

An Aspect of the Fe Distribution of $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_y$: Electrical and Mössbauer Studies.

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Oxygen-rich samples of $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_y$ with different concentrations have been prepared by solid state reaction in both superconducting (SC) and antiferromagnetic (AFM) phases. Electrical resistivity measurements indicated the preference of Fe to substitute Cu in Cu (1) sites for low iron concentrations in the SC phase. Mössbauer measurements have been carried out at room temperature, 77 K and 4.2 K in order to elucidate Fe distribution just below the SC-AFM phase transition of $x=0.45$ and up to $x=1$. From the analysis of the obtained MS spectra, it is concluded that in the SC phase with $x=0.4$, Fe substitutes Cu in both square planar and induced pyramidal Cu (1) sites. The latter is formed by oxygen filling the unoccupied O (5) site. With increasing iron content, Fe accommodated in Cu (2) sites prevail, together with the Cu (1) sites of pyramidal configuration. The obtained small QS values for Fe in Cu(2) sites suggest the formation of quasi-octahedral Fe site by additional oxygen atom insertion in the mid plane of the Cu (2)-O bilayer. At 4.2 K, a suppressed hyperfine ordering with B_{hf} value of 472 kOe is assigned to Fe in Cu (1) sites for the superconducting sample with $x=0.4$. On the other hand, a hyperfine field of 502 kOe, slightly increasing with x , is suggested to associate Fe in Cu (2) sites with subsequent increase in iron content.

Introduction:

Mössbauer technique (MS) has been widely utilized in studying oxide superconductors by substituting a part of Cu by ^{57}Fe in many superconducting systems [1-7]. On the basis of MS parameters one can differentiate between various lattice positions where MS probe atom is accommodated. After proper assignment information on the electronic, magnetic and vibrational properties of the host material may be obtained.

The high temperature superconducting $\text{YBa}_2\text{Cu}_3\text{O}_y$ ($y \approx 7$) possesses an orthorhombic structure with two different copper sites conventionally referred to as Cu (1) and Cu(2) with population of 1 to 2. Cu (1) has a square planar coordination due to the presence of two oxygen vacancies in the a-axis whereas Cu (2) has a tetragonal pyramidal coordination due to an oxygen vacancy in the c-axis.

^{57}Fe studies on this system indicated that iron always replaces copper in some general sense and can do so both in the unique Cu (2) site as well as in several, but not all, of the n-coordinated $2 \leq n \leq 6$ ligand geometries. The population trends of the allowed ligand coordination are function of both iron concentration and oxygen content.

Four sites for ^{57}Fe atoms to accommodate namely A, B, C and D have been assigned by Lines and Eibschutz[8]. The A site was concluded to be associated with iron substituting for Cu (2) as HS Fe^{3+} ($s=5/2$). On the other hand, sites B, C and D are considered to associate iron substituting for Cu (1) where the electronic configuration of iron in site B is almost certainly Fe^{3+} ($s=3/2$), site D is probably Fe^{2+} ($s=1$) and site C is most likely Fe^{4+} ($s=2$). Other subsequent MS studies where the sites were differently labeled agreed with these assignments [3,6].

Most of the reported MS studies were devoted to discuss Fe distribution in the superconducting phase with low iron concentrations where $x \leq 0.45$ in the formula $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_y$. In the present study MS measurements are discussed just below ($x=0.4$) the SC-AFM phase transition and up to $x=1$. Complementary studies in the superconducting phase with $0.0 \leq x \leq 0.1$ are presented through electrical resistivity measurements.

