

The structural-chemical state of ^{57}Fe in high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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Abstract. Mössbauer spectra using iron-57 and tin-119 nuclei in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ oxides are reported, using samples prepared under different conditions of heat and gas treatment. The separation of copper charge states between different structural positions is supported by these studies.

Keywords. High temperature superconductivity; Mössbauer spectra; structural-chemical state; copper charge separation.

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Doping of superconductive ceramics is one of the promising methods to control the physico-chemical properties of a new class of materials. The application of the modern resonance methods of investigations, which enables one to obtain the local structural-chemical information, is of special value. However, the electrical conducting properties of this substance make it difficult to effectively use the possibilities of NMR and NQR spectroscopies. In this connection Mössbauer spectroscopy on iron-57 and tin-119 isotopes has obvious advantages. These isotopes, we believe, will substitute copper ions, although the case of tin is less obvious and demands special analysis.

In the present work the attempt has been made to implant iron-57 and tin-119 in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ to study the states of these ions in the substance under different external effects.

Until this work was completed we had some general information about the effect of doping by the elements of interest or the elements close to them in their chemical properties. However, developments in this field have been so rapid that new research findings are continuously reported.

The substitution of copper in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ for Fe, Co, Ni, Zn, Ga, Al even by several percents causes a marked decrease in transition temperature into the superconducting state (Matsushita *et al* 1987; Moeno *et al* 1987). Doping by iron has been investigated in detail where T_c reaches about 80°K or lower for $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-\delta}$ at $x = 0.02$ (Matsushita *et al* 1987). The concentration increase above this value stabilizes the tetragonal phase under the normal conditions: 880–1000°C, 14–27 h in air.

In the present work $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-\delta}$ ceramics ($x = 0.02$ and 0.05 for Fe^{57} and $x = 0.05$ for ^{119}Sn) have been synthesized from metal stoichiometric mixture of yttrium

Table 1. Treatment of high-temperature superconductors and the unit cell parameters.

Sample No	Treatment characteristics	Unit cell parameters, Å		
1	Decomposition of homogenized mixture, 900°C, 30 min in air (contains ⁵⁷ Fe: $x = 0.02$)	3.863	11.733	
2	Annealing of the pressed sample No 1 at 900°C in air for 3 h, quenching in air	3.866	11.730	
3	Annealing of the sample No. 1, 900°C, 5 h in air			
4	Sample No 3, annealing in 9-atm. O ₂ at 550°C, 5 h	3.860	11.680	
5	Sample No 4, annealing for 1 h 500°C, vacuum (10^{-6} torr)			
6	Sample No 5, annealing for 1 h 600°C, vacuum (10^{-6} torr)	3.862	11.799	
7	Annealing after decomposition and pressing at 900°C, 3 h (⁵⁷ Fe content $x = 0.05$)	3.863	11.685	$\delta = 0.04$
8	Sample No 7, annealing in O ₂ under 3 atm, 2 h, 700°C	3.863	11.667	$\delta = -0.06$
9	Sample No 8, annealing at 700°C, 2 h, vacuum (10^{-2} torr)	3.863	11.761	$\delta = 0.46$

Note. Annealing was carried out at room temperature. In other cases the cooling rate was 150°/hour.

oxide (99.99), copper oxide (99.9) and barium nitrate (99.9) and the corresponding isotopes of 80–90%-enrichment in the form of oxides. The initial mixture was homogenized and dispersed to particles of about 1 μ , which was taken to the stage of decomposition of barium nitrate to produce practically the single-phase end product. For further treatment the conditions of guaranteeing the production of a well-crystallized single-phase sample (table 1) were chosen. The basis of this choice is the investigation of the structure and properties of YBa₂Cu₃O_{7- δ} ceramics thus produced and heat-treated under different conditions (annealing temperature, time and atmosphere, cooling conditions). The main characteristics of the treatment conditions for typical samples are listed in table 1.

All the presented values of chemical shifts of δ are given relative to pure iron and the temperatures of source and absorbent were the same. The Mössbauer spectra were processed on computer by the method of least squares.

