NMR Study of Zn Doping Effect in Spin Ladder System $SrCu_2O_3$

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Nuclear magnetic resonance spectra of Cu nuclei were measured in a typical spin ladder system, $Sr(Cu_{1-x}Zn_x)_2O_3$ ($x = 0\%$, 0.25%, and 0.5%) at temperatures ranging from room temperature to 20 K. The linewidth of the spectrum peaks drastically increased at temperatures below 100 K with x being only 0.25%. The width ΔW increased with the increase in Zn concentration and the decrease in temperatures ($\Delta W \sim x/T$). These facts prove that a quite minute amount of impurity breaks the singlet ground state and the effect of impurity is observed in the whole system. [S0031-9007(97)05089-8]

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The effects of impurity doping in low dimensional quantum spin systems have recently become interesting topics in terms of experiment and theory. One of the topics in the localized quantum spin system is the appearance of free edge spins with a freedom of $S = \frac{1}{2}$ in $S = 1$ Haldane gap system. In the case of a typical $S = 1$ Haldane gap system, $Ni(C_2H_8N_2)_2NO_2(ClO_4)$, the characteristics of EPR spectra of Cu- or Zn-doped samples have been explained by the existence of $S = \frac{1}{2}$ free edge spins [1,2]. Another topic in the localized system is the appearance of magnetic long range order in a spin-Peierls system $CuGeO_3$ [3–5]. It has been confirmed from neutron scattering that the antiferromagnetic order coexists with lattice dimerization at low temperatures in 0.7% Si doped samples [5]. Those results of the experiments on impurity doping have revealed novel features of low dimensional quantum spin systems.

Impurity doping in a spin ladder system has currently been attracting researchers since theoretical investigation has revealed that doping nonmagnetic impurity into the paramagnetic state could lead to superconductivity [6,7]. A typical spin ladder system, $SrCu_2O_3$ with spin gap $\Delta = 420$ K [8], has been intensively investigated for the last several years. Although superconductivity has not been observed, an unexpected anomaly corresponding to the magnetic order has recently been observed at temperatures below 8 K when the base material is doped with 1% Zn by Azuma *et al.* [9]. In the lightly doped region where the concentration of Zn is below 1%, the system is paramagnetic and the susceptibility shows Curie-like behavior at low temperatures. Although the susceptibility data are well explained by the unpaired free spins [9], the microscopic information has not been obtained yet.

It is of great interest to study the microscopic nature of the spin configuration which appears when the substance is doped with impurity such as Zn. We investigated the problem by measuring ^{63}Cu and ^{65}Cu nuclear magnetic resonance (NMR).

The oriented powder samples with very low concentration impurity (0.25%, 0.5% Zn) were prepared for the measurement. The detail of the synthesis procedure is shown in Ref. [10]. The NMR measurements were carried out mainly at the frequency of 83.55 MHz and with the field (H) parallel to the c axis, the direction of orientation, being applied. There appeared six separated NMR spectrum peaks, as shown in Fig. 1(a). The values of ν_Q and η are estimated as 9.9 MHz and 0.71, respectively. The results for the pure samples are consistent with the results of Ishida *et al.* [11]. The NMR linewidth for the pure samples is approximately 100 G at room temperatures and 200 G at 4.2 K. On the other hand, the drastic increase in the linewidth is observed for the samples doped with 0.25% Zn at temperatures below 100 K, as shown in Fig. 1(b). The NMR linewidth becomes narrower at room temperatures, but it is still twice as wide as that of the pure samples. It can easily be seen from Fig. 1(b) that the linewidth is field dependent when two side peaks caused by the ^{63}Cu transition ($I^Z = \pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2}$) around 64 and 82 kOe are compared. The linewidth at around 82 kOe is wider than the one at around 64 kOe. The H dependence of the linewidth for these peaks of 0.5% Zn doped samples is shown in Fig. 2. The linewidth ΔW shows linear dependence on H, $\Delta W(\mathrm{Oe}) \sim 200 + H(\mathrm{Oe})/T$. The dependence of ΔW on T and H shows that the cause of the broadening of the peaks is not electric but magnetic.

