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K XANES studies of 3d transition metal dopants in $\text{YBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_{7-\delta}$; $x \leq 0.10$ and $\text{M} = \text{Mn to Ni and Zn}$

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Abstract. In continuation of our earlier report on the EXAFS studies, we present here the results of K XANES measurements on the 3d dopants, Mn to Ni and Zn, in the 1–2–3 lattice. It is found, perhaps for the first time, that the Mn dopant in a 1–2–3 lattice is in a divalent state. It is inferred from the K XANES features that Mn occupies the Cu(1) chain site in the 1–2–3 lattice. The results of our consolidated K XANES measurements on the valence states of Fe, Co, Ni and Zn dopants are consistent with the earlier reports on these heavy 3d ions in 1–2–3 compounds.

1. Introduction

Substitutional studies of the 3d transition metal ions at the Cu sites in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (1–2–3) compound have been a subject of considerable interest [1–7]. We have made measurements on the K absorption edges and the associated fine structure of the heavy 3d ions in $\text{YBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_{7-\delta}$; $x \leq 0.10$ and $\text{M} = \text{Mn to Ni and Zn}$, using the synchrotron radiation source at Daresbury Laboratory. Valuable information on the environments of these dopants in 1–2–3 lattice obtained from the analysis of the extended x-ray absorption fine structure (EXAFS) data has been reported earlier [1]. Here, we discuss the results of our K XANES measurements on the 3d dopants, Mn to Ni and Zn, in the 1–2–3 system.

It is noted that several reports are available on the K edges and associated structure of Fe and Co dopants in 1–2–3 compounds [7–10]. Relatively, less attention has been paid to K XANES studies of 1–2–3 compounds with Ni and Zn dopants [10, 11]. This is, perhaps, the first report on the K XANES of Mn dopant in the 1–2–3 lattice.

2. Experiment

The samples of the 3d-ion-substituted 1–2–3 compounds, prepared by the standard solid state reaction route, were checked for single-phase formation using the XRD method. The details regarding preparation of the samples and their XRD analysis are given in our earlier paper [1]. The K XANES measurements were made with

a 2 GeV synchrotron radiation source at SERC, Daresbury Laboratory, UK. The experiments were performed on beam line 7.1 equipped with a Si(III) double-crystal monochromator. Since the dopant's concentrations in 1-2-3 compounds were rather low, the signals from dopants were collected in the fluorescence mode. In order to reduce the background, the fluorescence x-rays were filtered by a $15 \mu\text{m}$ ($Z-1$) metal foil placed in front of the scintillation counter. The experiments were performed at room temperature on finely powdered samples mounted on Scotch tape. The K XANES data were taken over a 300 eV pre-edge region and a closely spread edge region. Four to five spectra were taken for each sample. The spectral data were processed using the standard Daresbury programs [12] which take care of the background corrections.

3. Results and discussion

Figure 1 shows the K XANES of Mn ions in single-phase samples of $\text{YBa}_2(\text{Cu}_{1-x}\text{Mn}_x)_3\text{O}_{7-\delta}$: $x = 0.02, 0.04$ and 0.08 . The K absorption edge region of the Mn metal foil is included in the figure. It is apparent from the figure that the observed spectral features for $x = 0.02$ are weak and the intensity increases with an increase in Mn concentration (x) as is expected.

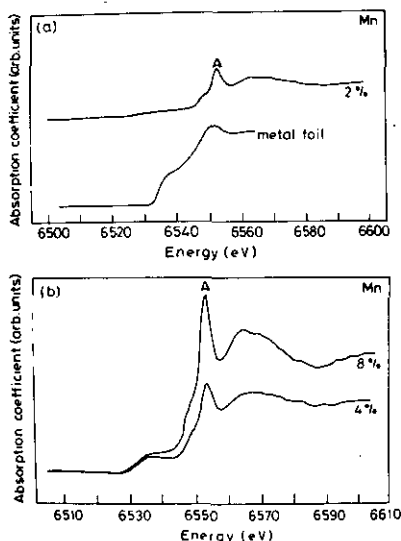


Figure 1. K XANES of the Mn ion in the single-phase samples of $\text{YBa}_2(\text{Cu}_{1-x}\text{Mn}_x)_3\text{O}_{7-\delta}$; (a) $x = 0.02$, (b) $x = 0.04$ and 0.08 . For comparison, the K edge region of Mn metal foil is included in (a).

The energy of the edge position is taken to be at the maximum in the first derivative of the absorption coefficient (μ) that corresponds to inflection point in the initial rise of the edge [13]. The changes in the energy of the Mn edge position (chemical shifts, ΔE) in $\text{YBa}_2(\text{Cu}_{1-x}\text{Mn}_x)_3\text{O}_{7-\delta}$ compounds measured with respect to the Mn metal edge position are given in table 1. For the purpose of comparison,

Table 1. Shifts of the K absorption edge and the main peak position of Mn dopant in $\text{YBa}_2(\text{Cu}_{1-x}\text{Mn}_x)_3\text{O}_{7-\delta}$ compounds (uncertainty in the oxygen estimation ($\text{O}_{7-\delta}$) is ± 0.02).

