Lawrence Berkeley National Laboratory

Recent Work

Title

An x-ray absorption spectroscopic study of $\text{Yb}_{1-x}\text{Fe}_x\text{O}_{7+y}$

Permalink

<https://escholarship.org/uc/item/6m8199ss>

Journal

Journal of Electron Spectroscopy and Related Phenomena, 103(SI)

Author

Ziq, Kh.A.

Publication Date

1998-08-01

AN X-RAY ABSORPTION SPECTROSCOPIC STUDY OF $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$

M. Faiz¹, X. Zhou², E. J. Moler², S. A. Kellar², Z. Hussain², N. M. Hamdan¹, and Kh. A. Ziq¹

¹ Physics Department, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

² Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

We report a study of x-ray absorption near-edge structure of the O K and Cu L_3 edges in $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$ for $x = 0.01, 0.05$ and 0.15 . We attribute the peaks below 529 eV in the O K edge spectra of $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$ to holes on the O sites. Our results show hole filling with increasing Fe content, which means that Fe enters the structure primarily in the formally trivalent oxidation state. Cu L_3 edge spectra reveal increased amount of Cu^{3+} with increasing Fe content. The results are discussed in terms of charge balancing.

KEY WORDS: High- T_c Superconductors, XANES, XRD, $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$

INTRODUCTION:

Metallic substitution studies have enhanced our understanding of the superconducting and normal state properties of high- T_C superconductors. Substitution of metals in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) usually depresses T_C and has other negative effects on the superconducting properties. The superconducting properties of YBCO depend not only on the oxygen stoichiometry but also on the oxygen ordering. Substitution of Cu can provide a selective tool to investigate the specific effects because depending on the dopant characteristics, the substituted compounds may exhibit modified microstructures without any substantial change in the overall oxygen content. Much work has been done in this direction. Trivalent metal ions like Fe, Co, or Al replace Cu in Cu(1) site on the Cu-O chain and depress T_C more slowly than divalent Zn and Ni which replace Cu in Cu(2) site in the CuO_2 plane [1]. Substitution of Cu by Fe may lead to (i) reduction of T_C , (ii) structural transformation with increasing impurity concentration, (iii) increase in oxygen content accompanied by a rearrangement of oxygen, and (iv) local magnetic ordering. When Cu is replaced by Fe, the oxygen atoms might rearrange themselves in order to provide the most stable Fe site. This modifies the local electronic densities of states. Little is known about the variation of electronic structure due to the substitution. Yang et al. [2] have studied the variation of electronic structure of YBCO upon Fe doping, at the Fe site using x-ray absorption spectroscopy (XAS). In this paper we compliment their work by investigating Cu and O sites using XAS. Furthermore, Zhang et al. [3] have studied the same system using x-ray photoelectron spectroscopy (XPS) and found that effective copper valence of the system increases with increasing Fe content. This is in contradiction with the oxygen iodometry results of Awana et al. [4]. We address this issue also in this paper.

While XPS probes the occupied electronic states, XAS probes the unoccupied electronic states in the most direct way. Thus these two experimental techniques compliment each other. With the advent of synchrotron radiation sources, XAS has

become a powerful technique used to investigate the empty states. It allows one to selectively study a particular species in a compound [5].

EXPERIMENTAL:

Stoichiometric amounts of high purity CuO, Y₂O₃, Ba(NO₃)₂ and Fe₂O₃ (at least 99.9%) were mixed followed by grinding in an agate mortar. The mixer was preheated at 1173 K for 18 hours. After regrinding the black powder, it was pressed into pellets of 1 cm diameter and heated at about 1203 K twice for 35 hours with intermediate grinding. The final annealing of the samples was performed at 1223 K for 24 hours in oxygen atmosphere, followed by slow cooling of the samples to 823 K and keeping it for 50 hours. Finally the samples were furnace cooled to room temperature in oxygen atmosphere. In this way, poly crystals of YBa₂Cu_{3-x}Fe_xO_{7+y} with starting x values of 0.01, 0.05 and 0.15 were prepared.

