# MÖSSBAUER SPECTROSCOPY OF HIGH $T_c$ $YBa_2(Cu_{3-x}Fe_x)O_y$

Li Shi(李 士) and Li Yinhua(李印华)

(*Institute of High Energy Physics, Beijing 100080, China*)

**ABSTRACT**

$YBa_2(Cu_{3-x}Fe_x)O_y$ ($x$ is 0.001, 0.005, 0.01, 0.1 and 0.3 respectively), of which Cu is replaced with $^{57}Fe$ are studied using Mössbauer spectroscopy to understand the crystal lattice property, the effects of the replacement on superconductivity of the High $Tc$ materials.

**Keywords** Mössbauer spectroscopy, High $Tc$ superconductor, Superconducting mechanism, Hyperfine interaction

## 1 INTRODUCTION

The discovery of high temperature superconducting materials has brought about worldwide interests. Nearly all the scientific methods are employed to study their superconducting mechanism in order to reach further exploration and application. Some results have been achieved[1–4] using Fe ions to replace Cu ions in high $T_c$ superconductor YBaCuO by Mössbauer spectroscopy. But so far some questions are not clear yet, such as up to which replaced fraction $x$ will destroy the superconductivity, what changes will take place on the Mössbauer spectra, and in which crystal lattice sites of Cu(1) and Cu(2) that the Fe ions locate determines the superconductivity characteristic, *etc.* In this study, we use different replaced fractions of $^{57}Fe$ (94.5 % enriched) as ion probes to study the superconduct or crystal lattice properties, superconductivity, and the effects of the replacement on the high $T_c$ $YBa_2(Cu_{3-x}Fe_x)O_y$ ($x$ is 0.001, 0.005, 0.01, 0.1 and 0.3 respectively). The results we obtained may give some information to understand the superconducting mechanism.

## 2 SAMPLE PREPARATION AND EXPERIMENTAL

The samples of $YBa_2(Cu_{3-x}Fe_x)O_y$ were prepared by mixing pure $Y_2O_3$, $BaCO_3$, CuO and $Fe_2O_3$ at the proportion of Y:Ba:Cu:Fe=1:2:(3–$x$):$x$ ($x$=0.001, 0.005, 0.01 and 0.3). In the case of minor replacement, enriched $^{57}Fe$ must be used to improve the signal-to-noise ratio of spectrum. The homogeneous mixtures were pressed to slice first, sintered for 6 h in oxygen atmosphere at 900°C, then pulverized and pressed to slice in 13mm diameter, sintered again in oxygen atmosphere at 960°C for 6 h, slowly cooling to room temperature[5]. A series of $YBa_2(Cu_{3-x}Fe_x)O_y$ samples with various replacement

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is prepared. The X-ray diffraction results show when the replacement is in $0 < x < 0.3$, the samples are in uniform phase.

The spectra were measured with a constant accelerating Mössbauer spectrometer with the source of 1.85 GBq $^{57}$Co(Rh). Vibration sample magnetometer is used for measuring the magnetic property.

## 3 RESULTS AND DISCUSSION

Fig.1 shows the curves of magnetic susceptibility $YBa_2(Cu_{3-x}Fe_x)O_y$ vs temperature at different replacement. Evidently $T_c$ is not affected much when $x$ is no more

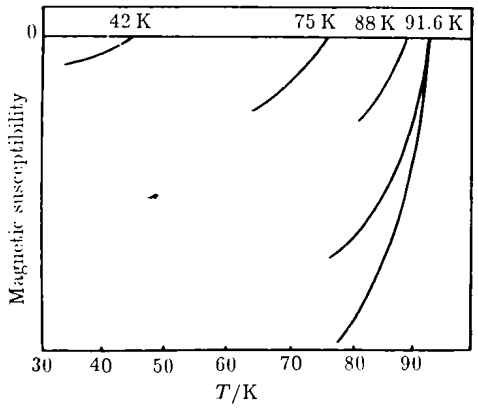


**Fig.1 The magnetic susceptibility curves of superconductor $YBa_2(Cu_{3-x}Fe_x)O_y$**
from right to left $x$=0.001, 0.005, 0.01, 0.1 and 0.3

