Crystal structure, magnetism, and superconductivity of $YBa_2(Cu_{1-x}Fe_x)_3O_{7+y}$ with $x=0.05-0.15$

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(Received 5 July 1989)

Neutron scattering experiments and magnetic-susceptibility measurements have been performed to investigate the structural and magnetic properties of $YBa_2(Cu_{1-x}Fe_x)_3O_{7+y}$ with $x=0.05$, 0.10 (superconductors), and 0.15 (nonsuperconductor). Rietveld refinements of neutron diffraction at room temperature indicate that the Fe atoms occupy both the Cu(1) "chain" and Cu(2) "plane" sites—the occupation of the Cu(2) sites is about 30% of the total Fe content. Neutron-diffraction measurements down to 5.5 K indicate no evidence of long-range magnetic order; however, neutron small-angle scattering as a function of temperature shows a cusplike anomaly around 20 K. This suggests that the Fe-doped $YBa_2Cu_3O_7$ system undergoes spin-glass ordering at low temperatures; accordingly, in the superconducting samples superconductivity and spin-glass coexist. Magnetic susceptibility for the nonsuperconducting sample gives further evidence for the spin-glass order. The results obtained are discussed in connection with the superconducting properties of this system.

I. INTRODUCTION

Since the discovery of the superconductor $YBa_2Cu_3O_{7-y}$,[1] intensive experimental and theoretical efforts have been made to elucidate the mechanism of the high-T_c superconductivity. In these works, investigations of the substitution effect of transition metals for Cu have provided significant information on the superconducting properties.[2,3] As is now well known, the undoped superconducting compound has an orthorhombic unit cell—a threefold stacked perovskite structure with two distinct Cu sites: Cu(1), which forms one-dimensional Cu-O chains and Cu(2), which forms two-dimensional CuO_2 planes. The results of the substitution effect first suggested that the superconducting current flows in the CuO_2 planes.[4] This was based on the fact that the doped compounds with a tetragonal structure, which *may not* have the linear chain, also show high-T_c superconductivity. Furthermore, these works suggested that the substitutional atoms, which induce the orthorhombic-tetragonal transition, such as Co and Fe, *would* preferentially occupy the Cu(1) sites, while the substitutional atoms, which retain the orthorhombic structure, such as Ni and Zn, *would* occupy the Cu(2) sites. Neutron-diffraction experiments indicated that the site occupation of Co and Ni is consistent with these suggestions, but different results were reported on the site occupation of Zn.[5,6] For the Fe substitution, ^{57}Fe Mössbauer spectroscopy suggested that Fe occupies both the Cu(1) and Cu(2) sites; nevertheless, there are considerable differences in the interpretation of the data obtained.[7–9] Subsequent neutron-diffraction experiments also gave different results for the site occupation of Fe.[10–12] On the other hand, electron microscopy on $YBa_2(Cu_{1-x}Fe_x)_3O_7$ with $x=0.04-0.1$, whose crystal structure was determined to be tetragonal by diffraction experiments, showed the existence of orthorhombic microdomains (about 20 Å in diameter); hence, in this case the tetragonal structure observed is only in a statistical sense.[11,13] Thus, the recent studies revealed more complicated aspects than the suggestions at the early stage. However, with several other pieces of experimental evidence the significance of the CuO_2 plane for the superconductivity has been recognized; it is considered that the superconducting current is being carried by hole pairs formed on the oxygen sites in the CuO_2 planes.[14]

In addition, work on the doped compounds has shown that a transition-metal substitution for Cu substantially changes the superconducting transition temperature T_c. These studies revealed that both magnetic and nonmagnetic ions reduce T_c in a similar manner.[3,15] Hence, the results indicate again that Cu is crucial for the superconductivity; furthermore, the superconducting properties are not sensitive to magnetic impurities, in contrast to conventional Bardeen-Cooper-Schrieffer (BCS) type superconductors. Moreover, Mössbauer spectroscopy on the Fe substituted compounds up to $x=0.07$ exhibited hyperfine field below about 20 K, suggesting that some magnetic order occurs in the superconducting state.[7,8] These experimental results might be related with the recent suggestions that magnetism plays a central role in high-T_c superconductivity.

In the present work, neutron scattering studies have been done to clarify the site occupation of the Fe atoms and the magnetic structure of $YBa_2(Cu_{1-x}Fe_x)_3O_{7+y}$ with $x=0.05$, 0.10, and 0.15. The magnetic susceptibility has also been measured to study the magnetism of these compounds.

II. EXPERIMENT

The samples were prepared by the solid-state reaction method starting from Y_2O_3, $BaCO_3$, CuO, and Fe_2O_3 powders. For each sample a mixture of these powders was heated twice at 900 °C for 10 h with intermediate grinding. The compound was ground again and heated at 920 °C for 10 h. Finally, the resultant compound was ground, further annealed at 400 °C for 10 h and then slowly cooled to room temperature in a furnace. All heat treatments were done in an oxygen atmosphere. X-ray diffraction showed that the materials were single phase; i.e., there were no impurity peaks with intensities more than 0.5% of the strongest peak of the majority phase. The diffraction data indicated that the crystal structure was tetragonal. The concentration and homogeneous distribution of Fe were checked by electron probe microanalysis (EPMA). The superconducting transition temperature T_c was determined by measuring resistivity and magnetization. The T_c's of the samples with $x=0.05$ and 0.10 were 64 and 36 K, respectively. For the sample with $x=0.15$ the superconducting transition was not observed down to 4.2 K. The results are in good agreement with many other experiments.[3,15] Some discrepancies in the concentration dependence of T_c between these results and a few other experiments[7] might be attributed to differences in the sample preparation.

