Mössbauer observation near the superconducting transition temperature in the $TlBaCa_3Cu_3O_{8.5}$ superconductor

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The $TlBaCa_3Cu_3O_{8.5}$ superconductor contains two main superconducting phases, 1:2:2:3 and 2:2:2:3, identified by powder x-ray analysis. Using ^{57}Fe Mössbauer nuclei as the probe, it has been confirmed that the results are the same as those furnished by x-ray analysis. It has also been proved that iron atoms in the lattice substitute two inequivalent sites of copper atoms for each main phase. We have observed a temperature dependence of the Mössbauer parameters, i.e., quadrupole splitting, isomer shift, and relative resonance area. Here several problems are discussed related to the lattice dynamics and the electric charge transfer, which takes place in the transition from normal state to superconducting state.

Since Sheng *et al.*[1] reported a superconducting transition in the Tl-Ba-Ca-CuO system with the onset temperature of 120 K in early 1988, attempts have been made to study the phase composition, the relevant crystal structures, etc.[2–4] In this paper we will discuss some significant and interesting results obtained using the ^{57}Fe Mössbauer effect on the micromechanism of $TlBaCa_3Cu_3O_{8.5}$ superconductor.

In order to explore the micromechanism of the Cu-O layer and the electronic structure around copper atoms, a small amount of iron atoms taken as the probe are introduced into $TlBaCa_3Cu_3O_{8.5}$. The nominal composition of the sample, $TlBaCa_3Cu_{2.93}Fe_{0.07}O_{8.5}$, is prepared by thoroughly mixing appropriate quantities of dry powders of Tl_2O_3, CaO, BaO, CuO, and Fe_2O_3 (90% enriched in ^{57}Fe). Then the mixture is pressed into a pellet and wrapped in a golden foil. The temperature of the open furnace in which all samples were heated was raised to 910 °C. Then this temperature was maintained for 10 min and the samples were heated in flowing oxygen. After that the furnace is cooled down slowly at the rate of 2 K per min to room temperature.

The resistive transition of these samples is examined by means of the standard dc four-probe technique, and their susceptibility is tested using the method of ac mutual inductance. The results indicate that the onset transition temperature is 110 K and the zero-resistance temperature is 100 K for $TlBaCa_3Cu_{2.93}Fe_{0.07}O_{8.5}$. While, for the iron-free sample, $TlBaCa_3Cu_3O_{8.5}$, the onset transition temperature is 123 K and the zero-resistance temperature is 116 K. Obviously, the effect of doping iron in $TlBaCa_3Cu_3O_{8.5}$ exists. However, its superconductivity is better than that of $Tl_2Ba_{1.7}Ca_{1.5}(Cu_{1-x}Fe_x)_3O_9$.[5]

Powder x-ray diffraction is carried out by Cu $K\alpha$ radiation using the Y-2 diffractometer. The results show that the samples consist of two main phases and a few impurity phases. Both dominant phases are identified. One of them has the component of 2:2:2:3, i.e., $Tl_2Ba_2Ca_2Cu_3O_{10}$ and the other has 1:2:2:3 corresponding to $TlBa_2Ca_2Cu_3O_{8.5}$. When iron atoms are added in the sample, the phase composition in the sample is roughly the same as the iron-free one. It is found that the 2:2:2:3 phase includes a bilayer of Tl-O units and is a body-centered tetragonal lattice with space group $I4/mmm$, while the 1:2:2:3 phase contains a monolayer of Tl-O units and is a simple tetragonal lattice with space group $P4/mmm$. Applying the least-squares fitting program, we obtained the lattice parameters of the two main phases for the composition of Fe, x, as follows: $x=0$: $a=3.985$ Å, $c=38.98$ Å; $x=0.07$, $a=3.983$ Å, $c=39.16$ Å for the 2:2:2:3 phase, and $x=0$: $a=3.850$ Å, $c=15.97$ Å; $x=0.07$: $a=3.996$ Å, $c=15.89$ Å for the 1:2:2:3 phase.

Both phases, 2:2:2:3 and 1:2:2:3, coexist and intergrowth appears in our samples. The appearance of better superconductivity might be due to the special heat treatment adopted in preparing the sample and the dominant phases being formed by the phases 1:2:2:3 and 2:2:2:3. There are two kinds of oxygen coordination numbers of copper: five in pyramidal and four in square plane. In other words, the copper atoms have inequivalent sites in each main phase.

