Transverse staggered moment in the Haldane-gap antiferromagnet [Ni(C$_2$H$_8$N$_2$)$_2$NO$_2$(ClO$_4$)] observed by proton nuclear magnetic resonance

M. Chiba

Institute of Atomic Energy, Kyoto University, Uji, Kyoto 611, Japan

Y. Ajiro

Department of Chemistry, Kyoto University, Kyoto 606, Japan

H. Kikuchi

Government Industrial Research Institute, Nagoya 462, Japan

T. Kubo

Nara University of Education, Nara 630, Japan

T. Morimoto

Institute of Atomic Energy, Kyoto University, Uji, Kyoto 611, Japan

(Received 16 April 1991)

A quasi-one-dimensional $S=1$ antiferromagnet NENP [Ni(C$_2$H$_8$N$_2$)$_2$NO$_2$(ClO$_4$)] has been studied through the measurement of proton NMR under an applied magnetic field, B_0, up to 12 T. At 4.2 K with the magnetic field parallel to the chain, a large transverse moment perpendicular to the magnetic field has been observed even below the critical field, $B_c = 9.8$ T. The moment increases with increasing applied field, showing no singularity at B_c. It is not caused by the three-dimensional order. It is due to the field-induced staggered moment caused by the combined action of the staggered inclination of the principal axes of the g tensor of Ni^{2+} ions from the crystal b axis (chain axis) and the large transverse staggered susceptibility. The induced transverse moment is estimated to be 1.5μ_B at $B_0 = 11.7$ T.

Haldane has predicted the existence of a quantum energy gap between the singlet ground state and the lowest excited state in a one-dimensional (1D) Heisenberg antiferromagnet when the spin S is integer.[1] The prediction has given an impetus to experiments on $S=1$, quasi-1D antiferromagnets. Several quasi-1D antiferromagnetic materials have been used to investigate the Haldane gap.[2-5] Among these materials Ni(C$_2$H$_8$N$_2$)$_2$NO$_2$(ClO$_4$) (NENP after Ref. 4) with Ni^{2+} spin, $S=1$, has been found to be one of the best candidates. The Ni^{2+} spin system in NENP has been reported to have an energy gap consistent with the Haldane gap through experiments on neutron diffraction,[5] and magnetic susceptibility.[5] Measurements of high-field magnetization[6,7] also provided evidence for the existence of the Haldane gap in NENP from the magnetization anomaly at the critical field, B_c (=9.8 T when B_0 is parallel to the chain). The results clearly showed that the Haldane gap decreases with increasing applied field and finally closes at B_c. Hence, the ground state of the Haldane state may be greatly modified by the presence of the magnetic field. In fact, the observation has stimulated theoretical works on the magnetic field effect.[8-10] In this context it is very important to study the properties of the Haldane gap microscopically and dynamically through the breaking of the singlet ground state with increasing field.[11] Recently we reported[12] experimental results of NMR on NENP under high magnetic field up to 12 T. The purpose of this paper is to analyze the structure of the proton spin-echo spectra and to discuss a possible mechanism for the anomalously large NMR shift.

The crystal structure[13] of NENP is shown in Fig. 1(a). The Ni^{2+} ions are covalently linked along the crystal b axis by bridging nitrate groups bounded on one side by the nitrogen atom and on the other side by one of the oxygen atoms, forming 1D magnetic chains of $S=1$. The chains are well isolated from each other by the perchlorate anions, resulting in much weaker interchain exchange coupling $J' \sim 10^{-4} J$, where J is the intrachain exchange coupling with $J/k = 50$ K. The basal plane, built with four nitrogen atoms from two ethylene diamine molecules as shown in Fig. 1(b), is roughly perpendicular to the b axis (chain axis). The NMR experiment was performed on the protons in these diamine molecules with the applied magnetic field B_0 parallel to the b axis.