Experimental**Samples preparation:**

Compounds with the stoichiometric compositions $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_y$ where $0.0 \leq x \leq 1.0$ have been prepared using the solid-state reaction technique. All raw materials were preheated at 150 C for two hours. The samples with different ratios of the $^{57}\text{Fe}_2\text{O}_3$ were mixed and then put under mechanical grinding for about an hour to get a homogeneous mixture. The samples were then heated at

500 C for 48 hours and the oven was switched off to cool to room temperature. After that the oven was turned on and adjusted at 900 C with the samples inside it for 9 hours in flowing oxygen. The obtained samples were secondly homogenated in good mixing powder form and then converted into pellets under a pressure of 8 tons/cm². These pellets were put in porcelain crucibles and introduced to an oven at 970 C for 12 hours with flow of oxygen gas for 8 hours from the beginning of this heating cycle. The resultant tablets were cooled to a temperature of 600 C with a rate of (1 C/min.), then the furnace was switched off to cool down to room temperature. The resultant materials were ground for an hour yielding a very fine powder and then converted again into pellets under a pressure of 10 ton/cm². These pellets were put into the furnace and heated at 980 C for 12 hours in air atmosphere. Then, the oven was left to cool down to 550 C with a cooling rate of 1.0 C/min. after which it was turned-off to cool down to room temperature.

The resistance measurements:

The resistance of the samples was determined using the conventional four-probe method. DC programmable current source "Keithley, Model 224" was used and a current of 10 mA was applied. The possibility of the disturbing thermopower was eliminated using a current source, which automatically changes the current polarity during the experiment. The measurements were done in the temperature range of 77- 290 K at a pressure of 10 torr A pt-100 No. 4097 thermocouple connected with a digital voltmeter "Keithley, Model 196 System DMM" was used for the temperature measurements. The voltage drop was detected using an accurate digital nanovoltmeter "Keithley Model 181". When the electric current I pass through the sample the voltage drop was recorded and the sample resistance R was obtained using Ohm's law. All the used system was computerized.

Mössbauer spectra measurements:

Mössbauer spectra were taken by a MS spectrometer having four cooling facilities: room-temperature, a continuous helium-flow cryostat for temperatures above 4.2 K, a liquid-helium with pumping facility for temperatures in the 1.3-4.2 K range and a 10 T superconducting magnet cryostat. In the flow cryostat measurements, the sample temperature was monitored using a carbon-glass resistor located in the sample mount. The uncertainty of the temperature measurements was ~ 0.1 K. The Mössbauer γ -ray sources were ⁵⁷Co/Rh and the constant acceleration spectrometer drives were operated in double-ramp (flat background) mode.

Results and Discussion:

Electrical resistivity:

Fig. (1) displays the temperature dependence of reduced resistivity $\rho(T)/\rho(300K)$ for the undoped and iron doped samples. It can be seen that samples with x -values up to 0.06 exhibit a metallic-like behaviour down to the onset temperature. On the other hand, a semiconducting behaviour which is reflected as an increase in resistivity with decreasing temperature just below T_c is observed for samples with higher x -values. This can be attributed to inhomogenities in the sampels or may reflect minor localization within the Cu-O planes due to increasing dopant content [9].

Fig. (2) illustrates the effect of iron substitution on the superconducting transition temperature T_c . The observed depression in T_c as a function of increasing x can be explained as follows: Iron is known to replace Cu preferentially in the Cu (1) sites and the oxygen content remains near 7 for $x \leq 0.03$ ⁽¹⁰⁾. For $x \geq 0.03$, the O (1) anion Fig. (3) along the b-axis in the Cu (1)-O chain becomes disordered partially occupying the O (5) site along the a-axis in the same plane which leads to an average tetragonality in the unit cell. Moreover, since Fe has a larger valence state than Cu, it attracts oxygen to maintain charge neutrality and tends to retain oxygen with y ranging from 6.9-7.2 as x increases [10,11]. Therefore, T_c remains constant and equal to ~ 90 K up to the orthorhombic-tetragonal transition and then decreases continuously due to:

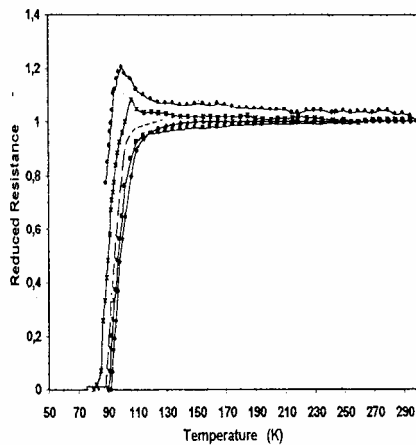


Fig. (1): Reduced resistivity as a function of temperature for undoped and iron doped samples: [$x=0$ (\bullet), $x=0.02$ (\circ), $x=0.04$ ($- -$), $x=0.06$ ($- -$), $x=0.08$ (x), and $x=0.1$ (\blacklozenge).

