Reduction of Ordered Moment and Néel Temperature of Quasi-One-Dimensional Antiferromagnets Sr_2CuO_3 and Ca_2CuO_3

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We report elastic neutron diffraction and muon spin relaxation (μSR) measurements of the quasi-one-dimensional antiferromagnets Sr_2CuO_3 and Ca_2CuO_3, which have extraordinarily reduced T_N/J ratios. We observe almost resolution-limited antiferromagnetic Bragg reflections in Sr_2CuO_3 and obtain a reduced ordered moment size of $\sim 0.06\mu_B$. We find that the ratio of ordered moment size $\mu(Ca_2CuO_3)/\mu(Sr_2CuO_3) = 1.5(1)$ roughly scales with their Néel temperatures, which suggests that the ordered moment size of quasi-one-dimensional antiferromagnets decreases continuously in the limit of vanishing interchain interactions. [S0031-9007(97)02480-0]

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One-dimensional spin systems with antiferromagnetic interactions have received considerable attention because of their pronounced quantum mechanical effects. In the absence of interchain interactions, both integer *and* half-odd integer spin-chain systems have spin-singlet ground states, rather than an antiferromagnetically ordered Néel state [1–3]. Yet, for half-odd integer spin chains, the spin excitations are gapless at momentum $k = 0$ and π [4]; this indicates that the ground state of a half-odd integer spin chain is closer to the Néel ordered state than the integer spin systems, which have a so-called Haldane gap [3].

Because of the gapless feature of half-odd integer spin chains, one interesting question is whether the ground state is ordered or disordered when interchain interactions are introduced. Previously, it was proposed that there is a nonzero critical coupling ratio ($J'/J = R_c$), below which the system retains a singlet ground state [5]. Recent renormalization group calculations, however, suggest that the ground state may depend on microscopic details of the model which describes the spin-spin interactions [6,7]. Numerical studies of the Heisenberg model suggested a vanishing critical coupling ratio ($R_c \sim 0$); namely, for infinitesimally small interchain couplings, half-odd integer spin chains should exhibit Néel order [7].

Experimentally, $KCuF_3$ is the most investigated quasi-one-dimensional $S = 1/2$ antiferromagnet. Unfortunately, this material has relatively large coupling ratio $R = J'/J \sim 2\ \mathrm{K}/203\ \mathrm{K} = 1.0 \times 10^{-2}$, as shown from neutron inelastic scattering measurements [8]. Probably reflecting the large coupling ratio R, the T_N/J ratio ($\sim 39\ \mathrm{K}/203\ \mathrm{K} = 0.2$) and the ordered moment size [$= 0.49(7)\mu_B$ [9]] were also found to be relatively large.

To investigate the regime of the critical coupling ratio, model materials with smaller interchain couplings are needed; the quasi-one-dimensional $S = 1/2$ antiferromagnets Sr_2CuO_3 and Ca_2CuO_3 are suitable candidates [10–14]. The intrachain interaction ($2J \sim 2600$ K) of these materials have been estimated from susceptibility [10,11] and infrared light absorption [12]. Néel ordering of these compounds was first observed in μSR measurements [13], with a significantly reduced T_N/J ratio of $\sim 5\ \mathrm{K}/1300\ \mathrm{K} = 4 \times 10^{-3}$ for Sr_2CuO_3 and $T_N/J \sim 11\ \mathrm{K}/1300\ \mathrm{K} = 8 \times 10^{-3}$ for Ca_2CuO_3. Since T_N/J is a measure of the coupling ratio R [7,15], the reduced T_N of these two compounds demonstrates their good one dimensionality. A previous elastic neutron scattering measurement of Ca_2CuO_3 [16] has found an extremely reduced size of ordered moments [$= 0.05(3)\mu_B$], although this result contains a systematic uncertainty due to extinction. In the case of Sr_2CuO_3, powder neutron measurements were unable to observe antiferromagnetic Bragg reflections, placing an upper limit of any ordered moment of $<0.1\mu_B$ [10]. In this Letter we report μSR and neutron scattering measurements of single crystalline Sr_2CuO_3 and Ca_2CuO_3 specimens, aiming to clarify the relationship between T_N/J and the size of ordered moments.

The crystal structure of Sr_2CuO_3 and Ca_2CuO_3 (Fig. 1) is similar to that of La_2CuO_4, but lacks oxygen ions between the Cu ions in one direction (c axis). As a result, chains of corner shared CuO_4 tetragons extend in the b-axis direction, with a strong antiferromagnetic interaction due to the 180° Cu-O-Cu coupling. The lattice parameters of Ca_2CuO_3 are smaller than those of Sr_2CuO_3 by 7.0% (c axis) and 3.6% (a and b axes) [10,17]. The reduced c-axis parameter of Ca_2CuO_3 probably enhances the interchain coupling (J'), as its higher T_N suggests.

