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Extended x-ray absorption fine-structure studies of 3d ions in YBa$_2$(Cu$_{1-x}$M$_x$)$_3$O$_{7-\delta}$ ($x \leqslant 0.10$; M $\equiv$ Mn, Fe, Co, Ni and Zn)

B D Padalia†, S J Gurman‡, P K Mehta† and Om Prakash§

† Department of Physics, Indian Institute of Technology, Bombay 400 076, India
‡ Department of Physics and Astronomy, University of Leicester, Leicester LE1 7RH, UK
§ Materials Science Centre, Indian Institute of Technology, Bombay 400 076, India

Abstract. EXAFS measurements on 3d ions in samples of nominal composition YBa$_2$(Cu$_{1-x}$M$_x$)$_3$O$_{7-\delta}$ ($x \leqslant 0.10$; M $\equiv$ Mn, Fe, Co, Ni and Zn) were made in fluorescence mode using the synchrotron radiation source at Daresbury Laboratory. The standard Daresbury packages including the EXCURV90 program were used to identify the dopant site occupancy and to evaluate the coordination number and bond lengths. It is found, perhaps for the first time, that the Mn^{2+} ion occupies the Cu(1) chain site in the 1:2:3 lattice. The occupancy of the Cu(1) site by Fe and Co dopants is confirmed. Ni ions are distributed nearly equally between Cu(1) chain and Cu(2) plane sites. For $x > 0.03$, some of the Ni separates out as NiO and the maximum Ni content in the 1:2:3 compound has been estimated to be 4 ± 1 at.%. No useful data could be obtained for Zn dopant owing to interference from the adjacent Cu K edge in the 1:2:3 compound. An attempt has been made to interpret the observed drop in T_c due to substitution on the basis of EXAFS findings.

1. Introduction

Amongst the existing high-T_c superconductors, the YBa$_2$Cu$_3$O$_{7-\delta}$ (1:2:3) compound provides an ideal opportunity for substitutional studies as it is relatively easy to prepare it in single-phase form with $T_c \simeq 91$ K. The unit cell of the 1:2:3 compound contains two structurally inequivalent Cu sites: the Cu(1) or chain site and the Cu(2) or plane site. It is this aspect of the structure which has attracted much attention for substitutional studies of 3d transition-metal ions at the Cu sites (Bridges *et al* 1989, 1990, Yang *et al* 1990, Mehta *et al* 1991, Padalia *et al* 1991). A considerable amount of work has been reported on the substitution of Fe and Co into the 1:2:3 lattice. The extent of Ni incorporation into the 1:2:3 compound has raised some questions (Qian *et al* 1989, Bridges *et al* 1990, Yang *et al* 1990). Relatively little attention has been paid to the substitution of Mn and other lighter 3d transition-metal ions in the 1:2:3 system. Thus motivated, we carried out a systematic study of substitutional effects of the entire 3d transition-metal series, Sc to Ni and Zn at the Cu sites in YBa$_2$Cu$_3$O$_{7-\delta}$. Special care was taken in the synthesis and characterization of the substituted samples. Some of the results of our XRD, iodometric titration, four-probe resistivity, AC susceptibility, Cu 2p XPS and Cu K edge measurements on these 3d-ion-substituted 1:2:3 compounds were reported recently (Padalia and Mehta 1989, Padalia *et al* 1991).

In order to determine the valence states and the environments of the 3d ions substituted in the 1:2:3 lattice, we have measured the K edges and the associated fine structures of Mn, Fe, Co, Ni and Zn in 1:2:3 compounds with the synchrotron radiation source at Daresbury Laboratory of the Science and Engineering Research Council (SERC). Here, we report the results of our EXAFS measurements on the 3d ions substituted in the 1:2:3 system.

2. Sample preparation

The samples of the 3d-ion-substituted compounds with nominal compositions $YBa_2(Cu_{1-x}M_x)_3O_{7-\delta}$ where $M \equiv$ Mn, Fe, Co, Ni ($x \leqslant 0.10$) and Zn ($x \leqslant 0.05$) were prepared by the solid state reaction route (Mehta 1991). Together with high-purity (greater than 99.9%) Y_2O_3, $BaCO_3$ and CuO, the respective substituent oxides MnO_2, Fe_2O_3, Co_3O_4, NiO and ZnO were used in appropriate quantities. The samples in pellet form were sintered, after multiple intermediate grindings, in an O_2 atmosphere at about 930 °C for about 36 h and then cooled slowly to about 550 °C. Between approximately 550 and 400 °C, extended oxygenation for about 72 h was carried out to improve the oxygen content and ordering in the samples.

The XRD analysis of the samples showed the formation of the 1:2:3 single phase in the case of Mn and Ni for $x \leqslant 0.08$ while for Fe, Co and Zn no impurity phases were found up to the substitution limits.

