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High Pressure Synthesis and Magnetic Properties of Quasi One Dimensional Systems $Sr_{n-1}Cu_{n+1}O_{2n}$ (n=3, 5)

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$SrCu_2O_3$ and $Sr_2Cu_3O_5$ containing two-leg and three-leg S=1/2 ladders made of antiferromagnetic Cu-O-Cu linear bonds, respectively, were synthesized at high pressure, and their crystallographic properties were investigated. Susceptibility of the 3-leg ladder system, $SrCu_2O_3$, is characteristic of thermal excitation from a nonmagnetic ground state with a spin gap of 420 K, while $Sr_2Cu_3O_5$, containing 3-leg ladders, had a finite susceptibility at the lowest temperature reflecting gapless spin excitation spectrum. $SrCu_2O_3$ has thus been found to be the first 2-leg ladder compound having a well-defined spin gap.

KEY WORDS: High pressure synthesis/ Heisenberg S=1/2 ladder/ Spin gap/ Magnetic susceptibility

1. INTRODUCTION

One dimensional (1D) quantum spin systems exhibit various interesting magnetic phenomena, and the recent discoveries of the spin-Peierls transition in $CuGeO_3$ (S=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. On the other hand, Daggoto *et al.* proposed another electronic origin of spin gap. They argued that an antiferromagnetic S=1/2 coupled chains (2-leg ladder) such as are realized in $(VO_2)P_2O_7$[3] should have a spin gap and that the ground state after hole-doping would be superconducting or a charge density wave.[4]

$Sr_{n-1}Cu_{n+1}O_{2n}$ (n=3, 5, 7 ...) 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] as shown for the first two members $SrCu_2O_3$ and $Sr_2Cu_3O_5$ in Fig.1. Figure 2 shows a $Cu_{n+1}O_{2n}$ sheet which can be obtained by shearing a regular CuO_2 sheet so that zigzag chains form periodically. In other words, the CuO_2 sheet is cut into strips (ladders) of $(n+1)/2 \cdot a$ in width, each containing $(n+1)/2$ Cu ions in its width, and these strips are connected again so that the Cu ions share oxygen edges at the interface. In each strip strong antiferromagnetic interactions should work through the linear Cu-O-Cu bond stretched along the a and c axes, while the

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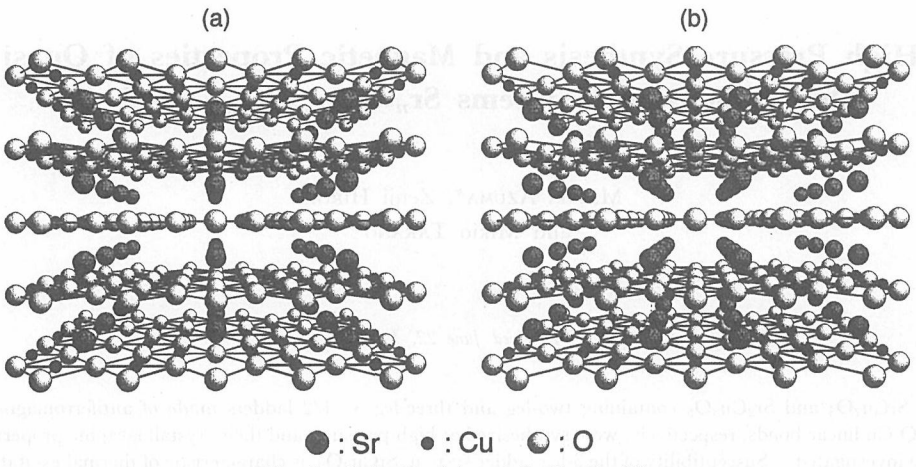

Fig. 1. $SrCu_2O_3$ (a) and $Sr_2Cu_3O_5$ (b).