The pulsed NMR experiment was carried out at 4.2 K up to an applied field of 12 T, greater than the critical field. The operating frequencies were from 35 to 500 MHz. In order to observe the resonance line shape of the proton NMR the two-pulse spin-echo signal was traced by scanning the applied field. At low field, the spectrum is characterized by an unresolved single line without structure as is shown in Fig. 2 (spectrum A). With increasing field, however, the resonance line begins to split into three components, indicating the appearance of the field-induced shift of the resonance field of satellite components. The structure of the resonance line is nearly symmetric. One of the typical spectrum at high field is shown in Fig. 2 (spectrum B). The difference in the resonance field between the central line and its satellites

(a) NENP

- ○ Ni
- ◉ Cl
- ⊕ O
- ○ N
- ○ C

(b) Ethylene-diamine in NENP
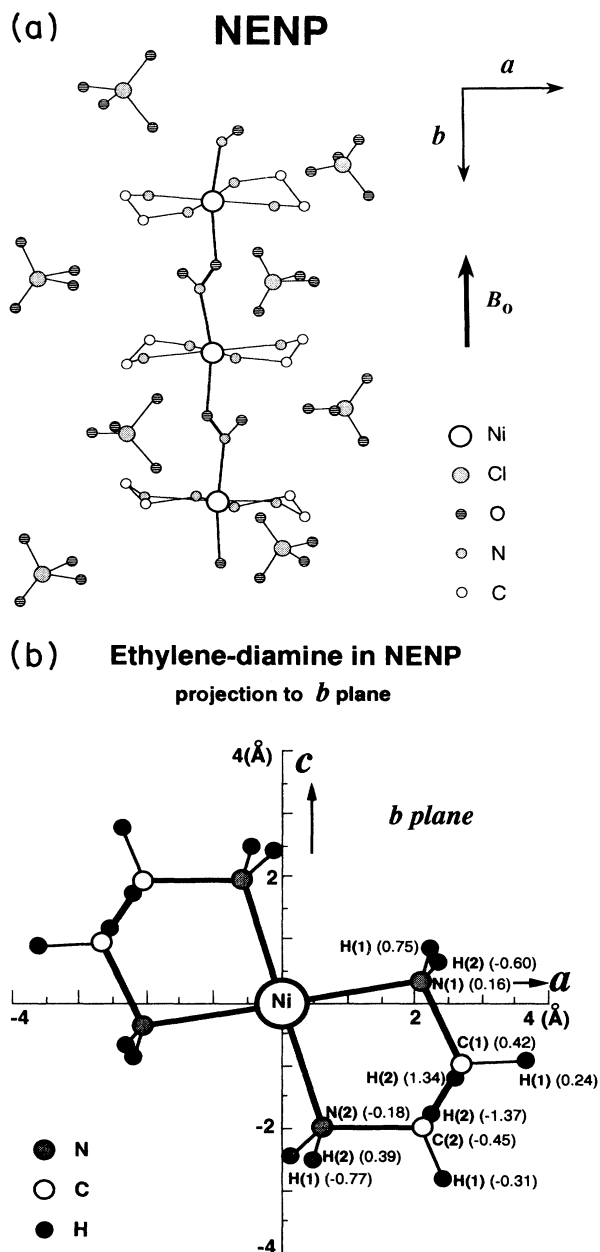
projection to *b* plane

- ● N
- ○ C
- ● H

FIG. 1. Crystal structure of NENP. (a) Perspective view. (b) The projection of the ethylene diamine molecules onto the *b* plane containing Ni^{2+}. The values in the parentheses are the distance between the atom and the *b* plane in the unit of Å.

(hereafter we call this the *satellite shift*) increases with increasing applied field as is shown in the lower part of Fig. 2. No singularity appears in the satellite shift at B_c except for a weak inflection of the curvature around B_c.

First, we show that the spectral structure cannot be explained by considering a contribution from a uniform moment of Ni^{2+}. In general, the origin of the NMR shift in magnetic materials is the local field at the nucleus produced by the magnetic ions. Assuming that the local field at the proton is the dipole field produced by a point dipole at the site of Ni^{2+}, the observed satellite shift is too large
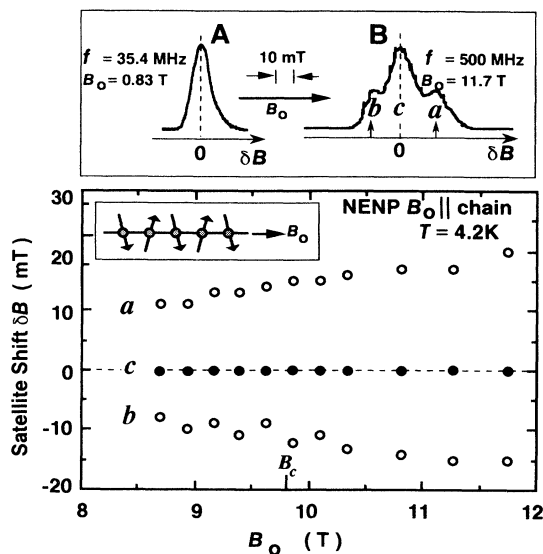