In order to check the elemental composition of the samples, a detailed energy-dispersive x-ray analysis (EDAX) study was undertaken within the grains and at the grain boundary regions for Mn ($x \leqslant 0.08$), Fe, Co and Ni ($x \leqslant 0.10$) and Zn ($x \leqslant 0.05$). The EDAX revealed fairly uniform distributions of Mn, Fe, Co and Zn in the grains with no clustering in the grain boundary regions. However, in the case of Ni-substituted 1:2:3 samples, it was found that the Ni content for $x = 0.06$ and 0.10 did not exceed 4 ± 1 at.% within the grains, suggesting that excess Ni is segregated at the grain boundaries (Mehta *et al* 1991).

3. Experimental details

3.1. EXAFS experiments

EXAFS measurements on the K edges of the substituted ions in 1:2:3 compounds were made at the 2 GeV synchrotron radiation source, SERC Daresbury Laboratory. The experiments were performed on beam line 7.1 which has a Si(111) double-crystal monochromator to define the x-ray energy. The signals from the substituent atoms were collected in fluorescence mode, using a single NaI:Tl scintillation counter. All experiments were performed at room temperature on finely powdered samples mounted on Scotch tape. EXAFS data were taken over an energy range corresponding to electron wavenumbers of 1–20 $Å^{-1}$. Four to five spectra, each taking about 30 min, were averaged to give the final data which had a fluorescence count of 10^6–10^7 photons per data point.

3.2. *Data analysis*

The software on beam line 7.1 produces as output the natural logarithms of I_f/I_0, i.e.
the fluorescence counts I_f divided by the incident beam count I_0, as a function of the
monochromator angle. This was calibrated in terms of the photon energy using the
EXCALIB program of Morrell *et al.* For background subtraction, we used the EXBACK
program by the same workers to fit low-order polynomials to the pre- and post-edge
data to represent the smooth absorption background. These were then subtracted
from the spectrum in the usual way to give the EXAFS function $\chi(k)$.
    For the dopant environments in the 1:2:3 compound, structural information was
obtained by multi-parameter fitting of the experimental EXAFS data to an EXAFS
function calculated using the single-scattering curved wave theory (Gurman *et al*
1984). The program used was the standard Daresbury package EXCURV90 (Binsted *et
al* 1990). For successful application of the theory, it is necessary to use a reliable set
of scattering data. The scattering phase shifts used were calculated within EXCURV90
for each atom type. These have been extensively tested on metal foils and oxide
samples and are known to give good results. In the present work, the values of
$A(k)$, a factor that corrects for amplitude reduction arising from events that result
in absorption but not EXAFS (such as multiple excitations), and the mean free path
factor, V_i, were taken from an earlier report on Cu in the 1:2:3 compound (Gurman
et al 1988).
    The EXCURV90 fitting routine uses a non-linear least-squares fit of the fast curved
wave theory to the experimental EXAFS data. The variable parameters are the inter-
atomic distances R and the energy offset E_0, which together fix the phase of $\chi(k)$,
the coordination number N and the Debye–Waller factor σ^2. These parameters con-
trol the amplitude of $\chi(k)$. The data range used in the fit was generally 15–600 eV
above the absorption edge corresponding to a k-range of 2.5–13 Å^{-1}. The program
varies selected parameters until a minimum is obtained in the fit index (FI) defined
by

$$FI = \frac{1}{100\,N_P} \sum_{i=1}^{N_P} \{[\chi_i(\text{calc}) - \chi_i(\text{expt})]k^n\}^2$$

where N_P is the number of data points and n is a k-weighting factor used to equalize
the contribution of all the points to the FI; $n = 3$ was used throughout this work.
    A non-trivial problem encountered when using this type of curve-fitting approach
is the estimation of the uncertainties in the fitted parameters. This problem is com-
plicated by the presence of correlation between parameters, especially the pairs (E_0,
R) and (N, σ^2), introduced by the finite data range. We have used the statistical
test described by Joyner *et al* (1987) to estimate these uncertainties. This test, which
is an integral part of EXCURV90, provides a plot of the 95% significance region ($\pm 2\sigma$
uncertainty) on a contour map of the FI when plotted as a function of two correlated
variables. It is these $\pm 2\sigma$ uncertainties which are given in the tables of our structural
parameters. This test may also be used to determine whether a shell of scattering
atoms gives a significant contribution to the fit. With the exception of Ni K edge data,
the addition of the Y scattering atoms was found not to improve the fit significantly
nor did the third oxygen shell at 2.3 Å.