The critical temperatures of these samples were determined by standard four-probe technique, using a constant current source and a Keithly-181 nano voltmeter. X-ray diffraction patterns of the samples were obtained using a Phillips PW1700 automated diffractometer. The analysis is computer assisted so that the interplanar spacing values can be corrected for the instrument error function by analyzing a silicon standard and subsequent phase identification.

X-ray absorption near edge structure (XANES) measurements were performed using Advanced Light Source at Lawrence Berkeley National Laboratory on beamline 9.3.2 [6]. High-resolution XANES spectra were taken in the Ba M, Cu L₃, Fe L_{2,3}, and O K absorption edge regions, while the monochromator was set at a resolving power (E/ΔE) of ≥ 7000 . The photon flux at the sample was about 10¹⁰ photons/s. The YBa₂Cu₃₋

$x\text{Fe}_x\text{O}_{7+y}$ poly crystal samples were cooled to about 90 K before scraping them in a vacuum of about 1×10^{-10} torr, in order to minimize oxygen loss from the fresh surface [7]. Note that cooling the sample below its T_c is not necessary for the scope of this study. Since the size of the synchrotron radiation photon beam at the sample was ≤ 1 mm, it was not difficult to align the system to make sure that only the sample was illuminated by the photon beam. XANES measurements were performed using a partial electron yield detector consisting of 40 mm channel plates in the pulse counting mode. I_0 signal from a freshly evaporated gold grid was used for normalization of spectra.

RESULTS AND DISCUSSION:

The samples used in this investigation were first characterized by monitoring their resistance as a function of temperature using the standard four-point contact method. The zero-resistance transition temperatures were 93, 92 and 71 K for $x = 0.01, 0.05$ and 0.15 respectively. The XRD patterns for all the samples are shown in Fig.1. Further XRD indexing and refinement was performed using a Powder Diffraction Package (PDP) program [8] which confirmed that they are all single phase with orthorhombic symmetry. This is clear from the (012) and (102) peaks. Although these two peaks get closer to each other in the sample with $x = 0.15$ they are still distinct. This means that the sample with $x = 0.15$ is still orthorhombic. This is consistent with the resistivity measurements that revealed all three samples were superconducting.

Fig.2 shows the O K edge of $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$ (YBCFO) poly crystals at 90 K as a function of x . Energy scale was corrected by comparing Ba M edge of the samples with that of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystal [9], with the assumption that the Fe substitution does not affect Ba site. A straight line fitted to the region before the peaks (below 523 eV) has been subtracted as background. The spectra shown in the figure have not been smoothed or filtered in any way. Two small peaks at 524.5 and 526.5 eV (labeled A and

B respectively) and a prominent peak at 530 eV (labeled C) precede the main edge which starts at about 531 eV. Multiple scattering calculations assign peak A and B to holes in O sites in the CuO₂ plane (O2 and O3) and Cu-O chain (O1) respectively [9]. Intensity of peaks A and B decreases with increasing Fe content, indicating hole filling in both CuO₂ plane and Cu-O chain. This result is in good agreement with M. Karppinen et al. and I. S. Lyubutin et al. [10,11]. This seems to support that T_c degradation with increasing iron substitution is due to hole filling. In other words, Fe enters the structure primarily in the formally trivalent oxidation state. We interpret the peak C as the signature of the O holes being removed and localized around the Fe sites in the compound. Note that the intensity of this peak increases with increasing Fe content. Our interpretation is further supported by the general observation that many of the insulating transition metal oxides exhibit such sharp peaks between 529 and 530 eV in the O K edge spectra [12]. Furthermore, the peak C resembles CuO rather than Iron oxide, suggesting that Fe actually enters Cu site.