Now, we focus on the central peaks ($I^Z = \frac{1}{2} \leftrightarrow -\frac{1}{2}$) in order to precisely investigate the T dependence of NMR shifts and linewidth. Hereafter we investigate only the central peak of ^{65}Cu since that of ^{63}Cu overlaps the side peak of ^{65}Cu ($I^Z = \frac{3}{2} \leftrightarrow \frac{1}{2}$). There appears a satellite signal or a hump in the central peak of around 68.9 kOe, as shown in Fig. 3. We decomposed the central peak into two Gaussians. The T dependence of the shift of the satellite signal is shown in the inset of Fig. 4. The value is about 0.2%–0.4% and increases with the

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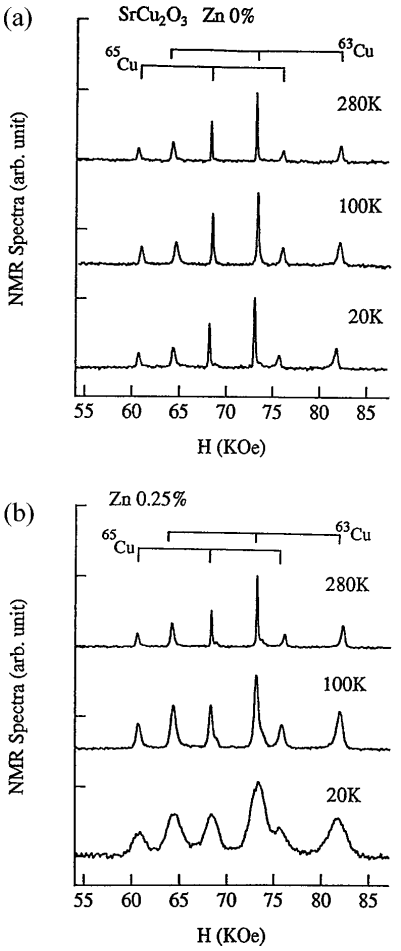


FIG. 1(a). NMR spectra for pure samples at 83.55 MHz. (b) NMR spectra for 0.25% Zn doped samples at 83.55 MHz.

increase in temperature. These features of the satellite signal have also been observed for the H perpendicular to the c axis [11]. Therefore, the satellite signal would be attributed to the imperfect orientation. The reason that the satellite signal is observed as a separate peak would be attributed to anisotropy of the orbital shifts for the crystal axes, i.e., c axis and the perpendicular direction. We, hereafter, focus only on the main signal. The T dependence of the shift is shown in Fig. 4. Here, we defined the shift as the center of the Gaussian since the peaks of the Zn doped samples become broader at lower temperatures. The shift of the pure sample becomes almost constant at lower temperatures, reflecting that the ground state is singlet. However, the shifts of Zn doped samples show Curie-like behavior in a way similar to the susceptibility data. The difference between the NMR and susceptibility lies in the fact that the NMR provides on-site microscopic information, while the susceptibility provides totally macroscopic information. In the localized free spin model, the susceptibility is given as $\chi = Nc(g\mu_B)^2 S(S+1)/3K_B T$, where c represents the concentration of the impurity, i.e., the localized

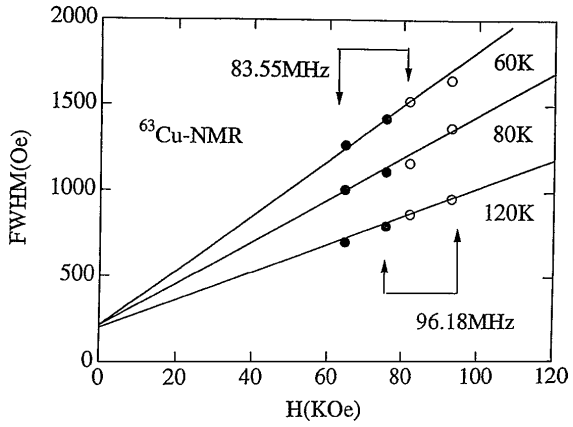
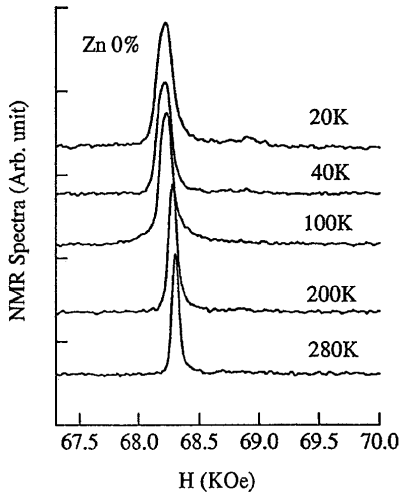


FIG. 2. Field dependence of NMR linewidth of the ^{63}Cu side peaks for 0.5% Zn doped samples. The closed (open) circles represent the side peaks caused by the transition $I^Z = -(+)\frac{3}{2} \leftrightarrow -(+)\frac{1}{2}$.



