Antiferromagnetism of La_2CuO_{4-y} Studied by Muon-Spin Rotation

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Zero-field spin precession of positive muons has been observed in the antiferromagnetic state of La_2CuO_{4-y}. Sharp onsets of the sublattice magnetization are found at temperatures close to those of the susceptibility maxima of different specimens. The long-lived precession signal indicates a microscopically homogeneous distribution of spin density at each Cu atom below the Néel temperature. Combination of the present results and neutron-scattering studies indicates the ordered moment per Cu atom to be significantly less than $1\mu_B$.

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The discovery and development of high-T_c oxide superconductors, e.g., $(LaSr)_2CuO_4$, $YBa_2Cu_3O_7$, etc.,[1-3] have prompted a burst of experimental and theoretical investigations on these and related systems.[4] In a parent nonsuperconducting compound La_2CuO_{4-y}, antiferromagnetic ordering has recently been confirmed by susceptibility[5] and neutron scattering[6-8] measurements. The Néel temperature T_N of this system is quite sensitive to the oxygen deficiency y ($T_N \approx 290$ K for $y \simeq 0.03$; $T_N \approx 0$ K for $y \simeq 0$),[5] and there are reports of bulk[9] and trace[5,10] superconductivity in some samples ($y \simeq 0$). In order to explore the possible connection between the antiferromagnetism and the high-T_c superconductivity,[11] it is very important to study the detailed magnetic properties of La_2CuO_{4-y}. In this Letter, we report a muon-spin-rotation (MSR) measurement on La_2CuO_{4-y}. In zero external magnetic field, we found a clear long-lived muon spin precession signal below T_N, which suggests that the ordering occurs with microscopically homogeneous spin distribution. The muon spin precession frequency yielded an accurate temperature dependence of the internal magnetic field which is proportional to the sublattice magnetization. The precession amplitude indicated a rather abrupt onset into the antiferromagnetic state. Combined with the neutron-scattering studies, the present experiment shows that the magnetic moment of Cu is noninteger and significantly less than $1\mu_B$.

We have studied three different polycrystalline specimens of La_2CuO_{4-y}. The synthesis technique[7] assured single-phase samples. Different oxygen stoichiometries were obtained by variation of the heat treatment. Sample 1 was heated to 950 °C and oven cooled in air. Sample 2 was heated under pure oxygen at 950 °C and then at 500 °C and oven cooled. Sample 3 was heated under 260 psi of O_2 at 500 °C and oven cooled. Thus, the oxygen-vacancy content and Néel temperature should both decrease with sample number. The MSR experiment[12] was performed at the muon channel at the Alternating Gradient Synchrotron (AGS) proton accelerator of Brookhaven National Laboratory. The spin-polarized positive-muon beam was stopped in the specimen placed in a Displex cryostat. The time histograms $F(t)$ and $B(t)$ of muon-decay positrons were recorded by two sets of counters placed forward and backward of the specimen with respect to the incoming muon beam.[13] Since positrons are emitted preferentially to the muon spin direction, there is an asymmetry in the counting rate as

$$F(t) \propto \exp(-t/\tau_\mu)[1+A(t)],$$

$$B(t) \propto \exp(-t/\tau_\mu)[1-A(t)],$$

where τ_μ is the muon lifetime of 2.2 μsec. After normalization for the counter efficiency, the time evolution of the muon-decay asymmetry $A(t)$ can be directly obtained as $A(t) = [F(t) - B(t)]/[F(t) + B(t)]$.

