Muon-Spin-Rotation Study of Magnetism in $La_{1.85}Sr_{0.15}CuO_4$ and $YBa_2Cu_3O_x$ below 90 mK

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Internal magnetic fields in $YBa_2Cu_3O_x$ and $La_{1.85}Sr_{0.15}CuO_4$ have been investigated below 90 mK using muon spin rotation. In $YBa_2Cu_3O_x$ the static internal magnetic field at the muon site due to magnetic ordering remains constant with increasing x up until $x=6.30$ and then rapidly approaches zero just above $x=6.44$. In heavily doped samples of $YBa_2Cu_3O_x$ ($x \geq 6.54$, $T_c \geq 52$ K) and $La_{2-y}Sr_yCuO_4$ ($y=0.15$, $T_c=37$ K) we find little evidence for static or slowly fluctuating electronic moments. These results clearly establish that static magnetic order is destroyed in regions of high carrier concentration.

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A central issue regarding high-T_c superconductivity is whether or not magnetic interactions are important in stabilizing the superconducting electronic ground state, as in many proposed theories.[1] The primary experimental facts which suggest that there may be a connection between magnetism and superconductivity are the following: (1) Neutron scattering and muon spin rotations (μSR) have shown that the insulating phases of $La_{2-y}Sr_yCuO_4$,[2,3] $YBa_2Cu_3O_x$ (Refs. 4-6), and $Bi_2Sr_2Ca_{1-y}Y_yCu_2O_x$ (Ref. 7), which have reduced carrier concentrations in the two-dimensional CuO_2 network, order antiferromagnetically. Recently, this has also been shown to be true for $Nd_{2-y}Ce_yCuO_4$, which is a high-T_c superconductor with electrons as carriers rather than holes.[8] (2) Raman and neutron scattering indicate that magnetic moments and correlations between them are present even in the superconducting phases of $La_{2-y}Sr_yCuO_4$ and $YBa_2Cu_3O_x$. In particular, neutron scattering on single crystals of $La_{2-y}Sr_yCuO_4$ has shown that the magnitude of the Cu moments is constant but the magnetic correlation length shortens as y increases.[9] In $YBa_2Cu_3O_x$ a broad peak in the Raman scattering attributed to spin-pair excitations is observed to broaden further and shift to lower energies with doping in the superconducting phase.[10] (3) μSR experiments indicate the coexistence of static magnetic order or spin freezing with superconductivity, although it is not clear that this is due to intrinsic coexistence or to inhomogeneities in the stoichiometry. For example, superconducting samples of $YBa_2Cu_3O_x$ near the metal-insulator transition appear to show static internal fields.[5] Similar observations have been made on single crystals of $La_{2-y}Sr_yCuO_4$ with y as high as 0.08.[11] Most recently it has been reported[12] that $La_{2-y}Sr_yCuO_4$ exhibits weak static magnetic ordering or spin freezing below 2 K up to and including $y=0.15$ while fully oxygenated $YBa_2Cu_3O_x$ does not order at 35 mK.

We report here μSR results on a different $La_{1.85}Sr_{0.15}CuO_4$ sample and a series of well-annealed $YBa_2Cu_3O_x$ samples ($x=6.04$, 6.28, 6.39, 6.44, 6.51, 6.54, and 6.74) below 90 mK. In $YBa_2Cu_3O_x$ we find that the static component of the internal field at the muon site, which is a measure of the magnetic order parameter, approaches zero just above $x=6.44$ in the superconducting phase. In more heavily doped samples where $x \geq 6.54$ and $T_c \geq 52$ K there is no evidence for static internal magnetic fields of electronic origin. A similar negative result in $La_{2-y}Sr_yCuO_4$ ($y=0.15$, $T_c=37$ K) establishes that static magnetic order is also destroyed in this system at high carrier concentrations.

