# Observation of a Spin Gap in $SrCu_2O_3$ Comprising Spin-$\frac{1}{2}$ Quasi-1D Two-Leg Ladders

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Magnetic properties of $SrCu_2O_3$ and $Sr_2Cu_3O_5$, containing two-leg and three-leg $S = \frac{1}{2}$ ladders made of antiferromagnetic Cu-O-Cu linear bonds, were investigated. The susceptibility of the two-leg ladder material, $SrCu_2O_3$, is characteristic of thermal excitation from a nonmagnetic ground state with a spin gap of about 420 K, while the susceptibility of $Sr_2Cu_3O_5$, containing three-leg ladders, reflects a gapless spin excitation spectrum. The temperature dependence of the nuclear-spin lattice relaxation rate, $1/T_1$, of $^{63}$Cu NMR also indicates the existence of a spin gap only for $SrCu_2O_3$. The spin gap we observed for $SrCu_2O_3$ confirms a recent theoretical prediction for the magnetic behavior of spin $= \frac{1}{2}$ antiferromagnetically coupled Heisenberg chains.

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One-dimensional (1D) quantum spin systems exhibit various interesting magnetic phenomena, and the recent discoveries of the spin-Peierls transition in $CuGeO_3$ ($S = \frac{1}{2}$) [1] and the Haldane gap in $Y_2BaNiO_5$ ($S = 1$) [2] have raised keen interest in this field. The spin-Peierls transition results from an interplay of the spin system and the lattice, leading to a structural transition from a uniform antiferromagnetic chain toward dimerization, while the Haldane gap, taking place in antiferromagnetic Heisenberg chains of integer spins, has a purely electronic origin. Both these systems have nonmagnetic ground states with energy gaps in their spin excitation spectra, i.e., spin gaps. Daggoto *et al.* [3] have recently proposed an additional possible electronic mechanism for the formation of spin gaps. They argued that $S = \frac{1}{2}$ antiferromagnetically coupled chains (two-leg ladders) such as are found in $(VO_2)P_2O_7$ [4] should have a spin gap and that the ground state after hole doping should be either superconducting or a charge density wave.

$Sr_{n-1}Cu_{n+1}O_{2n}$ ($n = 3, 5, 7, \ldots$) is a homologous series of high pressure phases in which $Cu_{n+1}O_{2n}$ sheets alternate with $Sr_{n-1}$ sheets along the $c$ axes of their orthorhombic cells [5]. These $Cu_{n+1}O_{2n}$ sheets are obtained by shearing a regular $CuO_2$ sheet such that zigzag chains form periodically. In other words, the $CuO_2$ sheet is cut into strips (ladders) of $[(n + 1)/2]a$ in width, each containing $(n + 1)/2$ Cu ions in its width, and these strips are connected again so that the $CuO_4$ squares share edges at the interface. The $Cu_4O_6$ and $Cu_6O_{10}$ sheets for $n = 3$ and 5, respectively, are illustrated in Fig. 1. In each ladder, strong antiferromagnetic interactions should occur through the linear Cu-O-Cu bonds aligned along the $a$ and $b$ axes, while the interactions via 90° Cu-O-Cu bonds across the interface between ladders must be much weaker and may even be ferromagnetic [6]. Moreover, the shearing causes spin frustration due to the symmetry at the interface [5]. Thus, quasi-1D $S = \frac{1}{2}$ ladders with almost homogeneous intraladder antiferromagnetic interactions are realized for small-$n$ phases, with a dimensional crossover to 2D behavior expected with increasing $n$ value.

Recently, Rice *et al.* [6] theoretically investigated the nature of the ground states of these compounds and concluded that those with $n = 3, 7, 11, \ldots$ should be frustrated quantum antiferromagnets with spin liquid ground states. Light doping with holes is predicted to keep the spin gap open and lead to singlet superconductivity. In contrast, the phases with $n = 5, 9, 13, \ldots$ should have gapless ground states. The difference comes from whether there is an even or odd number of Cu ions in the width of a strip, i.e., whether the $(n + 1)/2$ legs are even or odd in number.

In order to find new quantum spin systems exhibiting interesting physics, and possibly high $T_c$ superconductivity, we have carefully synthesized the first two compounds with $n = 3$ ($Sr_2Cu_4O_6$ or $SrCu_2O_3$) and $n = 5$ ($Sr_4Cu_6O_{10}$ or $Sr_2Cu_3O_5$). Briefly reported here are the results of magnetic susceptibility measurements and $^{63}$Cu NMR measurements which reveal a dramatic difference in the magnetic ground state in the two- and three-leg ladder materials.

