

# Proof of the metallic nature of the chemical bond and coexistence of magnetism and superconductivity in the $Y_{1-x}Fe_xBa_2Cu_3O_8$ system ( $0 \leq x \leq 0.5$ )

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Superconducting transitions have been observed in the  $Y_{1-x}Fe_xBa_2Cu_3O_8$  system at  $x \leq 0.3$ . In the interval  $0.1 \leq x \leq 0.3$ , a magnetic ordering of the Fe atoms in the "copper sublattice" is observed to coexist with a superconductivity. It has been established that all the cations in the 1–2–3 phase have a metallic chemical bond, so it is meaningless to discuss their valence states.

1. This letter reports the results of a synthesis of and study of the properties of, a metal-oxide superconducting ceramic based on the 1–2–3 phase that contains iron ions. In the synthesis of the samples, the yttrium ions were replaced by trivalent iron in order to avoid introducing additional charge perturbations in the "copper sublattice":  $Y_{1-x}^{3+}Fe_x^{3+}Ba_2Cu_3O_8$ , where  $x = 0.00, 0.01, 0.05, 0.1, 0.2, 0.3, 0.4, \text{ and } 0.5$ .

An x-ray analysis showed that at  $x \leq 0.2$  the samples are dominated by the 1–2–3 phase. The powder diagrams reveal no other phases containing iron. At  $x > 0.2$ , the basic 1–2–3 phase is joined by a small admixture of the  $Fe_2O_3$  phase, in an amount which reaches 5–8% at  $x = 0.5$ . An orthorhombic structure is retained at all concentrations; the parameters of the unit cell increase slightly.

2. Figure 1 shows the temperature dependence of the resistance  $R(T)$ . For the samples with concentrations  $0 \leq x \leq 0.2$  we observe a transition to a superconducting state at the temperatures listed in Table I. The point at which the superconducting transition begins varies only slightly in the interval  $0 \leq x \leq 0.2$ . As  $x$  is increased, the width of the transition along the temperature scale increases.

In the normal phase (at  $T > T_c$ ) the  $R(T)$  dependence is metallic at  $x \leq 0.05$ , and as  $x$  is increased, it gradually converts into a semiconductor dependence. A strict linearity of  $R(T)$  is not observed. At the concentrations  $x = 0.1, 0.2, \text{ and } 0.3$  the resistance typically increases just before the superconducting transition, with the result that a maximum appears on the  $R(T)$  curves (Fig. 1).

3. Figure 2 shows Mössbauer spectra of the samples at 295 K. The clearly expressed hyperfine structure in the spectra and its evolution with  $x$  allow an unambiguous resolution of the spectra into four components (three doublets and a singlet), which correspond to various crystallographic positions of the Fe atoms. We identify the doublet formed by the outermost lines of the spectrum with iron atoms which are replacing copper in tetragonal pyramids. These positions would be expected to have large gradients in the crystal electric field (and thus a large value of the quadrupole splitting  $QS$  in the  $Fe^{57}$  spectrum), due to a displacement of a cation from a central position in an oxygen pentavertex. We attribute the doublet formed by the inner pair

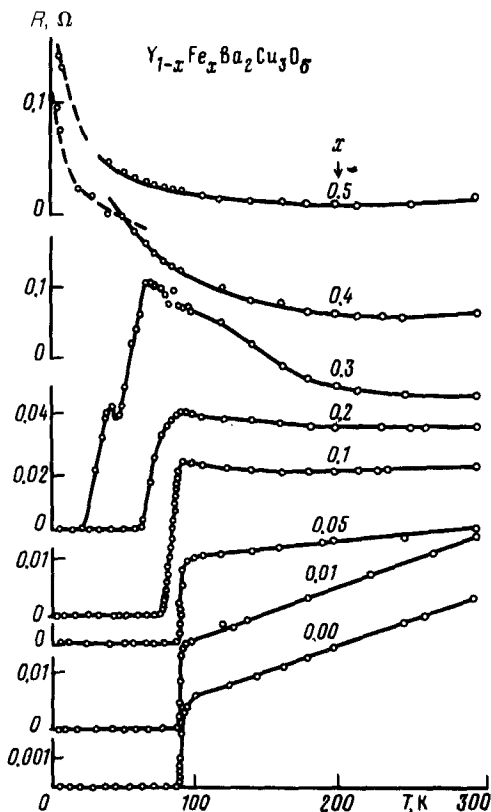


FIG. 1. Temperature dependence of the electrical resistance in the  $Y_{1-x}Fe_xBa_2Cu_3O_6$  system with various values of  $x$ .