Neutron scattering experiments were performed with the spectrometers installed at the Japan Research Reactor 2 (JRR-2), Japan Atomic Energy Research Institute (JAERI). Powder-diffraction data to study the crystal structure were collected at room temperature using a triple-axis spectrometer in the diffraction arrangement with 41-meV neutrons (wavelength 1.4125 Å). A pyrolytic-graphite filter was used to reduce the higher harmonics of those neutrons. The sample was placed in a cylindrical vanadium cell of thickness 0.05 mm. The data obtained were analyzed by a Rietveld refinement program.[16] Neutron-diffraction measurements to investigate the magnetic structure were carried out on another triple-axis spectrometer with a double-crystal pyrolytic-graphite monochromator. Most of the measurements were made with 13.6-meV neutrons (2.4526 Å) and a pyrolytic-graphite filter. Neutron small-angle scattering experiments were performed to further study the magnetic structure with the same spectrometer. Measurements at low temperatures were done using a conventional cryostat. The sample placed in an aluminum cylinder of thickness of 0.5 mm was enclosed in an aluminum can that was filled with helium exchange gas.

The magnetic-susceptibility measurements were made with a superconducting quantum interference device (SQUID) magnetometer and a conventional magnetic balance.

III. RESULTS

A. Crystal structure

The diffraction pattern obtained for the nonsuperconductor $YBa_2(Cu_{0.85}Fe_{0.15})_3O_{7+y}$ is shown by the points in Fig. 1 against both the scattering angle 2θ and the wave vector Q. The crystal structure is tetragonal with $P4/mmm$ space group. Compared with the undoped tetragonal sample,[17] changes in the relative intensity of the diffraction pattern are apparently seen. It is particularly clear that the intensity of (0 0 1) at 7.0° in 2θ is reduced and those of (0 0 2) at 14.0° and (1 1 2) at 33.1° are substantially increased. The profile refinement was started from the determination of atomic positions. Then the occupation factor of the oxygen was refined. The total oxygen content was obtained to be 7.2, which is larger than the value of the undoped superconductor $YBa_2Cu_3O_{7+y}$ ($y \sim -0.2$). This indicates that the Fe atoms have a larger valence than Cu, and hence attract oxygen to maintain a charge neutrality. Next the site that Fe atoms occupy was determined. When it was supposed that Fe substitutes in the Y or Ba site, the fitting was considerably poor compared with the substitution in the Cu sites. With the fact that the samples show no detectable impurity phase, the results indicate that Fe occupies only the Cu sites. In the next step, the occupation factors of Fe for the Cu(1) and Cu(2) sites were fixed in several ways. The results indicated that Fe preferentially substitutes in the Cu(1) site but it might occupy the Cu(2) site also. In the final refinement, therefore, the total content of Fe was fixed and the occupations of Fe on the Cu(1) and Cu(2) sites were calculated. Figure 1 and Table I show the results obtained. The global R factors were R_{WP} (the residual for the weighted total pattern)=5.38% and R_P (the residual for the total pattern)=3.87%, and the phase dependent R factors were R_B (the residual for the integrated intensity)=1.90% and R_F (the residual for

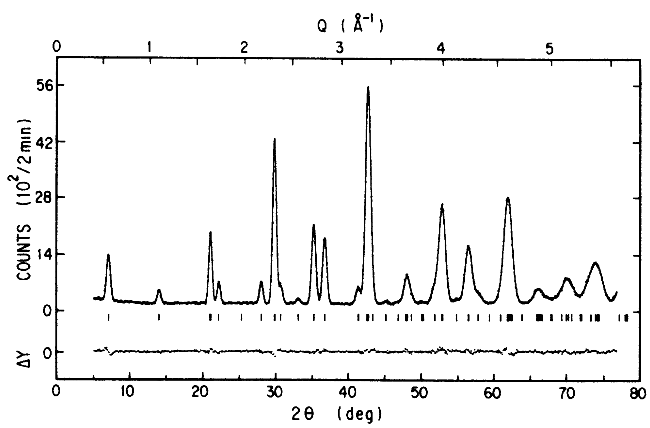

FIG. 1. Rietveld refinement of the neutron powder-diffraction data for $YBa_2(Cu_{0.85}Fe_{0.15})_3O_{7.2}$. The solid curve shows the calculated intensity, and Δy shows the difference pattern. The short vertical lines mark the positions of possible Bragg reflections.

TABLE I. Crystal parameters for $YBa_2(Cu_{0.85}Fe_{0.15})_3O_{7.2}$ at room temperature. B is the isotropic temperature factor, and g is the occupation factor. The estimated standard deviation is given in parentheses. The space group is $P4/mmm$. Lattice constants are $a=3.8814(4)$ Å and $c=11.695(2)$ Å.