4. Results and discussion

Figures 1 and 2 show the background-subtracted and k^3-weighted EXAFS functions $\chi(k)$ for Mn ($x = 0.08$) and Ni ($x = 0.03$, 0.06 and 0.10) in $YBa_2(Cu_{1-x}M_x)_3O_{7-\delta}$ samples. The corresponding Fourier transforms (FTS) are given below the EXAFS in the lower parts of the figures. For the purpose of comparison, the EXAFS curve for Cu in $YBa_2Cu_3O_{7-\delta}$ compound (unsubstituted) and the associated FT are given in figure 3. In figures 1–3, the full curves represent the experimental data, and the broken curves represent the theoretical fits. The FTS are phase corrected and, therefore, the peaks appear at the true interatomic distances R.
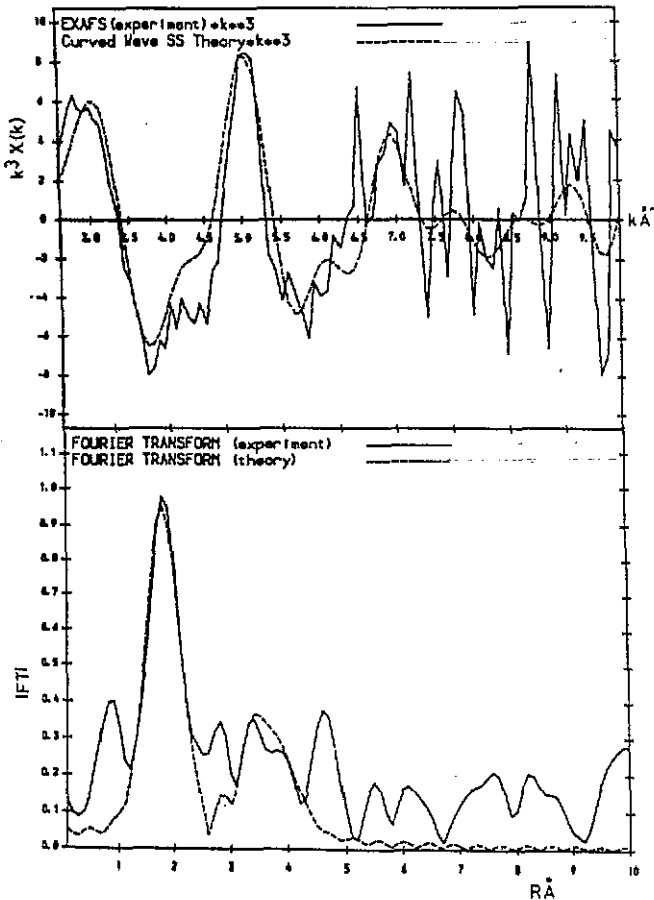

Figure 1.   EXAFS   spectrum   (upper)   and   associated   FT   (lower)   for   Mn   in $YBa_2(Cu_{1-x}Mn_x)_3O_{7-\delta}$, $x = 0.08$: ——, experimental data; – – –, theoretical fits.

It should be stated that we could not obtain useful data for Zn because of strong absorption from the adjacent Cu K edge. Even for 4 at.% Mn, we could not get a good background subtraction for $\chi(K)$ owing to interference from the Ba L_3 edge. We have, however, succeeded in obtaining reasonably good data for Mn ($x = 0.08$)
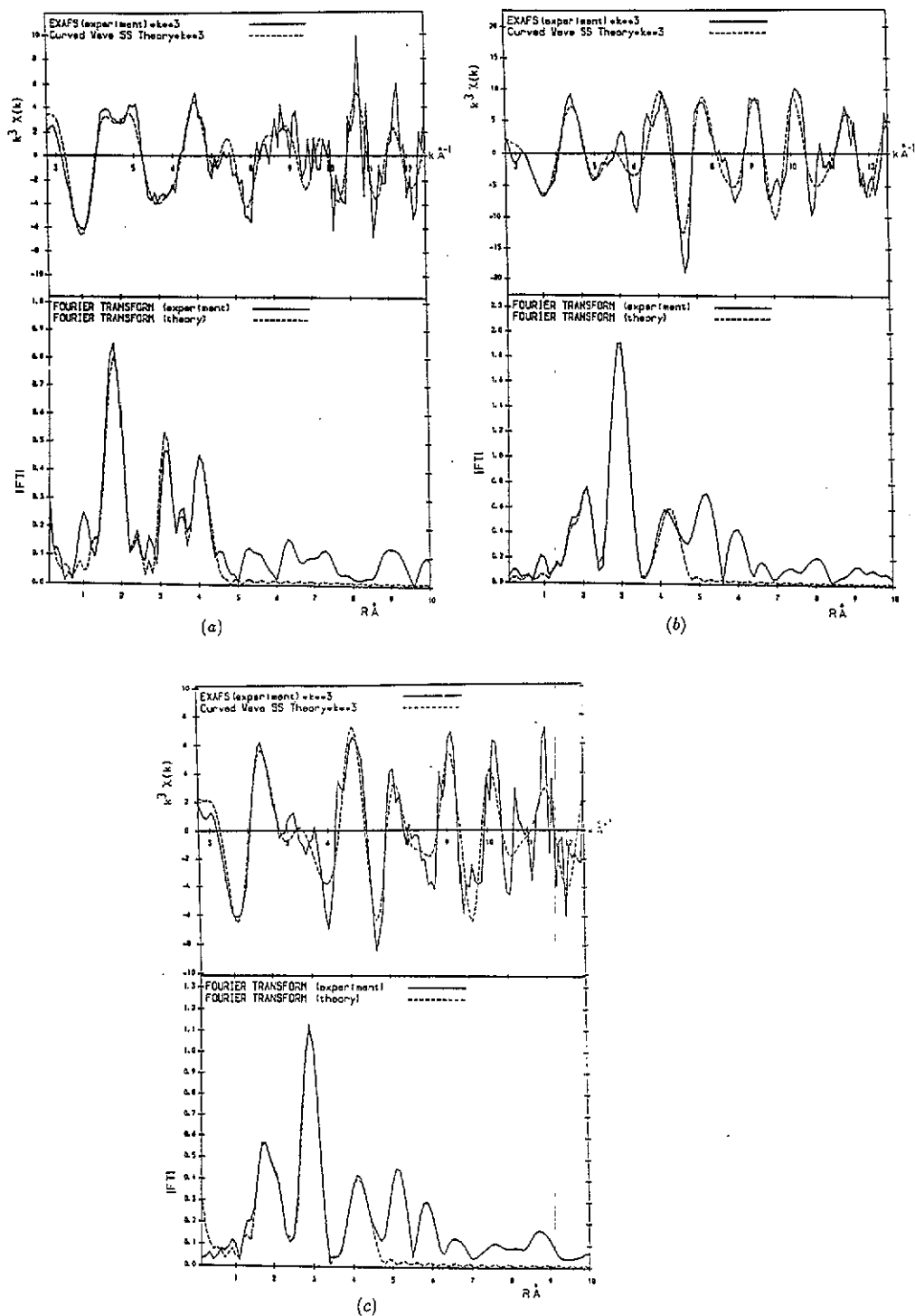
(a)