Samples	Shifts ^a of			
	K absorption edge, ΔE (eV) (± 0.5 eV)	Main peak position, ΔE^b (eV) (± 0.5 eV)	Valence state of Mn ion	Effective charge, q (electron per atom)
Mn (metal)	00.0	11.0		
MnO	5.4	16.2	2	0.64
Mn_3O_4	10.0	20.3	2, 3	1.16
Mn_2O_3	12.0	23.5	3	1.38
$\text{YBa}_2(\text{Cu}_{0.98}\text{Mn}_{0.02})_3\text{O}_{6.89}$	5.5	18.3		0.65
$\text{YBa}_2(\text{Cu}_{0.96}\text{Mn}_{0.04})_3\text{O}_{6.90}$	5.5	18.3	2 ^b	0.65
$\text{YBa}_2(\text{Cu}_{0.92}\text{Mn}_{0.08})_3\text{O}_{6.90}$	5.5	18.3		0.65

^a Shifts were measured with respect to the Mn metal edge position: $\Delta E = (E_{\text{K edge}})_{\text{compound}} - (E_{\text{K edge}})_{\text{metal}}$; $\Delta E^* = (E_{\text{main peak}})_{\text{compound}} - (E_{\text{K edge}})_{\text{metal}}$.

^b Estimated by comparison of shifts.

the chemical shifts (ΔE) for Mn oxides with well known valence states are included in the same table.

The effective charge (q) on the absorbing Mn ion calculated from the measured edge shifts (ΔE) using the semi-experimental method of Gianturco and Coulson [14] are listed in table 1. The method essentially requires a knowledge of the theoretically calculated values of binding energies (BE) as a function of oxidation number of the ion in question. Values of BE for several ions, calculated using an analytical self-consistent field procedure, are available in the form of tables [15]. Shifts in BE are plotted against the oxidation number. This plot is used to estimate the values of q corresponding to the measured value of edge shift (ΔE). The method has been used earlier effectively for estimating the q values on the absorbing ions in simple as well as complex systems [13, 16, 17].

We have also measured the energy shifts (ΔE^*) of the main peak, A (figure 1), with respect to the Mn metal edge position. The values of ΔE^* for Mn-doped 1-2-3 compounds are given in table 1. ΔE^* values measured for Mn oxides are also given in the same table.

A perusal of the data collected in table 1 indicates that the values of ΔE (and ΔE^*) for the Mn dopant in 1-2-3 compounds are of nearly the same magnitude as those obtained for the divalent Mn in MnO. The observation indicates that Mn dopant in the 1-2-3 lattice is in the divalent state. The trend in the estimated values of q lends support to this finding. The result of the present study, that Mn dopant in the 1-2-3 lattice is in a 2+ state, is new and has not been reported earlier.

Further, it is noted that ΔE and ΔE^* indicate no significant change in their values with x , the Mn concentration in 1-2-3 compounds. The results suggest that Mn, irrespective of its concentration, retains a divalent character in the 1-2-3 compounds.

It may be stated here that our earlier iodometric titration measurements, Cu K XANES [3, 7] and EXAFS studies [1] have revealed that: (i) the lattice oxygen content ($\text{O}_{7-\delta}$) remains unaffected; (ii) the Mn dopant occupies the Cu(1) chain site in the 1-2-3 lattice without any distortions; and (iii) the valence of Cu (2+) remains

unchanged on Mn substitution at the Cu site in the 1-2-3 lattice. Since the Mn dopant as well as the host Cu ion in the 1-2-3 lattice are in the 2+ state and have the same ionic radii, the above findings are not surprising. Further, the observed fall in T_c from ~ 91 K down to ~ 71 K with increasing Mn concentration, x , in the 1-2-3 lattice [3] can be attributed to the replacement of Cu(1) at the chain site by Mn^{2+} dopant in 1-2-3, thus affecting the Cu 3d-O 2p hybridization strength and thereby resulting in the fall of T_c .

Along lines similar to those followed for the Mn dopant, we have also analysed the K XANES data collected for the other 3d dopants, Fe to Ni and Zn in 1-2-3, to find the valence states of these ions. The present results have been found to be consistent with those reported by others [8-11] establishing that Ni and Zn exist in a 2+ state while Fe and Co ions are predominantly in the trivalent state. Since the present K XANES features of Fe, Co, Ni and Zn closely resemble those reported earlier [8-11], we are not reproducing the spectra here.

