# Magnetic Order in the Hole-Doped Two-Leg Ladder Compound $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$: Evidence from Cu-NMR and -NQR Studies on a Single Crystal

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We report from Cu-NQR and -NMR experiments that hole-doped two-leg ladder compound $Sr_{2.5}$-$Ca_{11.5}Cu_{24}O_{41}$ comprising $Cu_2O_3$ ladders and $CuO_2$ chains reveals three-dimensional (3D) magnetic order below $T_M = 2.2$ K. We found that small moments $\sim 0.02\mu_B$ are spontaneously ordered on the ladders, whereas large moments $\sim 0.56\mu_B$ are on the magnetic Cu sites occupying about one-fourth of the chain Cu sites. It is suggested that this 3D magnetic order is a cooperative phenomenon driven by the formation of pinned charge density wave–like state on the ladders which the optical conductivity measurement has clarified. [S0031-9007(99)09206-6]

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Ladder cuprates have attracted much interest since superconductivity was discovered with $T_c \sim 12$ K in a polycrystal $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41.84}$ [1] and $T_c \sim 10$ K in a single crystal $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$ [2], when pressure greater than 3 GPa is applied. Remarkably, these experiments appeared to support the theoretical prediction that singlet superconductivity would occur by doping a small amount of holes into even-leg spin-ladder compounds with a spin gap [3–5]. The substitution of Ca for Sr increases the conductivity of $Sr_{14-x}Ca_xCu_{24}O_{41}$ (Ca$x$) which comprises hole-doped $Cu_2O_3$ two-leg ladders and $CuO_2$ chains [6–8]. The optical conductivity experiment clarified that holes are transferred from the chains to the ladders upon the isovalent Ca substitution, and hole content $n$ increases progressively as $n \sim 0.14$, 0.2, and 0.22 for $x = 6$, 9, and 11, respectively [9].

Measurements of the Knight shift $K$ and the nuclear spin-lattice relaxation rate $T_1^{-1}$ on Ca$x$ revealed that the magnitude of the spin gap *decreases* progressively as $x$ increases from 0 to 11.5, with estimates of $\Delta_K = 270$ K and $\Delta_{T_1} = 350$ K for Ca11.5 [10]. From the Gaussian spin-echo decay rate $T_{2G}^{-1}$ measurement, spin correlation length $\xi$ was found to be determined by an average distance of doped holes. $n \sim 0.14$, 0.22, and 0.25 per $Cu_2O_3$ ladder were estimated for Ca6, Ca9, and Ca11.5, respectively. In an intermediate $T$ region of 60–200 K, hole pairs are formed accompanying the spin gap, but confined on each ladder. Below $T_L \sim 60$ K where the resistivity increases following $T^{-2}$, mobile hole pairs are, however, localized [2,11]. In this charge-localized regime, it was found that staggered spin fluctuations at low frequencies around $q \sim \pi$ dominate the $T_1$ process in the ladders for Ca6, Ca9, and Ca11.5, suggesting collapse of the spin gap [10].

Recent specific heat $C(T)$ measurement on Ca11.5 has found a sharp peak around $T_M \sim 2.2$ K well below $T_L$ at zero magnetic field ($H = 0$) and ambient pressure [12]. In addition, an elastic neutron diffraction (ND) experiment has suggested the development of magnetic neutron Bragg reflections upon cooling below $T_M$, proving that the peak in $C(T)$ is magnetic in origin [12]. It is remarkable that the peak in $C(T)$ becomes broader at $H = 1.8$ T and disappears under $H > 8$ T. These evidences assure an appearance of magnetic order below $T_M$. It is, however, not yet clear whether the charge-localized state emerging on the ladders below $T_L$ is relevant to the onset of long-range magnetic order.

In this Letter, we present extensive Cu-NMR and -NQR results on a single crystal Ca11.5 grown by the traveling-solvent floating-zone method [2]. We have found that the magnetic order takes place accompanying small spontaneous moments $M_a(L) \sim 0.02\mu_B$ along the $a$ axis on the ladders, whereas large moments $M_a^{\mathrm{mag}}(C) \sim 0.56\mu_B$ on the magnetic Cu sites and small moments $M_a^{\mathrm{dimer}}(C) \sim 0.02\mu_B$ on the seeming dimer Cu sites in the chains. The spin degree of freedom produced by the charge localization on the ladders is suggested to play an essential role in making a three-dimensional (3D) magnetically coupled network.

