PHYSICAL REVIEW B VOLUME 40, NUMBER 1 1 JULY 1989

^{57}Fe Mössbauer study of the $Tl_2Ca_{1.5}Ba_{1.7}(Cu_{1-x}Fe_x)_3O_9$ superconductor

Zeng Yiwei, Yan Xiaohua, Lin Mingzhu, Ren Yanru, Meng Xianren, Lu Yongning,
Tu Qingyun, Wu Xiaoshan, and Sang Lihua
Department of Physics, Beijing Normal University Beijing 100875, China

(Received 27 January 1989)

The results of ^{57}Fe Mössbauer-effect studies on high-T_c $Tl_2Ca_{1.5}Ba_{1.7}(Cu_{1-x}Fe_x)_3O_9$ with $x=0.01$, 0.05, and 0.07 are reported in this paper. The Mössbauer spectra depend on concentration and show three quadrupole doublets that can be related to different Cu sites at different phases and to the number of oxygen vacancies. The site preference of Fe is identified by fitted Mössbauer results. The parameter of a Mössbauer spectrum run at 77 K indicates that at the superconducting state the density of s electrons at Cu sites is different from that of the normal state. The data from x-ray diffraction are given for $x=0.01$ and 0.07 and the analyzed results show that the 2:1:2:2 and 2:2:2:3 phases have an intergrowth in our samples.

New rare-earth-free superconductors have been made in the past year.[1-3] This is a very significant breakthrough and will open a new way to provide deeper insight into the mechanism of high-temperature superconductivity. The crystal structure of a Tl-Ca-Ba-Cu-O system has been identified. It is known that there are two superconducting phases in a Tl-Ca-Ba-Cu-O system based on the work of Hazen *et al.*[4] One has a composition of the $Tl_2Ca_2Ba_2Cu_3O_{10+x}$ (2:2:2:3 phase) and the other has a composition of the $Tl_2CaBa_2Cu_2O_{8+x}$ (2:1:2:2 phase). In this Brief Report we report some interesting results obtained by means of a Mössbauer-effect study by using ^{57}Fe nuclei as a probe for the $Tl_2Ca_{1.5}Ba_{1.7}(Cu_{1-x}Fe_x)_3O_9$ superconductor. In order to analogize the effect of iron impurity on a Tl-Ca-Ba-Cu-O system, we prepared three samples with different iron content, i.e., $x=0.01$, 0.05, and 0.07, respectively.

A typical procedure for the synthesis of $Tl_2Ca_{1.5}Ba_{1.7}(Cu_{1-x}Fe_x)_3O_9$ samples with different contents of iron is as follows. Dry powders and appropriate amounts of Tl_2O_3, CaO, BaO, CuO, and Fe_2O_3 (90% enriched in ^{57}Fe) were completely mixed, ground, and cold pressed into pellets. An open Al_2O_3 boat containing the pellets for which the iron compositions were taken as $x=0.01$, 0.05, and 0.07, respectively, were then put into a tube furnace. The samples were heated to 800–880 °C for 3–6 h in flowing oxygen and then the temperature was lowered at a rate of 2–3 °C/min to 450 °C. Then power was turned off and the furnace was naturally cooled to room temperature.

The resistance and diamagnetic transitions of the samples were examined by a standard dc four-probe method and an ac mutual-inductance method, respectively. The examined results show that their T_c values are around

TABLE I. Powder x-ray-diffraction data for the high-T_c superconductor $Tl_2Ca_{1.5}Ba_{1.7}(Cu_{1-x}Fe_x)_3O_9$ ($x=0.01$).