Mössbauer measurements are performed using a MS-500 Mössbauer spectrometer. ^{57}Co is put in the Pd matrix to serve as a γ-ray source and the velocity of the driving unit of the spectrometer was measured by a Michelson interferometer. The Mössbauer spectra for $TlBaCa_3Cu_{2.93}Fe_{0.07}O_{8.5}$ at various temperatures, 290, 130, 115, 100, 90, and 80 K, are shown in Fig. 1. According to the x-ray-diffraction analysis, all Mössbauer spectra are fitted with four symmetric Lorentzian doublets that can be labeled *A*, *B*, *C*, and *D*. *A* and *B* represent the two kinds of inequivalent Cu sites, partially replaced by iron atoms, in the 2:2:2:3 phase. Similarly, *C* and *D* are in the 1:2:2:3 phase. Both *A* and *C* represent the four-coordinate square-planar Cu(1) site with a formal oxidation state of ^{57}Fe,[6] whereas *B* and *D* represent the five-coordinate square-pyramidal Cu(2) site. The Mössbauer parameters of each doublet at various temperatures are given in Table I, where the relative abundance listed in Table I is defined as the resonance area ratio of each doublet to total doublets.

The dependence of relative abundances on temperature is drawn in Fig. 2. Based on Table I and Fig. 2, the relative abundances of all doublets are almost the same at room temperature. Only the relative areas for *A* and *C* are slightly larger than that of *B* and *D*. However, the situation is different for *A* and *B*, especially at lower temperature. This can be seen from Fig. 2. The relative abundance of *A* increases by 18% as temperature decreases from 290 to 115 K and drops down by 6% as temperature decreases from 115 to 100 K. On the contrary, within the same ranges of temperature, the relative abundance of *B* decreases about 17% and successively increases about 6%. The variation of the relative abundance *A* and *B* compensate each other. It is worthy to note that such a situation mentioned above just occurs around the superconducting transition temperature (100 K). As for doublets of *C* and *D*, we can find a similar tendency accompanied with only a small deviation of relative abundance in comparison with that of *A* and *B*. With regard to the relative abundance, we can conclude that, in the sample, the quantity of the 2:2:2:3 phase is slightly more than one-half and the iron atoms in it should preferentially occupy the square-planar Cu(1) site at low temperature.

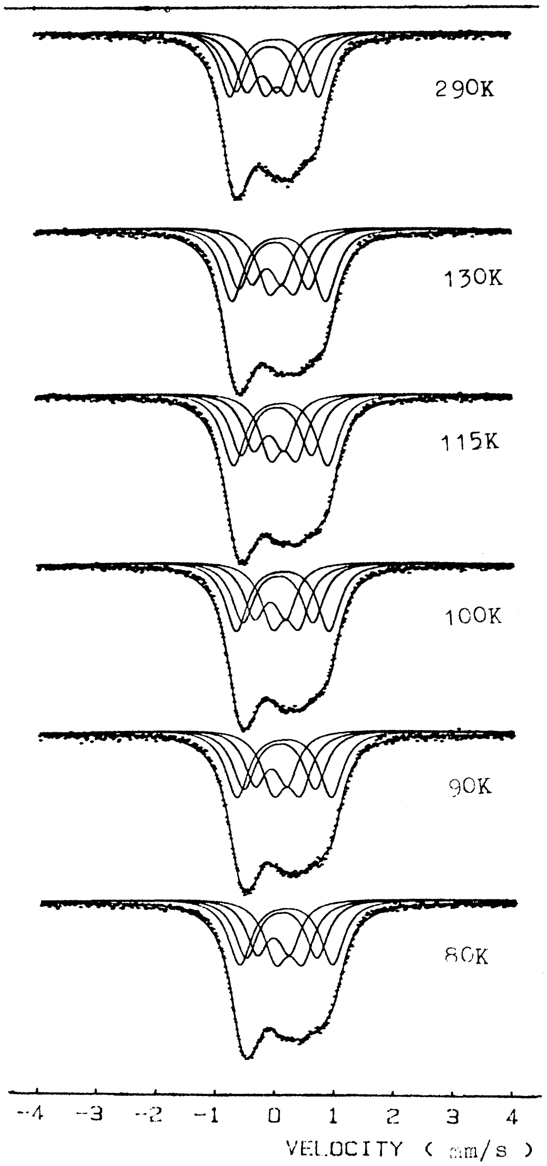

FIG. 1. Mössbauer spectra of $TlBaCa_3Cu_{2.93}Fe_{0.07}O_{8.5}$ at several temperatures.