(b)

(c)

Figure 2. EXAFS spectra (upper) and associated FT (lower) for Ni in $YBa_2(Cu_{1-x}Ni_x)_3O_{7-\delta}$: (a) $x = 0.03$; (b) $x = 0.06$; (c) $x = 0.10$.

in the $YBa_2(Cu_{1-x}Mn_x)_3O_{7-\delta}$ sample. This is, perhaps, the first EXAFS report on the Mn-substituted 1:2:3 system.

The FTs of the EXAFS for the substituted samples exhibit the first prominent peak at 1.8–2.0 Å which corresponds to the nearest-neighbour distance. Since the measured distance is far too short for the occupancy of a Y site (Y–O at 2.35 Å) or Ba site (Ba–O at 2.73 Å) by substitutional ions, it is clear that Mn and Ni ions substitute for Cu in 1:2:3 compounds. Further, a double peak appears in the FT at 3–4 Å for all the substituent ions except for Ni, in which case a triple-peak pattern is observed at the same position. In the unsubstituted $YBa_2Cu_3O_{7-\delta}$ compound, there are two Cu sites: the Cu(1) chain site between two Ba layers and Cu(2) plane site between the Ba and Y layers (figure 4). There are one Cu(1) and two Cu(2) positions in each unit cell. In the Cu EXAFS (Gurman *et al* 1988), the occupancy of the two sites gives a characteristic triple peak in the FT (figure 3) because of the three cation distances (Cu–Y at 3.2 Å, Cu–Ba at 3.4 Å and Cu–Cu at 3.85 Å). A comparison of the FT features for the substituted samples with those of the unsubstituted 1:2:3 compound (Gurman *et al* 1988) reveals that the short Cu–Y peak at 3.2 Å is missing from the FT for the Mn substituent. Thus, the simple observation suggests that Mn occupies entirely the Cu(1) site. It may be added that we have also observed similar EXAFS and FT features for the Fe and Co dopants in the 1:2:3 compound, confirming the results of Bridges *et al* (1989) and Yang *et al* (1990) that Fe and Co occupy the Cu(1) chain site. We have, therefore, not shown here the EXAFS and FT for these dopants.
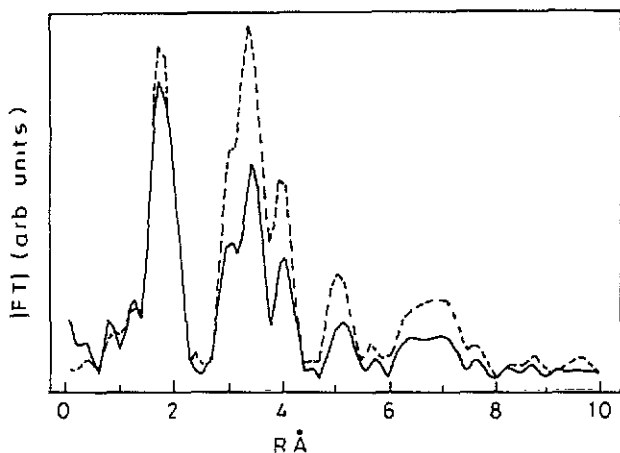
Figure 3. FT of EXAFS spectrum for Cu in $YBa_2Cu_3O_{7-\delta}$ (unsubstituted).

The coordination numbers N, the interatomic distances R and their mean square deviations σ^2 obtained from our EXAFS analysis are given in tables 1–7. For convenience, the N and R-values for the unsubstituted reference 1:2:3 compound determined by diffraction as well as EXAFS studies (Gurman *et al* 1988) are included in table 1.