Polycrystalline samples were prepared from mixtures of $SrCuO_2$ (the ambient pressure form) and CuO in a cubic-anvil-type high pressure apparatus [7]. The samples were synthesized in $\frac{1}{2}$ h treatments at 4.5 GPa at 1373 K and 3 GPa at 1323 K for $SrCu_2O_3$ and $Sr_2Cu_3O_5$, respectively (for structural details see Ref. [5]). Samples, as characterized by powder x-ray diffraction, showed no trace of impurities except for small amounts of CuO. This magnetic impurity [8] could be eliminated by decreasing CuO content of the starting materials. Most probably, a small amount of CuO tended to remain intact, as a result of the insufficiency of the one-shot reaction under pressure. Magnetic measurements were performed with a SQUID magnetometer (Quantum Design MPMS) in a magnetic field of $10^4$ Oe on cooling from 650 to 5 K.

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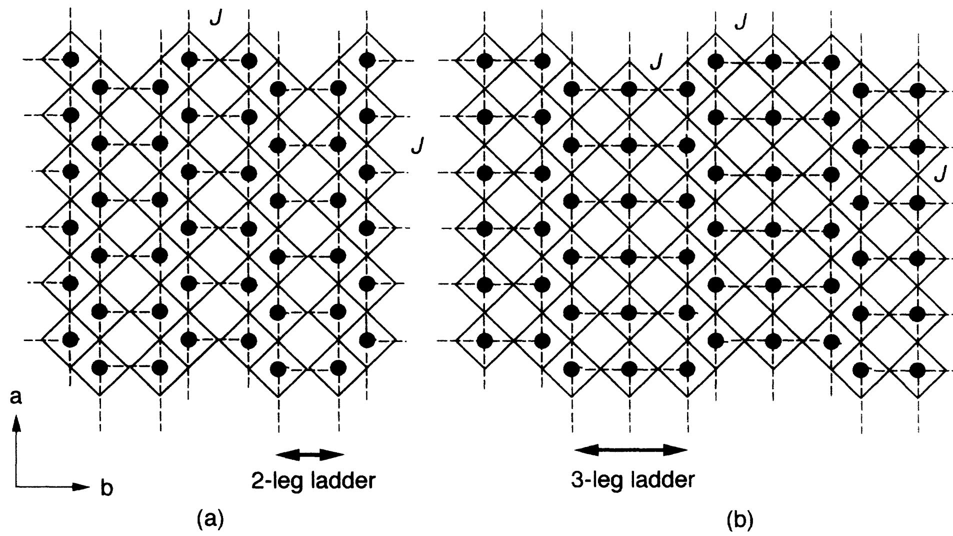


FIG. 1. Schematic drawings of the $Cu_2O_3$ sheet of $SrCu_2O_3$ (a) and the $Cu_3O_5$ sheet of $Sr_2Cu_3O_5$ (b). The filled circles are $Cu^{2+}$ ions, and $O^{2-}$ ions exist at the corners of the squares drawn with solid lines. Cu spins are strongly coupled with each other via an essentially uniform antiferromagnetic exchange within each ladder, while the ladders are separated from each other in effect because of the weakness of the exchange interaction via the 90° Cu-O-Cu bond plus the spin frustration due to symmetry at the interface.

Plotted with open circles in Fig. 2 is the temperature dependence of the magnetic susceptibility of a typical sample of $SrCu_2O_3$, where the data are normalized to 1 mol of Cu for convenience of comparison with $Sr_2Cu_3O_5$. The susceptibility decreases rapidly with decreasing temperature, while a Curie-like behavior appears clearly below 70 K. The data below 20 K were fitted to a Curie-Weiss law of

$$\chi = 9.86 \times 10^{-4}/(T + 2.03) \text{ emu/mol Cu}.$$

This small Curie component can be attributed to a contribution from 0.26% of $Cu^{2+}$ ions made free by lattice imperfections or impurity phases. After subtraction of the Curie term, a very small temperature independent susceptibility of $-4 \times 10^{-7}$ emu/mol Cu remains at low temperatures, 250 times smaller in magnitude than the susceptibility at 600 K and essentially zero within experimental resolution. The core diamagnetism for $SrCu_2O_3$ is estimated to be $-3.65 \times 10^{-5}$ emu/mol Cu by using literature values for $Sr^{2+}$, $Cu^{2+}$, and $O^{2-}$ and the Van Vleck paramagnetism to be $4.47 \times 10^{-5}$ emu/mol Cu, using NMR data concerning the isotropic orbital shift and $\langle r^{-3} \rangle$ ($r$: nucleus, $d$ electron distance) [9]. The sum of these, $8 \times 10^{-6}$ emu/mol Cu, is positive and considerably larger in magnitude than the low temperature experimental value mentioned above. However, we do not consider the difference to be significant, because the estimation itself includes some approximate factors such as $\langle r^{-3} \rangle$. As a first approximation, therefore, the intrinsic part of the susceptibility due to the $Cu^{2+}$ spin system ($\chi^{\text{bulk}}$) of $SrCu_2O_3$ is estimated by subtracting the Curie component and is plotted in Fig. 2 with closed circles. The continuous decrease of $\chi^{\text{bulk}}$ toward zero over a wide temperature range clearly suggests the presence of a large energy gap in the spin excitation spectrum.