A single crystal of Sr_2CuO_3 ($\sim \phi 3$ mm $\times$ 2 cm) was grown employing the traveling-solvent-floating-zone (TSFZ) method, as described in Ref. [11]. In order to search for antiferromagnetic Bragg reflections, we

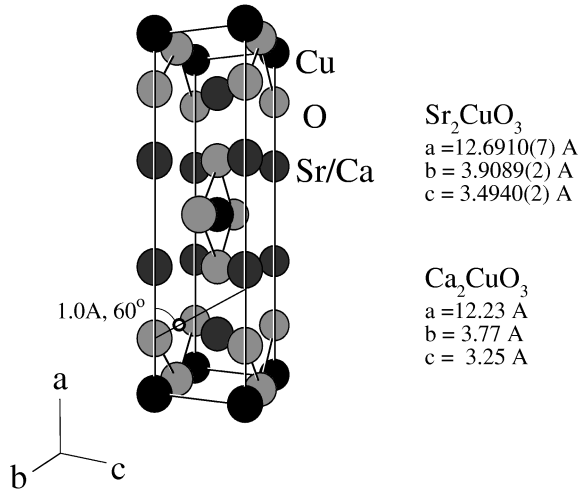

FIG. 1. The crystal structure of $(Sr, Ca)_2CuO_3$. The Cu-O chain runs in the b-axis direction. The circle is the off-chain O-μ^+ bond muon site. The lattice parameters are from Refs. [10,17].

performed elastic neutron scattering measurements at the High Flux Beam Reactor (HFBR) at Brookhaven National Laboratory, using the H4M and H7 triple-axis spectrometers. For the measurements, two pyrolytic graphite (PG) filters were employed to eliminate contamination of higher order reflections from the monochromator.

In Fig. 2(a), we show diffracted neutron counts around the point $(0, 1/2, 1/2)$, where an antiferromagnetic Bragg reflection was observed below $T_N = 5.41(1)$ K. We confirmed with tighter collimation (10'-40'-S-10'-80') that the width of this Bragg reflection is as narrow as that of a nuclear reflection (011). This is direct evidence of antiferromagnetic long range order in Sr_2CuO_3. We observed other antiferromagnetic Bragg reflections at $(h, k/2, l/2)$, where h is an integer and k and l are odd integers. We fit the $(0, 1/2, 1/2)$ reflection with a Gaussian form, and plot the peak intensity (I_0) and width (σ) in Fig. 2(b) as a function of temperature.

In order to determine the ordered spin direction and the moment size, we measured the integrated intensities of magnetic Bragg reflections in both the $0kl$ and hkk zones. The intensity distribution was best explained using the assumption that ordered moments are aligned along the b-axis direction, parallel to the chain. By normalizing the magnetic Bragg intensities with those of several relatively weak nuclear Bragg reflections, such as (200) and (400), we find the ordered moment size to be $0.06(3)\mu_B$. Because of extinction of nuclear reflections, the ordered moment size obtained here should be considered as an upper limit.

Since extinction of nuclear reflections depends on the quality of individual crystals, the size of ordered moments obtained by the above method contains a relatively large systematic error. With muon spin relaxation (μSR), on the other hand, we can compare the relative size of moments between isostructural materials quite accurately.

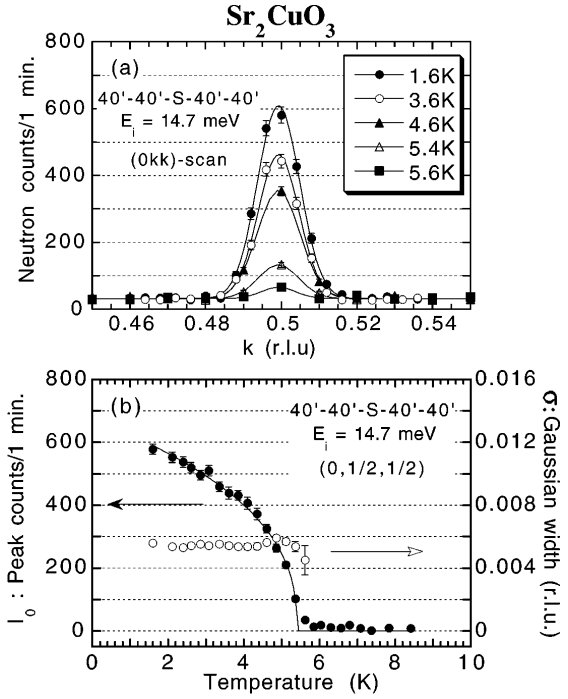

FIG. 2. (a) Antiferromagnetic Bragg reflection of Sr_2CuO_3. (b) Temperature dependence of the peak counts I_0 (filled circles), and the width σ (open circles). The solid line is a phenomenological power-law fit $[I_0 \propto (T_N - T)^{2\beta}]$ with $T_N = 5.41(1)$ K and $\beta = 0.20(1)$.

