Magnetic order induced by hydrogen in superconducting $RBa_2Cu_4O_8$ (R = Y,Gd) studied by Mössbauer and NQR techniques

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Magnetic susceptibility, Mössbauer spectroscopy, nuclear quadrupole resonance of Cu (NQR), nuclear magnetic resonance of Cu in the hyperfine field of the antiferromagnetic state (AFNMR), and x-ray diffraction measurements were performed to study the superconducting and magnetic properties of hydrogen charged bulk $YBa_2Cu_4O_8H_y$. For $y < 1$ the c lattice parameter decreases with y. In contrast to Fe-doped $YBa_2Cu_3O_7H_y$, where T_c decreases continuously with increasing y, we find here that for 1% Fe doped, T_c = 59 K is unaffected by hydrogen charging, but the shielding fraction is reduced sharply from 38% for y = 0 to 17% and 3% for y = 1 and 1.85, respectively. The Mössbauer spectra for y = 0 at T > 90 K contain one doublet. The spectra for hydrogen charged samples, in addition to this doublet, contain a magnetic pattern composed of two sextets, between 4.1 K and T_N = 360 K. The relative amount of the magnetic pattern depends on hydrogen concentration. The Mössbauer spectrum obtained for y = 1 is a superposition of spectra obtained for y = 0 and those for y = 2, showing a phase separation into magnetic and superconducting regions in $YBa_2Cu_4O_8H_y$. NQR-AFNMR studies of $YBa_2Cu_4O_8H_y$ and $GdBa_2Cu_4O_8H_y$ samples indicate that magnetic order is induced only in the Cu(2) planes.

INTRODUCTION

In the high-T_c superconducting cuprates Fe generally substitutes at the Cu sites. It is generally accepted that partial substitution of Fe for Cu in $YBa_2(Cu_{1-x}Fe_x)_3O_7$ (Y123) induces an orthorhombic-tetragonal phase transition and progressively reduces T_c. For Fe concentration exceeding x = 0.13, the materials are not superconducting.[1,2] Some contradictory results are reported in the literature concerning the distribution of Fe over the two Cu sites in Y123. However, Mössbauer spectroscopy studies (MS) on ^{57}Fe show that Fe atoms are found to occupy predominantly the Cu(1) site with an increasing fraction occupying the Cu(2) sites as the total amount of Fe increases. Since iron replacing Cu^{2+}, is either Fe^{3+} or even Fe^{4+}, it attracts oxygen to maintain charge neutrality. It was suggested that several different oxygen coordinations exist around the Fe residing in the Cu(1) site. The Mössbauer spectra above 90 K for the oxygen-rich superconducting material is composed of three or four doublets corresponding to these Fe sites, which are immediately identified by their isomer shifts and quadrupole splittings.[3–5] When oxygen is depleted the Y123 loses its superconducting properties and for $YBa_2Cu_3O_6$ the Cu(2) sites become antiferromagnetically ordered at T_N = 420 K. All Fe atoms residing in this site, have a five-fold pyramidal coordination. When Cu becomes magnetically ordered, it produces an exchange field at the Fe located at the Cu(2) sites, leading to a well-defined sextet in the

Mössbauer spectra. The magnetic hyperfine field at this site at 4.1 K is 505(5) kOe. We have shown that whenever various cations are doped in sites outside the Cu(2) planes in a sufficient amount to make superconductivity disappear, a static long-range antiferromagnetic ordering of spins at the Cu(2) sites is induced.[6] The effect of hydrogen doping on the superconducting properties of Y123 has been studied extensively. We have shown[7] that in $YBa_2Cu_{2.94}Fe_{0.06}O_7H_y$, T_c is reduced with increasing y and superconductivity is suppressed for y = 1.3. An analysis of the Mössbauer spectra shows that for this y value the Cu(2) sites become antiferromagnetically ordered at T_N = 420 K, in a very similar way as caused by the removal of oxygen. The phase diagram in the H-doped materials is similar to the well-known phase diagrams obtained in a wide family of cationic substitution in Y123.

