Competition between the singlet-spin liquid state and the magnetic ground state in a two-chain spin-$\frac{1}{2}$ antiferromagnetic ladder compound $LaCuO_{2.5}$: A ^{63}Cu NMR study

S. Matsumoto, Y. Kitaoka, K. Ishida, and K. Asayama
Department of Material Physics, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

Z. Hiroi, N. Kobayashi, and M. Takano
Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611, Japan

(Received 5 February 1996)

The magnetic characteristics of $LaCuO_{2.5}$ comprising an antiferromagnetic two-chain spin-$\frac{1}{2}$ ladder have been investigated by ^{63}Cu NMR measurements. The ground state of this compound was suggested from susceptibility measurements to be the singlet-spin liquid state. The present experiments have, however, revealed that $LaCuO_{2.5}$ is not in such a spin-liquid state, but rather a magnetic ordering takes place below $T_N \sim$ 110 K as evidenced by the large enhancement of the nuclear spin-lattice relaxation rate, $(1/T_1)$ and of the spin-echo decay rate, $1/T_2$ leading to the disappearance of the Cu NMR signal. This magnetic ordered state has been found to be suppressed by substituting Sr for La by 5%, i.e., by hole doping. [S0163-1829(96)51418-9]

The study of low-dimensional spin-$\frac{1}{2}$ antiferromagnets (AF) has drawn much interest since the discovery of high T_c in lightly doped cuprates of two-dimensional (2D) square lattice. A square lattice has a magnetically ordered ground state with a reduction of the ordered moment[1] and a true long-range order is destroyed by doping holes slightly. In the one-dimensional AF Heisenberg chain, the quantum effects overwhelm the long-range order but the ground state has a quasi-long-range nature with an inverse power-law decay in the spin-spin correlation function. What happens in the intermediate system between 1D and 2D systems? An answer was first given by numerical calculations which found that the crossover from chains to square lattices was far from smooth.[2,3] In such quasi-1D systems that have chains coupled with one next to the other to form ladders of increasing width, ladders with an even number of chains have a spin liquid ground state because of their short-range spin correlation decayed exponentially and then a finite spin gap is produced with its magnitude reduced progressively with an increase of chains.[3,4] By contrast, ladders made from an odd number of chains display magnetic properties similar to single chain, i.e., gapless spin excitation with a power-law decay of spin-spin correlations.

As a matter of fact, the presence of a spin gap was confirmed experimentally in such two-chain ladder compounds as $(VO)_2P_2O_7$ (Ref. 5) and $SrCu_2O_3$ (Refs. 6 and 7). By contrast, the three-chain ladder $Sr_2Cu_3O_5$ exhibited long-range development of the spin correlation upon lowering temperature and as a result the long-range order emerged around 60 K due to the weak interladder interaction and/or the interlayer coupling.[8,9] There is thus excellent consensus between theory and experiment confirming a dramatic difference between spin-$\frac{1}{2}$ Heisenberg AF even and odd ladders.

More interestingly, holes doped into ladders with even number chains are predicted to pair[2,10] and possibly superconduct or form bipolarons.[11] A clear contrast between even and odd ladders is again predicted upon doping. Doped even ladders are especially outstanding because hole pairing possibly belongs to a different universality class of 1D system than the Tomonaga-Luttinger liquid found in doped single and odd ladders. Because of the difficulty of carrier doping, $La_{1-x}Sr_xCuO_{2.5}$ has been the first system[12] where holes were doped into two-chain ladders. From the T dependence of the susceptibility very similar to that observed in $SrCu_2O_3$ (Ref. 6), $LaCuO_{2.5}$ was reported to be another model system of the two-chain ladder with a spin gap.[12] An insulator to metal transition was observed with increasing Sr content, but no superconducting transition took place down to 5 K.[12]

In this paper, the Cu NMR study is reported in order to clarify magnetic properties in the two-chain ladder compound $LaCuO_{2.5}$ and the Sr-doped compounds, $La_{1-x}Sr_xCuO_{2.5}$ with $x=0.025$ and 0.05. From the present experiment it is, however, shown that the parent compound $LaCuO_{2.5}$ is unexpectedly not in the spin gap ground state, but instead in a magnetically ordered state at low-T below $\sim$110 K, which is sensitive to Sr (holes) doping, suppressed by substituting Sr for La by 5%.

