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Cu-NMR/NQR Studies of Spin Gap in the Edge-Sharing CuO_2 Chains of $Ca_{2+x}Y_{2-x}Cu_5O_{10}$

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Abstract. We have studied ^{63}Cu-NMR of $Ca_{2+x}Y_{2-x}Cu_5O_{10}$ with edge-sharing CuO_2 chains. The Knight shift, ^{63}K, and nuclear spin-lattice relaxation time, $^{63}T_1$, of ^{63}Cu show spin gap behavior of $\Delta \sim$50K for x=1.5 and 1.67, which is relevant for the spin dimer formation of Cu^{2+} spins in the chains.

Keywords: NMR, Knight shift, spin gap, dimer, $Ca_{2+x}Y_{2-x}Cu_5O_{10}$
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INTRODUCTION

After the discovery of high-T_c superconductors, low-dimensional quantum spin systems have attracted much interest, because of their peculiar magnetic and electronic properties. In particular, the fascinating coexistence/competition of a spin dimer (spin gap) state and magnetically-ordered state of the cuprates has caused much attention, as those two different ground states are generally believed to be mutually exclusive. $Sr_{0.73}CuO_2$ [1, 2, 3] and Ca_xCuO_2 ($x \sim$0.85) [4] with edge-sharing CuO_2 chains are particular compounds which contain inherently holes with 40∼60 % Cu. Previous measurements reveal a gap behavior for Cu spins in the Ca- and the Sr-systems, indicating the existence of dimer spin configuration [3, 4]. Moreover, a magnetic order with small moments is reported at low temperature [5].

An isomorphic edge-sharing CuO_2 chain system $Ca_{2+x}Y_{2-x}Cu_5O_{10}$ is interesting, as x, hence, hole-doping can be largely changed [6, 7]. The end material $Ca_2Y_2Cu_5O_{10}$, which has no holes, shows an antiferromagnetic ordering of Cu moments below 29.5 K with ferromagnetic coupling along the chain [8]. With more hole doping (with increasing x) main magnetic interaction may become antiferromagnetic. Thus, the evolution of the magnetic ground state of this material is very important for clarifying magnetic properties in the hole-doped low-dimensional spin systems. Recently large single crystals of this material are successfully prepared [10, 11, 12]. In addition to thermodynamical properties, extensive studies on magnetic properties have yielded a detailed magnetic phase diagram [11, 12]. An appearance of a spin gap originating from the singlet dimers is suggested in a particular doping range in the vicinity of the AF ordered phase. Here we report results of Cu-NMR for single crystals of $Ca_{2+x}Y_{2-x}Cu_5O_{10}$. We have confirmed spin gap behavior from nuclear spin-lattice relaxation time and Knight shift for x=1.5 and 1.67.

EXPERIMENTAL

Samples were prepared by a traveling solvent floating method from a mixture of $CaCO_3$, Y_2O_3 and CuO in flowing oxygen of 10 atmosphere. Details of the crystal preparation and characterization were described in Ref.12. Cu-NMR/NQR was measured by a conventional phase coherent pulse method with a superconducting magnet up to H=9 T. We measured Cu-NMR for both single crystal and powdered sample. The Knight shift is obtained by fitting the whole spectrum (including satellite lines of both ^{63}Cu and ^{65}Cu isotopes) by using an nuclear quadrupole interaction of $\nu_Q \sim$32 MHz.

RESULTS AND DISCUSSIONS

The observed ^{63,65}Cu-NQR spectra are relatively sharp at high temperatures and become gradually broader at lower temperatures. At the lowest temperature (4.2K) the line width is as large as ∼1MHz. The accuracy for the value of the Knight shift was poorer below 10K. The nuclear quadrupole frequency, $^{63}\nu_Q$, is ∼32 MHz is confirmed by the the NQR spectra. $^{63}\nu_Q$ is nealy temperature-independent. The temperature dependence of the ^{63}Cu-Knight shift, ^{63}K, is shown in Fig. 1. At high temperature, ^{63}K obeys a Curie-Weiss relation and shows a peak around T=40K followed by a rapid decrease with decreasing temperature for both x=1.5 and 1.67. This result seems to indicate the spin gap behavior in this hole-doping range.

