NMR study of naturally occurring ^{13}C in the Haldane-gap material $Ni(C_2H_8N_2)_2NO_2ClO_4$

A. P. Reyes, H. N. Bachman, X. P. Tang,* M. W. Meisel,† and W. P. Halperin
Department of Physics and Astronomy, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208

N. Fujiwara‡ and T. Goto
Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606, Japan
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The spin-lattice relaxation time T_1 of naturally occurring ^{13}C in $Ni(C_2H_8N_2)_2NO_2ClO_4$, a Haldane-gap system commonly known as NENP, has been measured as a function of temperature ($T>4$ K), magnetic field ($H=3.46$ and 7.56 T), and crystal orientation [a, b (the Ni chains), and c axes]. Using the established magnetic-field dependence of the gap and the materials parameters known for NENP, the general trends of the T_1 data can be reproduced by standard analysis with the assumption that the relaxation is governed by the processes at $q=\pi$. Most importantly, an unusual feature in the $H(\|b)=7.56$ T data can only be explained by using a temperature-dependent gap. [S0163-1829(97)04714-0]

Ever since the $S=1$ quasi-one-dimensional Heisenberg antiferromagnetic material $Ni(C_2H_8N_2)_2NO_2[ClO_4]$,[1] commonly known as NENP, was first identified (Ref. 2) as a Haldane-gap system,[3,4] a wide variety of experimental probes have been used to study its static and dynamic magnetic properties. To date, most of the experimental results may be explained by a spin Hamiltonian written as

$$\mathcal{H}=-J\sum_i \vec{S}_i\cdot\vec{S}_{i+1}+D\sum_i (S_i^z)^2+E\sum_i [(S_i^x)^2-(S_i^y)^2]$$

$$-\mu_B\vec{H}\cdot\sum_i \overleftrightarrow{g}\cdot\vec{S}_i-J'\sum_j \vec{S}_j\cdot\vec{S}_{j+1}, \qquad (1)$$

where the nearest-neighbor spin intrachain interaction $J=-(46\pm2)$ K, the single-ion anisotropy $D/|J|=0.18\pm0.01$, the orthorhombic anisotropy $E/|J|=0.02\pm0.01$, and the nearest-neighbor spin interchain interaction J' is given as $|J'/J|\approx8\times10^{-4}$.[5] In addition, the presence of the finite anisotropy causes the Haldane gap $\Delta=0.41\ |J|$ to be distorted and to assume the values of $\Delta_x\approx14.3$ K, $\Delta_y\approx12.2$ K, and $\Delta_z\approx29.0$ K,[5,6] where it is important to note that x, y, z correspond to the a, c, b crystal axes, respectively, with the b axis being along the chains.

One of the microscopic probes used to investigate NENP has been ^1H NMR.[7–10] In fact, Chiba *et al.*[7] have discovered the presence of a staggered moment due to the $Pn2_1a$ crystal symmetry.[1] The existence of the this staggered moment has been discussed theoretically,[11,12] where the second and fourth terms in Hamiltonian (1) take the form of

$$\sum_{i\in(1)}[\vec{S}_i\cdot\overleftrightarrow{D}_1\cdot\vec{S}_i-\mu_B\vec{S}_i\cdot\overleftrightarrow{g}_1\cdot\vec{H}]$$

$$+\sum_{i\in(2)}[\vec{S}_i\cdot\overleftrightarrow{D}_2\cdot\vec{S}_i-\mu_B\vec{S}_i\cdot\overleftrightarrow{g}_2\cdot\vec{H}], \qquad (2)$$

where the subscripts 1 and 2 refer to the two possible orientations of the principal axes of the D and g tensors along the chain. Although some questions remain open, Hamiltonian (1), as amended by Eq. (2), provides an explanation for the observation of ''forbidden'' transitions in electron spin resonance (ESR) experiments.[11–14]

Although a self-consistent description of the important materials parameters of NENP has emerged, we have been motivated to pursue NMR experiments that probe the carbon and nitrogen atoms which are physically closer to the Ni spins. Our efforts to observe signals arising from naturally occurring ^{14}N and ^{15}N have not been successful to date; however, we have succeeded in measuring the temperature, field, and crystalline orientation dependences of the spectra and T_1 associated with the naturally occurring ^{13}C in a single crystal of NENP. Recently, nonproton NMR data have been reported on the Haldane-gap systems of Y_2BaNiO_5 (Ref. 15) and $AgVP_2S_6$.[16,17] In this paper, the dynamic aspects (i.e., T_1) of our measurements will be presented, and the static properties (i.e., spectra) will be reported elsewhere.