Fully oxygenated sintered pellets of $YBa_2Cu_3O_{6.99}$ were prepared by standard techniques at the University of British Columbia,[13] starting from a stoichiometric mixture of 99.999% pure Y_2O_3, $BaCO_3$, and CuO. Precise amounts of oxygen were then removed and the samples annealed at constant x at a relatively low oxygen pressure ($p \sim 1$ Torr) for 12 to 24 h to ensure a uniform concentration. The absolute uncertainty in the oxygen concentration is estimated to be 0.02. The sample of $La_{1.85}Sr_{0.15}CuO_4$, for which the superconducting onset temperature was 39 K and the midpoint 37 K, was prepared at the University of Tokyo using a spray-dry method, which achieves particularly good homogeneity in the Sr concentration and a precise stoichiometry.[14]

Polarized surface muons from the M15 beam line at TRIUMF were collimated to 7.5 mm diameter and then passed through a thin muon detector and a series of thin windows in the dilution refrigerator before stopping in the sample. The samples, which measured typically 13 mm diameter by about 1 mm thick, were epoxied onto a thin Cu foil which was bolted to the cold finger of an Oxford Instruments top-loading dilution refrigerator. A second foil was placed over the sample to reduce any heating of the surface from radiation. A thick-film RuO_2 resistor, attached to the front face of one sample, indicated that the temperature difference between the mixing chamber and samples mounted in this way was less than 10 mK after an equilibration time of 30 min.

Muon spin rotation provides information on the magnetic environment of the host similar to that furnished by NMR except that the spin-$\frac{1}{2}$ muon is an implanted probe. As a consequence of parity violation in muon decay, the muon spin polarization can be monitored without the use of externally applied magnetic fields.[15] In an *internal* local magnetic field **B** at an angle θ with respect to the z axis (the initial muon polarization direction) the z component of the muon polarization evolves as

$$G_z(t) = \cos^2\theta + \sin^2\theta \cos(\gamma_\mu B t) , \quad (1)$$

where $\gamma_\mu = 0.851$ MHz/mT is the gyromagnetic ratio of the muon. Note that while the amplitude of the oscillating term depends on θ, the orientation of the field, the frequency is determined solely by B. In an antiferromagnet the internal magnetic field at the muon site arises from the spontaneous magnetization below T_N and leads to coherent precission of the muon spins.[16] Well below T_N, the magnetic excitations are frozen out so that one expects negligible muon spin relaxation. In a polycrystal one observes the same frequency (or frequencies, if there is more than one muon site) but with a powder-averaged amplitude. If there is some spatial variation in the magnitude or relative orientation of the ordered moments then there will be a distribution of internal fields at the muon site. Carrying out the angular average of Eq. (1) and assuming a Gaussian distribution of fields one obtains

$$G_z(t) = \tfrac{1}{3} + \tfrac{2}{3} \exp[-\tfrac{1}{2}(\gamma_\mu \Delta B t)^2] \cos(\gamma_\mu B t) , \quad (2)$$

where B is now the average internal magnetic field and ΔB is the rms deviation. Note that $\frac{1}{3}$ of the muon polarization in a powder is time dependent due to the component of the internal field along the initial muon polarization direction.

Figure 1 shows the measured time evolution of the muon polarization (multiplied by a constant experimental factor A) in several of the $YBa_2Cu_3O_x$ samples below 90 mK in zero applied magnetic field. Coherent precision of the muon spins was observed at or below $x = 6.44$, providing unambiguous evidence of magnetic ordering. Similar spectra, observed above 4 K, were the first positive identification of antiferromagnetism in $YBa_2Cu_3O_x$.[4] The average internal field reported here is consistent with that seen at 4 K, indicating that there is no change in the magnetic ordering below 4 K. Considering that the experimental asymmetry factor A is about

