The influence of local structure on superconductivity in Fe\textsubscript{0.5}Cu\textsubscript{0.5}Ba\textsubscript{2}YCu\textsubscript{2}O\textsubscript{7.41}: a Mössbauer effect study

Y.H. Liu a,*, G.C. Che a, K.Q. Li a, Z.X. Zhao a, Z.Q. Kou b, N.L. Di b, Z.H. Cheng b

a National Laboratory for Superconductivity, Institute of Physics, Chinese Academy of Sciences, ZhongGuanCun, P.O. Box 603, Beijing 100080, PR China
b State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing 100080, PR China

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Abstract

In this paper, the Mössbauer effect of the Fe\textsubscript{0.5}Cu\textsubscript{0.5}Ba\textsubscript{2}YCu\textsubscript{2}O\textsubscript{7.41} superconductor with \( T_c = 80 \) K synthesized at 1000°C at high pressure of 6 GPa was reported. Results indicate that the high-pressure synthesis makes only a slight amount of Fe located at Cu(2) sites migrate to Cu(1) sites and there is no obvious magnetic pair-breaking effect induced by Fe located at Cu(2) sites. In addition, the high-pressure synthesis changed fourfold coordinated Fe to fivefold coordinated Fe in the chains. We argued that the fivefold coordinated Fe in CuO\textsubscript{x} chains favors the occurrence of superconductivity in Fe\textsubscript{0.5}Cu\textsubscript{0.5}Ba\textsubscript{2}YCu\textsubscript{2}O\textsubscript{7.41} superconductor.

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1. Introduction

It is well known that in YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{6+x} (YBCO) superconductor there are two different Cu sites: Cu(1) and Cu(2). The Cu(1) site is related to CuO\textsubscript{x} chains and the Cu(2) site exists in CuO\textsubscript{2} planes. In order to understand high-\( T_c \) superconductivity, a number of investigations focused on the influence of transition-metal substitution for Cu on superconductivity of YBCO. All of the substitutions depress superconducting transition temperature \( T_c \) due to decreasing hole concentrations, breaking pairs or localizing holes. On the other hand, some researchers paid attention to the effect of the change in local structure on superconductivity [1,2]. As far as the study of the local structure is...
concerned, it should unambiguously be said that the substitution of Fe for Cu in YBCO is very interesting because the Fe is a useful microscopic probe of structural, magnetic and electric properties by the measurements of Mössbauer spectroscopy. Mössbauer technique has been verified to be a powerful tool determining the assignment of Fe between Cu(1) and Cu(2) sites [3–8] and sensitive to local structure [2]. From previous investigations of Mössbauer spectra on Fe-doped YBCO compounds, some conclusions can be reached as follows: (1) The Fe preferentially substitutes for Cu (1) in CuO \(_x\) chains [2–13]. (2) Changing the heat-treatment conditions gives rise to the migration of partial Fe from Cu(1) to Cu(2) sites [7,10]. (3) The substitution of Cu(2) by Fe does not change the magnetic ordering temperature of YBa\(_2\)Cu\(_3\)O\(_{6.1}\) [5]. However, these conclusions were obtained by the Mössbauer effect measurements on nonsuperconducting Fe-doped YBCO samples or superconducting ones with low Fe content prepared at ambient pressure. Recently, we have successfully synthesized Fe\(_{0.5}\)Cu\(_{0.5}\)Ba\(_2\)YCu\(_2\)O\(_{7.41}\) superconductor with \(T_c = 80K\) at 1000°C under high pressure of 6GPa [14,15]. Why does not such a high amount of iron destroy superconductivity in this superconductor? In order to find the origin, it is necessary to study the Fe-site occupancies and the change of local structure of Fe\(_{0.5}\)Cu\(_{0.5}\)Ba\(_2\)YCu\(_2\)O\(_{7.41}\) superconductor using Mössbauer technique.