The temperature dependence of $1/T_1T$ of ^{63}Cu shown in Fig. 2 also reveals gap behavior, where the $1/T_1$

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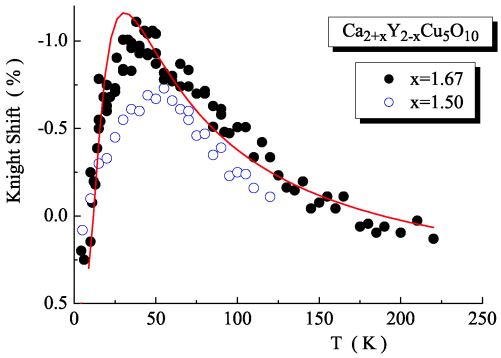

FIGURE 1. Temperature dependence of the Knight of ^{63}Cu for x=1.5 (○) and x=1.67 (●). The red line shows the fitting line for a non-interacting dimer model (see text).

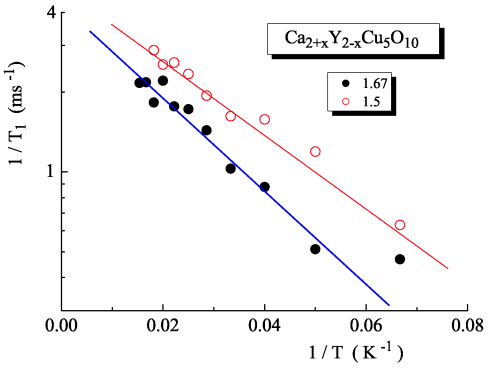

FIGURE 2. Reciprocal Temperature dependence of the nuclear spin-lattice relaxation rate $1/T_1$ of ^{63}Cu for x=1.5 (○) and x=1.67 (●).

obeys an activation type relation of $exp(-\Delta/kT)$ with Δ =40∼50K. These results show that the energy gap for the spin excitations does not change appreciably with hole-doping between x=1.5 and 1.67.

The Knight shift, which is proportional to the magnetic susceptibility, is calculated on the basis of the simple noninteractive dimer energy level scheme, as given by $K_{spin}(T) \propto \mu_{eff}^2(1/(3+exp(\Delta/k_BT))$. In spite of the crude function, the fitting to the experimental values for x=1.67 is satisfactory as shown in Fig. 1. We estimate the energy gap between the singlet and the triplet state to be $\Delta \sim$50K for x=1.67. In order to give insight into the hole-doping effects on the spin gap, one needs a microscopic theory, which takes into account the interchain coupling as well as the change of dimer interaction[13].

The small shoulder around 20K for x=1.5 and as well for x=1.67 is observed in the temperaure dependence of the magnetic susceptibility. Although the formation of spin glass state for x=1.5 and a spin dimer state for x=1.67 are suggested in the previous study [11, 12], the present NMR results imply the spin gap does not much depend on hole-doping and also on magnetic field. The recent neutron scattering measurement for the single crystal does not show the clear evidence of the spin gap state, instead indicates that an anomalous broadening of spin wave excitations along the chain in the undoped one (x=0) and also the hole doping is much more effective to broaden the excitations along the chain [14]. This may be caused by the progressive increase of antiferromagnetic interaction with increasing hole concentration.

The magnetic interaction between Cu^{2+} spins via corner oxygen is expected to be ferromagnetic, whereas, the interaction between the next neighbor Cu^{2+} spins is strongly antiferromagnetic, when a doped-hole occupies the adjacent Cu site. The spin systems are highly frustrated within the chain. As the hole concentration is 1/3 per Cu for x=1.67, the localized holes are located at every third site in the chain. Thus, all the Cu^{2+} spins are expected to form spin singlet dimers, Such arrangement of the spins in the 1D chain is already proposed for $Ca_{1-x}CuO_2$ from the structural analysis [15] and for the chain site in $Sr_{14}Cu_{24}O_{41}$ from the neutron scattering [16] and the NMR study [17].

In summary, we have observed spin gap behavior in the temperature dependence of the Knight shift and nuclear spin-lattice relaxation rate of ^{63}Cu in the edge-sharing CuO_2 chain system of $Ca_{2+x}Y_{2-x}Cu_5O_{10}$ for x=1.5 and 1.67. The appearance of the spin dimers relevant for the spin singlet state is confirmed in the hole-doped 1D cuprate from a microscopic point of view.

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