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Effect of $S=\frac{1}{2}$ fractional spin on nuclear magnetic relaxation in a $S=1$ Heisenberg antiferromagnetic linear chain system

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The spin-lattice relaxation time T_1 of proton in NENP was measured at low temperatures and at low fields for a single crystal involving natural defects of 5%, one doped with a nonmagnetic Zn^{+2} ion of 1%, and pure crystal. The magnetization recoveries exhibited $\exp\{-(t/\tau_1)^{1/2}\}$-type behaviors subsequent to exponential behaviors for initial time, which were qualitatively almost the same in all cases. The absolute values of the corresponding relaxation rates for the former two crystals were much larger than those for the latter. These features were reasonably explained by considering that fractional spins may play the role for thermal reservoir as if a magnetic impurity in a nonmagnetic solid. It is speculated that the spin-lattice relaxation of the fractional spin, the time of which is of the order of nuclear Larmor period, is determined by the collision with low-density Haldane excitations. [S0163-1829(97)00445-6]

There has been a considerable interest in the properties of the ground-state and magnetic excitations in $S=1$ Heisenberg antiferromagnetic linear chain (HALC), since Haldane proposed his conjecture that the HALC with integer spin values has an energy gap between the first excited triplet state and a nonmagnetic singlet ground state.[1] The nature of the ground state of $S=1$ HALC has been well understood in terms of the ''valence-bond-solid,'' so-called AKLT (Affleck-Kennedy-Lieb-Tasaki) model.[2] According to this model, at both terminals of an open chain, there appears a degree of freedom or fractional spin of $S=1/2$ which cannot participate in the singlet pair formed between the two neighboring sites of $S=1$. The linear chain of Ni^{+2} ion in the compound $\mathrm{Ni(C_2H_8N_2)_2NO_2(ClO_4)}$ (abbreviated as NENP) has been the subject of various experimental studies as the most typical system for the realization of Haldane gap for $S=1$ HALC.[3] The presence of the fractional spin has been evidenced clearly by the measurement of ESR in NENP doped with magnetic Cu^{+2} ion,[4] or a nonmagnetic ion such as Zn^{+2}.[5] In an undoped single crystal of NENP, the ESR signals due to the fractional spins caused by natural defects have been also observed.[6]

Previously it was found that the relaxation time T_1 of proton in NENP exhibits an anomalous behavior at low temperatures:[7] The relaxation rate T_1^{-1} deviates seriously from its remarkable and rather monotonous temperature dependence between about 6 and 70 K, which is due to contribution of thermally activated lowest magnetic excitations. Furthermore the relaxation rate T_1^{-1} accompanies a peak, which shifts to the lower-temperature side as the resonance frequency ν_N becomes smaller. Since such anomalous behaviors are found at low temperatures and at low fields where the nonmagnetic character of the system is well developed, the predominance of another relaxation mechanism has been suggested. The purpose of the present work is to clarify, in view of recent experimental findings of the fractional spin in NENP, the effect of the fractional spin on the proton nuclear magnetic relaxation at low temperatures. The measurements were made, using a phase-coherent pulsed NMR spectrometer, for a single crystal with defects of 5%, the value of which has already been confirmed by magnetization measurement,[4] and for a single crystal doped with a Zn^{+2} ion of 1%. For comparison, we also chose another pure single crystal. We observed the nuclear-magnetization recovery $m(t)=1-M(t)/M_0$, where M_0 is the magnetization at the thermal equilibrium, with low external field applied perpendicular to the linear chain along the b axis.

Typical examples of the temperature dependences of nuclear magnetization recoveries $m(t)$ for NENP with defects obtained at $\nu_N=12$ MHz are shown in Fig. 1, where (a) and (b) represent semilogarithmic plots of $m(t)$ vs t and $t^{1/2}$, respectively. As is seen, the behavior of $m(t)$ differs depending on the temperature: At the temperatures above about 8 K, the recovery is well described by a single-exponential function, thus determining the conventional relaxation time T_1, which is associated with thermal magnetic excitations. While, at lower temperatures, the recovery becomes nonsingle exponential as a whole. The long-time behavior of $m(t)$ is described well by the function of $\exp\{-(t/\tau_1)^{1/2}\}$, where τ_1 is taken to be constant, and during initial time $m(t)$ fits well a single-exponential function, which defines another time constant for the recovery of $m(t)$. Hereafter this time constant is also expressed as T_1.

