 123 system, and $T_c$ is suppressed due to the over doping effect. It is also known that the Ca doping cointroduces oxygen vacancies which reduces the number of generated holes. However, there is still some disagreement on the site where the oxygen vacancy is created, the plane or the chain site. There are also some arguments about the site which Ca occupies, the R or the Ba site. We performed the element specific extended x-ray absorption fine structure study at the Ca $K$ edge, Gd and Ho $L_{III}$ edge for a series of $R_{1-x}Ca_xBa_2Cu_3O_{7-\delta}(R = \text{Gd, Ho})$ samples with $x = 0, 0.1$ and 0.2. Our data indicate that Ca is located in the R site, there is no observable change of oxygen content in the CuO$_2$ plane and that the increased Ca concentration causes a higher disorder in the local environment around the rare earth site.

PACS: 61.10.Ht - X-ray absorption spectroscopy: EXAFS, NEXAFS, XANES, etc.
PACS: 74.72.Bk - $Y$-based cuprates.
PACS: 74.25.-q - General properties; correlations between physical properties in normal and superconducting states.

I. Introduction

It has been generally accepted that the superconducting transition temperature $T_c$ of $YBa_2Cu_3O_{7-\delta}$ (Y-123) system depends on the hole concentration in the CuO$_2$ plane [1,2]. By changing the oxygen content and/or doping cations into the Y site the hole concentration of the system can be controlled [1]. Ca doping in $RBa_2Cu_3O_{7-\delta}$ ($R = \text{rare earth}$) generates excess holes and the overdoping effect causes the suppression of $T_c$. The cointroduce of oxygen vacancies is also observed [3,4] which reduces the generation of excess holes. This counterbalance effect enables the revival of superconductivity in the oxygen deficient $YBa_2Cu_3O_{7-\delta}$ samples [5,6,7]. While Ca doping causes the increase of the hole concentration and the oxygen vacancies are confirmed by many groups, it is still an open question on the site of the cointroduced oxygen vacancies. As reported by Awana et al., based on x-ray diffraction, the coordination number of Ca depends on oxygen content [7]. In fully oxygenated Y-123 the incorporated Ca is sixfold coordinated which creates oxygen vacancies in the adjacent CuO$_2$ planes, resulting the suppression of superconductivity [6]. On the other hand, Yakabe et al. observed increasing lattice constant c with Ca content in both oxygen-depleted and fully oxygenated samples of doping level up to 50%, and
concluded that Ca is eightfold coordinated [8]. We report the study of the local environment around the rare earth site using element specific extended x-ray absorption fine structure (EXAFS) technique [9]. The structural information we obtained from this study includes the coordination number of oxygen around the rare earth atom, the interatomic distance between the rare earth atom and the surrounding oxygen and the Debye-Waller factors which contain the mean-square relative displacements due to static disorder or thermal vibration.

II. Experiment

Extended x-ray absorption fine structure (EXAFS) measurements were performed at Synchrotron Radiation Research Center. A series of fully oxygenated Gd1-xCaxBaxCu2O7-δ samples with x = 0, 0.1, and 0.2 were studied at room temperature. For the purpose of comparison, we have also studied Ho1-xCaxBa2Cu3O7-δ samples (x = 0 and 0.1). Gd and Ho LIII edge data were taken at the wiggler beamline and the Ca K edge data at the DCM beamline. All the data were taken using transmission mode. These samples were prepared by Prof. W. Guan using a conventional solid state reaction method as described elsewhere [10]. For the transmission experiments, the pellets were ground and sifted through a 30 μm filter. Single layers of the fine powder was then put onto scotch tapes, appropriate sample thickness was obtained by stacking multiple layers of the tapes for the measurements.

III. Results

The EXAFS data were analysed by the standard procedure [12]. The pre-edge background absorption was subtracted to yield the atomic absorption spectrum of the atom of interest. The background above the edge was removed from the spectrum using spline fit. The data is then converted from energy space to K space. A Fourier transform (FT) is applied to obtain the r-space data. Figs. 1-3 show the various stages of the data analysis. Structural parameters were obtained by fitting the experimental data to theoretical standards calculated by using FEFF6 program [11]. The least-square curve fitting procedure provided by FEFFIT program [12] was employed to extract the Gd-O and Gd-Cu distances, coordination numbers, and the Debye-Waller factors. We obtain the best fitting results by assuming that the first peak of Fig. 3 is composed of two different gadolinium-oxygen distances Gd-O(2) and Gd-O(3), while the second peak is fitted to a single Gd-Cu distance. As assigned by other authors [13], O(2) and O(3) are the two oxygen sites on the CuO2 plane their distances to Gd are unequal due to the orthorhombic splitting. Fig. 4 shows the best two-shell fit of the Gd LIII EXAFS data of the undoped GdBazCu2O7-δ sample, which is typical to all of our fitting results. We have also applied this data analysis procedure to the Ho LIII EXAFS data of the Ho1-xCaxBa2Cu3O7-δ samples, and obtained similar results. Table I summarises the results of the fittings. The distances Gd-O(2), Gd-O(3), and the corresponding coordination numbers are not affected by the Ca concentration indicating that the local environment around the Gd atom is unaffected by the dopings. The Debye-Waller factor increases with x, indicating the oxygen disorder increases with the Ca doping level. This is also evidenced by the decrease of amplitude of the FT peaks in
FIG. 1. Gd L III edge EXAFS spectra for Gd\textsubscript{1-x}Ca\textsubscript{x}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-δ} samples with \( x = 0, 0.1, \) and 0.2.