A field-swept Cu-NMR spectrum was obtained at $H \sim 11$ T by using a boxcar integrator and superconducting magnet (12 T at 4.2 K). Cu-NQR spectrum was obtained by plotting spin-echo intensity as a function of frequency. $T_1^{-1}$ and $T_{2G}^{-1}$ were measured by the saturation-recovery method and recording the spin-echo amplitude as a function of the time $\tau$ between the first and second pulses, respectively.

First we show from the Cu-NMR study that the spin degree of freedom manifests when the charge is localized below $T_L \sim 60$ K and takes part in the onset of magnetic order. Figure 1 indicates the $T$ dependence of the full widths at half maximum (FWHM) of the ladder $^{63}$Cu-NMR spectra for Ca9, Ca11.5, and Ca0 in $H \| b$ axis. Whereas the FWHM of Ca0 does not exhibit any significant $T$ dependence over an entire $T$ range, each $T$ dependence of FWHM for Ca11.5 and Ca9 is scaled to that of measured susceptibility down to $T_L$. It is considered that the Ca substitution enhances the transferred hyperfine-coupling constant between the ladder-Cu nuclei and magnetic moments on the chains. With further decreasing $T$ below $T_L$, the FWHM's of Ca9 and Ca11.5 increase markedly. It is noteworthy that the anisotropy of FWHM, which is displayed in the inset, coincides with the anisotropy of hyperfine form factor. Namely, $(\mathrm{FWHM})_b/(\mathrm{FWHM})_{a,c} \sim 2.8$ is compatible to $(A_b - 3B)/(A_{a,c} - 3B) \sim 2.8$ [10]. A continuous increase of FWHM is, hence, because field-induced staggered spin polarization develops on the ladders. It was reported from the optical conductivity measurement that hole pairs tend to form a charge-density-wave-like (CDW-like) regular array, although it is not truly 3D long-range order [13]. The localization of hole pairs is, however, not expected to induce unpaired spins near them. Therefore, the CDW-like state is anticipated to be formed by a regular array of *single hole*. As a consequence of localization of single hole breaking the collective spin-singlet state on the ladders, it is possible that unpaired spins are produced in the vicinity of localized single hole.

Figure 2(a) indicates that the NQR spectrum for the ladders undergoes an appreciable broadening as $T$ is lowered to 1.4 K across $T_M = 2.2$ K. Figure 3 indicates that the NQR intensity $I$ at 19.8 MHz multiplied by the temperature $T$, $I \times T$, and $T_{2G}^{-1}$ decreases below $T_M$. Reduction in both quantities below $T_M$ originates from a splitting in the NQR spectrum by the internal field $H(L)$ emerging at the ladders. The NQR spectrum at 4.2 K is well reproduced by assuming a Gaussian distribution of the electric field gradient (EFG) as indicated by the solid curves in the lower panel in Fig. 2(a). Here the $^{63}$Cu-NQR frequency $^{63}\nu_Q = 20.2$ MHz and $^{63}$FWHM $= 6.3$ MHz are deduced by using the natural abundance 69.09% (30.91%) and nuclear quadrupole moment $Q = -0.211$ $(-0.195)$ barn for $^{63}$Cu ($^{65}$Cu). Its spectral broadening at 1.4 K is well reproduced by adding the Zeeman splitting due to the appearance of the internal field $H_{a,b}(L) \sim 1.06$ kOe and $H_c(L) \sim 1.90$ kOe in case that $H(L)$ is along the $a$, $b$, and $c$ axes at the ladders, respectively. Here $H(L)$ is treated within the first-order approximation to the nuclear quadrupole interaction for $I = 3/2$ [14] with the asymmetry parameter $\eta = 0.46$ of EFG reported in the literature [10]. A spontaneous moment $M_a(L) \sim 0.022\mu_B$, $M_b(L) \sim 0.009\mu_B$, or $M_c(L) \sim 0.040\mu_B$ is estimated by using the