Figure 2 shows the temperature dependences of T_1^{-1} and τ_1^{-1} at $\nu_N=12$ MHz. The quite similar recovery curves of $m(t)$ were observed for the Zn^{+2}-doped NENP, and for pure NENP. Figures 3 and 4 show the results for the temperature dependences of T_1^{-1} and τ_1^{-1} obtained at $\nu_N=18$ MHz in these samples. As is seen in Figs. 2–4, the temperature dependences of the time constants T_1 and τ_1 are qualitatively almost the same: There appears a maximum in each of T_1^{-1} and τ_1^{-1} at the same temperature. Thus, fluctuations of the local fields which govern the nuclear magnetization recovery

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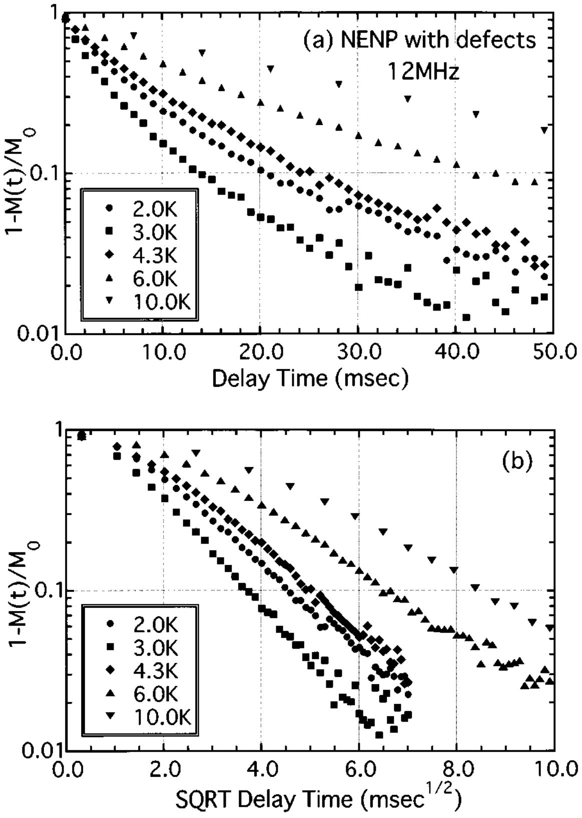

FIG. 1. Examples of nuclear-magnetization recovery $m(t)$ of proton in NENP with defects for various temperatures measured at $\nu_N = 12$ MHz with $H \perp b$ axis: Semilogarithmic plots of $m(t)$ vs t and $t^{1/2}$ are represented in (a) and (b), respectively.

may be essentially common. However, the absolute values of the corresponding relaxation rates for the crystal with defects and Zn^{+2}-doped crystal are much larger than those for pure crystal. It is probable that a small amount of defects may be involved even in pure NENP. Thus, these experimental features suggest strongly that the fractional spins at the terminals of finite Ni^{+2} linear chain play the role for the thermal reservoir for the proton magnetization recovery as if a magnetic impurity in nonmagnetic solid.

In the following we shall analyze the experimental results for $m(t)$ in view of the theory for the nuclear magnetic relaxation in nonmagnetic solid including paramagnetic impurity.[8] Let us first explain briefly the relevant theoretical background. This theory is based on taking into account, in addition to the interaction with the impurities via the anisotropic dipolar coupling, the effect of spin diffusion as a means of transporting the nuclear Zeeman energy to paramagnetic impurity. The dominant process is the one such that the nuclear-spin flip occurs without accompanying the electron spin flip. The relaxation rate of the nuclear spin $\boldsymbol{I}_\nu$ at the position $\boldsymbol{r}_\nu$ caused directly by the fluctuation of the impurity spin $\boldsymbol{S}_j$ at the position $\boldsymbol{r}_j$ is given as $(T_1^{-1})_{\nu j} = C/r_{\nu j}^6$ where the term C is given as

$$C = \frac{2}{5}(g\mu_B\gamma_N)^2 S(S+1)\frac{\tau_e}{1+\omega_N^2\tau_e^2}. \tag{1}$$

Here τ_e is the longitudinal relaxation time of the impurity electron spin which is introduced by taking the correlation function of the form like $\langle S_j^z(t)S_j^z\rangle = S^2\exp(-t/\tau_e)$. Then the behavior of $m(t)$ is determined by an ensemble average of the recoveries $m(r_\nu,t)$ for the nuclei in various different environments. Because of an average local-field produced by the impurity, the nuclei just in the neighborhood of each impurity site cannot contribute to NMR observation, and also they cannot take part in spin diffusion. Thus, for such a region around each impurity site, we may define spheres char-