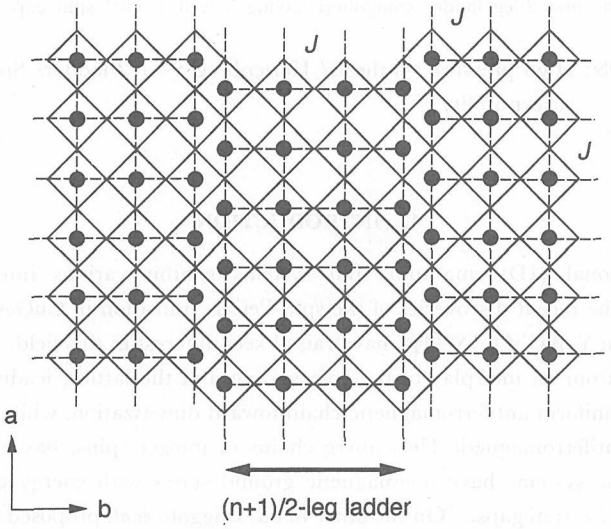

Fig. 2. Schematic drawing of the $Cu_{n+1}O_{2n}$ sheet of $Sr_{n-1}Cu_{n+1}O_{2n}$. The filled circles are Cu^{2+} ions, and O^{2-} ions exist at the corners of tge squares drawn with solid lines.

interactions via 90° Cu-O-Cu bonds across the interface must be much weaker, may even be ferromagnetic.[6] Moreover, the shearing causes spin frustration due to the symmetry at the interface.[5] Thus, a quasi-1D $S=1/2$ ladders with almost homogeneous intraladder antiferromagnetic interactions are realized for small-n phases and a dimensional crossover to 2D is expected with increasing n value.

Recently Rice *et al.*[6] investigated theoretically the nature of the ground states of these compounds and concluded that the stoichiometric compounds with $n=3$, 7, 11 ... would be frustrated quantum antiferromagnets with spin liquid ground states and that the spin gap would remain after light doping with holes. Occurrence of singlet superconductivity has thus been stressed. In contrast, phases with $n=5$, 9, 13 .... should have gapless ground states. The

difference comes from whether we have 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 out new quantum spin systems exhibiting interesting physics including high T_c superconductivity, we have carefully synthesized by using a high pressure technique the first two compounds with $n=3$ ($Sr_2Cu_4O_6$ or $SrCu_2O_3$) and $n=5$ ($Sr_4Cu_6O_{10}$ or $Sr_2Cu_3O_5$) containing 2- and 3-leg ladders, respectively. To be reported here briefly are the results of magnetic susceptibility measurements revealing the presence of a large spin gap for $SrCu_2O_3$ and gapless behavior of $Sr_2Cu_3O_5$.

2. EXPERIMENTAL

Polycrystalline samples were prepared from mixtures of $SrCuO_2$ *(the ambient pressure*