Atom	Site	x	y	z	B (Å^2)	g
Y	1d	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.4(3)	1.0
Ba	2h	$\frac{1}{2}$	$\frac{1}{2}$	0.1851(9)	0.0(3)	1.0
Cu(1)	1a	0	0	0	1.1(5)	0.68(5)
Fe(1)	1a	0	0	0	1.1(5)	0.32(5)
Cu(2)	2g	0	0	0.3567(6)	0.3(2)	0.93(3)
Fe(2)	2g	0	0	0.3567(6)	0.3(2)	0.07(3)
O(1)	2f	$\frac{1}{2}$	0	0	1.5(5)	0.59(2)
O(2)	2g	0	0	0.1581(9)	0.3(3)	1.0
O(3)	4i	$\frac{1}{2}$	0	0.3783(6)	0.7(3)	1.00(2)

the structure factor) = 1.79%. As shown in Table I, the occupation of Cu(1) and Cu(2) were 0.32 and 0.07, respectively. The refinements for the superconductive compounds with $x=0.05$ and 0.10 also indicated that Fe atoms occupy both the Cu(1) and Cu(2) sites in a similar proportion within experimental accuracy. Hence, the occupation of the Cu(2) sites is 30(±10)% of the total Fe. Because of the similarity of the scattering amplitude of Cu and Fe, there may be some error in these occupation factors. The results are, however, basically consistent with those of other neutron-diffraction experiments,[11] Mössbauer effect,[7] and so on.[3]

The refinement gives information on bond lengths also. The results show that the Cu(1)—O(2) bond lengths [O(2) being the apical oxygen between Cu(1) and Cu(2)] are 1.843, 1.832, and 1.848 Å for $x=0.05$, 0.10, and 0.15, respectively. These are shorter than the lengths in the undoped orthorhombic superconductor (1.856 Å) and longer than that in the tetragonal nonsuperconductor (1.829 Å).[17,18] (Note that these values were obtained from the data measured at 10 K.) In the case of the Co-doped system, Miceli *et al.*[19] observed that the Cu(1)—O(2) bond length systematically decreases with increasing Co content. From the results they correlated the change in the bond length with the depression of T_c; that is, they suggested that the decreased Cu(1)—O(2) separation, i.e.—the increased Cu(2)—O(2) separation—induces an electron transfer to the CuO_2 planes. As a result, the hole population decreases dramatically. This corresponds with the drastic increase in the electrical resistivity with Co doping, whose increase is considered to be due to the decrease in the hole concentration and the localization of the holes.[3] For the present compounds, no systematic change in the bond length was observed; however, the tendency to decrease the Cu(1)—O(2) length with Fe doping is noticed. Thus, Fe atoms substituted in the Cu(1) sites might play the similar role to Co for the depression of T_c. In fact, the resistivity of this system also increases dramatically with increasing Fe concentration, indicating the localization of holes.[3,15] However, the Fe atoms that occupy the Cu(2) sites would affect T_c distinctly. Thus, the difference in the depression of T_c between the Fe and Co system observed in the experiments[3] could be explained by the difference in the substitution for the Cu sites between these systems.

B. Magnetism

1. Neutron scattering

As mentioned previously, Mössbauer experiments suggested that the Fe-doped $YBa_2Cu_3O_7$ superconductor ($T_c \sim 80$ K) undergoes a certain magnetic order at low temperature (~6 K), and that ordering temperature rises to 20 K with decreasing T_c when the Fe content is increased.[7] If a long-range magnetic order really exist, it is important to determine the structure of that order in connection with superconductivity. In the present experiments, superlattice peaks associated with antiferromagnetic ordering were carefully searched for, since several such peaks have been established for the tetragonal nonsuperconductive $YBa_2Cu_3O_{6+y}$ with $y=0\sim0.35$: $(\frac{1}{2}\frac{1}{2}l/2)$ and $(\frac{1}{2}\frac{1}{2}l)$ (l=integer) type reflections.[20,21] The scans around the $(\frac{1}{2}\frac{1}{2}\frac{3}{2})$ and $(\frac{1}{2}\frac{1}{2}2)$ reflections measured at 5.5 K for $x=0.15$ are shown in Fig. 2 (closed

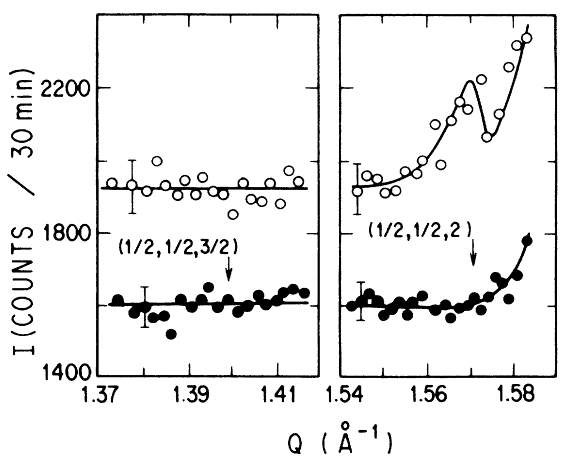

FIG. 2. Neutron-diffraction profiles around $(\frac{1}{2}\frac{1}{2}\frac{3}{2})$ and $(\frac{1}{2}\frac{1}{2}2)$ magnetic reflections for $YBa_2(Cu_{0.85}Fe_{0.15})_3O_{7.2}$ measured at 5.5 K (●). For comparison, the magnetic peaks of the tetragonal $YBa_2Cu_3O_{6.0}$ measured at 9 K are also shown (○).

circles), as typical examples. [For comparison, the results for the nonsuperconducting tetragonal $YBa_2Cu_3O_{6.0}$ (open circles) measured at 9 K are also shown. It is noted that the half-integer-type reflections reported for $y \sim 0.35$ were not detected in our undoped sample. This may be related to a difference in the O deficiency.] As seen in the figure, there is no indication of a similar type of antiferromagnetic order in this Fe-doped sample.