The structure of $YBa_2Cu_4O_8$ (Y124) is closely related to Y123 but with one additional CuO chain in the unit cell. Each unit cell contains two Cu-O chains [denoted Cu(1)], with four-fold square-planar coordination of oxygen and two CuO_2 planes [denoted Cu(2)] with a five-fold pyramidal coordination of oxygen. Partial substitution of Fe for Cu in $YBa_2(Cu_{1-x}Fe_x)_4O_8$ sharply reduces T_c which is totally suppressed for x > 0.04.[8] In contrast to Y123 the Mössbauer spectrum when T > 90 K for $0.005 < x < 0.025$ consists of a single quadrupole doublet, with a splitting of $\Delta \equiv eqQ/2$ = 0.8(1) mm/s and an isomer shift of 0.3 mm/s [Fig. 3(c)]. The site assignment of

this doublet is not straightforward. In recent papers we attributed this doublet to iron ions which reside in the Cu(1) sites. Our assumption is based on the fact that for $T < 30$ K a well-defined sextet appears,[9] suggesting that these samples exhibit coexistence of superconductivity in the Cu(2) planes and magnetic order in the Cu(1) chains. For $x > 0.05$, an additional sextet appears in the Mössbauer spectra indicating that magnetic order is formed in the Cu(2) sites. Thus, the Y124 system behaves similarly to the Y123 system discussed above.

An alternative (and less preferable) way is to assume that Fe in Y124 resides preferentially in the Cu(2) sites.[10,11] Supporting evidences for this determination are (1) the similarity of the values of the hyperfine parameters of this doublet to the values corresponding to Fe in the Cu(2) sites of Y123.[2-4] (2) The sharp decrease of T_c caused by Fe doping. However, if Fe enters the Cu(2) sites, it is very hard to accept that at low temperatures, one obtains superconductivity and magnetic order in the same planes. Recent NQR measurements on $x = 0.005$ and 0.01 Fe-doped Y124 samples show that the presence of Fe affects dramatically both Cu(1) and Cu(2) sites.[12] Thus, the location of Fe in the Y124 system remains unclear.

Here, detailed studies on the effect of hydrogen charging on the superconducting and magnetic properties of ceramic Y124 are reported. The main subject addressed here is the hydrogen-induced magnetic order in Y124, in a way which is similar to that obtained by other substitutions in this structure. Recently, the antiferromagnetic state was also detected by μsr measurements.[13] In contrast to the Fe-doped Y123 system,[7] T_c remains constant and the shielding fraction decreases sharply with the increase of the amount of H. Using the Mössbauer technique on 1 at. % Fe-doped Y124 samples we show that magnetic ordering is induced by hydrogen. We propose the formation of two phases in the system, namely, a superconducting and a magnetic phase[14] and their relative amount depends on the hydrogen concentration. The results presented here can be equally explained by the two scenarios of site location of Fe mentioned above. NQR studies on Gd124 confirm the antiferromagnetic order of the Cu(2) sites, induced by hydrogen.

EXPERIMENTAL DETAILS

$YBa_2(Cu_{0.99}Fe_{0.01})_4O_8$ was prepared by solid-state reaction of stoichiometric mixture of the constituent oxides, in high oxygen pressure following the procedure described in Ref. 7. First, Y(123) was prepared by conventional methods and the Y(124) phase was obtained by sintering the Y(123) with CuO at 850°C for 15 h at $P(O_2) = 150-200$ atm. X-ray-diffraction studies confirmed the purity of the compound. For Mössbauer studies, hydrogen absorption in 1 at. % ^{57}Fe-doped material was accomplished by direct contact with hydrogen gas at 200°C in a fixed volume and the amount of hydrogen absorbed was determined by noting the change in gas pressure. Samples with two concentrations were studied, one with 1.0 H and the second with 1.85 H atoms per formula unit (f.u.), denoted as H1 and H2, respectively. The

$GdBa_2Cu_4O_8$ sample for NQR measurements was prepared in the same manner.

Magnetic dc measurements on powder materials in 10 Oe as a function of temperature, in the zero-field-cooled process, were carried out in a PAR vibrating sample magnetometer, and determined T_c and the shielding fraction (SF) of the samples. Mössbauer spectroscopy (MS) was performed using of a 100 mCi ^{57}Co:Rh source, with a constant acceleration mode spectrometer. The spectra at various temperatures were least-square fitted with several subspectra corresponding to different sites in the materials.

