Magnetic Susceptibility of Ideal Spin 1/2 Heisenberg Antiferromagnetic Chain Systems, Sr_2CuO_3 and $SrCuO_2$

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Magnetic susceptibility is measured on the one-dimensional spin 1/2 antiferromagnets Sr_2CuO_3 and $SrCuO_2$ using single crystals. Large, nearly contamination-free single crystals enable us to measure the intrinsic spin susceptibility over a wide temperature range between 5 and 800 K. The results are in excellent agreement with the recent calculation by Eggert, Affleck, and Takahashi, and the exchange interaction energy J is estimated to be 2200 ± 200 and 2100 ± 200 K, respectively. In Sr_2CuO_3, an isotropic susceptibility drop is observed below about 20 K, which is also consistent with the result of this rigorous calculation.

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It is well known that one-dimensional (1D) quantum spin systems are expected to show many interesting magnetic properties originating from the low dimensionality and the quantum fluctuations. In particular, theoretical studies on these systems have achieved remarkable progress. After the exact evaluation of the value of the magnetic susceptibility at zero temperature [1], Bonner and Fisher (BF) [2] calculated the magnetic susceptibility of the $S = 1/2$ finite-length chain numerically, which is a good approximation at high temperatures and has been used to compare the experimental results of real materials. Recently, by applying conformal field theory, Eggert, Affleck, and Takahashi (EAT) have succeeded in calculating the magnetic susceptibility of the $S = 1/2$ antiferromagnetic (AF) Heisenberg spin chain system with high accuracy [3]. Their result has revealed a characteristic temperature dependence of the magnetic susceptibility at low temperatures as low as $0.01J$. Considering such theoretical progress, it is indispensable to evaluate the magnetic properties of 1D $S = 1/2$ AF systems over a wide temperature range using well-characterized single crystals.

In this Letter, we study the magnetic susceptibility of Sr_2CuO_3 and $SrCuO_2$ single crystals, which turns out to be almost ideal systems of 1D $S = 1/2$ AF Heisenberg chains. The result can be quantitatively compared with the recent theoretical calculation. It is shown that the experimental results are in excellent agreement with the theoretical calculation, and the exchange interaction J is estimated to be 2200 ± 200 K for Sr_2CuO_3 and 2100 ± 200 K for $SrCuO_2$, respectively. In particular, Sr_2CuO_3 exhibits a characteristic temperature dependence at low temperatures ($T < 0.01J$) as predicted by EAT.

Sr_2CuO_3 has the 1D chains composed of these CuO_4 quadrilateral structures with sharing corner oxygens together [Fig. 2(a)] [4]. The exchange interaction J between neighboring Cu^{2+} ions is expected to be large because of the superexchange interaction. In the previous study using polycrystalline samples, the J value was estimated to be more than 1000 K [5,6]. In spite of this large J value, the μSR experiment [5] shows that this material has the three-dimensional (3D) long range AF order only below $T_N \sim 5$ K; moreover recent neutron scattering measurements using the same single crystal used in the present study [7] shows that the crystal has the 3D long range AF order only below $T_N \sim 5.4$ K. This property enables us to observe the ideal 1D behavior over a wide temperature range. Thus the exchange interaction between the chains $J_\perp$ is expected to be extremely small, $J_\perp/J \sim 10^{-5}$ [8]. This situation has not been realized on most 1D systems which have been extensively studied so far, such as $CuCl_2\ 2NC_5H_5$ and $KCuF_3$, since these systems usually undergo Néel transition at a relatively high temperature compared to the exchange interaction J [9]. Furthermore, there is no indication that Sr_2CuO_3 shows phase transitions such as the spin-Peierls transition usually taking place in a 1D system [6]. Therefore, this system is expected to show an ideal 1D behavior of the $S = 1/2$ of Heisenberg antiferromagnet over a wide temperature range from 5 to 1000 K or higher.

The structure of $SrCuO_2$ has two CuO chains combining to each other by sharing their edges, thus forming one CuO zigzag chain [Fig. 2(b)] [10]. The intrachain exchange interaction (J) is expected to be as large as in Sr_2CuO_3. On the other hand, the exchange interaction between the diagonal Cu-Cu spins (J') is expected to be small $J' = (0.1-0.2)|J|$ [11] and even ferromagnetic. Hence, at higher temperatures, this zigzag chain can also be regarded as two independent chains as in Sr_2CuO_3. The situation would change, however, at low temperatures. The interaction J' would frustrate the Cu spin on the adjacent chains, preventing them from being AF coupled. Therefore, a qualitative difference in their magnetic properties between Sr_2CuO_3 and $SrCuO_2$ is expected at low temperatures.