The NENP specimen was grown according to the procedures outlined by Meyer *et al.*[1] The single crystal possessed nominal dimensions of $5\times10\times3$ mm^3, along the a, b (Ni chain axis), and c axes respectively, as indicated by x-ray measurements. Several NMR[8,9] and ultralow temperature susceptibility[18] experiments have been performed on crystals which have been produced from the same starting materials. The purity of one of the specimens made from these materials has been investigated, and the results are given by Avenel *et al.*[18]

The NMR measurements were made in two different superconducting magnets, one set persistent at 7.56 T and the other operating at 3.46 T. A continuous flow ^4He cryostat was used in conjunction with a homemade probe possessing low-temperature tunable capacitors and a sample rotating mechanism. A pulsed, quadrature-detected NMR spectrometer was utilized to obtain Fourier transformed spectra.[19] The spin-lattice relaxation times were obtained by integrating the spin echoes after variable delays and fitting the results with an exponential recovery curve. We used classic 90°–180° pulse sequences with a full 16 cycle phase alteration, where typically a 90° pulse was 2–3 μs. The phase cycling is used to eliminate spurious ringing from the two pulses since T_2 ($\approx$80–100 μs) was short. Owing to the 1.1% natural abun-

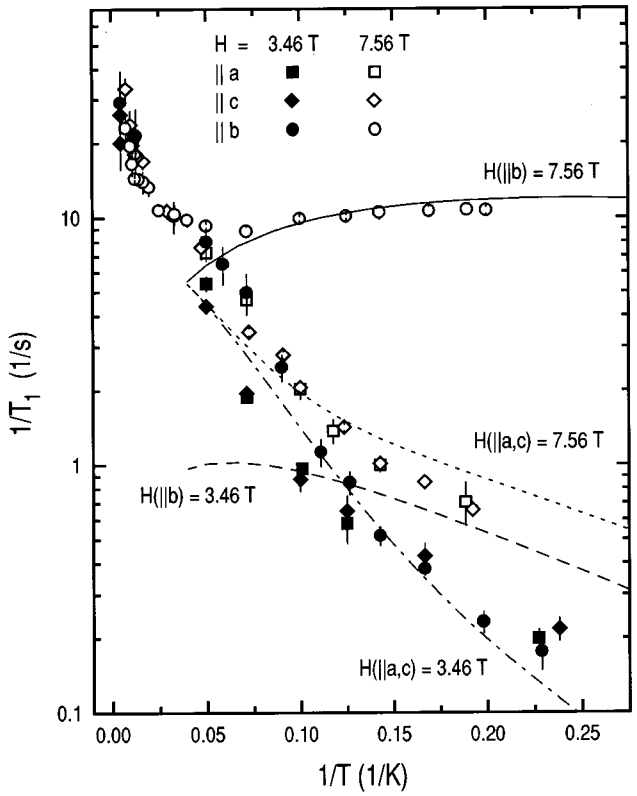

FIG. 1. The experimental data are shown in an Arrhenius plot $1/T_1$ vs $1/T$ for various fields and orientations as indicated. The results of the data analysis, as described in the text, are shown as various lines. With the exception of the $H(\|b)=3.46$ T line, the qualitative trends of the experimental data are reproduced by the fitting analysis, especially the ''bump'' in the $H(\|b)=7.56$ T data.

