

High Pressure Synthesis and Magnetic Studies of Quasi One Dimensional Systems $\text{Sr}_{n-1} \text{Cu}_{n+1} \text{O}_{2n}$ ($n = 3, 5$)

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ABSTRACT

SrCu_2O_3 and $\text{Sr}_2\text{Cu}_3\text{O}_5$ 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 and magnetic properties were investigated. Both susceptibility and T_1 data of NMR revealed the existence of a large spin gap only for SrCu_2O_3 . Superconductivity, which had been predicted theoretically for carrier-doped SrCu_2O_3 could not be realized although partial substitution of La^{3+} for Sr^{2+} seemed to be carried out successfully. Electron carriers injected seems to remain localized.

INTRODUCTION

$\text{Sr}_{n-1} \text{Cu}_{n+1} \text{O}_{2n}$ ($n = 3, 5, 7, \dots$) is a homologous series of high pressure phases in which $\text{Cu}_{n+1} \text{O}_{2n}$ sheets alternate with Sr_{n-1} sheets along the c axes of their orthorhombic cells [1] as shown for the first two members SrCu_2O_3 and $\text{Sr}_2\text{Cu}_3\text{O}_5$ in Fig.1. Figure 2 specifically shows a $\text{Cu}_{n+1} \text{O}_{2n}$ 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

Occurrence of singlet superconductivity has thus been stressed. In contrast, phases with $n = 5, 9, 14..$ would 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 which they called a spin ladder with $(n-1)/2$ rungs and $(n+1)/2$ legs.

In order to find out new quantum spin systems exhibiting interesting physics including high T_c superconductivity, we have carefully synthesized by a using high pressure technique the first two compounds with $n = 3$ ($\text{Sr}_2\text{Cu}_4\text{O}_6$ or SrCu_2O_3) and $n = 5$ ($\text{Sr}_4\text{Cu}_6\text{O}_{10}$ or $\text{Sr}_2\text{Cu}_3\text{O}_5$) 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 $\text{Sr}_2\text{Cu}_3\text{O}_5$, which have been supported by ^{63}Cu NMR measurements. Partial substitution of La^{3+} for Sr^{2+} was also attempted in order to dope SrCu_2O_3 with electrons and make it superconducting. Lattice parameters were changed systematically by the substitution, but no trace of superconductivity was observed.

SAMPLE PREPARATION

Polycrystalline samples were prepared from mixtures of SrCuO_2 (the ambient pressure form), La_2O_3 and CuO in a cubic anvil type high pressure apparatus [3]. Synthesis conditions were 4.5 GPa at 1373 K and 3 GPa at 1323 K for SrCu_2O_3 and $\text{Sr}_2\text{Cu}_3\text{O}_5$, respectively. Samples were characterized by Powder X-ray diffraction (XRD), electron diffraction (ED) and high-resolution electron microscopy (HREM, JEM-2000EX).

RESULTS

Figure 3 shows the HREM images and the corresponding ED patterns of $\text{Sr}_2\text{Cu}_3\text{O}_5$, in which its in-plane structure as illustrated in Fig. 2 can be seen. Two kinds of black dots are identified clearly; 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 located on the first and the third legs of the ladders and the other on the second leg.

Figure 4 shows powder XRD patterns of SrCu_2O_3 and $\text{Sr}_2\text{Cu}_3\text{O}_5$. All the intense peaks could be indexed assuming the orthorhombic cells of $a=3.930\text{\AA}$, $b=11.560\text{\AA}$, $c=3.492\text{\AA}$ and $a=3.932\text{\AA}$, $b=19.411\text{\AA}$, $c=3.462\text{\AA}$, respectively.

interactions should work through the linear Cu-O-Cu bond stretched along the a and c axes, while the interactions via 90° Cu-O-Cu bonds across the interface must be much weaker, may even be ferromagnetic [2]. Moreover, the shearing causes spin frustration by symmetry at the interface [1]. 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.