The EXAFS spectra recorded were not of the same quality; they were noisy for Mn, good for Fe and very good for Co and Ni. The data ranges used were also different: 15–360 eV ($k = 2.5$–10.0 Å^{-1}) for Mn, 15–530 eV ($k = 3$–12 Å^{-1}) for
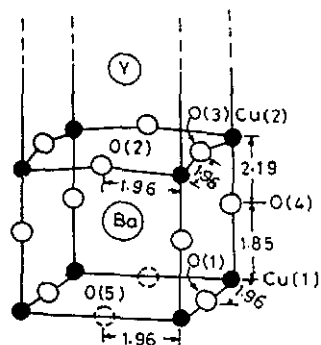
Cu(2) – Y → 3.20 Å
Cu(1)/Cu(2) – Ba → 3.40 Å

Figure 4. Typical Cu–O bond distances in the $YBa_2Cu_3O_{7-\delta}$ lattice as determined through EXAFS.

Table 1. The coordination number N, the interatomic distance R and the mean square deviation σ^2 obtained from the EXAFS analysis for $YBa_2Cu_3O_{7-\delta}$. The N-, R- and σ^2-values reported by others are included for comparison.

Neighbours	Balagurov et al (1991), diffraction		Gurman et al (1988), EXAFS[a]		
	N	R (Å)	N	R (Å)	σ^2 (Å^2)
Cu(1)–O(4)	0.67	1.83	1 ± 0.5	1.85	0.002 ± 0.001
Cu(1)–O(1)					
Cu(2)–O(2)	3.33	1.95	4 ± 1	1.96	0.002 ± 0.001
Cu(2)–O(3)					
Cu(2)–O(4)	0.67	2.3	$\simeq 1$	2.19	0.003
Cu(2)–Y		3.20		3.20	
Cu(1)–Ba		3.45		3.40	
Cu(2)–Ba					
Cu–Cu	4	3.85			

[a] AFAC $A(k) = 0.7$; VPI $V_i = -4.0$ eV; $E_0 = 0$ eV.

Fe, 15–540 eV ($k = 2.5$–12 Å^{-1}) for Co, and 15–600 eV ($k = 2.5$–13 Å^{-1}) for Ni. For Co and Ni spectra, the theoretical fits were excellent.

For Mn, Fe and Co, the Y-shell contributions are insignificant. The long-to-short oxygen ratios for Mn (3/4), Fe (2/3) and Co (2.5/3.0) are approximately unity. A perusal of the data in tables 1–4 suggests 100% Cu(1) site occupancy for Mn, Fe and Co. The Mn–O distances of 1.81 Å and 1.99 Å are almost identical to the Cu–O distance. The Mn–Ba distance (3.37 Å) is slightly shorter than the Cu–Ba distance (3.4 Å). Owing to the short data range and strong background, distances are less well

Table 2. The coordination number N, the interatomic distance R and the mean square deviation σ^2 obtained from the EXAFS analysis for $YBa_2(Cu_{0.92}Mn_{0.08})_3 O_{7-\delta}$.

Neighbours	Present work [a]		
	N	R (Å)	σ^2 (Å^2)
Mn–O	4 ± 2	1.81	0.007 ± 0.003
Mn–O			
Mn–O	3 ± 2	1.99	0.006 ± 0.003
Mn–O			
Mn–O			
Mn–Y			
Mn–Ba	8 ± 3	3.37	0.015 ± 0.005
Mn–Ba			
Mn–Mn			

[a] AFAC $A(k) = 0.7$; VPI $V_i = -4$ eV; $E_0 = 18$ eV.

Table 3. The coordination number N, the interatomic distance R and the mean square deviation σ^2 obtained from the EXAFS analysis for $YBa_2(Cu_{1-x}Fe_x)_3 O_{7-\delta}$. The N-, R- and σ^2-values reported by others are included for comparison.

Neighbours	Present work [a] $x = 0.02$			Yang *et al* (1989) $x = 0.05$		Bridges *et al* (1989) $x = 0.033$	
	N	R (Å)	σ^2 (Å^2)	N	R (Å)	N	R (Å)
Fe–O	3 ± 1.5	1.79	0.008 ± 0.002	2.0	1.84	4.2	1.84
Fe–O							
Fe–O	2 ± 1	1.86	0.005 ± 0.002	2.2	1.94		
Fe–O							
Fe–O				0.67	2.3	1	2.4
Fe–Y							
Fe–Ba	5 ± 3	3.18	0.015 ± 0.005		$\simeq3.50$		
Fe–Ba							
Fe–Fe	$\simeq2$	3.79	$\simeq0.001$				

[a] AFAC $A(k) = 0.7$; VPI $V_i = -4$ eV; $E_0 = 22$ eV.

defined (±0.05 Å) than usual. The coordination numbers of the Mn–O shells are 4 ± 2 at 1.81 Å and 3 ± 2 at 1.99 Å. The σ^2-values vary in a similar way to those for Cu; the Mn–O bonds are rigid and well defined.

For the 3 at.% Ni-substituted sample, the FT of the EXAFS is similar to that for Cu, showing a triple-peak cation correlation. The Ni–O correlation was fitted with 1.5 ± 1 atoms at 1.87 Å and 4 ± 1 atoms at 1.94 Å. The Debye–Waller factors for both are very small. The cation distances were fitted as Ni–Y at 3.27 Å, Ni–Ba at 3.32 Å and Ni–Cu at 3.95 Å, almost identical to those for Cu. The results suggest that in the 3 at.% Ni-substituted sample, Ni occupies both Cu(1) chain and Cu(2) plane sites in equal proportions.