Fig.3 shows the Cu L₃ edge of YBa₂Cu_{3-x}Fe_xO_{7+y} poly crystals at 90 K as a function of x. The spectra were acquired with 2-bunch beam implying less than 10¹⁰ photons/s at the sample. Again the energy scale was corrected using Ba M edge as stated earlier. The spectra clearly show a small peak at about 931 eV along with the main peak at about 929.5 eV. Note that the peaks shift to higher energy with increasing Fe content. This indicates that the average valency of Cu increases with increasing Fe content. While the main peak is ascribed to a transition from the 3d⁹ ground state (formally Cu²⁺) the higher energy shoulder is a signature of Cu³⁺ in the CuO₂ layers [13-17]. Cu can be found in the formal valence states of +1 (e.g. CuO₂), +2 (e.g. CuO), and +3 (e.g. NaCuO₂). Note that the integer valences are only meant to describe a nominal configuration of Cu, with covalency effects not included. The ground state of Cu¹⁺ is a 3d¹⁰ configuration, whereas that of Cu²⁺ is a mixture of 3d⁹ (~60%) and 3d¹⁰ $\underline{L}$ (~40%) configurations [18], where $\underline{L}$ denotes an oxygen ligand hole, and that of Cu³⁺ is a mixture of 3d⁸ and 3d⁹ $\underline{L}$ configurations [19]. It is, however, known from x-ray

photoemission spectroscopy (XPS) data that in CuO, which is electronically not too different from the situation found in the CuO₂ layers in the cuprates, the 3d⁸ configuration is about 10 eV above the 3d⁹+3d¹⁰ $\underline{L}$ ground state [20]. Therefore, if formally Cu³⁺ ions are present, their wave functions will be dominated by the 3d⁹ $\underline{L}$ component because of the high excitation energy of the 3d⁸ component. The components 3d⁹ for Cu²⁺ and 3d⁹ $\underline{L}$ for Cu³⁺ are almost degenerate [20]. This can rationalize the difficulty in detecting Cu³⁺ in the Cu 2p XPS spectra. Nonetheless, we have clearly observed the signature of Cu³⁺ in our x-ray absorption measurements at the Cu L₃ edge. Intensity of this Cu³⁺ peak increases with increasing Fe content. This confirms the XPS results by Zhang et al. [3]. In pure YBCO increased Cu³⁺ is taken as a sign of increased hole concentration and thus improved superconductivity. However, in YBCFO T_c decreases with increasing x because of increased O content. Therefore, in YBCFO increased Cu³⁺ is only due to charge balancing.

CONCLUSIONS:

In summary, our high-resolution XANES spectra at O K edge in YBa₂Cu_{3-x}Fe_xO_{7+y} for x = 0.01, 0.05 and 0.15 show hole filling with increasing Fe content in both CuO₂ plane and Cu-O chain. Our Cu L₃ edge spectra reveal increased amount of Cu³⁺ with increasing Fe content, which is due to charge balancing.

ACKNOWLEDGMENTS:

The authors acknowledge the support and help provided by the Physics Department of King Fahd University of Petroleum and Minerals at Dhahran, Saudi Arabia and Lawrence Berkeley National Laboratory at Berkeley, USA for this study. This work was partially supported by US-DOE.

REFERENCES:

