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Local structure distortion in a $YBa_{2-0.52}Sr_{0.52}Cu_3O_7$ superconductor

K. Zhang, G. Bunker, and B. Chance
Institute for Structural and Functional Studies, 3401 Market St., Philadelphia, Pennsylvania 19104

C. F. Gallo*
3M Industrial and Electronic Sector, St. Paul, Minnesota 55144-1000

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X-ray-absorption fine structure has been used to study local structure distortions of a Sr-doped superconductor $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ with $x=0.52$ and $T_c=95$ K. Direct comparison with the undoped superconductor shows that the local structure around the Sr atoms, which are directly observed to substitute for Ba atoms, was found to be distorted significantly, with four oxygen atoms located at the Ba/Sr plane shifted towards Sr atoms by 0.14 Å, and Sr shifted closer to the Cu(2) plane by 0.05 Å. No significant changes are found for the local structures around Cu and Y atoms, which implies that the Cu(2) plane and CuO_2-Y-CuO_2 sandwich structure is preserved.

One of the interesting features of the $Y_1Ba_2Cu_3O_7$ superconductor is that the yttrium atoms can be replaced fully by almost all rare-earth[1,2] atoms while still remaining superconducting, even if the rare earth has a large magnetic moment. On the other hand, no literature has reported the total replacement of barium atoms to maintain the superconducting transition. It has been reported, however, that partial replacement of barium by strontium does not destroy the transition.[3-6] Although the transition temperature T_c was found to monotonically decrease with increasing Sr concentration, the decrease of T_c was believed to be correlated with the oxygen content in the system.[6] The structure of the Sr-doped compound is almost identical with the undoped one except for the contraction of the unit-cell volume.[4] It has been speculated that the decrease of T_c is due to local structural distortions of the Ba/Sr sites.[4] However, no experiments have been reported to probe the local structure change upon the substitution.

Here we report a x-ray-absorption fine-structure (XAFS) experiment on a $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ superconductor with $x=0.52$. The XAFS technique has been used successfully as a probe for local structure, which is complementary to x-ray diffraction.[7] By tuning the x-ray energy to a particular absorption edge of selected metal atoms, one can study the local environment within a radius of about 5 Å from the absorbing atoms. The analysis of the XAFS experiment showed, by comparing the doped superconductor with the undoped one, that the substitution occurs at the Ba site. The average distance of the Sr atom to the oxygen atoms located at the Sr plane is 2.60 ± 0.02 Å, which is about 0.14 Å shorter than the Ba-O distance. The distance of Sr to Cu(2), which sandwich the yttrium atom, is also shortened by 0.05 ± 0.02 Å. Both distortions cause the unit-cell contraction as detected by x-ray diffraction. No significant changes are found for the local structure around Cu and Y atoms, except for a slight contraction of Cu-O and Y-O atomic distances, which implies that the Cu(2) plane and CuO_2-Y-CuO_2 sandwich structure is preserved.

The superconducting samples Y-(Ba/Sr)-Cu-O and Y-Ba-Cu-O used for the XAFS experiment were prepared by solid-state reaction by mixing Y_2O_3, CuO, $BaCO_3$, and $SrCO_3$ powders in appropriate proportion, firing in oxygen at 910 °C for 12 h and annealing at 450 °C for 4 h. The resultant material was reground and refired as described above. The final material was jet milled to a particle size 1–3 μm, mixed with 6% organic binder (carbowax), and pressed at about 65 000 psi. The pellets were sintered in oxygen at 960 °C for 16 h and the temperature was slowly decreased (7 h) to 400 °C.

The samples were characterized by resistivity and x-ray diffraction measurements. The resistance measurement for the two $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ samples with $x=0.52$ obtained different T_c's of 95 and 85 K, which probably are due to different oxygen contents, depending on the procedure and temperature of the sample preparation. X-ray diffraction showed that the samples contain a single 1:2:3 phase only, with lattice constants of $a=3.790$ Å, $b=3.840$ Å, and $c=11.520$ Å for the 95-K transition sample, and $a=3.812$ Å, $b=3.862$ Å, and $c=11.586$ Å for the 85-K transition sample.