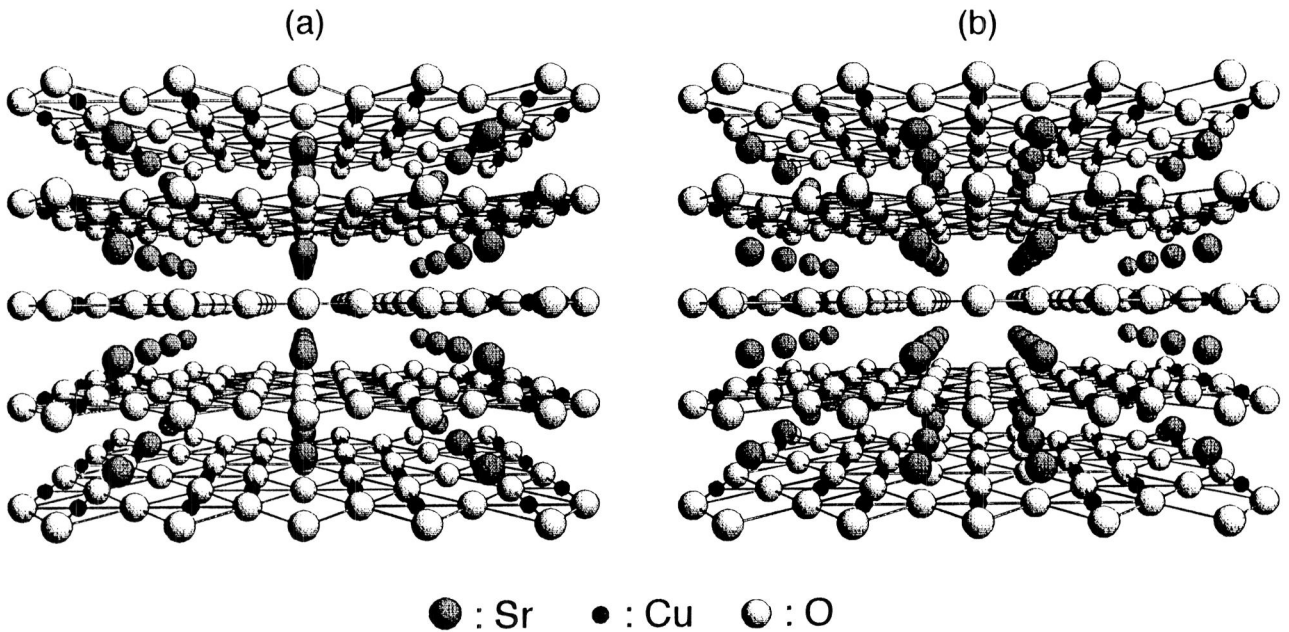


Fig. 1 Schematically illustrated structures of SrCu_2O_3 (a) and $\text{Sr}_2\text{Cu}_3\text{O}_5$

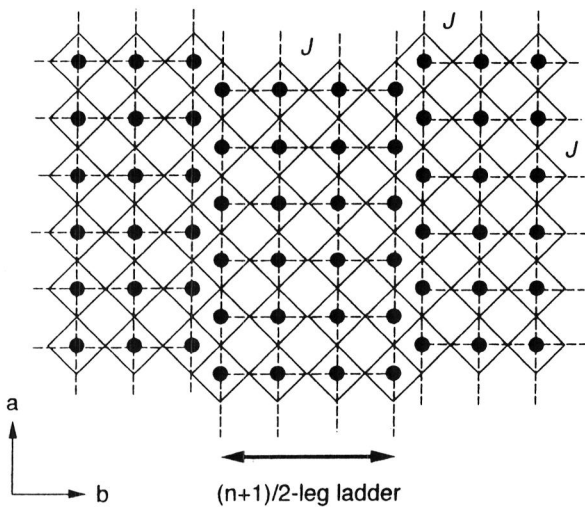


Fig. 2 Schematic drawings of the $\text{Cu}_{n+1}\text{O}_{2n}$ sheet of $\text{Sr}_{n-1}\text{Cu}_{n+1}\text{O}_{2n}$. The filled circles are Cu^{2+} ions, and O^{2-} ions exist at the corners of the squares drawn with solid lines.

