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Superconductivity and antiferromagnetism in the Cu(2) planes of $YBa_2Cu_3O_7H_x$

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Mössbauer, magnetic susceptibility, and powder x-ray diffraction measurements were performed to study the magnetic properties and superconductivity of hydrogen-charged $YBa_2Cu_3O_7H_x$ doped with 2 at.% ^{57}Fe. T_c is reduced with increasing H concentration and superconductivity was absent at $x=1.3$. An analysis of the Mössbauer spectra at different temperatures shows that antiferromagnetism at the Cu(2) sites is induced by hydrogen in a very similar way as the removal of oxygen. The phase diagram is very similar to the well-known phase diagrams obtained in a wide family of cationic substitutions in $YBa_2Cu_3O_7$.

I. INTRODUCTION

It is by now well established that in the $YBa_2Cu_3O_z$ (1:2:3) system there is competition between superconductivity and long-range antiferromagnetism (AF) in the Cu(2) planes.[1-4] In the orthorhombic $YBa_2Cu_3O_x$ system, the superconducting transition temperature T_c is dramatically affected by the oxygen content and for $z<6.4$ the samples are tetragonal, semiconducting, and the Cu(2) sites are antiferromagnetically ordered. The Néel temperature T_N increases sharply with decreasing z, from $T_N=0$ K for $z\approx6.5$ to $T_N=415$ K for $z\approx6.0$.[1] The magnetic structure is composed of strong nearest-neighbor AF coupling of the spins within the Cu(2) planes, with AF alignment of the nearest-neighbor spins in the adjacent planes. By using the Mössbauer technique on iron-doped samples, it was shown[2] that T_N is not affected by the presence of Fe and that Fe is thus a reliable probe of the magnetic behavior of the Cu(2) sites. This interrelation between superconductivity and magnetism is found in a wide family of cationic substitutions in the oxygen rich 1:2:3 system.[3,4] We have shown that whenever various cations are doped in sites outside the Cu(2) planes sufficiently to make superconductivity disappear, a static long-range AF ordering of spins at the Cu(2) sites is induced.[4]

The effect of hydrogen doping on the superconducting properties of 1:2:3 has been studied by several authors.[5-8] It was shown that similar changes in the properties can be induced in the material by either removing oxygen or adding hydrogen. NMR (Ref. 7) and μSR (Ref. 8) measurements indicate that, for high hydrogen concentration, the system is not superconducting and magnetic ordering is induced in the system. In the present study, $YBa_2Cu_3O_7H_x$ with x ranging from $x=0$ to $x=1.3$ is investigated. In order to perform Mössbauer studies, all the samples were doped with 2 at. % ^{57}Fe.

Several experimental techniques were used and a phase diagram which exhibits a region of superconductivity and a region of magnetic order of the Cu(2) atoms was obtained. It was seen that in the Fe-doped samples, the addition of hydrogen reduces T_c in the superconducting compound, in contrast to data obtained for Fe-free samples.[5-8] Moreover, for high hydrogen concentrations, a static magnetic ordering of the Cu(2) atoms is found. The observed magnetic order is probably antiferromagnetic, in analogy with the 1:2:3 system. Thus this system is another example of the delicate interplay between superconductivity and magnetism in high-T_c superconductors.

II. EXPERIMENTAL DETAILS

The ceramic compound $YBa_2Cu_3O_{7-\delta}$ doped with 2 at. % ^{57}Fe was prepared by conventional methods.[2] The oxygen-deficient sample was obtained by quenching the sample from 900 °C to liquid nitrogen. The oxygen concentration was obtained by weight loss and we assign it to be 6.1. Hydrogen absorption was accomplished by direct contact with the gas at 200 °C in a fixed volume and x was determined by noting the change in gas pressure. X-ray diffraction was performed to determine the crystallographic structure and to ensure the purity of the compounds. Mössbauer spectroscopy was performed with use of a conventional constant-acceleration spectrometer and a 100-mCi ^{57}Co:*Rh* source. The spectra at various temperatures were least-squares fitted with various spectra corresponding to the two inequivalent iron sites. Magnetic dc susceptibility measurements in low fields as a function of temperature in the field-cooled process, carried out in a *PAR* vibrating-sample magnetometer, determined T_c of the samples.