The x-ray absorption experiment was performed at the Cornell High Energy Synchrotron Source (CHESS), beamline C-1. The samples were ground using a mortar pestle to 400 mesh and uniformly coated on Scotch tape. Measurements were made on Sr, Cu, and Y K edges at 80 K for the 95-K T_c sample. The same measurements were also performed on the undoped 1:2:3 compound for comparison, along with model compounds. Additionally, the Ba-L_I edge of the undoped superconductor and BaO was measured. A double Si(111) crystal monochromator was used through the run. Appropriate detuning of the monochromator to reduce the harmonics was checked by monitoring the harmonics with a third ionization chamber covered in front by an aluminum attenuator to cut down the intensity of the fundamental.

Standard XAFS data analysis techniques were used.[7,8] We also generated the radial distribution function (RDF) from XAFS data using the "splice method," which served as a model check in some cases.[9,10] Starting from the filtered single-shell χ data, the backscattering amplitude and the central and backscattering phase shifts are removed by taking the amplitude ratio and the phase difference between the filtered χ data of the unknown and an appropriate model. The amplitude ratio and the phase difference are then extrapolated through the low k region using the cumulant expansion. These data are then inverted using a Fourier sine transform with a Gaussian damping factor to obtain a broadened RDF. This method provides a model-independent way to estimate the RDF for disordered distributions.

Figure 1 shows the Fourier transform modulus of Sr K-edge XAFS data compared with the Ba L_I edge Fourier transform. Despite the phase difference for different central atoms and different edges measured, all coordination shells around Sr shown by the transform are similar to those around Ba. The reduction of the magnitude of the Sr transform probably reflects an increase in the disorder in the doped system. The imaginary parts of the transform, which are not shown in the figure, are also similar in phase beyond the second shell except for a constant phase shift reflecting the phase difference between Sr K edge and Ba L_I edge. The transforms provide direct evidence that the Sr substitution occurs at the Ba site.

A nonlinear least-squares fitting method[8] was used for the first-shell Sr K-edge data and the results are shown in Table I along with the coordination numbers and interatomic distances for the Ba atoms in Y-Ba-Cu-O determined by x-ray diffraction. The first shell was modeled by two subshells of oxygen. The two coordination numbers, the two distances, and the two Debye-Waller factors were allowed to vary to obtain the best fit. We found that there are 4.0 ± 0.4 oxygen atoms located at 2.60 ± 0.02 Å from Sr atoms with the same Debye-Waller factor at 80 K as the Sr-O atomic pairs in SrO; and with other 5 ± 2 oxygen atoms located at an average distance of 2.84 ± 0.05 Å with a much larger Debye-Waller factor of 0.016 Å^2. Since the thermal disorder should be small at 80 K, the large Debye-Waller factor implies a large disorder for spatial distribution of the atoms.

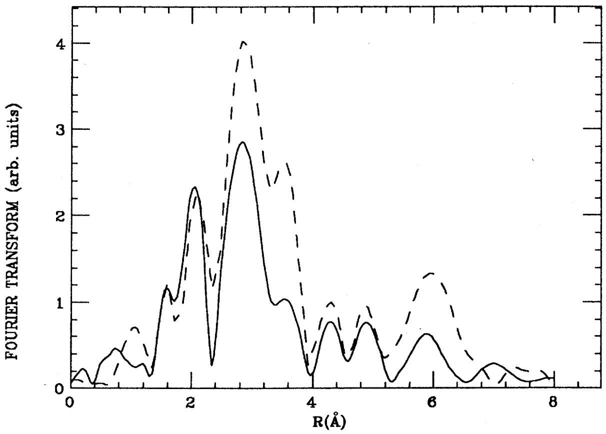

FIG. 1. The Fourier-transform magnitudes of the Sr K edge for Y-(BaSr)-Cu-O (line) and the Ba L_I edge for Y-Ba-Cu-O (dash). Both Sr and Ba local environments are similar except for magnitude reductions due to disorder.

