Gd^{3+} exchange interaction as measured by NMR in hydrogen-doped $GdBa_2Cu_3O_7H_{1.55}$

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Proton NMR in nonsuperconducting $GdBa_2Cu_3O_7H_{1.55}$ was measured at liquid-helium temperature by a spin-echo method. The negative shift of the resonance spectrum was found to be proportional to the dc magnetic field. This shift is shown to arise from the demagnetizing field due to a canted spin structure. The Gd exchange parameter is estimated to be $J \simeq 0.05$ K, showing that the exchange energy is higher than the dipole one. Hydrogen doping has no effect on the gadolinium ordering temperature.

The high-T_c superconductor $GdBa_2Cu_3O_7$ has a Néel temperature T_N of about 2.3 K which is the highest among the *superconducting* rare-earth-based series. The Gd^{3+} moments are oriented along the c axis in the antiferromagnetic phase. Each moment is then expected to experience a parallel dipole field of 3 kG. So far, the origin of the rare-earth ordering was not clearly demonstrated. At first sight, one may wonder whether the dipolar coupling alone can give rise to the magnetic ordering. Paul *et al.*[1] have excluded this possibility, on the ground of the calculated dipole energy. Recently Kistenmacher[2] has established parallel trends in T_N and de Gennes factor with the rare-earth ionic size and supported the idea that the rare-earth antiferromagnetic coupling is due to superexchange.

It is well known that nuclear magnetic resonance (NMR) is a powerful method to investigate the magnetic interaction. In the case of a hydrogen-doped sample, the proton NMR reveals the magnetic environment of H atoms. Thus we have shown that H atoms in $EuBa_2Cu_3O_7H_{0.9}$ are localized in the Cu(1) plane.[3] In this paper we describe the effect of gadolinium magnetic moments on proton NMR in $GdBa_2Cu_3O_7H_{1.55}$. The hydrogenization, as previously, was done at low H_2 pressure of about 10 cm of Hg.

The hydrogen-doped sample, like the vacuum-annealed one, is tetragonal and nonsuperconducting. The susceptibility measured using a superconducting quantum interference device magnetometer, as a function of temperature (Fig. 1) is close to that reported for the as-grown sample with the same T_N value.[4] This is coherent with the fact that the Cu(1) plane containing H atoms is fairly distant from the Gd^{3+} ions. At 295 K the ac susceptibility in zero external field was found to be 4.4×10^{-5} emu/g, whereas the differential susceptibility in a dc field of 3 kG was measured to be $3.5\ (\pm0.2)\times10^{-5}$ emu/g which is close to the susceptibility measured in a field of 10 kG for the undoped sample.[4] The Gd^{3+} free-ion susceptibility was calculated to be 3.6×10^{-5} emu/g at 295 K. It is clear that the susceptibility excess observed in zero dc field arises from a ferromagnetic phase for which the magnetization was easily saturated. Taking the ferromagnetic susceptibility per cm^3 as the inverse demagnetizing factor, the amount of this phase was evaluated to be 300 ppm, assuming spherical symmetry. Such a small quantity is expected not to alter the proton NMR in the $GdBa_2Cu_3O_7H_{1.55}$ phase. The sample compositions determined by electron probe microanalysis are coherent with the 1:2:3 phase.

The NMR measurements were carried out at liquid-helium temperature by using a variable-frequency spin-echo apparatus. The spin-echo signal was observed at 35 μs from the beginning of the first pulse. A powdered sam-

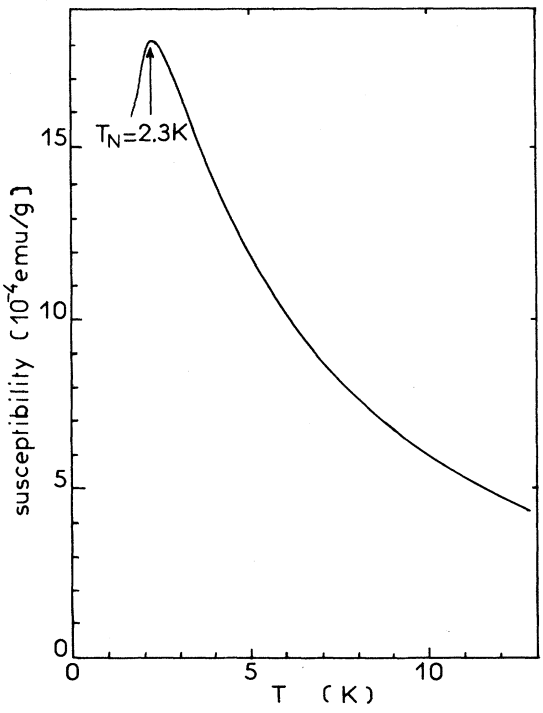

FIG. 1. Susceptibility in a magnetic field of 1 G as a function of temperature for the hydrogen-doped $GdBa_2Cu_3O_7H_{1.55}$ sample.

ple of about 1 g was used in this study. The particles whose size ranges from 5 to 20 μm are free to move in a glass tube.