To examine other possible types of order the diffraction patterns were measured over the Q range from 0.5 to 1.75 $Å^{-1}$ at 9 and 40 K, and several temperatures above these. However, neither additional Bragg peaks nor changes in the intensity were detected in this sample within experimental uncertainty. Thus it can be concluded that there is no long-range periodic magnetic order, such as antiferromagnetic, spiral, spin-density wave, or ferromagnetic. The hyperfine field found in Mössbauer experiments, therefore, might not be due to a long-range magnetic order. In the present experiments the existence of short-range order could not be studied since the samples were polycrystals.

In order to investigate the origin of the hyperfine field observed in Mössbauer spectroscopic studies, neutron small-angle scattering experiments were performed. The results for $x = 0.15$ are shown in Fig. 3, where the background from the container was subtracted from the observed intensity. As seen in this figure, the temperature dependence of the scattering intensity at several wave-vectors Q shows a small but clear anomaly at about 20 K. This indicates that some magnetic ordering certainly occurs at low temperatures. Since a similar cusplike anomaly is often observed in small-angle scattering for a spin-glass system[22] and there is no evidence for long-range magnetic order, the anomaly found here suggests that this system undergoes a spin-glass transition. As will be shown later, magnetic susceptibility of this nonsuperconducting sample shows a difference between zero-field-cooled (ZFC) and field-cooled (FC) magnetization, which gives clear evidence for the spin-glass transition in this system. Furthermore, as shown in Fig. 4, similar anomalies were observed in small-angle scattering experiments on the superconductive samples with $x = 0.05$ and 0.10. These measurements were done at the wave vector of $Q = 0.067$ $Å^{-1}$. [For comparison, the result on the undoped superconductor ($T_c = 94$ K) is shown in this figure, although the measurements below 5 K could not be done.] Since anomalies observed in the compounds with $x = 0.05$ and 0.10 are essentially the same as that for $x = 0.15$, these results indicate that Fe-doped system exhibits the spin-glass transition in the superconducting state also. That is, spin-glass order coexists with high-T_c superconductivity. This result is, basically consistent with the previous Mössbauer study.[7]

It is noted here that the temperature dependence of the intensity above the ordering temperature is rather weak; that is, the small-angle scattering intensity is still large at higher temperatures. The reason for the large temperature-independent intensity is not clear at present. In small-angle scattering, however, the signal due to mag-

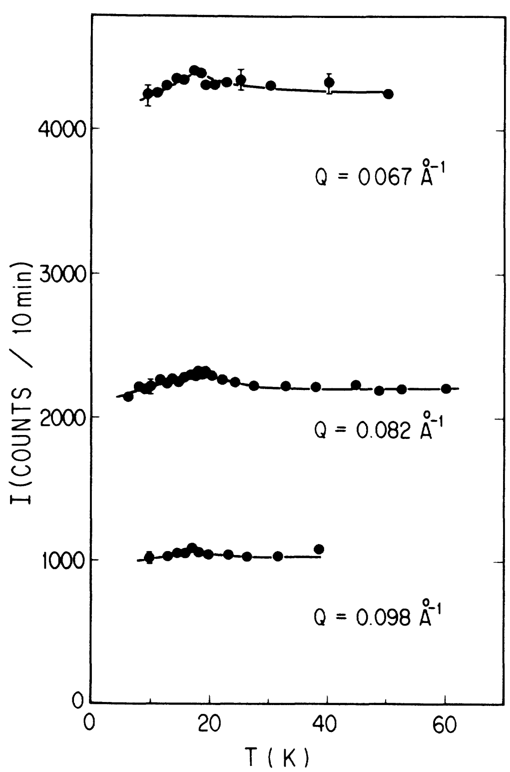

FIG. 3. Neutron small-angle scattering intensity at various wave vectors as a function of temperatures for $YBa_2(Cu_{0.85}Fe_{0.15})_3O_{7.2}$. The solid curves are guides to the eye.

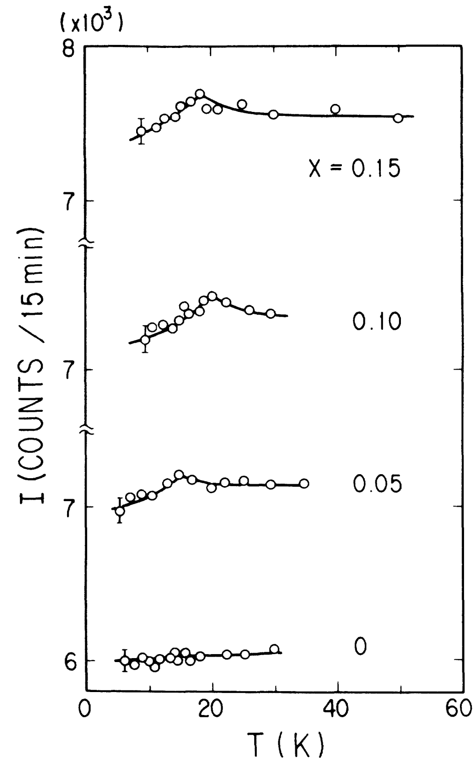

FIG. 4. Neutron small-angle scattering intensity at wave vector $Q = 0.067$ $Å^{-1}$ as a function of temperature for $YBa_2(Cu_{1-x}Fe_x)_3O_{7+y}$ with $x = 0$, 0.05, 0.10, and 0.15. The solid curves are guides to the eye.

