NMR/NQR Study on Magnetism of Spin Ladder $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$

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Z. Naturforsch. **55a**, 311–314 (2000); received October 27, 1999

Presented at the XVth International Symposium on Nuclear Quadrupole Interactions, Leipzig, Germany, July 25–30, 1999.

Long-range antiferromagnetic (AF) order in the doped spin ladder compound of $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$ is investigated by heat capacity, magnetization and Cu-NMR/NQR measurements. We suggest that this AF order is primarily responsible for the chain Cu moments.

Key words: NMR; NQR; Spin Ladder Compound; Antiferromagnetic Order; Charge Order.

1. Introduction

Strong quantum fluctuations of $S=1/2$ Heisenberg antiferromagnets have attracted interest after the discovery of high-T_c superconductors. Recently, spin excitations in spin ladders, i.e., coupled chain systems, were studied experimentally and theoretically [1, 2]. Among ladder compounds, $Sr_{14}Cu_{24}O_{41}$ is unique as in it the carriers are controlled by a substitution of Sr by Ca or La. $Sr_{14}Cu_{24}O_{41}$ consists CuO_2 layers with 1D chains of edge-sharing CuO_4 clusters and Cu_2O_3 layers with two-leg ladder configuration [3]. Some measurements [3, 4] show that when holes are transferred from the chain to the ladder site, the system becomes conductive with hole doping to the ladder by the substitution of Sr by Ca. When high pressure is applied, the compounds around $x=12$ become more conductive, and superconductivity appears [5].

However, an unexpected magnetic order was recently observed under ambient pressure for $Sr_{14}Ca_{11.5}Cu_{24}O_{41}$ [6]. The magnetic moments seem to be small and their magnetic structure seems to be complicated. The controversy about which sites of Cu spins are responsible for the magnetic order is not yet settled, although this magnetic order is an important issue for understanding the origin of superconductivity under high pressure. Thus, we have studied NMR and NQR together with heat capacity and magnetization measurements to elucidate the nature of the magnetism of Cu moments in $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$.

2. Experimental

Single crystals were prepared by a traveling-solvent floating-zone method under high oxygen pressure. NMR and NQR were measured by a conventional phase coherent pulse method. Heat capacities were measured by an Oxford cryostat with superconducting magnets of 12T, and magnetic susceptibilities were measured by a SQUID susceptometer.

3. Results and Discussion

Previous NMR studies on $Sr_{14}Cu_{24}O_{41}$ have provided clear evidence for the formation of gaps for low-lying spin excitations in both the chain and the ladder sites [7–9]. This spin gap formation in the 1D chain in $Sr_{14}Cu_{24}O_{41}$ is attributed to the charge order of Cu^{2+} and Cu^{3+} in the chain. Spin-dimers of magnetic Cu^{2+} are created in a particular array of Cu^{2+} and Cu^{3+} states [10].

The temperature dependence of the magnetic susceptibility for various x in our single crystals is shown in Figure 1. After subtracting the low temperature paramagnetic contributions, the magnetic susceptibility decreases rapidly with decreasing temperature below 80 K. This decrease of spin susceptibility at low temperature is due to the formation of singlet spin ground state in the 1D Cu-chains. The gap behavior of the magnetic susceptibility is obtained even in highly-doped samples of $x=11.5$. The decrease of the spin susceptibility at low temperature is shown more clearly by the present NMR measurement for $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$. The Cu-NMR shift of the chain site decreases below 80 K, as shown in Fig. 2, indicating the ex-