NMR and NQR studies at 1.2 and 4.2 K were performed using a standard pulse spectrometer in zero external field. The frequencies were scanned in discrete steps and the intensity was measured by spin-echo techniques.

EXPERIMENTAL RESULTS AND DISCUSSION

A. The effect of hydrogen on the lattice parameters

X-ray powder measurements on $YBa_2(Cu_{0.99}Fe_{0.01})_4O_8H_y$ samples indicate that they are single phases. Least-squares refinement of the orthorhombic crystallographic unit-cell parameters yield for $y = 0$, $a = 3.833$ Å, $b = 3.873$ Å, and $c = 27.28$ Å, in complete agreement with Ref. 8. The a and b crystallographic axes are independent of y, while the c axis decreases for $0 < y < 1$ and then increases for $y > 1$ (Fig. 1). For comparison, the effect of hydrogen on the c lattice parameter in H-doped in Y123 is also shown. It can be seen that for $0 < y < 1$ both systems behave similarly, however for $y > 1$ the c axis in Y123 remains constant and yields the pseudocubic structure $a = b = c/3$.[15] On the other hand, for Gd124H$_y$ all the unit-cell parameters expand with hydrogen loading and the lattice parameters for $y = 0$ are $a = 3.874$ Å, $b = 3.887$ Å, and $c = 27.14$ Å and $a = 3.912$ Å, $b = 3.927$ Å, and $c = 27.75$ Å for $y = 2$.

B. dc magnetization studies

Figure 2 shows the susceptibility curves as a function of temperature for $YBa_2(Cu_{0.99}Fe_{0.01})_4O_8H_y$. It is readily
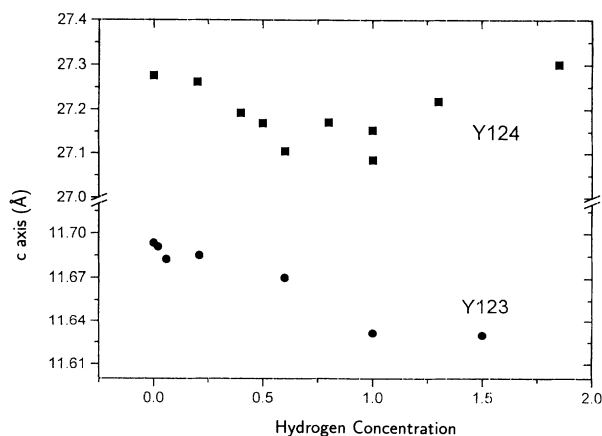

FIG. 1. The effect of hydrogen on the c lattice parameter in Y124 and Y123.

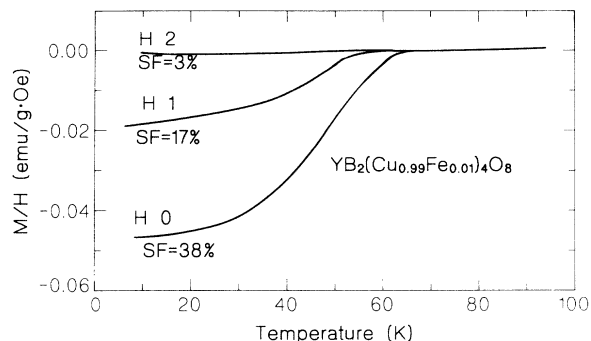FIG. 2. The temperature dependence of the susceptibility measured at 10 Oe in the zero-field-cooled process for $YBa_2(Cu_{0.99}Fe_{0.01})_4O_8H_y$ materials. SF is the diamagnetic shielding fraction deducted at 4.2 K.

observed that $T_c = 59(1)$ K is obtained for all samples measured regardless of hydrogen concentrations. This value is in perfect agreement with Ref. 8. However, it differs from results obtained for $YBa_2(Cu_{0.99}Fe_{0.01})_3O_7H_y$,[7] where increasing the hydrogen concentration causes T_c to decrease and for $y > 1$ superconductivity is totally suppressed. The relatively high SF observed for $y = 0$ gives strong evidence for bulk superconductivity of this material. A sharp reduction in the SF is observed for H1 and H2 materials. The SF numbers listed in Fig. 2 have to be taken with caution. (1) The dc measurements were not performed at the same time and there is some uncertainty in the applied field values. (2) The reduction in the diamagnetic SF also can be explained by geometric effects in the size of the powder particles caused by hydrogen loading. However, the same T_c for all samples and the reduced SF in H1 and H2 (which contains 1.85 H/f.u.) may indicate a phase separation into superconducting and magnetic regions. We suggest that hydrogen atoms are not randomly distributed and that 2 H/(f.u.) are needed to destroy completely superconductivity (in those unit cells where hydrogen is accumulated). Magnetic ordering is induced in those cells and the rest of the sample is unaffected by the presence of H and remains superconducting. The site location of H in the crystal structure is not known. In the light of the present picture, the relative amounts of the magnetic phases deducted from the Mössbauer studies, can be easily explained.