It was shown previously that the proton spectrum in a nonmagnetic Eu^{3+}-based sample is centered at a reference frequency given by proton NMR in a diamagnetic material. The Eu^{3+} Van Vleck susceptibility is too small to give rise to any observable shift. For the present Gd-based sample the proton spectrum at 1.8 K is shifted to the low-frequency side (Fig. 2). The shift was found to be proportional to the dc magnetic field (Fig. 3). The nuclear transverse relaxation time $T_2 = 50$ μs is independent of magnetic field and is practically constant up to 4.2 K. The spin-lattice relaxation time T_1 is 1 order of magnitude longer. The transverse relaxation rate due to the proton dipolar interaction at the vacant oxygen sites in the Cu(1) plane was calculated to be $1.4\times10^4\ s^{-1}$ approaching the observed value. On the other hand, the line shift decreases monotonically with increasing temperature (Fig. 4). It may be recalled that the short-range order exists well above the Néel temperature, especially for a low-dimensional system. Owing to the weak exchange coupling as revealed by the low T_N value the Gd antiferromagnetic structure would be easily canted in an applied magnetic field. On the contrary, such a canting is quite negligible for the Cu sublattice since the exchange parameter between Cu^{2+} nearest neighbors is as high as 1100 cm^{-1} (Ref. 5), leading to a Néel temperature higher than 400 K for nonsuperconducting samples.[6] This explains why the spectrum in an Eu-based sample is unshifted.

The field-induced magnetization M of the Gd sublattice gives rise to a demagnetizing field within each particle of the powdered sample. Consequently, the effective field experienced by the proton in the Gd-based sample is reduced, in agreement with the negative shift. The nuclear relaxation was found to be the same at the center and at both sides of the spectrum, showing that the latter arises from a single phase. Thus the proton NMR appears to be a suitable microscopic method of determining the induced magnetization and checking the sample homogeneity. It may be noted that an accurate measurement of the absolute magnetization by a macroscopic method is not so simple. To evaluate the canting angle as a function of the applied magnetic field H we assume that there is exchange

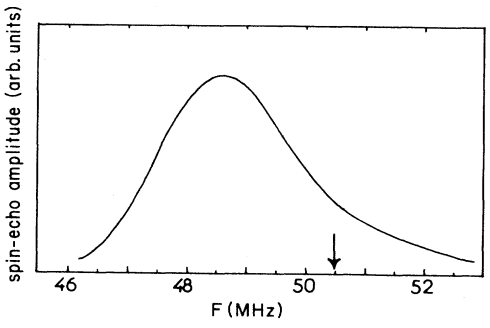

FIG. 2. Proton resonance spectrum at 1.8 K in a dc magnetic field of 11.86 kG. The arrow indicates the proton resonance frequency in a nonmagnetic sample.

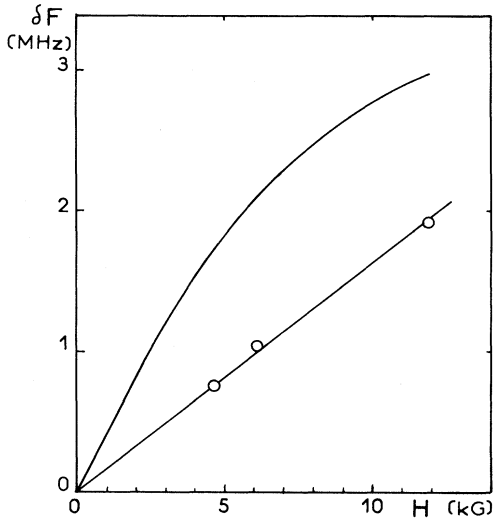

FIG. 3. Line shift at 1.8 K as a function of applied magnetic field. The upper curve is calculated for an uncoupled system deduced from the Brillouin function $B_{7/2}$ $(7\mu_B H/1.8k)$ (see text).

interaction only between nearest neighbors. Thus we consider a simplified Heisenberg model of a square lattice where each spin S is antiferromagnetically coupled with its four nearest neighbors. In the presence of a magnetic field the magnetic moments rotate such that their ferromagnetic component aligns along the field, at the expense of the exchange energy. Each magnetic moment then makes an angle α with the field. By minimizing the total energy it is straightforward to obtain the equilibrium

