Simultaneous magnetic ordering of the Gd and Cu subsystems in oxygen-deficient $GdBa_2Cu_3O_{6+x}$

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The simultaneous ordering of Gd and Cu magnetic moments was investigated in oxygen-deficient $GdBa_2Cu_3O_{6+x}$ ($x \approx 0.3$). The internal magnetic fields measured by the muon-spin-rotation technique show strong deviations from a mere superposition of the magnetic fields produced by the two magnetic subsystems separately. Above the ordering temperature ($T_N = 2.3$ K) of the Gd moments an increased relaxation rate and a negative frequency shift compared to the behavior of the ordered Cu system alone are observed. These deviations indicate the persistence of long-lived Gd spin fluctuations up to a temperature of approximately 100 K. The observed negative frequency shift is attributed to an interaction of the Gd moments with the Cu(II) magnetic subsystem.

I. INTRODUCTION

The superconducting properties of $GdBa_2Cu_3O_7$ are very similar to those of $YBa_2Cu_3O_7$.[1,2] However, the magnetic behavior of the two systems is different since the Gd atoms in $GdBa_2Cu_3O_7$ possess magnetic moments which order antiferromagnetically below $T_N = 2.3$ K.[3–7] The magnetic ordering does not affect the superconductivity.

In oxygen-deficient $YBa_2Cu_3O_{6+x}$ with x close to 0, the Cu atoms in the CuO_2 plane order antiferromagnetically at around 400 K.[8–10] In this case the superconductivity is suppressed by the magnetic ordering. Below $x = 0.4$ no superconductivity in $YBa_2Cu_3O_{6+x}$ is observed. The general assumption to explain this different behavior is that the Gd electrons have little or no overlap with the conduction electrons whereas those of Cu(II) in the CuO_2 planes are strongly involved in the conduction and superconductivity of the system.

In the present study we have investigated oxygen-deficient $GdBa_2Cu_3O_{6+x}$ where both the Gd and Cu spins order simultaneously. The main question was whether the two subsystems influence each other or order independently. In the latter case a linear superposition of the internal fields of the two subsystems would be expected whereas in the former case a deviation from the mere superposition should show up. In this experiment the muon-spin-rotation (μSR) method was used which allows an easy and precise detection of internal magnetic fields.

II. EXPERIMENTAL DETAILS

A polycrystalline disc of $GdBa_2Cu_3O_7$ with a superconducting transition temperature of $T_c = 91$ K was annealed in vacuum at 650 °C for 4 h, then slowly cooled down to 450 °C, and finally to room temperature. The result of this treatment was a reduction of the oxygen content to $x \approx 0.3$ as determined by the weight loss of the sample. X-ray diffraction showed that the final sample was single phase with a tetragonal structure.

The μSR measurements were performed at the Paul-Scherrer-Institut in Villigen, Switzerland. In these experiments spin-polarized positive muons are implanted into the sample with an energy of approximately 4 MeV. The muons stop at interstitial sites and start to precess with a Larmor frequency $\omega/2\pi$ corresponding to the local internal magnetic field B_μ. The relation between the two quantities is given by

$$\omega = \gamma_\mu B_\mu , \tag{1}$$

where $\gamma_\mu = 851.4$ MHz/T is the gyromagnetic ratio of the muon. The muon decays with a mean lifetime of 2.2 μs and emits a positron and two neutrinos. Since the emission probability of the positrons is anisotropic with respect to the muon spin direction, the muon spin precession can be easily monitored by counting the decay positrons in a fixed detector. The observation of a muon spin precession in zero external field is an unambiguous indication for the existence of an internal magnetic field at the muon site. This field is produced by the magnetic moments of the surrounding atoms and has to be static or slowly fluctuating on a time scale of microseconds in order to be seen by the muon. For a detailed description of the μSR technique see Ref. 11.