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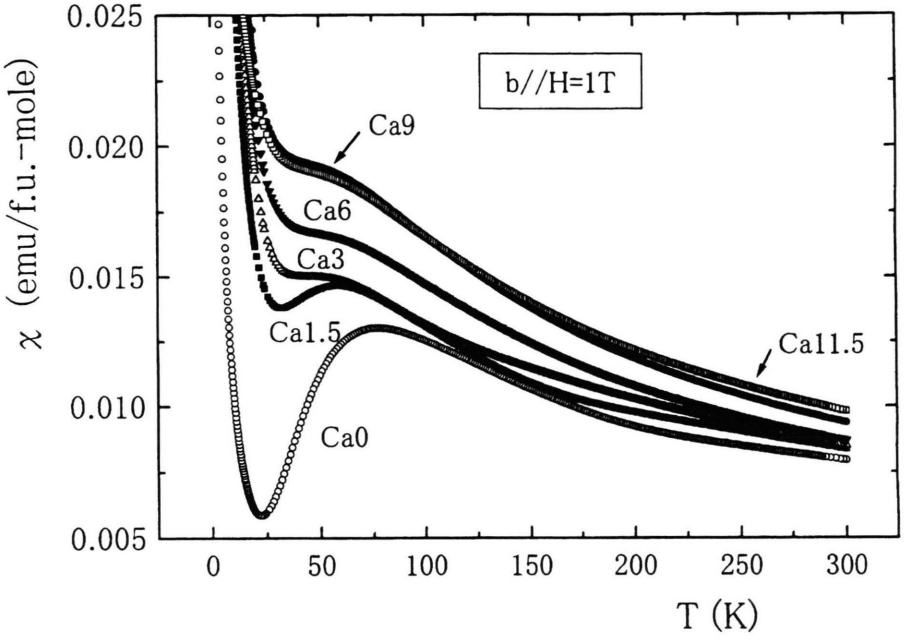

Fig. 1. Temperature dependence of the magnetic susceptibility of single crystal $Sr_{14-x}Ca_xCu_{24}O_{41}$.

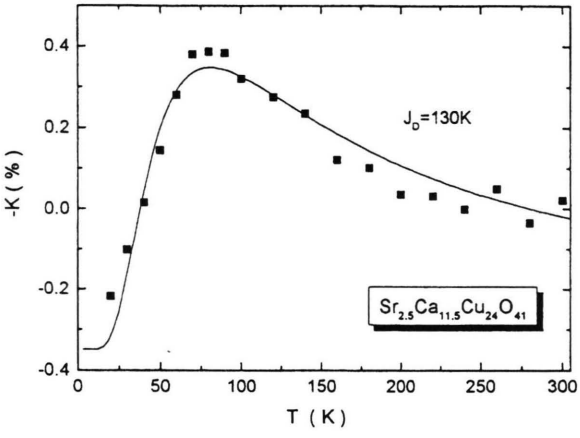

Fig. 2. Temperature dependence of the Cu-NMR shift at the chain site of single crystal $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$.

istence of a spin gap for the 1D Cu-chain of highly-doped $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$. These results mean that the spin dimers in the chain site survive in the range near $x=11.5$.

For very low temperatures we have found anomalies of the magnetization of $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$. Figure 3 shows the magnetic susceptibility as a function of temperature measured at $H_{ext}=50$ G for $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$. As clearly seen, χ decreases only for $H \| c$-axis, which indicates that the occurrence of an antiferromagnetic (AF) magnetic order at 2.3 K, and that the direction of AF ordered moments is along the c-axis. However, when a field above 1000 Oe is applied, the anomalies associated with the cusp are smeared out completely, and χ increases smoothly with decreasing temperature. Interestingly, we have confirmed meta-magnetic behavior at a low field of 600 Oe, as shown in the inset of Figure 3. A change of magnetization around 600 Oe is observed when the field is applied along the c-axis. On the other hand, no anomalies of magnetization are observed for $H \| a$ and $H \| b$-axis. These results show that the ordered moments flop to the a-axis from the c-axis at a small value of 600 Oe.

Furthermore, we have confirmed a sharp cusp of the heat capacity of $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$ at 2.3 K, as similar to the previous report [6]. This anomaly is attributed to AF magnetic order of Cu moments. Below T_N, the temperature dependence of the heat capacity seems to obey the T^2-relation in the magnetic ordered state. The cusp corresponding to the magnetic transition is shifted to lower temperatures by an external field, and is smeared out completely by high fields up to 6 T. It should be pointed out that the magnetically-ordered state disclosed by the heat capacity and magnetic susceptibility measurements coexists with the spin dimer state of the chain. The next question is which site is responsible for the magnetic order. In order to elucidate this point as well as the origin of this phase transition, Cu-NMR/NQR was performed.