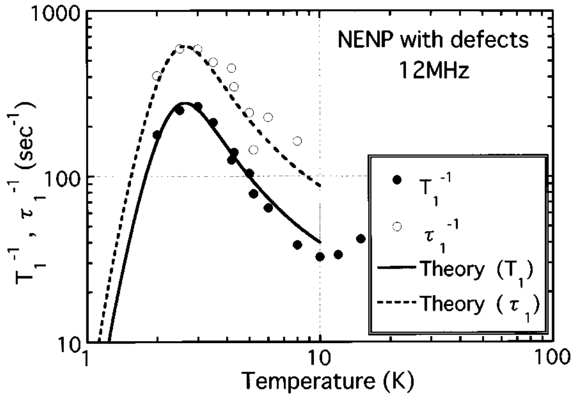

FIG. 2. Temperature dependences of T_1^{-1} and τ_1^{-1} for NENP with defects obtained at $\nu_N = 12$ MHz with $H \perp b$ axis.

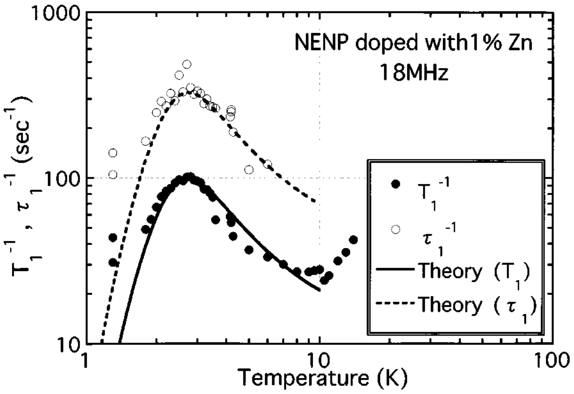

FIG. 3. Temperature dependences of T_1^{-1} and τ_1^{-1} for Zn^{+2}-doped NENP(1%) obtained at $\nu_N = 18$ MHz with $H \perp b$ axis.

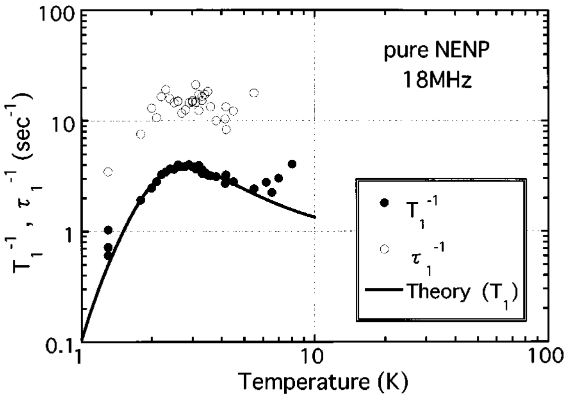

FIG. 4. Temperature dependences of T_1^{-1} and τ_1^{-1} for pure NENP obtained at $\nu_N = 18$ MHz with $H \perp b$ axis.

acterized by an exclusion radius b_0 and by a diffusion-barrier radius b. In general, the relation $b<b_0$ $(\approx 1.4b)$ holds. When the nuclear-spin system is saturated initially, the nuclear magnetization recovers most rapidly at $r_\nu \sim b_0$ due to the relatively strong dipolar couplings. This results in a difference in spin temperature of the nuclear-spin system, which gives rise to the nuclear-spin diffusion. There are two limiting cases: In the diffusion-limited case, the bottleneck in the relaxation process is the rate at which the nuclear Zeeman energy can diffuse to the impurity sites. During the time when the diffusion effect does not emerge, the configurations of the impurities which the nucleus sees differ at the nuclear site, thus $m(t)$ is not expected to be exponential. The use of the continuum approximation yields an $\exp\{-(t/\tau_1)^{1/2}\}$-type recovery of $m(t)$ except for short initial time.[9,10] While in the rapid-diffusion-limit case, since the nuclear Zeeman energy can be redistributed among the nuclear spin system fast enough to maintain the internal equilibrium, the bottleneck is the rate at which the nuclei locating near the vicinity of the exclusion radius relax to the nearest impurity. In this case, the recovery of the nuclear magnetization would follow an exponential function over the whole time, thus the nonexponential behavior is missing.

