# Use of the isotope $^{57}$Fe for neutron-diffraction determination of positions of iron atoms in the superconductor $Y_1Ba_2(Cu_{1-x}Fe_x)_3O_y$

A. M. Balagurov, I. S. Lyubutin, G. M. Mironova, Huan Chan Gen, and A. Ya. Shapiro

*Joint Institute for Nuclear Research; Institute of Crystallography, Academy of Sciences of the USSR*

A neutron-diffraction structural analysis has been made of the system $Y_1Ba_2(Cu_{1-x}Fe_x)_3O_y$ $(0.0 \leqslant x \leqslant 0.27)$, in which the iron was enriched to 95.7% in the isotope $^{57}$Fe. Up to $x_0 = 0.10$, the iron atoms lie exclusively at Cu1 sites. At a higher concentration $x = x_0 + \Delta x$, the "excess" iron $\Delta x$ is distributed equiprobably between Cu1 and Cu2 sites. The introduction of iron results in the capture of additional oxygen, in an amount of 0.5 of an oxygen atom per iron cation.

The $YBa_2(Cu_{1-x}Fe_x)_3O_y$ system is attracting particular research interest since a magnetic ordering of iron atoms has been observed in the superconducting state of this system.[1-3] The location of the Fe atoms in the structure of this superconductor, however, is ambiguous and is the subject of an active debate.[4] Contradictions are seen in not only data from Mössbauer spectroscopy[4] but also in data from neutron diffraction.[5-7]

In the present letter we are reporting a neutron diffraction study of $Y_1Ba_2(Cu_{1-x}Fe_x)_3O_y$ samples with $x = 0.0, 0.05, 0.10, 0.15, 0.20, 0.23$, and $0.27$ containing iron enriched to 95.7% in the isotope $^{57}$Fe. For the natural mixture of isotopes the coherent neutron scattering length $b_{coh}$ of copper ($b_{Cu} = 0.772 \times 10^{-12}$ cm) is only 20% different from $b_{coh}$ of iron ($b_{Fe} = 0.954 \times 10^{-12}$ cm), but when the isotope $^{57}$Fe is used ($b_{Fe-57} = 0.230 \times 10^{-12}$ cm), the change in the structure factors is intensified considerably, and the accuracy of an analysis of diffraction data improves sharply.

The samples were synthesized by the standard ceramic procedure, with annealing

TABLE I. Lattice constants and superconducting transition temperatures $T_c$ (at the level of 50% of $R_N$) of $YBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$. The standard deviations for the constants $a$ ($b$) and $c$ are $\pm 0.003$ Å and $\pm 0.005$ Å, respectively.

| $x$ | $a$, Å | $b$, Å | $c$, Å | $T_c$, K |
|---|---|---|---|---|
| 0.00 | 3.819 | 3.891 | 11.674 | 91 |
| 0.05 | 3.864 | | 11.682 | 69 |
| 0.10 | 3.867 | | 11.675 | 42.7 |
| 0.15 | 3.872 | | 11.616 | 9 |
| 0.20 | 3.874 | | 11.637 | |
| 0.233 | 3.872 | | 11646 | |
| 0.266 | 3.873 | | 11.640 | |

and slow cooling in oxygen. To monitor the composition of the samples, and to determine whether they were of a single phase, we used electron-probe x-ray microanalysis (with a CAMEBAX spectrometer) and also x-ray phase analysis. According to the x-ray data, all the samples containing iron have a tetragonal structure. Table I lists the lattice constants. The electrical resistance of the samples was measured by the four-probe method and also by a contactless method over the temperature range $4.2 \leqslant T \leqslant 300$ K. In the iron concentration range $0.0 \leqslant x \leqslant 0.15$ we observed transitions t~
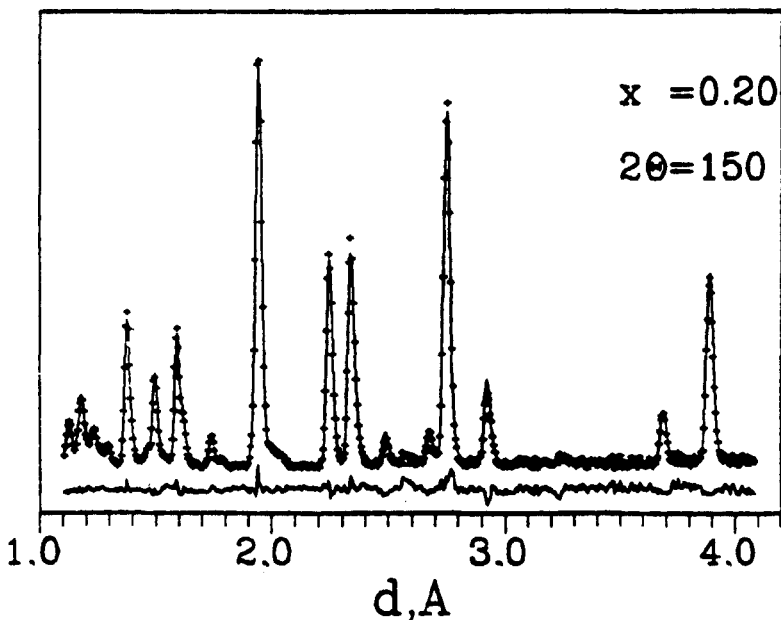