We used the same polycrystalline samples for the NMR measurement as in the previous work, where the detailed procedures to prepare the sample were reported.[12] The crystal structure of $LaCuO_{2.5}$ is one of the prototypes of anion-deficient perovskites with orthorhombic structure where $a \sim \sqrt{2}a_p$, $b \sim 2\sqrt{2}a_p$, $c \sim a_p$ (a_p is the lattice parameter of the primitive perovskites structure). Figure 1(a) indicates the perspective view of the structure projected to the a-b plane in which the La coordination is omitted. Two-chain ladders are along the c axis where the distances of linear Cu-O bonds within ladders shown by the thick solid lines are short (1.95 Å), whereas the distances of Cu-O_{apex} bonds among ladders indicated by the dashed lines are long (2.29 Å). These unbalanced Cu-O bonds lead to a strong AF interaction of order 10^3 K for the intraladder 180° Cu $(3d_{x^2-y^2})$-O $(2p_\sigma)$-Cu $(3d_{x^2-y^2})$ bonds as in $SrCu_2O_3$ indicated in Fig. 1(b), but lead to a weak interaction for the interladder 152.2° Cu-O_{apex}-Cu bonds indicated by the dashed lines. In contrast to this complicated coupling *among*

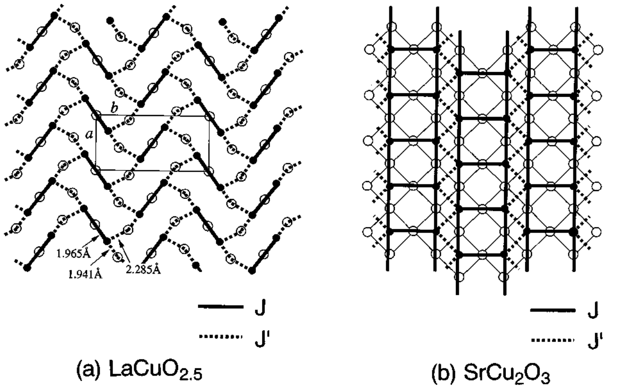

FIG. 1. (a) Perspective view of structure of $LaCuO_{2.5}$ projected to the a-b plane in which La coordination is omitted and two-chain ladders are along the c axis. (b) Structure of $SrCu_2O_3$ projected to the a-b plane in which Sr layers are stacked along the c axis and two-chain ladders are along the b-axis.

ladders in $LaCuO_{2.5}$, each ladder in $SrCu_2O_3$ is coupled through the 90° Cu-O-Cu bond at the interface *between* ladders as indicated by dashed lines in Fig. 1(b) and hence the interaction across the interface between ladders must be ferromagnetic.[6] Furthermore, the shearing causes spin frustration due to the symmetry at the interface [see dashed lines in Fig. 1(b)]. This may be one of the reasons why the experimental value of the spin gap ($\Delta = 450 \sim 650$ K) in $SrCu_2O_3$ (Refs. 6 and 7) is in agreement with the theoretical prediction calculated to be about $J/2 \sim 650$ K on the assumptions that the interladder interaction is ignored and J is nearly 1300 K for the linear Cu-O-Cu bond in the square lattice.[2,3] Consequently, this difference of interladder interaction turns out to lead to a contrast of ground states between $SrCu_2O_3$ and $LaCuO_{2.5}$.

