

Mössbauer Study of High T_c $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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^{57}Fe -Mössbauer spectra of $\text{GdBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-\delta}$ ($x = 0.005$) are studied in a wide temperature range (1.4–700 K), and the valence states and surroundings of iron cations are analyzed. There are four sites for Fe: A, B, C and D. Fe(A), Fe(B) and Fe(C) occupy Cu(1) sites with different O-coordinations. Fe(D) is attributed to a Cu(2) site with only one definite O-surrounding. The Fe cations are identified as high spin 4+ at site B and 3+ at site D. Alignment of polycrystalline powder absorber in a magnetic field leads to small texture effects.

1. INTRODUCTION

Investigations have been focused on the microstructures and characteristics of the high T_c $\text{RBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_{7-\delta}$ (abbr. 1-2-3 compound) since its discovery [1-6]. Here R is rare earth ions (Y, Gd, Eu, etc.); the substitutions within them produce little effect on the transition temperature T_c . Improvement elements or probes M (such as Ti, V, Cr, Mn, Co, Fe, Ni and Zn) are substituted for Cu in order to further investigate the superconductive structures and mechanisms. The transition temperature decreases when Cu is substituted by some content of Fe, Co, Ni, and Zn, while T_c changes very little when Cu is substituted by the same content of Ti, V, Cr and Mn [7]. But the superconductivities of 1-2-3 compound will be damaged and change from a superconductive state into a semiconductive if the content of substitutes is too high (for Fe ~ 5%). Moreover, T_c depends on the oxygen content significantly. Usually T_c remains around 92 K when $\delta \rightarrow 0$ and 1-2-3 compound changes from an orthorhombic to a tetragonal phase when $\delta \rightarrow 0.5$.

Neutron diffractions studies indicate the existence of two Cu sites in 1-2-3 compound, i.e., Cu(1) and Cu(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, as shown in Fig. 1. Recently, the magnetism of 1-2-3 compound was studied [8-10] with ^{57}Fe as a probe. Generally, superconduction and magnetic ordering excludes each other in traditional

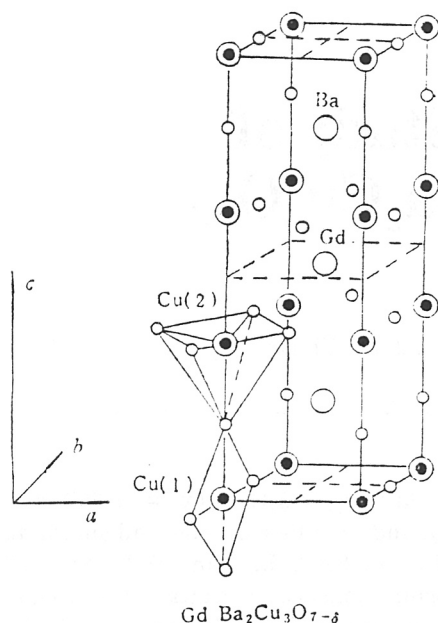


Fig. 1
Structure of $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

metals and alloys. But 1-2-3 compound has both properties below the temperature of liquid helium. It may be due to the fact that the rare earth ion is located between two CuO_2 planes (Fig. 1). Although some work has been done through ^{57}Fe Mössbauer spectroscopy, the valence states and locations of Fe in the compound are not very clear. It is necessary to make further research on the compound.

2. EXPERIMENT

Samples of $\text{GdBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-\delta}$ ($x = 0.5\%$) were prepared by traditional methods. The small percentage of Fe was chosen to provide a good probe and to reduce its effect on superconductivities and Fe-Fe interactions. X-ray diffraction analysis showed that the samples were in a single orthorhombic phase. A measurement of the magnetic susceptibility $\chi_g = M_g/M$ indicated $T_c \rightarrow 90.6$ K (here we obtained T_c when $\chi_g = 0$ [11]). The spectra at the temperature range of 1.4–700 K were collected with a 100 mCi $^{57}\text{Co}(\text{Rh})$ source kept at room temperature by a Mössbauer spectrometer driven by sine wave. The linearization of velocity axes and fits of the spectra according to Lorentz lines were carried out on a VAX computer. The experiment and calculation were made at the Freie Universität, Berlin. Since the spectra vary in a large temperature range, we can investigate the superconductivity of 1-2-3 compound with the ^{57}Fe spectra corresponding to the temperature.

3. ANALYSIS

The ^{57}Fe spectra of $\text{GdBa}_2(\text{Cu}_{0.995}\text{Fe}_{0.005})_3\text{O}_{7-\delta}$ are shown in Fig. 2. The temperature range is from 1.4 K to 700 K. From the reasonable linewidth, we analyze the different spectra by four symmetric quadruple doublets, labelled as A, B, C and D in the sequence of their quadruple splitting. This means that Fe occupies four sites in 1-2-3 compound, Fe(A), Fe(B), Fe(C) and Fe(D), respectively. Table 1 shows their Mössbauer parameters at 80 K. The site D has the lowest relative intensity — only about 9.5%.

