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Magnetic phase transition in the $S=\frac{1}{2}$ zigzag-chain compound $SrCuO_2$

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We have studied the magnetic properties of the $S=\frac{1}{2}$ quasi-one-dimensional Heisenberg antiferromagnet $SrCuO_2$, which has zigzag chains of Cu^{2+} ions. We have observed a static magnetic ordering below $T_c \sim 2$ K. The weak internal field in the muon spin relaxation spectra and the absence of the magnetic Bragg peaks below T_c suggest that the Cu^{2+} moments are largely reduced probably due to the quantum fluctuation. The remarkable suppression of the ordering temperature ($kT_c/J_2 = 1.1\times 10^{-3}$), where J_2 is the dominant exchange constant, probably originates from the combined effects of quantum fluctuation and frustration. [S0163-1829(97)51318-X]

Lower dimensional antiferromagnets have attracted many researchers since they exhibit novel phenomena originating from quantum fluctuations. Quantum effects are most prominent in one-dimensional (1D) systems. The most striking effect in a 1D Heisenberg antiferromagnet (HAF) is that integer and half-odd-integer spins show qualitatively different properties, as first suggested by Haldane.[1] In high-T_c superconducting copper oxides, which are realizations of the spin (S) $\frac{1}{2}$ two-dimensional (2D) HAF with carrier doping, many studies support the importance of 2D magnetic fluctuations to an understanding of these mechanisms.[2] Based on the t-J model, superconductivity is also expected in the carrier doped $S=\frac{1}{2}$ Heisenberg ladder[3] which is a system intermediate between one and two dimensions.

The compound $SrCuO_2$ has the orthorhombic crystal structure (space group $D_{2h}^{17}-Cmcm$).[4] This material has a unique structure consisting of zigzag chains of Cu ions. A section of such a zigzag chain in the bc plane is shown in Fig. 1. Copper spins are coupled by the nearly 180° Cu-O-Cu interaction (J_2) and also by the nearly 90° Cu-O-Cu interaction (J_1). Judging from the exchange interactions in similar copper oxides such as La_2CuO_4, J_2 is expected to be strongly antiferromagnetic. In this case, there exists a competition between J_1 and J_2 irrespective of the sign of J_1. Since the nearly 180° Cu-O bond length and the nearly 90° Cu-O bond length in $SrCuO_2$ are similar to those in $SrCu_2O_3$,[5] the interaction constants are expected to be similar with each other. Theoretically, the ratio of $|J_1/J_2|$ was calculated to be 0.1–0.2 (Ref. 6) in $SrCu_2O_3$, where J_1 and J_2 are ferromagnetic and antiferromagnetic, respectively. Therefore, the zigzag chain in $SrCuO_2$ can be viewed as composed of two loosely coupled $S=\frac{1}{2}$ antiferromagnetic chains with frustration.[7] A similar frustrated coupling can also be seen in the two-leg spin ladder compound $SrCu_2O_3$.[5,8] The ladders, where spins are coupled by the 180° Cu-O-Cu interaction, are coupled by the 90° Cu-O-Cu interaction. The 90° interaction introduces a frustration into the interladder coupling. The frustration does not significantly change the spin gap in the excitation spectrum, which originates from the ladders, and helps in retaining the spin-fluid nature.[9]

The ground state of an $S=\frac{1}{2}$ 1D system with competing nearest-neighbor (J_1) and next-nearest-neighbor interactions (J_2) has been studied by Haldane.[10] He argued that there exists a transition from a spin-fluid state to a spontaneously dimerized state at $J_2/J_1 \sim \frac{1}{6}$ in the Heisenberg case. Recently, White and Affleck[11] have studied theoretically an $S=\frac{1}{2}$ zigzag chain. They showed that the system exhibits both dimerization and incommensurate spiral spin correlations.