III. RESULTS AND DISCUSSION

Figure 1 shows μSR spectra and their Fourier transforms for an oxygen-depleted $GdBa_2Cu_3O_{6+x}$ sample at three different temperatures. In the upper spectrum, which was measured at 121 K, a clear oscillation is visible. The frequency of 4 MHz is the same as in

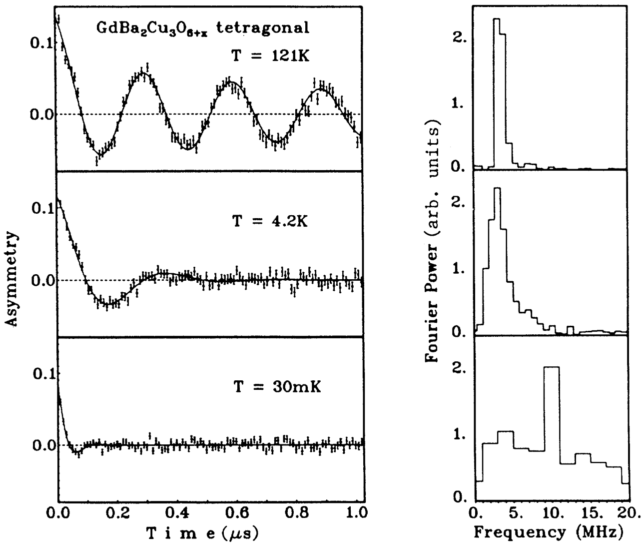

FIG. 1. μSR spectra and their Fourier transforms for a nonsuperconducting $GdBa_2Cu_3O_{6+x}$ ($x \approx 0.3$) sample at three different temperatures.

$YBa_2Cu_3O_6$ and originates from the ordering of the Cu moments in the CuO_2 planes.

In the middle of Fig. 1 the spectrum at 4.2 K is shown. Although this temperature is still well above the Néel temperature $T_N = 2.3$ K of the Gd magnetic ordering, the shape of the spectrum has clearly changed: the average frequency is slightly lower than at 121 K and the signal is strongly damped. This can be seen also on the line shift and broadening in the Fourier transform.

The lowest spectrum in Fig. 1 was taken at 30 mK and shows a very rapidly relaxing signal indicating the presence of high frequencies and a large frequency distribution. This can be seen more clearly in the corresponding Fourier transform on the right side. The fit of the time spectrum gives an average frequency of 8 MHz.

The μSR frequencies and depolarization rates are displayed in Figs. 2 and 3 (solid circles) as a function of temperature. The solid lines are guides to the eye and have no theoretical significance. In addition, data points of an oxygen-deficient $YBa_2Cu_3O_{6+x}$ ($x \approx 0.3$) are shown. The dashed lines which connect these points are considered as representative for the Cu moments ordering alone. It can be seen that the two data sets coincide in the higher temperature range, say above 100 K. However, at lower temperatures strong deviations show up, not only below 2.3 K where, due to the ordering of the Gd moments, such changes are expected but also in the intermediate region well above the ordering temperature of the Gd moments.

Dipolar field calculations can serve as a useful guide for the discussion of the data. Assuming a magnetic structure for the surrounding atoms and a site for the muon, the magnetic dipolar field and the corresponding μSR frequency can be calculated. Uncertainties exist concerning the site assignment as well as the neglect of hyperfine contributions to the local field and therefore these calculations can provide only qualitative arguments.

The calculations were done assuming antiferromagnetically ordered Gd moments ($\mu_{Gd} = 7.4\mu_B$) parallel to the c axis of the unit cell[6,7] and antiferromagnetically ordered Cu moments ($\mu_{Cu} = 0.64\mu_B$) with the spin direction in the a-b plane.[10] The orientations of the spins in the plane are not known. For definiteness we chose the Cu spins parallel to the diagonal of the a-b plane. For the muon site we assumed the so-called Balmer(2) site[12] which has the coordinates ($0.274a$,$0.011b$,$0.137c$). The Balmer(2) site corresponds to muon bonding to the apical oxygen and is suggested as the probable muon site in oxygen-deficient $RBa_2Cu_3O_x$ (R = rare earth) systems.[12–14]

The calculated dipolar field at the Balmer(2) site from the Cu subsystem alone gives the μSR frequency of 4 MHz and that of the Gd subsystem alone of 7.3 MHz. The vectorial superposition of the two fields is displayed in Fig. 4. It results in two magnetically inequivalent Balmer(2) sites with calculated dipolar fields of 6.4 and 9.9 MHz, respectively.

