

Mössbauer study of 3d-ion-substituted $\text{YBa}_2(\text{Cu, Fe, M})_3\text{O}_{7-\delta}$; $\text{M} = \text{V, Mn}$

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Abstract. ^{57}Fe Mössbauer investigations at 300 K have been carried out on V, Mn substituted $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ system. Preliminary studies show that for small concentration of V (4%), Fe occupies preferentially the Cu(1) site whereas for the same concentration of Mn, Fe prefers the Cu(2) site. It is suggested that for low concentrations V has a preference for Cu(2) site whereas Mn prefers Cu(1) site in the 1-2-3 lattice.

Keywords. ^{57}Fe Mössbauer; $\text{YBa}_2\text{Cu}_3\text{O}_7$ substituted; manganese; vanadium.

1. Introduction

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (1-2-3) is a well-established oxide superconductor (SC) with $T_c \sim 92$ K for $\delta \leq 0.1$. This system is extensively investigated for its superconducting behaviour as a function of ionic substitution on the various sites. The 3d character of the ionic substitution onto the Cu-site has been observed to influence the superconducting behaviour in a significant manner. Several transport and susceptibility studies have been reported in the literature on this aspect (Xiao *et al* 1987; Tarascon *et al* 1988; Mehta *et al* 1989). These studies, however, do not reveal the relative site occupancy of the substituted 3d-ion on the two inequivalent copper sites. Neutron diffraction, Mössbauer and NMR techniques can be fruitfully employed to get an insight into the structural and site occupancy aspects. For example, neutron diffraction has revealed in Fe-substituted 1-2-3 that the vacant chain sites are partly filled by an excess of oxygen commensurate with Fe-substitution (Howland *et al* 1989). A careful NMR and Mössbauer study allows us to distinguish between the two inequivalent Cu sites in the 1-2-3 compound.

In our earlier paper on $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-\delta}$; $0.02 \leq x \leq 0.08$ by Mössbauer studies, we have shown (Shringi *et al* 1989) that Fe substitutes Cu on both the pyramidal-coordinated Cu(2) and 4-oxygen coordinated Cu(1) chain sites in varying proportions depending upon the amount of Fe substitution. In this paper we report the ^{57}Fe Mössbauer studies on the vanadium and manganese-substituted 1-2-3 compound.

2. Experimental

Samples of $\text{YBa}_2(\text{Cu}_{0.98-x}\text{Fe}_{0.02}\text{M}_x)\text{O}_{7-\delta}$; $\text{M} = \text{Mn, V}$ and $x = 0.0, 0.04, 0.08$ were prepared by the standard ceramic technique (Prakash *et al* 1988) using proportionate quantities of high purity ($\geq 99.9\%$) Y_2O_3 , BaCO_3 , Fe_2O_3 , CuO , MnO_2 and V_2O_5 as starting materials. The sintered pellets were annealed in oxygen for several hours at 650–450°C. All the samples characterized by XRD (CuK_α radiation) were found to be

single-phase (phase purity $\geq 96\%$) orthorhombic 1-2-3. The structure, however, was driven close to tetragonal for all the compositions.

For the Mössbauer measurement the samples were crushed to powder form and then glued to celloctapes to form the absorber. A 10 mCi Co^{57} (Rh) source was used in the experiment. An electromechanical transducer employed in constant acceleration mode was calibrated using 25 μm thick $\alpha\text{-Fe}$ absorber. The MCA used a PC to control the data acquisition operation. The 14.4 keV γ -ray peak was very carefully selected using a 1024 channel ADC. As the absorbers contained a very small fraction of non-enriched iron, around 2.5 million counts were collected per channel to give statistically significant spectra. The data reported here were collected at 300 K.

A computer program was utilized to deconvolute the four Lorentzian in a typical spectrum. The parameters like base line counts and intensities of individual doublets were evaluated by this program using a non-iterative optimization whereas an iterative grid search procedure was employed to determine the linewidths and peak positions of the Lorentzians. The doublets were subjected to constraints such that the intensity ratio within a doublet was taken to be 1:1 and linewidths for Lorentzians within a doublet were taken to be equal. The goodness-of-fit parameter was better than 1 for all the spectra.

3. Results and discussion

Mössbauer spectra (MS) of $\text{YBa}_2(\text{Cu}_{0.98-x}\text{M}_x\text{Fe}_{0.02})_3\text{O}_{7-\delta}$; $\text{M} = \text{Mn}, \text{V}$ are shown in figure 1. The Mössbauer spectrum for $x = 0$ sample was earlier reported (Shringi *et al* 1989). The parameters from the analysis of the MS are given in table 1. All the spectra were fitted with two quadrupole doublets which indicate that Fe ions occupy the two inequivalent Cu(1) and Cu(2) sites albeit in different concentrations. Neither of the two sites has a quadrupole splitting (QS) characteristic of an octahedral co-ordination of oxygen around Cu. On the basis of isomer shift systematics and quadrupole splitting we have assigned Fe substituting Cu(2) site to be in high spin Fe^{3+} state and Fe-substituting Cu(1) site having valence state between Fe^{3+} and Fe^{4+} state. This suggests that a small fraction of Fe ions on the Cu(1) site is in the Fe^{4+} state (Shringi *et al* 1989). We further see from table 1 that the area ratio at the resonance lines for outer and inner doublets, $A_{\text{I}}/A_{\text{II}}$, is 0.41. This indicates that Fe substitutes almost statistically on both the Cu(1) and Cu(2) sites. This area ratio gets significantly altered on the substitution of V and Mn at the Cu-site. For small concentration of V ($x = 0.04$), Fe occupies

Table 1. Mössbauer parameters for $\text{YBa}_2(\text{Cu}_{0.98-x}\text{M}_x\text{Fe}_{0.02})_3\text{O}_{7-\delta}$.