2. Experimental

The Fe\(_{0.5}\)Cu\(_{0.5}\)Ba\(_2\)YCu\(_2\)O\(_{7.41}\) superconductor was prepared in two steps. In the first step, high-purity (99.99%) powders of Y\(_2\)O\(_3\), BaCO\(_3\), CuO and Fe\(_2\)O\(_3\) in appropriate molar proportion were thoroughly mixed in a mortar. The mixture was heated in air in the temperature range 880 \(\leq T \leq 930^\circ\)C for at least 70 h with a few intermediate grindings. Then, the heated mixture was reground and pressed into pellets, which were sintered at 930°C for about 40 h in air and slowly cooled to room temperature at a rate of 30°C/h. The resultant product was named AM-sample, which is not superconducting. In the second step, the AM-sample was powdered, mixed with 5wt% KCIO\(_4\) powder as oxidant and compacted into pellets with diameter of 7 mm and thickness of 5 mm, which were wrapped in gold foil and synthesized at 1000°C under high pressure of 6 GPa for 0.5 h in belt-type apparatus reported in detail in Refs. [14,15]. The resultant product was named HP-sample.

Both the AM- and HP-samples were characterized by powder X-ray diffraction (XRD) using MXP18A-HF diffractometer with Cu K\(\alpha\)-radiation. The temperature dependence of electrical resistance was measured by standard four-probe method. DC magnetic measurements were performed using SQUID magnetometer (Quantum Design, MPMS type). \(^{57}\)Fe Mössbauer spectra of the AM- and HP-samples were recorded by a Wissel System constant acceleration Mössbauer spectrometer with \(^{57}\)Co (Pd) source at room temperature. The velocity was calibrated using a \(\alpha\)-Fe foil. The values of isomer shift given here were relative to \(\alpha\)-Fe at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of AM-(A) and HP-(B) samples of Fe\(_{0.5}\)Cu\(_{0.5}\)Ba\(_2\)YCu\(_2\)O\(_{7+x}\), indicating that the two samples are of single phase. Structural analysis confirmed that both of them
have tetragonal structure belonging to space group \(P4/mmm\). The lattice parameters of AM- and HP-samples are \(a = 0.3874\), \(c = 1.167\)\(\text{nm}\) and \(a = 0.3865\), \(c = 1.1598\)\(\text{nm}\), respectively, indicating that the HP-sample has smaller unit-cell volume than the AM-sample. This is due to the increase of oxygen content in the HP-sample \([14,15]\). The oxygen contents per unit cell of AM- and HP-samples are 7.23 and 7.41, respectively \([15]\).

Fig. 2(A) shows the \(M-T\) and \(R-T\) curves of the superconducting HP-sample and Fig. 2(B) shows the \(R-T\) curve of the AM-sample. These results indicate that the HP-sample has superconducting transition temperature \(T_c = 80\)\(K\) and the shielding and Meissner fraction are about 50\% and 24\%, respectively \([14]\). The AM-sample has a semiconductor-like behavior, even after oxygenation at 350\(^\circ\)C for 40\(h\) in flowing oxygen at ambient pressure.

Room-temperature Mössbauer spectra of the AM-sample and HP-sample are shown in Fig. 3 (1) and (2), respectively. The spectra can be better fit to three symmetric quadrupole-split sites (A–C). The hyperfine parameters of isomer shift (\(\delta\)), quadrupole splittings (\(\Delta\)), full-width-at-half-maximum, or FWHM (\(\Gamma\)) and site intensity ratio (\(I/A\)) of the three subspectra are summarized in Table 1. The Mössbauer spectrum of the AM-sample is very similar to those obtained elsewhere \([2,6,12]\).