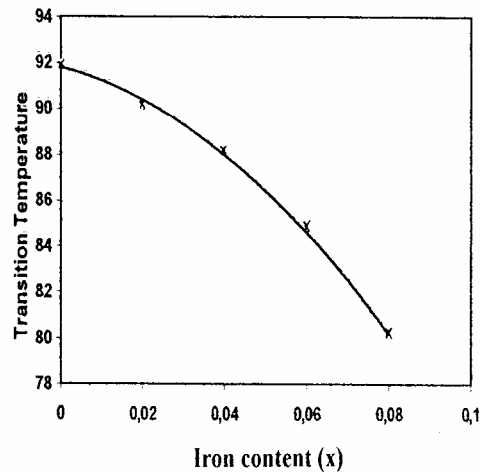


Fig. (2): Variation in the superconducting transition temperature T_c for samples with different iron content (x) in $YBa_2Cu_{3-x}Fe_xO_y$.

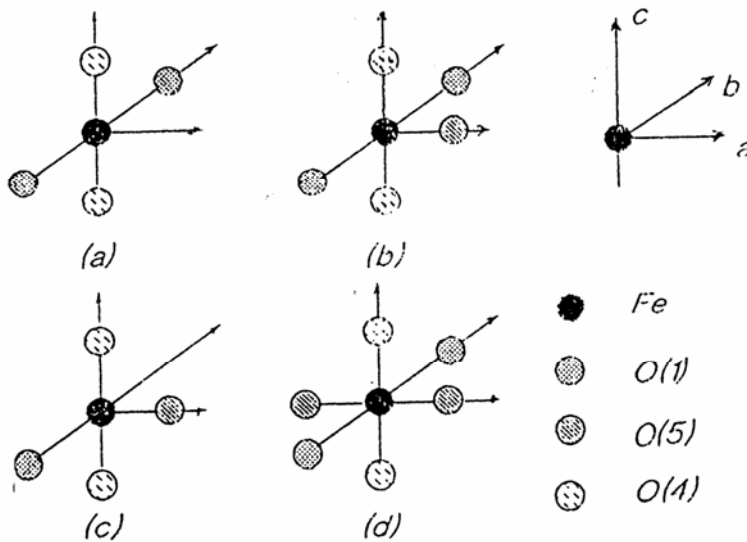


Fig. (3) : Possible local environment of Fe at the Cu (1) site.

- i. The above disordered structure in the Cu-O chains may weaken the coupling between Cu-O chains and Cu-O planes and consequently decreases T_c .
- ii. A reduced current density as confirmed by Hall coefficient experiments [12] which indicate a smooth decrease in carrier density as Fe concentration is increased.
- iii. Even minor population of Fe in Cu (2) sites is expected to suppress the superconductivity since Cu-O planes are considered to carry the superconducting current.

B-Mössbauer spectra:

Figure (4) depicts the MS spectra at room temperature for iron doped samples with different concentrations. Each spectrum is resolved into a number of subspectra. The corresponding isomer shift (IS) and quadrupole splitting (QS) for each subspectrum are listed in Table (1).