The present work was performed using single crystals grown by the traveling-solvent-floating-zone (TSFZ) method. By adopting the TSFZ method, we can obtain contamination-free single crystals unlike the flux method. CuO was used as a solvent in the growth. Details will be described elsewhere. The magnetic susceptibility

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measurements were done using a superconducting quantum interference device (SQUID) dc magnetometer between 2 and 800 K. Above 400 K, we used an oven attachment equipped with the SQUID.

As shown in Fig. 1, the susceptibility of as-grown crystals has a considerable Curie term as reported in [5,6]. By annealing under Ar atmosphere we succeeded in reducing the Curie term for both compounds. From this result the Curie term is considered to be due to excess oxygens. In Sr_2CuO_3, the Curie term, which amounts to about 0.063% of free Cu^{2+} ions in as-grown crystal, decreases to about 0.013% by annealing at 870 °C for 72 h. In $SrCuO_2$, the impurities decrease from 0.11% to 0.018% by annealing at 870 °C for 36 h.

Figures 2(a) and 2(b) show the temperature dependence of the magnetic susceptibility χ along three principal axes of Sr_2CuO_3 and $SrCuO_2$, respectively, annealed under the best conditions. In both systems, χ has the following characteristic features: (1) as small as 10^{-5} emu/mol, the same order as Van Vleck paramagnetic and core diamagnetic contribution, (2) anisotropic with one larger value in one direction and almost the same values in the other two directions, (3) increase with raising temperature over 800 K, which indicates that the AF coupling is strong enough to suppress χ even at 800 K. It is found that the major temperature dependent part of χ is isotropic in both systems, which provides an evidence that the spin system in both compounds can be regarded as a Heisenberg systems. As for the temperature independent anisotropic part, χ for both systems is largest when the magnetic field is applied perpendicular to the CuO_4 squares ($H \parallel c$ in Sr_2CuO_3, and $H \parallel a$ in $SrCuO_2$).

For a more quantitative analysis, we decomposed χ into

$$\chi = \chi_{\text{Curie}} + \chi_{\text{core}} + \chi_{\text{VV}} + \chi_{\text{spin}}, \qquad (1)$$

where χ_{Curie} represents an extrinsic Curie contribution which remained after the annealing. χ_{core} is the diamagnetic contribution from the ionic cores, and χ_{VV} is the Van Vleck paramagnetic term which results in the anisotropy in these two systems. They are independent of temperature. χ_{spin} represents the contribution from the 1D $S = 1/2$ chains in which we are interested.

Since χ was measured over a wide temperature range, the exchange interaction J can be estimated accurately from a comparison with the theoretical calculation. It should be noted that the J values can be determined almost uniquely from the slope of χ. As demonstrated in Fig. 3, the experimental data (with χ_{Curie} removed) can be reproduced well by the EAT theoretical calculation with $J = 2100 \pm 200$ K for Sr_2CuO_3 and $J = 2100 \pm 200$ K for $SrCuO_2$. Now that the value J can be determined, the zero temperature spin susceptibility $\chi_{\text{spin}}(0)$ can be estimated using the theoretical result $\chi_{\text{spin}}(0) = 0.101\,32 g^2 \mu_B^2 / J$ [1]. From this we can determine the temperature independent contribution, χ_{VV} and χ_{core}, by subtracting $\chi_{\text{spin}}(0)$ from the experimental value using Eq. (1). Using the value $\chi_{\text{core}} = 10.7 \times 10^{-5}$ emu/mol for Sr_2CuO_3, and 6.6×10^{-5} emu/mol for $SrCuO_2$[12], χ_{VV} for each axis can be extracted. The estimated values of χ_{VV} are listed in Table I. The result for Sr_2CuO_3 is quantitatively consistent with those by NMR study on the CuO chain contribution of $YBa_2Cu_3O_7$ [13].

Nearly the same values of the exchange interaction J for the two compounds are reasonable considering a nearly similar Cu-O configuration. It is interesting to compare these values with those of the 2D analogs such

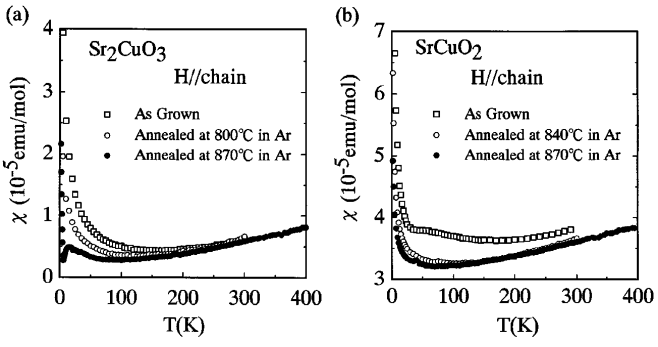

FIG. 1. The temperature dependence of χ of (a) Sr_2CuO_3 and (b) $SrCuO_2$ annealed under different conditions.