FIG. 1. Diffraction spectrum of the compound $Y_1Ba_2Cu_{2.4}Fe_{0.6}^{57}O_{7.25}$ measured at $2\theta = 150°$. Shown here are experimental points, a calculated profile, and a difference curve.

TABLE II. Structural results on $YBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$. The standard deviations of the values shown here are 0.001 for the z coordinates, 0.02 for x, and 0.015–0.025 for $n(Fe1)$ and $n(Fe2)$. The last column shows the R-factor of a profile analysis.

| x | z(Ba) | z(Cu2) | z(02) | z(03) | y | n(Fe 1) | n(Fe2) | R |
|------|-------|--------|-------|-------|------|---------|--------|-------|
| 0.00 | 0.184 | 0.356 | 0.161 | 0.380 | 0.95 | − 0.03 | 0.03 | 0.037 |
| 0.05 | 0.187 | 0.357 | 0.159 | 0.379 | 1.01 | 0.15 | 0.00 | 0.037 |
| 0.10 | 0.186 | 0.357 | 0.160 | 0.380 | 1.07 | 0.26 | 0.00 | 0.039 |
| 0.15 | 0.182 | 0.357 | 0.162 | 0.380 | 1.18 | 0.32 | 0.12 | 0.042 |
| 0.20 | 0.184 | 0.356 | 0.160 | 0.379 | 1.25 | 0.40 | 0.14 | 0.038 |
| 0.23 | 0.179 | 0.355 | 0.164 | 0.380 | 1.21 | 0.42 | 0.15 | 0.047 |
| 0.27 | 0.179 | 0.352 | 0.164 | 0.379 | 1.29 | 0.43 | 0.23 | 0.058 |

a superconducting state at the temperatures $T_c$ listed in Table I. At $x \geqslant 0.2$, we observed a conductivity of a semiconductor nature.

The neutron diffraction studies were carried out on a DN-2 time-of-flight diffractometer in the Neutron Physics Laboratory of the Joint Institute for Nuclear Research at the IBR-2 pulsed reactor. The data were analyzed by the Rietveld method. The spectra were analyzed for interplanar distances in the interval $1.3 \leqslant d \leqslant 4.0$ Å. They contained 40 diffraction peaks (space group $P4/mmm$). Figure 1 shows examples of the measured and calculated spectra.

In the analysis we varied, in addition to the experimental parameters (the normalization factor, the peak width, etc.) and the lattice constants, the z coordinates of the Ba, Cu2, O1, and O2 atoms and the population factors of the Cu1, Cu2, and O4 positions (the designations of the atoms of Ref. 6 correspond to space group $Pmmm$). The thermal factors were taken from Ref. 5 and were fixed. Some constraints were imposed on the content and coordinates of the copper and iron atoms: $n(Cu1) + n(Fe1) = 1$, $n(Cu2) + n(Fe2) = 2$, and $z(Cu2) = z(Fe2)$.

The structural data found are summarized in Table II. It follows from these data that even at high iron concentrations the structure of the compound $Y_1Ba_2 Cu_{1-x}Fe_x)_3O_y$ remains essentially the same. The maximum atomic displacements do not exceed $\pm 0.03$ Å; this figure lies within the possible systematic errors. The sum of the iron concentrations in the two positions, Cu1 and Cu2, is described well by the straight line $f(x) = 3x$ up to at least $x = 0.2$, supporting the suggestion that copper is replaced by the iron.