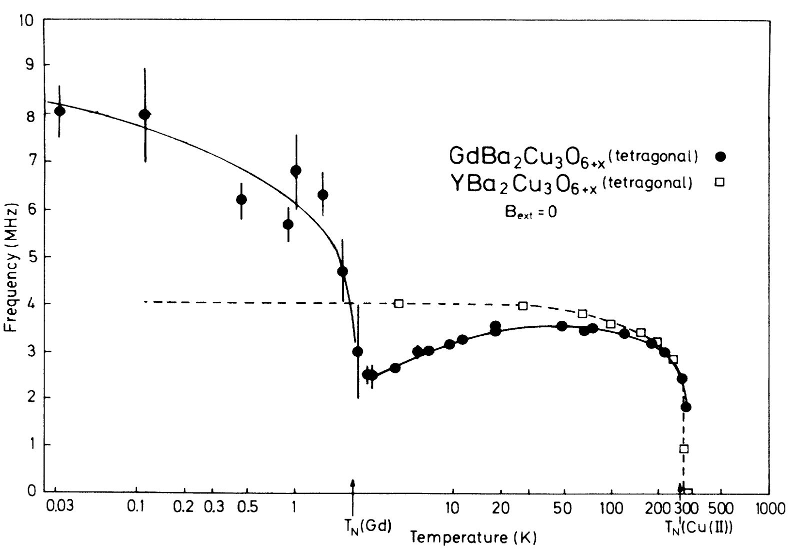

FIG. 2. Temperature dependence of the μSR frequency for $GdBa_2Cu_3O_{6+x}$ (solid circles) and $YBa_2Cu_3O_{6+x}$ (open squares). In both cases $x \approx 0.3$. The solid line and the dashed line are guides to the eyes. T_N(Gd) and T_N[Cu(II)] mark the Néel temperatures of the Gd and Cu(II) subsystems.

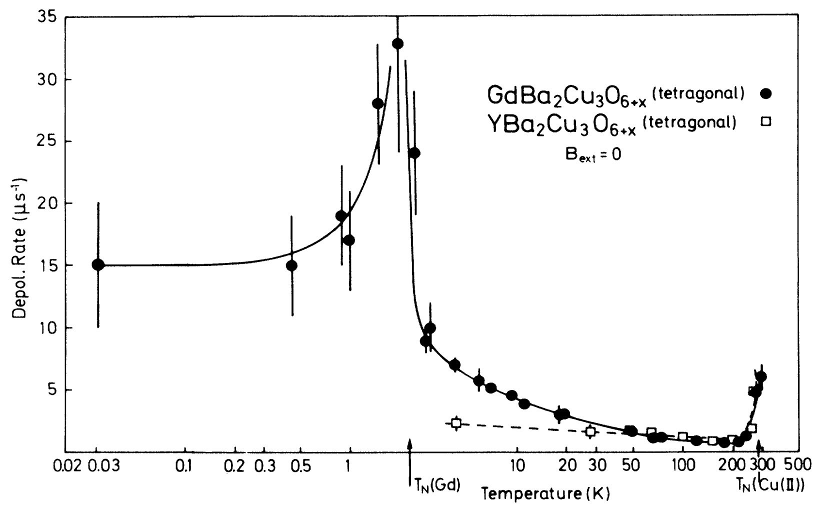

FIG. 3. The μSR depolarization rate for $GdBa_2Cu_3O_{6+x}$ (solid circles) and for $YBa_2Cu_3O_{6+x}$ (open squares) as a function of temperature. In both cases $x \approx 0.3$. The solid line and the dashed line are guides to the eyes. T_N(Gd) and T_N[Cu(II)] mark the Néel temperatures of the Gd and Cu(II) subsystems.

A. High-temperature region ($T > 100$ K)

The coincidence of the data points of the Y- and Gd-based systems above 100 K (Figs. 2 and 3) suggests that the Cu moment ordering is the same in the two systems and that the muons occupy the same site. The effect of the Gd atoms on the local magnetic field is apparently negligible at these temperatures. The calculated dipolar field of the Cu subsystem alone gives for the Balmer(2) site 4 MHz in accordance with the data.