The FTs of EXAFS for 6 and 10 at.% Ni show a strong Ni–Ni peak at about 3 Å dominating the spectra. We identify this peak as due to the presence of NiO in these samples. We used the known NiO crystal structure (NaCl type with Ni–O at 2.07 Å and Ni–Ni at 2.95 Å) and the results of our fit to determine the amount

Table 4. The coordination number N, the interatomic distance R and the mean square deviation σ^2 obtained from the EXAFS analysis for $YBa_2(Cu_{1-x}Co_x)_3O_{7-\delta}$. The N-, R- and σ^2-values reported by others are included for comparison.

| | Present work [a] | | | | | | Bridges et al (1989) | | | |
| | x = 0.04 | | | x = 0.08 | | | x = 0.03 | | x = 0.07 | |
Neighbours	N	R (Å)	σ^2 (Å²)	N	R (Å)	σ^2 (Å²)	N	R (Å)	N	R (Å)
Co–O	3±1.5	1.75	0.004±0.002	3±1.5	1.74	0.003±0.001	3.6	1.80	3.4	1.81
Co–O										
Co–O	2.5±1	1.88	0.002±0.002	2.5±1	1.86	0.002±0.001				
Co–O							1.6	2.42	1.4	2.35
Co–Y										
Co–Ba	3±3	3.13	0.010±0.005	5.5±3	3.11	0.020±0.005				
Co–Ba										
Co–Co	≃4	3.77	≃0.01	≃4	3.76	≃0.01				

[a] AFAC $A(k) = 0.7$; VPI $V_i = -4$ eV; $E_0 = 11$ eV.

Table 5. The coordination number N, the interatomic distance R and the mean square deviation σ^2 obtained from the EXAFS analysis for $YBa_2(Cu_{1-x}Ni_x)_3O_{7-\delta}$. The N-, R- and σ^2-values reported by others are included for comparison.

| | Present work [a], x = 0.03 | | | Bridges et al (1990), x = 0.033 | |
Neighbours	N	R (Å)	σ^2 (Å²)	N	R (Å)
Ni–O	1.5±1	1.87	0.002±0.002	0.76	1.85
Ni–O					
Ni–O	4±1	1.94	0.011±0.004	3.8	1.95
Ni–O					
Ni–O	1±1	2.23	0.005±0.003	0.85	2.42
Ni–Y	2±1	3.27	0.005±0.002	3.1	3.26
Ni–Ba	7±2	3.32	0.007±0.004	3.1	3.33
Ni–Ba				3.1	3.49
Ni–Ni	≃4	3.95	≃0.007	≃4	3.97

[a] AFAC $A(k) = 0.7$; VPI $V_i = -4$ eV; $E_0 = 18$ eV.

of Ni present as NiO. The remaining Ni is assumed to be in the 1:2:3 lattice. We scaled our measured coordinates (to allow for the NiO fraction) before trying to identify the site occupancy. The corrected Ni contents in the $YBa_2(Cu_{1-x}Ni_x)_3O_{7-\delta}$ samples with $x = 0.03$, 0.06 and 0.10 were found to be 3 at.%, 4±1 at.% and 4±1 at.%, respectively. The EDAX also reveals that Ni incorporation in the grains of the 1:2:3 compound is limited to about 4 at.% (Mehta et al 1991). The proportion of segregated NiO in the 1:2:3 compound estimated by us is similar to that found by neutron diffraction (Balagurov et al 1991) as well as by EXAFS studies (Bridges et al 1990).

For all the three Ni-substituted 1:2:3 samples, clear occupancy of Ni on both Cu(1) and Cu(2) sites is evident. The Ba-to-Y ratio of 3/4 and long-to-short oxygen ratio of 3/5 both indicate roughly equal occupancies of Cu(1) and Cu(2) sites. The contribution of the Y shell is always significant (the third oxygen shell is marginally

Table 6. The coordination number N, the interatomic distance R and the mean square deviation σ^2 obtained from the EXAFS analysis for $YBa_2(Cu_{1-x}Ni_x)_3O_{7-\delta}$.

	Present work [a]					
	$x = 0.06$			$x = 0.10$		
Neighbours	N	R (Å)	σ^2 (Å^2)	N	R (Å)	σ^2 (Å^2)
Ni–O	1±0.5	1.87	0.002±0.002	0.5±0.5	1.87	0.002±0.002
Ni–O						
Ni–O	3±1	1.94	0.011±0.004	2.5±1	1.94	0.011±0.004
Ni–O						
Ni–O	1±1	2.24	0.007±0.005	1±1	2.24	0.007±0.005
Ni–Y	1.5±1	3.27	0.007±0.004	1±1	3.27	0.007±0.004
Ni–Ba	4.5±1.5	3.32	0.007±0.004	4±2	3.26	0.022±0.005
Ni–Ba						
Ni–Ni	≃2	3.95	0.007	≃3	3.91	≃0.010

[a] AFAC $A(k) = 0.7$; VPI $V_i = -4$ eV; $E_0 = 18$ eV.

