Magnetic phase diagrams of the system $YBa_2(Cu_{1-x}Fe_x)_3O_y$

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The magnetically ordered states in oxygen-saturated and -depleted specimens of the system $YBa_2(Cu_{1-x}Fe_x)_3O_y$ with $0.01 \leqslant x \leqslant 0.30$ have been studied by Mössbauer spectroscopy. It was found that a magnetic ordering of the Fe ions on Cu1 sites occurs in the superconducting state. The loss of superconductivity due to a high degree of doping and also due to removing oxygen leads to the appearance of magnetic order on Cu2 sites. In oxygen-depleted specimens, for small iron concentrations ($x \leqslant 0.05$) the Cu1 and Cu2 sublattices are magnetically unconnected and two magnetic phase transitions are observed: a low-temperature transition at $T_{m1} \approx 20$ K for the Cu1 sublattice and a high-temperature transition at $T_{m2} \approx 400$ K for the Cu2 sublattice. On increasing the iron concentration a strong exchange interaction between the Cu1 and Cu2 sublattices arises and the whole matrix is antiferromagnetically ordered with a single magnetic transition point $T_{m2} \approx 460$ K. The phase diagrams have been constructed, delineating the regions of existence of magnetism and superconductivity and also the regions for various magnetic phases in oxygen-saturated and -depleted $YBa_2(Cu_{1-x}Fe_x)_3O_y$ systems as a function of iron concentration.

1. INTRODUCTION

One of the main trends in the research into the nature of high-temperature superconductivity is the study of the magnetic mechanism for pairing.[1,2] Great attention is paid to the existence of layer structures in HTSC materials of the $RBa_2Cu_3O_7$ type (R is a rare earth), where magnetic ordering of layers containing rare earth ions alternate with superconducting layers containing copper.[3] The experimental observation, in the superconducting layer, of magnetic ordering of iron and cobalt atoms introduced into copper sites in the system $YBa_2(CuM)_3O_7$ (M = Fe, Co) aroused special interest.[4–14] Of the experimental methods for studying the magnetically ordered state in the superconducting region the most effective are Mössbauer spectroscopy and neutron diffraction since they do not require application of an external magnetic field to obtain "magnetic" information.

We report here new results on the existence of magnetically ordered states in the system $YBa_2(Cu_{1-x}Fe_x)_3O_y$ and on the correlations between magnetism and superconductivity, obtained mainly by Mössbauer spectroscopy. In addition, some results which we published in part previously are summarized and extended.

2. EXPERIMENTAL METHOD

Two series of specimens of the $YBa_2(Cu_{1-x}{}^{57}Fe_x)_3O_y$ system were studied, in which the concentration of iron replacing copper atoms was varied over the wide limits $0.01 \leqslant x \leqslant 0.30$. The specimens of the first series were saturated with oxygen to the maximum ($y \geqslant 7$). It was established by neutron diffraction studies and by iodometry that the overall oxygen content in a specimen increases with a rise in the Fe concentration and even exceeds seven oxygen atoms per formula unit. This comes about on account of the capture of additional oxygen by the iron ions in its immediate neighborhood. To prepare the second series, all the specimens of the first series were heated at ~650 °C in a furnace with pure helium for 6–10 h. In this way oxygen was removed to the value $y < 6.5$. To increase the accuracy of the Mössbauer studies all specimens contained iron enriched to 96% with the ^{57}Fe isotope. The details of the synthesis are the same as those described previously.[15,16] X-ray analysis, electron-probe x-ray microanalysis, measurement of electrical conductivity (by resistive and inductive methods) and magnetic susceptibility, and neutron diffraction were used to certify the specimens, while iodometry, thermogravimetry, and neutron diffraction were used for determining the oxygen content. X-ray and neutron diffraction examinations show that a small amount of extraneous phases of the YBa_2CuFeO_5 type can appear for $x \geqslant 0.23$.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Suppression of superconductivity on introducing iron into the 1-2-3 phase

On replacing copper by iron ions in the oxygen-saturated system $YBa_2(Cu_{1-x}{}^{57}Fe_x)_3O_{\simeq 7}$ the superconducting transition temperature is reduced (see Fig. 1) and the temperature range of the transition is broadened. According to our measurements the critical concentration x_c at which superconductivity is completely suppressed by the doping is $x_c \approx 0.17$ (or Fe/Cu ≈ 17%). This value is much higher than the critical concentration of paramagnetic impurity in the usual (low-temperature) superconductors where $x_c \approx 1\%$ (Ref. 17).