2	d_{obs}	d_{ref}	h	k	l	I/I_0	Phase
27.8	3.21	3.228	1	0	9	54	2:2:2:3
29.4	3.04	3.021	0	0	12	23	2:2:2:3
30.2	2.96	2.96	0	0	10	16	2:1:2:2
31.6	2.83	2.81	1	0	9	100	2:1:2:2
32.8	2.73	2.77	1	1	9	36	2:2:2:3
33.0	2.72	2.72	2	0	0	75	2:1:2:2
33.6	2.67	2.669	2	0	2	14	2:2:2:3
35.7	2.52	2.529	2	0	5	23	2:2:2:3
36.9	2.44	2.433	2	1	0	30	2:1:2:2
38.8	2.32	2.319	2	0	8	32	2:2:2:3
47.2	1.93	1.924	2	2	0	48	2:1:2:2
54.7	1.68	1.726	0	0	21	32	2:2:2:3
55.7	1.65	1.621	3	1	7	34	2:2:2:3
56.2	1.82	1.814	3	0	0	32	2:1:2:2
57.9	1.59	1.588	3	10	9	45	2:1:2:2
58.7	1.57	1.573	1	0	18	18	2:1:2:2
61.3	1.51	1.511	1	1	18	30	2:1:2:2
65.2	1.43	1.438	3	2	7	32	2:2:2:3

95–105 K and decrease with increments of the iron content. The crystal structures of two samples ($x = 0.01$ and 0.07) were determined by x-ray-powder diffraction taken with a Philips APD-10 x-ray diffractometer at room temperature. The analyzed result of the diffraction pattern for the iron content $x = 0.01$ is given in Table I (the result of $x = 0.07$ is similar to that of $x = 0.01$), and shows that the 2:1:2:2 and 2:2:2:3 phases coexist and take an intergrowth in the sample. The proportion of the 2:1:2:2 phase in the two samples is larger than that of the 2:2:2:3 phase. According to the data, the ratio of the 2:1:2:2 phase to the sum of both phases is about 65% for $x = 0.01$ and the ratio will increase slightly with each increment of iron (69% for $x = 0.07$). Most of the reflection lines could be indexed to a tetragonal unit cell with lattice parameters $a = 5.51$ Å and $c = 29.5$ Å on the 2:1:2:2 phase, and $a = 5.56$ Å and $c = 35.3$ Å on the 2:2:2:3 phase for $x = 0.01$. But for $x = 0.07$, the lattice parameters of the 2:1:2:2 phase are the same as the $x = 0.01$'s, and on the 2:2:2:3 phase the a and c then become equal to 5.42 and 36.1 Å, respectively. It is reasonable to reduce the parameter a with an increase of the iron composition since the atomic radius of Fe is less than that of Cu. However, the reason for the increase of the parameter c needs to be explored further.