TABLE I. Results for the first two shells of Sr edge in Y-(Ba/Sr)-Cu-O compared with the results for Ba first and second neighbor determined by x-ray diffraction.

Atomic pair	N	R (Å)	σ^2 ($\times 10^{-3}$ Å^2)[a]
Sr-O	4.0(4)	2.60(2)	0.0(5)
	5(2)	2.84(5)	16(4)
Ba-O[b]	4	2.741	
	6	2.937	
Sr-Cu	4	3.33(2)	1.3(5)
	4	3.46(6)	20(4)
Ba-Cu[b]	4	3.376	
	4	3.471	

[a] Compared with Sr-O in SrO and Y-Cu in $YBa_2Cu_3O_7$.
[b] Reference 15.

The radial distribution function for Sr first shell was constructed from the XAFS data by a method following Stern, Ma, Hanske-Petitpierre, and Bouldin[9], which is shown in Fig. 2. The RDF around Ba atoms was also constructed from Ba L_I edge XAFS data for the superconductor and BaO model, and is plotted in the same figure. The data were premultiplied by Gaussian damping factor, $\exp(-2k^2\sigma_c^2)$ with $\sigma_c^2 = 0.012$, to minimize artifacts from truncating the data at high k.[9] This has the effect of artificially increasing the σ^2 of the RDF by 0.012 Å^2. It can be seen from the figure that the distribution of the oxygen atoms around both Sr and Ba are very broad. Although the Gaussian damping factor introduces peak broadening itself, the width of the distribution is 0.22 Å which is significantly larger than the width of 0.11 Å from the damping. The true width σ is $[(0.22)^2 - (0.11)^2]^{-1/2} = 0.19$ Å. The main peak of the distribution is located at an average distance 2.64 Å, with more oxygen atoms dis-

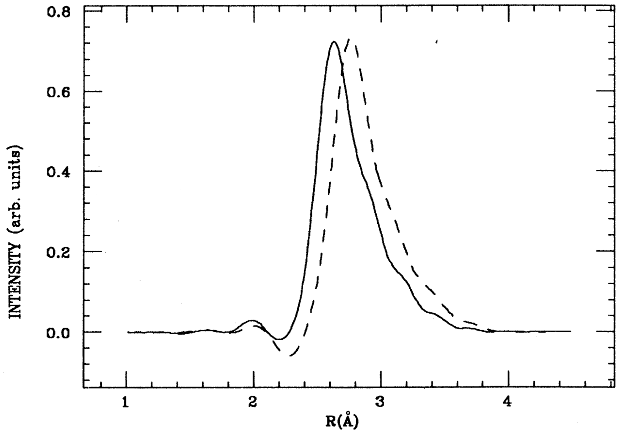

FIG. 2. Radial distribution function obtained by the splice method (Refs. 9 and 10) for the first and second shells around Sr (line) and Ba (dash) atoms determined from Sr K edge and Ba L_I-edge XAFS data. A Gaussian damping factor of $\sigma_c^2 = 0.012$ Å^2 was used in Fourier transforms to reduce truncation ripple, which artificially broadens the peak by this amount.

tributed further away, appearing as a long tail of the distribution. The distribution around Sr atoms is similar to that around Ba atoms, except that all oxygen atoms are shifted closer to Sr atoms by 0.14 Å. The areas of the distributions, which were obtained by the same procedure, indicates the first-shell coordination numbers are the same within 5% which is within the errors. The tail of the distribution extending well beyond 3 Å could be due to the leakage from the second shell, since the first two shells were not well separated in the Fourier transform. The reason that we cannot resolve two distances could be due to the limited data range in *k* space, and to the very large disorder of the atoms at longer distances. Nonetheless, the results from standard XAFS data analysis and the RDF method are mutually consistent. Here we would like to emphasize that the result determined by XAFS least-squares fitting method could be substantially in error if a wrong model were assumed or the atomic distribution cannot be approximated by a Gaussian or a few Gaussians. The RDF method, which does not require one to assume a hypothetical model, is valuable for checking the fitting results.