III. EXPERIMENTAL RESULTS

A. Crystal-structure determination and dc magnetization measurements

Substitution of Fe for Cu in $YBa_2Cu_3O_{7-\delta}$ results in an orthorhombic-tetragonal transition at about 2 at. % Fe, and causes a considerable reduction of T_c. Several groups have measured the variation of T_c as a function of Fe in the 1:2:3 system and have obtained varying results that lie between some upper and lower limit.[9] Our starting material which contains 2 at. % Fe is superconducting with $T_c = 73(1)$ K and is in fair agreement with the published data.[9] The quality of the fit to the experimental diffractogram for the hydrogen-free sample is the same whether we assume an orthorhombic ($a = 3.843$ Å and $b = 3.858$ Å) or a tetragonal ($a = 3.852$ Å) structure. In both cases we obtain a lattice parameter of $c = 11.66$ Å. The quenched sample is definitely tetragonal with $a = 3.853$ Å and $c = 11.72$ Å [Fig. 1(a)]. This elongation along the c axis is a result of oxygen vacancies in the basal planes which induce an increase of the Cu—O bonds along the c axis.[10] The diffraction pattern of our $YBa_2Cu_3O_7H_x$ samples showed a tetragonal structure have lattice parameters $a = 3.860$ Å and $c = 11.72$ Å with no change within the experimental error of up to a hydrogen concentration of $x = 1.3$. Evidence of some amorphization is also seen. Note the expansion of the unit-cell volume for both the oxygen-deficient and hydrogen-charged systems (Fig. 1). This shows that hydrogen charging and oxygen removal affect the crystal structure similarly.

The variation of T_c with x is shown in Fig. 1(b). Increasing the hydrogen concentration causes T_c to decrease at a rate of about 40 K/mole-atom-hydrogen, up to $x \approx 1.0$. This differs from the results of other studies[5-8] where it is claimed that T_c is independent of x in the superconducting compound. The differences are perhaps due to the presence of 2 at. % Fe in our samples. Upon increasing x further, the compound becomes nonsuperconducting and, as will be seen from our Mössbauer measurements, shows long-range antiferromagnetism.

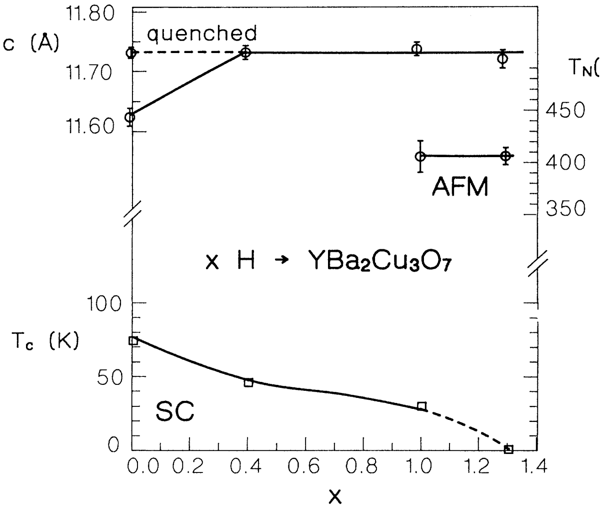

FIG. 1. Hydrogen-concentration dependence of the lattice parameter c for $YBa_2Cu_3O_{7-\delta}H_x$. The initial charge of H extends c the same as the removal of O. (b) The superconducting transition temperature T_c for the superconducting region and the Néel temperature T_N for the antiferromagnetic region as a function of hydrogen concentration.

B. Mossbauer measurements

It is well accepted that Fe atoms occupy predominantly the Cu(1) sites.[2,11] Mössbauer studies show[2] that a fraction of the iron enters the Cu(2) sites and in the nonsuperconducting quenched (oxygen-deficient) material, orders magnetically with the same Néel temperature as the undoped material. Thus ^{57}Fe is a reliable probe of the magnetic behavior at the Cu(2) sites. When the Cu(2) sites are magnetically ordered, they produce an exchange field at the iron located at the Cu(2) sites. The iron nuclei experience a magnetic field leading to a well-defined sextet in the observed Mössbauer spectra. In Fig. 2 we show the Mössbauer spectrum of our quenched (oxygen-deficient) starting sample measured at $T = 90$ K. The six line pattern accounts for 22% of the spectral area. The central part of this spectrum is composed of several quadrupole doublets,[2-4] corresponding to inequivalent iron sites due to different oxygen-neighbor configurations at the Cu(1) site.