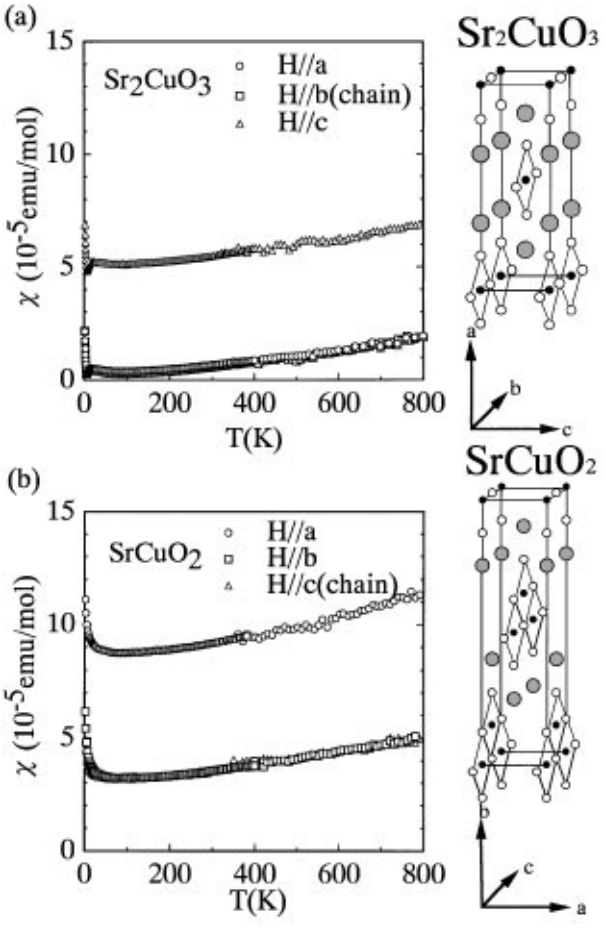

FIG. 2. The temperature dependence of χ with the magnetic field applied along the three axes for the crystals with the smallest Curie term, (a) Sr_2CuO_3 and (b) $SrCuO_2$. The schematic crystal structures are shown in the right hand side of each panel.

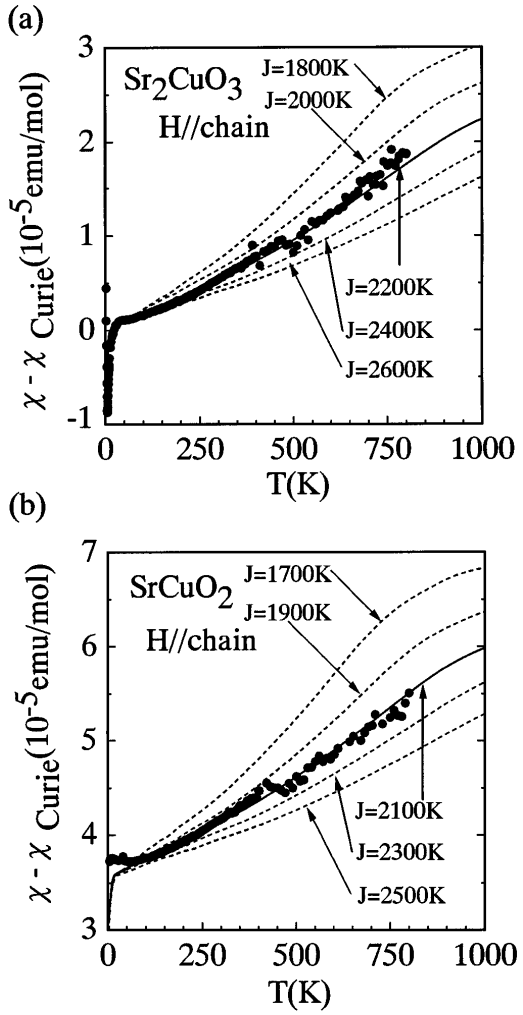

FIG. 3. $\chi - \chi_{\text{Curie}}$ and the theoretical curves by EAT [3] for various values of J for (a) Sr_2CuO_3 and (b) Sr, respectively.

as La_2CuO_4. In La_2CuO_4, J is estimated to be 1730 K by the inelastic neutron scattering experiment [14]. This value is significantly smaller than that in 1D analogous systems. Even if comparing the difference in their Cu-O bond length and other structural difference [15], the significant difference in the J value suggests that there might be some other factors to determine the value J, such as the difference in dimensions.