It would be very interesting to study the magnetic properties of the zigzag chain experimentally. In particular, whether long-range magnetic ordering exists or not should be investigated. In this paper we report the results of magnetic susceptibility, heat capacity, neutron diffraction and

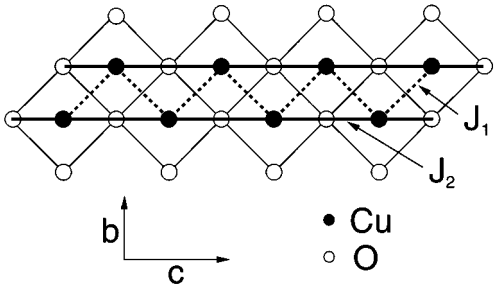

FIG. 1. The zigzag chain of Cu^{2+} ions along the c axis in $SrCuO_2$. The filled circles represent copper atoms and the open circles represent oxygen atoms.

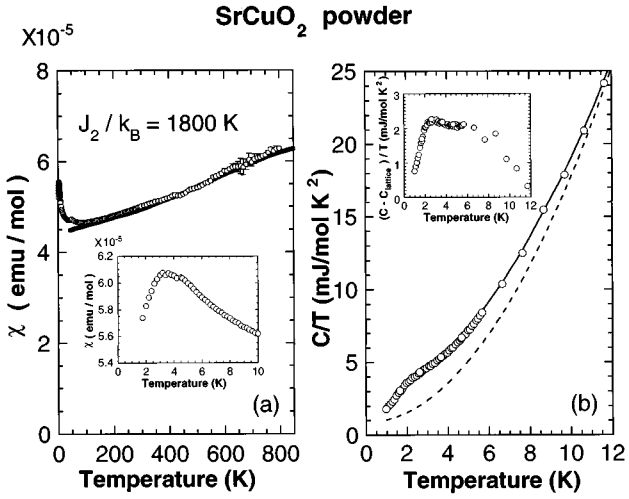

FIG. 2. (a) Temperature dependence of magnetic susceptibility in a polycrystalline sample of $SrCuO_2$. The solid line represents the theoretical susceptibility discussed in the text with $J_2/k_B=1800$ K and $\chi_{VV}=3.35\times10^{-5}$ emu/mol Cu. (b) Temperature dependence of heat capacity in a polycrystalline sample of $SrCuO_2$. The broken line represents the lattice heat capacity. The inset shows the heat capacity after the lattice contribution was subtracted.

muon spin relaxation (μSR) measurements on $SrCuO_2$, from which we get evidence for magnetic ordering at $T_c\sim2$ K.

Ceramic samples of $SrCuO_2$ were prepared by firing a stoichiometric ratio of $SrCO_3$ (99.99%) and CuO (99.99%) at 980 °C for 30 h in air with intermittent regrinding. A single crystal of $SrCuO_2$ grown by the traveling solvent floating zone (TSFZ) method was used for neutron-diffraction experiments. The dimension of the crystal is about 3, 3, and 30 mm along the a, b, and c axes, respectively.

The magnetic susceptibility was measured using a superconducting quantum interference device magnetometer (Quantum Design MPMS2). The heat capacity was measured using a MagLab^{HC} microcalorimeter of Oxford Instruments. The neutron-scattering experiments were carried out on the H4M and H7 triple-axis spectrometers at the High Flux Beam Reactor at Brookhaven National Laboratory. The μSR measurements were done at the M13 and M15 beam lines at TRIUMF (Vancouver).

The temperature dependence of the magnetic susceptibility in $SrCuO_2$ powder is shown in Fig. 2(a). The susceptibility increases with increasing temperature (T) for $50\leqslant T\leqslant800$ K. A broad peak in the temperature dependence of susceptibility characteristic of an $S=\frac{1}{2}$ 1D HAF (Refs. 12 and 13) is assumed to appear above 800 K. The magnetic impurity density, assuming Cu^{2+} as impurities, is estimated from the low-temperature Curie tail to be $\sim0.02\%$. The peak at ~3 K indicates a magnetic transition. We have observed no difference between field-cooled and zero-field-cooled magnetization measurements, suggesting that the peak does not originate from a spin-glass transition. The solid line in Fig. 2(a) represents the theoretical susceptibility.[13] In analyzing the data we fixed the diamagnetic susceptibility (-5.00×10^{-5} emu/mol Cu) (Ref. 14) and fitted the Van Vleck susceptibility χ_{VV} and J_2/k_B. The observed susceptibility is well fitted by the theoretical calculation with $\chi_{VV}=3.35\times10^{-5}$ emu/mol and $J_2/k_B=1800$ K. This result of the susceptibility is consistent with that reported recently.[15]