netic origin would be superimposed on scattering caused by particles or other inhomogeneities in the material. Although these nonmagnetic scattering centers are suggested for the large background, some magnetic fluctuations may still exist even at high temperatures. It was, however, difficult to estimate such a magnetic contribution to the total intensity. The wave-vector dependence of the small-angle scattering is shown in Fig. 5. The intensity steeply increases at small angles; however, as mentioned earlier, the temperature dependence of the intensity is fairly weak. Here again, thus, the separation of the nonmagnetic and magnetic scattering was difficult. Accordingly, the fitting to an Ornstein-Zernike form [$I=I_0/(Q^2+\kappa^2)$, where I is the intensity, Q is the wave vector, and κ is the inverse of the correlation length] to evaluate magnetic correlations could not be done reasonably. As seen in the insert of Fig. 5, the Q dependence of the total intensity is rather fitted to a power law of Q^{-a}, where $a=4.4\pm0.7$. This result suggests that clusters of some kind (nonmagnetic particles or magnetic clusters, for example) may form.

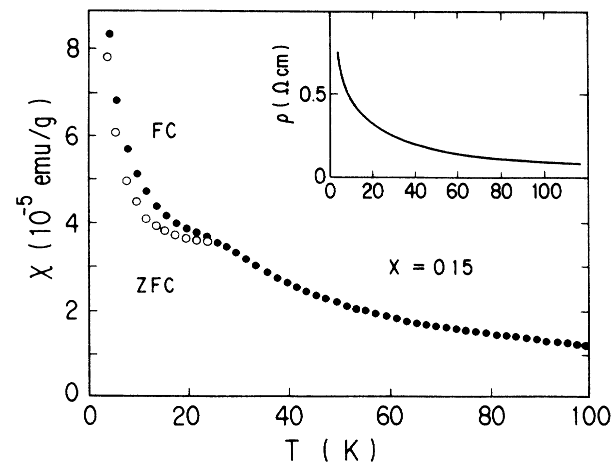

FIG. 6. The ZFC and FC magnetic susceptibility of the sample with the Fe content $x=0.15$. The measurement was done under the magnetic field of 10 G. The insert shows the resistivity of this compound.

2. Magnetic susceptibility

In order to clarify the magnetic properties of this system magnetic susceptibility was measured carefully. The results for the nonsuperconductive sample ($x=0.15$) are shown in Fig. 6. This clearly indicates that an anomaly appears at about 27 K. Furthermore, the results show that the zero-field-cooled and the field-cooled magnetization differ significantly. These reveal further evidence for the spin-glass transition of this system. It is noted that the cusp-like anomaly is superimposed on a paramagnetic component. (As shown in the insert of this figure, the resistivity of this compound indicated no anomaly around 27 K. Thus, the anomaly observed in the susceptibility is not caused by any trace of superconductivity.) Although the transition temperature obtained here is different from that in the neutron scattering experiment, such a difference is often observed; that is, the temperature where an anomaly is observed in neutron scattering depends on the wave vector of the measurements, and that temperature is lower than that obtained in susceptibility measurements, as shown in Ref. 22.

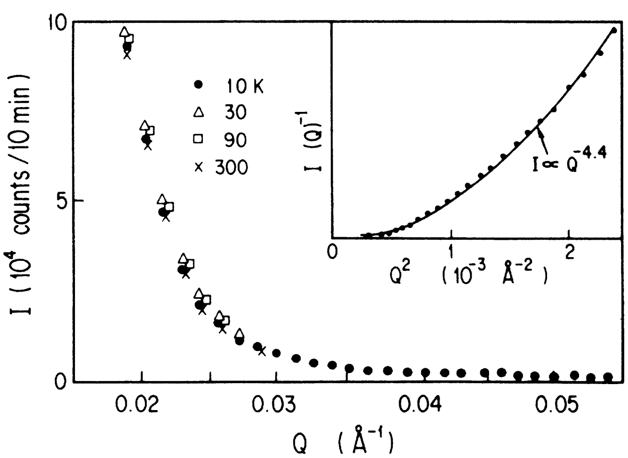

FIG. 5. The wave-vector dependence of the small-angle scattering of the sample with the Fe content $x=0.10$. The insert shows the fitting to the Ornstein-Zernike form: $I=I_0/(Q^2+\kappa^2)$; however, the intensity is rather represented by a power law of $I\propto Q^{-a}$, where $a=4.4\pm0.7$.

The temperature dependence of the magnetic susceptibility between 30 and 120 K is well characterized by the Curie-Weiss law: $\chi=\chi_0+C/(T-\Theta)$, where χ_0 is the temperature-independent susceptibility, C and Θ are the Curie constant and the Weiss temperature, respectively. The values obtained by least-squares fits are shown in Table II, with those for the samples with $x=0.05$ and 0.10.

A part of the results for $x=0.15$ under various magnetic fields is shown in Fig. 7. The arrows display the temperature T_g, which is defined as the temperature that separates the irreversible ZFC and reversible FC branches. The result under the field above 100 G indicates that $[T_g(0)-T_g(H)]$ depends on the applied field as H^a, where $a=\frac{1}{3}(\pm0.04)$. However, the data under the field below 100 G deviate from this form, suggesting a stronger dependence on H. Although this field dependence was not obtained precisely because of the difficulties in the data analysis at low magnetic fields, the result which indicates a stronger field dependence would be compared with the $H^{2/3}$ dependence at a low-field region in the regular spin-glass state.