Recently Rice *et al.* [2] investigated theoretically the nature of the ground states of these compounds and concluded that the stoichiometric compounds with $n = 3, 7, 11\dots$ would be frustrated quantum antiferromagnets with spin liquid ground states and that the spin gap would remain after light doping with holes.

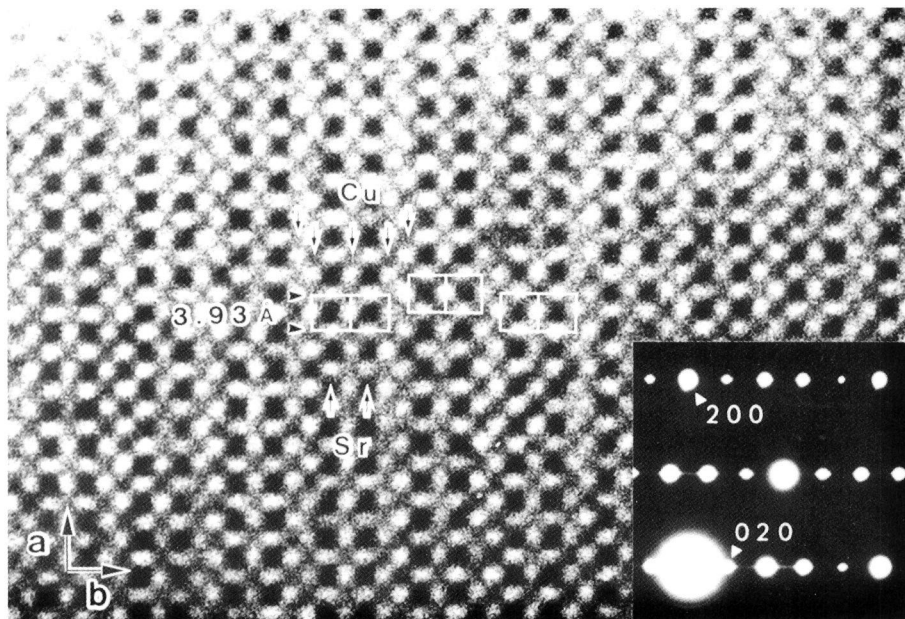


Fig. 3 High resolution electron microscopic image and the corresponding Electron diffraction patterns (inset) of $\text{Sr}_2\text{Cu}_3\text{O}_5$.