The heat capacity data are shown in Fig. 2(b). The broken line represents the lattice heat capacity estimated using the data in the range of $15\leqslant T\leqslant30$ K. The inset shows the heat capacity after the lattice contribution was subtracted. A broad peak is observed at ~2 K, indicating a magnetic transition. This transition temperature (T_c) is consistent with that obtained in the susceptibility measurement since T_c corresponds to the temperature at which derivative of susceptibility with respect to temperature is maximum.[16] We estimate the magnetic entropy below 12 K as ~20 mJ/(mol K). This amount corresponds to less than $\sim0.5\%$ of the total magnetic entropy $N_Ak_B\ln(2)$ expected for $S=\frac{1}{2}$, where N_A is Avogadro's number. This is natural because in a 1D magnet a large amount of magnetic entropy is lost in the short-range ordered state above the magnetic ordering temperature. In fact, the entropy below 12 K is consistent with that calculated theoretically for 1D HAF below 12 K with $J/k_B=1800$ K.[17]

From the susceptibility and heat-capacity measurements, we confirmed that static magnetic ordering takes place in $SrCuO_2$ at ~2 K. A feature of this magnetic ordering is that the ordering temperature is extremely low compared with what one expects from the large exchange interaction constant. We first tried neutron powder diffraction to study this magnetic ordering. No distinct magnetic Bragg peak was observed down to 1.4 K. We then performed neutron-diffraction measurements using the single crystal. No distinct magnetic Bragg peak was observed in the $(h,0,l)$, $(0,k,l)$, $(h,k,0)$, and $(h,k,3k)$ zone down to 0.3 K. One way to explain this would be that the spin structure is incommensurate. However, magnetic Bragg peaks should be observed in at least one of the scattering planes mentioned above when the spin correlation along the chain direction (the c axis) is incommensurate as predicted theoretically.[11] To explain the absence of magnetic Bragg peaks, incommensurate spin correlation along the a or b axis should also be taken into consideration, which is unlikely in the present system. Therefore, it is probable that the ordered Cu^{2+} moments are very small. The moments are estimated to be $\leqslant0.01\mu_B$, assuming that the spins point along the chain direction antiferromagnetically as in Sr_2CuO_3.[18] Other spin structures also give a similar limit.

In order to study the magnetic ordering of $SrCuO_2$ in more detail, we have performed μSR experiments. We show in Fig. 3(a) the temperature dependence of μSR spectra obtained in $SrCuO_2$. At high temperatures, where the effect of local fields from Cu^{2+} spins is negligible due to the fast spin fluctuations, the spectra can be fitted with the static Gaussian function $G_{KT}(t,\Delta)$ given by Kubo and Toyabe.[19] The spectra originate from static nuclear dipole fields of copper. The observed width Δ is $\sim0.15\ \mu s^{-1}$ at 100 K. When the temperature is decreased, the depolarization rate rapidly increased, reflecting the slowing down of random fields from Cu^{2+} electron spins. When the fluctuation is relatively fast, this field works as an independent channel of muon spin relaxation, in addition to the nuclear dipolar fields. Then the muon spin relaxation function should be given by a product of the two functions[20] as