The second-shell around the Sr atoms was analyzed, and the fitting results are shown also in Table I. The model compound used for the second-shell Sr-Cu central and backscattering atom pair is the second-shell Y-Cu atomic pair in the yttrium 1:2:3 compound. The error introduced in the data analysis due to approximating the central atom Sr by Y is negligible, since the central atom phase shifts are about the same for neighboring atoms in the periodic table. A two-distance fit, which is a reasonable model to start with, determined that four copper atoms are located at 3.33(2) Å and another four at 3.46(6) Å with a Debye-Waller factor difference 0.0013 Å^2 and 0.020 Å^2, respectively. The radial distribution function for the second shell around Sr atoms was also determined (not shown), with a broad distribution of $\sigma=0.012$ Å^2 at an average distance of 3.40 Å, which is consistent with the fitting results.

Figure 3 plots the Fourier transform of the Sr-doped superconductor Cu *K*-edge EXAFS compared with the Cu edge for the undoped Y-Ba-Cu-O superconductor. From the figure, one can see that the local structure around Cu atoms in the Sr doped and undoped systems are very similar. Detailed analysis by the ratio method or fit[8] indicate the first-shell coordination number and the Debye-Waller factor are unchanged in the doped material. The Cu-O distance was found to be shortened by 0.01 Å, although the change is within the experimental error (Table II).

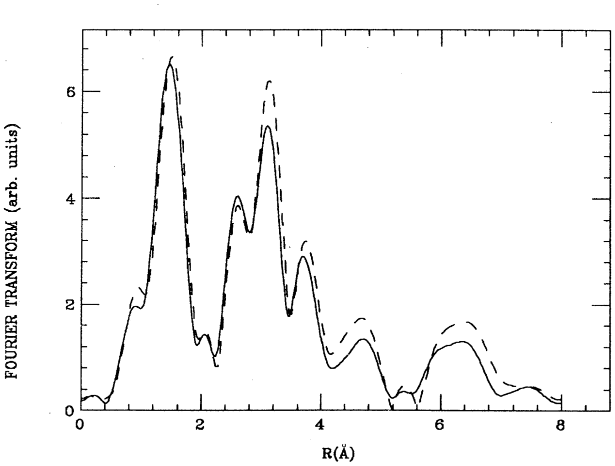

FIG. 3. The Fourier-transform magnitudes of the Cu *K* edge of Y-(BaSr)-Cu-O (line) and Y-Ba-Cu-O (dash).

The Fourier transform of Y *K* edge of Y-(BaSr)-Cu-O is shown in Fig. 4 compared with the Fourier transform of the Y-Ba-Cu-O sample. The two curves are almost identical up to 4 or 5 Å from the Y atoms. As shown in Table II, the detailed analysis for the first shell (Y-O) and second shell (Y-Cu) showed that no coordination number and Debye-Waller factor changes were detected. The Y-O and Y-Cu interatomic distance, however, were found shortened by 0.01 Å, respectively. Although the shortening is consistent with the lattice parameters determined by x-ray diffraction, the change is within our experimental error.

To summarize, the analysis for the XAFS experiment observed that Sr atoms substitute for Ba, and the local structure is distorted in the Sr-doped superconductor Y-(BaSr)-Cu-O. For the results obtained from the different edges to be consistent, the four oxygen atoms at 2.60 Å from the Sr atom must be the oxygen atoms located in the Ba-Sr plane. The significant distance shift of 0.014 Å of the oxygens towards Sr greatly distort the structure and are responsible for the unit-cell shrinkage along both *a* and *b* directions. The Sr atoms are also closer to the Cu(2) plane by 0.05 Å, causing the reduction of the unit-cell dimension in the *c* direction. The determined structures around Cu and Y atoms are very similar to the undoped material, except for the slight decreases of the interatomic distances which are consistent with the lattice constant obtained from x-ray diffraction. No changes were found for the first few shells around yttrium atoms, except for slight distance shrinkages of Y-O and Y-Cu pairs. Since the atoms on the first two shells around yttrium are all located on the Cu(2) plane, this implies that the Cu(2) planes are identical in the doped and undoped systems, for either atomic arrangement or bonding strength which reflect the electronic configuration.