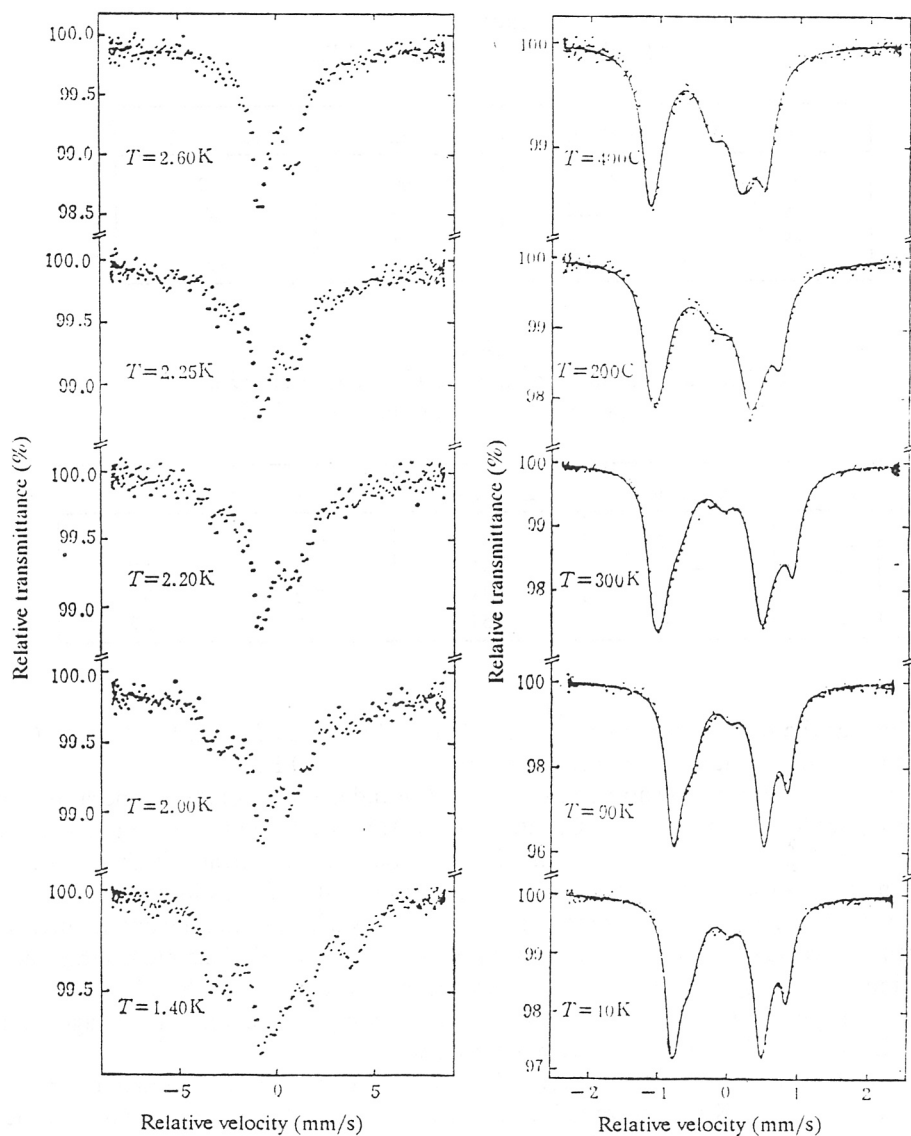


Fig. 2
Mössbauer spectra (1.4—700 K).

From Fig. 2, we find that a magnetic split of the ^{57}Fe spectra occurs at the same temperature where the Gd sublattice orders ($T_N = 2.25\text{ K}$). The magnetic broadening emerges at low temperature ($T < 2.6\text{ K}$). An analysis of the magnetic line broadening indicates positive signs of the EFG (electrical field gradient) for sites A, B, and C, which is consistent with the results of Brand *et al.* [12]. In the range from 10 K to 300 K, the relative intensity of subspectrum D is rarely dependent on the temperature, and the intensity for site B increases ($\sim 30\%$) at the cost of the reduced intensity of sites A and C (Fig. 3). The relationship of Debye temperatures is

$$\theta_D(\text{B}) > \theta_D(\text{D}) > \theta_D(\text{A}), \theta_D(\text{C})$$

Table 1
Mössbauer parameters at 80 K.

