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Annealing, quenching and substitution effects on $YBa_2Cu_3O_{7-\delta}$: An XAS study

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Abstract. K-absorption edge region of copper in oxygen and air-annealed high T_c (~ 91 K) superconducting (SC) samples, $YBa_2Cu_3O_{7-\delta}$, has been investigated. The spectra exhibit a weak structure at ~ 23 eV. To understand its origin, the spectra have been recorded for quenched Ce-substituted and semiconducting Y_2BaCuO_5 samples. It is argued that the weak structure (~ 23 eV) is not a characteristic feature of an SC compound but appears to be a final state effect.

Keywords. High temperature superconductivity; annealing; quenching; substitution effect; $YBa_2Cu_3O_{7-\delta}$; X-ray absorption spectra.

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1. Introduction

The discovery of high temperature superconductivity in the Y-Ba-Cu-O system has generated a great deal of interest among scientists and technologists. In this system, $YBa_2Cu_3O_{7-\delta}$ has emerged as the only superconducting (SC) phase with $T_c \sim 90$ K. The other possible phases, Y_2BaCuO_5, $Y_2Cu_2O_5$ and $BaCuO_2$ are either semiconducting or insulating. $YBa_2Cu_3O_{7-\delta}$ ($\delta < 0{\cdot}5$) crystallizes in the distorted orthorhombic perovskite structure. It has been observed that partial substitution of Ce (< 10%) for Y ions commensurately suppresses T_c and the high temperature quenching of $YBa_2Cu_3O_{7-\delta}$ ($\delta > 0{\cdot}5$) leads to samples being in tetragonal phase and non-SC (Schnemeyer *et al* 1987; Prakash *et al* 1988; Rao *et al* 1988).

X-ray absorption spectroscopic (XAS) studies have revealed a prominent absorption peak at ~ 17 eV and an associated structure at ~ 23 eV in the K-absorption edge region of Cu in SC, $YBa_2Cu_3O_{7-\delta}$. The prominent peak at ~ 17 eV is assigned to Cu^{2+} while assignment of the structure at ~ 23 eV is controversial. It is, therefore, considered worthwhile to investigate the effects of oxygen-annealing, quenching and substitution on the weak structure at ~ 23 eV. These results are discussed in this paper.

2. Experimental

Samples of $YBa_2Cu_3O_{7-\delta}$ were prepared by the standard ceramic technique using proportionate quantities of Y_2O_3, $BaCO_3$ and CuO powders of $\sim 99{\cdot}9\%$ purity. The

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samples of the precalcined powder in the pellet form were annealed at 930 ± 10°C for 12 hours in oxygen atmosphere as well as in air and cooled down slowly to room temperature (Prakash *et al* 1988). A few pellets of $YBa_2Cu_3O_{7-\delta}$ from the above batch were quenched from the elevated temperature (> 870°C). Samples were also prepared in O_2 atmosphere with Ce substitution (~ 7·5%) on the yttrium site. For comparison, semiconducting samples of Y_2BaCuO_5 were prepared at ~ 1050°C in air atmosphere. The samples were characterized by X-ray diffraction and the impurity phases were found to be less than 4%. The oxygen and air-annealed $YBa_2Cu_3O_{7-\delta}$ samples including Ce-substituted, $Y_{0.925}Ce_{.075}Ba_2Cu_3O_{7-\delta}$ showed an orthorhombic structure while the quenched samples exhibited a tetragonal phase. From the resistivity measurements on oxygen and air-annealed samples T_c was found to be 91 ± 1 K, while for the Ce-substituted samples, Meissner effect was not observed down to ~ 77 K. The quenched sample remained non-SC down to 4·2 K (Prakash *et al* 1988).

The X-ray absorption spectra (XAS) were recorded with a conventional X-ray spectroscopic set-up using laboratory source of continuous radiation (Darshan *et al* 1984; Padalia *et al* 1973). Both the photographic and the electronic counting techniques were used to record the spectra.

3. Results and discussion

The K-absorption near edge structure (K-XANES) of Cu in $YBa_2Cu_3O_{7-\delta}$ recorded at room temperature for oxygen-and air-annealed samples is shown in figure 1 (c and d).

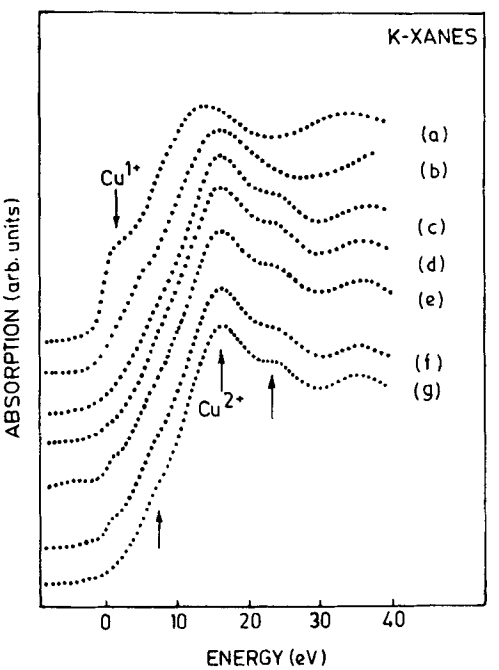

Figure 1. K-absorption edge region of Cu in (a) Cu_2O, (b) CuO, (c) $YBa_2Cu_3O_{7-\delta}$ annealed in oxygen, (d) $YBa_2Cu_3O_{7-\delta}$ annealed in air, (e) $Y_{0.925}Ce_{0.075}Ba_2Cu_3O_{7-\delta}$, (f) $YBa_2Cu_3O_{7-\delta}$ quenched from > 870°C and (g) Y_2BaCuO_5.