FIG. 2. Field dependence of the satellite shift of the proton NMR from the main line across the critical field ($B_c = 9.8$ T). Solid circles show the main line and open circles show the satellite line. No singularity appears at B_c.

compared with the dipole field due to the induced uniform moment of Ni^{2+} obtained by high-field magnetization.[6] For example, the longitudinal uniform moment induced parallel to the direction of the applied field is estimated to be only $0.05\mu_B$ at $B_0 = 11.7$ T, even at magnetic fields higher than B_c. The satellite shift is evaluated to be at most 5 mT using the estimated proton position in Fig. 1(b), which is one order of magnitude smaller than the observed shift. In addition, the observed shift increases continuously with increasing field without showing any singularity at B_c, while the longitudinal uniform moment increases abruptly at B_c. Further, we cannot expect symmetrical structure in the spectrum from the longitudinal Ni^{2+} moment. Since all the protons are located near the plane perpendicular to the direction of the induced moment, the local field along the *b* axis should have the same sign for all proton sites.

A recent measurement[14] of the temperature dependence of the satellite shift also supports the above considerations. With decreasing temperature below 4.2 K the satellite shift increases, in contrast to the uniform susceptibility[4] which decreases with decreasing temperature by reflecting the property of the singlet ground state. Summing up the above discussion, the origin of the structure of the resonance line is by no means due to the longitudinal moment.

We turn now to a possible effect of the transverse moment. The symmetric structure of the resonance line can be explained by considering the presence of the transverse moment perpendicular to the applied field. In order to estimate the absolute value of the transverse moment, we simulate the observed spectrum, assuming the following two cases. The direction of the transverse moment in the *b* plane should be one of the principal axes of the *g* tensor (see below). From the inspection of the local symmetry of the crystal structure the transverse moment will be for

$\varphi = 58°$ or $\varphi = 148°$, where φ is the angle between the direction of the Ni^{2+} moment projected onto the b plane and the a axis. As is clear in Fig. 3(b), the calculated line shape due to the transverse Ni^{2+} moment of $1.5\mu_B$ with $\varphi = 58°$ fits well the observed proton resonance line shape. From the agreement we conclude that the Ni^{2+} spin has the transverse moment of $1.5\mu_B$ (75% of the full moment) at 11.7 T. As is shown in the inset of Fig. 2 the spin will make an antiferromagnetic alignment due to the strong interchain antiferromagnetic coupling. It also shows a slight canting to the direction of the applied field to present the small uniform magnetization of $0.05\mu_B$.

Why does the transverse moment of Ni^{2+} appear? One might think that such a huge moment would be due to either well-developed short-range order or 3D long-range order. This is, however, not true. Although the intrachain exchange coupling, $J/k \sim 50$ K is much larger than the experimental temperature of 4.2 K and some short-range order may occur, the fluctuating moment in the short-range ordered state produces no NMR shift. Then one might expect 3D long-range order, in which the static moment produces a large shift. Indeed, it is theoretically shown[10] that the Haldane system with weak interchain coupling is in 3D ordered state above B_c at 0 K. In the present situation, however, the experimental temperature of 4.2 K is too high to expect 3D order, in view of the usual estimation for the Néel temperature, $(JJ')^{1/2}/k \sim 0.5$ K.