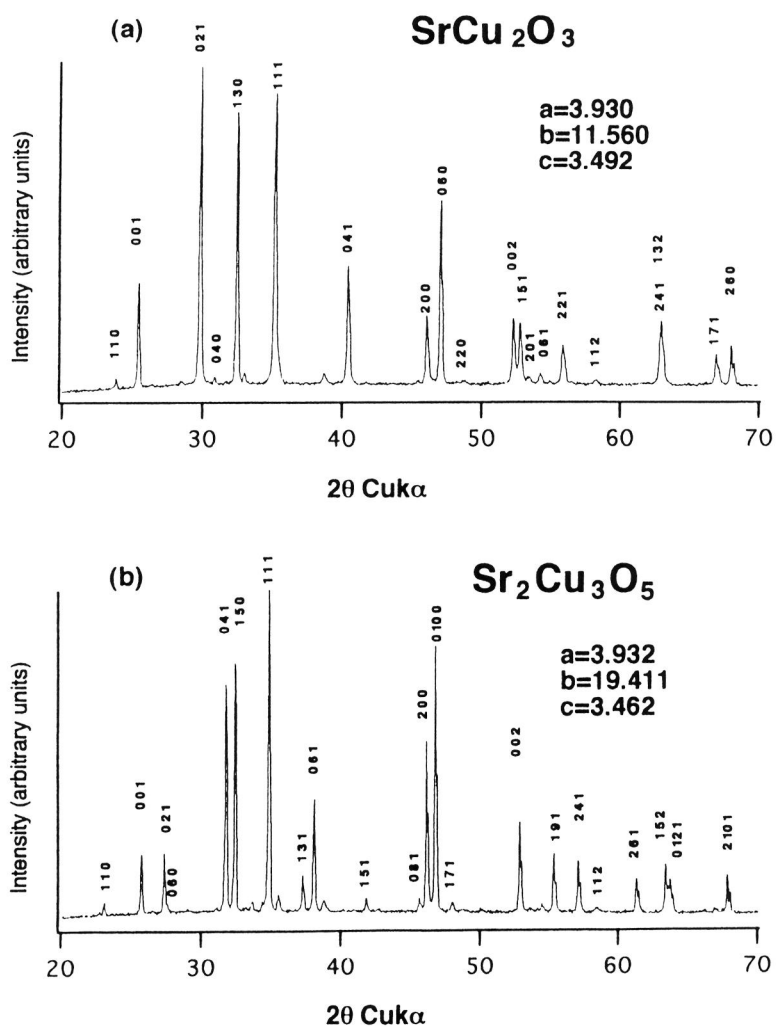


Fig. 4 Powder X-ray diffraction patterns of SrCu_2O_3 (a) and $\text{Sr}_2\text{Cu}_3\text{O}_5$ (b).

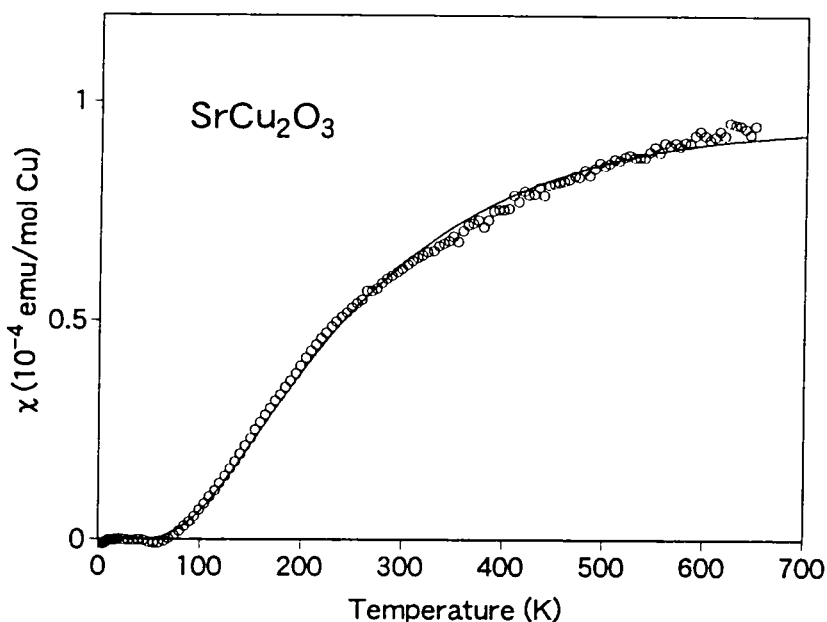


Fig.5 Temperature dependence of magnetic susceptibility of SrCu_2O_3 after subtraction of the Curie component and the small orbital contribution. Solid line stands for the calculated susceptibility assuming a spin gap of 420 K using an equation $\chi(T) \propto T^{1/2} \exp(-\Delta / T)$ given in ref. 5.