To ensure additional control over the doping isostructure compositions with high iron content ($x = 0.33, 0.67, 1.00$) were synthesized. The samples were prepared using the same methods, the annealing time being 200 h at 900°C with $x = 0.33$. The substance contains 80% of the basic cubic phase of perovskite with $a = 3.866$ Å. At room temperature the Mössbauer spectra consist of two components: magnetic— $\delta = 0.29$ mm/s, $\epsilon = 0.06$ mm/s, $H = 357$ kOe (64%) and doublet— $\delta = 0.13$ mm/s, $\epsilon = 1.14$ mm/s (36%). At 78° K one state with $H = 483$ kOe was observed. For $x = 0.67$ the mixture of two perovskite-like phases with $a = 3.866$ and 4.050 Å were obtained. At room temperature. The two components observed in spectra were magnetic (52%),

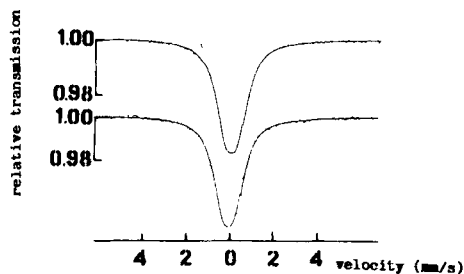


Figure 1. Mössbauer spectra of ^{119}Sn samples Nos 11 (bottom) and 12 (top) at room temperature.

$\delta = 0.31$ mm/s, $\varepsilon = 0.12$ mm/s, $H = 382$ kOe and doublet, $\delta = 0.27$ mm/s, $\varepsilon = 0.81$ mm/s. At 78°K the effective magnetic field of the first component increases to 500 kOe. For $x = 1.00$ the basic phase was perovskite-like with $a = 3.94$ Å. At room temperature the magnetic phase (80%) is observed ($\delta = 0.35$ mm/s, $\varepsilon = 0.06$ mm/s, $H = 484$ kOe). Iron states in doped samples with $x = 0.02$ and 0.05 were not observed.

The results of Mössbauer investigations of the sample nos. 10–12 for ^{119}Sn reveal that the spectral parameters are close to similar values for SnO (figure 1); there are additional reflections in the X-ray patterns which are hard to identify. Probably Sn does not normally enter the structure of the compound under these synthesizing conditions. Special annealing for 200 h in air (900°C) resulted in insignificant broadening of the lines in spectrum (by 30%) with insignificant variations in X-ray patterns. In table 1 the parameters of the basic component (orthorhombic modification) (figure 3) are listed for the 200-hours annealing. The substance transforms into superconducting state at temperatures higher than the liquid nitrogen temperature. For Sn to fully enter the lattice, it is probably necessary to substantially decrease the concentrations and use the prolonged annealing regimes (hundreds of hours) at 900 – 950°C . However, in this case, it is difficult to control the existence of a single phase in the samples using the customary X-ray diffraction methods, and further investigations are necessary.

Mössbauer investigations of $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-\delta}$ for $x = 0.02$ and 0.05 showed qualitatively similar results. Of all the samples described in table 1 only sample no. 5 exhibits the Meissner effect, and the temperature measurements of resistance showed the existence of a broad (estimates: $\Delta T = 10^\circ$) transition into the superconducting state in liquid nitrogen temperature region and this transition did not end completely by 78°K . At used concentrations of Fe the tetragonal phase is stabilized including the superconductive sample No 5. As is to be expected, in the pure tetragonal phase $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, the transition into the superconductive phase above 1.6°K is not observed (Nakazawa *et al* 1987, 1988). Comparison of the results of Nakazawa *et al* with our data (table 1) leads us to the conclusion that heat-treatment in oxygen under high pressure increases T_c . Such a behaviour in ceramics corresponds to similar results in undoped samples (Pavlyuhin *et al* 1988a, b).

In figure 2 the change of structural-chemical state of Fe ions in the samples under different conditions is shown. In tables 2 and 3 the parameters of the observed ^{57}Fe states are presented. In spectra three different structural-chemical states of iron ions are distinguished. One of them (III, tables 2 and 3) corresponds to the high-spin state of Fe^{3+} (chemical shift $\delta = 0.30$ – 0.35 mm/s). Under the present conditions its content

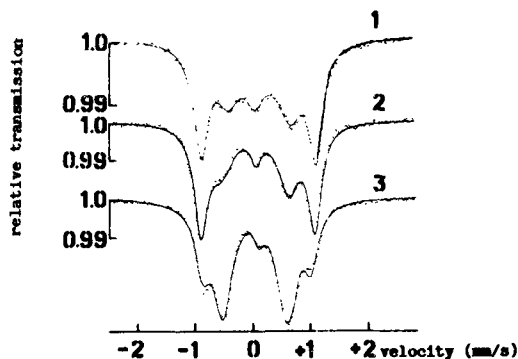


Figure 2. Mössbauer spectra of the ^{57}Fe samples Nos 9(1), 7(2) and 8(3) at room temperature.