Figure 1 shows a few examples of the oscillating component of the asymmetry $A(t)$ thus obtained in La_2CuO_{4-y} sample 1 with zero external magnetic field. The clear precession at lower temperatures is due to a static internal magnetic field H_{int} from the ordered magnetic moments surrounding the muon site. In powder specimens, the direction of H_{int} is random, but its magni-

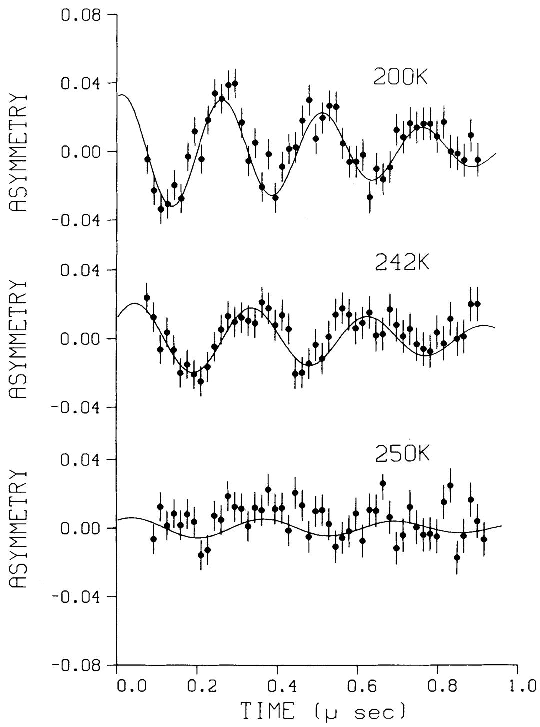

FIG. 1. Muon spin precession signal observed in La_2CuO_{4-y} sample 1 in zero external magnetic field. Solid lines represent the fit with the precession frequency and amplitude shown in Fig. 2.

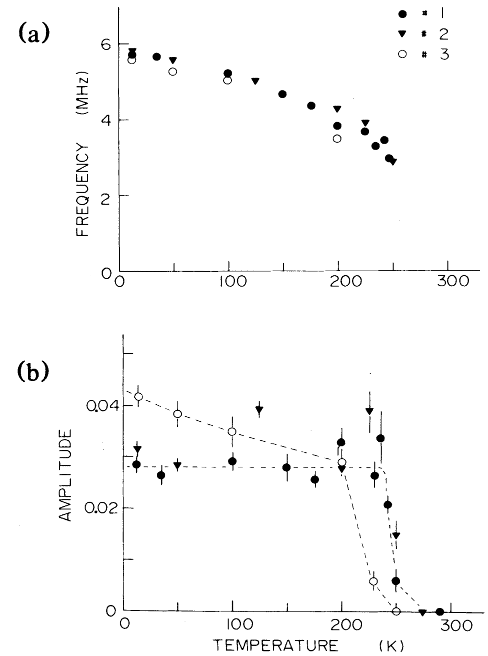

FIG. 2. Temperature dependence of (a) the frequency and (b) the amplitude of the muon spin precession signal observed in the three different specimens of La_2CuO_{4-y}. The statistical error in (a) is within the size of the points. The broken lines in (b) are guides to the eye.

tude $|H_{\text{int}}|$ is often unique. Then the muon spins precess coherently as long as H_{int} is *static*. The extent to which we infer that H_{int} is *static* is determined by the time scale of the precession signal: i.e., a few microseconds in the present case. The precession signal disappears at higher temperatures, indicating that the system becomes paramagnetic. The relaxation rate of the precession signal ranged between 0.5 and 2 μsec^{-1} without showing any obvious tendency towards divergent behavior.

