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Magnetic ordering induced by hydrogen doping of $YBa_2Cu_3O_7$

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Superconducting $YBa_2Cu_3O_7$ samples doped with hydrogen were investigated by the muon-spin-rotation technique. For a hydrogen concentration larger than 0.5 per formula unit, we find a well-defined precession signal in zero external field. This is a clear indication of magnetic ordering in these samples. The precession frequency of 2 MHz is distinctly different from the 4-MHz signal observed in magnetically ordered oxygen deficient $YBa_2Cu_3O_6$ and thus excludes that the effect is due to oxygen removal from the sample. The data are consistent with the assumption that hydrogen acts as an electron donor filling the hole states in $YBa_2Cu_3O_7$.

$YBa_2Cu_3O_y$ shows a large variation of physical properties, if the oxygen stoichiometry is changed: The material is metallic and superconducting for $y=7.0$ (Ref. 1) but semiconducting and antiferromagnetic for $y=6.0$.[2,3] The transition between these two regimes occurs around $y=6.4$.[4,5] The conductivity in $YBa_2Cu_3O_7$ is of p-type (holes)[6] and the transition from the conducting to the magnetically ordered state is due to the removal of holes by taking out oxygen.[7] In this paper we show that a similar change of the physical properties can be achieved by adding hydrogen to the system but leaving the oxygen stoichiometry unchanged. We found that hydrogen doping of $YBa_2Cu_3O_7$ induces magnetic ordering in a very similar way as the removal of oxygen from this system. Our data suggest that hydrogen acts as an electron donor filling the hole states in $YBa_2Cu_3O_7$.

The effect of hydrogen doping on the superconducting properties of $YBa_2Cu_3O_7$ was studied in detail by Reilly and co-workers,[8,9] Nicolas *et al.*,[10] and Fujii *et al.*[11] Reilly and co-workers showed that the superconducting properties of $YBa_2Cu_3O_7H_x$ are little changed up to $x=0.13$, but then for higher hydrogen concentrations, the superconducting volume fraction decreases indicating a phase separation in a superconducting and nonsuperconducting region above this concentration limit. No characterization of the nonsuperconducting volume fraction is given by these authors. In a recent NMR paper,[12] local magnetic ordering in hydrogen-doped $YBa_2Cu_3O_7$ was reported.

In the present paper we present evidence for hydrogen-induced magnetic ordering in $YBa_2Cu_3O_7$ measured by the muon-spin-rotation (μSR) technique. The fact that a spin precession signal is observed in zero external field is an unambiguous signature of an internal magnetic field and therefore of magnetic ordering in the sample. The H-concentration dependence of this effect is investigated.

The sample preparation started from well-characterized $YBa_2Cu_3O_7$ materials with superconducting transition temperatures above 90 K. The hydrogen charging was done from the gas phase at hydrogen pressures of several bars and at a temperature of 168 °C. The hydrogen uptake took several hours to days depending on the desired hydrogen concentration in the sample. As expected, the uptake was faster in the powders than in the pellets but choosing the appropriate charging time, the same charging state, and also the same μSR results were obtained for both types of material. The hydrogen concentration in the sample was calculated from the pressure difference in the charging cell before and after hydrogen uptake. X-ray powder diffraction showed that the hydrogen-charged samples with $x<1.17$ remained orthorhombic with no change of the lattice parameters within experimental errors.

Measurements of the magnetic susceptibility showed an onset of superconductivity at 90 K also in the hydrogen charged samples and a decrease of the diamagnetic signal with increasing hydrogen concentration. These data are in good agreement with the results obtained by Fujii *et al.*[11] Resistivity measurements resulted in a metallic behavior with a transition to zero resistivity at 90 K for hydrogen concentrations $x<0.2$ but showed a semiconducting behavior for $x>0.2$.

The muon-spin-rotation experiments were performed at the low-momentum beam of the Paul Scherrer Institut (Switzerland) in zero external field with a usual μSR setup.[13] In these experiments, positive muons with an energy of 4 MeV are implanted into the sample and come to rest approximately 100–200 μm below the sample surface.