of lines (which is clearly expressed in Fig. 2 for  $x = 0.2$  and  $0.3$ ) to iron atoms which have replaced copper ions in oxygen-incomplete octahedra: "squares" (these are positions of copper between two barium layers). The broadening of the lines of this doublet (the width is  $\Gamma = 0.6$  mm/s) is evidently due to some distribution of the Mössbauer parameters ( $QS$  and  $IS$ ) resulting from mobility of oxygen vacancies in these polyhedra. The broadened singlet at the center of the spectrum can naturally be linked with Fe atoms at positions of yttrium ions in nearly ideal oxygen cubes. The high local symmetry of the surroundings of the cation in these positions should lead to an unsplit

TABLE I. Temperature intervals of the superconducting transition; points of the magnetic ordering,  $T_N$ , in the  $Y_{1-x}Fe_xBa_2Cu_3O_6$  system.

$x$	0.0	0.01	0.05	0.1	0.2	0.3	0.4
$T_c$ interval, K	95 - 91	93 - 90	95 - 87	92 - 76	92 - 60	65 - 21	-
$T_N$ , K	-	-	-	~10	~25	~35	56

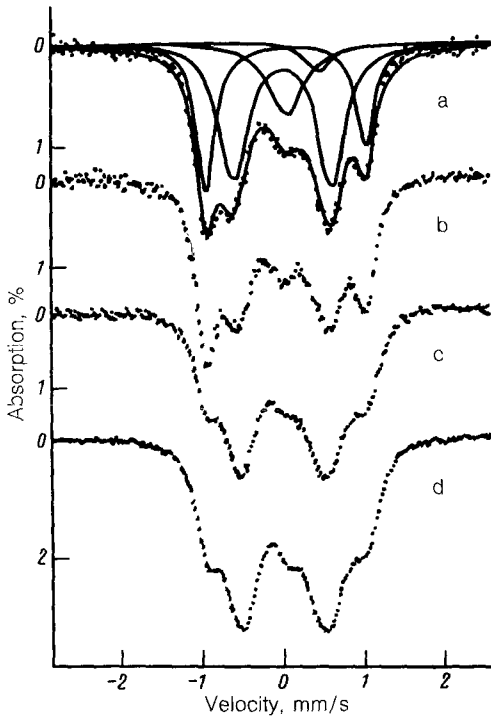


FIG. 2. Mössbauer absorption spectra of  $\text{Fe}^{57}$  nuclei at  $T=295$  K in the  $\text{Y}_{1-x}\text{Fe}_x\text{Ba}_2\text{Cu}_3\text{O}_6$  system at various values of  $x$ : a— $x=0.05$ ; b— $x=0.1$ ; c— $x=0.2$ ; d— $x=0.3$ .

resonant line. A careful analysis of the spectra for various values of  $x$  and for various temperatures showed that the fourth component of the spectrum, with a positive isomer shift, is due to iron ions which are not part of the crystal structure of the 1-2-3 phase. This component should be attributed to an impurity  $\text{Fe}_2\text{O}_3$  phase.

The parameters of the Mössbauer spectra for each position of the iron atoms are shown in Table II. Three basic conclusions can be drawn from an analysis of these parameters.

TABLE II. Concentration of iron atoms ( $A$ ) at the cationic sites of the 1-2-3 phase (expressed as a percentage of the total amount of Fe in the sample); isomer chemical shifts ( $IS$ ) (with respect to the metallic  $\alpha$ -Fe); and quadrupole splittings ( $QS$ ) for  $\text{Fe}^{57}$  nuclei at 295 K.

