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Nickel Impurities in the 90K Superconductor

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1. Introduction

With the goal of obtaining more insight into the unique role of Cu, there are many experiments on substituting for the various metal atoms in the 1-2-3 superconductor. Among them, the experiments on Cu substitution by Ni[1−6] either have not been able to verify where the impurity atom actually resides or claimed that Ni atoms are at Cu(2) sites. We present here a detailed investigation combining the XAFS technique with a careful characterization of the morphology of the sample $YBa_2(Cu_{1-x}Ni_x)_3O_{7-\delta}$ with $x = 0.02, 0.05, 0.09$ and conclude that Ni does not substitute in either Cu site.

2. Sample Characterization, XAFS Measurements and Analysis

The samples were made using Y_2O_3,BaO_2,CuO and Ni acetate powders with standard procedures. The samples were characterized by X-ray diffraction, ac magnetic susceptibility, electrical resistance, optical and electron microscopy. The results are that the 2% sample has $T_c = 86.5K$, over 90% of the volume of the sample is shielded in an ac susceptibility measuremant, 94% of the Ni dissolved in the 1-2-3 phase with $x = 0.02$; the 5% sample has T_c= 79.5K, Ni atoms significantly mixed between the 1-2-3 phase with $x = 0.04$ and NiO precipitates; the 9% sample is multiphase and no T_c was found.

XAFS measurements on the 2% and 5% samples were made at room temperature on the Ni and Cu K-edges at SSRL . The Cu K-edge measurements were made in transmission while the Ni K-edge measurements were made in fluorescence.

The data were analyzed by standard methods, the resulting $\chi(k)$ weighted by k^3 is displayed in Fig. 1. The magnitude of the transforms for the $k^3\chi(k)$ data are shown in Fig. 2.

3. Results and Discussion

Fig.1 and 2 indicate that Ni is not simply substituting in the Cu site. The second and more distant peaks appear to be significantly different around the Ni and Cu atoms. For more quantitative comparison, the ln-ratio were taken between various shells. Fig. 3(a),(b) show the first shell ln-ratio and phase differences between the 2% Ni and the models NiO, Ni acetate and Cu 1-2-3 phase. From these comparison, we find that there are 4.75 ± 0.4 oxygen neighbors around the Ni at a distance of $1.95 \pm 0.03Å$ with $\sigma^2 = 0.004 \pm 0.003Å^2$

To determine the atom in 2nd shell of 2% Ni sample,fits were made with theoretical calculations using spherical wave and Dirac-Hara energy dependent muffin

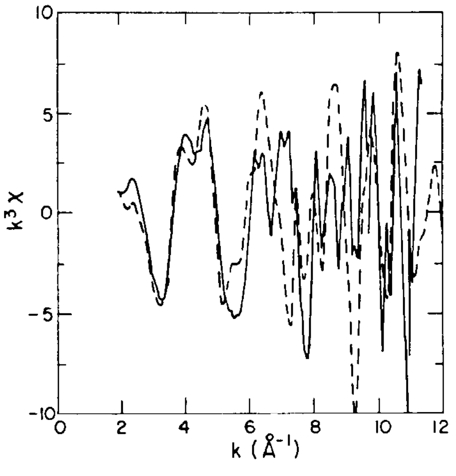


Fig.1

Plots of $k^3\chi(k)$ for the Ni K-edge (solid) and for the Cu K-edge (dashed) of $YBa_2(Cu_{0.98}Ni_{0.02})_3O_{7-\delta}$.