Figure 2(a) shows the behavior of the coherent scattering length b in the Cu1 site. In general, we would have $b_1 = b_{Cu} + 3p_1(b_{Fe} - b_{Cu})x$, where $p_1$ is the probability for the replacement of copper by iron at a Cu1 site. With a uniform distribution of iron between Cu1 and Cu2 sites we would have $p_1 = 1/3$, while if iron were exclusively in the Cu1 site, we would have $p_1 = 1$. The dashed lines in Fig. 2(a) correspond to these two cases (the slope of the straight lines is negative because of the relation $b_{Fe} < b_{Cu}$). Up to $x = 0.1$, the experimental points correspond to $p_1 = 1$, and at higher values of x they approach the line with $p_1 = 1/3$.
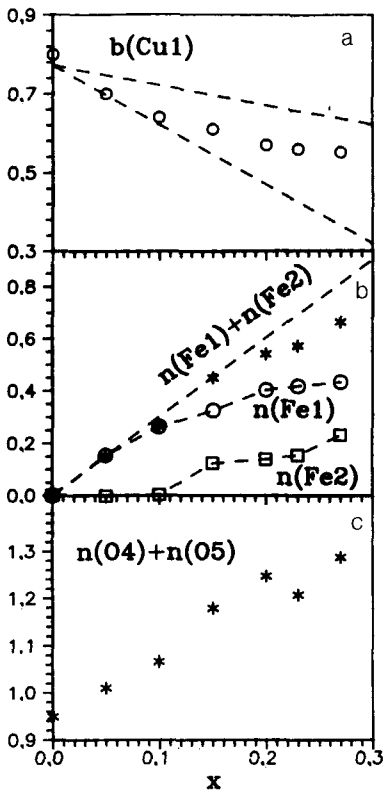
FIG. 2. Structural parameters versus the concentration $(x)$ of iron atoms in the $Y_1Ba_2(Cu_{1-x}Fe_x)_3O_y$ system at room temperature. a: Points—Coherent neutron scattering length for the Cu1 site; dashed lines—calculations for (upper line) $p_1 = 1/3$ and (lower) $p_1 = 1$. b: Circles—iron content in Cu1 sites; squares—the same, in Cu2 sites; asterisks—total iron content; straight line—$f(x) = 3x$. c: Iron content in Cu1—O chains.

Figure 2(b) shows experimental points on the iron content in the Cu1 and Cu2 sites and on the total iron content in the two sites; the independent variable is the iron concentration in the sample. Up to $x = 0.10$ the iron content in the Cu2 sites [n(Fe2)] is zero within the experimental error, while n(Fe1) increases in proportion to $3x$. In the interval $0.1 \leqslant x \leqslant 0.2$, the slopes of these plots are approximately $2x$ and $1x$, respectively; i.e., in this interval there is an approximately equiprobable filling of the two sites. At $x \leqslant 0.23$ the error in these results becomes greater because of the appearance of additional peaks on the neutron diffraction patterns. The nature of these peaks is magnetic, according to Mössbauer studies.

It thus follows from the experimental results that in the $Y_1Ba_2(Cu_{1-x}Fe_x)_3O_y$ system the iron atoms are in exclusively Cu1 sites at concentrations up to $x_0 = 0.1$. With a further increase in the concentration, $x = x_0 + \Delta x$, the excess iron $\Delta x$ begins to be distributed approximately uniformly between the two sites, Cu1 and Cu2. At $x = 0.20$, for example, the cation distribution can be described by $Y_1Ba_2(Cu_{0.6}Fe_{0.4})[Cu_{1.8}Fe_{0.2}]O_{7.25}$, where the parentheses and square brackets refer to the Cu1 and Cu2 sites, respectively.

Figure 2(c) shows the experimental dependence of the oxygen content in the samples on the iron concentration. Here we clearly see a tendency for Fe atoms to

capture additional oxygen. For all the samples containing iron, the amount of O is greater than 7 per formula unit (Table II). The increase in the amount of oxygen calculated from these results is 0.4–0.5 of an oxygen atom per iron cation.

Similar structural data were recently found[8] for a system containing cobalt, $Y_1Ba_2(Cu_{1-x}Co_x)_3O_y$. The high quality of the neutron diffraction patterns (recorded with the D2B high-resolution diffractometer at ILL, in Grenoble) made it possible to obtain information in Ref. 8 about both small systematic changes in coordinates and the thermal parameters of the atoms. The change in the thermal factor for the Cu1 sites, which contain most of the Co, does not exceed 0.06 $Å^2$ at $x \leqslant 0.10$; only at $x = 0.22$ does it increase by 0.4 $Å^2$. A comparison of our own results with the data of Ref. 8 shows that the structural characteristics of the iron-substituted and cobalt-substituted 1–2–3 systems are essentially the same up to $x = 0.20$.

[1] Q. A. Pankhurst *et al.*, Phys. Lett. A **127**, 231 (1988).
[2] I. S. Lyubutin *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **47**, 196 (1988) [JETP Lett. **47**, 238 (1988)].
[3] T. Tamaki *et al.*, Solid State Commun. **65**, 43 (1988).
[4] *International Conference on the Applications of the Mössbauer Effect* (ICAME-89), Budapest, Hungary, September 1989, *Book of Abstracts*, **1**, p. 6.1–6.66.
[5] G. Roth *et al.*, Z. Phys. B **71**, 43 (1988).
[6] P. Bordet *et al.*, Solid State Commun. **66**, 435 (1988).
[7] P. Glazkov *et al.*, Sverkhprovod. Fiz. Khim. Tekh. **1**, 5 (1988).
[8] R. Sonntag *et al.*, Physica C **159**, 141 (1989).