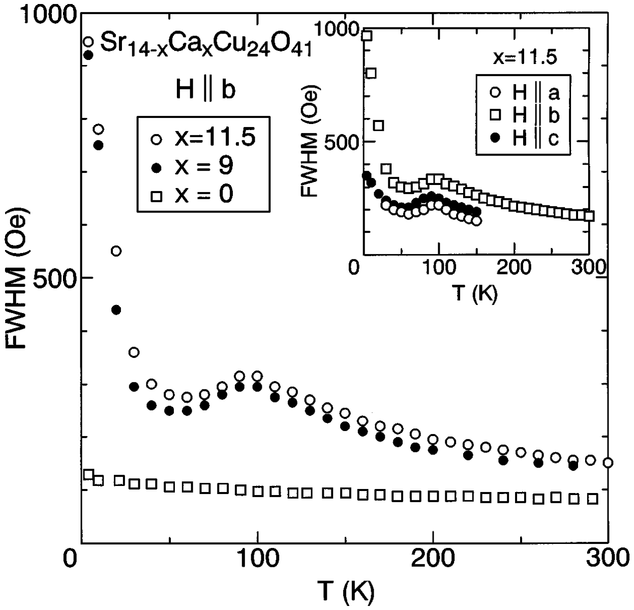

FIG. 1. $T$ dependence of the full widths at half maximum (FWHM) of the ladder-$^{63}$Cu NMR spectra for $x = 0$, 9, and 11.5 in $\mathrm{Sr}_{14-x}\mathrm{Ca}_x\mathrm{Cu}_{24}\mathrm{O}_{41}$ for $H \| b$ axis. The inset shows the $T$ dependence of FWHM for $H \| a, b$, and $c$ in $x = 11.5$.

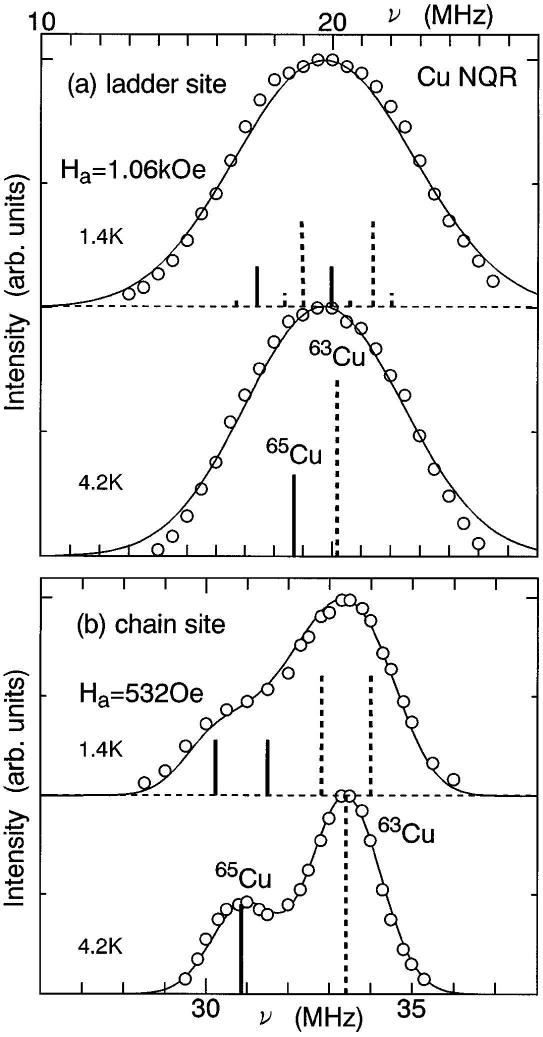

FIG. 2. Cu-NQR spectra for (a) the ladder sites and (b) the Zhang-Rice sites in the chains in Ca11.5 at 1.4 K (upper panel) and 4.2 K (lower panel). $^{63}$Cu ($^{65}$Cu) NQR intensities are marked by the dashed (solid) lines. Solid curves indicate calculated Cu-NQR spectral shapes at 1.4 K (upper panel) and 4.2 K (lower panel) (see text for details).

hyperfine-coupling constants $A_{a,c} = (48\ \mathrm{kOe})/\mu_B$ and $A_b = (-120\ \mathrm{kOe})/\mu_B$ estimated for the ladder-Cu sites in $SrCu_2O_3$ [15]. The ND experiment has revealed spontaneous moments along the $a$ axis on the chains [12]. Therefore a likely direction of $M(L)$ on the ladders is expected to lie along the $a$ axis, since an interlayer superexchange interaction may be responsible for the 3D magnetically coupled network. The integrated value of $I \times T$ over the frequency, $II \times T$, at 1.4 K remains about 90% of the value at 4.2 K as shown in Fig. 3. This result assures us that $M(L)$ is not so widely distributed.