always decreased both in vacuum and in oxygen under pressure (figure 3 and tables 2 and 3). According to the available data the samples were single-phase, therefore the presence of the high-spin Fe^{3+} ought to be attributed to some structural position of small cations in the layered perovskite-like structure $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Probably, in a temperature range 500–900°C, iron cations have marked mobility so that high-temperature treatment (900°C) leads to occupancy of energetically less favourable structural positions, in which iron ions have the degree of oxidation 3+. When the temperature decreases to $\approx 500^\circ\text{C}$ the degree of occupancy of these positions substantially decreases. The change of occupancy of oxygen structural sites $4i$ for the space group of tetragonal phase P4/mmm (Izumi *et al* 1987; Pavlyuhin *et al* 1988b) according to the used atmosphere of treatment and substantial redistribution of the I and the II components intensities in Mössbauer spectra (tables 2 and 3, figures 2 and 3) enable one to attribute the I and the II components to the structural site Cu(1) and the III state to Cu(2).

The chemical shift of the I and the II states under all treatment conditions did not vary substantially and was 0.00–0.05 mm/s (tables 2 and 3). In literature low-spin ($\delta \approx 0.00$ mm/s) and high-spin ($\delta \approx -0.19$ mm/s) states of Fe^{4+} are described for close

Table 2. Parameters of the observed ^{57}Fe states.

Sample No	Concentration of iron ions state (%)			Superfine interaction parameters of iron ions at room temperature (mm/s)					
				I state		II state		III state	
	I	II	III	δ	ϵ	δ	ϵ	δ	ϵ
1	42	45	13	0.05	1.96	0.06	1.01	0.33	0.66
2	58	29	13	0.07	1.96	0.04	0.91	0.33	0.60
3	51	37	12	0.03	1.95	-0.02	1.09	0.31	0.60
4	29	66	5	0.03	1.89	-0.01	1.10	0.37	0.58
6	80	20	—	0.01	1.99	0.01	0.66	—	—
7	34	58	8	0.04	1.97	0.00	1.09	0.35	0.61
8	21	78	1	0.04	1.94	-0.01	1.04	—	—
9	65	35	—	0.07	1.98	0.10	0.74	—	—

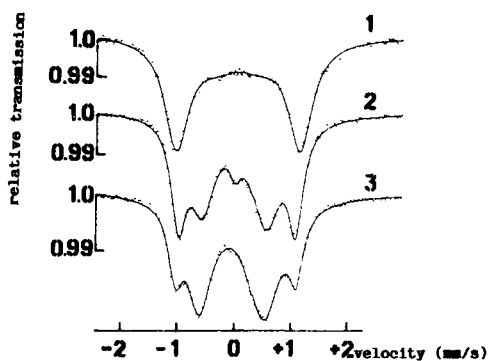
Table 3. Parameters of the observed ^{57}Fe states.

Sample No	Concentration of iron ions state (%)			Superfine interaction parameters of iron ions at 78 K (mm/s)					
				I state		II state		III state	
	I	II	III	δ	ϵ	δ	ϵ	δ	ϵ
2	63	23	14	0.03	2.02	-0.02	0.84	0.30	0.65
4	30	62	8	0.00	1.94	-0.05	1.10	0.35	0.56
6	—	—	—	0.05	2.06	—	—	—	—
7	36	56	8	0.02	2.04	-0.05	1.07	0.28	0.61
8	22	77	1	0.01	1.93	-0.06	1.02	—	—
9	67	33	—	0.04	1.93	0.03	0.69	—	—

systems (Grenier *et al* 1981; Demazeau *et al* 1984; Takeda *et al* 1986). This is attributed to the observed states to low-spin Fe^{4+} . Considering that the oxygen content in a layer may vary within a significant range (Izumi *et al* 1987a, b; Pavlyuhin *et al* 1988a, b), it is necessary to assign different oxygen ambience (different coordination numbers in Cu(1)-plane) to the I and II states. According to tables 2 and 3, vacuum treatment increases the I phase content. Therefore the coordination numbers of this state must be less than those of the II state. The probable cause of the Fe^{4+} existence in a low-spin state is the comparatively small cation-oxygen distances for the position 1a Cu(1) (2×1.808 and 4×1.927 Å) (Izumi *et al* 1987a).