The temperature dependence of magnetic susceptibility of SrCu_2O_3 is plotted in Fig. 5 after the subtraction of a Curie component due to Cu^{2+} ions made free by lattice imperfections and also a small constant term due to Van Vleck paramagnetism and ionic diamagnetism [4]. The data are normalized at 1 mol of Cu for convenience of comparison with $\text{Sr}_2\text{Cu}_3\text{O}_5$. The continuous decrease of susceptibility toward zero over a wide temperature range suggests a large energy gap in the spin excitation spectrum. According to quite a recent theoretical study of the 2-leg Heisenberg ladder system, susceptibility is given as a function of temperature and the magnitude of the spin gap, Δ , with an equation

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

if the intraladder interaction is homogenous and if the continuum of the first excited states has a parabolic dispersion [5]. We have performed the fitting of the obtained susceptibility data as shown in Fig. 5 with the solid line and obtained $\Delta = 420$ K.

Figure 6 shows the temperature dependence of Curie-term subtracted susceptibility of $\text{Sr}_2\text{Cu}_3\text{O}_5$. The susceptibility continuously decreases with

decreasing temperature but remains at a large finite value of about 3.5×10^{-5} emu/mol Cu at 0 K in contrast to the case of SrCu_2O_3 . This suggests that the 3-leg ladders in $\text{Sr}_2\text{Cu}_3\text{O}_5$ have a gapless spin excitation spectrum as expected theoretically.

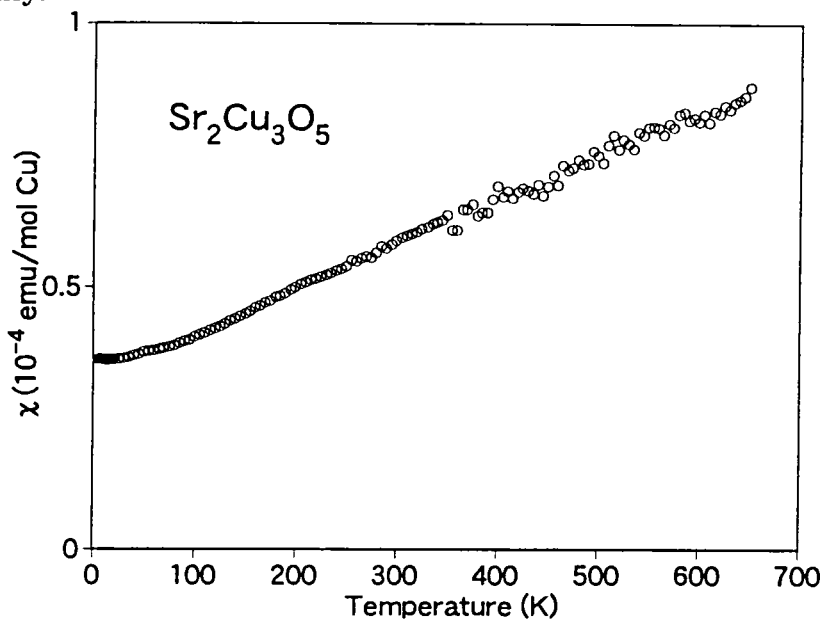


Fig. 6 Temperature dependence of magnetic susceptibility of $\text{Sr}_2\text{Cu}_3\text{O}_5$ after subtraction of the Curie component from the raw data. In contrast with the case of SrCu_2O_3 , a relatively large susceptibility remains at the lowest temperature after the correction.

A microscopic investigation by means of ^{63}Cu NMR also has revealed the existence of a spin gap in SrCu_2O_3 [6]. A very sharp peak appeared and the Knight shift varied with temperature in parallel with χ . Interestingly, however, the Arrhenius plot of T_1 data has shown that the spin gap is 680 K as shown in Fig. 7. Fitting the T_1 data to a refined theoretical equation [5],

$$1/T_1 \propto (0.80908 - \ln(0.003/T)) \cdot \exp(-\Delta / T)$$

gives almost the same value of 700 K. Theoretically the spin gap is calculated to be about $J/2$ [2,5]. Although the accurate value of the intraladder antiferromagnetic exchange J is not known, it would be about 1300 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, while the gap estimated

by the susceptibility measurement is considerably smaller than the expectation. The reason is not clear at the present stage.