The dependence of T_c on iron concentration in the system $YBa_2(Cu_{1-x}Fe_x)_3O_{\simeq 7}$ is shown in Fig. 1. For comparison, the experimental dependence of T_c on the oxygen content in $YBa_2Cu_3O_{7-y}$ containing only 1% iron is shown in the same figure. Our studies showed[18] that the presence of one percent iron does not change the overall form of the $T_c = f(y)$ curve observed for un-substituted specimens. The coincidence of these dependences in the range of change of $3x$ (iron) and of y from 0 to 0.2 (see Fig. 1) is worthy of note. If we take into account that for small x all the iron goes onto Cu1 sites, then the agreement of the $T_c = f(y)$ and $T_c = f(3x)$ curves indicates that with respect to its influence on T_c the introduction of one Fe ion instead of Cu is equivalent to the removal of one oxygen ion from Cu1–O chains. This points to the identity of the mechanisms for the

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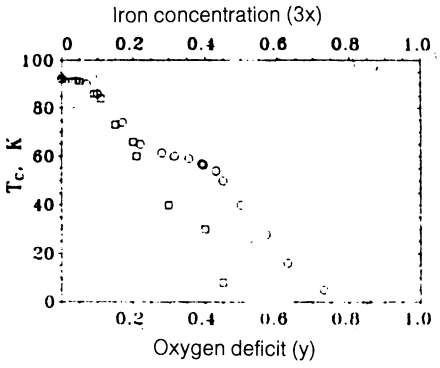

FIG. 1. Dependence of superconducting transition temperature T_c (determined by the induction method[16]) on Fe concentration in the system $YBa_2(Cu_{1-x}Fe_x)_3O_{\approx 7}$ (□) and on oxygen content in the system $YBa_2(Cu_{0.99}Fe_{0.01})_3O_{7-y}$ (○).

suppression of superconductivity in these systems. In all probability the mechanism for suppression of superconductivity by a paramagnetic impurity is not of a magnetic nature, but is associated with a reduction in the number of carriers due to localization of holes on high-valency iron ions.

In the oxygen-depleted system $YBa_2(Cu_{1-x}Fe_x)_3O_{y<6.5}$ superconductivity is absent for all values of x and the temperature dependence of the electrical resistance is semiconductorlike.

3.2. Structural positions, charged and spin states of Fe ions

Mössbauer studies[16,19] and neutron diffraction[15] showed convincingly that in oxygen-saturated specimens of $YBa_2(Cu_{1-x}Fe_x)_3O_{y>7}$ the iron ions are situated on copper sites and that at small concentrations ($x \leqslant 0.1$) they occupy mainly Cu1 sites. Typical Mössbauer spectra of ^{57}Fe nuclei in the paramagnetic temperature region are shown in Fig. 2. The most intense components $D1$ and $D2$ belong to iron ions in Cu1 sites corresponding to fourfold oxygen square planar coordination ($k = 4$) and fivefold square pyramidal coordination ($k = 5$) (Ref. 16). Such pyramids are formed at Cu1 sites either by attachment of additional O5 oxygen to Fe ions (see Fig. 3) or in twin domain walls.[20]

In all probability it is just the distribution of the Fe ions on Cu1 sites that causes the weak suppression of superconductivity when the 1-2-3 phase is doped with paramagnetic ions, if it is recognized that the main channels for superconductivity lie in the Cu2–O planes.

The values of the isomeric chemical shifts IS of the Mössbauer spectra (IS$\approx$0.0 mm/s relative to α-Fe) have already indicated in the first experiments[4–9] that the electronic states of iron ions in Cu1 sites were unusual for oxidized compounds. Further analysis of the magnitudes of IS and of the magnetic fields H_{hf} for ^{57}Fe nuclei at low temperatures showed that high-spin states of Fe^{4+} ($S = 2$) are possible here, as are also states of Fe^{3+} with low ($S = 1/2$) and intermediate ($S = 3/2$) spins.[21] For small iron concentrations ($x \leqslant 0.05$) in superconducting specimens highly saturated with oxygen, a $D4$ component appears in the Mössbauer spectra (see Fig. 2) with a small isomeric shift IS≈ -0.1 mm/s, which can be correlated with the low-spin diamagnetic state of Fe^{4+} ions ($S = 0$). It is probably associated with a coordination $k = 5$ in Cu1 sites.[22] Investigation