C. The antiferromagnetism: Mössbauer studies (MS)

It is well accepted that Fe in Y(124) resides preferentially in one of the crystallographic sites, namely, Cu(1) or Cu(2). The results presented here can be explained by either of the two possibilities. For Fe concentrations exceeding 4 at.% in Y(124), superconductivity is destroyed and a static magnetic ordering is induced in the Cu(2) planes.[8] We propose that hydrogen induces a magnetic ordering in the same manner. Assuming that Fe is located in the Cu(2) site, when these sites become magnetically ordered, they produce an exchange field at the

iron ions. The Fe nuclei experience a magnetic field leading to a sextet in the MS. If Fe is located in the Cu(1) (our preferred site assignment of Fe), we assume that an exchange-field transferred via the hydrogen atoms from the Cu(2) planes is acting on the Fe ions. For the sake of clarity, we shall discuss briefly at first the MS of the unloaded Y(124) sample (H=0). After that the detailed MS of H2 and H1 at various temperatures will be described. It is shown that the MS of H1 are a superposition of spectra obtained in H=0 and H2.

1. Mössbauer studies of Y(124) with H=0

For all low-iron-doped concentrations studied[8,9] (0.5–2.5 at.%) the MS at $T > 90$ K show basically one symmetric doublet [Fig. 3(c)] with a quadrupole splitting $\Delta = 0.8$ mm/s and an isomer shift I.S.=0.30 mm/s. These parameters can be assigned to Fe^{3+} in a high spin state. Previously we attributed this doublet[8] to Fe in the Cu(1) site. This single doublet indicates that, in contrast
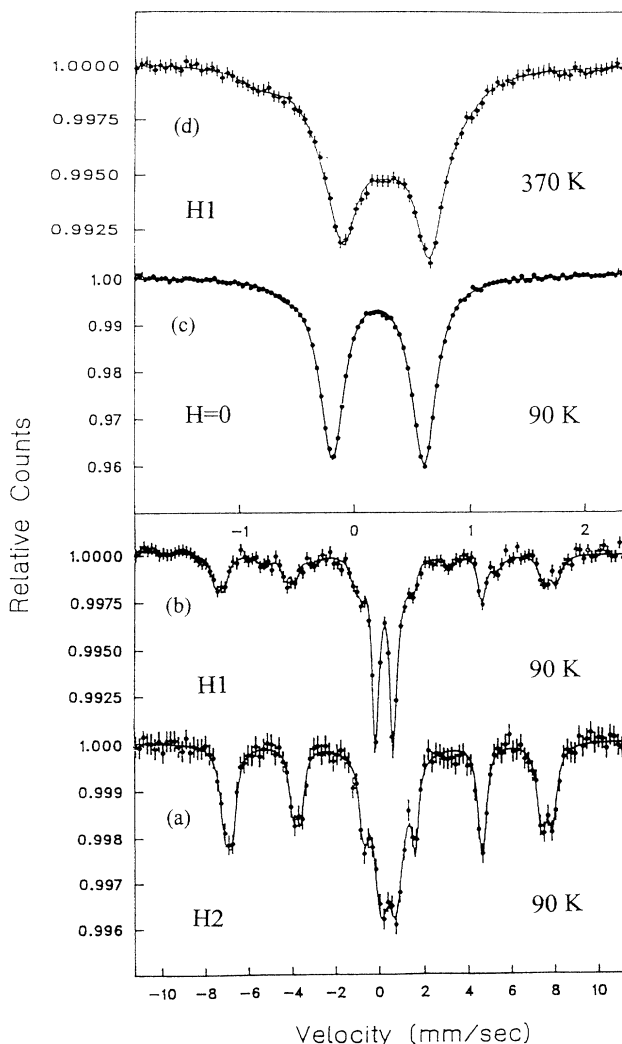

FIG. 3. Mössbauer spectra at 90 K for $YBa_2(Cu_{0.99}Fe_{0.01})_4O_8H_y$ and of H1 at 370 K (note the expanded scale in upper part of the figure).

to Y(123), all iron ions are equivalent in terms of oxygen environment and therefore only one doublet is observed.