Composition (x)	Sq. planar site outer doublet(I)		Pyramidal site inner doublet(II)		Area ratio $A_{\text{I}}/A_{\text{II}}$
	IS(mm/s)	QS(mm/s)	IS(mm/s)	QS(mm/s)	
0.00	0.01	2.01	0.23	0.48	0.41
0.04 M = V	-0.125	1.69	0.155	0.37	0.66
0.06 M = V	-0.01	1.76	0.13	0.36	0.39
0.04 M = Mn	-0.08	1.83	0.18	0.39	0.12
0.06 M = Mn	-0.05	1.84	0.15	0.36	0.35

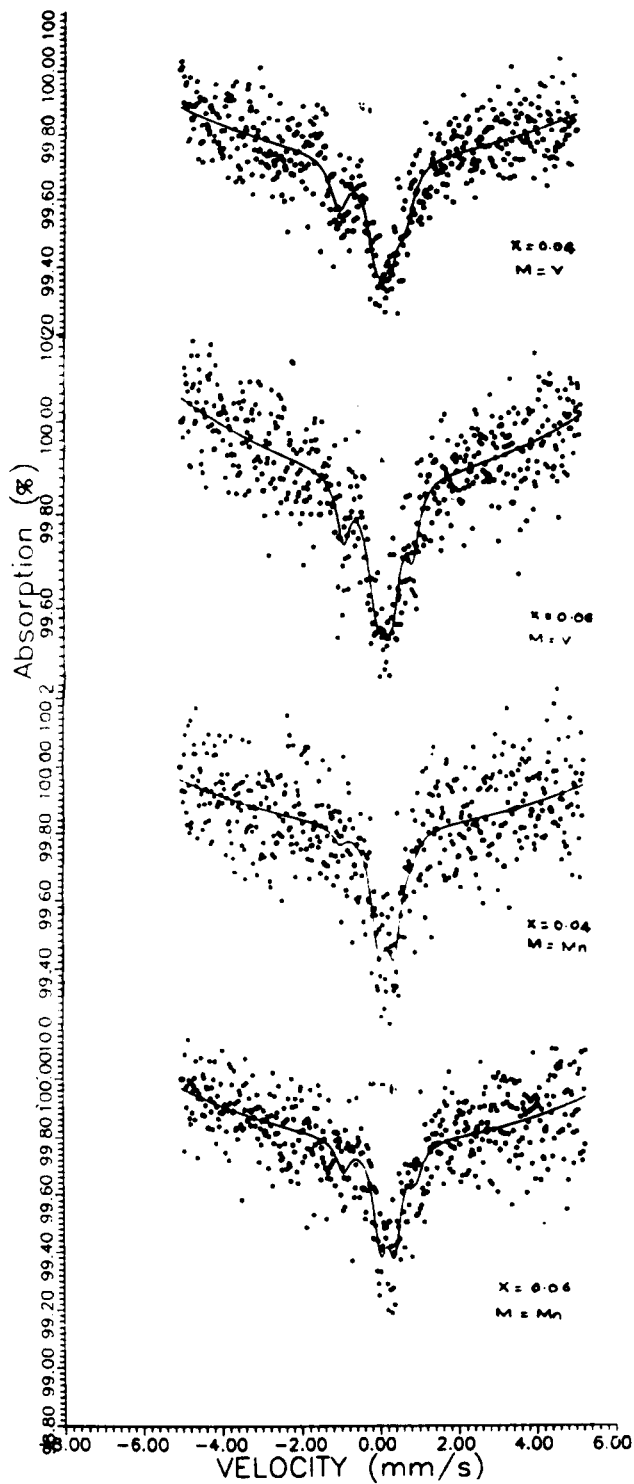


Figure 1. Mössbauer spectra of $YBa_2(Cu_{0.98-x}M_xFe_{0.02})_3O_{7-\delta}$ at 300 K. $M = V, Mn$; $x = 0.04, 0.06$.

preferentially the Cu(1) chain site, whereas, for the same concentration of Mn, Fe occupies preferentially the pyramidal coordinated Cu(2) site. Further increase in the concentration of the substituted ion ($x = 0.06$), the preferential occupation of Fe in case of Cu(1) chain site for V and Cu(2) site for Mn is no longer observed. Fe appears to approach the statistical distribution on both the sites for larger V and Mn ($x \geq 0.06$) concentrations.

A tentative explanation on the basis of ionic radii can be offered for the above observations. Our XPS data (Mehta *et al* 1989) indicate that V and Mn in the samples are in pentavalent and divalent states respectively. It is not surprising therefore that V^{5+} which has ionic radius of 0.59 \AA could prefer to occupy the smaller interstitial pyramidal Cu(2) site and in turn drives Fe on to the chain site. For Mn^{2+} which has larger ionic radius (0.80 \AA), one expects it to occupy the Cu(1) chain site. This is indeed observed. In case of $x = 0.06$, a near statistical distribution of Fe on both the sites is rather intriguing and is not well understood. This needs an extensive investigation of the system substituted with V or Mn over a large range.

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