Figure 2 also shows that no magnetic splitting is ob-

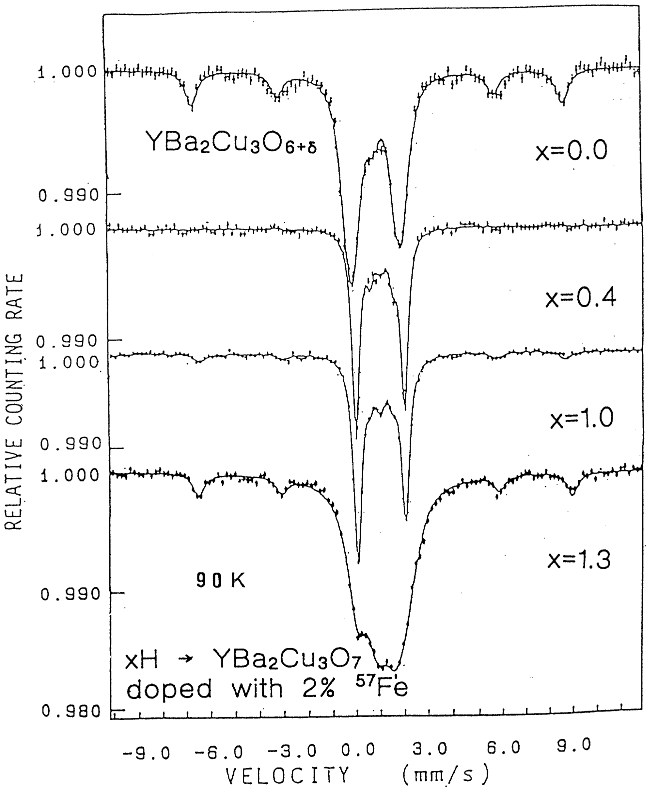

FIG. 2. Mössbauer spectra of 2 at. % ^{57}Fe–doped $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_{7-\delta}H_x$ at 90 K. The magnetic splitting is attributed to Fe at the Cu(2) sites. Note the absence of magnetic splitting in the superconducting material $x = 0.4$. The central portion of the spectra are due to quadrupole interactions at the primarily Cu chain sites. They will be analyzed elsewhere.

served in the superconducting sample $YBa_2Cu_3O_7H_{0.4}$ ($T_c=47$ K). In $YBa_2Cu_3O_7H_{1.3}$, which is not superconducting, we observe a well-defined magnetic sextet which accounts for about 13% of the spectral area. We attribute this sextet to iron which replaced Cu at the Cu(2) sites and orders antiferromagnetically. All iron atoms at this site are equivalent in terms of local oxygen environment and yield a well-defined magnetic spectrum. At 90 K, the magnetic hyperfine field is 490(5) kOe in both the oxygen-deficient and the hydrogen-charged samples (Fig. 2). But as mentioned above, the intensities of the magnetic sextet in the latter compound are significantly smaller, even though the Fe concentration is the same. We will return to this fact later. Figure 3 shows the temperature dependence of the Mössbauer spectrum for $x=1.3$. The main effect to be seen is that as the temperature is raised, the magnetic splitting decreases and, above $T_N=415$ K, the sextet disappears. The long-range magnetic order at the Cu(2) sites induced by the hydrogen, occurs at a concentration where the material becomes nonsuperconducting, exemplifying again the competition between the two states.[3] In this respect, hydrogen charging induces magnetic order in a way similar to oxygen removal and this result is in accord with other measurements.[7] The central part of the $x=1.3$ spectrum in Figs. 2 and 3 differs from that of all the other concentrations. A detailed analysis of this will be presented elsewhere.