Next we present results on the chains. The Cu-NQR spectra around 33 MHz in Fig. 2(b) are assigned to the Zhang-Rice (ZR) singlet sites in the chains according to the previous works on Ca0 [16,17]. The Cu-NQR spectral width for the ZR sites increases at 1.4 K across $T_M$ as well as that for the ladders does. The $T_1^{-1}$ at $H = 0$ exhibits a sharp peak around 2.8 K close to $T_M$ as seen in Fig. 4. This peak originates from critical magnetic fluctuations towards a magnetic phase transition, suppressed by an application of $H$ and eventually collapsing at $H$ greater than $H = 4.7$ T. It is, therefore, evident from the measurements of $T_1^{-1}$, $C(T)$ [12], and $\chi(T)$ [18] that the magnetic order is suppressed by the magnetic field.

The NQR spectrum at 4.2 K is well reproduced by assuming a Gaussian distribution of EFG as indicated by the solid curves in the lower panel in Fig. 2(b). Here ${}^{63}\nu_Q = 33.4$ MHz and ${}^{63}$FWHM $= 2.0$ MHz are deduced. From the NQR spectral broadening at 1.4 K, the internal field $H_{a,b,c}^{ZR}(C) \sim 0.532$ kOe along the $a$, $b$, and $c$ axes at the ZR sites is deduced. Since $\eta$ is ignored here because of the small value of 0.043 [10], $H^{\mathrm{ZR}}(C)$ is independent of its direction.

The Cu nucleus at the ZR site is coupled through the transferred hyperfine interaction with the nearest-neighbor dimer-Cu spins. The dimer-Cu spins in Ca0 were reported to form the spin singlet with the gap $\Delta \sim 125$ K from the $T_1$ measurements [16,17]. Likewise in Ca11.5, $T_1^{-1}$ is well fitted in $T = 15-40$ K to the activation form of $T_1^{-1} \propto \exp(-\Delta/T)$ with the gap $\Delta = 100$ K without any appreciable $H$ dependence as indicated by the solid line in Fig. 4. Note that the $\Delta = 100$ K in Ca11.5 is close to the $\Delta \sim 125$ K in Ca0. Accordingly, the Cu nucleus at the ZR site is also expected to be coupled with the dimer-Cu spins on the chains in Ca11.5. Furthermore, we should remark that each spin on the dimers in Ca11.5 is magnetically coupled with spins on "magnetic Cu sites" in the chains. Otherwise, we cannot expect the appearance of $H^{\mathrm{ZR}}(C)$ at the ZR sites. Holes existing on the ZR sites in Ca0 ($n \sim 0.5$) are transferred onto the ladders in Ca11.5 by Ca substitution, in which as a result $n \sim 0.25$ was estimated [10]. Therefore, about one-fourth of the Cu sites of the chains are converted into the magnetic Cu sites. If the transferred hyperfine-coupling constants in Ca11.5 are assumed to be the same as $A_{a,c} = (-14.8\ \mathrm{kOe})/\mu_B$ and $A_b = (-18.9\ \mathrm{kOe})/\mu_B$ in Ca0 [16], a spontaneous moment on the dimer $M_{a,c}^{\mathrm{dimer}}(C)$ $[M_b^{\mathrm{dimer}}(C)]$ is estimated to be $0.018\mu_B$ $(0.014\mu_B)$ when the dimer-Cu spins are assumed to be equivalently coupled with the Cu nucleus at the ZR site. The ND experiment revealed that spontaneous moments along the $a$ axis on the chains were $\langle\mu\rangle_a \sim 0.15\mu_B$ on an average on the assumption that the direction of all the moments is parallel to the $a$ axis dominated by the superexchange interaction [12].