In the spectrum of the AM-sample there are three subspectra (A–C) while only two subspectra (B and C) exist in the spectrum of the HP-sample. This indicates that the iron atoms in the AM-sample have three different oxygen environments while the iron atoms in the HP-sample have two different oxygen environments. Moreover, the relative intensities of three quadrupole doublets in the spectrum of the AM-sample are different from those of the HP-sample. Specifically, the intensity of doublet C increases at the expense of that of doublet A in going from the AM-sample to the HP-sample and the doublet A disappears in the spectrum of the HP-sample (see Fig. 3). These can reasonably be interpreted if the site occupancies of Fe in the AM- and HP-samples are taken into account. There is a general consensus of site assignment that doublets A and C are attributed to Fe at the Cu (1) sites and doublet B is attributed to Fe in CuO\(_2\) planes \([2,10–13]\). According to these assignments, doublet A is thought to be the Fe
having fourfold-oxygen coordination in the chains as suggested by Dunlap et al. [16] and confirmed by Smith et al. [12,13] and Shi et al. [2]. The iron corresponding to doublet B should have the same pyramidal-oxygen configuration as Cu(2) [2,10,12,13]. Doublet C, known to exist in oxygen-rich samples [2,10–13], is thought to be the Fe with fivefold-oxygen coordination [2,11] in CuO\(_x\) planes. From Table 1, one can also find that the quadrupole splitting (\(\Delta\)) of B site of HP-samples is smaller than that of the AM-sample, suggesting that the symmetry of oxygen environment about Fe(2) in the HP-sample is higher as compared with the AM-sample.

In Mössbauer spectroscopy, site-integrated intensities \(I\) are proportional to site occupancy \(N\) if we assume the recoil-free fraction is the same. In view of this, from Table 1 it can be found that about 76% of Fe content occupy C site in the HP-sample much higher than those in the AM-sample (see Table 1). After the high-pressure synthesis A site disappears. It seems to suggest that the presence of A site with fourfold-oxygen coordination in the chains suppresses superconductivity in Fe-doped YBCO and the high-pressure synthesis probably favors the atomic scale transformation of A \(\rightarrow\) C site in bulk materials [2]. The increase of Fe having fivefold-oxygen coordination (i.e., C site) in the chains apparently promotes superconducting coupling between CuO\(_2\) planes. Additionally, we also noted the fact that the antiferromagnetic (AFM) ordering temperature \(T_N\) decreases with increasing oxygen content in undoped YBCO and it was suggested [17] that increasing oxygen changes the interplane AFM coupling between CuO\(_2\) planes, which is necessary to establish the long-range AFM order. This effect has been found in Fe-doped YBCO [5] by the measurements of Mössbauer spectroscopy. A molecular-field model calculation indicates that the Cu–Fe exchange is only 0.26 of the Cu–Cu exchange in the planes [7,18]. From Table 1 it can also be seen that the isomer shift \(\delta\) of doublet B decreases to 0.213 mm/s from 0.331 mm/s after the high-pressure synthesis. This implies that the Fe(2)–O(2,3) bonds in CuO\(_2\) planes contract after the high-pressure synthesis [9] and the Fe related to doublet B (Fe(2)) is Fe\(^{3+}\) species with high spin (\(s = 5/2\)) [2]. Thus, it is possible that the increase of oxygen content and number of C sites and the contraction of Fe(2)–O(2,3) bonds lead to further weakening of Cu–Fe and Cu–Cu exchange at Cu(2) sites and favors the occurrence of superconductivity in Fe-doped YBCO.

Can Fe located at Cu(2) sites produce pair-breaking effect? From our present work, it could be speculated that the pair-breaking effect of Fe(2) is not obvious. Moreover, this conclusion can also be inferred from the work of Smith et al. [10]. In Ref. [10], the Fe-doped YBCO samples were prepared by conventional solid-state reaction method and subsequently were annealed in flowing O\(_2\) after annealing in flowing N\(_2\) and then were slowly cooled down to room temperature. Hereafter, we name these samples AL-samples. They found that for the AL-samples the Fe located at Cu(2) sites is increased and the superconducting transition temperature \(T_c\) is higher than that of the samples prepared conventionally. Comparing with the undoped YBCO, they found that there was only a relatively mild reduction in \(T_c\) of AL-samples, indicating that the Fe at