The theoretical result by BF has been used for the quantitative comparison with the experimental data on the real 1D AF systems. There is a significant difference between BF and EAT below $T \sim 0.23J$ ($\sim$500 K in the present systems). In this temperature range, BF shows a steeper rise with temperature. Hence, fitting the experimental result with BF always yields a larger J value than that with EAT. This situation is shown in Fig. 4. The experimental data fit rather well with BF for $J = 2800$ K, but a significant discrepancy shows up below 100 K.

Although χ_{spin} of Sr_2CuO_3 and $SrCuO_2$ shows similar behavior at high temperatures, a qualitative difference between the two is clearly observed at low temperatures. In particular, χ shows an isotropic drop below $T \sim 20$ K in Sr_2CuO_3 as shown in Fig. 2. It should be noted that this feature shows up as a cusp in the experimental data shown in Fig. 1 even before the Curie term is reduced. This drop seems to correspond to an onset of 3D AF long range order. However, the Néel temperature T_N of this compound, 5 K [5,7], is significantly lower than the temperature where this drop is observed. Furthermore, no anisotropy is seen in this temperature dependent part, in contrast to that expected in antiferromagnets below T_N. In this regard, this drop is difficult to explain by the onset of AF 3D long range order. The possibility of spin-Peierls transition at this temperature does not explain this drop. In the case of spin-Peierls transition, magnetic susceptibility should decrease to zero. Therefore the amount of this decrease should have the same value as the spin susceptibility at zero temperature $\chi_{\text{spin}}(0) = 6.9 \times 10^{-5}$ emu/mol [1]. In the present case, however, the decrease in χ_{spin} is $\sim 1 \times 10^{-5}$ emu/mol, too small to be expected from the spin-Peierls transition scenario. The absence of the spin-Peierls

TABLE I. The estimated value of χ_{VV} for Sr_2CuO_3 and $SrCuO_2$. The values estimated from the NMR on the CuO chains in $YBa_2Cu_3O_7$ are also shown for comparison. All susceptibilities are in units of 10^{-5} emu/mol.

Material	Axis	Present result	Ref. [13]
Sr_2CuO_3	a	3.4 ± 0.2	1.9
	b	3.3 ± 0.2	2.0
	c	7.2 ± 0.2	8.1
$SrCuO_2$	a	7.9 ± 0.2	...
	b	2.3 ± 0.2	...
	c	2.3 ± 0.2	...

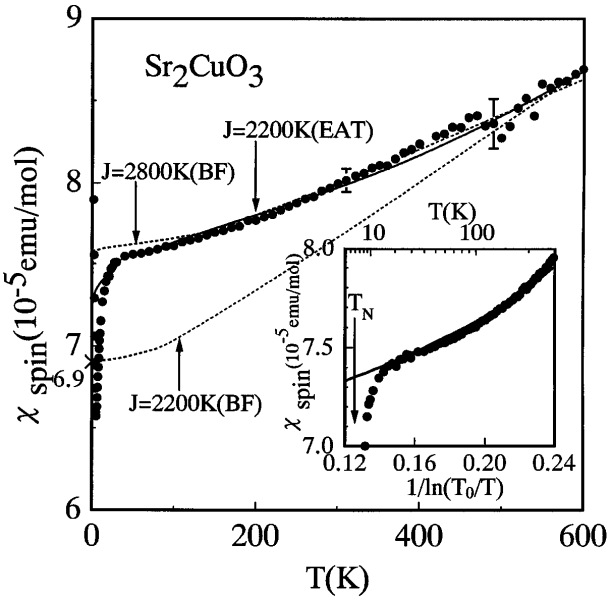

FIG. 4. χ_{spin} for Sr_2CuO_3 compared to theoretical calculations by EAT [3] with $J = 2200$ K (solid line) and by BF with $J = 2200$ and 2800 K (dotted line) in the temperature range below 600 K. The cross ($\times$) at $T = 0$ K indicates the theoretical susceptibility at $T = 0$ K for $J = 2200$ K. Inset: the experimental (dot) and theoretical (line) χ_{spin} as a function of $[\ln(T_0/T)]^{-1}$.

transition is also supported by the neutron scattering measurements by Ami *et al.* [6]. The other explanation should be necessary for understanding this susceptibility drop.