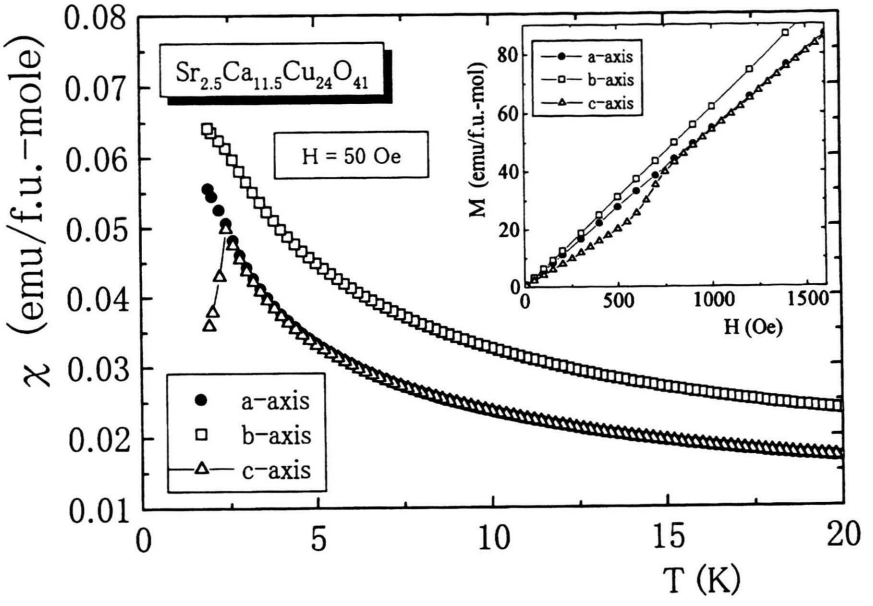

Fig. 3. Temperature dependence of the magnetic susceptibility of single crystal $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$ at $H_{ex}=50$ G applied along the *a*-, *b*-, and *c*-axis. The inset shows the magnetization as a function of the external field at 1.8 K.

For single crystals of $Sr_{14}Cu_{24}O_{41}$, the NMR and NQR spectra are sharp enough to resolve some peaks [10]. For the chain site, the spectra of the chain Cu are classified into three kinds of signals for which the NMR shifts show distinct temperature dependences. From the NMR shift together with the magnetic susceptibility at low temperature, the hyperfine coupling constants, H_{hf}, of Cu are evaluated to be -220, -25 and -12 kOe/μ_B. The component with the largest H_{hf} is attributed to Cu^{2+} ($S=1/2$). The other two components with the small H_{hf} are attributed to two kinds (different configurations) of the transferred hyperfine interactions at Cu^{3+} (non-magnetic state with $S=0$). Among the non-magnetic components, the spin echo decay time, T_2, of one of them is very small and shows Gaussian behavior, and T_2 of the other one is large and shows Lorentzian behavior. This fact shows clearly that the signal with the Gaussian T_2 arises from Cu^{3+} with two adjacent Cu^{3+} configurations, and the other one arises from the separated Cu^{3+} configuration. Thus, the present NMR results show that charge ordering of Cu^{2+} and Cu^{3+} is realized for the chain Cu's at low temperature, where the holes are localized $Sr_{14}Cu_{24}O_{41}$. The proposed charge and spin configuration for the chain in $Sr_{14}Cu_{24}O_{41}$ is shown in Figure 4(a).

For the paramagnetic state ($T>T_N$) of the doped $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$, the $^{63/65}$Cu-NQR spectrum of the chain (the component of $\mu_Q=33$ MHz) is relatively broad compared to that of the starting $Sr_{14}Cu_{24}O_{41}$, which arises partly from the inhomogeneity of the electric

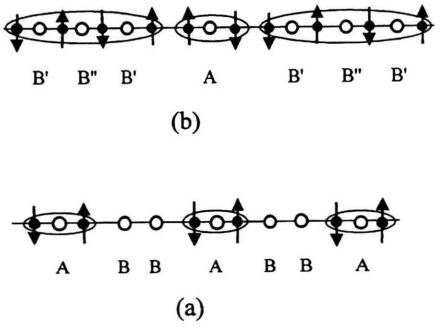

Fig. 4. Proposed configuration for spin and hole of the chain Cu sites (a) of $Sr_{14}Cu_{24}O_{41}$, and of (b) $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$. A, B, B', and B'' represent Cu^{3+} ($S=0$) sites with hole, and ↑ and ↓ represent magnetic Cu^{2+} ($S=1/2$) ions.