Commonly in $SrCu_2O_3$ and $LaCuO_{2.5}$, the temperature dependence of the susceptibility was well fitted to the following relation:

$$\chi(T) = \chi_0 + \frac{C}{(T-\theta)} + \alpha \frac{1}{\sqrt{T}} \exp\left(-\frac{\Delta}{T}\right), \tag{1}$$

where χ_0 is a T-independent term and the second is a Curie-Weiss contribution ascribed to impurities and/or Cu^{2+} ions. The third represents the bulk spin susceptibility inherent to the two-chain $S=\frac{1}{2}$ ladder, where α is a constant factor and Δ is the magnitude of the spin gap. The values are obtained as $\chi_0 = -4\times10^{-7}$ and -3.8×10^{-6} emu/mole Cu, $C = 9.86\times10^{-4}$ and 14.2×10^{-4} emu/mole Cu, $\theta = -2$ and -5 K, $\alpha = 4\times10^{-3}$ and 4.11×10^{-3}, and $\Delta = 420$ and 473 K for $SrCu_2O_3$ (Ref. 6) and $LaCuO_{2.5}$ (Ref. 12), respectively. Apparently, all these values are quite similar to one another, indicative of a large reduction of the spin susceptibility associated with the development of the spin-gap state with lowering temperature for both compounds.

The Cu NMR measurements have been made in a T range of 4.2–300 K at a constant frequency of 125.1 MHz by using a homemade coherent pulsed NMR spectrometer. The NMR spectrum was obtained by sweeping the magnetic field generated by a superconducting magnet (12 T at 4.2 K). The nuclear spin-lattice relaxation time T_1 was measured by the saturation recovery method with a single T_1 component. The spin-echo exponential decay rate $1/T_2$ was obtained by plotting the spin-echo intensity $M(2\tau)$ as function of time duration τ between the first and second rf pulses as follows:

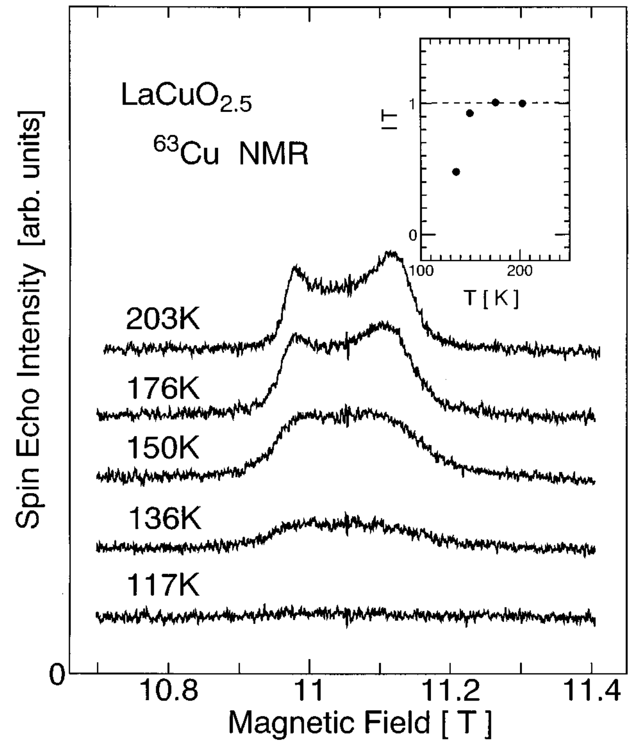

FIG. 2. T dependence of ^{63}Cu NMR spectrum for $LaCuO_{2.5}$ taken at 125.1 MHz. Inset indicates the T dependence of integrated Cu NMR intensity multiplied by temperature.

$$M(\tau) = M(0)\exp\left(-\frac{2\tau}{T_2}\right).$$

Figure 2 illustrates the T dependence of the ^{63}Cu NMR spectrum, which arises from the $(\frac{1}{2} \leftrightarrow -\frac{1}{2})$ transition split into two peaks by the second-order electric-quadrupole effect with the nuclear quadrupole frequency, $\nu_Q = 20$ MHz. With lowering temperature, the spectrum does not shift at all, but starts to broaden and its integrated intensity multiplied by temperature is progressively reduced below around 150 K as indicated in the inset of Fig. 2. As displayed in Fig. 3, since $1/T_2$ is largely enhanced below 150 K, its intensity is evaluated from an extrapolation to $\tau = 0$ for the spin-echo decay curve. Nevertheless, the total Cu sites whose NMR signals are observed are significantly reduced upon cooling. This is considered because spin-spin correlations and/or a short-range order begin to markedly develop towards a possible magnetic transition temperature, making it difficult to observe the NMR signal partially. As a result the NMR signal disappears near ~ 117 K. Correspondingly to these anomalies of the NMR spectrum and $1/T_2$, the T dependence of $^{63}(1/T_1)$ in $LaCuO_{2.5}$ does not bear resemblance at all to the typical spin-gap behavior observed in $SrCu_2O_3$ indicated together in Fig. 4.[7] $^{63}(1/T_1)$ decreases down to 230 K being in the process of seemingly forming a spin-gap-like state, but it tends to be constant and begins to be enhanced below