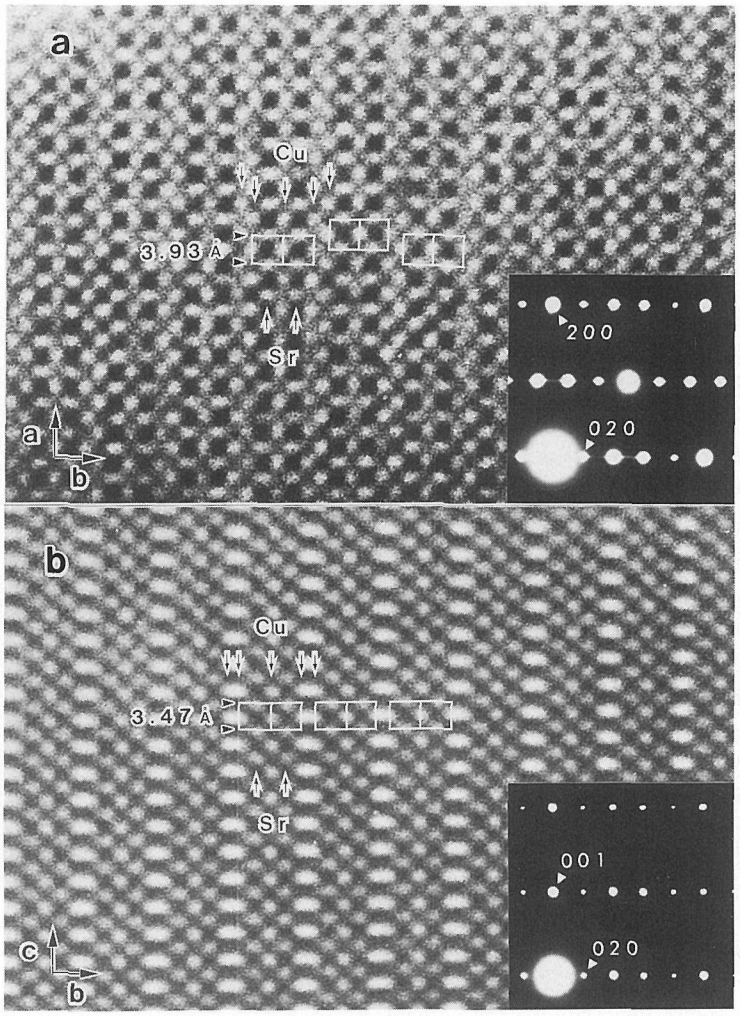

Fig. 3. High resolution electron microscopic images and the corresponding Electron diffraction patterns (inset) of $Sr_2Cu_3O_5$ along the c-axis (a) and the a-axis (b).

form) and CuO in a cubic anvil type high pressure apparatus.[7] Synthesis conditions were 4.5 GPa at 1373 K and 3 GPa at 1323 K for $SrCu_2O_3$ and $Sr_2Cu_3O_5$, respectively. Samples were characterized by Powder X-ray diffraction (XRD), electron diffraction (ED) and high-resolution electron michroscopy (HREM, JEM-2000EX). Crystal parameters were refined by a Rietvelt method using Rietan program.[8] Magnetic measurements were performed with a SQUID magnetometer (Quantum Design MPMS) in a magnetic field of 10^4 Oe on cooling from 650 K to 5 K.

3. RESULTS

3.1 *Crystallographic features*

Figure 3 shows the HREM images and corresponding ED patterns of $Sr_2Cu_3O_5$, from which its real-space structure as already illustrated in Fig. 1 and 2 can be seen. Two kinds of black dots are identified clearly in the charge density map reflecting the in-plane structure, Fig. 3(a); the large one is a Sr atom and the small one a Cu atom. In further detail, two different crystallographic sites are seen for Cu; one within a zigzag chain along the *a*-axis and the other between a pair of zigzag chains. In Fig. 3(b), which shows a cross-sectional view of the layer stacking, the Cu-Cu distance within chain is only about 1.9 Å. It is evident that both kinds of Cu sites are within a plane sandwiched by Sr layers. As seen from the HREM image in Fig. 4, the Cu-O sheet of $SrCu_2O_3$ is made of 2-leg ladders shifted by $a/2$ from each other.