At 4.2 K the MS spectra (not shown) for low Fe concentration 0.5–1 at. % exhibit a complicated structure which may be analyzed either, by using three magnetic sextets and one doublet, a picture which is not consistent with the single doublet shown in Fig. 3(c), or, by assuming long-range paramagnetic relaxation phenomena. However, this is of little interest in the present paper, and for comparison we shall present the most informative and revealing data at 4.2 K obtained for 2.5 at. % Fe doped in Y(124),[9] assuming that Fe resides in the Cu(1) sites.

According to magnetization measurements, this sample is superconducting below $T_c = 27$ K. Nevertheless it exhibits a well-defined magnetic sextet below 30 K. The saturated hyperfine field at 4.2 K is 461(2) kOe and the effective quadrupole interaction is -0.4 mm/s, just $-\frac{1}{2}$ of the value obtained at $T > 90$ K, proving that the ordered magnetic moments lie perpendicular to the electric-field gradient—the c axis. Thus, this sample exhibits coexistence of superconductivity in the Cu(2) planes and antiferromagnetism of Fe in the Cu(1) chains in almost the same temperature range.
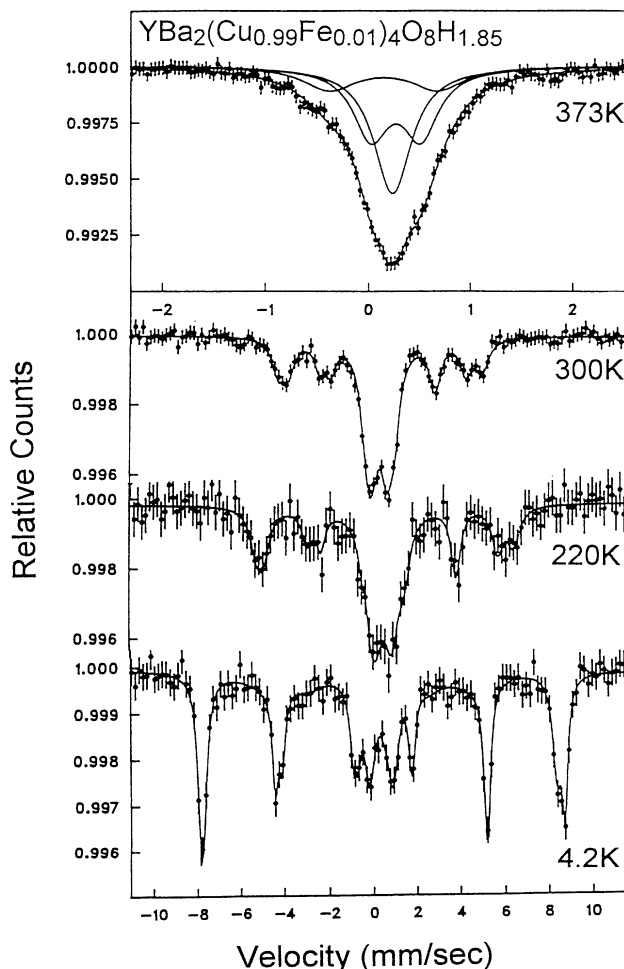

FIG. 4. Mössbauer spectra of H2 below and above $T_N = 360$ K (note the expanded scale in upper part of the figure).