The MS spectrum of the sample with $x=0.4$ Fig. (4a) exhibits a paramagnetic behaviour, with a minor undetectable fraction of magnetic order, which imply that Fe ions are preferentially accommodated at Cu (1) sites in this sample. Increasing the x -value to 0.6 and up to $x=1.0$ causes the appearance of a simultaneous magnetic phase of well defined Zeeman sextet at room temperature (component III). Since Fe ions in Cu (2) sites in $YBa_2Cu_3O_6$ present an antiferromagnetic order with $T_N=450$ [2], the observed magnetic phase can be attributed to iron which replaces copper in this site. Also, it is

worthy to notice that the values of IS at room temperature are 0.18, 0.15, 0.15 for samples doped with $x=0.6$, 0.8 and 1.0 respectively. These values are unusual for 123 type superconducting system (where IS is almost zero or small -ve value), which reflect changes in the electronic density compared to that in superconducting state. Therefore, this difference in IS values can be considered as a consequence of suppression of superconductivity similar to that reported in iron doped $\text{PrBr}_2\text{Cu}_3\text{O}_{7-\delta}$ [13]. In addition the small QS of Fe in Cu (2) sites may be attributed to an important displacement, by $\sim 0.5\text{-}0.6 \text{ \AA}$, of the iron towards the apex of the pyramid which permits an additional oxygen atom to be inserted in the mid plane of the Cu (2)-O bilayer to form a quasi-octahedral Fe site [14].

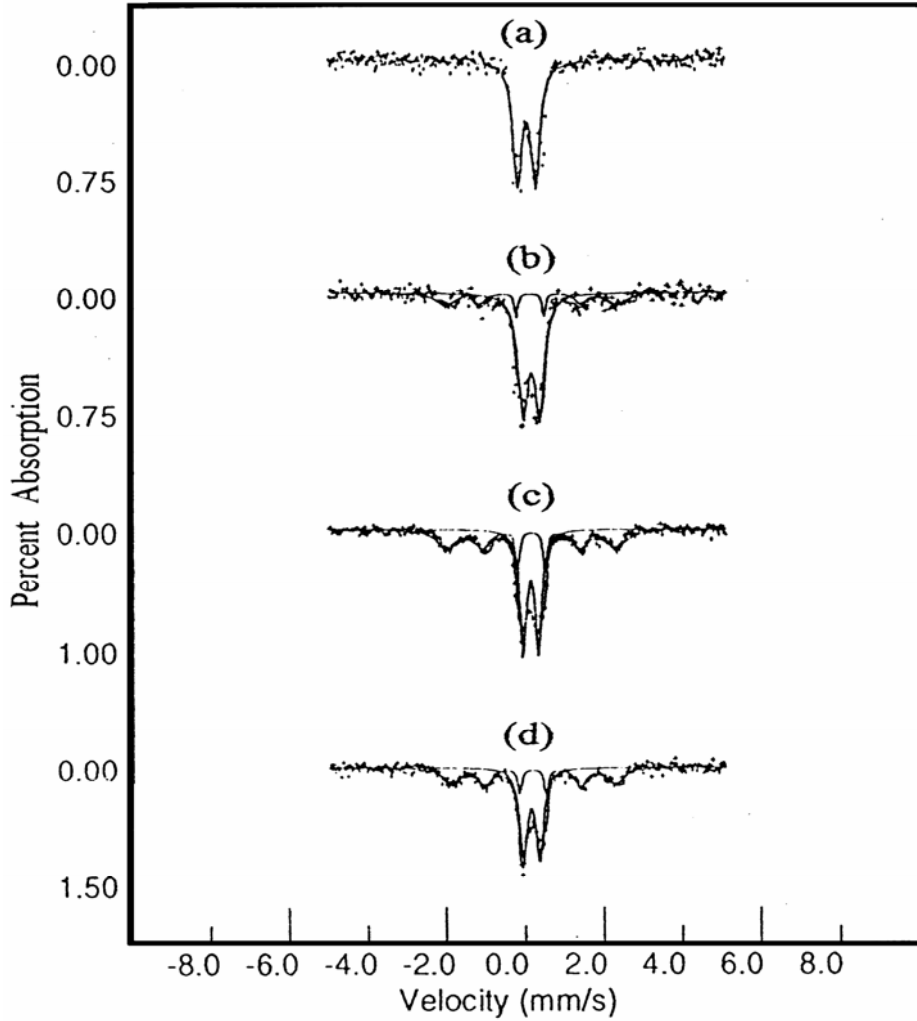


Fig. (4) : Mössbauer spectra at room temperature for the studied samples with different x -values: $x=0.4$ (a), 0.6 (b), 0.8 (c) and 1.0 (d).