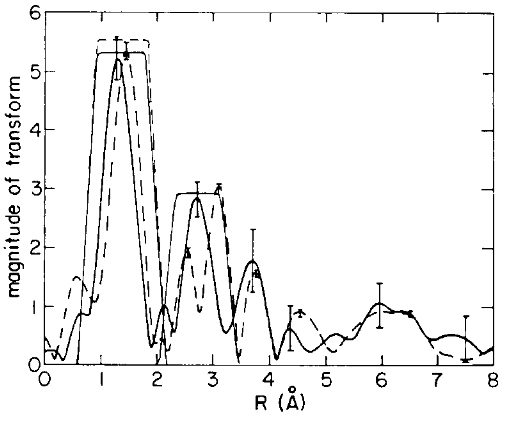
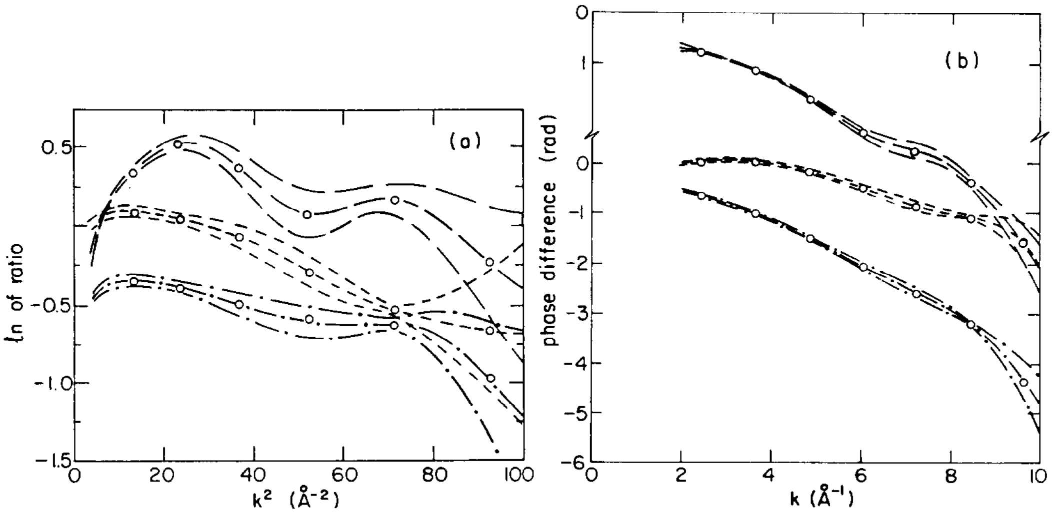


Fig.2

The magnitude of the transform of the $k^3\chi(k)$ of Fig.1. The Ni edge (solid) and the Cu edge (dashed) are transformed over the renge $1.9 \leq k \leq 11.4$Å with Hanning function of width 1.0Å^{-1} and 4.0Å^{-1} at the low and high ends of the range, respectively. The windows used for isolating particular shells are shown.



(a) Fig.3 (b)

The ln-ratio vs. k^2 of the Ni K-edge XAFS of the 2% sample divided by the Ni edge data of NiO (long dash), Ni acetate (dash-dot) and the Cu edge data of the 2% sample (short dash).

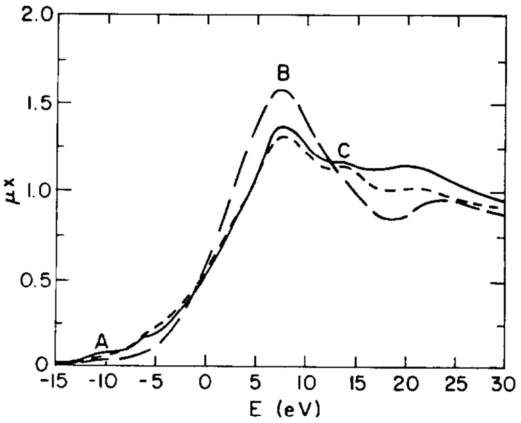
The difference in phase of the Ni K-edge XAFS of the 2% sample with Ni edge data of NiO (long dash), Ni acetate (dash-dot), and the Cu edger data of the 2% sample (short dash).

tin potential for the Ni center atom and Cu,Ni,Y,and Ba backscattering atoms. The results are that there are 5.1 ± 1.2 Y at $2.96 \pm 0.02\AA$ with $\sigma^2 = 0.011\AA^2$. A satisfactory fit also occurred for a mixture of Y at $2.96 \pm 0.02\AA^2$ and Ba at $3.10 \pm 0.02\AA^2$. These Ni-Y and Ni-Ba distances differ from Cu-Y and Cu-Ba about $0.24\AA$ and $0.3\AA$ respectively. To make our results consistent with substitution on either Cu site requires an unphysical assumption, namely, that the Ni distorts the second and more distant neighbor environment much more than the first neighbor environment. If the only perturbation is a substitution of Cu by Ni, the perturbation will decrease with distance from Ni. This is not the case indicating that the perturbation is not just localized at the Ni atom but occurs also in its surroundings, i.e., the surroundings also are changed and the Ni is not in a Cu-site.

Fig.4 shows near edge scans of the Ni K-edge for NiO, and the 2% Ni. Also shown is a corresponding Cu K-edge for 1-2-3 phase . The Cu K-edge for 1-2-3 phase shows a feature marked C which is caused by a-b plane of the Cu atoms[7]. The absence of feature C about the Ni atoms indicates that they are not in either Cu site since each would produce a feature C and this is confirms the extended XAFS result.

Fig.4

Near edge scans of the K-edge of the Ni edges of the 2% sample (solid), NiO (long dash) and the Cu edger of the 2% sample (short dash). The K-edge step has been normalized to one using the data beyond 30 eV. The onset of the 3d "pip" denoted by A has been aligned for all three edge scans.The features B and C are discussed in the text.



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