Table 7. The coordination number N, the interatomic distance R and the mean square deviation σ^2 obtained from the EXAFS analysis for NiO. The N-, R- and σ^2-values reported by others are included for comparison.

Shells in NiO	Structural parameters	Balagurov *et al* (1991) neutron diffraction	Present work		
			3 at.% Ni	6 at.% Ni	10 at.% Ni
O	N	6	0	2±1	3.5±1.5
	R (Å)	2.08	—	2.06	2.06
	σ^2 (Å^2)	—	—	0.005±0.002	0.005±0.002
Ni	N	12	0	3.5±1.5	6±1
	R (Å)	2.98	—	2.93	2.93
	σ^2 (Å^2)	—	—	0.005±0.002	0.005±0.002
O	N	8	—	—	—
	R (Å)	3.6	—	—	—
	σ^2 (Å^2)	—	—	—	—
Ni	N	6	0	2±1	4±1
	R (Å)	4.2	—	4.24	4.24
	σ^2 (Å^2)	—	—	0.005±0.002	0.005±0.002

so). The Ni–O distances are 1.87, 1.94 and 2.24 Å. The σ^2-values are rather large especially for the 1.94 Å shell; the Ni–Ba distance is short but σ^2 is very similar to that for Cu–Ba. The Ni–Y distance is the same as the Cu–Y distance with small σ^2. The NiO shells are all well ordered with σ^2 very similar to those in the pure crystal.

The data collected in table 3 for Fe and in table 4 for Co dopants indicate that our Fe–O and Co–O distances are shorter than those reported by others (Bridges *et al* 1989, Yang *et al* 1989). The shortening of the Fe–Ba and Co–Ba bond lengths accompanied by variations in the coordinations gives an impression of a distorted site. The possibility of a distortion has been predicted by Bridges *et al* (1989) from their model calculations, but we find that the σ^2-values for oxygen in both the Fe and the Co cases are very small and very similar to those found for Cu–O, indicating a well defined environment with very rigid bonds and thus contradicting the idea of

distortion. This aspect, however, requires further investigation.

It is of interest to find the way in which the valuable structural information obtained from our EXAFS experiments helps us to understand the superconducting behaviour of the 1:2:3 system. EXAFS studies of the 3d-ion-substituted 1:2:3 compounds have revealed that Mn, Fe and Co dopants occupy only the Cu(1) site; Ni goes to both the Cu(1) and the Cu(2) sites in the ratio of 1:1. Since the 1:2:3 unit cell has two Cu(2) sites and only one Cu(1) site, the Ni concentration at the Cu(1) chain site is nearly twice that of the Cu(2) plane site. Although EXAFS has not been able to provide site occupancy information for Zn because of the strong background resulting from the interference of the adjacent Cu K edge, it has been inferred from XANES studies (Yang *et al* 1990, Mehta 1991) that Zn occupies the Cu(2) plane site. Further, the ionic radius of Zn^{2+} (0.68 Å) for five coordination allows little possibility that Zn occupies the interstitial defect site in the 1:2:3 lattice.

Our XRD measurements have shown that Mn, Ni and Zn in the 1:2:3 compound retain an orthorhombic structure while Fe- and Co-substituted samples exhibit a structural phase transition from orthorhombic to tetragonal (Padalia *et al* 1991). The oxygen content remains nearly the same (i.e. $O_{6.90}$) for Mn, Ni and Zn substitutions but increases to more than $O_{6.90}$ commensurate with the Fe and Co concentrations; for example for 8 at.% Fe and Co, the oxygen contents are 6.95 and 7.04, respectively (Mehta 1991, Padalia *et al* 1991). It is found that the effect of any of these 3d ion substitutions on T_c has been detrimental. The extent of the decrease in T_c and its rate of decrease with increasing concentration x are dependent on the dopant ions although no definite trend is apparent from the T_c versus x plots shown in figure 5. For Mn- and Zn-substituted samples with $x = 0.04$, the T_c-value and the slopes of the T_c versus x plots are quite different. This observation is difficult to explain on the basis of structure (orthorhombic) and oxygen concentration ($O_{6.90}$) which remain the same for both Mn and Zn. It appears that T_c is relatively more sensitive to substitution at the plane site as in the case of Zn than at the chain site as in the case of Mn. This contention is also true for the case of Ni substitution in the 1:2:3 compound in which Ni goes to both the Cu(1) and the Cu(2) sites, as revealed by EXAFS studies. The slope of the T_c versus x plot for Ni falls between those of Mn and Zn (figure 5).

Further, it is apparent from figure 5 that, for small concentrations $x \leqslant 0.02$, the decreases in T_c for Mn, Ni and Zn are nearly the same (i.e. $T_c \simeq 81$ K for $x = 0.02$), suggesting that statistically one Cu ion replacement (for either the chain or the plane site) out of 14 unit cells has not reflected the relative importance of the Cu chain or Cu plane site in affecting T_c. However, it may be stated that one of the common problems in 1:2:3 samples (both substituted and unsubstituted) synthesized in different laboratories or at different times in the same laboratory is that of slight variation in the lattice oxygen content and the possibility of a wide variation in oxygen ordering at the Cu(1) site leading to a scatter in the values of T_c.