2. Mössbauer studies of H2 sample

The hydrogen concentration in this sample is 1.85 atom/(f.u.) and a small (SF=3%) superconducting phase with $T_c = 59$ K exists (Fig. 2). MS at various temperatures are displayed in Figs. 4 and 3(a). Although the site assignment of Fe is not conclusive, useful information concerning the effect of hydrogen charging can be deducted easily. The spectra in Fig. 4 consist of at least three subspectra. The main information to be seen, is the magnetic six line pattern obtained at low and elevated temperatures. As the temperature is raised the magnetic splitting decreases and the ordering temperature $T_N = 360(5)$ K is determined (see Fig. 5). We attribute this magnetic pattern to magnetic order induced by hydrogen in that fraction of the material which accommodates 2H/f.u. This T_N value is very similar to $T_N = 380$ K obtained for the magnetic ordering of the Cu(2) sites induced by 10 at. % of Fe in the Y(124) system.[8] In that respect hydrogen charging affects the Y(124) system in a way similar to Fe doping.

The detailed computer analysis of the spectrum obtained at 4.2 K (Fig. 4) shows that the magnetic pattern is composed of two magnetic sextets with I.S.=0.42(2) mm/s which account for 72% of the spectral area with relative intensity of 1:1. The hyperfine fields at 4.2 K are 514(2) and 499(2) kOe and the two subspectra differ only in their effective quadrupole interactions which are 0.07(4) and $-0.20(2)$ mm/s, respectively. Note that the hyperfine values of H2 are completely different from those of Fe-doped Y(124) described above. The narrow lines of the well-defined sextets (linewidth 0.27 mm/s) indicate that the hydrogen atoms absorbed in the unit cell occupy crystallographic positions (their locations are not known yet) and are not randomly distributed. In addition, the central part of the spectrum contains a broad doublet with relative intensity of 28% and I.S.=0.33(3) and $\Delta = 1.05(3)$ mm/s. This doublet belongs to the fraction which remains superconducting in this material. In this fraction the small amount of hydrogen, is randomly distributed and leads to the change and spread in the quadrupole values.

The same general picture holds for the MS measured at higher temperatures, but the relative amount of the dou-
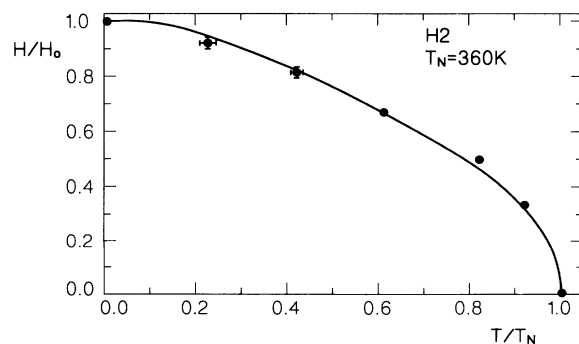

FIG. 5. Temperature dependence of the average normalized hyperfine field for H2. The solid line is the theoretical curve for Fe-Cu exchange strength (see text).

blet increases at the expense of the magnetic pattern which reduces to 57% at 90 K [Fig. 3(a)] and to 47% at 300 K (Fig. 4). This reduction in the intensity of the magnetic subspectra, can be the result of a lower Mössbauer recoil free fraction for these particles containing hydrogen and also a result of some distribution in T_N according to the exact concentration of hydrogen present.

The temperature dependence of H_{eff} for the two magnetic sextets has the same shape. The variation of the normalized average H_{eff} values, as a function of the reduced temperature, is exhibited in Fig. 5. It was shown theoretically,[16] that for all Fe-doped Y(123) based materials, the normalized H_{eff} values fall on one universal curve, regardless of Fe or oxygen concentration and whether Y is replaced by Pr. The model assumes that the temperature dependence of the magnetization of Cu and Fe^{3+} as a probe, behave like spin-$\frac{1}{2}$ and spin-$\frac{5}{2}$ systems and that the Fe-Cu exchange is only 26% of the Cu-Cu exchange strength. The solid line in Fig. 5 is the universal theoretical curve calculated in this way. The fit of the experimental data to this curve is our conclusive proof that the magnetic pattern in Fig. 4 is due to Fe in the Cu sites in the Y(124) structure.

The feature of the MS measured at 373 K (above T_N) is noteworthy. One would expect that similar to Fig. 3(c) both sextets will collapse to one doublet, since all Fe are equivalent in terms of oxygen environment. Unexpectedly, Fig. 4 shows that the high hydrogen concentration in first or second close neighbor positions to Fe lead to different quadrupole interactions. Consistent with the three subspectra observed at low temperatures, we fitted the spectrum at 373 K with three doublets. The major doublet (44%) has similar hyperfine parameters values ($\Delta=0.68$ and I.S.$=0.26$) as those obtained in the uncharged material [Fig. 3(c)]. The magnetic sextets collapse to two equal (28%) doublets with the same I.S.$=0.25$ mm/s and with $\Delta=0.09(7)$ and $0.47(3)$ mm/s. Thus one of the Fe positions is almost cubic.