<table>
<thead>
<tr>
<th>Sample</th>
<th>Site</th>
<th>(\delta) (mm/s)</th>
<th>(\Delta) (mm/s)</th>
<th>(\Gamma) (mm/s)</th>
<th>(I_{AM}/I_{HP})</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM-</td>
<td>A1(4):</td>
<td>0.062(2)</td>
<td>1.996(4)</td>
<td>0.136(4)</td>
<td>0.23(8)</td>
</tr>
<tr>
<td></td>
<td>B2(5):</td>
<td>0.331(3)</td>
<td>0.599(4)</td>
<td>0.154(4)</td>
<td>0.28(0)</td>
</tr>
<tr>
<td></td>
<td>C1(5):</td>
<td>−0.045(1)</td>
<td>0.889(3)</td>
<td>0.159(3)</td>
<td>0.48(5)</td>
</tr>
<tr>
<td>HP-</td>
<td>B2(5):</td>
<td>0.213(4)</td>
<td>0.163(7)</td>
<td>0.097(0)</td>
<td>0.24(1)</td>
</tr>
<tr>
<td></td>
<td>C1(5):</td>
<td>−0.015(3)</td>
<td>0.889(3)</td>
<td>0.161(4)</td>
<td>0.76(0)</td>
</tr>
</tbody>
</table>
Cu(2) sites has only a mildly detrimental effect on superconductivity. It was proposed that the Fe located at Cu(2) sites does not produce pair-breaking effect, but probably participate in the valence fluctuations helpful to superconductivity [10]. This phenomenon can also be found in the work of Katsuyama et al. [4]. Thus superconductivity in our superconducting samples synthesized by high pressure cannot be attributed to the slight decrease of the Fe located at Cu(2) sites. The number of fivefold coordinated Fe at Cu(1) sites in the AL-samples is larger [10] compared with the samples prepared conventionally. Moreover, those AL-samples have higher superconducting transition temperature though they contain more Fe in CuO$_2$ planes. Additionally, Shi et al. [2] found that the values of $T_c$ increase with increasing the relative intensity C-site in Fe-doped YSr$_2$Cu$_2$O$_{7+x}$. Based on these mentioned above, we are tempted to conclude that the increased oxygen and the presence of Fe with fivefold-oxygen coordination in CuO$_x$ chains are important to give rise to such a high $T_c$ in Fe$_{0.5}$Cu$_{0.5}$Ba$_2$YCu$_2$O$_{7.41}$ superconductor. This is possibly related to the local ordering of oxygen (or rearrangement of oxygen atoms in chains). That is to say, the high-pressure synthesis promotes a preferred site occupancy of oxygen atoms in CuO$_x$ chains. This kind of local oxygen ordering is favorable to transformation of holes to CuO$_2$ planes from CuO$_x$ chains. Thus, the $T_c$ of Fe$_{0.5}$Cu$_{0.5}$Ba$_2$YCu$_2$O$_{7.41}$ superconductor can be enhanced up to 80 K.

4. Summary

We successfully synthesized Fe$_{0.5}$Cu$_{0.5}$Ba$_2$Y-Cu$_2$O$_{7.41}$ superconductor with the value of $T_c$ as high as 80 K. Mössbauer technique was used to study the properties of local structure. Results indicate that the presence of Fe with fivefold-oxygen coordination in CuO$_x$ chains plays an important role in the occurrence of superconductivity in Fe$_{0.5}$Cu$_{0.5}$Ba$_2$YCu$_2$O$_{7.41}$ superconductor. That is to say, the high-pressure synthesis gives rise to the ordering the oxygen atoms in CuO$_x$ chains. On the other hand, Fe in Cu(2) sites has only mildly detrimental effect on superconductivity in Fe-doped YBCO, i.e., the pair-breaking effect of Fe(2) with high spin is not obvious.

References