For the superconducting sample ($x=0.10$), a different type of irreversibility, which is caused by the superconductivity was observed. In this case T_g approximately scales as $H^{1/4}$, consistent with the result that was previously reported.[23] This magnetic irreversibility was first explained by a superconducting glassy state because of its granular nature.[24] Recently, however, a flux-creep model was proposed for this magnetic anomaly on the basis of experiments for single crystals.[25] The anomaly in the susceptibility caused by the spin-glass transition was not clear in this superconducting sample because of its diamagnetism.

TABLE II. The parameters obtained from a fit to a Curie-Weiss law: $\chi=\chi_0+C/(T-\Theta)$.

x	T_c (K)	C (10^{-4} emu/g K)	χ_0 (10^{-6} emu/g)	Θ (K)	P_{eff} (μ_B/Fe ion)	Fitting range (K)	Magnetic field (G)
0.05	64	4.52	0.8	−3.9	3.77	75–200	7000
0.10	36	8.14	1.1	−12.1	3.79	50–200	7000
0.15		9.59	2.1	−2.5	3.35	30–120	10

IV. DISCUSSION

Up to now, several possibilities concerning the magnetism of the Fe-doped system have been proposed. The results obtained here, however, show that Fe-doped $YBa_2(Cu_{1-x}Fe_x)_3O_{7+y}$ with $x=0.05-0.15$ exhibits a spin-glass transition at low temperatures. The phase diagram obtained in the present work is shown in Fig. 8. Taking into account the fact that no magnetic transition has been observed in undoped high-T_c superconductors, and that the magnetic transition appears even for very low Fe content,[7] a speculated transition curve extrapolated to $x=0$ is shown by the dotted line. As seen in this figure, the spin-glass state and superconductivity coexist.

The existence of a spin-glass phase in relation to high-T_c superconductors was first predicted by Aharony *et al.*[26] Normally Cu ions interact antiferromagnetically through superexchange via the O ions in the two-dimensional CuO_2 plane. However, the presence of holes on the O sites gives rise to a ferromagnetic interaction between the Cu ions. The predicted spin-glass phase results from a frustration effect between these antiferromagnetic and ferromagnetic interactions. Such a spin-glass behavior has already been suggested experimentally for undoped compounds near the phase boundary between the antiferromagnetic and superconducting phase.[27–29] The present experiments, however, clarified that spin-glass order exists in the high-T_c superconducting state also. If antiferromagnetic interactions are enhanced, the magnetic frustrations mentioned earlier could be induced even in the superconducting phase. The experimental results suggest that the magnetic moments of Fe atoms might enhance the antiferromagnetic correlations between atoms, and eventually induce the spin-glass order. The magnetic susceptibility of the Fe-doped high-T_c superconductors actually shows antiferromagnetic interactions; that is, the Weiss temperatures evaluated from the data above T_c are negative.

In this experiment, the magnetic susceptibility of the sample with an Fe content of $x=0.15$ clearly shows an anomaly indicating spin-glass order. Although not mentioned in detail in a previous paper, a similar deviation from the Curie-Weiss law was noticed for $x\sim0.17$.[3] The present results indicate that the deviation observed in the previous experiment is caused by the spin-glass order. For the Co substituted system, however, such a deviation from the Curie-Weiss law was not clear. Moreover, the Weiss temperatures obtained for the Fe system do not exceed the order of 10 K; however, those for the Co system increase to reach a value as high as 100 K at $x=0.27$, which indicates that the superexchange between Co atoms is strongly enhanced.[3] These characteristics could be attributed to the difference in site occupation between the Fe- and Co-doped systems. Since the Co atoms occupy the Cu(1) sites preferentially,[3,5] the Curie-Weiss behavior in this compound might be caused by the paramagnetic or disordered Co moments on these sites. For the Fe system, as indicated in the structural analysis,

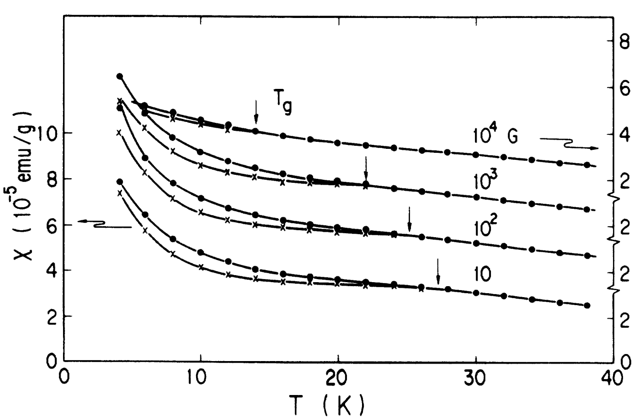

FIG. 7. The field dependence of the magnetic susceptibility of the sample with the Fe content $x=0.15$. The arrows show the temperature T_g, which separates the ZFC and FC branches. For clarity the curves are displaced vertically.