The muons are 100% polarized and the spin starts precessing after the implantation in the local magnetic field at the stopping site. Due to the spin-$\frac{1}{2}$ property of the muon only magnetic interactions are possible. The muon spin precession is recorded by counters detecting the decay positrons in forward and backward directions. The oscillation frequency of the decay rate as a function of time is a direct measure of the local magnetic field at the muon site:

$$\nu_\mu(\mathrm{MHz}) = 135.5 B_\mu(\mathrm{T}) . \quad (1)$$

The amplitude of the oscillation bears information on the fraction of muons experiencing a certain local field.

Figure 1 shows μSR spectra and their Fourier transforms for an uncharged and a hydrogen-charged $YBa_2Cu_3O_7$ sample. The main feature of the hydrogen-charged sample is an oscillation of approximately 2 MHz superimposed on exponentially decaying asymmetry. In addition, a weak but clearly visible oscillation of approximately 4 MHz is present. In the uncharged sample, the oscillations are absent and the asymmetry is essentially constant in the time range shown; the slight decay of the asymmetry is due to nuclear moments.

The temperature dependence of the two frequencies (2- and 4-MHz signal) is shown in Fig. 2. The data follow a Brillouin function with a Néel temperature of approximately 320 K. The ordering temperatures were very similar for all samples with H concentrations above $x = 0.5$. For lower hydrogen concentrations no oscillations were found in the μSR spectra. The fraction of muons experiencing either one of the two frequencies is plotted in Fig. 3. A continuous increase of this fraction with increasing H concentration and a possible saturation is visible.

The three different μSR signals (2 and 4 MHz, and the exponentially decaying part) are tentatively assigned to the following muon stopping sites:

The 2-MHz signal is attributed to muons bound to oxygen in the Cu-O chains of the $YBa_2Cu_3O_7$ structure. Such a site was proposed by Dawson *et al.* [14] on the basis of potential-energy and magnetic-dipolar-field calculations for muons in antiferromagnetically ordered $GdBa_2Cu_3O_7$.[15] Assuming the same muon stopping sites in the present case and that the Cu moments order in the same way as known for $YBa_2Cu_3O_6$, we calculate a dipolar field corresponding to $\nu_\mu = 2.2$ MHz which is in excellent agreement with the experimental value of 2 MHz. Thus, the present data suggest that the Cu moments in $YBa_2Cu_3O_7H_x$ order in the same way as in $YBa_2Cu_3O_6$. The 4-MHz signal which is very weak here, is the same as the one observed in $YBa_2Cu_3O_6$ where this is the dominant frequency. In the paper of Dawson *et al.*,[14] it was proposed that in the absence of chain oxygen atoms the muons would bind to oxygens in the Ba plane. The calculated dipolar field at this site for the known Cu moment ordering in $YBa_2Cu_3O_6$ gives a μSR frequency of 4.4 MHz in good agreement with the experimental value of 4

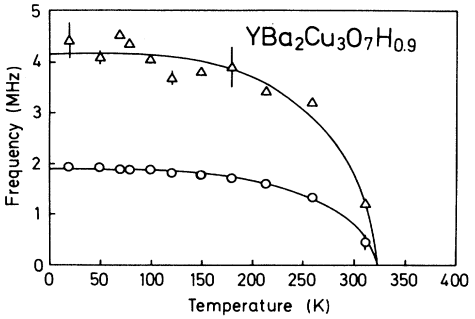

FIG. 2. Temperature dependence of the μSR frequencies in a hydrogen-charged $YBa_2Cu_3O_7$ sample. The solid line represents a fit to the data with the prediction of the $S = \frac{1}{2}$ molecular-field model. The Néel temperature of the sample is approximately 320 K.

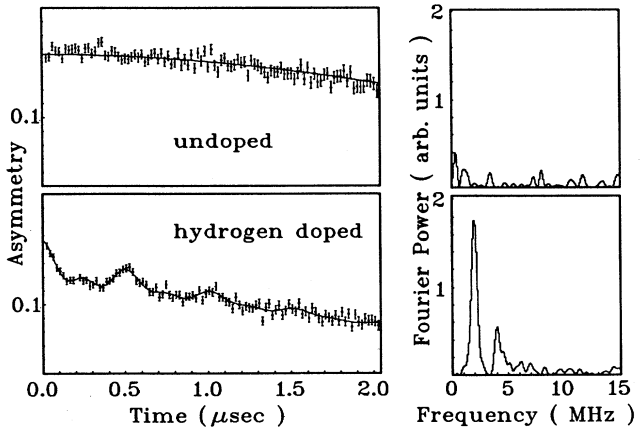

FIG. 1. μSR spectra and their Fourier transforms for an uncharged and a hydrogen-charged sample in zero external field. The oscillation in the lower spectrum is a clear indication of magnetic ordering in the sample. In the uncharged sample (upper spectrum) the oscillation is absent.