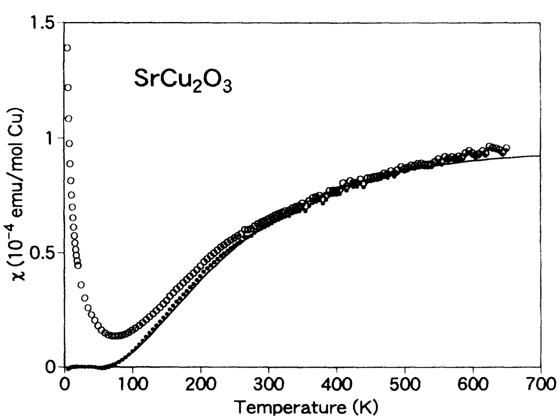


FIG. 2. Temperature dependence of magnetic susceptibility of $SrCu_2O_3$. The open circles are the experimental raw data, while the data after subtraction of the Curie component are shown as closed circles. The solid line represents the calculated susceptibility assuming a spin gap of 420 K, using the equation $\chi(T) \propto T^{-1/2}\exp(-\Delta/T)$ given in Ref. [10] (see text).

According to a recent theoretical study of the two-leg Heisenberg ladder system [10], the susceptibility as a function of temperature should be

$$\chi(T) = \alpha T^{-1/2}\exp(-\Delta/T),$$

if the intraladder interaction along the leg ($J$) is smaller than that along the rung ($J', J' > J$) and if the continuum of the first excited states has a parabolic dispersion. In this equation, $\alpha$ is a constant corresponding to the dispersion of the excitation energy, and $\Delta$ is the magnitude of the spin gap. Since we do not have an exact solution in which all the parameters needed to reproduce the behavior of the real system are included, such as $J'/J$, and the effect of weak interladder interactions along the $b$ and $c$ axes, we performed, as a tentative but rather realistic approach, the fitting of the experimental data to this equation. As seen in Fig. 2, the solid line calculated using $\Delta = 420$ K and $\alpha = 4 \times 10^{-3}$ reproduces the experimental data rather well.

Figure 3 shows the temperature dependence of observed (open circles) and corrected (closed circles) susceptibility of $Sr_2Cu_3O_5$, where the correction involves subtraction of the Curie component of magnitude

$$\chi = 2.35 \times 10^{-4}/(T + 1.51) \text{ emu/mol Cu}.$$

The corrected susceptibility (minus 0.06% free $Cu^{2+}$ spins) continuously decreases with decreasing temperature but remains at a large finite value of about $3.5 \times 10^{-5}$ emu/mol Cu at low temperatures, in contrast to the case of $SrCu_2O_3$. This suggests that the three-leg ladders in $Sr_2Cu_3O_5$ have a gapless spin excitation spectrum as expected theoretically.

A microscopic investigation by means of $^{63}Cu$ NMR also has revealed the existence of a spin gap in $SrCu_2O_3$ and will be reported in further detail elsewhere [9]. A very sharp peak appears, and the Knight shift varies with temperature in parallel with $\chi^{\text{bulk}}$ as shown in Fig. 4. An Arrhenius plot of the temperature dependence of the nuclear-spin lattice relaxation rate $1/T_1$, depicted in the inset of Fig. 4, shows that the spin gap is 680 K. Theoretically, the spin gap is calculated to be about $J/2$ $(= J'/2)$ [6,10]. Although an accurate value of the intraladder antiferromagnetic exchange is not known, this should be about 1300 K, judging from the resemblance of the ladder to the usual $CuO_2$ sheet with respect to the linear Cu-O-Cu bond configuration. The above magnitude of the spin gap is therefore approximately in