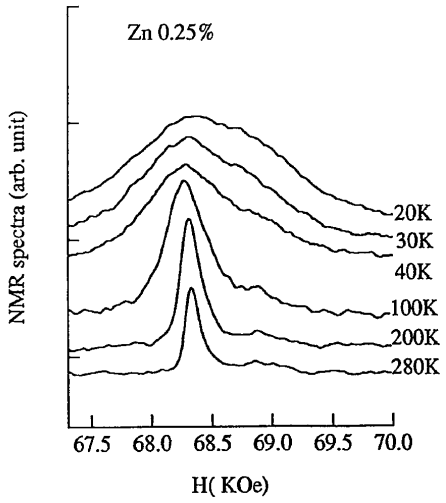


FIG. 3. The ^{65}Cu central peak $(I^Z = -\frac{1}{2} \leftrightarrow +\frac{1}{2})$ at 83.55 MHz for 0% and 0.25% Zn doped samples.

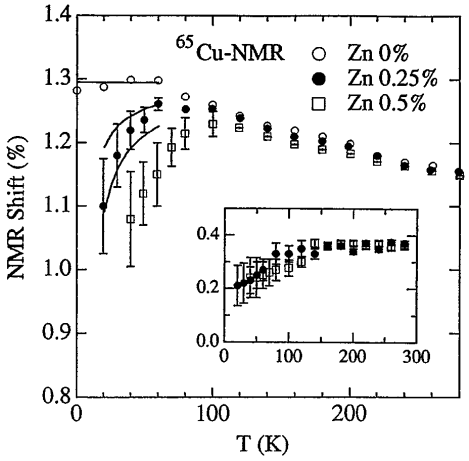


FIG. 4. Temperature dependence of the shift for the main signal in the ^{65}Cu central peak. The curves represent Eq. (1). The inset is the temperature dependence for the satellite signal.

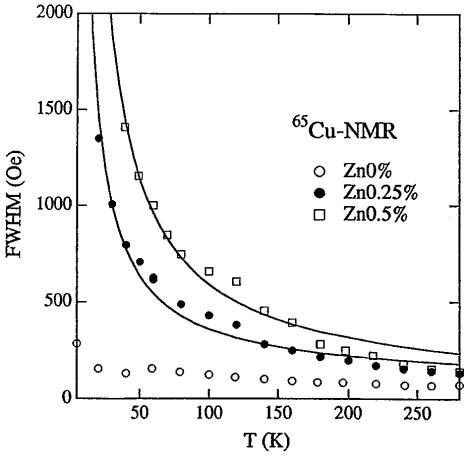


FIG. 5. Temperature dependence of the linewidth of the ^{65}Cu central peak. The curves represent Eq. (2).

unpaired free spins with $S = 1/2$. If the localized free spin model is valid, the shift due to the impurity doping should be zero ($\Delta K = 0$) because the majority of Cu sites remain in a nonmagnetic state with Zn being doped at a concentration of 0.25%–0.5%. On the contrary, if the uniform moments observed in the susceptibility measurements originate from a whole system, the shift should show Curie-like temperature dependence. The aforementioned susceptibility is rewritten in this case as $\chi = N(g\mu_B)^2[cS(S+1)]/3K_BT$ where $\sqrt{cS(S+1)}$ is the uniform effective moment at each lattice site. The shift is given as $\Delta K = A_{\rm hf}\chi/N\mu_B$.

$$\Delta K = A_{\rm hf} g^2 \mu_B [cS(S+1)]/3K_BT\,. \qquad (1)$$

Thus it is obtained as $8.1c/T$ with the hyperfine coupling of $A_{\rm hf} = -120$ kOe/μ_B obtained from $K - \chi$ plot at high temperatures being substituted to Eq. (1). The calculated values are plotted as solid curves in Fig. 4. The values obtained from the experiments are about twice as big as the calculated values of both Zn doped samples, 0.25% and 0.5%. It can be said that the deviation is within an experimental error since the peak broadens at low temperatures and the shifts are less well defined. The experimental results suggest that the uniform moments appear in the whole system rather than in finite lattice sites near impurity.