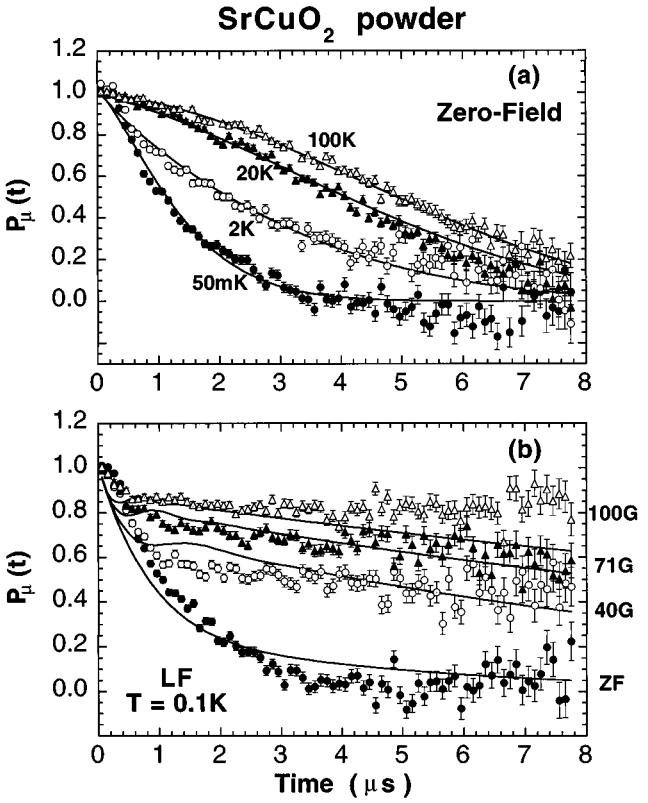

FIG. 3. (a) Zero-field μSR spectra in $SrCuO_2$ at various temperatures. The solid lines are the fit with the model function, Eq. (1). (b) Longitudinal field (LF) decoupling measurements on $SrCuO_2$ at 100 mK. The solid lines represent nearly static relaxation functions for Lorentzian local fields.

$$P_\mu(t)=\exp[-(\lambda t)^\beta]\times G_{KT}(t,\Delta), \qquad (1)$$

where λ represents the muon spin relaxation rate. The exponent β should be 0.5 for dilute fluctuating moments, 1 for bulk fluctuating moments, and approaches 2 when the spin fluctuations become more static. The solid lines in Fig. 3(a) are fits with the model function, Eq. (1). In the fitting, λ was varied and Δ was fixed at the value at 100 K. The value of β was varied below 5 K and fixed at 1 above 5 K, where the Gaussian term $G_{KT}(t,\Delta)$ is dominant and the relaxation function is insensitive to β. Equation (1) reproduces the observed data quite well. It is noted that the spectrum below $\sim$0.5 μs is rather like Gaussian and that above $\sim$0.5 μs becomes exponential below $T\sim 2$ K, suggesting that a large number of spins contributes to the spin fluctuations.

Figure 4 shows the temperature dependence of muon spin relaxation rate (λ) in $SrCuO_2$. A sudden increase of λ at $T\sim 2$ K indicates static magnetic ordering. This temperature also corresponds to the one below which β exceeds 1 as shown in the inset of Fig. 4. This supports that there is static magnetic ordering below $T\sim 2$ K. The ordering temperature is the same as that obtained from the magnetic susceptibility and the heat-capacity measurements. In order to determine whether the source of this relaxation is static or dynamic, we performed longitudinal field (LF) measurements, which investigate spin fluctuations by applying the external magnetic field parallel to the initial muon polarization.[21] Figure 3(b) shows μSR spectra from LF decoupling measurements. A