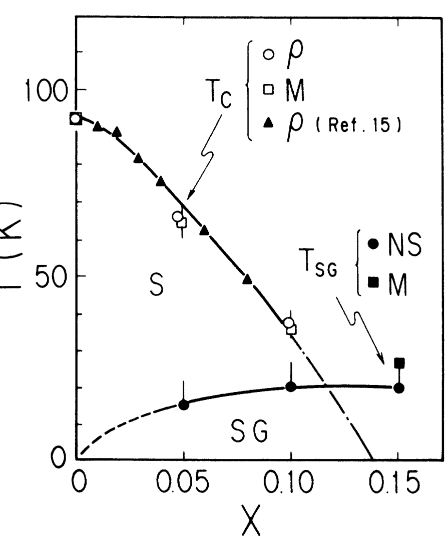

FIG. 8. The phase diagram obtained by neutron scattering (NS), magnetization (M), and resistivity (ρ). The superconducting state is denoted by S, and the spin-glass state is shown by SG.

Fe atoms occupy both Cu(1) and Cu(2) sites even for a low content of Fe. Hence, some magnetic moments of Fe substituted in the Cu(1) sites would contribute to the Curie-Weiss behavior as a background for the magnetic susceptibility, as in the case of the Co substitution. On the other hand, Fe on the Cu(2) site is possibly responsible for the magnetic anomaly due to the spin-glass order. Recently neutron-diffraction experiments showed antiferromagnetic order for a Co substituted system with $x \sim 0.27$.[30,31] As mentioned before, Co situated on Cu(1) sites would decrease the hole concentration; and this leads to the localization of holes on the oxygen sites.[19] The antiferromagnetic order observed suggests that the Co atoms substituted in the Cu(1) sites induce magnetic moments on the Cu(2) sites, and enchance antiferromagnetic coupling between Cu(1) and Cu(2) sites.[30,31] In the case of the Fe-doped system, antiferromagnetic order seems to be suppressed at least up to $x=0.15$. Some of the Fe atoms in this system occupy the Cu(2) sites, and they would have large magnetic moments on these Cu(2) sites. Such large magnetic moments might enhance magnetic frustrations, which would lead to the spin-glass order. A nuclear-quadrupole-resonance (NQR) study of Fe- and Co-doped compounds also indicated a different magnetic behavior in these systems.[32] That is, the temperature dependence of the nuclear spin-relaxation time T_1 shows broad peaks for Cu in both the Cu(1) and Cu(2) sites in the Fe-doped system, but the anomaly observed for the Cu(2) sites is fairly small compared with that for the Cu(1) sites in the Co-doped compounds. Thus, many experiments suggest that the magnetic properties differ between the Fe- and Co-doped system.

The results obtained in this study may suggest that the magnetism in the present system is closely related with the occurrence of superconductivity. Aharony *et al.*, who predicted the existence of the spin-glass state, further argued that an attraction between the O holes via the frustration for the antiferromagnetic order leads to high-T_c superconductivity.[26] If their theory is assumed to be correct, the magnetic frustration should occur dynamically in the superconducting state because holes are moving in the superconductor and the magnetic spins would flip whenever a hole passes through. The present work indicates that only a few percent of Fe induces the spin-glass state; hence, it suggests that the spins in the undoped system strongly fluctuate but are ready to order, as Tamaki *et al.* also suggested.[7] With Fe doping some holes will localize, and the spins around them would begin to order. Because of the large magnetic frustrations the order will be of a spin-glass type. Such spin-glass order is developed at the expense of the superconductivity. This is a possible explanation of the coexistence of high-T_c superconductivity and spin-glass order in this system.

Up to the present, several theories based on magnetic mechanisms have been proposed for high-T_c superconductivity. Since the electrons are highly correlated, owing to strong on-site Coulomb repulsion U, antiferromagnetism will be produced. Such antiferromagnetic correlations might provide an effective interaction for the hole pairing. However, some computer simulations indicated that a model with only U does not exhibit pairing of holes, but a model with U and an intersite Coulomb repulsion V induces the pairing; accordingly, Hirsch *et al.* suggested that a charge transfer excitation, which relates with a small energy difference between Cu and O levels, is essential for high-T_c superconductivity.[33] Thus, although antiferromagnetism certainly plays an important role in superconductivity, the situation is still unclear.

In conclusion, neutron scattering experiments and magnetic-susceptibility measurements clarified the structural and magnetic properties of the Fe-doped $YBa_2Cu_3O_{7+y}$. The results showed that the spin-glass order is induced by Fe doping; hence, the magnetic frustrations may be related with the origin of superconductivity in the oxide superconductors. However, to establish the essential mechanism of high-T_c superconductivity, more systematic and quantitative experiments will be necessary, in particular, investigations of magnetic correlations using single crystals would be important.

Note added: After submitting this paper, it was learned that a time-of-flight neutron scattering experiment has been done which gives more evidence for spin-glass ordering in this system.[34]

[1] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[2] G. Xiao, F. H. Streitz, A. Gavrin, Y. W. Du, and C. L. Chien, Phys. Rev. B **35**, 8782 (1987).

[3] J. M. Tarascon, P. Barboux, P. F. Miceli, L. H. Greene, and G. W. Hull, Phys. Rev. B **37**, 7458 (1988).

[4] Y. Maeno, M. Kato, Y. Aoki, and T. Fujita, Jpn. J. Appl. Phys. **26**, L1982 (1987).

[5] T. Kajitani, K. Kusaba, M. Kikuchi, Y. Syono, and M. Hirabayashi, Jpn. J. Appl. Phys. **27**, L354 (1988).

[6] G. Xiao, M. Z. Cieplak, D. Musser, A. Gavrin, F. H. Streitz, C. L. Chien, J. J. Rhyne, and J. A. Gotaas, Nature **332**, 238 (1988).