Muons in Sr_2CuO_3 and Ca_2CuO_3 are expected to occupy the same crystallographic position and experience dipolar fields from the ordered moments below T_N. The relative size of ordered moments can be deduced from the muon spin precession frequencies.

The μSR measurements were performed at the M15 surface-muon channel at TRIUMF (Vancouver, Canada), using a conventional μSR spectrometer [18] combined with a dilution refrigerator and a "low-background" apparatus [19] with a ^{4}He gas-flow cryostat. We evaluated the time evolution of muon spins, using the conventional ZF/LF-μSR technique [18,20].

In Fig. 3(a), we show the spectrum for Sr_2CuO_3. Below T_N, we observe spontaneous muon spin precession in zero external magnetic field; this is a signature of a well-defined static local field from ordered moments. We analyzed the spectra assuming two muon sites,

$$P_\mu(t) = A_1 P_{\mu 1}(t) + A_2 P_{\mu 2}(t), \qquad (1)$$

where $A_{1,2}$ is the fractional site population of the muons $(A_1 + A_2 = 1)$. We assumed the following conventional form for the signal from each site:

$$P_{\mu i}(t) = A_{\mathrm{osc}\,i} \exp(-\Delta_i t) \cos(\gamma_\mu H_{\mu i} t + \phi_i) + A_{\mathrm{rlx}\,i} \exp(-t/T_{1i}), \qquad (i = 1, 2), \quad (2)$$

where the first (second) term presents the muon spin precession (T_1 relaxation), due to the local field component perpendicular (parallel) to the initial muon spin direction.

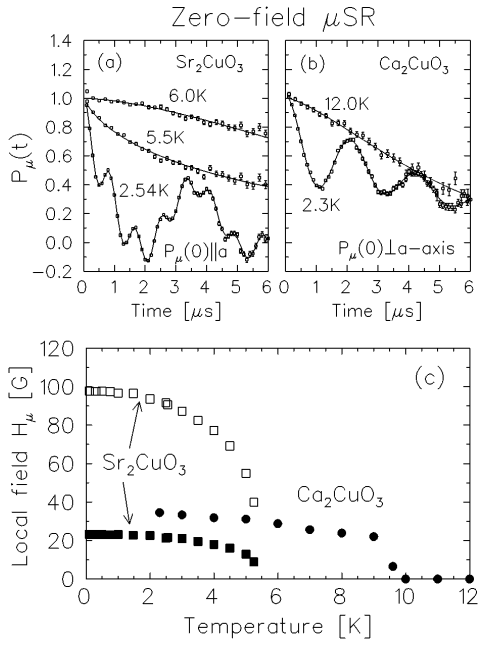

FIG. 3. Zero-field μSR spectra of (a) SrSRCuO$_3$2 and (b) Ca_2CuO_3. The solid lines on the data below T_N are fits to the function described in the text. (c) The local fields at the muon sites ($H_{\mu 1,2}$) are shown.

In Fig. 3(c), we show the local fields ($H_{\mu 1,2}$) as a function of temperature. In Sr_2CuO_3, the ratio of the two local fields was independent of temperature; this suggests that both of the muon sites are stable and that muons do not hop on the time scale of the muon lifetime. In Fig. 3(b), we show μSR spectra of Ca_2CuO_3. Because of the shape of our Ca_2CuO_3 specimen, we performed the μSR measurements with a crystal orientation [$P_\mu(0) \perp a$ axis] which was different from that of the Sr_2CuO_3 case [$P_\mu(0) \parallel a$ axis $\perp$ chain]. Consequently, we observed only one signal in the ordered phase. We confirmed, from independent measurements of polycrystalline Ca_2CuO_3 pellets, that the higher frequency signal also exists and that the signal observed in the single crystalline sample corresponds to the lower frequency signal. The muon local fields are plotted in Fig. 3(c). The ratio of the local fields of the two systems, which is equal to the relative size of ordered moments, was $\mu(Ca_2CuO_3)/\mu(Sr_2CuO_3) = 35(3)\ \mathrm{G}/23.2(1)\ \mathrm{G} = 1.5(1)$ in the $T \to 0$ limit.