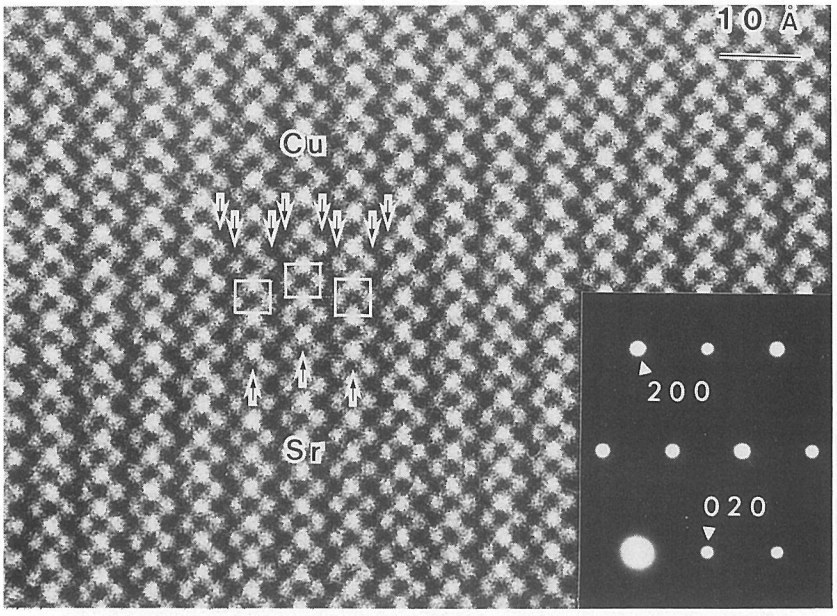

Fig. 4. High resolution electron microscopic images and the corresponding Electron diffraction patterns (inset) of $SrCu_2O_3$ along the *c*-axis.

Figure 5 shows observed (dots) and calculated (solid line) powder XRD patterns of $SrCu_2O_3$ and $Sr_2Cu_3O_5$. Tick marks represent the positions of possible Bragg refletions. In the excluded regions were small peaks due to CuO which remained in samples probably because of

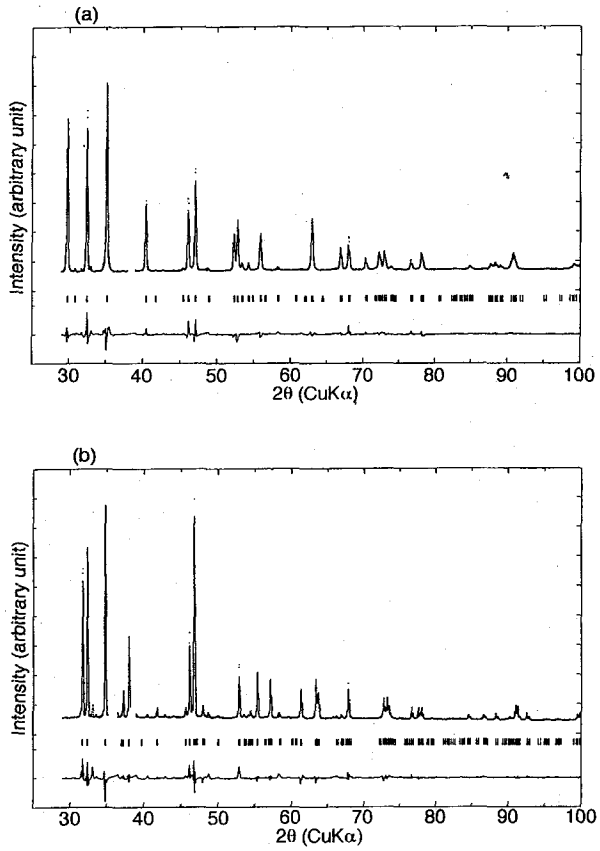

Fig. 5. Observed (dots) and calculated (solid line) powder XRD patterns of $SrCu_2O_3$ (a) and $Sr_2Cu_3O_5$ (b). Tick marks represent the positions of possible Bragg reflecitons.

insufficiency of the one-shot reaction under pressure. This magnetic impurity[9] could be eliminated by decreasing CuO content of the starting materials. Both samples were plate like crystals with a preferred orientation vector of (010). Refinement of the crystal structure were proceeded with space group Cmmm for both. Atomic coordinates were taken as follows : Sr, 2a (0, 0, 1/2) ; Cu, 4i (0, 1/3, 0) ; O, 2b (1/2, 0, 0) for $SrCu_2O_3$ and Sr, 4j (0, 1/10, 0) ; Cu1, 2a (0, 0, 0) ; Cu2, 4i (0, 1/5, 0) ; O1, 2b (1/2, 0, 0) ; O2, 4i (0, 1/10, 0), O3 (0, 3/10, 0) for $Sr_2Cu_3O_5$. The refinement was done in stages with thermal parameters held fixed in the initial calculations and allowed to vary only after the scale, background, halfwidth, preferred orientation and unit-cell parameters were convergent to their optimum values. Atomic coordinates, occupations and thermal parameters of oxygen were fixed during the refinement. The results of the refinement are summarized in Table 1.