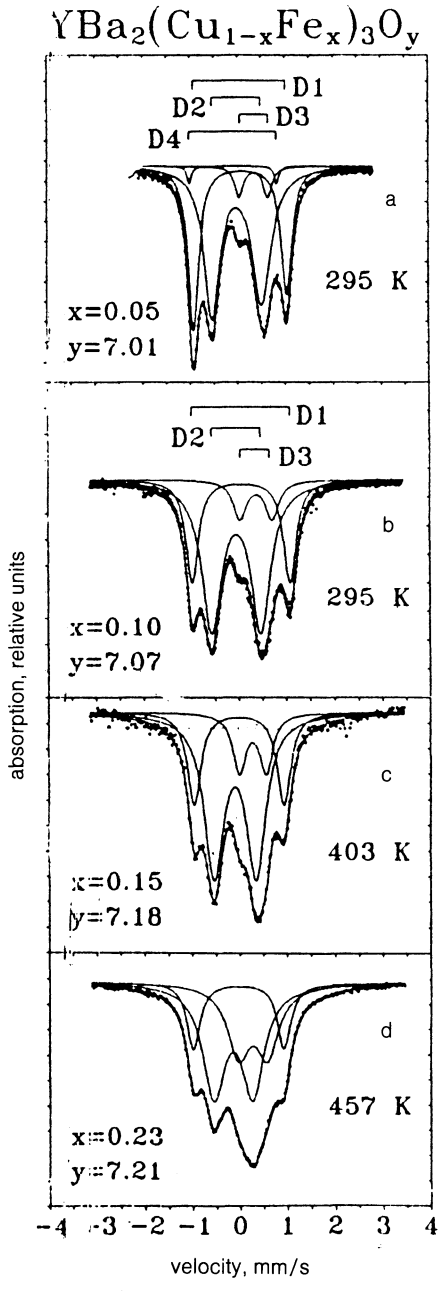

FIG. 2. Mössbauer spectra of ^{57}Fe nuclei in the paramagnetic temperature region of several specimens of the oxygen-saturated system $YBa_2(Cu_{1-x}Fe_x)_3O_{\approx 7}$. The deconvolution of the experimental spectra into the constituent doublet components $D1$, $D2$, $D3$ and $D4$ is shown.

of the magnetic susceptibility of $YBa_2(Cu_{1-x}Fe_x)_3O_7$ single-crystals gave a value of the magnetic moment of iron ions, averaged over all the structural positions, equal to $p_{\text{eff}}^{\text{Fe}} = 2.18\mu_B$ (see Ref. 23). This value corresponds to the low-spin state of Fe^{3+} ions.

If we recognize that in a "magnetic sense" a superconductor is a strong diamagnet, then the appearance of low-spin states on Fe impurity ions can be interpreted as the effect of diamagnetism induced on the paramagnetic impurity ions. However, the values of the parameter IS in fact remains unchanged even above the superconducting transition temperature T_c. This indicates that the low-spin states of

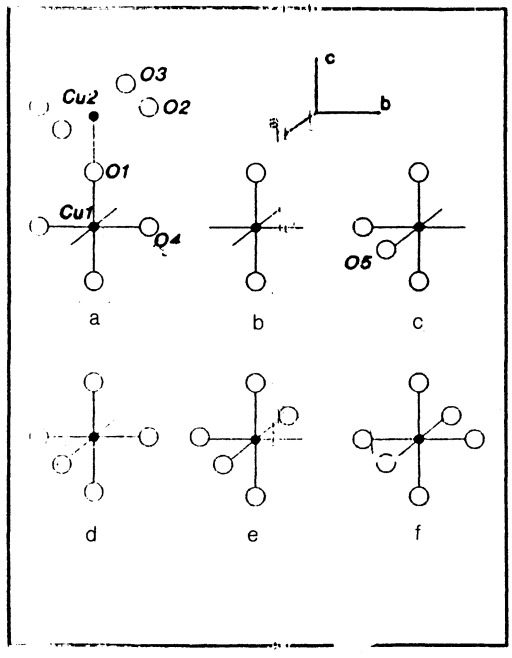

FIG. 3. Possible types of local oxygen surroundings for iron ions in Cu1 sites of the 1-2-3 phase.

iron ions are not a direct result of superconductivity but have a character in common with it. Evidently one and the same mechanism leads to both superconductivity and to "forced" intra-atomic pairing of the $3d$ spins of the Fe impurity ions.

3.3. Magnetic ordering of Fe ions on Cu1 sites. Low temperature magnetic phase transition in oxygen-saturated specimens

A hyperfine Zeeman splitting of the resonance lines appears in the Mössbauer spectra of ^{57}Fe nuclei at helium temperatures, indicating magnetic ordering of iron atoms in all structural positions (Fig. 4). Such magnetic ordering arises in the two systems: oxygen-saturated and oxygen-depleted. Computer analysis using a special program shows that in each low-temperature spectrum there can be resolved at least four magnetic components belonging to iron atoms in different structural positions. Components $M1, M2, M4$ and $M5$ are present in oxygen-saturated specimens and have the following magnetic-field values H_{hf} at ^{57}Fe nuclei: $H_{hf}(M1) \approx 210$ kOe, $H_{hf}(M2) \approx 265$ kOe, $H_{hf}(M4) \approx 465$ kOe, and $H_{hf}(M5) \approx 511$ kOe. Components $M2$, $M3$ [with the field $H_{hf}(M3) \approx 350$ kOe], $M4$, and $M5$ are present in oxygen-depleted specimens. Analysis shows that components $M1$ and $M2$ can be identified with iron atoms in Cu1 positions, having the corresponding four- and five-fold oxygen square planar and square pyramidal coordination ($k = 4$ and 5). The low values of the fields H_{hf} for components $M1$ and $M2$, as also of the magnitude of the isomer chemical shifts, indicate that the electronic states of iron ions in these structural positions differ from the high-spin states (see the preceding Sec. 3.2). The relative areas of all components, i.e., the number of Fe atoms in different structural positions, depend on the iron concentration and oxygen content.