The temperature dependences of the frequency and amplitude of the precession signal for the three samples are shown in Figs. 2(a) and 2(b), respectively. The frequency is proportional to H_{int} and consequently to the sublattice magnetization M_s. The statistical accuracy of the data points in Fig. 2(a) is within the size of the points. The present MSR measurements provide a much more accurate temperature dependence of M_s than the neutron-scattering studies. The three different samples show very similar variations of frequency over a wide temperature range, with $H_{\text{int}}(T \rightarrow 0) \approx 410-425$ G. As shown in Fig. 2(b), the precession amplitude undergoes a sudden change at $T \approx 250$ K for samples 1 and 2, while at $T \approx 200-225$ K for sample 3. We denote these temperatures as the Néel temperature T_N(MSR) determined by MSR. The frequencies at and just below T_N(MSR) are still about half that at low temperature ($T \rightarrow 0$). This suggests a rather sharp transition into the antiferromagnetic state, taking place at different temperatures for different specimens. We note that the sharp change in Fig. 2 at T_N resembles MSR results[14] on V_2O_3 and MnO which undergo first-order phase transitions at T_N. The second-order transitions in two-dimensional antiferromagnets,[15] e.g., K_2NiF_4, however, also show very sharp changes[16] of M_s near T_N, which can easily be misidentified as first-order transitions. Therefore, one needs to study La_2CuO_{4-y} further to determine the order of the phase transition at T_N. The precession amplitude for sample 3 shows a slow increase with decreasing temperature even below 200 K. This may be due to an inhomogeneity of the oxygen deficiency, and therefore to a distribution of Néel temperatures in sample 3.

In Fig. 3, we present the dc susceptibility χ measured on samples 1 and 3 using the Faraday method. The peak temperatures $T(\chi_{\max})$ are 258 and 222 K, and the temperatures of maximum $d\chi/dT$ are 249 and 207 K, respectively, for samples 1 and 3. These temperatures are very close to the Néel temperature T_N(MSR) found by MSR. We also note that χ decreases rapidly with increasing temperature above T_N, much faster than expected for an antiferromagnet. In contrast, the susceptibilities of known 2D Heisenberg antiferromagnetic insulators[15] like $CuF_2 \cdot 2H_2O$ show broad maxima[17] at $T \gtrsim 2T_N$. This feature suggests that La_2CuO_{4-y} is dis-

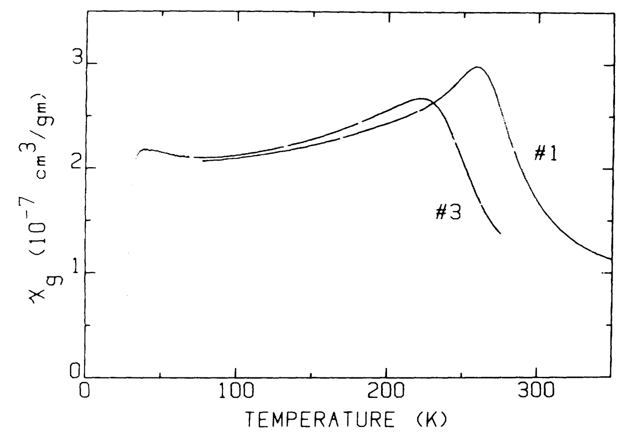

FIG. 3. dc magnetic susceptibility measured on samples 1 and 3 of La_2CuO_{4-y} used in the present MSR measurements.

tinctly different from conventional spin-$\frac{1}{2}$ 2D Heisenberg antiferromagnets.

The observed muon precession amplitude corresponds to a powder-averaged signal from about 50%–60% of the muons stopped in the specimen. In an independent MSR measurement with a transverse external magnetic field of 500 G, we also noticed that about 30%–40% of the muons are stopped at sites where H_{int} is very small (≤ 10 G) even at low temperatures ($10 \text{ K} \leq T \leq 200$ K). At the moment, we do not know whether this is due to the possible existence of macroscopic regions without static spin ordering or to the possibility that the internal field at some muon sites in the antiferromagnetic state is canceled by the crystal symmetry.[18]

With regards to the microscopic distribution of moments around μ^+, the observation of zero-field muon precession in Figs. 1 and 2 indicates that the ordered magnetic moments are distributed with a high symmetry so that more than 50% of the muon sites have the same magnitude of internal field H_{int}. The inhomogeneity of H_{int} estimated from the relaxation rate is less than 20 G, which corresponds to only 5% of H_{int} itself. If the moments at different Cu atoms were different in a random fashion (e.g., some Cu with a full $1\mu_B$ moment and others with no moment), one would not have observed the muon precession signal. An example of such a microscopically random magnet can be found in the diluted antiferromagnet $(Mn_{0.5}Zn_{0.5})F_2$ where Mn atoms with spin $\frac{5}{2}$ are substituted randomly by nonmagnetic Zn atoms. Indeed, no precession signal was observed[19] in zero-field MSR in $(Mn_{0.5}Zn_{0.5})F_2$, in contrast to a clear precession signal in pure MnF_2. Therefore, the present MSR results on La_2CuO_{4-y} rule out a random distribution of moments at Cu sites, and strongly suggest that equal moments are possessed homogeneously by all Cu atoms in the ordered state of La_2CuO_{4-y}.

