

Oxygen surroundings of impurity iron atoms in ceramic $\text{YBa}_2\text{Cu}_3\text{O}_7$

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The Mössbauer spectra of the system $\text{YBa}_2\text{Cu}_{3(1-x)}^{57}\text{Fe}_{3x}\text{O}_{7-\delta}$ ($x = 0.01, 0.02,$ and 0.10) with various degrees of oxygen deficiency δ have been measured. The results show that the spectra are a superposition of four quadrupole doublets, which are identified with positions of iron atoms in the matrix. The changes caused in the chemical surroundings of the iron by the loss of oxygen are analyzed.

Our purpose in this study was to learn about the oxygen surroundings of iron atoms added to the superconducting ceramic by analyzing the changes in the Mössbauer spectrum of iron as the oxygen content in the system was reduced. For the measurements we used two lots of samples. From the first lot we studied one sample with an iron concentration $x = 0.01$; from the second lot we studied three samples, with $x = 0.01, 0.02,$ and 0.10 .

The characteristic parameters of the superconducting transition found from the first sample were $T_c = 83.9$ K and $\Delta T_c = 6.3$ K. The samples were made from a powder deposited on a aluminum foil and mounted with BF-6 cement. We used a Mössbauer source consisting of Co^{57} in a chromium matrix.

We measured each of the Mössbauer spectra twice: before and after vacuum treatment (evacuation at room temperature for a day). The vacuum treatment led to a change in the spectrum for only the sample from the first lot (Fig. 1).

We used a computer to analyze the spectra in an effort to find the smallest set of symmetric doublets for which each of the Mössbauer spectra available could be represented as a sum of these doublets with various weights. It turned out that a set of three doublets could not solve this problem. Table I shows the results of a resolution into four doublets. The errors indicated here correspond to the scatter in the values of the parameters over the various samples.

According to the present understanding,¹ an impurity iron atom takes one of two copper positions in the matrix, Cu1 or Cu 2 (Fig. 2). The first of these positions is characterized by orthorhombic surroundings of oxygen atoms, while the second has pyramidal surroundings. Estimates yield an electric-field gradient for Cu1 which is twice that for Cu 2 (see also Ref. 2). On this basis it can be suggested that the position Cu1 corresponds to doublet D1, and Cu 2 to either D 3 or D 4.

A more accurate identification of the doublets which we found with possible positions of iron atoms in the matrix would require comparing the weights of the various doublets in the spectra (Table II). A comparison of M1 and M 2 is particularly informative here, since the only possible distinction between them would be a de-

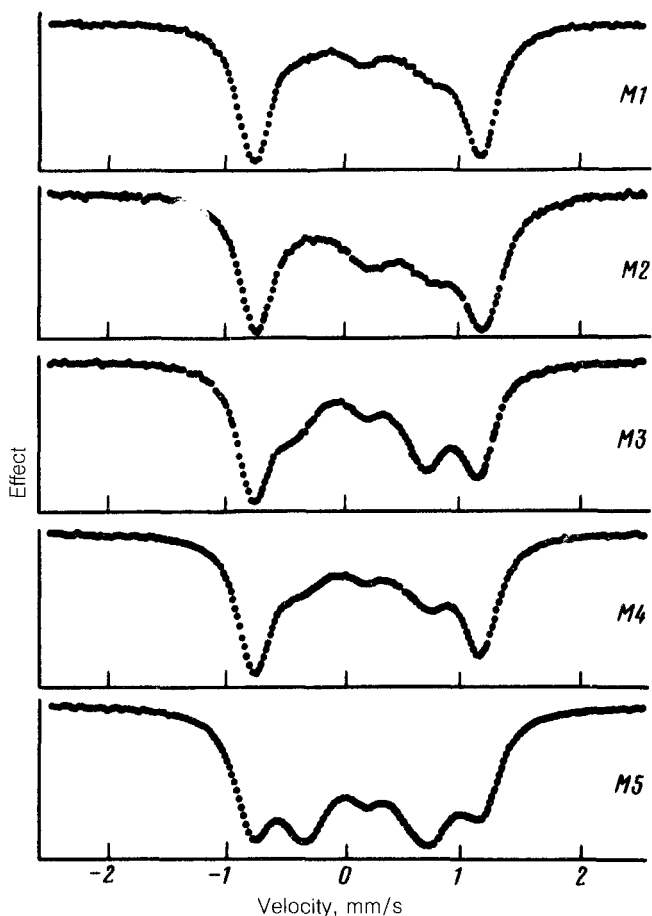


FIG. 1. Mössbauer spectra of the samples. M1, M2—Samples from the first lot, respectively before and after the vacuum treatment ($x = 0.01$); M3, M4, M5—samples from the second lot ($x = 0.01, 0.02, \text{ and } 0.10$).

crease in the oxygen concentration for M 2. It can be seen from Table II that 30% of the initial D1 and D 4 signals went into the D 3 and D 2 signals, respectively (within the indicated error in the determination of the partial contributions). It can thus be concluded that D1 and D 4 are signals of iron atoms from the Cu1 and Cu 2 positions,

TABLE I. Isomer shift (IS), quadrupole splitting (QS), and linewidth (LW) of doublets D1–D4.