We should note the large width of the resonance lines in the components $M1$ and $M2$. Special investigations[24–26] rule out spin relaxation as a possible source of broadening of

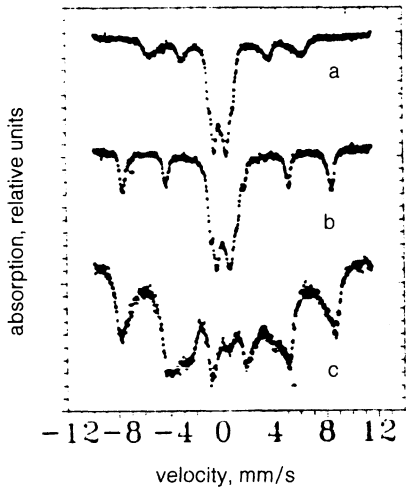

FIG. 4. Mössbauer spectra of ^{57}Fe nuclei in the compound $YBa_2(Cu_{0.77}Fe_{0.23})_3O_{7.21}$ at different temperatures. At $T = 41.5$ K part of the Fe ions have gone into the paramagnetic state.

Mössbauer lines in such specimens. Analysis shows that this broadening is caused by dispersion of the parameters of the hyperfine interaction and mainly of the magnitudes and directions of the static magnetic fields at ^{57}Fe nuclei. Such a state is typical for spin-glass type magnetic ordering, where the magnetic moments of Fe atoms are frozen in random directions relative to the crystallographic axes and have nonuniform magnetic and structural immediate surroundings.

As the temperature increases, a transformation of the spectra occurs and in the region of T_{m1} a transition of part of the iron atoms into the paramagnetic state is observed (see Fig. 4). The nature of this transition and the value of T_{m1} depend appreciably on the iron and oxygen concentrations. In the region of T_{m1} several parameters of the Mössbauer spectra change sharply together: the areas of the magnetic and paramagnetic components S, the magnetic field H_{hf} at a nucleus, the quadrupole shift QS and also the chemical isomer shift IS. The temperature T_{m1} can be determined from the change in any of these parameters. The temperature dependences of the magnetic fields at ^{57}Fe nuclei are shown in Figs. 5 and 6 for different components of the spectrum.

In oxygen-saturated specimens the value of T_{m1} increases from 0 to ≈ 35 K on increase of the iron concentration from $x = 0.00$ to the critical concentration $x_c \approx 0.17$

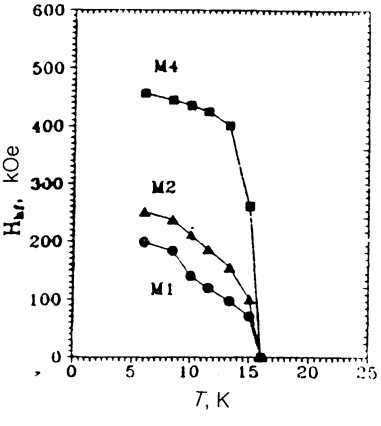

FIG. 5. Temperature dependence of hyperfine magnetic fields at the nuclei of iron ions in different structural positions in the compound $YBa_2(Cu_{0.9}Fe_{0.1})_3O_{7.07}$.

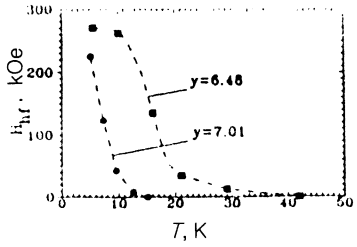

FIG. 6. Temperature dependence of hyperfine magnetic fields at the nuclei of iron ions in Cu1 sites for oxygen-saturated ($y = 7.01$) and depleted ($y = 6.48$) specimens of $YBa_2(Cu_{0.95}Fe_{0.05})_3O_y$.

(see Fig. 7). With further increase $x > x_c$, after losing superconductivity, the value of T_{m1} practically does not change and is stabilized at the level $T_{m1} \approx 30$–35 K. The neutron-diffraction results show that in this concentration region some saturation of Cu1 sites with iron ions takes place and active filling of Cu2 sites starts.[15] Both the loss of superconductivity and the features of the $T_{m1} = f(x)$ behavior for $x > x_c$ are associated with this.

At the point T_{m1} the magnetically split Mössbauer spectra are transformed into paramagnetic doublets, mainly $D1$ and $D2$ (see Figs. 4 and 2), which are typical of Cu1 sites. It follows unambiguously from this that magnetic ordering for $T > T_{m1}$ is due to iron ions on Cu1 sites.