A careful look at the T_c versus x plots (figure 5) reveals that the drop in T_c is steeper for Fe than for Mn beyond $x = 0.04$. On the other hand, Mn^{2+} and Fe^{3+} have the same ($3d^5$) electronic configuration as revealed by our XANES and XPS studies (Padalia and Mehta 1989, Mehta 1991). Further, the present EXAFS studies reveal that both Fe^{3+} and Mn^{2+} dopants occupy only the Cu(1) chain site. The observed steeper decrease in T_c for Fe^{3+} than for Mn^{2+} can, therefore, be attributed to an enhanced oxygen content ($O_{6.95}$) in the case of the Fe-substituted 1:2:3 compound. Fe in the trivalent state favours higher oxygen coordination (coordination of five),
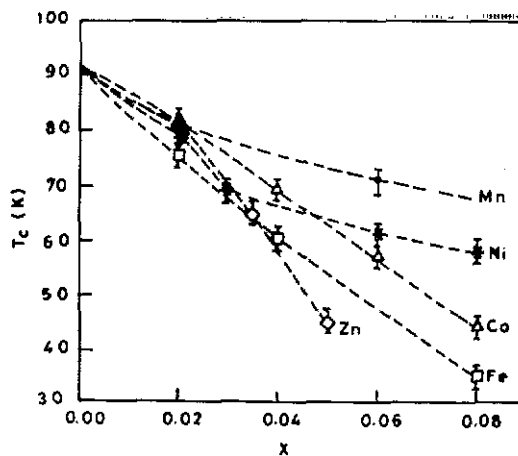
Figure 5. Variation in T_c with 3d ion dopant concentration x in the samples of nominal composition $YBa_2(Cu_{1-x}M_x)_3O_{7-\delta}$ ($M \equiv$ Mn, Ni, Co, Fe and Zn): – – –, guide to the eye. The samples are of 1:2:3 single phase except for those containing Ni for which the Ni content in the 1:2:3 compound is limited to about 3 at.% (for details, see text).

leading to disordering of oxygen along the *b* direction in the Cu(1) chain site and driving the structure from orthorhombic to tetragonal. The disruption of oxygen ordering in the presence of Fe^{3+} leads to the breaking of some of the Cu 3d–O 2p bonds, resulting in a steeper drop in T_c. A similar argument can be extended to the case of Co substitution at the Cu(1) site in the 1:2:3 compound. The way in which the magnetic character of the substituent 3d ions influences T_c in the 1:2:3 compound is not obvious, however.

It may be stated that there are not many reports on the study of the 1:2:3 system with Mn substitution. Jardim and Gama (1989) have observed no change in T_c with Mn substitution to the extent of 20 at.% Mn in the nominal 1:2:3 composition. However, the extent to which Mn forms solid solutions in the 1:2:3 matrix is not clear from their studies. Further, they have reported single-phase 1:2:3 formation for less than 5 at.% Mn substitution. Our 1:2:3 samples with a Mn substitution of 8 at.% or less have revealed no impurity phase by XRD. The EXAFS data on 8 at.% Mn-substituted samples of nominal composition $YBa_2(Cu_{0.92}Mn_{0.08})_3O_{7-\delta}$ have also not indicated any Mn clustering and impurity phases as observed in the case of Ni (above 3 at.%). Further, our EXAFS results indicate only a slight change in the Mn–Ba distance (3.37 Å) compared with that of the Cu–Ba distance (3.40 Å), and the σ^2-values are very similar to those for Cu, suggesting that the 8 at.% Mn has not created any significant lattice distortions in the 1:2:3 structure.

5. Conclusions

The results of our EXAFS studies on Mn, Fe, Co, Ni and Zn ions substituted in the 1:2:3 compound lead to the following conclusions.

(i) The EXAFS findings on the Mn dopant are new and are reported for the first

time. It is found that Mn which is in the 2+ state occupies only the Cu(1) chain site without producing any significant distortion of the 1:2:3 lattice.

(ii) Our EXAFS results agree with the earlier reports and firmly establish the fact that Fe and Co dopants occupy only the Cu(1) site but we do not support the idea of distortion of the lattice.

(iii) It is found that Ni ions are distributed nearly equally between Cu(1) chain and Cu(2) plane sites in the 1:2:3 lattice. For $x > 0.03$, some of the Ni separates as NiO. The identification of the NiO impurity phase exhibits the strength of EXAFS in the study of dopants. The maximum Ni content in the Ni-substituted 1:2:3 samples has been estimated to be 4 ± 1 at.%.

(iv) No useful data could be obtained for Zn dopant owing to interference from the adjacent Cu K edge.

(v) T_c is relatively more sensitive to substitution at the Cu(2) plane site than at the Cu(1) chain site.

(vi) Oxygen disorder in the lattice due to doping leads to a steeper decrease in T_c.

(vii) Finally, it may be stated that the present EXAFS data have provided valuable structural information on 3d ion dopants in 1:2:3 compounds although direct correlation with superconducting behaviour is yet to be established.

Acknowledgments

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