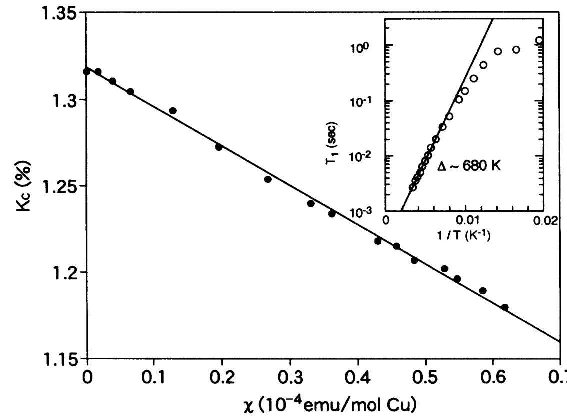


FIG. 4. $K$-$\chi$ plot of $SrCu_2O_3$. The Knight shift data were taken from a sample containing preferentially oriented ($c \parallel H$) powder. The orientation was carried out in a magnetic field of 11 T at room temperature, making use of a strong anisotropy in the orbital part of the susceptibility. The inset is an Arrhenius plot of the temperature dependence of the nuclear-spin lattice relaxation rate $1/T_1$, showing that the spin gap is 680 K.

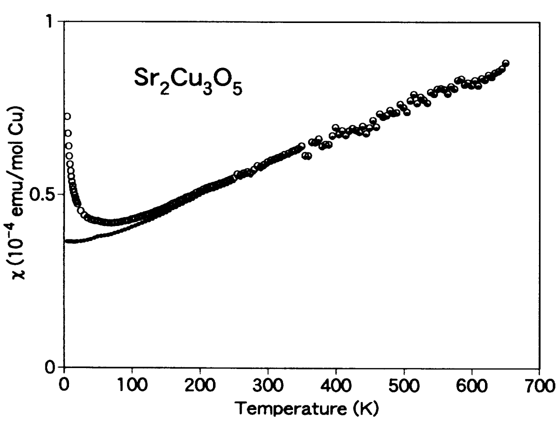


FIG. 3. Observed (open circles) and corrected (closed circles) magnetic susceptibility of $Sr_2Cu_3O_5$. The correction involves subtraction of the Curie component from the raw data. In contrast with the case of $SrCu_2O_3$, a large susceptibility remains at the lowest temperature after the correction.

agreement with the theoretical estimate, while the gap estimated by fitting the susceptibility data is considerably smaller than the expectation. The reason for the disagreement is not clear at the present stage.

In contrast with the case of the two-leg ladder system, $1/T_1$ of the three-leg system increases with decreasing temperature, and no NMR signal was detected below 100 K. As suggested by the magnetic measurement, $Sr_2Cu_3O_5$ does not have a spin gap, and therefore the magnetic coherence length should continue to increase down to the lowest temperature. This prevents us from observing an NMR signal below 100 K, by making the spin-echo decay rate $T_2$ too short.

In conclusion, we have observed a large spin gap in the two-leg ladder compound $SrCu_2O_3$, while $Sr_2Cu_3O_5$, comprising three-leg ladders is gapless, in good agreement with the conjecture of Rice *et al.*

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[1] M. Hase, I. Terasaki, and K. Uchinokura, Phys. Rev. Lett. **70**, 3651 (1993).

[2] J. Darriet and L. P. Regnault, Solid State Commun. **86**, 409 (1993).

[3] E. Dagotto, J. Riera, and D. Scalapino, Phys. Rev. B **45**, 5744 (1992).

[4] D. C. Johnston, J. W. Johnson, D. P. Goshorn, and A. J. Jacobson, Phys. Rev. B **35**, 219 (1987).

[5] Z. Hiroi, M. Azuma, M. Takano, and Y. Bando, J. Solid State Chem. **95**, 230 (1991).
[6] T. M. Rice, S. Gopalan, and M. Sigrist, Europhys. Lett. **23**, 445 (1993); S. Gopalan, T. M. Rice, and M. Sigrist, Phys. Rev. B **49**, 8901 (1994); M. Sigrist, T. M. Rice, and F. C. Zhang, Phys. Rev. B **49**, 12 058 (1994).
[7] M. Azuma, Z. Hiroi, M. Takano, Y. Bando, and Y. Takeda, Nature (London) **356**, 775 (1992).
[8] K. Muraleedharan, C. K. Subramaniam, N. Venkataramani, T. K. Gunda Rao, C. M. Srivastava, V. Sankaranarayanan, and R. Srinivasan, Solid State Commun. **76**, 727 (1990).
[9] K. Ishida, Y. Kitaoka, K. Asayama, M. Azuma, Z. Hiroi, and M. Takano (to be published).
[10] M. Troyer, H. Tsunetsugu, and D. Warts, Phys. Rev. B **50**, 13 515 (1994).