Reduction of ordered moment and Néel temperature of quasi one-dimensional antiferromagnets Sr$_2$CuO$_3$ and Ca$_2$CuO$_3$

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We report elastic neutron diffraction and muon spin relaxation ($\mu$SR) measurements of the quasi one-dimensional antiferromagnets Sr$_2$CuO$_3$ and Ca$_2$CuO$_3$, which have extraordinarily reduced $T_N/J$ ratios. We observe almost resolution-limited antiferromagnetic Bragg reflections in Sr$_2$CuO$_3$ and obtain a reduced ordered moment size of $\sim$0.06$\mu_B$. We find that the ratio of ordered moment size $\mu(Sr_2CuO_3)/\mu(Ca_2CuO_3) = 1.5(1)$ 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 inter-chain interactions.

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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 inter-chain interactions, both integer and half-odd integer spin-chain systems have spin-singlet ground states, rather than an antiferromagnetically ordered Néel state [3,4]. Yet, for half-odd integer spin-chains, the spin-excitations are gap-less at momentum $k = 0$ and $\pi$ [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 gap-less feature of half-odd integer spin-chains, one interesting question is whether the ground state is ordered or disordered when inter-chain interactions are introduced. Previously, it was proposed that there is a non-zero critical coupling ratio ($J'/J = R_c$), below which the system retains a singlet ground-state [4]. Recent renormalization group calculations however suggest that the ground state may depend on microscopic details of the model which describes the spin-spin interactions [4,5]. Numerical studies of the Heisenberg model suggested a vanishing critical coupling ratio ($R_c \sim 0$); namely, for infinitesimally small inter-chain couplings, half odd-integer spin-chains should exhibit Néel order [6].

Experimentally, KCuF$_3$ is the most investigated quasi-one-dimensional $S=1/2$ antiferromagnet. Unfortunately, this material has relatively large coupling ratio $R = J'/J \sim 2K/203K = 1.0 \times 10^{-2}$, as shown from neutron inelastic scattering measurements [8]. Probably reflecting the large coupling ratio ($\sim 39K/203K = 0.2$) 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 inter-chain couplings are needed; the quasi one-dimensional $S=1/2$ antiferromagnets Sr$_2$CuO$_3$ and Ca$_2$CuO$_3$ are suitable candidates. The intra-chain interaction ($2J \sim 2600K$) of these materials have been estimated from susceptibility [10,11] and infrared light absorption [12]. Néel ordering of these compounds was first observed in $\mu$SR measurements [13], with a significantly reduced $T_N/J$ ratio of $\sim 5K/1300K = 4 \times 10^{-3}$ for Sr$_2$CuO$_3$ and $T_N/J \sim 11K/1300K = 8 \times 10^{-3}$ for Ca$_2$CuO$_3$. Since $T_N/J$ is a measure of the coupling ratio $R$ [14,15], the reduced $T_N$ of these two compounds demonstrates their good one-dimensionality. A previous elastic neutron scattering measurement of Ca$_2$CuO$_3$ [16] has found an extremely reduced size of ordered moments (=0.05(3)$\mu_B$ [17]), although this result contains a systematic uncertainty due to extinction. In the case of Sr$_2$CuO$_3$, powder neutron measurements were unable to observe antiferromagnetic Bragg reflections, placing an upper limit of any ordered moment of $< 0.1\mu_B$ [18]. In this Letter we report $\mu$SR and neutron scattering measurements of single crystalline Sr$_2$CuO$_3$ and Ca$_2$CuO$_3$ specimens, aiming to clarify the relationship between $T_N/J$ and the size of ordered moment.

The crystal structure of Sr$_2$CuO$_3$ and Ca$_2$CuO$_3$ (Fig.1) is similar to that of La$_2$CuO$_4$, 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$_2$CuO$_3$ are smaller than those of Sr$_2$CuO$_3$ by 7.0% (c-axis) and 3.6% (a- and b-axis) [16,17]. The reduced c-axis parameter of Ca$_2$CuO$_3$ probably enhances the inter-chain coupling ($J'$), as its higher $T_N$ suggests.

A single crystal of Sr$_2$CuO$_3$ ($\sim 3mm \times 2cm$) was grown employing the traveling-solvent-floating-zone
(TSFZ) method, as described in Ref. [1]. In order to search for antiferromagnetic Bragg reflections, we 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. 2a, we show diffraction 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 \(\text{Sr}_2\text{CuO}_3\). We observed other antiferromagnetic Bragg reflections at \((h, k/2, 1/2)\), 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 \((\sigma)\) in Fig. 2b 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 \(0k\) and \(kk\)–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 (\(\mu\)SR) on the other hand, we can compare the relative size of moments between iso-structural materials quite accurately. Muons in \(\text{Sr}_2\text{CuO}_3\) and \(\text{Ca}_2\text{CuO}_4\) are expected to occupy the same crystallographic position and experience well-defined static local field from ordered moments. We assumed the following conventional form for the signal from each site:

\[
P_{\mu}(t) = A_{\text{祭}} \exp(-\Delta t) \cos(\gamma_\mu H_{\mu} t + \phi_1) + A_{\text{祭}} \exp(-t/T_1) \quad (i = 1, 2)
\]