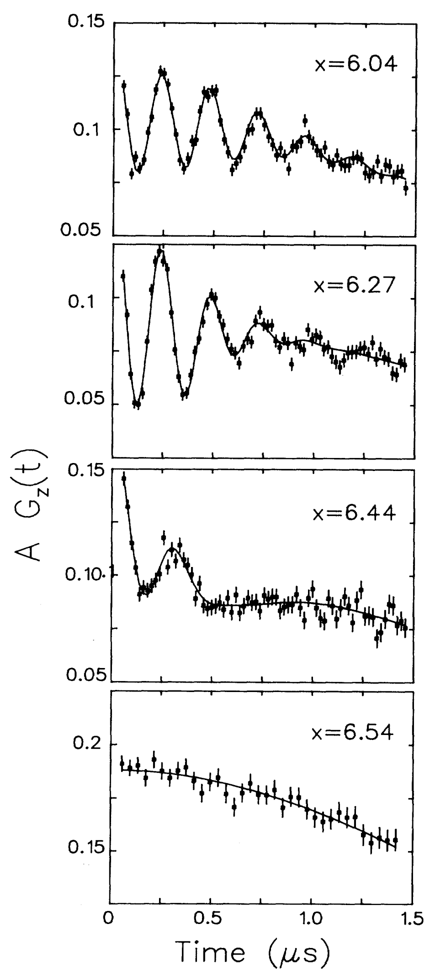

FIG. 1. The time evolution of the muon polarization in zero external field for various values of $YBa_2Cu_3O_x$. The temperature is 20 mK in all cases except for $x = 6.04$ for which $T = 90$ mK. The frequency of the oscillation is proportional to the average internal field at the muon site.

0.18, it is apparent from Fig. 1 that in addition to the observed oscillating component there is a rapidly depolarized component due to muons which stop at sites where the internal fields are higher and not well defined. A third term was introduced into the fitting function to account for the $\frac{1}{3}$ nonprecessing component in Eq. (2) and a well understood background signal from a fraction of the muons stopping in the Cu cold finger. Using the fact that nearly all the muons see an internal field in the antiferromagnetic phase of $YBa_2Cu_3O_x$ (Ref. 5), we deduce the Cu background to be 25(5)% of our total signal. The data for samples with $x \leq 6.44$ were fitted assuming these three components. In one sample ($x=6.51$), $G_z(t)$ was better represented by a single exponential function, $e^{-\lambda t}$, with a damping rate $\lambda = 0.24\ \mu s^{-1}$. This indicates a Lorentzian-type distribution of very weak internal magnetic fields centered about zero. The rms deviation, which is infinite for a true Lorentzian distribution, was estimated by assuming a cutoff in the internal field in the range 5–15 mT where the upper bound is close to the internal field observed in the $x=6.44$ sample and the lower bound is based on the fact that we observe an exponential-like relaxation. The response to selected external magnetic fields along the muon polarization direction confirms that the internal fields responsible for the depolarization are static. For higher values of x, $G_z(t)$ is Gaussian shaped at early times (see bottom of Fig. 1) with a ΔB close to that expected from weak muon-nuclear dipolar interactions.

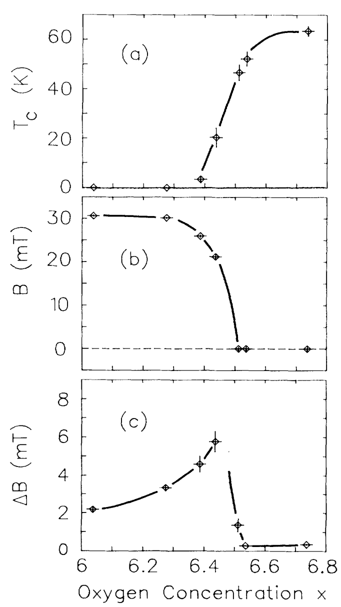

FIG. 2. The x dependence of (a) the midpoint of the superconducting transition in $YBa_2Cu_3O_x$ where the error bar represents the 10%-90% width, (b) the average internal field at the muon site B, and (c) the rms deviation ΔB. The curves are meant to guide the eye.