One of the distinguishing features of the Mössbauer spectra of the I and II states is the values of the linewidth. For the I state they are 0.28–0.31 mm/s, and for the II state they are 0.40–0.50 mm/s. This reveals that the II state probably corresponds to the superposition of different crystallographic positions with similar Mössbauer parameters. If we assume that oxygen with concentration c is distributed randomly in Cu(1) plane by the $4i$ positions the probability of realization of the coordination number K near the cation chosen of five possible cations, is

$$P_K(c) = \frac{4!}{K!(4-K)!} c^K (1-c)^{4-K}. \quad (1)$$

**Figure 3.** Mössbauer spectra of the ^{57}Fe samples Nos 1(1), 3(2) and 4(3) at room temperature.

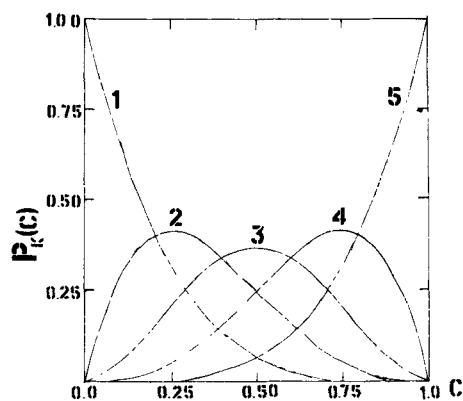


Figure 4. Function (1) of concentration c appearance depending on possible coordination number 1, $k = 0$; 2, $k = 1$; 3, $k = 2$; 4, $k = 3$; and 5, $k = 4$.

This is the well-known binomial distribution used for similar studies Mössbauer spectroscopy. Calculation of the value (1) is given in figure 4. Execution of the relationship (1) in practice demands the absence of correlations in Fe^{4+} and O^{2+} sites. This is not evident owing to the high oxygen mobility and as a consequence the impossibility of quenching of the occasional distribution of ions, existing at high temperatures, to its lower values. However the experimental results give the large effects, and probably it is reasonable to ignore the correlation effects while discussing possible conclusions.

The analysis of the I and II component intensities shows that their ratio varies at studied treatments 15 to 16 fold. Using the relationships in figure 4 it is easily seen that the only reasonable solution is to attribute the I state with $K = 0$ to (1). Then the II state is the superposition of all $K \neq 0$, which explains the more broad lines in the II state. As seen from figure 4 the concentration of oxygen ions in Cu(1) plane may change from 0.05 for sample No. 1 to 0.33 for sample No. 9. By considering the correlation of the unit cell sizes with the oxygen content for these samples we estimate the oxygen content to be $\delta = 0.78$ and 0.21 respectively (Pavlyuhin *et al* 1988b). Discrepancy between these values is outside the experimental errors and assumptions in Pavlyuhin *et al* (1988b). At the same time, for sample nos. 6, 9, 4 and 8, (samples treated at low temperatures and containing relatively smaller number of Fe^{3+}) a good correlation between the I state content — 0.80, 0.65, 0.29 and 0.21 (table 2) and $\delta = 0.78, 0.61, 0.28$ and 0.21 respectively is observed (see Pavlyuhin *et al* 1988a, b) where the second estimation is obtained). Note, that it is not easy to estimate the I state content when its concentration is high. In this case the computer processing of Mössbauer spectra (tables 2 and 3) shows that the II state manifests itself in a particular way different from the previous case.

The correlation seen may be explained by coexistence of two phases with oxygen content (6.0 and 7.0) in a sample, their ratio changes depending on treatment conditions. However, X-ray analysis indicates only one phase in a substance. The non-overlapped reflections (012), (113), (112) and (115) are always narrow and without splitting. In these substances the existence of microdomain structure is real (Pavlyuhin *et al* 1988b). However, it is extremely improbable that these domains will have the same structural characteristics in terms of X-ray analysis, but quite different compositions ($\delta = 0.0$ and 1.0).

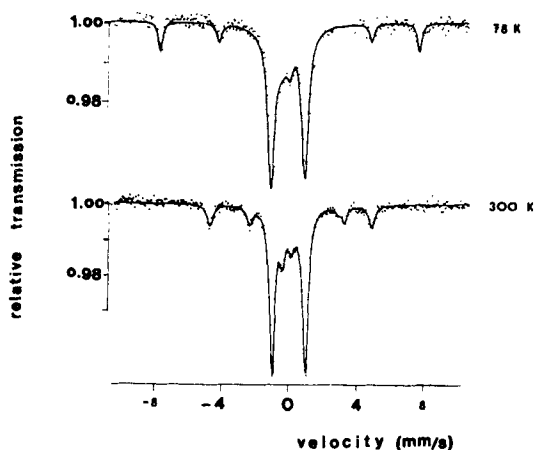


Figure 5. Mössbauer spectra of $\text{YBa}_2(\text{Cu}_{0.97}\text{Fe}_{0.03})_3\text{O}_{7-\delta}$, quenched from 900°C , illustrating the antiferromagnetic ordering in Cu(II)-layers.