Parameter	D1	Doublets		
		D2	D3	D4
$IS, \text{mm/s}$	0.17 ± 0.02	-0.01 ± 0.01	0.57 ± 0.01	0.07 ± 0.01
$QS, \text{mm/s}$	1.97 ± 0.01	1.46 ± 0.02	0.88 ± 0.02	0.87 ± 0.12
LW, G	3.30 ± 0.02	3.46 ± 0.04	3.31 ± 0.04	5.52 ± 0.06

● Cu2 ● Cu1 ○ O

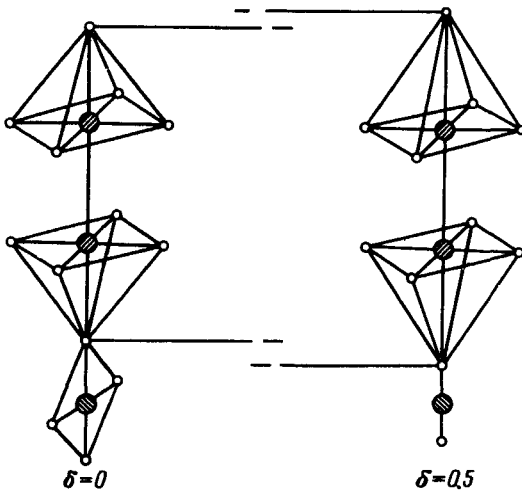


FIG. 2. Change in the chemical surroundings of the impurity iron atoms upon the loss of oxygen.

while D 3 and D 2 are signals from the same positions, but under conditions of an oxygen deficiency. The reason for the observed difference in the spectra for samples having the same iron concentration becomes clear: In samples 1 and 3, there is a difference in the relative populations of the Cu1 and Cu 2 positions. The fact that this ratio is substantially smaller than 2—the ratio of the numbers of Cu 2 and Cu1 positions in the matrix—in all the samples is evidence that the impurity iron atoms “go” into the orthorhombic oxygen surroundings far more actively than they go into the pure metal surroundings. Under these conditions, the relatively high population of Cu 2 positions in sample 3 may indicate the presence of “purely iron” clusters of $\text{Yba}_2\text{Fe}_3\text{O}_{7-\delta}$ in the third sample (in the tetragonal phase). It may be that a stronger binding of the oxygen atoms in such clusters was the reason why there were no changes in the Mössbauer spectra of the samples of the second lot during the vacuum treatment.

TABLE II. Relative weights of the doublets in the Mössbauer spectra.

Spectrum	Doublets			
	D1	D2	D3	D4
M1	8.08	2.49	2.34	1.69
M2	5.47	3.10	4.81	1.32
M3	4.69	2.93	1.97	4.98
M4	6.55	1.83	1.12	5.21
Statist. error	1.4%	5.0%	3.6%	6.4%

Working from the correspondence established between the doublets and the positions of iron atoms in the matrix, we can analyze the changes in the oxygen surroundings of the iron during the vacuum treatment. The reduction of the quadrupole splitting by a factor of two as we go from D1 to D 3 agrees with the interpretation that when an oxygen is lost from the surroundings of Cu1, two symmetrically positioned oxygen atoms remain near the copper atom.¹ Further evidence for this conclusion comes from the significant change in the isomer shift in the positive direction, which indicates a decrease in the electron density at the iron nucleus. The slight change in the chemical shift as we go from D 4 to D 2 forces us to assume that oxygen atoms do not leave the surroundings of Cu 2 and simply undergo a redistribution in space. In this case, the observed increase in the quadrupole splitting can be associated with a displacement of the oxygen atom at a vertex of a pyramid along the direction away from the base of the pyramid (Fig. 2).

The strong effect of the vacuum treatment in the first sample (30% of the iron atoms in Cu1 positions experience a change in their chemical surroundings) is evidence that in this case the oxygen atoms move away from the impurity iron atoms far more actively than on the average from the matrix. The "iron" and "copper" components of the system may thus be quite different from each other in terms of the oxygen deficiency δ .

¹Z. Yang, L. Wang *et al.*, Phys. Lett. **26**, 58 (1987).

²H. Tang, Z. Q. Qiu *et al.*, Phys. Rev. **B36**, 4018 (1987).

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