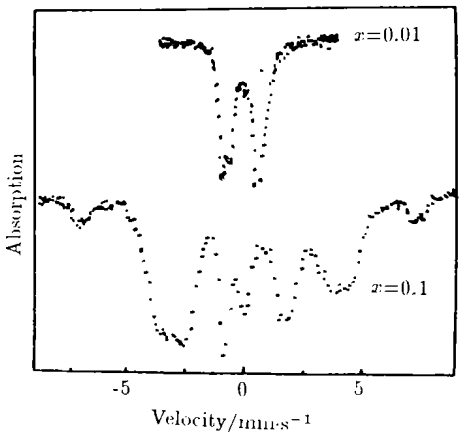


**Fig.2 Mössbauer spectra of superconductor $YBa_2(Cu_{3-x}Fe_x)O_y$ at 4.2 K with the replacement $x$=0.01 and 0.1**

than 0.01. If $x$ getting larger, $T_c$ declines notably and the diamagnetism becomes worse, and so does the superconductivity. In Fig.2, it can be seen that when $x = 0.01$, the Mössbauer.spectrum in 4.2K shows some analogy to that in room temperature (Fig.3), mainly existing doublet. While $x$=0.1, the Mössbauer spectra are totally different between 4.2 K and room temperature, the low temperature spectrum shows magnetic splitting. These indicate that we can neglect the influence from Fe ions substitution in the superconductor with minor replacement. So we can use minor replacement Fe as probe to study the Cu lattices; On the other hand, when replacements in the superconductor are higher, the wide sextet appeared at low temperature, it indicates that Fe is in magnetic order and probably has the spin relaxation. It proved that in YBaCuO superconductor the higher the replacement ($x > 0.01$), the worse the superconductivity of YBaCuO occured.

It can be seen from Fig.3 that for the lower replacement ($x$=0.001, 0.005, 0.01) the Mössbauer spectra are similar, all consist of 3 doublets after computer analysis. It

indicates in $YBa_2(Cu_{3-x}Fe_x)O_y$ there exist 3 Fe subcrystal sites Fe(1), Fe(2) and Fe(3), named $D_1$, $D_2$ and $D_3$. Their hyperfine interaction parameters are listed in table 1. For the sample of $x$=0.001, its hyperfine interaction parameters, isomer shift ($\delta$) and quadruple splitting (QS), corresponding to Mössbauer line $D_1$ and $D_2$ and $D_3$, are 0.04, 1.95; 0.36, 0.58 and -0.03, 1.00 mm/s, respectively. $D_1$ and $D_3$ have higher QS while smaller for $D_1$ and $D_2$, we ascribed Fe(1) and Fe(3) to lower spin $Fe^{3+}$, Fe(2) to higher spin $Fe^{2+}$ according to their values of $\delta$ and QS.

**Table 1**

**The hyperfine interaction parameters of $YBa_2(Cu_{3-x}Fe_x)O_y$**

| $x$ | $T_c$ | $\delta$ | $D_1/Q_s$ | A | $\delta$ | $D_2/Q_s$ | A | $\delta$ | $D_3/Q_s$ | A |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.001 | 91.6 | 0.04 | 1.95 | 0.51 | 0.36 | 0.58 | 0.06 | -0.03 | 1.00 | 0.43 |
| 0.005 | 91.6 | 0.05 | 1.93 | 0.49 | 0.37 | 0.65 | 0.06 | -0.04 | 1.33 | 0.45 |
| 0.01 | 88.0 | 0.06 | 1.97 | 0.50 | 0.38 | 0.70 | 0.07 | -0.01 | 1.22 | 0.43 |
| 0.1 | 75.0 | 0.02 | 2.00 | 0.46 | 0.36 | 0.82 | 0.11 | 0.00 | 1.07 | 0.43 |
| 0.3 | 42.0 | 0.07 | 1.94 | 0.40 | 0.35 | 0.68 | 0.12 | 0.08 | 1.13 | 0.48 |