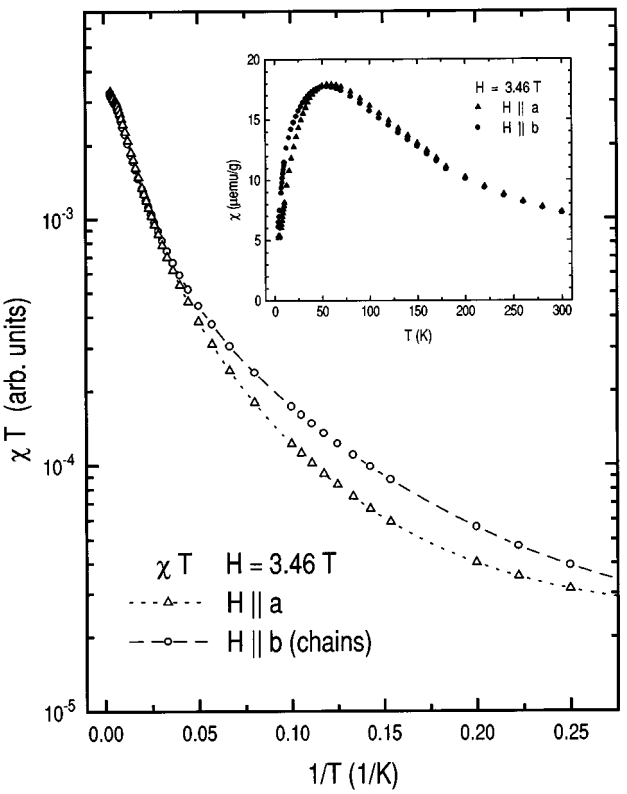

FIG. 2. The susceptibility $\chi(T)$ as multiplied by T and measured in a magnetic field of 3.46 T applied parallel to the a or b (chain) axes, is shown as a function of $1/T$, and the lines are guides for the eyes. The inset shows the $\chi(T)=M(T)/H$ data.

dance of ^{13}C and our minimum repetition time of four times T_1, it was necessary to signal average for long periods of time, e.g., up to 12 h at 5 K, and our results are shown in Fig. 1. It is noteworthy that our data are in the $\mu_B(H_C-H)<k_BT$ limit, where H_C is the critical field needed to destroy the Haldane phase. For $T>30$ K, the data are independent of field and crystal orientation. At approximately 30 K, the T_1 data evolve toward their low-temperature values with no observable differences between the $H\|a$ and $H\|c$ orientations for a given field. All of these general trends have been observed in the ^{1}H NMR work,[9,10] and the ''bump'' in the $H\|b$ data in 7.56 T is the most distinguishing feature. This behavior was not observed in the ^{1}H NMR studies,[9,10] although the $1/T_1$ ($H\|b$ in 8 T) data of Gaveau *et al.*[10] indicate a flat trend below ~25 K and a sudden drop at ~5 K. The discrepancies between the ^{1}H results[9,10] and our ^{13}C data may be due to the difference in the probe sites. Since the ^{13}C atoms are closer to the Ni ions and far apart from each other, they are a better probe of the Ni antiferromagnetic fluctuations. Furthermore, the ^{1}H $1/T_1$ values contain dipolar contributions from neighboring ^{1}H spins, and this effect may mask the ''bump'' feature. The ''bump'' behavior is not permitted by constant gap values which would be represented by straight lines on an Arrhenius plot. In other words, the smallest possible gap of nearly zero would be given by a horizontal line on such a plot, and as a result, the ''bump'' feature would not be explained. In fact, Gaveau *et al.*[10] used a temperature-dependent gap to explain their data, and we will use a similar procedure to model our results.

The temperature dependence of the magnetic susceptibility $\chi(T)=M(T)/H$ was studied from 3.5 to 300 K in a commercial superconducting quantum interference device magnetometer, Fig. 2. The sample was housed in a gelcap which was held by a plastic straw. The background signal of the measurement is small compared to the magnetization coming from the sample, and no correction is necessary for the data presented herein.

The analysis of the nuclear spin-lattice relaxation time data, Fig. 1, begins with the expression[20]

$$\frac{1}{T_1}(H_{\hat{i}},T)=\sum_{\substack{\alpha=\hat{j},\hat{k}\\0\leqslant q\leqslant\pi}}|A_\alpha(q)|^2S_\alpha(q,\omega_N)n_\alpha(q), \qquad (3)$$

where $A_\alpha(q)$ is the electron-nuclear hyperfine coupling, $S_\alpha(q,\omega_N)$ is the dynamic structure factor of the magnetic excitations, ω_N is the nuclear resonance frequency, and $n_\alpha(q)$ is the corresponding occupation function. At high temperatures, where $\hbar\omega_N\ll k_BT$, this expression may be written as[20]

$$\frac{1}{T_1}(H_{\hat{i}},T)=\gamma_N^2k_BT\sum_{\substack{\alpha=\hat{j},\hat{k}\\0\leqslant q\leqslant\pi}}|A_\alpha(q)|^2\frac{\chi''_\alpha(q,\omega_N)}{\omega_N}, \qquad (4)$$

where γ_N is the nuclear gyromagnetic ratio and $\chi''_\alpha(q,\omega_N)$ is the dissipative portion of the dynamic susceptibility. In the

Haldane phase, the dynamic structure factor of Eq. (3) is thought to possess a double-Lorentzian form given as[5,10]

$$S_\alpha(q,\omega_N)=\frac{S_{\alpha 0}}{\kappa_\alpha\Gamma_\alpha}\frac{1}{1+[(q-\pi)/\kappa_\alpha]^2+\{[\hbar\omega_N-\Delta_\alpha]/\Gamma_\alpha\}^2}, \tag{5}$$

where $S_{\alpha 0}$ represents a normalization coefficient, κ_α is the inverse correlation length, Γ is the fluctuation rate (i.e., the intrinsic energy width), and Δ is the Haldane energy gap.