Table (1): Mössbauer parameters for different concentrations at R.T, 77 K and 4.2 K, IS is the isomer shift relative to iron metal at R.T and QS is the quadrupole splitting. Accuracy of final decimal place shown in brackets.

T(K)	Component	x=0.4		x=0.6		x=0.8		x=1.0	
		IS mm/s	QS mm/s	IS mm/s	QS mm/s	IS mm/s	QS mm/s	IS mm/s	QS mm/s
R.T	I,II	0.07(9)	-0.45(7)	0.18	0.40(5)	0.15	-	0.15	-
	III	-	-	0.17(5)	0.04(1)	0.16(8)	0.37(9) 0.01(6)	0.19(8)	0.41(1) 0.02(7)
77 K	I	0.18(7)	2.22	0.18(2)	2.21	-	-	-	-
	II	0.13(8)	1.00	0.18(5)	1.10	0.24	0.99	0.23(9)	1.08
	III	-	-	0.42	-0.01(2)	0.38(8)	-0.04(1)	0.39	-0.06
4.2 K	I	0.42	-0.30	-	-	-	-	-	-
	II	0.34	0.29	0.34(4)	0.29(5)	0.34	0.30	0.34(4)	0.29(5)
	III	-	-	0.43(3)	-0.17(8)	0.40(5)	-0.09(8)	0.38(9)	-0.09(3)

More information can be obtained from the MS spectra measured at liquid nitrogen temperature Fig. (5). The paramagnetic doublet of the sample (x=0.4,

Fig. 4a) has been resolved into two doublets which reflect two different micro-environments of the Fe nucleus with QS values of 2.22 and 1 mm/s. As discussed earlier in section A, an orthorhombic-tetragonal structural transition occurs at $x > 0.03$ where O (1) anion becomes partially occupying the O (5) site. This process is a consequence of the tendency of Fe to create tetrahedral or octahedral oxygen coordination (pyramidal) about itself as indicated by neutron diffraction measurements [15]. Therefore, the doublet with the higher QS reflects a square planar oxygen coordination while the doublet with the smaller QS reflects a pyramidal one. The obtained QS values are comparable with those of sites D and B of reference (8) for which the valence and spin states are Fe^{2+} ($s=1$) and Fe^{3+} ($s=\frac{3}{2}$) respectively. Moreover, the relative spectral areas of the two doublets (Figs. 5a) point to the preference of Fe for the pyramidal Cu (1) sites than the square planar ones.

Increasing the iron content to x=0.6, the obtained MS spectrum is a combination of three subspectra. These include the above two components of x=0.4 (Fig. 5a) due to Fe in two Cu (1) sites, in addition to the antiferromagnetic sextet due to Fe in Cu (2) sites which was found to survive up to R.T (Fig. 4b). Inspecting Fig. (5b), it is to be noticed that both the intensity and spectral area of component I has been largely reduced relative to those of component II, followed by its disappearance with subsequent increase in Fe content as shown in Fig. (5, c-d). Thus, it can be concluded that for higher iron concentrations, Fe

accommodated in Cu (2) sites prevails, together with the Cu (1) sites of pyramidal configuration.

The MS spectra of iron doped samples at 4.2 K are depicted in Fig. (6). All samples show a more or less degree of ordering in such a way that reflects an increase in ordering temperature with increasing x .