A: Relative intensity

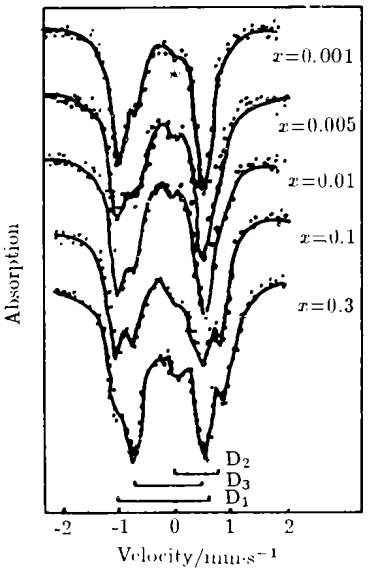


**Fig.3 The room temperature Mössbauer spectra of $YBa_2(Cu_{3-x}Fe_x)O_y$**

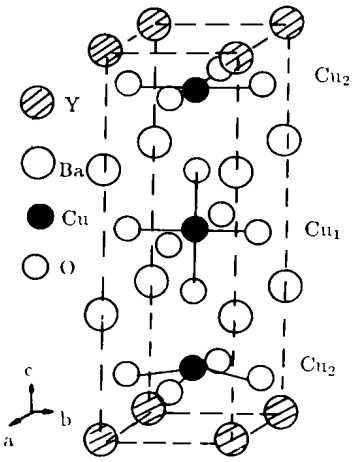


**Fig.4 Scheme of the crystal structure of $YBa_2(Cu_{3-x}Fe_x)O_y$**

Fig.3 also shows that when $x$ increases ($x$=0.1 and 0.3), the area of $D_2$ increases obviously, from 6% -7% up to 11% -12%, $D_1$ decreases gradually, and $D_3$ increases a little. This fact supports that the increasing $x$ will make the superconductivity of high $T_c$ materials getting worse. It is already known that Fe can only replace Cu in $YBa_2(Cu_{3-x}Fe_x)O_y$, and there are only two obviously different sites, Cu(1) of $Cu^{3+}$ and Cu(2) of $Cu^{2+}$[6] (see Fig.4). The number of oxygen around Cu(2) is fixed, but the number of oxygen ions ($O^-$) is unstable. According to the Mössbauer spectroscopy result, there are 3 lattice sites Fe(1), Fe(2) and Fe(3) in $YBa_2(Cu_{3-x}Fe_x)O_y$, so it is probably

the Fe ions located in one of Cu lattice site surrounded by two different environments. According to the $\delta$ and QS of $D_1$, $D_2$ and $D_3$, and Ref.[7], it can be said that Fe ions corresponding to $D_2$ situate at Cu(2), while $D_1$ and $D_3$ are the contributions from Fe at Cu(1), but their coordinating distribution oxygen ions are different, that is what we say their surroundings are different. As to why does the increasing $x$ accompany a rising area of $D_2$ doublet? We thought it is the critical point. Because $Cu^{2+}$ is more stable than $Cu^{3+}$, the Fe ions will occupy the Cu(1) sites first. When $x$ is less than 0.01, only a few number of Fe enter Cu(2) sites, the superconductivity is not affected obviously; when $x$ is larger than 0.01, more Fe ions occupy the Cu(2) sites, causing the degradation of superconductivity. So it may be said that the Fe ions on Cu(2) sites are one of the factors that spoil the superconductivity of $YBa_2(Cu_{3-x}Fe_x)O_y$, and the Fe ions on Cu(1) sites do not play a significant rule on the superconductivity. The relative intensities of $D_1$, $D_2$ and $D_3$ in Table 1 also show that when the replacement of Fe is small ($0.001 < x < 0.01$), about 94% of Fe ions replaced the Cu at Cu(1), only 6% of Fe ions replaced the Cu at Cu(2) crystal lattice sites.

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