Experimental evidence for the lowest excitation mode in the $s = 1$ Haldane-gap system: High-field proton magnetic relaxation in $Ni(C_2H_8N_2)_2NO_2ClO_4$

N. Fujiwara
Department of Physics, Faculty of Science, Kyoto University, Kyoto 606, Japan

T. Goto, S. Maegawa, and T. Kohmoto*
Department of Physics, College of Liberal Arts and Sciences, Kyoto University, Kyoto 606, Japan
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The nuclear spin-lattice relaxation time T_1 of the proton in the $s=1$ Haldane-gap system $Ni(C_2H_8N_2)_2NO_2ClO_4$ (NENP) has been measured at low temperatures in high magnetic fields (4 T $< H <$ 8 T) below the critical field. From the experimental results below 4 K, the field dependence of the energy gap for the lowest-energy mode of the three excitation modes, which has been predicted theoretically in NENP, are obtained. The results of T_1 below 4 K are well explained by treating the magnetic excitations as free fermions rather than free bosons.

Recently, there has been considerable interest in Haldane's prediction[1] that the one-dimensional Heisenberg antiferromagnet (1DHAF) with integer spin has an excitation gap between the singlet ground state and first excited state. This prediction has been supported by a number of numerical calculations for $s=1$ 1DHAF.[2–4] It is pointed out that the first excited state is a triplet which splits into a doublet and a singlet in the presence of single-ion anisotropy.[2]

Experimentally, the $s=1$ quasi-1DHAF compound $Ni(C_2H_8N_2)_2NO_2C1O_4$ (NENP) has been studied extensively as a typical compound for the Haldane-gap system by susceptibility,[5] neutron scattering,[5,6] and high-field magnetization.[7,8] The critical field H_c, where the lowest-excitation branch crosses the ground-state level, has been reported to be 9.8 and 13.1 T for the applied field **H** parallel and perpendicular to the linear chain along the b axis, respectively.[8]

For the study of low-frequency spin dynamics in the Haldane-gap system, the nuclear spin-lattice relaxation is a useful probe.[9–12] In previous works,[9,10] we measured the relaxation time T_1 of the proton in NENP at temperatures down to 0.5 K in the field range below 1 T. The remarkable decrease of the relaxation rate T_1^{-1} with decreasing temperature was interpreted on the basis of the conventional theory for paramagnets by using static-susceptibility data.[5] Gaveau *et al.*[11] also measured T_1 of ^1H at temperatures above 5 K between 1 and 4 T, and above 2 K at 8 T. They explained their experimental results, considering the low-frequency magnetic fluctuation associated with the damping of the excitation on the basis of the free-boson model proposed by Affleck for NENP.[13]

One of the interesting problems for the Haldane-gap system is the behavior of magnetic excitations in the presence of an applied field, particularly near H_c. Theoretically, it has been discussed that the magnetic excitation near H_c may be described by free fermions[14] or 1D bosons with a hard-core potential[15,16] which is equivalent to free fermions. In view of this, it is worthwhile studying the nuclear magnetic relaxation in NENP at low temperatures in the presence of high magnetic fields.

In the present work, we have measured T_1 of ^1H in NENP in the field range between 4 and 8 T at temperatures between 1.4 and 30 K. The temperature dependence of the relaxation rates T_1^{-1} below about 4 K have exhibited the existence of an excitation gap. In the following we show that this gap gives experimental evidence for the lowest-energy mode of the three excitation modes and that our results are well explained by treating the magnetic excitations as free fermions rather than free bosons.

The experiment has been performed by using a pulsed-NMR method for a single crystal of NENP in an external field applied parallel (‖) and perpendicular (⊥) to the Ni^{2+} linear chain. The nuclear spins of ^1H, which are included in $C_2H_8N_2$, are coupled with the Ni^{2+} spins via the dipolar interaction. Several NMR lines corresponding to nonequivalent proton sites were observed around the resonance field for a free proton at a fixed NMR frequency. The shift of the resonance field in each line becomes larger with increasing field or with decreasing temperature. The relaxation time T_1 for the central line was measured by using the saturation-recovery method for the spin-echo signal.

Figures 1(a) and 1(b) show the temperature dependences of the relaxation rate T_1^{-1} for the $\mathbf{H}\parallel b$ and $\mathbf{H}\perp b$ axes, respectively. The temperature dependences of T_1^{-1} change drastically around 4 K in both cases. Below 4 K the values of T_1^{-1} at a constant field exhibit an exponential decrease with decreasing temperature, expressed as

$$T_1^{-1} \propto \exp(-E_g/T) , \tag{1}$$

where the value of E_g depends on H. Figure 2 shows the field dependences of E_g obtained by fitting Eq. (1) with the experimental data, as is indicated by the dashed lines in Figs. 1(a) and 1(b).