We consider instead the effect of the staggered field in the *crystallographic sublattice* system.[15] A close inspection of the crystal structure shows that the individual chain is composed of two crystallographically inequivalent Ni^{2+} sites. The local symmetry axes of Ni^{2+} sites are not parallel to the b axis (chain axis), but slightly inclined from it with an angle $+$ or $-\theta$ changing its sign as one moves down the chain from one Ni^{2+} site to the next. The principal axis of the g tensor should also incline, reflecting the local crystal symmetry. Thus the sites of Ni^{2+} in a chain are divided into two sublattices and effectively experience a staggered transverse field as illustrated in Fig. 4. In order to clarify the physical image of two crystallographic sublattices we consider a two-spin system with spins S_1 and S_2. The Zeeman Hamiltonian $\mathcal{H}$ of this system is

$$\mathcal{H} = \mu_B B_0 \cdot (g_1 \cdot S_1 + g_2 \cdot S_2), \tag{1}$$

where g_1 and g_2 are the g tensors. When one of the principal axes of g_1 (g_2), the ζ_1 (ζ_2) axis, is inclined from the crystal b axis (i.e., z axis is parallel to B_0) with the tilting angle $\pm\theta$, the Hamiltonian becomes

$$\mathcal{H} = \mu_B B_0 [(g_{1\zeta}\cos^2\theta + g_{1\xi}\sin^2\theta)S_{1z} + (g_{1\zeta} - g_{1\xi})\sin\theta\cos\theta S_{1x}$$
$$+ (g_{2\zeta}\cos^2\theta + g_{2\xi}\sin^2\theta)S_{2z} - (g_{2\zeta} - g_{2\xi})\sin\theta\cos\theta S_{2x}], \tag{2}$$

where ξ_1 (ξ_2) axis are the other principal axes of the g tensors. Thus we have an x component of S_1 (S_2) as well as the z component even though the applied field is along z axis. More explicitly, the spin experiences the effective transverse field

$$B_{1\perp} = B_0\sin\theta\cos\theta(g_{1\zeta} - g_{1\xi})/g_{1\zeta}, \tag{3}$$

and

$$B_{2\perp} = -B_0\sin\theta\cos\theta(g_{2\zeta} - g_{2\xi})/g_{2\zeta}, \tag{4}$$
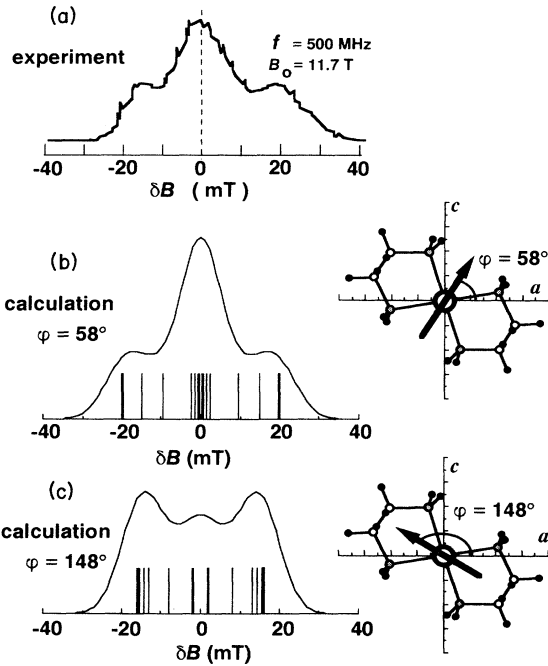

FIG. 3. Observed and calculated spectral line shapes. (a) Observed line shape at $B_0 = 11.7$ T. (b) Calculated line shape for the transverse moment of $1.5\mu_B$ with $\varphi = 58°$. (c) Calculated line shape for the transverse moment of $1.5\mu_B$ with $\varphi = 148°$. Here φ is the angle between the direction of the Ni^{2+} moment projected onto the b plane and a axis.
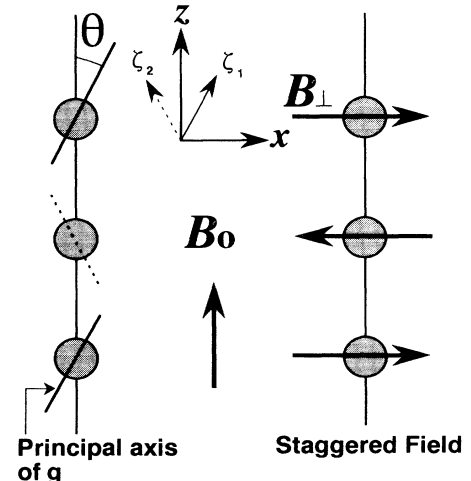

FIG. 4. An illustration of the crystallographic sublattice and the effective transverse magnetic field.