Some reports have appeared recently[27–29] where magnetic anomalies were observed at low temperatures in experiments on small-angle and quasielastic neutron scattering by specimens of the $YBa_2(CuFe)_3O_y$ system. From the nature of these anomalies and also from the features of the behavior of the magnetic susceptibility in an external magnetic field[27] they could be associated with a transition to a spin-glass type of state. There is also a suggestion[30] that ordering of magnetic moments of the iron, observed at low temperatures, is a quasi-one-dimensional Ising ordering and is associated with clustering of iron ions at twin domain walls in the form of linear chains along [110] directions. We consider this a suggestion to be less valid since the magnetic ordering refers to iron ions situated in square planar coordination on Cu1 sites. These coordinations are only present within twin domains and are absent in domain walls.[20]

We can, evidently, conclude from all this data that a spin-glass type of magnetic ordering of Fe ions on Cu1 sites

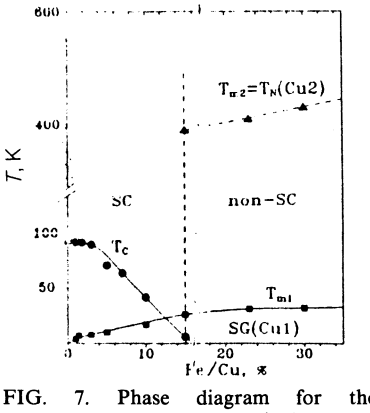

FIG. 7. Phase diagram for the oxygen-saturated system $YBa_2(Cu_{1-x}Fe_x)_3O_{y>7}$. T_c is the superconducting-transition temperature, T_{m1} the transition temperature to a magnetically ordered state in Cu1 sites, T_{m2} the transition temperature to a magnetically ordered state in Cu2 sites. SC is the region of existence of superconductivity, non-SC the region where superconductivity is suppressed by Fe doping, SG(Cu1) the region of a spin-glass type of magnetic state in the Cu1 sublattice.

takes place in the $YBa_2(Cu_{1-x}Fe_x)_3O_{y>7}$ system at low temperatures $T < T_{m1}$.

3.4. Magnetism—superconductivity phase diagram in the $YBa_2(Cu_{1-x}Fe_x)_3O_{y>7}$ system

Putting together all our data on the dependence of the superconducting transition temperature T_c and the spin-freezing temperature T_{m1} on the iron concentration, the phase diagram for the system of oxygen-saturated $YBa_2(Cu_{1-x}Fe_x)_3O_{y>7}$ specimens can be constructed (see Fig. 7). This phase diagram determines the regions of existence of superconductivity and magnetic ordering in the iron concentration range $0.00 \leqslant x \leqslant 0.30$.

The $T_{m1} = f(x)$ dependence determines the region of spin-glass type magnetic ordering on Cu1 sites. Extrapolation of this dependence to zero iron concentration gives the value $T_{m1} = 0$ at $x = 0$. This, evidently, indicates that in the undoped compound $YBa_2Cu_3O_7$ there is no local magnetic moment on copper ions in Cu1 sites. On the other hand, introduction of a small amount of paramagnetic iron atoms leads to a relatively high-temperature magnetic transition T_{m1}. This can indicate magnetic moments on nearest neighbor Cu atoms induced by Fe atoms. We can suggest that spin fluctuations existing in the copper sublattice are frozen on copper ions positioned in the vicinity of Fe ions. An estimate of the copper magnetic moment $p_{\text{eff}}^{\text{Cu1}} = 0.84\mu_B$ was obtained from measurements[23] of the magnetic susceptibility at temperatures above T_c of superconducting specimens, and the antiferromagnetic character of the interaction of iron ions was established.

It can be seen from Fig. 7 that the spin-glass state (SG) at Cu1 sites coexists with superconductivity up to a critical concentration $x_c \approx 0.17$, at which superconductivity is suppressed by doping. However, the low-temperature magnetic transition at T_{m1} continues to be observed even after the loss of superconductivity.

Since the SG state is realized in Cu1 sites, it is clear from the simplest structural considerations that magnetic ordering in the region of its existence should be quasi-two dimensional, since exchange interaction between two Cu1–O layers, essential for three-dimensional order, would require the participation in this interaction of a superconducting Cu2–O layer. In this way it is evident that a new type of layer structure is realized here. The magnetic layers in the basal *ab* plane $z = 0$, consisting of Cu1 sites, alternate with superconducting layers in $z = 1/3$ layers consisting of Cu2 sites. Essentially, unlike the rare-earth compounds $RBa_2Cu_3O_7$, where magnetically ordered states exist in the R layers, in the $YBa_2(Cu_{1-x}Fe_x)_3O_7$ system ordering is observed in the copper Cu1 sublattice.