In the recent calculation by EAT, $\chi_{\rm spin}$ shows an asymptotic $(\ln T)^{-1}$ dependence at low temperature. They suggest that $\chi_{\rm spin}$ of the 1D AF $S = 1/2$ Heisenberg model at low temperatures below $\sim 0.1J$ has

$$J\pi^2\chi(T) = 1 + 1/[2\ln(T_0/T)], \qquad (2)$$

as far as the SU(2) and translational symmetry is preserved. In this formula, T_0 is a parameter which depends on the second nearest neighbor interaction. Without the second nearest neighbor interaction, $T_0 \sim 7.7J$. This $(\ln T)^{-1}$ dependence shows up as a rapid decrease to $\chi_{\rm spin}(0)$ with infinite slope, when the temperature is lower than $T \sim 0.01J$. In Sr_2CuO_3, such a rapid decrease is expected to occur below 20 K, considering the J value 2200 K. The observed drop at $\sim$20 K is consistent with this calculation. In Fig. 4 the comparison between the experimental result and EAT calculation with $J = 2200$ K and $T_0 = 7.7J$ is shown. The experimental $\chi_{\rm spin}$ shows a steep decrease at around 20 K with a minimum value 6.5×10^{-5} emu/mol, consistent with the EAT calculation which shows a rapid decrease at 20 K and ends up at $T = 0$ with 6.9×10^{-5} emu/mol. Considering these similarities, the isotropic drop in $\chi_{\rm spin}$ at low temperature is a direct observation of the asymptotic $(\ln T)^{-1}$ term calculated by EAT. A more quantitative comparison is made in the inset of Fig. 4, where $\chi_{\rm spin}$ is plotted against $[\ln(T_0/T)]^{-1}$. As can be seen, the experimental and theoretical result coincide with each other in the temperature range above $\sim$10 K. At the lowest temperature range the coincidence is not as good. The reason for this is the presence of the Néel order of $T_N \sim 5$ K, and also due to an ambiguity in subtracting the extrinsic Curie term from the experimental data. Indeed the coincidence can be improved by changing T_0 or introducing the Weiss temperature in order to fit the impurity contribution. However, it is difficult to determine all of these parameters uniquely by fitting the experimental data since there are too many adjustable parameters and the Néel transition should be taken into account. Considering the above mentioned items, the experimental result precisely reproduces the theoretical calculation over such a wide temperature range, from 10 to 800 K or higher. Therefore, Sr_2CuO_3 can be regarded as an almost ideal 1D AF Heisenberg system. The extremely large J favored the observation of the "low temperature" behavior at experimentally accessible temperatures ($T < 0.01J$). It was also favored by the absence of a spin-Peierls transition and the severe suppression of 3D long range AF order due to extremely weak interchain coupling.

In $SrCuO_2$, the corresponding low temperature feature is not observed. This is not due to the Curie contribution. In fact, the impurity concentration in $SrCuO_2$ is 0.018%, almost the same as that of Sr_2CuO_3, 0.013%. Therefore, if the low temperature drop were present in $SrCuO_2$, it should have been observed as in Sr_2CuO_3. This indicates that χ is qualitatively different between the two systems at low temperatures. As described before, in $SrCuO_2$, there exists the direct Cu-Cu exchange interaction J' together with the superexchange interaction J. At low temperatures, however, the interaction J' would have some effect. Since J' frustrates the intrachain AF coupling, it would resist against the decrease in χ. The result shown in Fig. 3 seems to be consistent with the speculation.

In summary, we have successfully grown high quality single crystals of Sr_2CuO_3 and $SrCuO_2$. By fitting the temperature dependence of χ with the recent theoretical calculation by EAT, it is demonstrated that both systems can be regarded as 1D $S = 1/2$ Heisenberg systems, and the exchange interaction J is estimated to be 2200 ± 200 K for Sr_2CuO_3 and 2100 ± 200 K for $SrCuO_2$, respectively. In addition, very small contamination together with the absence or strong suppression of a spin-Peierls or AF transition enable us to see the intrinsic $\chi_{\rm spin}$ in the low temperature region which is in excellent agreement with the rigorous theoretical calculation and the 1D $S = 1/2$ Heisenberg AF magnet in the case of Sr_2CuO_3. $SrCuO_2$ shows different χ at low temperatures. The difference may be ascribed to the direct Cu-Cu interaction in a zigzag chain.

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