Magnetic ordering of Fe atoms in the superconductor $YBa_2(Cu_{0.95}Fe_{0.05})_3O_{7.01}$

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Magnetic ordering of iron atoms in the superconducting state ($y = 7.01$) and in the nonsuperconducting state ($y = 6.48$) has been observed in a $YBa_2(Cu_{0.95}Fe_{0.05})_3O_y$ sample by means of Mössbauer spectroscopy. In a superconducting sample the superconductivity was found to coexist with the magnetic ordering of Fe atoms at the Cu(1) sites. In a semiconductor sample the Fe atoms at the Cu(1) sites become magnetically ordered at a temperature $T_M \cong 20$ K. This temperature decreases by 10 K upon transition to the superconducting state.

The magnetic ordering of iron atoms below the superconducting transition temperature in a $YBa_2(Cu_{1-x}Fe_x)_3O_y$ system has been observed in many studies.[1-9] To determine whether magnetism and superconductivity can coexist, the conditions under which this effect arises must be carefully analyzed and the exact location of Fe atoms in the structure of the 1-2-3 phase must be known. We will show, by means of Mössbauer spectroscopy, that at low temperatures magnetic ordering of iron atoms occurs at Cu(1) sites in $YBa_2(Cu_{0.95}{}^{57}Fe_{0.05})_3O_y$ samples in the superconducting state ($y = 7.01$) and in the nonsuperconducting state ($y = 6.48$). The nature of the

magnetic ordering and its temperature dependence charge markedly when the superconductor undergoes a transition to a semiconductor, and partial suppression of magnetism by superconductivity is observed.

The technology used to synthesize the samples, to control elimination of oxygen, and to determine the oxygen content is described in detail in Ref. 10. X-ray data showed that the initial sample of $YBa_2(Cu_{0.95}{}^{57}Fe_{0.05})^3O_{7.01}$ was a single-phase sample and had a tetragonal structure ($a = b = 3.864$ Å, $c = 11.682$ Å). The temperature of the transition to the superconducting state was $T_c = 69$ K at the 50% level of R_H at $\Delta T_c = 7$ K. A reverse transition to the normal state at low temperatures was not observed. Upon reduction of oxygen to $y = 6.48$, the electrical resistance of the sample showed semiconductor nature down to $T = 4.2$ K. Mössbauer spectra of ^{57}Fe nuclei were recorded in the absorption mode in the temperature interval $5 \leqslant T \leqslant 500$ K.

At room temperature the spectrum of the initial sample with $y = 7.01$ (see Fig. 1a) revealed a superposition of four quadrupole doublets D1, D2, D3, and D4, corresponding to iron ions in various local structure sites. It was established in several papers[8,10–13] that the components D1, D2, and D4 belong to iron atoms at the Cu(1) copper sites, and that they differ in the number of oxygen atoms and the manner in which they are localized in the nerest neighborhood. It was shown recently[10] that of the two dominant components in the spectrum, D1 and D2, the component D1 corresponds to the oxygen coordination of a plane square [the Cu(1) sites are comprised of two O1 atoms along the c axis and two O4 atoms along the b axis] and the component

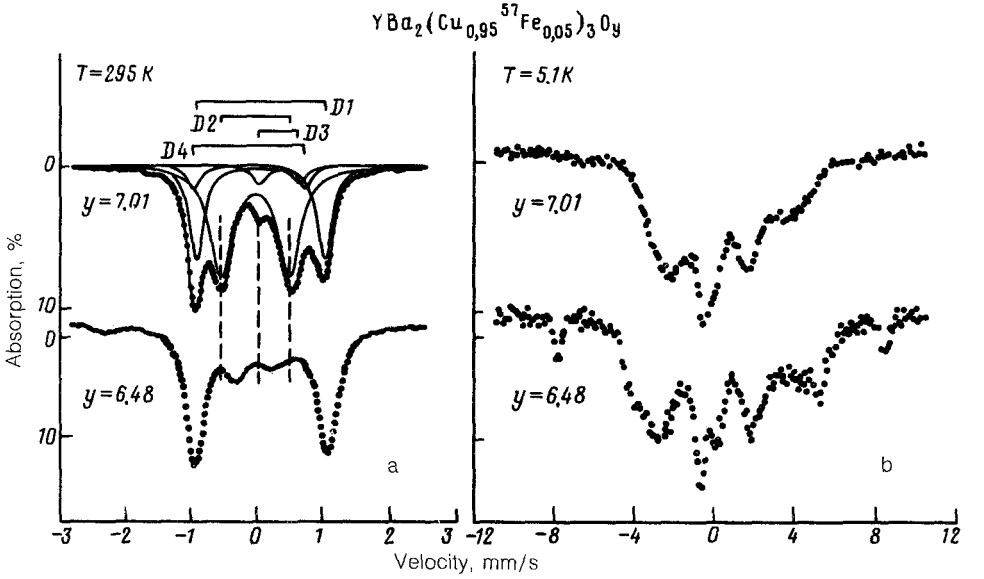

FIG. 1. Mössbauer spectra of $YBa_2(Cu_{0.95}{}^{57}Fe_{0.05})_3O_y$ for the superconducting state ($y = 7.01$) and the nonsuperconducting state ($y = 6.48$). (a) $T = 295$ K and (b) $T = 5.1$ K. Decomposition of the spectra into the compounds D1, D2, D3, and D4 is shown. The dashed lines indicate that the components D2 and D3 have vanished in the sample with $y = 6.48$.