Let us here consider the field dependence of E_g. Because of the presence of the longitudinal single-ion anisotropy term $D\sum_i (s_i^z)^2$, the triplet excited state splits into a lower-energy doublet with the z component of the total spin S^z $(=\sum_i s_i^z)=\pm 1$ and a higher-energy singlet with $S^z=0$ at zero field. In the presence of an applied

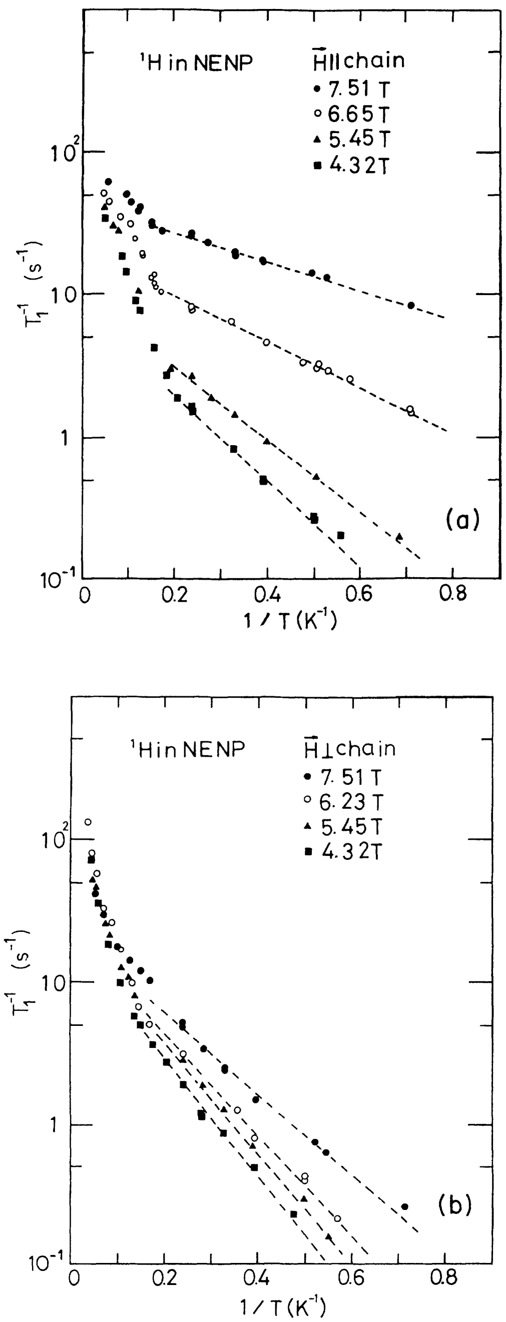

FIG. 1. Temperature dependence of T_1^{-1} for various experimental fields **H**. The dashed lines are drawn by the fitting of Eq. (1) with experimental results. (a) The field **H** is parallel to the linear chain. (b) The field **H** is perpendicular to the chain.

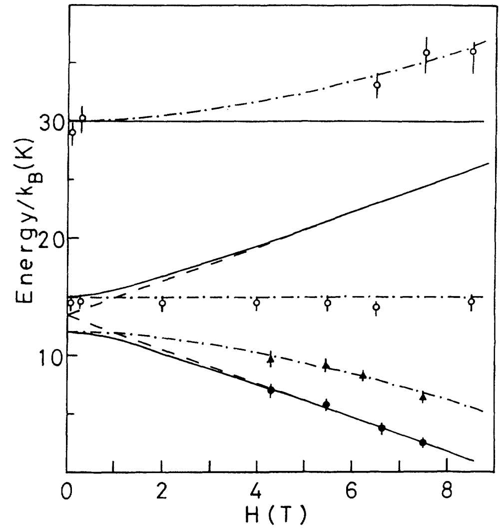

FIG. 2. Field dependence of energy levels of the excited state. Solid circles (●) and triangles (▲) show the energy gap obtained from T_1^{-1} with the field **H** parallel or perpendicular to the chain, respectively. The solid and dot-dashed lines represent the calculated curves with longitudinal (D) and transverse (E) anisotropies with **H** parallel or perpendicular to the chain, respectively. The dashed lines represent energy levels without the E anisotropy. Open circles (○) show the neutron-scattering data (Ref. 6).