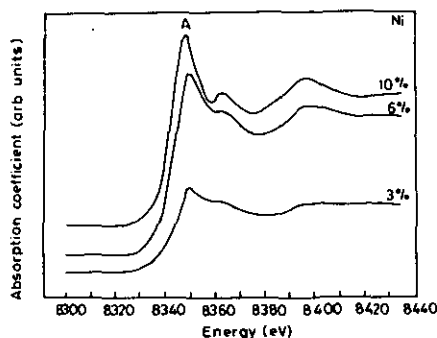


Figure 2. K XANES of Ni dopant in the samples of nominal composition $YBa_2(Cu_{1-x}Ni_x)_3O_{7-\delta}$; $x = 0.03, 0.06$ and 0.10 . For $x = 0.10$, the Ni K XANES features closely resemble the spectrum of NiO (not shown).

However, our observations on Ni dopant in 1-2-3 are not quite the same as those reported by Yang *et al* [10] and Qian *et al* [11]. The results on K XANES of Ni dopant, therefore, require some discussion. Figure 2 shows the K XANES of Ni dopant in the samples of nominal composition $YBa_2(Cu_{1-x}Ni_x)_3O_{7-\delta}$, $x = 0.03, 0.06$ and 0.10 . All the spectra are plotted to the same energy scale (100 eV in 10 cm). It is apparent from figure 2 that the spectral features change and the spectra shift towards the lower energy side with increase in the Ni dopant concentration from $x = 0.03$ to $x = 0.10$. The spectral features for $x = 0.03$ are similar to Cu K XANES in a 1-2-3 lattice while those for $x = 0.10$ closely resemble the K XANES of Ni in NiO [10]. The Ni K edge for $x = 0.06$ exhibits a shift and lies between the K edges for $x = 0.03$ and 0.10 (figure 2).

Our Ni K XANES results for $x = 0.03$ agree well with those of Yang *et al* [10] and Qian *et al* [11] for 2 at.% Ni in a 1-2-3 lattice. However, the present observations for 6 at.% Ni dopant in a 1-2-3 lattice are different from those reported by Yang *et al*. It is noted that Yang *et al* have not observed any change in their K XANES of 6 at.% Ni in 1-2-3 compounds. They have argued that their Ni-doped samples did not contain an NiO impurity and that the discrepancy between their results and

those of Qian *et al* was due to differences in their samples. On the other hand, our observations suggest the presence of an NiO impurity. Support for this contention has been obtained from the analysis of our EXAFS data on the same Ni-doped 1-2-3 samples showing that for $x > 0.03$, a part of the Ni separates out as NiO [1]. It is interesting to note that the EXAFS reports of Bridges *et al* [18] and the neutron diffraction studies of Balagurov *et al* [19] lend further support to our findings.

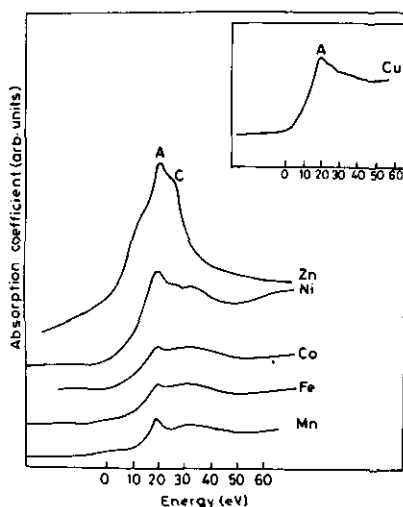


Figure 3. K XANES features of Mn along with the spectra of Fe, Co, Ni and Zn dopants in 1-2-3. The inset shows the K XANES of Cu in the 1-2-3 compound. For comparison, the K edge position for each dopant (as well as for host Cu ion) is taken as zero of the energy scale.

An attempt to obtain information on the site occupancy from the K XANES of Fe, Co, Ni and Zn dopants in 1-2-3 lattice has been made by Yang *et al* [10]. It is of interest to see if such information on the site preference of Mn in a 1-2-3 lattice can be extracted from the K XANES of Mn. We have, therefore, collected in figure 3, the K XANES of Mn along with the spectra of Fe, Co, Ni and Zn dopants. For the purpose of comparison, K XANES of Cu in a 1-2-3 lattice is also shown in the inset. Here, the K edge position for each dopant is taken as zero on the energy scale. A comparison of the gross spectral features reveals that the K XANES of Mn is similar to those of Fe and Co. Since Fe and Co are known to occupy the Cu(1) chain site [8, 9], it can be inferred that the Mn dopant also goes to the Cu(1) chain site in a 1-2-3 lattice. It should be mentioned here that our EXAFS findings [1] support the inference drawn from the present Mn K XANES studies.

4. Conclusions

(i) The K XANES measurements on the Mn dopant in a 1-2-3 lattice are reported, perhaps for the first time. It is found that the Mn ion exists in the divalent state and occupies the Cu(1) chain site in the 1-2-3 lattice.

(ii) For Ni concentrations $x > 0.03$ in nominal 1–2–3 composition samples, a part of Ni segregates as NiO impurity.

(iii) Results of the present consolidated K XANES studies on the heavy 3d dopants in 1–2–3 are consistent with earlier reports, confirming that Ni and Zn are in a 2+ state while Fe and Co dopants are predominantly in the trivalent state.

Acknowledgments

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