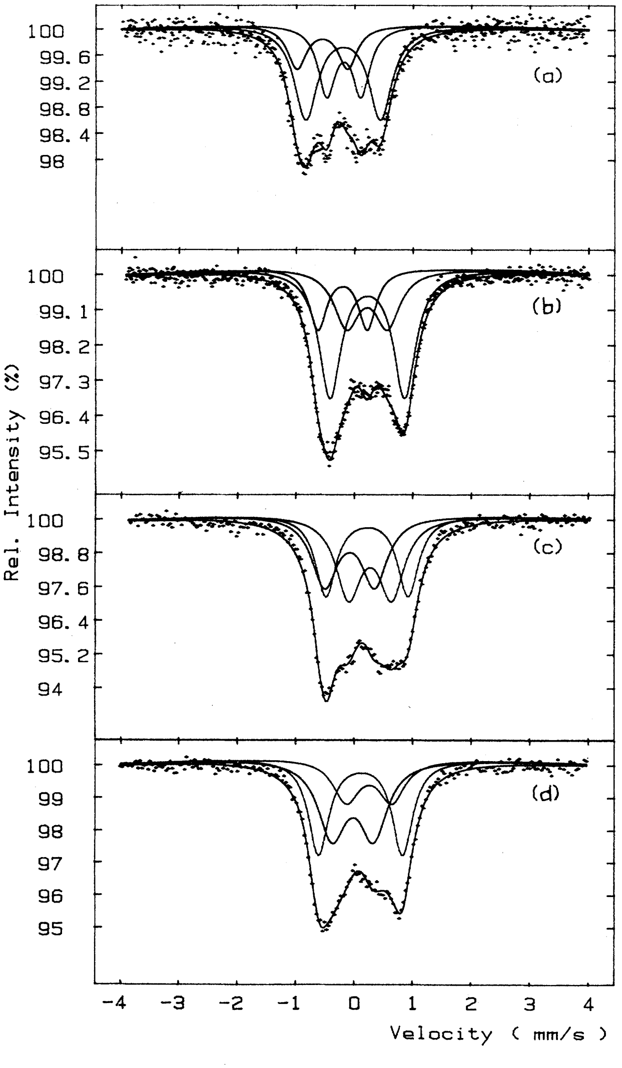

FIG. 1. The Mössbauer spectra of $Tl_2Ca_{1.5}Ba_{1.7}(Cu_{1-x}Fe_x)_3O_9$; (a) $x = 0.01$, (b) $x = 0.05$, and (c) $x = 0.07$ at room temperature, and (d) $x = 0.07$ at 77 K.

Mössbauer spectra of polycrystal absorbers with different iron compositions ($x = 0.01$, 0.05, and 0.07) at room temperature and the Mössbauer spectrum of $x = 0.07$ at 77 K (superconducting state) are shown in Fig. 1. These spectra were obtained by a MS-500 Mössbauer spectrometer, ^{57}Co in a Pd matrix served as a γ-ray source, and the four inner lines of natural iron foil were used for calibration. In each case, the spectra comprise three symmetric Lorentzian doublets which can be assigned as A, B, and C and represent the different Cu sites by partial substitution with Fe at both phases in these samples. As shown in Fig. 2, the Cu atom has only one site in the 2:1:2:2 phase and two unequivalent sites in the 2:2:2:3 phase, then we make the doublets A and B characterize the Cu sites in the square plane and octehedron of the 2:2:2:3 phase, respectively, and the doublet C in the 2:1:2:2 phase. The fitted Mössbauer parameters of these doublets are listed in Table II. Based on this table, the ratio of the subspectrum area of doublet A to the total spectra area increase appreciably with the decrement of iron. This fact reveals that the iron atom is favored to occupy this special Cu site characterized by the doublet A. From the results of Refs. 1–3, the T_c value of the 2:2:2:3 phase is higher than that of the 2:1:2:2 phase and will become lower with an increment of iron. The above fact would give us a significant result. We could confirm that the Cu atom in the square-planar site plays an important role in Tl-Ca-Ba-Cu-O superconductivity.

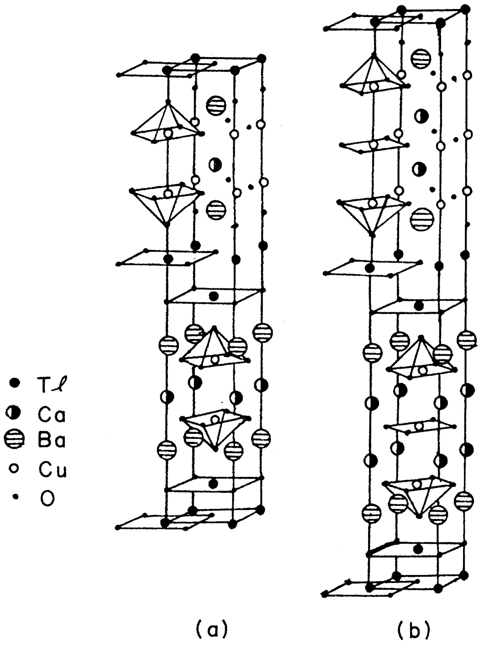

FIG. 2. Primitive cell for tetragonal Tl-Ca-Ba-Cu-O; (a) 2:1:2:2 phase and (b) 2:2:2:3 phase.

TABLE II. Fit parameters for the $Tl_2Ca_{1.5}Ba_{1.7}(Cu_{1-x}Fe_x)_3O_9$ powder samples spectra measured by the ^{57}Fe Mössbauer effect. (RT, room temperature; IS, isomer shift; QS, quadrupole splitting; FWHM, full width at half maximum; S_i, subspectrum area; S, total spectrum area.)