Now we shall examine our experimental results. As is seen in Fig. 1, the $\exp\{-(t/\tau_1)^{1/2}\}$-type behavior of $m(t)$ is clearly observed, while the appearance of the effect of spin diffusion is not obvious. So our result seems to correspond primarily to the diffusion-limited case. In the present case, the fractional spin may be regarded as a magnetic impurity, and the fractional spins of $S=1/2$ appear always as a pair of two effective spins at each of the defects or dopant Zn^{+2} ions. Here we assume for simplicity that b_0 and b can be defined around each of fractional spins in a pair. Neglecting the effect of spin diffusion, and using the continuum approximation for the nuclear-spin system, we obtain the following expressions for $m(t)$;[9,10] $m(t)=\exp(-t/T_1)$ with

$$T_1^{-1}=4\pi N_0 c_e C/3b_0^3 \quad (t<b_0^6/C) \tag{2}$$

and $m(t)\sim\exp\{-(t/\tau_1)^{1/2}\}$ with

$$\tau_1^{-1}=[(4/3)\pi^{3/2}N_0 c_e]^2 C \quad (t>b_0^6/C), \tag{3}$$

where N_0 is density of the Ni^{+2} lattice sites of NENP, and c_e is the concentration of the effective fractional spins. The initial exponential recovery is due to the dipolar coupling with only the nearest effective spin of $S=1/2$. At $t\sim t_0=b_0^6/C$, it turns into the subsequent $\exp\{-(t/\tau_1)^{1/2}\}$-type behavior, which results from the couplings with the ensemble of the surrounding effective spins. The above expressions predict that T_1^{-1} and τ_1^{-1} are proportional to the term C, and to c_e and c_e^2, respectively. Thus the temperature dependences of T_1^{-1} and τ_1^{-1} come only from τ_e in the term C, and the absolute values of T_1^{-1} and τ_1^{-1} depend on c_e.

As is evidenced in Figs. 2–4, the relaxation time τ_e should increase with decreasing temperature. Then there appears a peak in both T_1^{-1} and τ_1^{-1} at the temperature where the relation $\omega_N\tau_e=1$ is satisfied. This relation yields the maximum value $C_{\max}$ of the term C for each ω_N. Then using the peak values $(T_1^{-1})_{\max}$ and $(\tau_1^{-1})_{\max}$, we can determine the values of c_e and b_0 from Eqs. (3) and (2). Other numerical values necessary for this evaluation are $S=1/2$, $N_0=1.54\times10^{21}/\mathrm{cm}^3$, and $g=2.2$. Referring to Fig. 2, we obtain $(C)_{\max}=5.9\times10^{-40}$ cm^6/s, $b_0=11\times10^{-8}$ cm and $c_e=0.084$. Using these values, the crossover time t_0 is evaluated as 2.7 ms, which is close to the experimental value. Note also that t_0 should take the minimum at $(T_1^{-1})_{\max}$ and $(\tau_1^{-1})_{\max}$. We find such features in Fig. 1. Considering the fact that one defect produces two fractional spins, the concentration c of the defects in this sample is evaluated to be $c=0.042$. This value of c is reasonably compared with the anticipated value of 0.05. As for the temperature dependence of τ_e, we tentatively assume an activation-type equation with the activation energy of Δ;

$$\tau_e=\tau_0\exp(\Delta/k_BT). \tag{4}$$

The solid and dashed lines in Fig. 2 represent, respectively, theoretical curves for T_1^{-1} and τ_1^{-1} obtained on the basis of Eq. (4) by choosing $\Delta/k_B=9.4$ K as the best-fit value. Then τ_0 is evaluated to be 3.8×10^{-10} s.

We can evaluate similarly the values of b_0 and c_e for the case of the Zn^{+2}-doped NENP. We obtain $b_0=13\times10^{-8}$ cm and $c_e=0.082$. This value is much larger as compared with the value of $c_e=0.02$ expected from the doping concentration c' of 1%. This may be ascribed to the presence of natural defects apart from the defects produced by dopant. Then, if we tentatively assume $c'=0.01$, the concentration c of the natural defects is evaluated to be $c=0.036$. The solid and dashed lines in Fig. 3 represent, respectively, theoretical curves for T_1^{-1} and τ_1^{-1} obtained by choosing the best-fit value of $\Delta/k_B=8.4$ K. As for pure NENP, we get $c=0.001$ using $b_0=11\times10^{-8}$ cm determined for NENP with defects. The solid line is the best-fit theoretical curve with $\Delta/k_B=6.7$ K. As is seen in Figs. 2–4, Eq. (4) for τ_e yields satisfactory agreement between the experiment and the calculation by choosing an appropriate value of Δ, although the chosen value of Δ scatters somewhat depending on the sample. It turns out that the anomaly of the relaxation time provided in Ref. 7 should correspond to the behavior of the time constant T_1 introduced in the present analysis. It is added that the behaviors of T_1^{-1} are very close to those reported in Ref. 7 quantitatively as well as qualitatively.