The T dependence of the linewidth is shown in Fig. 5. The linewidth increases with the increase in the Zn concentration and the decrease in temperature, while the linewidth of the pure samples remains almost constant. As a result, ΔW is simply expressed as

$$\Delta W \sim c/T + \alpha\,, \qquad (2)$$

where c and α represent the Zn concentration and a constant, respectively. The solid curves in Fig. 5 represent $\Delta W = 2.75 \times 10^4/T + 83.6$ and $\Delta W = 5.74 \times 10^4/T + 42.8$ (Oe) for 0.25% Zn and 0.5% Zn, respectively. The singlet ground state is almost perfectly realized in the pure samples, but the state is easily broken by a quite minute amount of the impurity. The increase in the linewidth according to the increase in the concentration also shows that a quite minute amount of impurity affects the whole system. The broadening of the linewidth originates from the staggered part of the spin configuration which is included by the applied field, whereas the uniform part gives the NMR shift as shown in Eq. (1).

The NMR linewidth is analyzed from the sum of the signals with a different internal field at each lattice site and, then, the intensity of the NMR spectra $g(H)$ is given by the following expression:

$$g(H) = \Sigma_i f\big(H - (H_0 + A_{\rm hf} g\mu_B \langle S_i^Z\rangle)\big)\,, \qquad (3)$$

where $f(H)$ is the NMR line shape with natural linewidth at each lattice site and $\langle S_i^Z\rangle$ is a local moment at a lattice site which appears with impurity doping and H_0 represents the NMR shifts for the pure samples. Since the dipole coupling is ~1–2 kOe, this effect is neglected. Theoretically, it is known from several investigations that the correlation length ξ of the pure spin ladders with the low concentration of impurity is about 3 [12–14] and, then, $\langle S_i^Z\rangle$ is given as $(-1)^i S_0 \exp(-i/3)$, where the index i represents the distance from the impurity. The NMR spectrum $g(H)$ is easily calculated when $f(H) = \exp(-H^2/2w^2)$ is assumed and the natural linewidth, w, of about 200 G obtained from the pure samples is applied. The line shape of $g(H)$ is not sensitive to the value of S_0 for such a short correlation length like this and ΔW becomes below 300 Oe. Therefore, the experimental results are not definitely explained by the aforementioned theoretical investigations. The NMR spectrum is calculated for the staggered spin configuration $S_i^Z = (-1)^i S_0 \exp(-i/\xi)$. The simulation of $g(H)$ in Eq. (3) for the chains of 400 lattice sites with $\xi \sim 100 \pm 10$ and $S_0 = 0.005 \pm 0.001$ gives rise to ΔW by about 0.8 kOe, and for the chains of 200 lattice sites with

$\xi \sim 35 \pm 5$ and $S_0 = 0.013 \pm 0.001$, it gives rise to ΔW by about 1.4 kOe. The width w of $f(H)$ is assumed as about 300 ~ 400 G in order to keep the line shape of $g(H)$ Gaussian-like structure. For much larger S_0 or ξ, a double peak structure appears in $g(H)$, whereas for much smaller S_0 or ξ, a large ΔW which is presented here cannot be explained. These simulations correspond to the measurements at a temperature of 30–40 K for the doped Zn concentrations of 0.25% and 0.5%, respectively. In the case where $\xi = 100$ for 400 lattice sites, $\langle S_i^Z \rangle$ is still $0.135 S_0$ at the middle position between impurities. The value is not negligibly small as compared to the nearest adjacent sites of the impurities. These simulations give a rough estimation of ξ, and the results suggest the existence of the long distance tail of the staggered moments. The long distance tail may be deeply related with the magnetic order in the region where Zn $> 1\%$. The order may be caused by the freezing of the staggered moments due to three dimensional smaller interactions.

The large value of ξ is expected to appear in a gapless spin system such as $S = \frac{1}{2}$ Heisenberg linear chain [15] or a spin system with small spin gap as compared to the exchange coupling. The large ξ in the present case could arise from the weak coupling for the rungs. In this case, the characteristics of linear chains become dominant in the spin ladder and the large ξ is expected under the existence of the impurities [16]. On the contrary, in the case of the weak coupling for the legs, the characteristics of the rung dimers become dominant and the development of ξ is hardly expected. Moreover, the interladder coupling would promote the development of ξ since the coupling has the effect of reducing the spin gap of the pure spin ladder system [17]. Zn doping plays a roll of small perturbation at local lattice sites but causes a large effect on the whole system. The fact would be caused under the background that $SrCu_2O_3$ itself locates adjacent to the critical region for the gapless state due to the weak coupling for the rungs or the interladder coupling, although the spin singlet is realized.

In summary, the authors have shown from the NMR spectra that a very minute amount (~0.25%–0.5%) of impurity breaks the singlet ground state in a ladder system $SrCu_2O_3$. The existence of the long distance tail of the staggered moments and the uniform moments with a constant value is suggested from the NMR linewidth and the shifts at lower temperatures.

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