- 1 M. W. Ruckman and A. F. Hepp, *Superconductivity And Its Applications*, ed. by Y. H. Kao, P. Coppens, and H. S. Kwok, (1990)
- 2 C. Y. Yang, S. M. Heald, J. M. Tranquada, Y. Xu, Y. L. Wang, A. R. Moodenbaugh, D. O. Welch, and M. Suenaga, *Phys. Rev. B* 39, 6681 (1989)
- 3 H. Zhang, Q. R. Zhang, Z. P. Su, and M. R. Ji, *Phys. Rev. B* 42, 2248 (1990)
- 4 V. P. S. Awana , R. Lal, D. Varandani, A. V. Narlikar, and S. K. Malik, *Supercond. Sci. Technol.* 8, 745 (1995)
- 5 J. Stohr, “NEXAFS Spectroscopy”, Springer-Verlag, New York (1992)
- 6 Z. Hussain, W. R. A. Huff, S. A. Kellar, E. J. Moler, P. A. Heimann, W. McKinney, H. A. Padmore, C. S. Fadley, and D. A. Shirley, *J. Electron Spectrosc. Relat. Phenom.* 80, 401 (1996)
- 7 R. S. List, A. J. Arko, Z. Fisk, S. W. Cheong, S. D. Conradson, J. D. Thompson, C. B. Pierce, D. E. Paterson, R. J. Bartlett, N. D. Shinn, J. E. Schirber, B. W. Veal, A. P. Paulikas, and J. C. Campuzano, *Phys. Rev. B* 38, 11966 (1988)
- 8 M. Calligaris and S. Gevemia, Department of Chemistry, University of Trieste, Italy (1990).
- 9 E. E. Alp, J. C. Campuzano, G. Jennings, J. Guo, D. E. Ellis, L. Beaulaigue, S. Mini, M. Faiz, Y. Zhou, B. W. Veal, and J. Z. Liu, *Phys. Rev. B* 40, 9385 (1989)
- 10 M. Karppinen, J. Linden, J. Valo, A. Kareiva, A. Kozlov, K. Terryll, L. Niinisto, M. Leskela, and K. V. Rao, *Supercond. Sci. Technol.* 8, 79 (1995)
- 11 I. S. Lyubutin, S. T. Lin, C. M. Lin, K. V. Frolov, T. V. Dmitrieva, A. M. Balagurov, F. Bouree, and I. Mirebeau, *Physica C* 248, 222 (1995)
- 12 F. M. F. de Groot, M. Grioni, J. C. Fuggle, J. Ghijsen, G. A. Sawatzky, and H. Petersen, *Phys. Rev. B* 40, 5715 (1989)

- 13 T. A. Faltens, W. K. Ham, S. W. Keller, K. J. Leary, J. N. Micaels, A. M. Stacy, Hans-Conard zur Loe, D. E. Morris, T. W. Barbee, III, L. C. Bourne, M. L. Cohen, S. Hoen, and A. Zettl, *Phys. Rev. Lett.* 59, 915 (1987)
- 14 D. D. Sarma, O. Strebel, C. T. Simmons, U. Neukirch, G. Kaindl, R. Hoppe, and H. P. Müller, *Phys. Rev. B* 37, 9784 (1988)
- 15 A. Bianconi, M. DeSantis, A. Di Ciccio, A. M. Flank, A. Fontaine, P. Legarde, H. Katayama-Yoshida, A. Kotani, and A. Marcelli, *Phys. Rev. B* 38, 7196 (1988)
- 16 P. Kuiper, G. Kruizinga, J. Ghijsen, M. Grioni, P. J. W. Weijs, F. M. F. de Groot, G. A. Sawatzky, H. Verweij, L. F. Feiner, and H. Petersen, *Phys. Rev. B* 38, 6483 (1988)
- 17 J. Fink, N. Nücker, H. Romberg, M. Alexander, S. Nakai, B. Scheerer, P. Adelmam, and D. Evert, *Physica C* 162-164, 1415 (1989)
- 18 G. van der Laan, C. Vestra, C. Haas, and G. A. Zawatsky, *Phys. Rev. B* 23, 4369 (1981)
- 19 G. Kaindl, D. D. Sarma, O. Strebel, C. T. Simmons, U. Neukirch, R. Hoppe, and H. P. Müller, *Physica C* 153-155, 139 (1988)
- 20 P. Steiner, S. Hufner, V. Kinsinger, I. sander, B. Siegwart, H. Schmitt, R. Schulz, S. Junk, G. Schwitzgebel, A. Gold, C. Politis, H. P. Müller, R. Hoppe, S. Kemmler-Sack, and C. Kunz, *Z. Phys. B* 69, 449 (1988)

FIGURE CAPTIONS:

FIGURE 1: XRD patterns of $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$ poly crystals for $x = 0.01, 0.05$ and 0.15 .

FIGURE 2: O K edge of $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$ poly crystals at 90 K as a function of x .

FIGURE 3: Cu L_3 edge of $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7+y}$ poly crystals at 90 K as a function of x .