3.2 *Magnetic propeties*

The temperature dependence of magnetic susceptibility of $SrCu_2O_3$ is plotted in Fig. 6, where the data are normarized at 1 mol of Cu for the comparison with $Sr_2Cu_3O_5$. The susceptibility rapidly decreases 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

Table 1. Crystal parameters of $SrCu_2O_3$ and $Sr_2Cu_3O_5$ refined by a Prietvelt method.

	$SrCu_2O_3$	$Sr_2Cu_3O_5$
Color	Black	
Radiation	CuKα (λ=1.5405 Å)	
Temperature (K)	290	
Monochromator	Graphite	
2θ range (°)	30 to 100	
Step width (°)	0.03	
Preset time (sec)	10	
Crystal system	Orthorombic	
Space group	Cmmm	
Lattice paraneters (Å)	a=3.9298 (1)	3.9302 (9)
	b=11.559 (9)	19.401 (0)
	c=3.4916 (3)	3.4605 (5)
B (Sr) (Å^2)	0.99 (6)	1.08 (5)
B (Cu1) (Å^2)	0.47 (4)	0.69 (2)
B (Cu2) (Å^2)		1.02 (7)
R_{wp} (%)	4.02	5.06
R_p (%)	2.51	3.72
R_e (%)	2.78	3.14
R_I (%)	3.87	6.56
R_F (%)	3.41	5.40

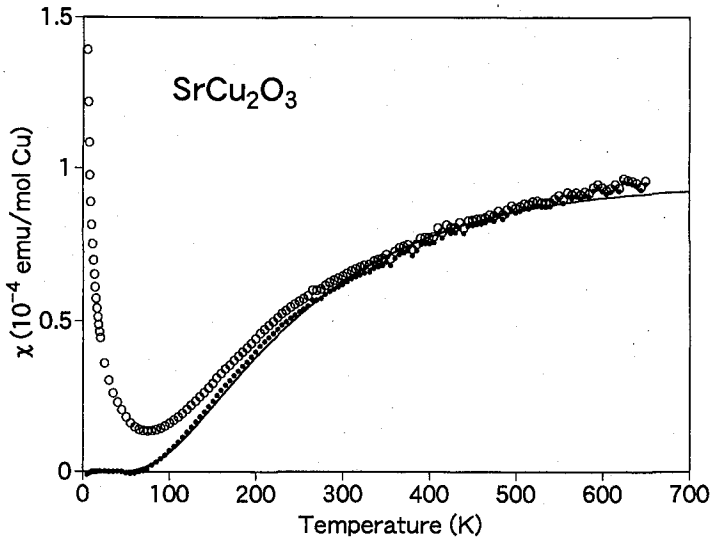

Fig. 6. Temperature dependence of the magnetic susceptibility of $SrCu_2O_3$. The open circles are the experimental raw data, while the data after subtraction of the Curie component and the small orbital contribution are given with the dark dots. Solid line stands for the calculated susceptibility assuming the spin gap of 420 K using an equation $\chi(T) \propto T^{-1/2} \exp(-\Delta/T)$ given in Ref. 10 (see text).

$\chi=9.86\times10^{-4}/(T+2.03)$ 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. After subtraction of the Curie term, a temperature independent susceptibility of -4.05×10^{-7} emu/mol Cu remains at low temperature, which may be due to the sum of the Van Vleck paramagnetism and ionic diamagnetism, each of the order of 10^{-5} emu/mol Cu. The intrinsic part of the susceptibility due to the Cu^{2+} spin system (χ^{bulk}) of $SrCu_2O_3$ was thus obtained by subtracting the Curie component and the constant term and are plotted in Fig. 6 with dots. The continuous decrease of χ^{bulk} toward zero over a wide temperature range suggests a large energy gap in the spin excitation spectrum.