field, the doublet split into two branches. Affleck[13] and Tsvelik[14] have calculated independently the dispersion relations for the three excitation modes, on the basis of free-boson and -fermion models, respectively. For the $\mathbf{H}\|b$ axis, both theories give the same result, and the energy branches at $q=\pi$ with $S^z=\pm 1$ are expressed as $E_\pi(H)=\Delta^{\pm}\mp g\mu_B H$, where $\Delta^{\pm}$ is the energy gap of the doublet at zero field. The experimental values of E_g fit well the above equation for the lowest-energy branch, which is shown by the dashed line in Fig. 2, when we choose $\Delta^{\pm}=13.5\pm 0.5$ K and $g=2.2\pm 0.1$. For the $\mathbf{H}\perp b$ axis, on the other hand, there appears an appreciable difference between the two theoretical treatments. By comparing the field dependence of E_g with these treatments, it turned out that our results fit rather well with the expression for the lowest-energy branch at $q=\pi$ presented by Tsvelik, if the values of the gaps at zero field are chosen as $\Delta^y=12.0$ K and $\Delta^z=30.0$ K for the doublet and singlet, respectively. The lowest-energy branch calculated by using these parameters is represented by the dot-dashed line in Fig. 2. The difference between the values of $\Delta^{\pm}$ and Δ^y may be attributed to the presence of the transverse single-ion anisotropy term $E\sum_i[(s_i^x)^2-(s_i^y)^2]$.

If the transverse anisotropy term exists, the doublet splits into two levels at zero field. The contribution of this anisotropy can be included in the values of the energy gaps at zero field. The energy difference between the two lower-energy levels is estimated to be about 3 K from the difference between $\Delta^{\pm}$ and Δ^y, and so the values of the energy gaps at zero field for the two lower-energy levels are 12 and 15 K. The energy levels obtained on the basis of Tsvelik's expression in the presence of the trans-

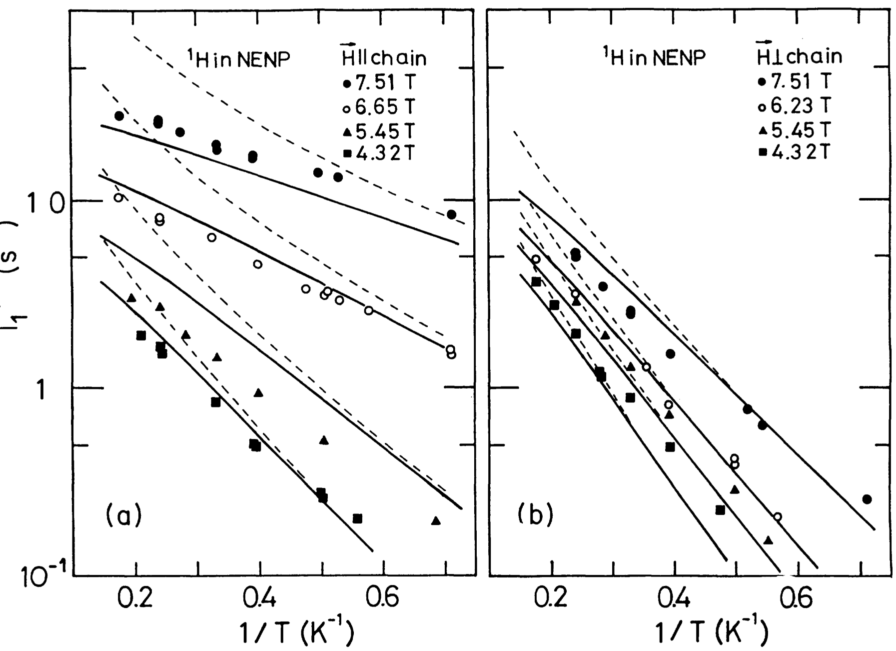

FIG. 3. Temperature dependence of T_1^{-1} below about 4 K. The solid and dashed lines represent the curves of T_1^{-1} calculated from Eq. (2) by using the fermion and boson occupation numbers for n_q, respectively, for each applied field. (a) The field **H** is parallel to the linear chain. (b) The field **H** is perpendicular to the chain.

verse anisotropy are shown in Fig. 2. For the **H**⊥b axis, the two higher-energy levels as well as the lowest-energy level are shown by the dot-dashed lines. As for the case of the **H**∥b axis, the energy levels can be estimated by considering the mixing of the two modes with $S^z=\pm 1$ as in the case of the **H**⊥b axis. The energy levels are shown by the solid lines in Fig. 2. As seen in the figure, the effect of the transverse anisotropy is negligibly small in our experimental field range. In Fig. 2 we also plot the neutron-scattering data at $q=\pi$,[6] which correspond to the two higher-energy modes for the **H**⊥b axis. The critical fields $H_c^{\parallel}$ and $H_c^{\perp}$ for the **H**∥b and **H**⊥b axes, respectively, are evaluated to be 9.2 and 13.3 T, from the theoretical expressions[14] $H_c^{\parallel}=\Delta^{\pm}/g\mu_B$ and $H_c^{\perp}=(\Delta^Y\Delta^z)^{1/2}/g\mu_B$. These values correspond to the critical fields estimated from high-field magnetization.[7,8]