There is a relation between the resonance area S' of the Mössbauer spectrum and the Debye-Waller factor f. In a harmonic solid it is given by

$$-\ln S' \propto -\ln f \ .$$

In order to eliminate the error of data treatment, we use the temperature dependence of the relative resonance area η to reflect the temperature dependence of Debye-Waller factor; here η can be expressed by

$$\eta = \frac{\sum_i S_i}{S} \ ,$$

where S_i is the resonance absorption area of the ith subspectrum and S denotes the total area of Mössbauer spectrum, i.e., $S = 2N_\infty v_{\max}$, here $v_{\max}$ is the maximum velocity of the Mössbauer source which is fixed at the electromagnetic driving unit and N_∞ is the base count of the spectrum. It is shown in Fig. 3 that an abnormal change of $\ln\eta$ appears near the transition temperature. The abnormal change of $\ln\eta$ at 90 K reveals that the lattice changes when the sample transforms from the normal state to the superconducting state. The lattice of the sample might be softened, similar to the report of Kimball.[7]

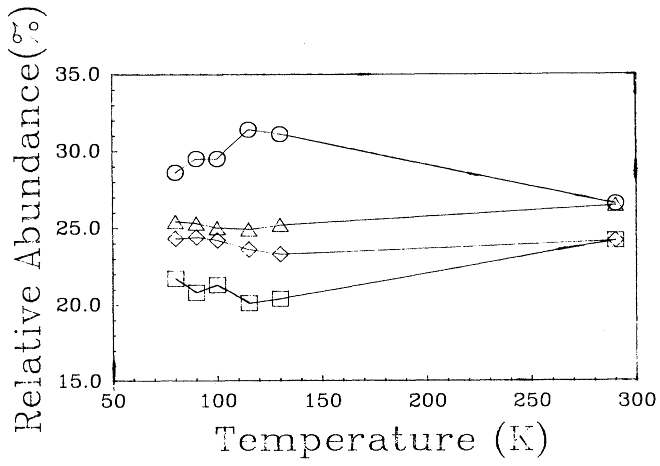

FIG. 2. The temperature dependence of the relative abundance for the doublets *A*, *B*, *C*, and *D*. Where the open circle and square denote doublets *A* and *B*, the open triangle and diamond stand for doublets *C* and *D*.

TABLE I. The fitting results of the Mössbauer data for $TlBaCa_3Cu_{2.97}Fe_{0.03}O_{8.5}$ at several temperatures. (IS, the shift of the gravity center of the subspectrum, relative to α-Fe; QS, quadrupole splitting; FWHM, full width at half maximum. Relative abundance is defined as the ratio of the area for a subspectrum to the total resonance area for all subspectra.)

Temperature (K)		80	90	100	115	130	290
IS (mm/s)	*A*	0.271	0.264	0.258	0.249	0.243	0.178
	B	0.059	0.050	0.050	0.049	0.037	−0.020
	C	0.197	0.187	0.179	0.177	0.158	0.104
	D	0.320	0.310	0.307	0.298	0.292	0.225
QS (mm/s)	*A*	1.57	1.58	1.55	1.58	1.58	1.49
	B	0.54	0.54	0.53	0.51	0.51	0.53
	C	1.20	1.20	1.17	1.18	1.18	1.13
	D	0.45	0.44	0.44	0.44	0.44	0.42
Relative abundance	*A*	29.6	29.5	29.5	31.4	31.1	26.6
	B	20.7	20.8	21.3	20.1	20.4	24.2
	C	25.4	25.3	25.0	24.9	25.2	26.5
	D	24.3	24.4	24.2	23.6	23.3	22.7
Linewidth (mm/s)	*A*	0.47	0.47	0.46	0.48	0.48	0.42
	B	0.44	0.43	0.43	0.44	0.44	0.46
	C	0.45	0.46	0.45	0.46	0.46	0.46
	D	0.45	0.46	0.46	0.45	0.45	0.43

Presumably, some important information on electric density around iron nuclei will be given from the temperature dependence of the shift of the gravity center of each doublet. In general, the position of the centroid of the Mössbauer pattern, $\delta(T)$, is determined by two factors:

$$\delta(T)=\delta_{\rm IS}+\delta_{\rm th}(T)\ .$$

Here $\delta_{\rm IS}$ is the isomer shift and $\delta_{\rm th}(T)$ is the second-order Doppler thermal shift. The thermal shift is proportional to the mean-square velocity of the Mössbauer atom, $\langle v^2\rangle$, i.e.,

$$\delta_{\rm th}(T)=\langle v^2\rangle/2c\ ,$$

where c is the light velocity. Considering our experimental conditions, we can use the Debye model in the low-temperature approximation to our samples; that is,

$$\langle v^2\rangle=\frac{9K_B\Theta_D}{8M}\left[1+\frac{8\pi^4}{15}\left[\frac{T}{\Theta_D}\right]^4\right]\ .$$