It has been speculated[4] that the local structure distortion would occur in the Sr-doped superconductor causing the monotonic decrease of T_c with increase of Sr concentration. However, our sample for which the Sr-Ba site is very distorted, retains the same 95-K transition temperature. Therefore, the distortion, at least to the present lev-

TABLE II. XAFS interatomic distance and Debye-Waller factor differences between Y-(Ba/Sr)-Cu-O and Y-Ba-Cu-O superconductors for Cu and Y *K* edges.

Atomic pair	Y-(Ba/Sr)-Cu-O-Y-Ba-Cu-O ΔR (Å)	$\Delta\sigma^2$ ($\times10^{-3}$ Å^2)
Y edge: Y-O	−0.01(1)	0.0(3)
Y-Cu	−0.01(1)	0.0(5)
Cu edge: Cu-O	−0.01(1)	0.0(3)

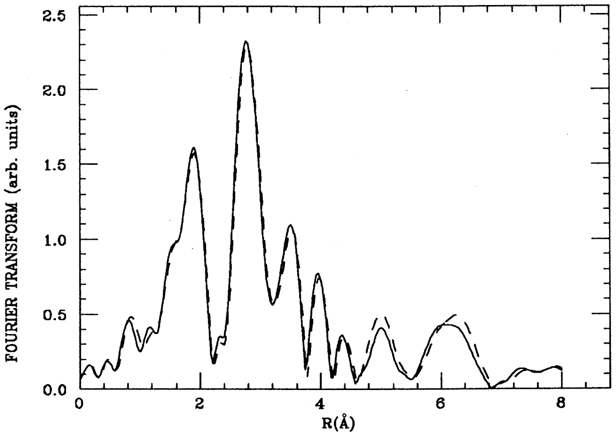

FIG. 4. The Fourier-transform magnitudes of the Y K edge of Y-(BaSr)-Cu-O (line) and Y-Ba-Cu-O (dash).

el, is not responsible for the decrease of T_c.

The question remains which structural feature is most directly responsible for the superconducting transition. It has been generally accepted, although it needs to be further proven theoretically, that the Cu(2) plane in the 1:2:3 compound is directly related to the superconductivity. Our observation that the Cu environment, particularly the distance and strength of the Cu(2)—O bond, remained the same upon Sr doping provides additional support that the Cu(2) plane is required for superconductivity.

It has been proposed that the copper chains in the 1:2:3 compound served as an electron reservoir for maintaining the O $2p$ holes in the Cu(2) planes upon oxygen reduction. Based on the observation that the Cu(2) planes are strongly coupled with each other through the Y—O bond in the 1:2:3 compound[11] and the couplings are significantly weakened in the tetragonal phase and nickel substituted nonsuperconductors[12] we have speculated that the CuO_2-Y-CuO_2 sandwich structure may be responsible for the 90-K superconducting transition.[11,12] Indeed, the coupling may reflect the charge-transfer process in the novel superconductor, which has been regarded as a possible mechanism for the superconductivity.[13] It is interesting to note the newly discovered high-T_c superconductors all have the same kind of sandwich structure,[14-16] although CuO_2-Y-CuO_2 is replaced by CuO_2-Ca-CuO_2. Our observation that the identity of the CuO_2-Y-CuO_2 structure for the Sr doped and nondoped superconductor provides further evidence of the importance of the sandwich structure. Further works will be undertaken to explore the relationship between the change of the sandwich structure and the change of the superconductivity.

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*Present address: Superconix Inc., Box 31, 261 East 5th St., St. Paul, MN 55101.

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