Sites	$ISO(\text{mm/s})$	$\Delta E_O(\text{mm/s})$	Rel. $A(\%)$
Fe(A)	0.003	2.00	27.0
Fe(B)	-0.156	1.49	31.0
Fe(C)	-0.008	1.31	32.5
Fe(D)	0.205	0.50	9.5

Table 2
Mössbauer parameters at 80 K after alignment (θ is the angle between the γ -ray and magnetic field).

Sites	$ISO(\text{mm/s})$	$\Delta E_O(\text{mm/s})$	Rel. $A(\%)$	$\theta(^{\circ})$
Fe (A)	0.003	2.03	27.4	63.8
Fe (B)	-0.164	1.45	40.6	61.8
Fe (C)	0.055	1.35	27.0	63.0
Fe (D)	0.343	0.54	5.0	40.2

Meanwhile, as the temperature increases, the O-coordinations of F(A), F(B) and F(C) seem to change slightly, and the change becomes more obvious above 400 K.

As the sum of the intensity of subspectra A, B and C is independent of the temperature, Fe(A), Fe(B) and Fe(C) are located in the same Cu site and Fe(D) is attributed to another Cu site. In the four Fe sites, Fe(B) has the highest O-coordination, its isomer shift indicates high spin Fe^{4+} . The O-coordination of Fe(A) seems to be the lowest. The isomer shift of Fe(D) indicates Fe^{3+} .

From Fig. 2, we observe a sudden decrease of the intensity of site C and the appearance of new structures around zero velocity after the temperature rises above 500 K. This means that the local O-concentration decreases, as evidenced by reference measurements of the absorber at lower temperatures. The spectra above 700 K indicate that 1-2-3 compound enters the tetragonal phase since oxygen diffuses significantly (the spectra are not shown here).

Now we analyze the spectra from polycrystalline powder absorbers aligned in a magnetic field of 6T. The parameters at 80 K are shown in Table 2. Calculation and analysis indicate that the sign of V_{zz} for site D is negative (V_{zz} : main axial component of EFG). As indicated previously, the signs of V_{zz} for A, B and C are also negative. Because the Cu(2) has negative V_{zz} in 1-2-3 compound [13], Fe(A), Fe(B) and Fe(C) enter Cu(1), and Fe(D) occupies Cu(2) site. From the analysis of the spectra, we find small texture effects, and the main axis of the EFG is oriented perpendicular with respect to the c -axis for site A and B, while site D exhibit an orientation parallel to the c -axis. Our findings for the Gd-system agree with the study by Boolchand *et al.* [13,14] on fully aligned Y-systems.

4. DISCUSSION AND CONCLUSION

Cu-O chains of Cu(1) layers used to be considered important for the superconductivity mechanism of 1-2-3 compound. But no one found the Cu-O chains of Cu(1) in the high T_c Bi-system since the system was discovered [15]. Usually Cu(2) is considered most important for superconduction. Recently, it was supposed that O(4) plays a great role in superconductivities,

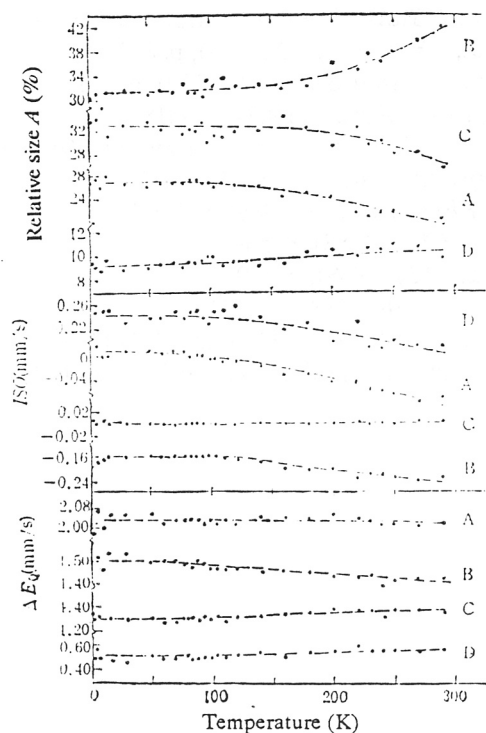


Fig. 3

Experimental plots of parameters vs. temperature.

because it connects Cu(1) and Cu(2) to make the crystalline structure steady [16]. But we do not observe the phenomenon from the ^{57}Fe spectra, and this hypothesis is incapable of explaining the effect on the transition temperature by different contents of Fe. From our work, we think that Cu(2) is important.

Now we conclude:

- 1) There are four sites for Fe: Fe(A), Fe(B) and Fe(C) occupy Cu(1) site, and Fe(D) is attributed to Cu(2) site. $\theta_D(B) > \theta_D(D) > \theta_D(A), \theta_D(C)$.
- 2) Fe cations are identified as high spin 4+ at site B and 3+ at site D.
- 3) Alignment of polycrystalline powder absorbers in a magnetic field leads to small texture effects.

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