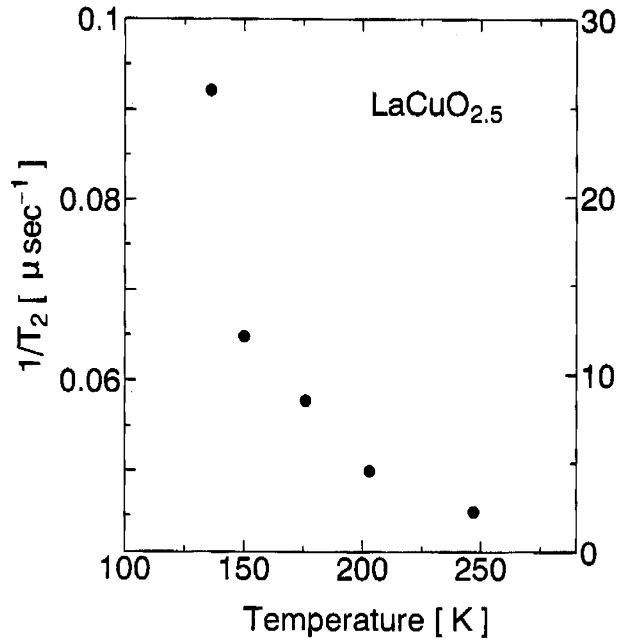

FIG. 3. T dependence of the exponential spin-echo decay rate, $1/T_2$, in $LaCuO_{2.5}$.

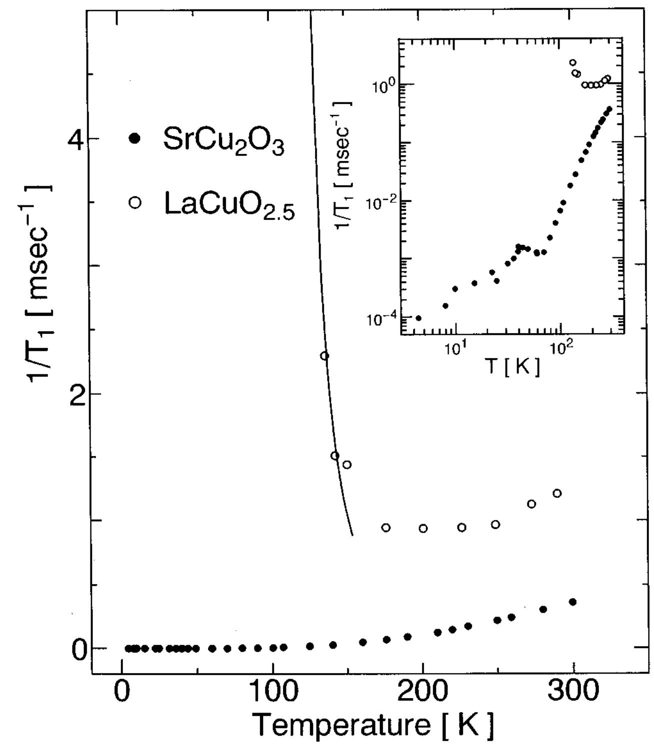

FIG. 4. T dependence of $^{63}(1/T_1)$ for $LaCuO_{2.5}$ and $SrCu_2O_3$ (Ref. 7). The inset indicates plots in logarithmic scales. The solid line is a fit of data below 150 K to $1/T_1 \propto 1/\sqrt{T-T_N}$ with $T_N \sim 110$ K.