when $g_{1\zeta} \approx g_{1\xi}$ ($g_{2\zeta} \approx g_{2\xi}$). In NENP the inclination of the principal axis of the g tensor is alternating in direction along the chain axis. Therefore, the spin in a chain experiences a staggered transverse field which is conjugate to the antiferromagnetic order parameter. Although the precise parameter of the g tensor is not known, we assume that $\theta = 10°$ because the angle between the z axis and the normal of the plane including the four nearest N atoms is $10°$. With reasonable assumptions that $g_{1\zeta} = g_{2\zeta} = 2$ and $|g_{1\zeta} - g_{1\xi}| = |g_{2\zeta} - g_{2\xi}| \approx 0.1$, the effective transverse field is $B_{1\perp}(B_{2\perp}) \approx \pm B_0/100$ [i.e., at $B_0 = 10$ T, $B_{1\perp}(B_{2\perp})$ $\approx \pm 0.1$ T]. Since the transverse staggered susceptibility is theoretically known[10] to be large near the critical field, the staggered field causes a transverse antiferromagnetic alignment. What is important in the present model is that the staggered inclination of the principal axis of g tensor and the intrachain antiferromagnetic coupling are essential. Unlike the usual antiferromagnetic case, the external uniform field couples to the antiferromagnetic fluctuation via the effective staggered field and induces the transverse

staggered moment. This situation reminds us of the case where a ferromagnetic alignment can be observed in the short-range ordered 1D ferromagnet under the external field. The externally induced spin alignment of our model should be contrasted with the "spontaneous" Néel order in the magnetic field where both intra- and interchain couplings are relevant.

In conclusion, the proton NMR spectra in NENP revealed the appearance of the moment of Ni^{2+}-ion perpendicular to the applied field. The transverse moment appears below B_c and increases with increasing field. The magnitude is, for example, $1.5\mu_B$ (75% of the full moment) at 11.7 T. The present model suggests the spin alignment should be antiferromagnetic. However, the results of the NMR experiment are not conclusive. The proposed spin alignment will be observed more directly by neutron diffraction in high magnetic fields.

[1]F. D. M. Haldane, Phys. Rev. Lett. **50**, 1153 (1983).

[2]W. J. L. Buyers, R. M. Morra, R. L. Armstrong, M. J. Hogan, P. Gerlach, and K. Hirakawa, Phys. Rev. Lett. **56**, 371 (1988).

[3]M. Steiner, K. Kakurai, J. K. Kjems, D. Petitgrand, and R. Pynn, J. Appl. Phys. **61**, 3953 (1987).

[4]J. P. Renard, M. Verdaguer, L. P. Regnault, W. A. C. Erkelens, J. Rossat-Mignod, and W. G. Stirling, Europhys. Lett. **3**, 945 (1987).

[5]J. P. Renard, M. Verdaguer, L. P. Regnault, W. A. C. Erkelens, J. Rossat-Mignod, J. Ribas, W. G. Stirling, and C. Vettier, J. Appl. Phys. **63**, 3538 (1988).

[6]Y. Ajiro, T. Goto, H. Kikuchi, T. Sakakibara, and T. Inami, Phys. Rev. Lett. **63**, 1424 (1989).

[7]K. Katsumata, H. Hori, T. Takeuchi, M. Date, Y. Yamagishi, and J. P. Renard, Phys. Rev. Lett. **63**, 86 (1989).

[8]I. Affleck, Phys. Rev. B **41**, 6697 (1990).

[9]A. M. Tsvelik (unpublished).

[10]T. Sakai and M. Takahashi (unpublished).

[11]P. Gaveau, J. P. Boucher, L. P. Regnault, and J. P. Renard, Europhys. Lett. **12**, 647 (1990).

[12]M. Chiba, Y. Ajiro, H. Kikuchi, T. Kubo, and T. Morimoto, J. Magn. Magn. Mater. **90 & 91**, 221 (1990).

[13]A. Meyer, A. Gleizes, J. Girerd, M. Verdaguer, and O. Kahn, Inorg. Chem. **21**, 1729 (1982).

[14]N. Fujiwara, T. Goto, T. Kohmoto, and S. Maegawa (unpublished).

[15]M. Matsuura and Y. Ajiro, J. Phys. Soc. Jpn. **41**, 44 (1976).