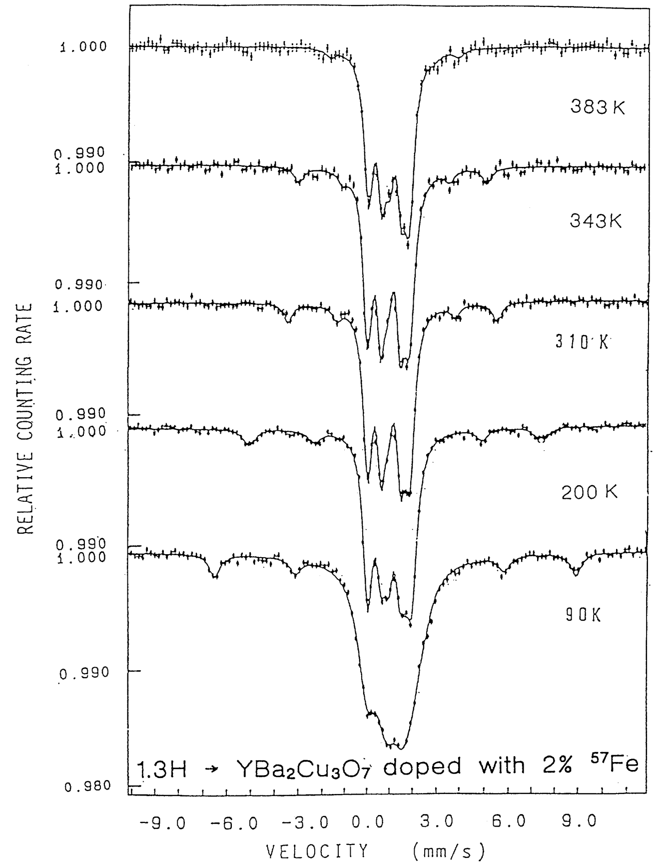

FIG. 3. Mössbauer spectra of 2 at.% ^{57}Fe-doped $YBa_2Cu_3O_{7-\delta}H_{1.3}$ at several temperatures. The magnetic splitting, which is attributed to Fe at the Cu(2) sites, decreases with increase of temperature and disappears at the temperature of 415 K.

We also obtained the Mössbauer spectra for $x=1.0$, which are very similar to those for $x=1.3$. At 90 K, the magnetic hyperfine field—which represents about 7% of the spectral area (Fig. 2)—is 480(5) kOe. T_N for this sample was determined in the same manner described previously. Figure 4 displays the temperature dependence of the effective field for both samples and shows that they are essentially identical having the same Néel temperature. Magnetic-susceptibility measurements indicated that the sample is superconducting with $T_c=30$ K. Our magnetic susceptibility data are consistent with the presence of only a small superconducting volume for this sample. It has, however, been shown that these measurements are not reliable indicators of the superconducting fraction (see, e.g., Ref. 12 and the references cited therein).

$x=1.0$ is the concentration near which the superconducting–long-range-AF-order transition occurs. The fact that both superconductivity and AF is seen in this sample may lead one to propose that either there is a phase separation between superconducting and magnetically ordered material or that superconductivity and AF overlap. The fact that the Mössbauer splitting remains the same while the intensity of the signal is so weak may lead one to conclude that there is a phase separation with only part of the material being antiferromagnetic. We would then, however, expect T_c to remain largely unaffected, but in actuality T_c dropped to 30 K. It is possible, however, that this drop in T_c is a reflection of the reduction in T_c for increasing hydrogen concentration in

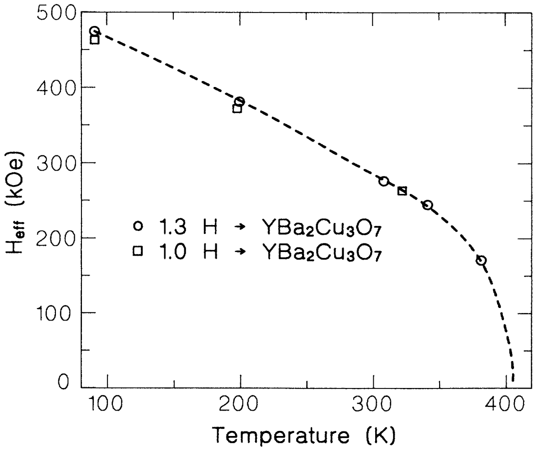

FIG. 4. Temperature dependence of the magnetic hyperfine field acting on Fe at the Cu(2) sites in $YBa_2Cu_3O_{7-\delta}H_x$ for $x=1.0$ and 1.3.

these Fe-doped samples. In any event, for concentrations other than $x = 1$ the usual observation of noncoexistence of superconductivity and AF remains valid.

While the $x = 1.3$ sample clearly shows AF and is nonsuperconducting, the relative intensity of the Mössbauer signal is less than that obtained for the oxygen-deficient sample.

Note added in proof. We are aware of a recent publication by V. V. Sinitsyn *et al.* (Fiz. Tverd. Tela (Leningrad) **31**, 54 (1989) [Sov. Phys. Solid State **31**, 2056 (1989)]) which shows that T_c remains independent of hydrogen concentration as long as it is above 90 K, corresponding to an oxygen concentration of ~7. However, for an oxygen concentration of 6.54, T_c for the undoped materials is ~60 K and decreased linearly with hydrogen concentration.

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