Since we do not know the hyperfine coupling constant nor the location of the μ^+ site in the crystal, it is not possible to deduce the magnitude of the moment at Cu atoms accurately. One can, however, crudely estimate the moment value based on experience from MSR in other magnetic oxides, e.g., MnO, where the hyperfine coupling is due mainly to the dipolar interaction and the μ^+ occupies a high-symmetry site surrounded by oxygen atoms.[14] If we assume the muon site to be at the center of four oxygen atoms in a CuO layer, the observed internal field $H_{int} \approx 420$ G in La_2CuO_{4-y} corresponds to the dipolar field from Cu moments of $\simeq 0.15\mu_B$ aligned with the antiferromagnetic spin structure proposed in Ref. 6.

Macroscopically, the muons stop uniformly throughout the specimen. Therefore, the observed zero-field precession amplitude indicates that more than 50% of the volume fraction of the specimen undergoes the magnetic ordering. This information can be combined with the results from neutron scattering to estimate the microscopic moment S at Cu atoms. The Bragg-peak intensity I_B of neutron scattering is proportional to $\langle S^2 \rangle$ as $I_B \propto \langle S^2 \rangle$, where $\langle \ldots \rangle$ denotes the spatial average. If 100% of the specimen magnetically orders, S is equal to the averaged moment $\simeq 0.4\mu_B$/Cu as determined by the neutron experiments.[6-8] If only 50% orders, the moment in the ordered region would be $\sqrt{2} \times 0.4 \approx 0.6\mu_B$. This argument gives the upper limit of S as $S \leq 0.6\mu_B$.

In summary, the present MSR experiment indicates that a noninteger moment, significantly less than $1\mu_B$, is distributed homogeneously at the Cu sites in the long-range ordered state of La_2CuO_{4-y}. Such a large reduction from the integer Bohr magneton number is rarely found in conventional ionic insulator antiferromagnets.[15] This result encourages a picture in which the magnetism of La_2CuO_{4-y} is related to an antiferromagnetic spin-density wave. We also found a sharp behavior of the sublattice magnetization and muon precession amplitude around T_N(MSR), and notice a rapid decrease of the susceptibility above $T(\chi_{max})$ which is very close to T_N(MSR). These results, together with the extreme sensitivity of the ordering temperature on the oxygen-defect density,[5] suggest that the antiferromagnetism of La_2CuO_{4-y} is different from that of conventional ionic spin systems.

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Note added.—Very recently with J. H. Brewer *et al.* at TRIUMF (Vancouver), we have extended the measurement to a few more specimens (samples 0, and 4–6) of La_2CuO_{4-y}. The observed Néel temperature T_N(MSR) and muon precession frequency $\nu(0)$ at $T \rightarrow 0$ are, for sample 0, $T_N(\text{MSR}) \simeq 295$ K, $\nu(0) = 5.8$

MHz; for sample 4, T_N(MSR)$\simeq$210 K, $\nu(0)$ =5.6 MHz; for sample 5, T_N(MSR)$\simeq$90 K, $\nu(0)$ =5.3 MHz; and for sample 6, T_N(MSR)$\simeq$10 K, $\nu(0)$ =5.1 MHz. Thus, $\nu(0)$ does not depend much on T_N. This indicates that different specimens with different T_N possess approximately equal microscopic ordered moment at $T \rightarrow 0$. The "ordering" we described in this paper corresponds to the three-dimensional static magnetic ordering.

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