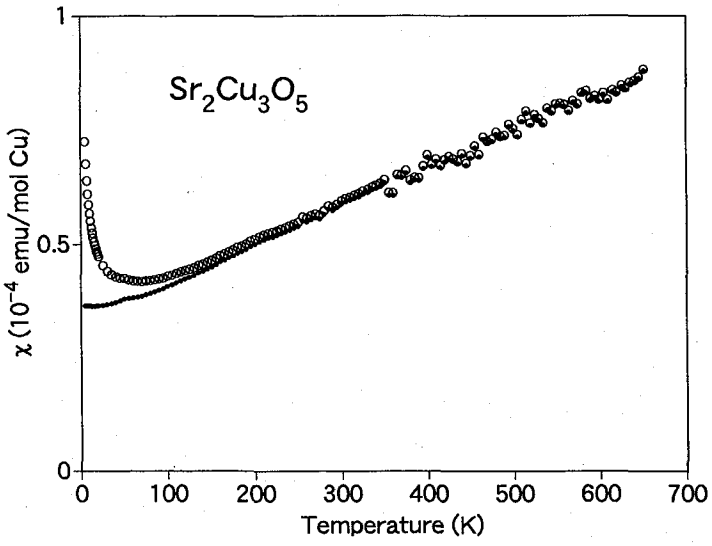

Fig. 7. Observed (open circles) and corrected (dots) magnetic susceptibility of $Sr_2Cu_3O_5$. The correction means subtraction of the Curie component from the raw data. In contrast with the case of $SrCu_2O_3$, a relatively large susceptibility remains at the lowest temperature after the correction.

Figure 7 shows the temperature dependence of observed (open circles) and corrected (dots) susceptibility of $Sr_2Cu_3O_5$, where the correction means subtraction of the Curie component only. The corrected susceptibility continuously decreases with decreasing temperature but remains at a large finite value of about 3.5×10^{-5} emu/mol Cu at low temperature in contrast to the case of $SrCu_2O_3$. This suggests that the 3-leg ladders in $Sr_2Cu_3O_5$ have a gapless spectrum as expected theoretically.

4. DISCUSSION

According to quite a recent theoretical study of 2-leg Heisenberg ladder system, the susceptibility is given as a function of temperature with the equation

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

if the intraladder interaction along the leg (J) is smaller than the rung ($J', J' > J$) and if the continuum of the first excited states has a parabolic dispersion. In this equation, α is a constant corresponding to the dispersion of the excitation energy and Δ is the magnitude of the spin gap.[10] We have performed the fitting of the obtained susceptibility data as shown in Fig. 6 with a solid line and obtained a spin gap value of 420 K. A microscopic investigation by means of ^{63}Cu NMR also has revealed the existence of a spin gap in $SrCu_2O_3$. A very sharp peak appeared and the Knight shift varied with temperature in parallel with χ^{bulk}. Interestingly, however, T_1 data have shown that the spin gap is 700 K as reported in detail elsewhere.[11] Theoretically the spin gap is calculated to be about $J/2$.[6,10] Although the accurate value of the intraladder antiferromagnetic exchange J is not known, it would be about 1,300 K as judged from the resemblance of the ladder to the usual CuO_2 sheet with respect to the linear Cu-O-Cu bond configuration. So, the magnitude of spin gap obtained from the T_1 data is in quantitative agreement with the theoretical estimation, but the gap estimated by the susceptibility measurement is considerably smaller than the expectation, but the reason is not clear.

In conclusion, we have observed a large spin gap in the 2-leg ladder compound $SrCu_2O_3$, while $Sr_2Cu_3O_5$ comprising 3-leg ladders is gapless, in good agreement with Rice's conjecture.

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