TABLE I. Hyperfine interaction parameters obtained from the Mössbauer spectra of ^{57}Fe at $T = 295$ K for $YBa_2(Cu_{0.95}Fe_{0.05})_3O_y$.

y		QS, mm/s	IS, mm/s	S, %	Γ, mm/s	H_{hf}, kOe
7.01	$D1$	1.95	0.056	32	0.27	0
	$D2$	1.04	-0.024	55	0.42	0
	$D3$	0.60	0.338	6	0.23	0
	$D4$	1.62	-0.092	7	0.24	0
6.48	$D1$	2.02	0.073	64	0.35	0
	$D5$	0.58	-0.025	29	0.61	0
	DM	0.21	0.254	7	0.39	296
Error		0.01	0.007	0.5	0.02	2

QS is the quadrupole splitting, IS is the isomeric shift with respect to α-Fe, S is the relative area of the component, Γ is the linewidth, and H_{hf} is the magnetic field at the ^{57}Fe nucleus.

D2 corresponds to a fivefold pyramidal coordination of the Cu(1) sites, which is formed when iron atoms capture additional oxygen which is situated at the O5 sites in the basal plane along the a axis. The nature of the component D3 and D4 has not yet been definitively determined. The Fe atoms at the Cu(2) sites and the Fe atoms in the coordination of the complete octahedron at the Cu(1) sites are now being discussed as two alternative sources of the component D3 (see Ref. 10). The hyperfine interaction parameters for all the components are shown in Table I.

A reduction of oxygen to $y = 6.48$ eliminates the components D2 and D3; gaps are seen in their places in Fig. 1a. At the same time, the intensity of component D1 increases and two new components appear: a quadrupole component D5 and a magnetic component DM. The latter manifests itself particularly clearly when the spectrum is recorded in a broad velocity range (see Fig. 2, $T = 297$ K), while the left wing of the spectrum in Fig. 1a shows only the traces of the magnetic hyperfine structure. The hyperfine interaction parameters of this magnetic component (see Table I) make a compelling case to link it with the component D3 which is present in the saturated oxygen sample and which vanishes after reducing the oxygen.

Analysis of the sample with $y = 6.48$ at high temperatures shows that the magnetic hyperfine splitting of the component DM remains up to $T \simeq 405$ K (see Figs. 2 and 3a). This temperature is close to the Néel temperature, which is associated with the antiferromagnetic order of the copper atoms at the Cu(2) sites of an oxygen-depleted $YBa_2Cu_3O_{6.2}$ compound.[14] The component DM (D3) thus belongs to the Fe atoms which directly "feel" the magnetic state of the Cu atoms at the Cu(2) sites.

Upon lowering the temperature to 5.1 K, the spectrum of the $YBa_2(Cu_{0.95}Fe_{0.05})_3O_{6.48}$ sample revealed a magnetic hyperfine splitting of all components (Fig. 1b). This suggests that all iron atoms become magnetically ordered. The magnetic field at the nucleus of iron atoms ($H_{hf} \simeq 275$ K Oe) is much lower for the main group of lines than for the component DM ($H_{hf} \simeq 500$ Oe) (see Fig. 3a). In Refs. 5 and 7 we have assumed and substantiated the assumption that the low value of the field H_{hf} stems from the fact that the iron ions at the Cu(1) sites are in a low-spin state or a state with an intermediate spin ($S = 3/2$ and 1).

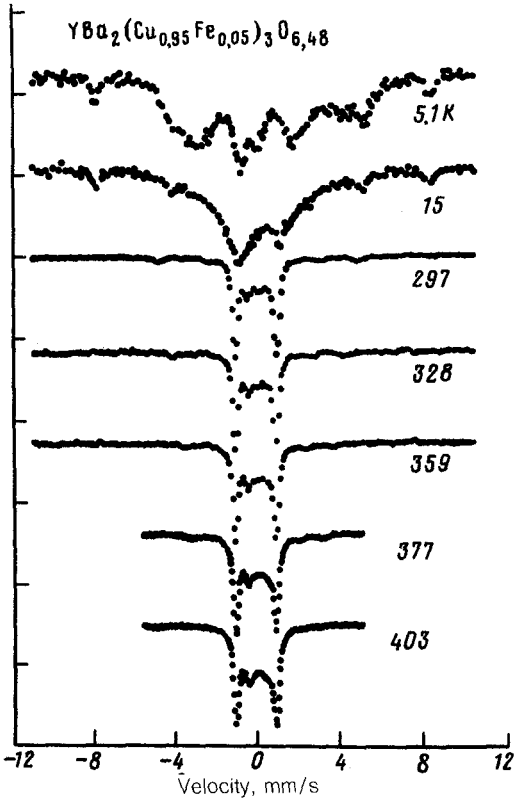

FIG. 2. Variation of the Mössbauer spectra of $YBa_2(Cu_{0.95}{}^{55}Fe_{0.05})_3O_{6.48}$ in the temperature interval $5 < T < 403$ K.