~ 150 K. From a sharp increase of $1/T_1$ below 150 K, one may remind that a critical behavior of $1/T_1$ near the Néel temperature, T_N, is described by the formula $1/T_1 \sim 1/\sqrt{(T-T_N)}$.[14] Accordingly, although the data are not enough for a precise determination of T_N, such a fit to the data below 150 K allows us to give a rough estimation of T_N being around 110 K as indicated by the solid line in Fig. 4. Recently, the μSR experiment on $LaCuO_{2.5}$ has also confirmed a sharp magnetic transition below ~ 120 K (Ref. 13) being consistent with the Cu NMR results. It is thus evident that $LaCuO_{2.5}$ is not in the singlet-spin liquid state, but instead a magnetic ordering occurs below ~ 110 K.

In striking contrast to $LaCuO_{2.5}$, $^{63}(1/T_1)$ for $SrCu_2O_3$ revealed an exponential decrease close to 100 K as shown in the inset of Fig. 4, although dominated at low temperatures by spin fluctuations caused by small amounts of $Sr_2Cu_3O_5$ presenting impurity phases.[6,7] Furthermore, the Cu NMR spectrum in $SrCu_2O_3$ was observable at low temperatures. These results gave firm evidence that $SrCu_2O_3$ is in the short-range resonating valence bond (RVB) ground state, where the spin correlation is exponentially decayed. In spite of the seeming similarity of the susceptibility between $LaCuO_{2.5}$ and $SrCu_2O_3$, it is considered that the antiferromagnetic interladder interaction in $LaCuO_{2.5}$, which is not frustrated, makes a spin liquid state unstable in contrast to the case of $SrCu_2O_3$. Actually, Rice *et al.* have recently shown that the interladder exchange constant, J', in $LaCuO_{2.5}$ is not so small with a value of $\sim 0.2J$ where J is the intraladder exchange constant, and pointed out a possibility of magnetic ordering because of the system being close to the quantum critical point.[15]

In order to obtain further evidence on the magnetic anomaly at low T, we have carried out the Cu NMR experiment on the Sr-doped compounds $La_{1-x}Sr_xCuO_{2.5}$ with $x=0.025$ and 0.05. Whereas the temperature below which the Cu NMR signal disappears is decreased from ~ 117 K for $LaCuO_{2.5}$ to ~ 50 K for $x=0.025$ as indicated in Fig. 5, the Cu NMR signal for $x=0.05$ is observable down to 4.2 K. As seen in Fig. 5, the NMR spectrum with a two-peak structure

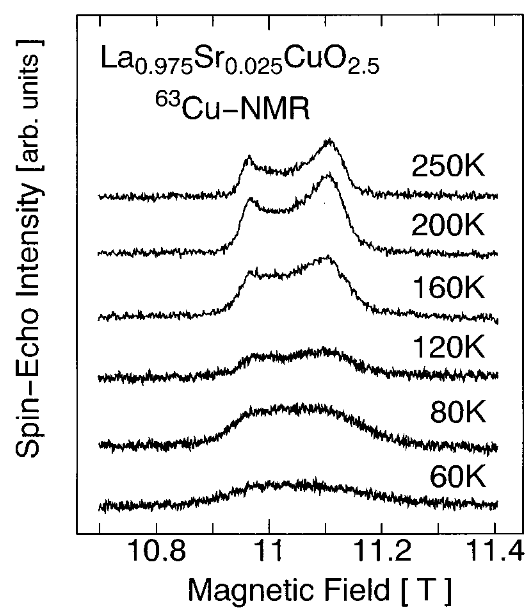

FIG. 5. T dependence of ^{63}Cu NMR spectrum for $La_{0.975}Sr_{0.025}CuO_{2.5}$. The NMR signal is observable down to ~ 50 K in contrast to the undoped $LaCuO_{2.5}$.