3.5. High-temperature magnetic phase transition in the oxygen-saturated system for $x > x_c$

An additional magnetic component $M5$ with magnetic field $H_{hf}(4.5\text{ K}) = 506$–$512$ kOe appears in Mössbauer spectra of oxygen-saturated specimens of $YBa_2(Cu_{1-x}Fe_x)_3O_{y>7}$ which have lost their superconductivity due to the high degree of doping ($x > x_c$). Judging from the magnitude of the parameters H_{hf} and IS the $M5$ component should be ascribed to a high-spin state of trivalent Fe^{3+} iron ions ($S = 5/2$). A similar component has been observed by others.[21,31,32] In our experiments the $M5$

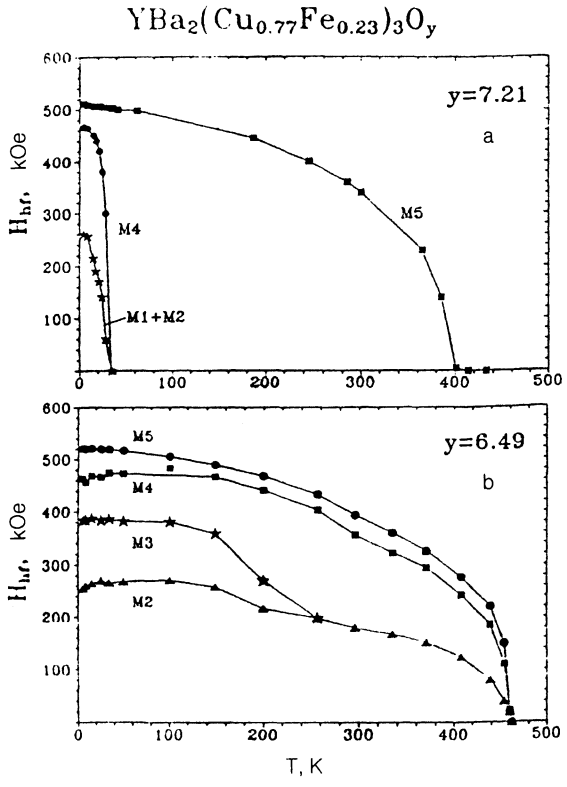

FIG. 8. Temperature dependence of hyperfine magnetic fields at ^{57}Fe nuclei for different components of the Mössbauer spectrum in (a) oxygen-saturated ($y = 7.21$) and (b) depleted ($y = 6.49$) $YBa_2(Cu_{0.77}Fe_{0.23})_3O_y$ specimens.

component remains magnetically ordered above T_{m1} (see Fig. 4) and goes over to the paramagnetic state only at a fairly high temperature T_{m2} (Fig. 8a).

The value of T_{m2} increases from 390 to 430 K with increase of iron concentration in the range $x_c \leqslant x \leqslant 0.3$ (see Fig. 7). The high-temperature magnetic transition point is thus close to the Néel temperature for copper atoms in Cu2 sites for the oxygen-deficient tetragonal $YBa_2Cu_3O_{\approx 6}$ ($T_{m2}^{Fe} \approx T_N^{Cu2}$) phase. It is curious that the magnetic transition was observed at T_{m2} for the Cu2 sublattices of maximally oxygen-saturated specimens which did not lose their superconductivity because of the large iron content.

The appearance of the magnetically ordered state in the Cu2 sublattice, due to loss of superconductivity from doping, was also seen recently with the help of NMR on copper nuclei.[33] This confirms the existence of such an effect in oxygen-saturated specimens. Alloying the 1-2-3 phase with iron at concentrations $x \geqslant x_c$ thus also plays the same role as the removal of oxygen in a "magnetic" sense. Iron also has a similar effect on superconductivity for $x < x_c$ (see Sec. 3.1). The appearance of magnetism in the Cu2 sublattice at the instant that superconductivity is lost through doping indicates the close association between these two phenomena, while the appearance of one or other is only associated with a change in the number of charge carriers. Attention is also paid to this feature by Nowik and Felner.[34]

The question of the origin of the $M5$ component is very important. We observed earlier that the $M5$ component with a high-temperature magnetic transition temperature also appears in Mössbauer spectra of specimens with low iron concentration, but only after driving off oxygen ($O_{y<6.5}$) and the loss of superconductivity.[35] In superconducting specimens this component is absent. The $M5$ component is thus directly associated with the magnetic state of copper ions in Cu2 sites. The contaminant phase $YBaCuFeO_5$, which can appear for large iron concentrations has a magnetic ordering temperature[36] above T_{m2} ($T_N \approx 450$ K) and we allowed for its possible influence when analyzing the spectra. The appearance of the $M5$ component in oxygen-depleted specimens with low iron content is an additional argument in favor of it not being associated with the impurity phase. For $T > T_{m2}$ the $M5$ component changes to quadrupole doublets $D1$, $D2$ and $D3$ typical of the paramagnetic state of the system $YBa_2(Cu_{1-x}Fe_x)_3O_{y\approx 7}$ (Ref. 16). The most intense of these is the doublet $D3$ (see Fig. 2) which is usually associated with the iron ions in Cu2 sites.[37] On the whole, therefore, the magnetic behavior of the $M5$ component is determined by the magnetic state of the Fe ions in Cu2 sites. However, the doublets $D1$ and $D2$, also partially contained in the $M5$ component, belong to Fe ions on Cu1 sites. This can indicate that the $M5$ component pertains to some magnetic clusters including, besides iron ions on Cu2 sites, also part of the Fe ions on Cu1 sites "magnetized" by the Cu2 sublattice.