$x$	0.05			0.1			0.2			0.3		
	$A$ , %	$IS$ , mm/s	$QS$ , mm/s	$A$ , %	$IS$ , mm/s	$QS$ , mm/s	$A$ , %	$IS$ , mm/s	$QS$ , mm/s	$A$ , %	$IS$ , mm/s	$QS$ , mm/s
Pyramids	30	+0.03	1.96	33	+0.04	1.96	18	+0.05	1.99	19	+0.05	1.98
Squares	49	0.00	1.23	50	0.00	1.17	65	-0.03	1.03	66	-0.02	1.02
Cubes	16	+0.03	0.20	17	+0.04	0.20	4	-0.02	0.16	6	-0.03	0.19
Error	$\pm 1$	$\pm 0.01$	$\pm 0.02$	$\pm 1$	$\pm 0.01$	$\pm 0.02$	$\pm 1$	$\pm 0.01$	$\pm 0.02$	$\pm 1$	$\pm 0.01$	$\pm 0.02$

a) The iron atoms in the structure of the 1-2-3 phase are situated primarily ( $\sim 90\%$ ) at positions of copper ions—in tetragonal pyramids and “squares.” Only an insignificant fraction of these atoms goes into positions of yttrium ions (cubes). In the copper sublattice itself, most of the iron is in the “squares.” The pyramids contain a number of Fe atoms smaller by a factor of two or three (depending on the value of  $x$ ). (We recall that the unit cell of the 1-2-3 phase has twice as many pyramids as “squares.”) With increasing  $x$ , the relative concentration of Fe atoms in the “squares” becomes progressively greater.

b) At  $x = 0.05$  and  $0.1$  we observe a significant asymmetry of the lines of the quadrupole doublet that belongs to the pyramids. We suggest that this asymmetry stems from a Gol'danskii-Karyagin effect<sup>1</sup> and is evidence of an anisotropy of the thermal vibrations of the atoms in the pyramids. At  $T = 78$  K, i.e., at the transition to the superconducting state, this asymmetry is preserved. Rough estimates based on the data of Ref. 2 yield, for  $x = 0.05$ , for example, a value of  $0.09$  or  $0.03 \text{ \AA}^2$  for  $[\langle r_{\parallel}^2 \rangle - \langle r_{\perp}^2 \rangle]$  at  $295$  K and  $78$  K, respectively ( $\langle r_{\parallel}^2 \rangle$  is the mean square amplitude of the vibration of the Fe atom along the  $c$  axis). The asymmetry of the lines of the doublet decreases with increasing  $x$  and disappears at  $x = 0.2$ .

c) The most interesting conclusion follows from an analysis of the isomer chemical shifts  $IS$  (Table II). The values which we found for  $IS$  for iron atoms in the 1-2-3 phase have nothing in common with the shifts for the known oxidizing states of iron,  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$ , in various oxygen coordinations.<sup>1)</sup> On the other hand, they are very close to the shift in metallic iron. The quantities  $IS$  are approximately the same for all