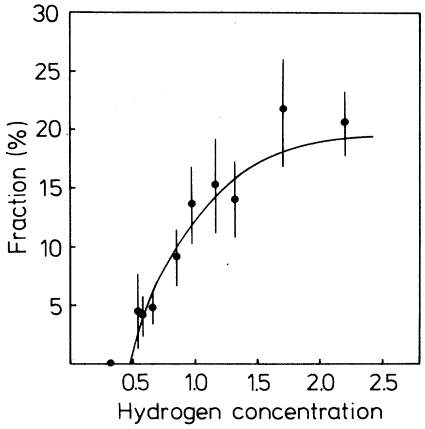

FIG. 3. Fraction of muons which contribute to the 2- and 4-MHz signal as a function of the hydrogen concentration. The fraction of the exponentially decaying signal, which is less well determined, is not included here. For $x > 1.2$ the total fraction (2 and 4 MHz, and exponentially decaying part) is approximately 1.

MHz. The fact that this signal is observed also in hydrogen-charged $YBa_2Cu_3O_7H_x$ can be explained by assuming that the oxygen stoichiometry in our sample is not completely 7 (some chain oxygens are missing). However, the main point is that the 4-MHz signal is very weak here, indicating that in the major part of the sample, the O_7 structure is preserved.

The exponentially decaying part is assigned to a third muon stopping site (besides the 2- and 4-MHz sites) in the magnetically ordered structure. The internal field at this site is weak (several G) and the corresponding μSR signal is only slightly different from that caused by nuclear moments. This exponentially decaying part which is also seen in oxygen-deficient Y-Ba-Cu-O samples[2,4] appears only in connection with the 2- and 4-MHz signals and therefore belongs to the magnetically ordered state. The fraction of muons stopping at this site is in the order of 75%. Muon-spin-rotation studies of magnetic order in systems with the O_7 structure as $HoBa_2Cu_3O_7$ do not reveal such a large fraction of weak magnetic order.[16] A possible explanation for the low amplitude of the oscillating component could be that hydrogen blocks some muon stopping sites. It is indeed very likely that hydrogen occupies the same sites as the positive muon.

Summarizing the experimental data we come to the following conclusion: Hydrogen doping of $YBa_2Cu_3O_7$ creates a well-defined magnetic state which is characterized in the μSR experiment by a strong 2-MHz and a weaker 4-MHz signal. The values of the observed frequencies indicate that the magnetic structure in $YBa_2Cu_3O_7H_x$ is the same as in $YBa_2Cu_3O_6$, i.e., that the Cu moments order antiferromagnetically in the Cu-O planes. A check of this structure assignment by neutron diffraction would be desirable.

The formation of the magnetic state starts at a hydrogen concentration of $x=0.5$ and reaches a saturation in the volume fraction at around $x \approx 1.2$ (see Fig. 3). Adding the fraction of muons in the exponentially decaying part, the data indicate that the sample is fully magnetic if the hydrogen concentration exceeds approximately $x=1.2$. The present data are in qualitative agreement with the assumption that each hydrogen atom donates one electron into the conduction band, thereby compensating for $\frac{1}{2}$ an O atom. In this simple model the doping of $YBa_2Cu_3O_7$ with $x=1.2$ hydrogen is equivalent to the removal of 0.6 oxygens and therefore $YBa_2Cu_3O_7H_{1.2}$ and $YBa_2Cu_3O_{6.4}$ should be equivalent. The magnetic structures of these two systems are indeed very similar.

For lower hydrogen concentration the comparison of hydrogen doping and oxygen removal shows some differences in details which are probably due to the phase separation by the H-doped samples but nevertheless the general trends remain valid.

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