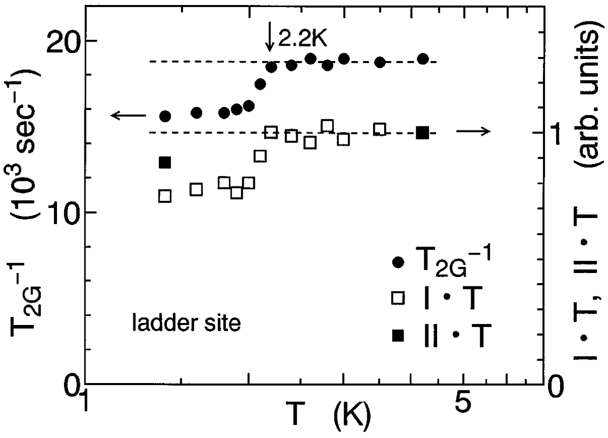

FIG. 3. $T$ dependence of the ladder-Cu NQR intensity $I$ in Fig. 2(a) at 19.8 MHz multiplied by the temperature $T$, $I \times T$ (open square), and the Gaussian spin-echo decay rate $T_{2G}^{-1}$ (closed circle). The intensities of $II \times T$ (closed square) integrated over the frequency at 4.2 and 1.4 K are plotted.

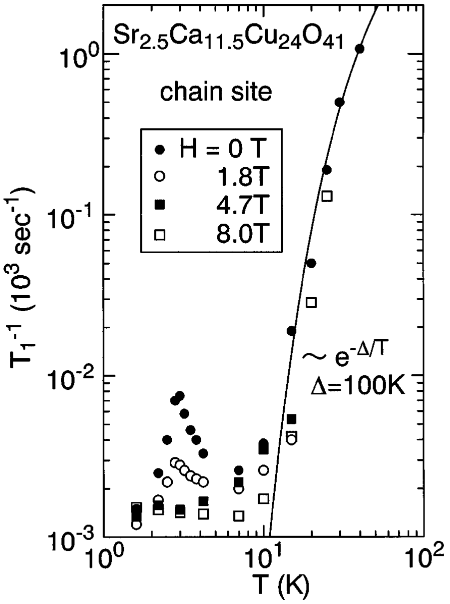

FIG. 4. $T$ dependence of $T_1^{-1}$ for the Zhang-Rice ${}^{63}$Cu site in Ca11.5 at 33.1 MHz in $H = 0$ together with those in $H = 1.8$, 4.7, and 8 T for $H \| b$ axis. The solid line is a fit to the activation type of $\exp(-\Delta/T)$ with a seeming dimer gap $\Delta = 100$ K.

From this result, $M_a^{\rm mag}(C)$ on the magnetic Cu sites is estimated to be $0.56\mu_B$. Here we assume that one-fourth (a half) of the chain Cu sites has $M_a^{\rm mag}(C) \sim 0.56\mu_B$ [$M_a^{\rm dimer}(C) \sim 0.018\mu_B$].

Note that $M_a(L) \sim 0.02\mu_B$ on the ladders are 1 order of magnitude smaller than $M_a^{\rm mag}(C) \sim 0.56\mu_B$ on the chains. We hence expect that the ND intensity originates primarily from the periodic array of moments distributed on the chains [12]. This feature of the magnetic order on the ladders resembles those in the gapped-1D systems doped with slight impurities such as $\rm CuGe_{1-x}Si_xO_3$ [19], $\rm Cu_{1-x}Zn_xGeO_3$ [20], and $\rm Sr(Cu_{1-x}Zn_x)_2O_3$ [21]. In the disordered spin-Peierls $\rm CuGeO_3$ systems, the antiferromagnetic long-range order with tiny saturation moments and spin-Peierls lattice dimerization were revealed to coexist with spatially varying order parameters [22,23].

In conclusion, the Cu-NMR and -NQR studies on the single crystal Ca11.5 have unraveled several unusual characteristics in the 3D magnetically ordered state below $T_M \sim 2.2$ K. Small moments $\sim 0.02\mu_B$ are spontaneously ordered on the ladders, whereas large moments $\sim 0.56\mu_B$ on the magnetic Cu sites occupy about one-fourth of the sites of the chains. The tiny spontaneous moments on the ladders reveal that most magnetic spectral weight exists in a high-energy region comparable to the spin gap $\Delta_K \sim 270$ K. Dissociation of hole pairs into single hole which is localized below $T_L \sim 60$ K was suggested to be responsible for the manifestation of the spin degree of freedom on the ladders. We propose that the development of pinned CDW-like periodic array *over long-range distance* upon cooling plays an essential role in making the 3D magnetically coupled network in Ca11.5. It is desired to be addressed by future theoretical work whether or not a cooperative interplay between the charge and spin order takes place in such the highly doped two-leg spin-ladder system.

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