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

\[
P_{\mu}(t) = A_{\text{祭}} \exp(-\Delta t) \cos(\gamma_\mu H_{\mu} t + \phi_1) + A_{\text{祭}} \exp(-t/T_1) \quad (i = 1, 2)
\]

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. In Fig. 2b, we show the local fields \((H_{\mu1,2})\) as a function of temperature. In \(\text{Sr}_2\text{CuO}_3\), 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. 3b, we show \(\mu\)SR spectra of Ca\(_2\)CuO\(_3\). Because of the shape of our Ca\(_2\)CuO\(_3\) specimen, we performed the \(\mu\)SR measurements with a crystal orientation \((P_y(0) \perp a\)-axis) which was different from that of the \(\text{Sr}_2\text{CuO}_3\) case \((P_y(0) \parallel a\)-axis \(\perp\) chain). Consequently, we observed only one signal in the ordered phase. We confirmed, from independent measurements of polycrystalline \(\text{Ca}_2\text{CuO}_3\) 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. 3c.

The ratio of the local fields of the two systems, which is equal to the relative size of ordered moments, was \(\mu(\text{Ca}_2\text{CuO}_3)/\mu(\text{Sr}_2\text{CuO}_3) = 35(3)G/23.2(1)G = 1.5(1)\) in the \(T \rightarrow 0\) limit.

In high-\(T_c\) related oxides, muons generally form an O–\(\mu^+\) bond with a bond length of \(~1.0\) Å [2]. Assuming such O–\(\mu^+\) bond formation, we performed an electrostatic potential calculation, and determined the stable muon positions in \((\text{Sr,Ca})_2\text{CuO}_3\). Fig. 4 shows the off-chain O–\(\mu^+\) 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 \(\text{Sr}_2\text{CuO}_3\) and \(\text{Ca}_2\text{CuO}_3\). 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 1. The moment sizes obtained by \(\mu\)SR and neutron techniques agreed within the errors, suggesting that uncertainties due to extinction or muon site ambiguity are, in fact, rather small.

In Fig. 5, we plot the ordered moment size of several quasi 1d antiferromagnets 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 \(R = J'/J \rightarrow 0\) limit, rather than maintaining a limiting size (dashed line in Fig. 5) as has been proposed theoretically [2].

The solid lines in Fig. 5 are predictions of ordered moment size from (1) linear spin-wave theory [26] (2) spin-wave theory with kinematical interactions [29-31] and (3)
chain mean-field (CMF) theory. 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 ($T_N/J \approx 2.1S(S+1)\sqrt{J'/J}$ for the spin-wave theories and $T_N/J \approx J'/J$ for chain mean-field theory.) We found that the CMF approach best explains the ordered moment size of Sr$_2$CuO$_3$ and Ca$_2$CuO$_3$. 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$_2$CuO$_3$ 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$_2$CuO$_3$ and Ca$_2$CuO$_3$ 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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FIG. 1.
The crystal structure of (Sr,Ca)$_2$CuO$_3$. The Cu-O chain runs in the $b$-axis direction. The circle is the off-chain O-$\mu^+$ bond muon site. The lattice parameters are from Ref. [10,17].

**FIG. 2.**
(a) Antiferromagnetic Bragg reflection of Sr$_2$CuO$_3$. (b) Temperature dependence of the peak counts $I_0$ (filled circles), and the width $\sigma$ (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 $\beta = 0.20(1)$.

**FIG. 3.**
Zero-field $\mu$SR spectra of (a) Sr$_2$CuO$_3$ and (b) Ca$_2$CuO$_3$. 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 ($H_{\mu1,2}$) are shown.

**FIG. 4.**
K. Kojima et al., Fig.4

K. Kojima et al., Fig.3
Ordered moment size as a function of $T_s/J$. The points for Sr$_2$CuO$_3$ and Ca$_2$CuO$_3$ are from this work (see Table I). KCuF$_3$ is from Ref. [8] and Cu$_{1-x}$Zn$_x$GeO$_3$ ($x = 0.034$) is from Ref. [22,23]. 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.

**TABLE I.** Ordered moment size of 1d and 2d antiferromagnets

| compound         | $\mu$SR local fields | $\mu$SR moment size | neutron moment size |
|------------------|-----------------------|----------------------|---------------------|
| Sr$_2$CuO$_3$    | 23.2 G, 97.7 G        | 0.06(1) $\mu_B$     | 0.06(3) $\mu_B$   |
| Ca$_2$CuO$_3$    | 35 G                  | 0.09(1) $\mu_B$     | 0.05(3) $\mu_B$   |
| YBa$_2$Cu$_3$O$_7$ | 310 G, 1330 G        | 0.6 $\mu_B$         |                     |
| La$_2$CuO$_4$    | 430 G                 |                      | 0.5 $\mu_B$        |

*a* this work.

$b$ $\mu$SR: this work, and neutron: Ref. [16].

$c$ $\mu$SR: from Ref. [24], and neutron: Ref. [25].

$d$ $\mu$SR: from Ref. [26], and neutron: Ref. [27].