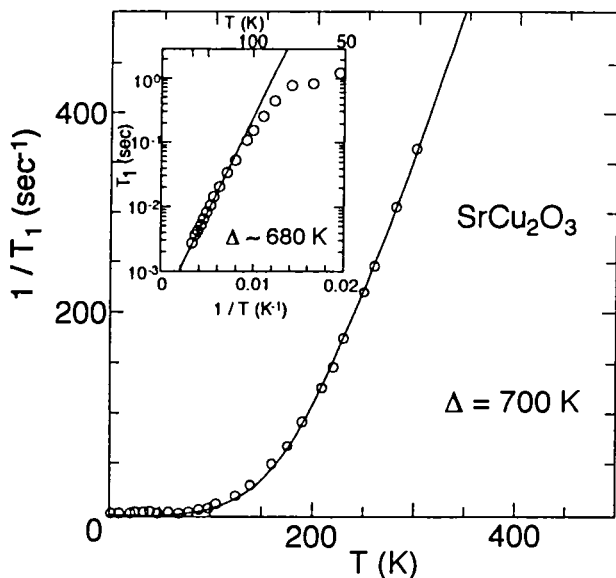


Fig 7 Temperature dependence of $1/T_1$ fitted to a refined theoretical equation assuming a spin gap of 700 K. Inset is the Arrhenius plot of T_1 of SrCu_2O_3 from which the magnitude of the spin gap is estimated to be 680 K.

Following Rice *et al.*'s conjecture suggesting the occurrence of superconductivity in carrier-doped SrCu_2O_3 , we attempted to dope SrCu_2O_3 with electron carriers by substituting La^{3+} for Sr^{2+} . Lattice parameters of $\text{Sr}_{1-x}\text{La}_x\text{Cu}_2\text{O}_3$ are plotted in Fig. 8 for the a and c axes. The length of the c axis shrinks with the substitution, while the a -parameter expands, reflecting the electrons being added into the antibonding $\sigma_{x^2-y^2}$ orbitals of the Cu_2O_3 sheet. Unfortunately, however, no trace of superconductivity was

observed. Injected electrons seemed to be localized randomly.

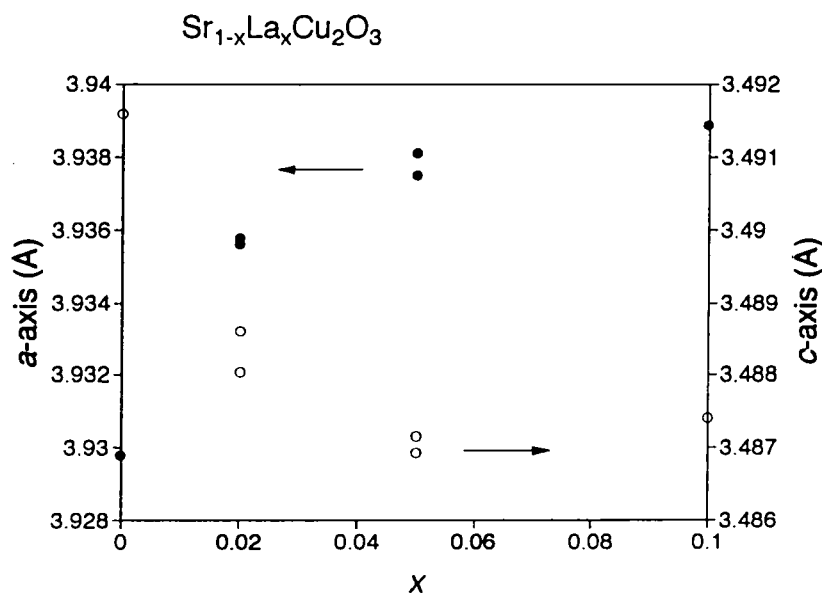


Fig. 8 Lattice parameters of $\text{Sr}_{1-x}\text{La}_x\text{Cu}_2\text{O}_3$

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