		0.01	0.05	0.07	0.07
Temperature		RT	RT	RT	77 K
IS (mm/s)	*A*	0.10(2)	0.17(1)	0.12(4)	0.16(1)
	B	−0.27(3)	−0.25(2)	−0.18(8)	0.00(1)
	C	0.11(2)	0.17(3)	0.17(4)	0.30(7)
QS (mm/s)	*A*	1.26(4)	1.28(4)	1.41(9)	1.44(8)
	B	0.85(5)	0.84(2)	0.85(10)	0.71(10)
	C	0.56(4)	0.70(10)	0.74(8)	0.78(10)
FWHM (mm/s)	*A*	0.49(7)	0.46(4)	0.43(7)	0.42(5)
	B	0.39(8)	0.37(4)	0.53(10)	0.58(10)
	C	0.34(7)	0.52(12)	0.52(7)	0.54(11)
S_i/S (%)	*A*	56	53	31	38
	B	18	20	32	41
	C	26	27	37	21

It is not difficult to estimate the quadrupole splitting of doublets *A*, *B*, and *C* according to the simple point-charge model. Obviously, the quadrupole splitting of doublet *A* must be larger than that of doublets *B* and *C*. Our experimental results are basically consistent with the theoretical calculation. The effect of an oxygen vacancy at an Fe nearest neighbor on the electric quadrupole splitting of different sites is very different. For the square-planar Cu site denoted by the doublet *A*, the increment of oxygen vacancies will reduce the value of the quadrupole splitting, while for the doublets *B* and *C*, corresponding to similar octahedral sites in different phases, the electric quadrupole splitting would increase with the decrement of the oxygen vacancies if they were positioned in the plane of the octahedron, or would decrease with the decrement of the oxygen vacancies if they were in the top of the octahedron. From the above discussion we can understand the variation of the electric quadrupole splittings of doublets *A* and *C* in terms of the increment of iron. The quadrupole splitting 0.85 mm/s of doublet *B* is a typical value of octahedral Fe^{3+}.[5] It implies that this doublet may correspond to the Cu sites at which all the nearest-neighbor sites are occupied, including those oxygen sites that are normally vacant. So these values of the electric quadrupole splitting do not vary with the content of iron.

The isomer shifts of doublets *B* and *C* are very different due to the unlike nearest-neighbor environments, although both Fe nuclei corresponding to doublets *B* and *C* are in similar octahedral interstitial sites. It is worth pointing out that the shifts of the center of gravity in doublets *B* and *C* of the sample with $x = 0.07$ have increased obviously since the sample is in the superconducting state. These variations might roughly come from the second-order Doppler thermal shift. However, the change of the shift of doublet *A* is rather small (0.04 mm/s), so there might be another factor to compensate for the thermal shift. Perhaps it is the difference of the density of *s* electrons at the Fe nuclei between the superconducting and normal state. The values of the linewidths are much larger than the natural linewidth owing to the inhomogeneous hyperfine interaction caused by the wide range of nearest-neighbor environments.

The authors would like to acknowledge Professor Li Zhe for the Mössbauer-effect measurements at 77 K.

---

[1] Z. Z. Sheng and A. M. Hermann, Nature (London) **332**, 55 (1988).

[2] C. W. Chu, J. Bechtold, L. Gao, P. H. Hor, Z. J. Huang, R. L. Meng, Y. Y. Sun, Y. Q. Wang, and Y. Y. Xue, Phys. Rev. Lett. **60**, 941 (1988).

[3] Z. Z. Sheng and A. M. Hermann, Nature (London) **332**, 138 (1988).

[4] R. M. Hazen, L. W. Finger, R. J. Augel, C. T. Prewitt, N. L. Ross, C. G. Hadidacos, R. J. Heaney, D. R. Vebley, Z. Z. Sheng, A. El Ali, and A. M. Hermann, Phys. Rev. Lett. **60**, 1657 (1988).

[5] Q. A. Pankhurst, A. M. Morrish, M. Raudsepp, and X. Z. Zhou, J. Phys. C **21**, L7 (1988).