3. Mössbauer studies of H1 sample

This material contains one hydrogen atom per formula unit and its SF is intermediate between the uncharged and H2 samples (Fig. 2). The magnetic pattern observed in the MS is similar to that of H2 but with smaller intensity. Both H1 and H2 materials have the same T_N. The comparison between the MS at 90 K for all samples studied is exhibited in Fig. 3. The magnetic pattern for H1 [Fig. 3(b)], which accounts for 39% of the spectral area is also composed of two sextets with the same hyperfine values of that of H2 [Fig. 3(a)]. The readily observed doublet in the central part is fitted with I.S.$=0.40$ and $\Delta=0.80$ mm/s values which are very similar to those of the doublet obtained in the uncharged materials [see Fig. 3(c)]. At 4.2 K a complicated spectrum (not shown) is obtained. Our analysis shows that it is a superposition of the spectrum shown in Fig. 4 at 4.2 K for H2 and the magnetic spectrum obtained for pure Fe-doped Y(124) described above.[9] It is interesting to notice that the spectrum obtained at 370 K, (above T_N), [Fig. 3(d)] is also a

superposition of the Fig. 3(c) and the spectrum observed for H2 at 373 K (Fig. 4).

D. NQR studies on $GdBa_2Cu_4O_8H_{1.96}$

NQR technique provides a complementary direct method to MS, to study the different quadrupole splittings of the two Cu sites in Y124. Natural Cu contains two isotopes, ^{63}Cu and ^{65}Cu both with nuclear spin of $I=\frac{3}{2}$. We mention here only the lines of the ^{63}Cu isotope. The frequency lines of the less abundant ^{65}Cu (31%) are shifted downward by about 10%. When Cu becomes antiferromagnetically ordered, the frequencies of the antiferromagnetic nuclear resonance (AFNMR) can be observed at much higher values than the NQR lines.

The NQR spectra of Y124 at 1.2 and 4.2 K are quite similar. On the other hand, the antiferromagnetic transition of the Gd sublattice at ($T_N=2.2$ K) in pure Gd124, induces a difference in the spectra below and above T_N [Fig. 6(a)], which permits separation of the NQR lines of Cu(1) from Cu(2). At 1.2 K the two signals at 20.3 and 31 MHz, are readily observed but at 4.2 K the latter peak disappears. Above T_N(Gd), the Cu(2) nuclei are severely distorted by the fast relaxation of the nearby paramagnetic Gd moments, and the 31-MHz line is suppressed. At 1.2 K the magnetically ordered Gd moments do not relax the Cu(2) sites and the full spectrum of both sites is obtained. Thus, only the lines corresponding to Cu(1) ap-
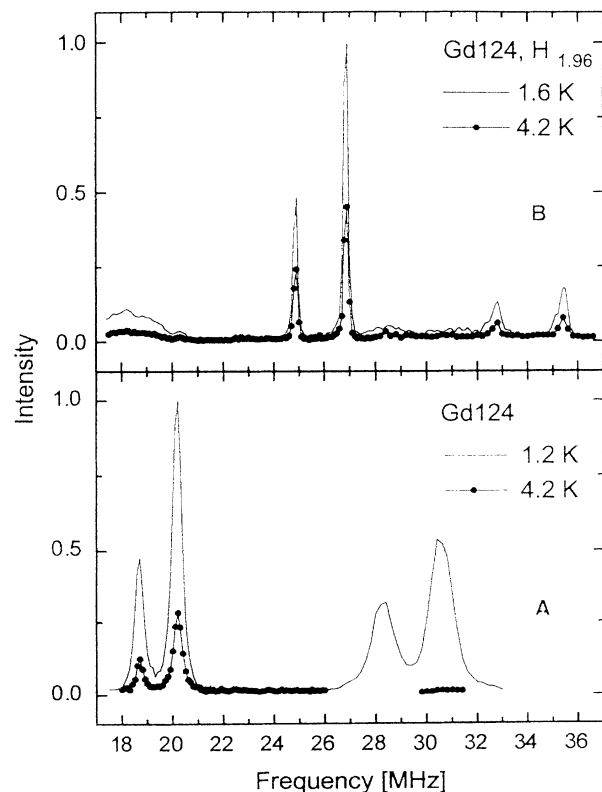