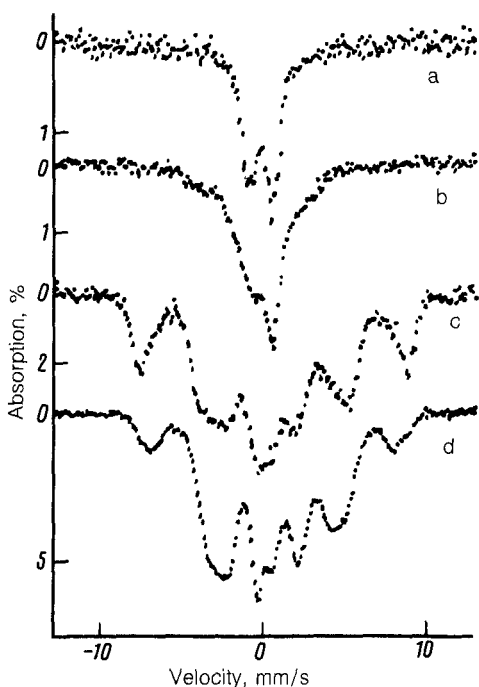


FIG. 3. Mössbauer absorption spectra of  $\text{Fe}^{57}$  nuclei at  $T = 4.2$  K in the  $\text{Y}_{1-x}\text{Fe}_x\text{Ba}_2\text{Cu}_3\text{O}_8$  system at various values of  $x$ : a— $x = 0.05$ ; b— $x = 0.1$ ; c— $x = 0.2$ ; d— $x = 0.3$ .

three positions of the iron atoms (the pyramid, the squares, and the cubes). This similarity implies that the valence electrons in the 1-2-3 phase are not localized atoms and are instead delocalized along the entire crystal. The density of  $s$  electrons is roughly the same at all lattice sites and approximately equal to its value in metallic  $\alpha$ -Fe. This result indicates that all the cations in the 1-2-3 phase (primarily copper in the squares) have a chemical binding of a metallic nature, and there is no point in discussing their valence state.

As the temperature is lowered to 78 K, the shifts of all the lines increase by an amount between +0.1 and +0.15 mm/s, apparently because of a temperature shift, since this value is approximately equal to the temperature shift in  $\alpha$ -Fe in the same temperature interval.<sup>4</sup> It follows that the chemical binding remains metallic in the superconducting state.

4. As the temperature is lowered from 295 K to 78 K, no substantial changes of any sort occur in the nature of Mössbauer spectra. This result implies that no structural or crystal-chemistry conversions occur in this temperature range. At 4.2 K, however, the spectra acquire a completely different shape (Fig. 3). In the samples with  $x = 0.2$  and  $0.3$  we can clearly see an additional line splitting, which is magnetic in nature. Traces of a magnetic splitting of the lines can also be seen in the sample with  $x = 0.1$ . Only at  $x \leq 0.05$  do we fail to find a magnetic interaction. Working from the temperature dependence of the magnetic splitting of the spectra, we estimated the temperatures at which the magnetic ordering appears,  $T_N$  (Table I). At 4.2 K the magnetic field at the  $\text{Fe}^{57}$  nuclei is  $\sim 330$  kOe. This value agrees with the field in metallic  $\alpha$ -Fe and is yet one more piece of evidence for a metallic state of the 1-2-3 phase.

We would like to call attention to the following circumstances: First, the fact that a superconductivity coexists with a magnetic order of the Fe atoms, which are in the copper sublattice, as was shown above, is interesting. Second, the comparatively high values of  $T_N$  at such low concentrations of Fe atoms could hardly be explained on the sole basis of an exchange interaction between iron atoms (Fe-Fe). Exchange interactions between iron and copper (Fe-Cu) apparently also arise here and lead to a magnetic ordering of the copper atoms. It may be that the destruction of the superconductivity with increasing iron concentration occurs because copper atoms become involved in an exchange interaction with iron.

<sup>1</sup>Typical values of  $IS$  for  $\text{Fe}^{3+}$  ions in oxygen octahedra and pentaverices range from +0.20 to +0.55 mm/s (with respect to metallic  $\alpha$ -Fe); the range of shifts for  $\text{Fe}^{2+}$  is from +0.95 to +1.5 mm/s (Ref. 3).

<sup>2</sup>V. I. Goldansky and R. H. Herber (editors), *Chemical Applications of Mössbauer Spectroscopy*, Academic Press, Orlando, 1968 [Russ. transl., Mir, Moscow, 1970, p. 86].

<sup>3</sup>R. S. Flinn, S. L. Ruby, and W. L. Kehl, *Science* **143**, 1434 (1964).

<sup>4</sup>F. Menil, *J. Phys. Chem. Solids* **46**, 763 (1985).

<sup>5</sup>R. S. Preston, S. S. Hanna, and J. Heberle, *Phys. Rev.* **128**, 2207 (1962).

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