Taking into account the results on the high-temperature phase transition at the point T_{m2}, one can add to the phase diagram of Fig. 7 a new region associated with magnetic ordering in Cu2 sites. A feature of the magnetic state of the oxygen-saturated system $YBa_2(Cu_{1-x}Fe_x)_3O_{y>7}$ for $x > x_c$ is the absence of strong interactions between the magnetic spin-glass state in the Cu1 sublattice and the magnetism of the Cu2 sublattice, as a result of which different magnetic ordering temperatures are observed for these sublattices, T_{m1} and T_{m2}. A similar effect was observed by Hechel *et al.*[38]

3.6. Magnetic phase transitions in the oxygen-depleted system $YBa_2(Cu_{1-x}Fe_x)_3O_{y<6.5}$

After removing the oxygen, the magnetic state of the system $YBa_2(Cu_{1-x}Fe_x)_3O_7$ changes sharply. Several magnetic components are observed in the Mössbauer spectra, some of which, belonging to Cu1 sites, go over into the paramagnetic state at low temperatures at T_{m1}, while the others do so at high temperatures at T_{m2}. For specimens with small iron content ($x < 0.1$) an increase by about 10 K in the magnetic phase transition temperature in the Cu1 sublattice (the value of T_{m1}) is observed in the transition from the superconducting into the semiconducting state as a result of the removal of oxygen. For example, for $x = 0.01$ the value of T_{m1} increases from 3 to 12 K, and for $x = 0.05$ from 10 to ≈ 20 K (see Fig. 6).

We note that a magnetic phase transition for copper ions in the Cu1 sublattice in undoped $YBa_2Cu_3O_{\approx 6}$ was observed by NMR (Ref. 39) and by neutron diffraction[40] (besides the low-temperature magnetic transition for the Cu2 sublattice). It is possible that the increase in T_{m1} on removal of the oxygen, which we found in the system $YBa_2(Cu_{1-x}Fe_x)_3O_y$, is associated with the appearance of a magnetic moment on copper ions in Cu1 sites. The effect of an increase of T_{m1} on removing oxygen was also established

by Katsuyama *et al.*[41] From the Mössbauer results we cannot establish unequivocally whether a spin-glass type state is preserved in the Cu1 sublattice after the loss of superconductivity or a transition to the antiferromagnetic state occurs. Some types of antiferromagnetic states in the Cu1 sublattice have been discussed.[40,13,14]

At the same time a high-temperature magnetic phase transition with $T_{m2} \approx 400$ K is observed for iron ions in the Cu2 sublattice. The absence of strong interactions between the Cu1 and Cu2 sublattices and the existence of a number of magnetic ordering temperatures is an important feature of the magnetic state of the oxygen-depleted system at small Fe concentrations: a low-temperature point T_{m1} for the Cu1 and a high-temperature T_{m2} for the Cu2 sublattice. This state is analogous to the magnetic state of oxygen-saturated specimens with $x > x_c$.

However, on increasing the iron concentration the situation changes and for $x \geqslant 0.1$ only one transition point to the paramagnetic state is observed for all components of the Mössbauer spectrum. For example, it can be seen from Fig. 8b that in the specimens $YBa_2(Cu_{0.77}Fe_{0.23})_3O_{6.49}$ the components $M2$ and $M3$ refer to Cu1 sites as though they are magnetizing the Cu2 sublattice and the transition point of these components to the paramagnetic state is extended to the high-temperature T_{m2} corresponding to the Néel point for the Cu2 sublattice ($T_{m2}^{Fe} \approx 460\ K \approx T_N^{Cu2}$). This points to strong exchange interaction arising between the Cu1 and Cu2 sublattices, leading to the appearance of long-range antiferromagnetic ordering of the whole matrix. Neutron diffraction fixes the appearance of long-range antiferromagnetic ordering in these specimens.[15] Evidently, the spin-glass state in the Cu1 sublattice, existing for small Fe concentrations, goes over to antiferromagnetic long-range ordering. The scheme of the development of magnetic states on changing x and y which we established in the $YBa_2(Cu_{1-x}Fe_x)_3O_y$ system by Mössbauer spectroscopy does not, as a whole, contradict the scheme for the transformation of the magnetic structure (by the formation of phases of the $AF1$ and $AF2$ type) established earlier[13,14] by neutron diffraction for the analogous cobalt-doped system $YBa_2(Cu_{1-x}Co_x)_3O_y$.