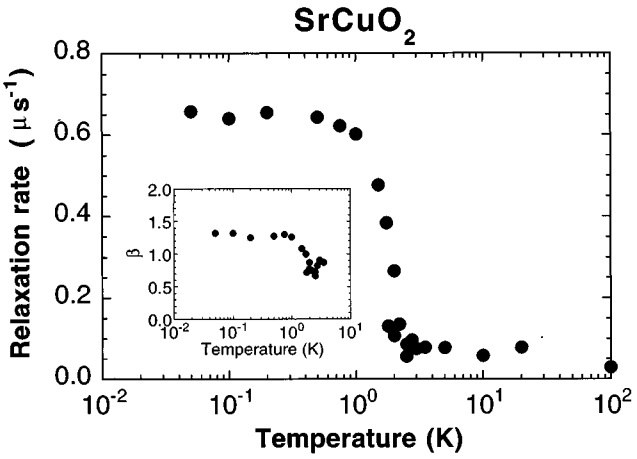

FIG. 4. Temperature dependence of muon spin relaxation rate (λ) in $SrCuO_2$. The inset shows the temperature dependence of β.

small field of 100 G almost decouples the muon relaxation, suggesting that the ordered moments are static. The solid lines represent nearly static relaxation functions for Lorentzian local fields.[20] This function reproduces the observed data reasonably well. The relaxation rate is estimated to be 0.4 MHz at 100 mK from the fitting.

We now discuss the origin of the static magnetic ordering at $\sim$2 K. The results of the magnetic susceptibility and the heat-capacity measurements demonstrate that a magnetic transition occurs. As mentioned above, the μSR spectrum below $\sim$0.5 μs is rather Gaussian-like, which suggests that a large number of spins contributes to the relaxation. However, the magnitude of the internal field at low temperatures is much smaller than that in Sr_2CuO_3 (Refs. 18 and 22) and Ca_2CuO_3 (Refs. 18 and 23) and no precession in the muon spectra is observed. It should be noted that an anomalously reduced ordered moment has been observed in Ca_2CuO_3 ($\sim 0.09\mu_B$) (Ref. 18) and in Sr_2CuO_3 ($\sim 0.06\mu_B$) (Ref. 18). This is consistent with the result of the neutron measurements, which show that the Cu^{2+} moments is $\leqslant 0.01\mu_B$ in $SrCuO_2$. The greatly reduced moment is probably caused by quantum fluctuations enhanced by frustration. Note that the absence of the precession signal in zero-field μSR does not necessarily preclude the existence of long-range spatial magnetic order. Generally, a pointlike magnetic probe in real space, such as μ^+, is rather insensitive to details of long-range spin configurations. Possible causes for smearing of the precession include (a) multiple muon sites with different strengths of local fields, and (b) a spread of impurity/imperfection concentration in the specimen which results in spread of the size of the ordered moment. Therefore, the spin structure of $SrCuO_2$ cannot be determined by the present results only.

We compare the static ordering temperature to those in the related compounds Sr_2CuO_3 and Ca_2CuO_3, which have simple chains of Cu^{2+} spins. Both compounds have strong intrachain interactions (an order of 10^3 K) via the 180° Cu-O-Cu path. This interaction is similar to that in $SrCuO_2$ as mentioned above. Although the one-dimensionality is quite good in the former two compounds, they show an antiferro-

magnetic long-range ordering because of the finite interchain coupling. The ordering temperature (T_N) is 5.41 K for Sr_2CuO_3(Ref. 18) and ~11 K for Ca_2CuO_3 (Refs. 18, 23, and 24), showing a suppression of T_N with $k_BT_N/J=2.5\times10^{-3}$ for Sr_2CuO_3. The suppression of the magnetic ordering temperature is more remarkable in $SrCuO_2$ ($kT_c/J_2=1.1\times10^{-3}$). The suppression probably originates from the combined effects of quantum fluctuation and frustration. This reminds us that the frustration effect between spin chains is similar to that between two-leg spin ladders, where the frustrations help in retaining the spin-fluid nature.[9]

In conclusion, we have observed a static magnetic ordering at $T_c\sim2$ K in $SrCuO_2$. The weak internal field in the muon spectra and the absence of the magnetic Bragg peaks suggest that the Cu^{2+} moments are reduced probably due to the quantum fluctuation enhanced by frustration. This is the lowest transition temperature ever observed in Cu-O chain compounds. The suppression of the static ordering temperature probably originates from the combined effects of quantum fluctuation and frustration.

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