[7] T. Tamaki, T. Komai, A. Ito, Y. Maeno, and T. Fujita, Solid State Commun. **65**, 43 (1988).

[8] E. R. Bauminger, M. Kowitt, I. Felner, and I. Nowik, Solid State Commun. **65**, 123 (1988).

[9] S. Nasu, H. Kitagawa, Y. Oda, T. Kohara, T. Shinjo, K. Asayama, and F. E. Fujita, Physica **148B**, 484 (1987).

[10] B. D. Dunlap, J. D. Jorgensen, W. K. Kwok, C. W. Kimball, J. L. Matykiewicz, H. Lee, and C. U. Segre, Physica **153-155C**, 1100 (1988).

[11] G. Roth, G. Heger, B. Renker, J. Pannetier, V. Caignaert, M. Hervieu, and B. Raveau, Z. Phys. B **71**, 43 (1988).

[12] P. Bordet, J. L. Hodeau, P. Strobel, M. Marezio, and A. Santoro, Solid State Commun. **66**, 435 (1988).

[13] Z. Hiroi, M. Takano, Y. Takeda, R. Kanno, and Y. Bando, Jpn. J. Appl. Phys. **27**, L580 (1988).

[14] Recently, however, the polarized x-ray absorption spectroscopy indicated the possibility that holes enter in the p_z band of oxygen atoms situated above the Cu(2) sites. A. Bianconi, M.

A. Bianconi, M. De Santis, A. DiCicco, A. M. Flank, A. Fontaine, P. Lagarde, H. K. Yoshida, A. Kotani, and A. Marcelli, Phys. Rev. B **38**, 7196 (1988).

[15]A. Matsushita, H. Aoki, Y. Asada, T. Hatano, K. Kimura, T. Matsumoto, K. Nakamura, and K. Ogawa, Physica **148B**, 342 (1987).

[16]F. Izumi, J. Cryst. Soc. Jpn. **27**, 23 (1985).

[17]S. Katano, S. Funahashi, T. Hatano, A. Matsushita, K. Nakamura, T. Matsumoto, and K. Ogawa, Jpn. J. Appl. Phys. **26**, L1049 (1987).

[18]S. Katano, S. Funahashi, T. Hatano, A. Matsushita, K. Nakamura, T. Matsumoto, and K. Ogawa, Jpn. J. Appl. Phys. **26**, L1046 (1987).

[19]P. F. Miceli, J. M. Tarascon, L. H. Greene, P. Barboux, F. J. Rotella, and J. D. Jorgensen, Phys. Rev. B **37**, 5932 (1988).

[20]J. M. Tranquada, D. E. Cox, W. Kunnmann, H. Moudden, G. Shirane, M. Suenaga, P. Zolliker, D. Vaknin, S. K. Sinha, M. S. Alvarez, A. J. Jacobson, and D. C. Johnston, Phys. Rev. Lett. **60**, 156 (1988).

[21]H. Kadowaki, M. Nishi, Y. Yamada, H. Takeya, H. Takei, S. M. Shapiro, and G. Shirane, Phys. Rev. B **37**, 7932 (1988).

[22]A. P. Murani, Phys. Rev. Lett. **37**, 450 (1976).

[23]I. Felner, Y. Wolfus, G. Hilscher, and N. Pillmayr, Phys. Rev. B **39**, 225 (1989).

[24]K. A. Müller, M. Takashige, and J. G. Bednorz, Phys. Rev. Lett. **58**, 1143 (1987).

[25]Y. Yeshurun and A. P. Malozemoff, Phys. Rev. Lett. **60**, 2202 (1988).

[26]A. Aharony, R. J. Birgeneau, A. Coniglio, M. A. Kastner, and H. E. Stanley, Phys. Rev. Lett. **60**, 1330 (1988).

[27]N. Nishida, H. Miyatake, D. Shimada, S. Okuma, M. Ishikawa, T. Takabatake, Y. Nakazawa, Y. Kuno, R. Keitel, J. H. Brewer, T. M. Riseman, D. Ll. Williams, Y. Watanabe, T. Yamazaki, K. Nishiyama, K. Nagamine, E. J. Ansaldo, and E. Torikai, J. Phys. Soc. Jpn. **57**, 597 (1988).

[28]K. Kumagai, I. Watanabe, H. Aoki, Y. Nakamura, T. Kimura, Y. Nakamichi, and H. Nakajima, Physica **148B**, 480 (1987).

[29]H. Kitazawa, K. Katsumata, E. Torikai, and K. Nagamine, Solid State Commun. **67**, 1191 (1988).

[30]P. Zolliker, D. E. Cox, J. M. Tranquada, and G. Shirane, Phys. Rev. B **38**, 6575 (1988).

[31]P. F. Miceli, J. M. Tarascon, L. H. Greene, P. Barboux, M. Giroud, D. A. Neumann, J. J. Rhyne, L. F. Schneemeyer, and J. V. Waszczak, Phys. Rev. B **38**, 9209 (1988).

[32]Y. Kohori, Y. Oda, H. Shibai, N. Okamoto, T. Kohara, and K. Asayama, J. Phys. Soc. Jpn. **57**, 2632 (1988).

[33]J. E. Hirsch, S. Tang, E. Loh, Jr., and D. J. Scalanpino, Phys. Rev. Lett. **60**, 1668 (1988).

[34]M. Hennion, I. Mirebeau, G. Coddens, A. Menelle, T. E. Phillips, K. Moorjani, and M. Hervieu, Physica C **159**, 124 (1989).