At this stage one should admit the proposal (Pavlyuhin *et al* 1988a) to be more convincing. It is proposed that in the Cu(I) layer there are two types of oxygen: chemical O^{2-} in a customary form, and the other intercalated, neutral one, the effect of which on Mössbauer parameters is insignificant compared to O^{2-} . This explanation satisfies the Mössbauer, structural (Pavlyuhin *et al* 1988b) and DTA (Pavlyuhin *et al* 1988a) data at the same time.

The study of neutron diffraction in HTSC with extremely low oxygen content Tranquada *et al* 1987) revealed the anti-ferromagnetic ordering of Cu^{2+} ions in Cu(II) planes. Thus attributing the Mössbauer component of Fe^{3+} to the structural position of Cu(II) means that during the quenching from high temperatures in inert medium (liquid nitrogen) it is possible, using Mössbauer spectroscopy, to discover the magnetic transition that was found for the samples $\text{YBa}_2(\text{Cu}_{0.97}\text{Fe}_{0.03})_3\text{O}_{7-\delta}$. This transition is shown in figure 5. In the case of quenching from $900\text{--}940^\circ\text{C}$ the content of high-spin Fe^{3+} in Cu(II) structural position is $\approx 20\%$. In accordance with quenching temperature the value of effective field on the iron nuclei is 245 and 451 kOe for 900°C , 266 and 465 kOe for 920°C , and 294 and 477 kOe for 940°C (measurement temperature is 300 and 78 K respectively). For the magnetically ordered component of Mössbauer spectra, the chemical shift corresponds exactly to the III state (table 2). The comparison of the value of the quadrupole splitting of this component ($\varepsilon = 0.31 \pm 0.01$ mm/s) with similar values for the paramagnetic state (Table 2) shows

$$(3 \cos^2 \theta - 1)/2 = -\frac{1}{2}. \quad (2)$$

For Fe^{3+} , in the form of square pyramid, the z -axis of the tensor of electric field gradient is directed along the C axis, so for the effective field direction from (2) we obtain $\cos^2 \theta = 0$. Therefore, the axis of the easiest magnetization lies in the Cu(II)-plane, in accordance with conclusions of Tranquada *et al* (1987). The Mössbauer experiments at temperatures higher than room temperature enabled us to estimate the Néel temperature $T = 410 \pm 10$ K (the effective field at room temperature was 282 ± 4 kOe). The effect of quenching conditions on the magnetic field at room temperature reveals the dependence of Néel temperature on the oxygen content in

the samples, hardly controlled under these conditions. The estimation of the Néel temperature from the Brillouin dependence for $S = 1/2$ gives too low a value: $T_N = 340\text{--}350$ K, that is probably associated with the complex character of electron–electron correlations.

The antiferromagnetic ordering for tetragonal structures $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)\text{O}_{7-\delta}$ at quenching from $900\text{--}940^\circ\text{C}$ in liquid nitrogen was observed for $x = 0.03$ ($a = 3.855(3)\text{ \AA}$, $c = 11.788(6)\text{ \AA}$) and $x = 0.01$ ($a = 3.851(3)\text{ \AA}$ and $c = 11.790(5)\text{ \AA}$).

The unusual behaviour of quadrupole splitting for the II state (tables 2 and 3) is its marked decrease at low oxygen contents in a substance. For the samples quenched from 900, 920 and 940°C the splitting is obtained as 0.67 (0.64), 0.64 (0.58) and 0.57 (0.52) mm/s at 300°K (78 K). So this value varies depending on the oxygen content, from 1.10 mm/s to 0.57 mm/s.

Therefore the separation of the copper charge states between different structural positions may be considered to be well established. In the position with quintuple coordination there are Cu^{2+} ions, and in the Cu(I)-plane there are Cu^{1+} ions for the $\text{YBa}_2\text{Cu}_3\text{O}_6$ composition. The increase of oxygen content leads to producing Cu^{3+} in Cu(II)-layers. So in a substance Cu^{1+} , Cu^{2+} and Cu^{3+} ions exist simultaneously (in other words, the distribution of conduction electrons corresponds to this charge state).

Probably, the electron–electron correlations, resulting in transition into the superconducting state, are preceded by such concentrations of Cu^{3+} in Cu(II)-layer, when the antiferromagnetic transition becomes impossible.

Besides, the results obtained show that intercalation of neutral oxygen in Cu(I)-plane is probable for high temperature superconductivity.

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