quadrupole interactions due to random atomic distribution of Sr and Ca. Nevertheless, comparing the Cu-NQR spectrum above and below T_N, magnetic broadening appears obviously below T_N, as shown in Figure 5(a). The spectrum below T_N can not be fitted by a unique Gaussian or Lorentzian component but is well fitted by two components. One comes from Cu nuclei which do not feel any magnetic hyperfine field, and the other comes from Cu nuclei for which a finite hyperfine field exist along the *c*-axis. As shown in Fig. 5, the observed spectrum, shown by the dots solid line, can well be fitted by a sum of broken lines obtained from the 2nd order perturbation calculation (the split component) and a dashed

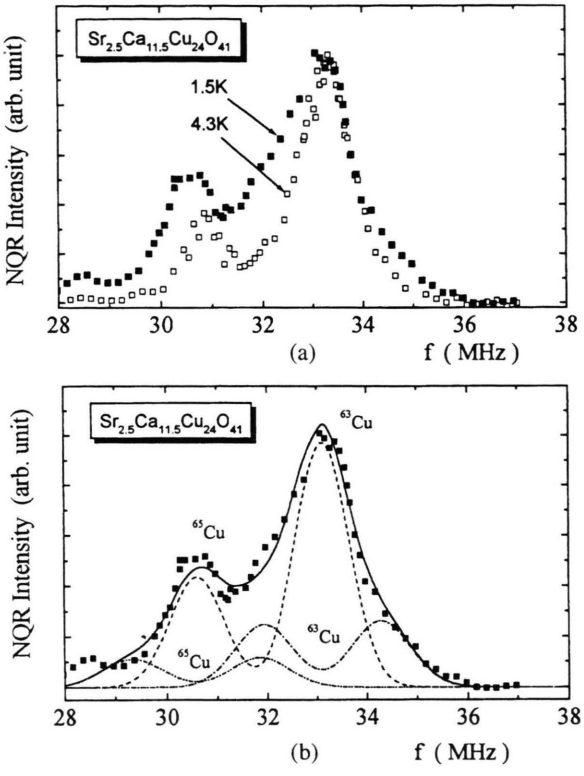

Fig. 5. $^{63/65}$Cu-NQR spectra around 33 MHz of single crystal $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$. (a): the spectra are normalized at the peak obtained above T_N and below T_N. (b): the spectrum with fitting lines (broken lines) for $T<T_N$.

line (the unchanged component). The transferred hyperfine field is uniform at the non-magnetic chain Cu^{3+} sites.

This result indicates that the B site (or the Zhang-Rice singlet state) of Cu^{3+} in Fig. 4(a) becomes two distinct magnetic states in the chain below T_N. As mentioned already, holes in the compound are transferred to the ladder site from the chain site with increasing x. The number of holes is reduced and the magnetic spin states increase at the chain Cu sites. And the remaining holes in the chains are expected to be localized at low temperature. Thus, we propose a possible charge and spin configuration for the chain Cu sites in $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$ as shown in Figure 4(b). In this configuration, we expect that dimers survive. As the B″-site is located at a symmetrical surrounding of the spin array, and the B′-site is situated in non-symmetric sites, the transferred hyperfine field from Cu^{2+} is cancelled at the B″-site, but a finite value of H_{hf} exists at the B′-site. As the hyperfine field is obtained to be 1.1 kOe, we estimate that the magnitude of moments of chain Cu^{2+} is 0.06 μ_B with using a transferred hyperfine coupling constant of -19 kOe/μ_B for the chain Cu^{3+} site. Thus, we conclude that the magnetic order can be attributed to the chain Cu^{2+} moments in the configuration among localized non-magnetic Cu^{3+} ions, and that the magnetic order observed for $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$ is responsible for the chain Cu^{2+}.

As for the spontaneous moments at the ladder site, we do not detect any indication of a sizable hyperfine field at the ladder Cu site in the Cu-NQR/NMR measurement. This means that vanishingly small magnetic ally ordered moments are induced at the ladder Cu sites, if any.

In conclusion, magnetic order of the chain Cu in highly doped $Sr_{2.5}Ca_{11.5}Cu_{24}O_{41}$ is confirmed by NMR/NQR, heat capacity and magnetization measurements. We found a uniaxial meta-magnetic behavior at low field of 600 Oe from magnetization measurement. At 1.8 K, spins in the chain flop from the c-axis to the a-axis by a small external field of ~1 kOe. Based on the NQR/NMR results, we conclude that the magnetic order is attributed to the chain Cu^{2+} moments in the configuration among localized non-magnetic Cu^{3+} ions.

Acknowledgement

This work was supported in part by a grant-in-aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

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