In addition to the field H_{hf} (which is proportional to the magnetic moment of Fe atoms), its temperature dependence for this group of lines also differs appreciably from the behavior of the component DM. This field decreases sharply in the temperature interval 15–20 K and then a long "tail" extends to $T \simeq 40$ K (see Figs. 3a and 3b) which indicates that strong magnetic correlation exist even in this temperature interval. The curve cannot be described by the Brillouin law, and the point at which the transition to magnetically ordered state occurs is roughly estimated to be $T_M \simeq 20$ K. In contrast with the component DM, the magnetic behavior of Fe atoms at D1 and D5 of the Cu(1) sites is therefore not the same as the behavior of the magnetic moments of copper at the Cu(2) sites.

At $T = 5.1$ K a superconducting sample with $y = 7.01$ also reveals a magnetic splitting of all components of the Mössbauer spectrum (Fig. 1b). The shape of the spectrum for the basis group of lines is similar to that of the spectrum of a sample with $y = 6.48$ (Fig. 1b), and the magnetic field H_{hf} at the ^{57}Fe nuclei is also low (see Fig. 3b). Since at least 90% of the iron atoms in the $YBa_2(Cu_{0.95}Fe_{0.05})_3O_{7.01}$ sample are situated at the Cu(1) sites, it follows from this result that at liquid-helium tempera-

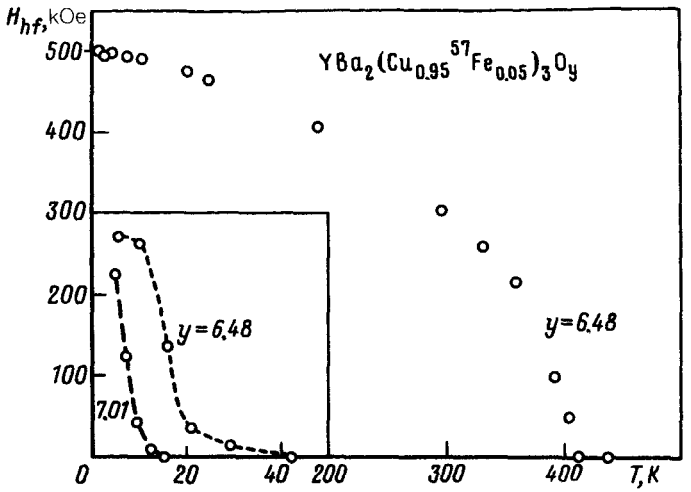

FIG. 3. Temperature dependence of the hyperfine magnetic fields at ^{57}Fe nuclei in $YBa_2(Cu_{0.95}Fe_{0.05})_3O_y$ for a superconducting sample ($y = 7.01$) and nonsuperconducting sample ($y = 6.48$). In the inset the scale along the abscissa is enlarged.

tures the superconductivity coexists with the magnetic order of Fe atoms at the Cu(1) sites. The Fe atoms at the D1-type sites and at D2-type sites in this case are ordered.

An increase in temperature causes the magnetic field H_{hf} to rapidly decrease (Fig. 3b) and at $T \geqslant T_M \simeq 10$ K the spectra acquire a shape characteristic of the paramagnetic state. Note that in a superconducting sample the temperature at which Fe atoms at the Cu(1) sites undergo a transition to a magnetically ordered state is lower by approximately ten degrees than it is in the same sample in the nonsuperconducting state after the reduction of oxygen (see Fig. 3b).

As can be seen in Fig. 1b, the spectrum of a sample with $y = 7.01$, which was carefully recorded with good statistics at $T = 5.1$ K, does not show a low-intensity magnetic component DM. Such a component was observed, however, at $T = 0.1$ K and 4.2 K in Refs. 4, 8, and 15 for superconducting samples, but it quickly vanished as the temperature was raised. Clearly, the Fe ions in our sample, which correspond to these lines at $T = 5.1$ K, have already undergone a transition to the paramagnetic state. Their lines are part of the general background and cannot be resolved because of their low intensity. The magnetism of the component DM was strongly suppressed as The shift in the temperature T_M, which occurs as a result of transition to the superconducting state, can be attributed either to the magnetization in the nonsuperconducting state of Fe atoms at the Cu(1) sites by the magnetic sublattice of copper atoms in the Cu(2) sites, or to a partial suppression of the magnetism [of Fe atoms at the Cu(1) sites] as a result of the onset of superconductivity. Because of the antiferromagnetic ordering of copper atoms in the neighboring Cu(2)–O planes,[14] the magnetization of atoms at the Cu(1) sites, which lie between two such planes, clearly should be weak due to the cancellation of the effects produced by the neighboring planes. The

mechanism for the suppression of magnetism by the superconductivity should be discussed, however, only when the nature of high-T_c superconductivity is understood.

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