FIG. 2. \( k^3\chi(k) \) of the spectra in Fig. 1.

FIG. 3. Magnitude of Fourier transform of the data shown in Fig. 2.

FIG. 4. The Fourier transform of \( k^3\chi(k) \) for GdBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-δ} plotted with the result of the best 3 shell fit.
Fig. 5. A comparison of the Fourier transforms of Ho L\textsubscript{III} edge and Ca K edge data taken from \textit{Ho}_{0.9}\textit{Ca}_{0.1}\textit{Ba}_{2}\textit{Cu}_{3}\textit{O}_{7-\delta}.

Fig. 3 as Ca doping increases. The Fourier transform of Ho L\textsubscript{III} EXAFS obtained from \textit{Ho}_{0.9}\textit{Ca}_{0.1}\textit{Ba}_{2}\textit{Cu}_{3}\textit{O}_{7-\delta} sample shows a similar Ho local environment as that of Gd. A comparison to the Fourier transform of Ca K edge is shown in Fig. 5. The Ca K edge data is much noisier, and is not possible to be analysed quantitatively, due to the low Ca concentration. However, the radial distribution of neighbours of the absorbing atom can be observed by inspecting the peaks of the FT. In the range between 0 and about 3.3 \text{Å}, it is clearly shown that the local structure of Ca is very similar to that of the Ho. Therefore we believe Ca is incorporated into the rare-earth site, except that all the peaks are shifted to the lower \text{r} side. The shorter local bond length of the Ca atom compared to that of the rare earths is due to the distortion of the CuO\textsubscript{2} plane caused by the increased oxygen disorder, this is also indicated by the increasing Debye-Waller factor on the rare earth site upon Ca doping.

IV. Conclusions

We summarise the results of our study as follows:

(1) The number of oxygen on the CuO\textsubscript{2} plane is not affected by the Ca dopings.
(2) The bond lengths Gd-O(2) and Gd-O(3) around the gadolinium are not significantly altered by the Ca dopings.
(3) The bond length Gd-Cu is not affected.
(4) There is an increasing disorder in oxygen environment due to the Ca dopings.
(5) The comparison of the Ca K edge data with the rare earth L\textsubscript{III} data indicate that the Ca is incorporated into the rare earth site.
TABLE I. The parameters including the number of neighbours, the interatomic distances (R), and Debye-Waller factors ($\sigma^2$) obtained from the best fitting results of Gd$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_{7-\delta}$, and Ho$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_{7-\delta}$ samples.

<table>
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<tr>
<th>Neighbors</th>
<th>R(Å)</th>
<th>$\sigma^2(10^{-3}\text{Å}^2)$</th>
<th>Neighbors</th>
<th>R(Å)</th>
<th>$\sigma^2(10^{-3}\text{Å}^2)$</th>
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<tr>
<td></td>
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<tr>
<td>Gd-O(2)</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>0</td>
<td>4</td>
<td>2.39 ± 0.03</td>
<td>0</td>
<td>4</td>
<td>2.36 ± 0.07</td>
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<td>2.39 ± 0.03</td>
<td>0.1</td>
<td>4</td>
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<tr>
<td>0.2</td>
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<tr>
<td>Gd-0(3)</td>
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<td></td>
<td></td>
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<tr>
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<td>0</td>
<td>4</td>
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<td>3.24 ± 0.02</td>
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<td>3.24 ± 0.03</td>
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<td>3.21 ± 0.04</td>
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</table>

The oxygen environment in the CuO$_2$ plane is not affected in terms of the bond distances and the coordination numbers. However, the oxygen disorder increases with the amount of Ca doping which is critical to superconductivity [14]. The disorder introduced by Ca doping could be attributed to the accompanied deoxygenation of the CuO chains [15,16] resulting the suppression of superconductivity.

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References

(1989).