Then $\delta(T)$ can be written as

$$\delta(T)=a+bT^4\ ,$$

where a and b are constants. The relation between $\delta(T)$ and T^4 is a linear one. If we make a linear fitting for the above formula in the temperature range from 130 to 80 K, the linear correlation coefficients for *A*, *B*, *C*, and *D* doublets can be obtained, i.e., −0.958, −0.919, −0.961, and −0.945, respectively. The linearity of $\delta(T)$ versus T^4 (Fig. 4) is not very good. This situation suggests that we should think over the assumption mentioned above: whether it is true and whether the a in the equation is

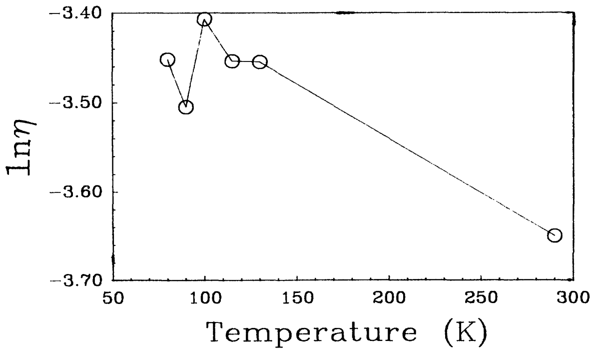

FIG. 3. The temperature dependence of $\ln\eta$, where η denotes the ratio between the sum of the resonance area for all subspectra and the total area of Mössbauer spectrum.

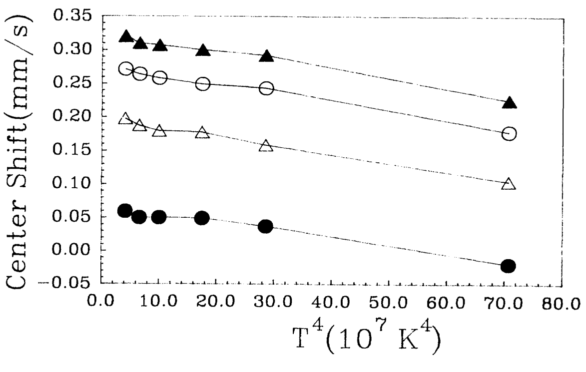

FIG. 4. The dependence of the shift of gravity center on the temperature to fourth power for the doublets *A*, *B*, *C*, and *D*. Where the open and solid circles denote doublets *A* and *B*, the open and solid triangles stand for doublets *C* and *D*.

constant. In other words, δ_{IS} is probably dependent on the temperature. In fact, we hardly think that the isomer shift under our condition is independent of temperature, since the volume should vary as the temperature changes. So, the isomer shift should also change. With respect to our situation, the value of δ_{IS} of ^{57}Fe should decrease as the temperature drops down. However, referring to Table I and Fig. 4, we find that the value of δ_{IS} of all doublets increases with the decreasing of temperature. This makes us look for another reason which causes the variation of δ_{IS} with temperature. We think that the significant increasing the isomer shift of all doublets from the normal states to the superconducting state deducts an effect of thermal shift. This means that significant changes of the electron density and oxidation occur. Such an interesting result indicates that the electric-charge-transfer phenomena emerges when the sample transits from the normal state to the superconducting state. Otherwise, it is difficult to explain the above experimental results.

According to the simple point-charge model, we obtain the quadrupole splittings of doublets *A*, *B*, *C*, and *D*, respectively. The quadrupole splittings of doublets *A* and *C* must be larger than that of *B* and *D*. In view of the effect of either an oxygen vacancy at the iron nearest neighbor on the quadrupole splitting or the oxygen content for the 2:2:2:3 phase being larger than that of the 1:2:2:3 phase, we conclude that the quadrupole splitting of doublet *A* should be larger than that of doublet *C*. In Table I, the quadrupole splittings of the most doublets, except *B*, increase at the beginning as the temperature decreasing from room temperature to superconducting transition temperature. Then all of them change in almost the same way.

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