B. Low-temperature ($T < 2.3$ K)

At low temperatures, e.g., at 30 mK, a superposition of the internal magnetic fields from the two subsystems (Fig. 4) yields the following results. The calculated dipolar field at the assumed muon site gives two different frequencies, namely, 6.4 and 9.9 MHz with equal statistical weight. Thus, the predicted average frequency is 8.15 MHz in reasonable agreement with the observed frequency at low temperatures. The fact that the predicted two μSR lines cannot be resolved might be attributed to a broad field distribution in the separate subsystems. The difference of the two predicted frequencies of 3.5 MHz corresponds to a damping rate ($\lambda = \Delta\omega = 2\pi\Delta\nu$) of 22 μs^{-1}, a value which is in reasonable agreement with the observed depolarization rate. Thus, at the lowest temperatures the assumption of an independent ordering of the two magnetic subsystems without mutual influence is in accord with the present data.

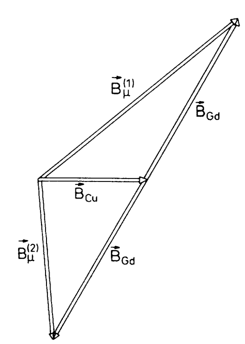

FIG. 4. Superposition of the calculated magnetic dipolar fields from the ordered Gd and Cu subsystems at the assumed muon site [Balmer(2) site, see text].

C. Intermediate-temperature region ($2.3 < T < 100$ K)

The most interesting part is the temperature region above the ordering temperature ($T_N = 2.3$ K) of the Gd moments. It can be seen (Fig. 2) that the frequency shows a negative shift compared to that of the Cu system alone and that the depolarization rate λ is very large near and above $T_N = 2.3$ K (Fig. 3). We draw two conclusions from this observation: (i) There exist long-lived correlations in the Gd spin system which contribute to the local magnetic field at the muon site. Above 100 K, these fluctuations are so fast that the contribution to the local field becomes negligible. Long-lived spin correlations have been observed in other μSR studies (e.g., Refs. 15 and 16) and are discussed there in detail. They are attributed to the formation of spin clusters which slow down the fluctuations of the individual moments. (ii) From a mere superposition of the local fields from the Cu(II) moments with the fluctuating field from the Gd moments we would expect a continuous transition from the 8-MHz frequency below 2.3 K to 4 MHz far above 2.3 K. In reality we observe a surprising undershoot in the frequency. We think that this is an indication of the interaction of the two subsystems, but have no detailed picture of this interaction yet.

IV. CONCLUSIONS

The magnetic ordering of Gd moments alone is known from studies of fully oxygenated $GdBa_2Cu_3O_7$ and that of the Cu(II) moments alone from investigations of oxygen-deficient $YBa_2Cu_3O_x$. In the present work we have investigated the simultaneous ordering of Gd and Cu moments in oxygen-deficient $GdBa_2Cu_3O_x$. We found strong deviations from a mere superposition of the internal magnetic fields from the two magnetic subsystems. The data indicate that in the oxygen-deficient $GdBa_2Cu_3O_x$, the Gd spins remain correlated at temperatures far above the Néel temperature of 2.3 K. These correlations persist on a time scale of the μSR frequency of approximately 4 MHz.

Correlations in the Gd spin system above the ordering temperature were found before in μSR experiments[5] in a 60 K superconducting $GdBa_2Cu_3O_x$ sample. Since in this case no static ordering of the Cu moments existed, the correlations of the Gd spins are apparently not bound to a static Cu spin ordering. It seems that fluctuations in the Cu(II) spin system, or reduced conductivity in the CuO_2 planes, are sufficient to induce magnetic correlations in the Gd spin system above T_N. In fully oxygenated $GdBa_2Cu_3O_7$, no such Gd spin correlations were observed above $T_N = 2.3$ K. Thus, the Gd spin correlations above T_N depend on the oxygen stoichiometry, but the exact interaction between the magnetic subsystems is not known yet.

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