FIG. 6. Cu NQR spectra of (a) $GdBa_2Cu_4O_8$, (b) $GdBa_2Cu_4O_8H_{1.96}$.
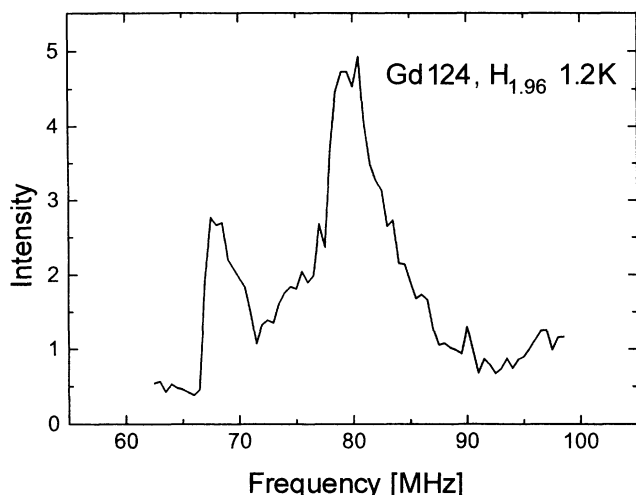
FIG. 7. AFNMR spectrum of $GdBa_2Cu_4O_8H_{1.96}$ at 1.2 K.

pear at 4.2 K.[17] At 1.2 K, no systematic difference is found in the NQR lines of Y124 and Gd124.

The NQR spectra vary with hydrogen loading. Figure 6(b) exhibits the NQR spectra of $GdBa_2Cu_4O_8H_{1.96}$ at 1.6 and 4.2 K, and all the lines are attributed to the Cu(1) sites. The smeared peaks at low frequencies are a result of unloaded Gd124 material. Hydrogen (2 H/f.u.) shifts the 20.3-MHz peak of Cu(1) to 27 MHz, in a very similar way as observed in the Y123-H system.[18,19] This line is very close to the frequency for Cu in Cu_2O, suggesting local reduction of Cu caused by hydrogen. The narrowness of this line may indicate some long-range order of the hydride configuration in the Cu(1) planes. There is no x-ray evidence for the Cu_2O phase, and we are convinced that the 27-MHz line belongs to the host material. The peak at 35.5 MHz [Fig. 6(b)] probably belongs to Cu(1) with different hydrogen concentration with higher quadrupole splitting. This line was also observed in the Y123-H (Ref.

19) system but not so clear as here.

Figure 7 shows the AFNMR spectrum of $GdBa_2Cu_4O_8H_{1.96}$ at the high-frequency region. This spectrum is found only at 1.2 and not at 4.2 K and therefore must be related to Cu(2) sites as described above. This supports our assumption that magnetic ordering in the Cu(2) planes is induced by hydrogen in those unit cells where 2 H/f.u. is accumulated. Fe serves only as a probe and the presence of 1% Fe does not affect the position of Cu NQR and AFNMR lines, but reduces their intensity by a factor of 2. The spectrum of 1% Fe-doped $GdBa_2Cu_4O_8H_y$ resembles that of Fig. 6(b),[12] but the line at 35.5 MHz is broadened.

Summarizing the data shown in this paper, we may say with high confidence that in both H1 and H2, charging of hydrogen leads to phase separation to superconducting and magnetically ordered regions. The fraction of the magnetic phase ($T_N = 360$ K) depends strongly on hydrogen concentration. NQR-AFNMR studies show clearly that the induced magnetic order is confined to the Cu(2) planes. We assume that the main effect of hydrogen is the reduction of charge carrier concentration which leads to suppression of superconductivity.[20] The present study shows that the hydrogen-doped Y(124) system behaves in a way similar to other high-T_c superconductors, namely, in compositions which are not superconducting, a long-range magnetic ordering is induced. The magnetic state in this system is not induced by depletion of oxygen, since in Y124 the oxygen concentration is fixed and not affected by hydrogen charging.

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