In high-T_c related oxides, muons generally form an O-μ^+ bond with a bond length of $\sim$1.0 Å [21]. Assuming such O-μ^+ bond formation, we performed an electrostatic potential calculation, and determined the stable muon positions in (Sr, Ca)$_2$CuO$_3$. Figure 1 shows the off-chain O-μ^+ bond site, which is responsible for the lower-field signal. We calculated the magnetic dipolar field for this site, and found that the local field from a given size of ordered moment agrees within 10% in Sr_2CuO_3 and Ca_2CuO_3. Therefore, the local field ratio in these two compounds reflects the relative size of their moments. We estimated the ordered moment sizes from the dipolar fields, as summarized in Table I. The moment sizes obtained by μSR and neutron techniques agreed within the errors, suggesting that uncertainties due to extinction or muon site ambiguity are, in fact, rather small.

TABLE I. Ordered moment size of 1D and 2D antiferromagnets.

Compound	Local fields (G)	μSR Moment size	Neutron Moment size
Sr_2CuO_3 [a]	23.2, 97.7	0.06(1) μ_B	0.06(3) μ_B
Ca_2CuO_3 [b]	35	0.09(1) μ_B	0.05(3) μ_B
$YBa_2Cu_3O_7$ [c]	310, 1330		0.6 μ_B
La_2CuO_4 [d]	430		0.5 μ_B

[a]This work.
[b]μSR: this work, and neutron: Ref. [16].
[c]μSR: from Ref. [22], and neutron: Ref. [23].
[d]μSR: from Ref. [24], and neutron: Ref. [25].

In Fig. 4, we plot the ordered moment size of several quasi-1D antiferromagnets [8,9,26,27] as a function of T_N/J. As expected, the ordered moments shrink as the T_N/J ratio decreases. Moreover, the ordered moment size continuously decreases in the regime of extremely reduced ratio $T_N/J = 4 \times 10^{-3} \sim 10^{-2}$. This suggests that the ordered moment vanishes smoothly in the $R = J'/J \to 0$ limit, rather than maintaining a limiting size (dashed line in Fig. 4) as has been proposed theoretically [28].

The solid lines in Fig. 4 are predictions of ordered moment size from (1) linear spin-wave theory [29], (2) spin-wave theory with kinematical interactions [29,30], and (3) chain mean-field (CMF) theory [7,31,32]. These theories predict the relationship between the coupling ratio ($R = J'/J$) and the ordered moment size; we estimated R from T_N/J within the framework of each theory [$T_N/J \approx 2.1S(S+1)\sqrt{J'/J}$ [15] for the spin-wave theories and

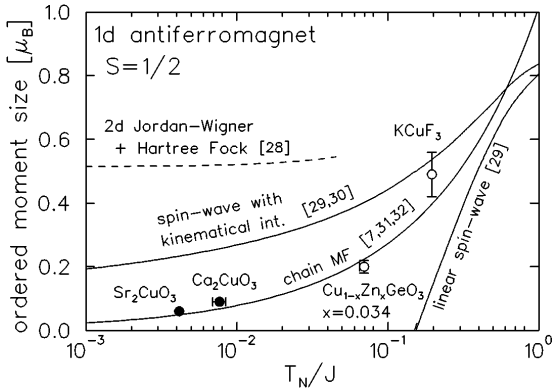

FIG. 4. Ordered moment size as a function of T_N/J. The points for Sr_2CuO_3 and Ca_2CuO_3 are from this work (see Table I). $KCuF_3$ is from Refs. [8,9] and $Cu_{1-x}Zn_xGeO_3$ ($x = 0.034$) is from Refs. [26,27]. The lines are theoretical relations, which have zero moment (solid lines from Ref. [29,31]) or finite moment (dashed line from Ref. [28]) in the $R \to 0$ limit.

$T_N/J \approx J'/J$ [6,7,31] for chain mean-field theory]. We found that the CMF approach best explains the ordered moment size of Sr_2CuO_3 and Ca_2CuO_3. Since the CMF approach is based on the exact solution of an isolated spin chain, it takes more quantum mechanical effects into account than the spin-wave approaches which presume an antiferromagnetic ordered state. Probably, this is the reason why the CMF approach presented the most successful account for $R \rightarrow 0$ region, where moment reduction is dominated by quantum spin fluctuations.

Summarizing our results, we observed long range antiferromagnetic order in Sr_2CuO_3 with a remarkably reduced ordered moment ($\sim 0.06\mu_B$). The relative size of ordered moments $\mu(Ca_2CuO_3)/\mu(Sr_2CuO_3) = 1.5(1)$ roughly scales with their Néel temperatures. We have shown that Sr_2CuO_3 and Ca_2CuO_3 lie in the regime of extremely reduced T_N/J ratio, where quantum mechanical moment reduction dominates. Further studies of these systems, for example, probing their spin excitations, will be of great interest.

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