at higher temperatures becomes progressively broader with decreasing temperature and then vanishes below $\sim$50 K. Although the NMR signal for $x=0.05$ is observable at 4.2 K, the spectrum is distributed over a broader field range and its integrated intensity is multiplied by temperature is significantly reduced upon cooling. The T-dependent broadening of the Cu NMR spectrum does not follow the Curie law observed in the susceptibility measurement and hence cannot be interpreted *only* by the dipole fields induced by extrinsic impurity spins and/or intrinsic Cu^{2+} spins produced by Sr doping, i.e., the magnetic inhomogeneity effect caused by the paramagnetic spins. The NMR intensities in the undoped and 2.5% Sr-doped $LaCuO_{2.5}$ disappear sharply below around 117 and 50 K, respectively, whereas that in 5% Sr doped compound is gradually wiped out upon cooling, which may be related to the development of short-range magnetic order associated with the inhomogeneous distribution of Sr content. A spin-glass-like disordered magnetic phase may produce distributed internal fields at the Cu nuclei so that the Cu NMR intensity is wiped out. The latter possibility shows the spin-glass phase existing in the concentration range of $x=0.025-0.05$ for the 2D square lattice system, $La_{2-x}Sr_xCuO_4$. It is apparent that the magnetic anomaly observed in $LaCuO_{2.5}$ is significantly suppressed and a paramagnetic ground state tends to be stabilized by introducing Sr or holes, although some magnetic inhomogeneity remains largely.

In conclusion, the present Cu NMR experiments have revealed that the ground state of $LaCuO_{2.5}$ is not in the spin liquid state with a spin gap in disagreement with the previous suggestion from the susceptibility measurement.[12] Alternatively, it has been shown that a magnetic ordering takes place below $T_N \sim 110$ K as evidenced by the large increase of $1/T_1$ and the divergent behavior of $1/T_2$ leading to the disappearance of the Cu NMR signal. Recent μSR experiment has confirmed a magnetic transition below around 120 K.[13] Furthermore, it has been found that T_N is strongly reduced upon doping and the paramagnetic state is stabilized by substituting Sr for La by 5%. The present NMR experiments have found a contrast of the ground state between the two-chain ladder compounds, $SrCu_2O_3$ and $LaCuO_{2.5}$. The antiferromagnetic interaction among the ladders in $LaCuO_{2.5}$, which is not frustrated, has been shown to lead to the magnetically ordered state. This statement may be supported by the recent theoretical analysis that the system is close to the quantum critical point due to not so small interladder exchange interaction with a value of $\sim 0.2J$.[15] No signature of superconductivity in the Sr-doped $LaCuO_{2.5}$ compound may be partially responsible for the lack of a spin gap in the parent compound $LaCuO_{2.5}$.

We would like to thank T.M. Rice, B. Normand, and J. Akimitsu for communicating their results to us in advance of publication and for stimulating discussions. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

[1] S. Chakraverty, B.I. Halperin, and D.R. Nelson, Phys. Rev. B **39**, 2344 (1989).
[2] E. Dagotto, J. Riera, and D.J. Scalapino, Phys. Rev. B **45**, 5744 (1992).
[3] T.M. Rice, S. Gopalan, and M. Sigrist, Europhys. Lett. **23**, 445 (1993).
[4] R.M. Noack, S.R. White, and D.J. Scalapino, Phys. Rev. Lett. **73**, 882 (1994); S.R. White, R.M. Noack, and D.J. Scalapino, *ibid.* **73**, 886 (1994).
[5] R.S. Eccleston, T. Barnes, J. Brody, and J.W. Johnson, Phys. Rev. Lett. **73**, 2626 (1994).
[6] M. Azuma, Z. Hiroi, M. Takano, K. Ishida, and Y. Kitaoka, Phys. Rev. Lett. **73**, 3463 (1994).
[7] K. Ishida, Y. Kitaoka, K. Asayama, M. Azuma, Z. Hiroi, and M. Takano, J. Phys. Soc. Jpn. **63**, 3222 (1994).
[8] K. Kojima *et al.*, Phys. Rev. Lett. **74**, 2812 (1995) .
[9] K. Ishida *et al.*, Phys. Rev. B **53**, 2827 (1996).
[10] M. Sigrist, T.M. Rice, and F.C. Zhang, Phys. Rev. B **49**, 12 058 (1994).
[11] N. Nagaosa (private communication).
[12] Z. Hiroi and M. Takano, Nature **377**, 41 (1995).
[13] J. Akimitsu *et al.* (private communication).
[14] T. Moriya, Prog. Theor. Phys. **28**, 371 (1962).
[15] T.M. Rice and B. Normand (private communication).