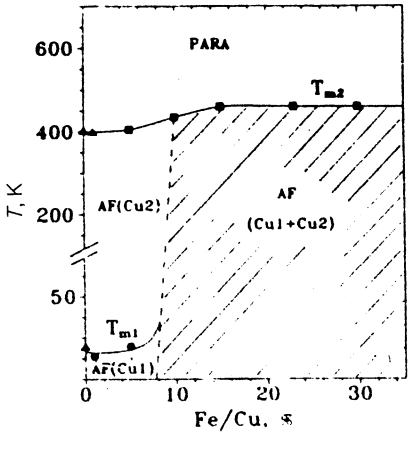

FIG. 9. Phase diagram for the oxygen depleted system $YBa_2(Cu_{1-x}Fe_x)_3O_{y<6.5}$. T_{m1} is the magnetic ordering temperature for the Cu1 sublattice. T_{m2} is the magnetic ordering temperature for the Cu2 sublattice. AF(Cu1) is the region of the magnetically ordered state in the Cu1 sublattice, AF(Cu2) is the region of antiferromagnetic ordering in the Cu2 sublattice, AF(Cu1 + Cu2) is the region of existence of long-range antiferromagnetic order over the whole matrix, PARA is the paramagnetic region.

The phase diagram determining the regions of existence of different magnetic states for the oxygen-deficient system $YBa_2(Cu_{1-x}Fe_x)_3O_{y<6.5}$ is shown in Fig. 9. The experimental points on this diagram indicate the temperatures of magnetic phase transitions mainly obtained by Mössbauer spectroscopy. Only for $x = 0$ are the results for Cu1 and Cu2 taken, respectively, from Matsumura *et al.*[39] and Tranquada *et al.*[42] On this phase diagram the regions AF(Cu1) and AF(Cu2) are weakly connected and have different magnetic phase transition points. A similar type of magnetic state was found by neutron diffraction in the analogous cobalt-doped system $YBa_2(Cu_{1-x}Co_x)_3O_y$ (Refs. 13, 14). It was established for this system that for fixed values of y different types of magnetic ordering ($AF1$ and $AF2$ phases) are realized and the Cu1 and Cu2 sublattices can have different magnetic phase-transition temperatures. Because of the competition between Cu1–Cu2 and Cu2–Cu2 antiferromagnetic exchange interactions, frustration of magnetic order in the Cu2 sublattice and the appearance of a canted spin structure are possible.[40]

The region AF(Cu1 + Cu2) on the phase diagram of Fig. 9 is determined by the existence of long-range antiferromagnetic order over the whole system, including both the Cu1 and Cu2 sublattices. In this region strong exchange interaction arises between the Cu1 and Cu2 sublattices. It is not impossible that the type of magnetic ordering in this region corresponds to the $AF2$ phase, established for the cobalt-doped 1-2-3 system.[13,14]

4. CONCLUSIONS

In conclusion we will enumerate the "magnetic" effects in the system $YBa_2(Cu_{1-x}Fe_x)_3O_y$ as established by the present experiments.

1. At low temperatures in the superconducting state Fe ions on Cu1 sites order magnetically, probably in a spin-glass arrangement. It is possible that the iron-doped 1-2-3 phase forms a layer structure in which the superconducting layers in *ab* Cu2–O planes alternate along the *c* axis with magnetic layers in the *ab* Cu1–O planes.

2. In the "pure" undoped 1-2-3 phase copper ions in Cu1 sites in the superconducting state have no local magnetic moment. On doping with iron a local moment is induced on the copper ions closest to iron and the Fe–Cu interaction is then antiferromagnetic. This explains, in particular, the small value of the effective moment on iron ions found from measurements of magnetic susceptibility.

3. Low-spin or diamagnetic states (intra-atomic pairing of $3d$ electrons) are induced in the matrix of the 1-2-3 phase on Fe impurity ions in Cu1 sites. This effect and the appearance of superconductivity evidently have a common character.

4. In a "magnetic" sense, doping of the 1-2-3 phase with iron plays the same role as removing oxygen. Namely, in specimens with high oxygen content the magnetic ordering of Cu2 sites with a high-temperature magnetic phase transition $T_{m2} \approx 400$ K appears as soon as the iron concentration reaches the critical x_c and superconductivity disappears. In the Cu2 sublattice at temperatures $T < 400$ K either a super-

conducting or a magnetically ordered state can thus be realized, with the appearance of one or the other determined only by the number of charge carriers.

5. In oxygen-saturated specimens of $YBa_2(Cu_{1-x}Fe_x)_3O_{y\geqslant 7}$ the exchange interaction between the Cu1 and Cu2 magnetic subsystems is either absent or appears very weak.

6. The loss of superconductivity on removing oxygen and the appearance of magnetism in the Cu2 sublattice leads to an increase in the temperature of the freezing-in of Fe spins in Cu1 sites. This is evidently associated with the appearance of a magnetic moment on copper ions in Cu1 sites.

7. In the oxygen-depleted system $YBa_2(Cu_{1-x}Fe_x)_3O_{y<6.5}$, for small iron concentrations, the Cu1 and Cu2 sublattices are magnetically independent and two magnetic phase transitions are observed for them, respectively at $T_{m1}\approx 20$ and $T_{m2}\approx 400$ K. For $x\geqslant 0.1$ strong exchange interaction arises between the Cu1 and Cu2 magnetic sublattices and only one magnetic phase transition is observed at $T_{m2}\approx 460$ K.

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