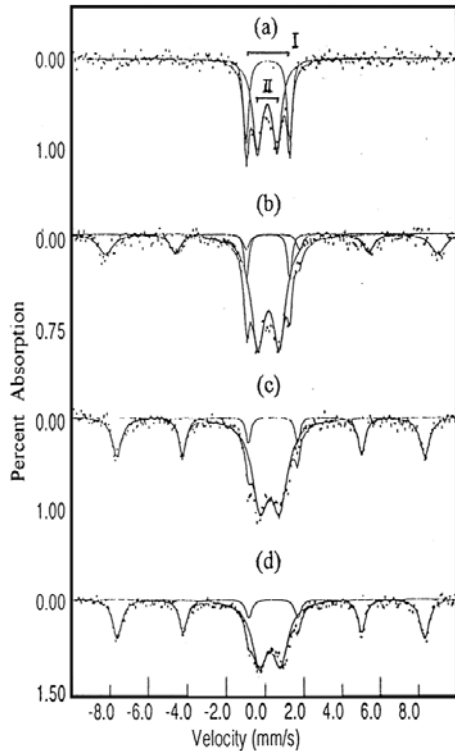


Fig. (5) : Mössbauer spectra at 77 K for the studied samples with different x -values: $x=0.4$ (a), 0.6 (b), 0.8 (c) and 1.0 (d).

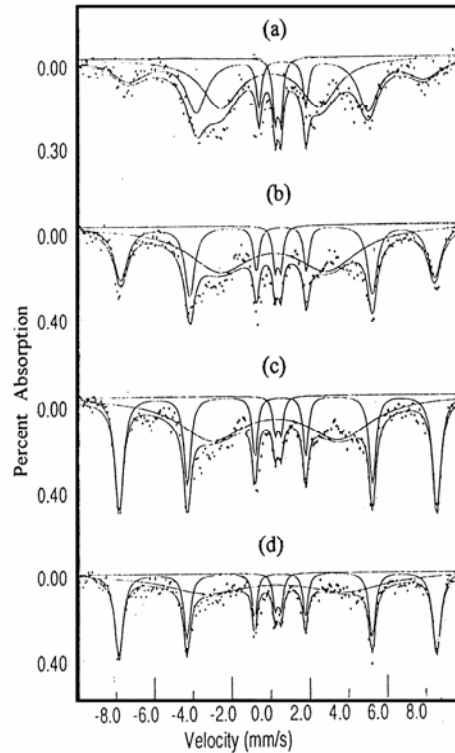


Fig. (6) : Mössbauer spectra at 4.2 K for the studied samples with different x -values: $x=0.4$ (a), 0.6 (b), 0.8 (c) and 1.0 (d).

As can be seen from Fig. (6a), the MS spectrum for the sample with $x=0.4$ exhibits very broad lines which are evidence of spin-glass-like moment arrangement with high anisotropy [15]. On the basis of neutron studies, some authors[10] conclude that this magnetic ordering arises from short-chain Fe clusters formed along the basal plane diagonal of Cu (1)-O. Again, referring to Fig. 6a, the observed broadening also imply that magnetic ordering and superconductivity seem to coexist at 4.2 K in this sample.

The hyperfine field B_{hf} of this Zeeman splitting is estimated to be 472.7 kOe which is in agreement with other reported values of B_{hf} associated with Fe in Cu (1) sites.

On the other hand, the above observed broadening of Fig. (6a) spectrum is found to develop gradually into resolved magnetic spectra with subsequent increase in iron content Fig. (6, b-d). The associated increase in the relative intensity of the outermost lines with increasing x indicates an increase in iron species with the highest hyperfine fields. The estimated values of B_{hf} for samples with $x=0.6, 0.8$ and 1.0 are 502.6, 508 and 508.5 kOe respectively. These higher values of B_{hf} indicate that these fields correspond to Fe accommodated in Cu (2) sites which prevail with increasing iron concentration. However, the electric field gradient (as reflected from the sign of QS) at Cu (2) site should be positive and point along the C-axis [11]. The measured -ve effective quadrupole interaction Table (1) indicates that the direction of B_{hf} is \perp to the C-axis. Therefore, it may be concluded that the Fe moments are ordered along the ab plane, as also reported in semiconducting $\text{La}_2\text{CaCu}_2\text{O}_6$ and $\text{YBa}_2\text{Cu}_3\text{O}_6$ [14]. Moreover, it is to be noticed that in Fig. (6, a-d), an additional doublet with IS value of 0.06 was added to obtain a better fit to the spectrum. This subspectrum is very likely to be expected for Fe clustering occurring at high concentrations.

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