Of interest here are the magnitude of the internal field B and the rms deviation ΔB associated with the oscillating component evident in Fig. 1. These two quantities are displayed in Figs. 2(b) and 2(c) as a function of oxygen concentration. In samples with $x \geq 6.51$, where no coherent oscillation was observed, the average field is taken to be zero but the rms deviation is finite [see Fig. 2(c)]. Note that as x approaches 6.50 from below there is simultaneously a dramatic *decrease* in the *magnitude* of the average internal field and an *increase in the rms deviation*. A similar phenomenon was seen in the $La_{2-y}Sr_yCuO_4$ system[3,12] as a function of Sr doping, which increases the carrier concentration in the CuO_2 planes in much the same way as adding oxygen does in $YBa_2Cu_3O_x$. Note the sharp cutoff in the internal field B, providing strong evidence against any sort of static magnetic order or spin freezing in the heavily doped superconducting phase where T_c exceeds about 52 K. In samples with lower values of T_c there are internal fields of electronic origin. In particular we estimate that 90(10)% of the muons in the $x=6.44$ sample ($T_c=20$ K) see an average internal field greater than or equal to 20 mT. Considering the uncertainty with regard to variations in the stoichiometry on a microscopic scale, one cannot conclude from this that there is true overlap of the superconducting and magnetic order parameters. One would have to first verify the uniformity of the sample on the scale of a few coherence lengths.

In a previous study Weidinger *et al.*[12] reported that internal fields of electronic origin are presented in the superconducting phase of $La_{2-y}Sr_yCuO_4$, including $y=0.15$ with a $T_c=32$ K. We studied a different sample of $La_{1.85}Sr_{0.15}CuO_4$ with a well controlled stoichiometry prepared by a spray-dry technique for which $T_c=37$ K.[14] The spectrum obtained at 20 mK (see Fig. 3) indi-

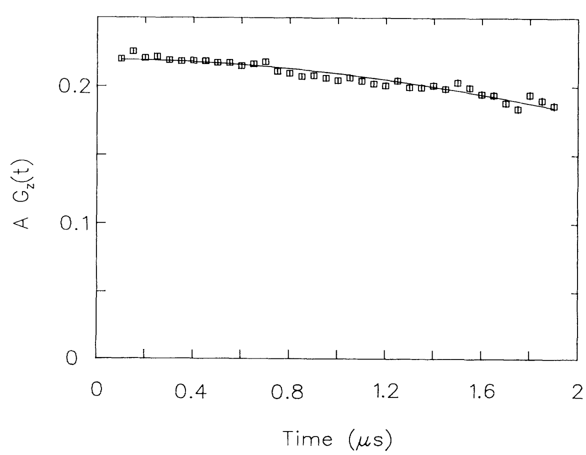

FIG. 3. The time evolution of the muon polarization function in $La_{1.85}Sr_{0.15}CuO_4$ in zero applied field at 20 mK. The functional behavior is characteristic of muon-nuclear dipolar interaction and the absence of static electronic moments.

cates that there are no such internal fields in our sample. The Gaussian-type relaxation function at early times and the fitted rms magnitude in the internal field distribution [0.30(5) mT] are close to what is expected from randomly oriented nuclear dipoles (0.24 mT).[17] Thus if we assume a dense concentration of electronic moments in $La_{1.85}Sr_{0.15}CuO_4$ they must be less than Cu nuclear dipole moments or they are fluctuating too rapidly to be observed.

In conclusion, we find little or no evidence for static electronic moments in heavily doped $La_{2-y}Sr_yCuO_4$ ($y=0.15$) and $YBa_2Cu_3O_x$ ($x \geq 6.54$) at temperatures as low as 20 mK. This clearly demonstrates that static magnetic order is absent in the regions of high carrier concentration in both $YBa_2Cu_3O_x$ and $La_{2-y}Sr_yCuO_4$. Internal fields of electronic origin are observed in some superconducting samples with reduced carrier concentrations. However, this could be due to variations in the stoichiometry on a microscopic scale such that the magnetic and superconducting order parameters do not actually overlap.

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