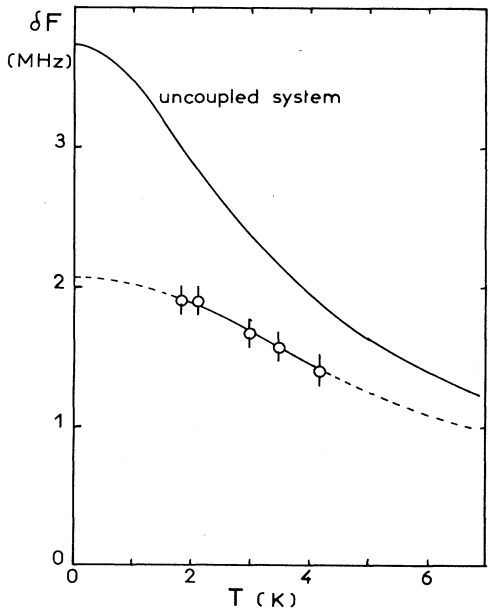

FIG. 4. Temperature dependence of the line shift in a dc magnetic field of 11.86 kG. The theoretical variation for uncoupled gadolinium moments is represented by the Brillouin function $B_{7/2}$ $(5.6/T)$ (see text).

angle α as

$$\cos\alpha = \frac{\mu_B H}{8JS}, \quad (1)$$

where J is the exchange parameter.

This relation reveals that the induced magnetization is proportional to H until complete alignment. The saturated magnetization arising from the Gd^{3+} moments of $7\mu_B$ was calculated to be 366 G.

We have calculated, on the other hand, the magnetization induced by a dc field of 11.9 kG in the case of uncoupled Gd moments. The temperature dependence of the reduced magnetization is then given by the Brillouin function $B_{7/2}$ (a) with $a = g\mu_B SH/kT$. At high temperature, the Brillouin function represents a good approximation for the actual Gd sublattice magnetization. At 77 K the proton linewidth at half maximum and line shift are reduced to about 0.5 and 0.1 MHz, respectively. This shift is consistent with a demagnetizing factor of 2.4. Using this value we calculated the shifts at low temperature. The theoretical results were found to be higher than the experimental points, in agreement with the fact that the antiferromagnetic coupling tends to reduce the magnetization (Fig. 4). In the same way, the field dependence at 1.8 K of the magnetization, i.e., of the line shift for uncoupled spins, was compared to the experiments (Fig. 3). Again, the observed linear variation reflects the antiferromagnetic behavior, in contrast with a system without interaction.

The line shift extrapolated to 0 K corresponds to an induced magnetization of 204 G. Using Eq. (1) the exchange parameter was estimated to be $J \simeq 0.05$ K. We thus deduced an exchange energy of $-4JS^2 = -2.45$ K as compared to the dipole energy of -1.4 K. The paramagnetic Curie temperature was deduced to be -2.1 K, which is in the range of the reported values of -2 and -3 K for the as-prepared and vacuum-annealed samples, respectively.[4]

We have shown previously that the proton linewidth in $EuBa_2Cu_3O_7H_{0.9}$ sample arises from the Cu^{2+} dipole fields. For the Gd-based sample the spectrum is more than four times broader. Electron microscopy has shown that the particle shapes are quite irregular so that the demagnetizing field H_d is necessarily inhomogeneous. If we take, for example, the H_d dispersion value as $4\pi M/3$, the effective spread at 1.8 K in a dc field of 11.9 kG would be 780 G. On the other hand, the magnitude of the dipole field due to the Gd^{3+} sublattice in zero external field, was calculated to be 640 G at the vacant oxygen site in the Cu(1) plane. Thus the demagnetizing and dipole fields are believed to be the main origins of the observed width, in field units, of about 650 G at half maximum. At 77 K the Cu^{2+} sublattice is expected to remain antiferromagnetic and the reduced linewidth is due to the Cu^{2+} dipole fields as for the Eu-based sample. On the other hand, the echo signal becomes very weak, due to a short relaxation time T_2 of about 17 μs, which is much smaller than the value at 4 K where thermal fluctuations of magnetic ions are negligible.

In summary, we have shown that the negative shift in the proton resonance frequency in $GdBa_2Cu_3O_7H_{1.55}$ is due to the demagnetizing field originated from the induced magnetization of the gadolinium sublattice. By using a simplified Heisenberg model with only nearest-neighbor interaction, the exchange parameter has been evaluated. The corresponding exchange energy is larger in magnitude than the dipole energy. It is concluded that the gadolinium magnetic ordering results from the antiferromagnetic exchange interaction together with the dipole coupling which tends to align the magnetic moment along the c axis.

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