For purposes of comparison, K-XANES of Cu in monovalent Cu_2O and divalent CuO are also included in the figure. The K-edge position ($\sim$ 8980·2 eV) of Cu in metallic state has been taken as the zero of the energy scale. The value of K-edge of Cu metal measured by us agrees well with the value reported by Bearden and Burr (1967). The main K-absorption peak measured with respect to the Cu metal appears at $\sim$ 17 eV and is assigned to Cu^{2+}. A weak structure is evident at $\sim$ 23 eV on the higher energy side of the main peak for the high T_c SC samples. Such a structure at $\sim$ 23 eV has also been observed by others. It is tempting to assign this structure to Cu^{3+} on the basis of (i) charge neutrality consideration, (ii) the possibility of dismutation of $2Cu^{2+}$ to $Cu^{1+} + Cu^{3+}$ as discussed by Pauling (1987) and (iii) charge transfer model of Varma *et al* (1987), wherein Cu ion fluctuating between Cu^{1+}, Cu^{2+} and Cu^{3+} is proposed. The assignment of the structure is still controversial and, therefore, needs some discussion.

The K-XANES studies on $YBa_2Cu_3O_{7-\delta}$ compound carried out by several investigators (Bianconi *et al* 1987; Boyce *et al* 1987; Jeon *et al* 1987) provide no convincing evidence of Cu^{3+} in this SC system. On the other hand Lytle and Greegor (1988) find evidence of simultaneous presence of Cu^{2+} and Cu^{3+} by chemical analysis.

In order to understand the origin of the structure at $\sim$ 23 eV, we extended the K-XANES study to 7·5% Ce-substituted (Y, Ce) $Ba_2Cu_3O_{7-\delta}$ samples in which T_c is suppressed ($T_c < 77$ K). The choice of Ce-substitution is dictated by the fact that Ce can exist in trivalent, tetravalent of mixed valent state. If Ce is driven towards Ce^{4+} state in the Ce-substituted sample, it is likely to reduce the trivalent component in Cu, if at all it exists, in the $YBa_2Cu_3O_{7-\delta}$ compound. This is likely to be reflected in the structural features associated with the absorption edge of Cu in (Y, Ce) $Ba_2Cu_3O_{7-\delta}$ sample. It may be stated that our preliminary results on the core level XPS of Ce in (Y, Ce) $Ba_2Cu_3O_{7-\delta}$ give an indication of Ce being in the mixed valent (3+ and 4+) state. However, the K-XANES study of Cu in the same Ce-substituted sample exhibit no detectable change in the intensity and the position of the weak structure at $\sim$ 23 eV (figure 1e).

It is of interest to see if the structure at $\sim$ 23 eV is affected by lowering the oxygen concentration and by the associated structural phase transition in $YBa_2Cu_3O_{7-\delta}$. We, therefore, quenched the samples from the elevated temperature (> 870°C). It is found that the structure at $\sim$ 23 eV in the K-XANES of Cu remains unaffected in the quenched samples (figure 1f). This supports the results obtained for the Ce-substituted samples. Further, the K-XANES of Cu in non-SC Y_2BaCuO_5 samples also exhibits the structure at $\sim$ 23 eV (figure 1g). It is, therefore, inferred that this structure is not a characteristic feature of the SC compounds. Further, the possibility of appearance of a final state effect (shake-up satellite) at $\sim$ 23 eV due to charge transfer mechanism cannot be ruled out. Since a weak structure has been observed at $\sim$ 7 eV below the main Cu^{2+} peak in the XAS spectra of these compounds, being assigned to shake down the satellite (Jeon *et al* 1987), it appears that the structure at $\sim$ 23 eV is due to the shake-up satellite.

References

Bearden J A and Burr A F 1967 *Rev. Mod. Phys.* **39** 125

Bianconi A, Castellano A C, Santis M De, Politis C, Marcelli A, Mobilio S and Savoia A Z 1987 *Phys. Rev.* **B67** 307

Boyce J B, Bridges F, Claeson T, Howland R S and Geballe T H 1987 *Phys. Rev.* **B36** 5251
Darshan B, Padalia B D, Nagarajan R, Dhar S K, Malik S K and Vijayaraghavan R 1984 *Phys. Rev.* **B30** 4031
Jeon Y, Lu R, Jhans H, Shabeen S A, Liang G, Croft M, Ansari P H, Ramanujachary K V, Hayri E A, Fine S M, Li S, Feng X H, Greenblatt M, Green L H and Tarascon 1987 *Phys. Rev.* **B36** 3891
Lytle F W and Greegor R B 1988 *Phys. Rev.* **B37** 1550
Padalia B D, Krishnan V, Patni M J, Radhakrishnan N K and Gupta S N 1973 *J. Phys. Chem. Solids* **34** 1173
Pauling L 1987 *Phys. Rev. Lett.* **59** 225
Prakash R, Prakash O and Tavare N S 1988 *Pramana – J. Phys.* (In press)
Rao C N R, Ganapathi L and Ram R A M 1988 *Mater. Res. Bull.* **23** 125
Schnemeyer L F, Waszczuk J V, Zahurak S M, Van Dover R B and Siegrist T 1987 *Mater. Res. Bull.* **22** 1467
Varma C M, Schmitt-Rink S and Abrahams E 1987 *Solid State Commun.* **62** 681