The establishment of the spin temperature and the nuclear-spin diffusion, which occurs extending over the crystal, must be due to the proton-proton interactions between the different $\mathrm{C_2H_8N_2}$ molecules in the neighboring chains as well as along the chain. If we use the average distance of 2.5×10^{-8} cm for the relatively short distances of intermolecule protons, we obtain approximate value of $T_2=40\times10^{-6}$ s. This value is consistent with the experimental values of $30\text{–}40\times10^{-6}$ s. As for the diffusion constant D, the expression for the configuration of simple cubic lattice of the nuclear spins of $I=1/2$ is given as $D=a^2/50T_2$, where a is the lattice spacing and T_2 is the transverse relaxation time.[8] Applying this expression to the case of NENP, we obtain roughly $D=6.3\times10^{-13}$ cm^2/s, using an average value of 2.5×10^{-8} cm for a and 4×10^{-5} s for T_2. We can define, around each fractional spin, a sphere of radius r_0 in which the nuclei reach thermal equilibrium during the time t, we have the relation $r_0=(Ct)^{1/6}$, where

C is given by Eq. (1). On the other hand, the spin temperature near the fractional spin may transfer, during the time t, to the distance $\sim r_d=(Dt)^{1/2}$. Thus, for $r_d>r_0$, or for the time $t>t_1=C^{1/2}D^{-3/2}$, the spin diffusion becomes effective, and $m(t)$ approaches a single-exponential recovery with a relaxation rate given as $(T_1^{-1})_d=4\pi N_0 c_e \rho D$, where ρ is pseudopotential given as $0.7(C/D)^{1/4}$.[8] Then, using the above values for T_2 and D, we obtain, for NENP with defects, the value of $t_1=140$ msec for $(T_1^{-1})_{\max}$. It turns out that the relation $t_0 \ll t_1$ holds at the relevant temperatures. The relaxation rate $(T_1^{-1})_d$ is calculated to be 0.16 s^{-1} for $(T_1^{-1})_{\max}$. This value is much smaller as compared with experimental values of T_1^{-1}. So the diffusion effect is found to be negligibly small, thus the $\exp\{-(t/\tau_1)^{1/2}\}$-type behavior lasts for a long time. This is the reason why the effect of nuclear-spin diffusion is not observed obviously in the present cases.

Finally we discuss the spin-lattice relaxation time τ_e of the fractional spin. The value of τ_e, which is of the order of $1/\omega_N$, is much shorter as compared with the spin-lattice relaxation time of the paramagnetic impurity in the usual nonmagnetic solid or intermetallic compound, which is of the order of microseconds or of seconds at liquid N_2 or liquid He temperature, respectively.[9,10] As the most probable reason, we suppose that the spin-lattice relaxation of the fractional spin is governed by the collision with the thermal Haldane excitations in the linear chain, which propagate on the linear chain with an average spin-wave velocity. Then by assuming that the density of Haldane excitations and their average velocity does not depend on the length of the chain, we may speculate that the fractional spin is relaxed by one collision with the excitation, and the relaxation time τ_e is interpreted as the average collision time. It also follows that Eq. (4) represents the temperature dependence of the probability for the appearance of thermal excitation. Then the parameter Δ may be taken to be the effective gap energy. The values of Δ are somewhat smaller as compared with the established value of 14 K. At the present the reason for this is not certain. The above speculation seems to be consistent with the intensity of the ESR signal due to the fractional spins: The intensity increases rapidly with decreasing temperature because the resonance line is shifted largely out of the observation by collision with thermal excitation, thus the number of chains without thermal excitations increases.[11] The reason for the fact that the evaluated collision time τ_e does not depend on the length of the chain in contrast to the ESR signal intensity may be ascribed to the difference in time scale of the Larmor period between the nuclear and electron spins.

In conclusion, we have explained the anomalous behaviors of the nuclear magnetization recovery of proton in NENP with defects at low temperatures in terms of the effect of fractional spins of $S=1/2$ at the terminals of an $S=1$ HALC of finite length by considering that the fractional spins may play roles for thermal reservoir. As the most probable reason for the dynamics of the fractional spins, the collision with the low-density thermal Haldane excitations has been speculated.

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