Now we analyze the field and temperature dependences of T_1^{-1} below 4 K in view of the particle description for the magnetic excitation in the $s=1$ Haldane-gap system. Following the treatment of Gaveau *et al.*,[11] we consider the dominant contribution to T_1^{-1} to result from the low-frequency fluctuation associated with the energy damping of quasiparticles in the lowest-energy mode. This energy damping gives the magnetic fluctuation, which is expressed as the Fourier component of $\exp[iE_q(H)t-\Gamma t]$, where $E_q(H)$ is the excitation energy of the lowest-energy mode and Γ is the damping factor. Here we assume that the spatial spin correlation is simply expressed as $\exp(-\kappa r)$ with inverse correlation length κ. Then T_1^{-1} is expressed as

$$T_1^{-1}=\frac{A}{N}\sum_q \frac{\kappa}{(q-\pi)^2+\kappa^2}\,\frac{\Gamma}{[E_q(H)-\hbar\omega_N]^2+\Gamma^2}n_q\ , \tag{2}$$

where n_q is the occupation number of the quasiparticle and A is the geometrical factor due to the dipolar coupling between the nuclear and Ni^{2+} spins.

We have discussed that the excitation levels are well explained by the free-fermion model. Here we treat the quasiparticles as free fermions and apply the fermion occupation number $f_q=\{\exp[E_q(H)/T]+1\}^{-1}$ to n_q in Eq. (2). As for the expression of $E_q(H)$ for the **H**∥b axis, we apply the dispersion relation for the case with axial anisotropy, which is given as $E_q(H)=\hbar\omega_q^{\pm}-g\mu_B H$,[13,14] where $\hbar\omega_q^{\pm}=[(2Js)^2(q-\pi)^2+(\Delta^{\pm})^2]^{1/2}$, since the effect of transverse anisotropy for $E_q(H)$ can be negligible in the relevant field range. The value of $\Delta^{\pm}$ has been determined to be 13.5 K in the preceding analysis. For the **H**⊥b axis, the dispersion relation presented by Tsvelik is used (see Ref. 14). The values of energy gaps at zero field have been also determined in the preceding analysis to be 12.0 and 30.0 K for the lowest- and highest-energy modes, respectively. We used the values of $J=55$ K, $\kappa\simeq 1/8$,[5,6] and $g=2.2$. If the damping factor Γ is assumed to be temperature and field independent, the temperature dependence of T_1^{-1} results from the occupation number in Eq. (2). The value of Γ is estimated to be 2 and 3 K for the **H**∥b and **H**⊥b axes, respectively, from comparison between the calculated and observed field dependences of T_1^{-1}. These values seem to be reasonable, since they satisfy the condition that $\Gamma\leq E_q(H)$. The values of T_1^{-1} calculated from Eq. (2), by choosing the value of A to be 4.7×10^{13} and 9.9×10^{13} s^{-2} for the **H**∥b and **H**⊥b axes, respectively, are represented by the solid lines in Figs. 3(a) and 3(b). As seen in the figures, the temperature dependences of T_1^{-1} below 4 K are well explained by using the fermion occupation number f_q in

Eq. (2) under the condition that the damping factors are constant. With respect to the field dependence of T_1^{-1}, the agreement between the experimental results and calculations is rather good for the $\mathbf{H}\perp b$ axis, while for the $\mathbf{H}\|b$ axis there appears a slight difference between the experimental results and calculations.

Next we examine our experimental results by treating the quasiparticles as free bosons. The values of T_1^{-1} were calculated from Eq. (2) by applying the boson occupation number $\{\exp[E_q(H)/T]-1\}^{-1}$ to n_q and using the preceding values of Γ. The temperature dependence of T_1^{-1} for the values of the applied field are represented by the dashed lines in Figs. 3(a) and 3(b). The dashed lines do not fit the experimental results, and the deviation at high temperatures has a trend to become more serious as the applied field approaches the critical field. If this deviation is ascribed to the temperature dependence of Γ, it is necessary to assume that Γ decreases as the temperature increase. But this is unreasonable.

In summary, the proton nuclear spin-lattice relaxation time T_1 below 4 K in NENP has exhibited experimental evidence for the existence of the lowest-energy mode of the three excitation modes that have been predicted in the $s=1$ Haldane-gap system with single-ion anisotropy. Our experimental results were interpreted reasonably by treating the magnetic excitations as free fermions rather than free bosons. This fact means that the magnetic excitations are regarded as 1D bosons with hard-core repulsion or free fermions in the high magnetic fields.

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* Present address: Department of Physics, College of Liberal Arts, Kobe University, Kobe 657, Japan.

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