In the following discussion, we will make the following general assumptions or approximations: (a) the ^{13}C spins only couple to the nearest Ni ions, (b) the coefficients $A_\alpha(q)\approx A'^2\{1-(4z/A')\sin(q_z b/2)\cos(q_x a/2)\}$, and (c) $\Delta_\alpha \gg \hbar\omega_N$. In addition, we will assume that $q=\pi$ is where all the spectral weight is located, and this approximation is on sound footing based upon experimental results[5,21] and numerical work.[22–24] In other words, the spin-lattice relaxation time, which in principle sums over all q values, is dominated by the processes at $q=\pi$. This last approximation is not valid when $k_B T \ll \Delta$, where the main contribution to the T_1 arises from the region near $q=0$ as required by energy conservation.[25] For example, this limit is achieved in the NMR work on $AgVP_2S_6$.[17] For our and other[9,10] NMR experiments on NENP, energy conservation is maintained by interactions with phonons and other processes. Furthermore, we will also assume that the density of magnetic excitations is given by the Fermi-Dirac distribution. Our choice is made for consistency with the magnetic-field dependence of the Haldane gap that will be discussed later. In fact, our data is not capable of distinguishing between the appropriateness of our choice versus Bose-Einstein or Boltzmann statistics. Finally, we will assume that the inverse correlation length is given by the simple expression $\kappa_\alpha=\Delta_\alpha/c_0$, where c_0 is the spin wave velocity. Granting these points, Eq. (3) becomes

$$\frac{1}{T_1}(H_{\hat{i}},T)=\sum_{\alpha=\hat{j},\hat{k}}\frac{A'_\alpha}{\Delta_\alpha(H,T)}\frac{\Gamma_\alpha(H,T)}{[\Gamma_\alpha{}^2(H,T)+\Delta_\alpha{}^2(H,T)]}\times\frac{1}{(\exp[\Delta_\alpha(H,T)/T]+1)}, \tag{6}$$

where all the magnetic-field and temperature dependencies have been explicitly noted and the coefficients A'_α have absorbed the constants.

The question of the field dependence of the gap has been addressed by neutron,[5] ESR,[13,14] and specific-heat[27] experiments and numerous theoretical treatments. So, we will take this dependence from the literature, see for example Eqs. (7) and (9) of Ref. 5 or Eq. (2.14) of Ref. 6. Additional choices for the values of the necessary materials parameters will be guided by the neutron-scattering results obtained on a standard, i.e., nondeuterated,[21] specimen,[5] and the values of the Haldane gaps in zero magnetic field have been given in the opening paragraph. From Fig. 1, it is clear that we have not been able to discriminate differences between the $H\|a$ and $H\|c$ data. Consequently, we have taken $\Delta_x=\Delta_y=13$ K and $\Delta_z=29$ K. In addition, we will take $g_z=2.08$ (slightly different than what one gets from susceptibility) and $g_x=g_y=2.16$.[5]

Since one of the gaps is much larger than the other when H is perpendicular to the chains, Fujiwara *et al.*[9] and Gaveau *et al.*[10] only keep the term with the smallest gap in their analyses of Eq. (6). In addition, whereas Fujiwara *et al.*[9] took the damping contribution to be a constant, Regnault *et al.*[5] and Gaveau *et al.*[10] suggest a more complete approximation is to consider

$$\Gamma_\alpha(H,T)=\Gamma_\alpha(0)n_\alpha(H,T), \tag{7}$$

where experimental evidence suggests that $\Gamma(0)<\Delta$.[5,9,10,21] However, as suggested by Zheludev *et al.*[28] who performed neutron-scattering experiments on the Haldane gap material known as NINAZ, a constant term should dominate the $T\to 0$ behavior such that

$$\Gamma_\alpha(H,T)=\Gamma_{\alpha,1}(0)+\Gamma_{\alpha,2}\exp[-\Delta(H,0)/T]. \tag{8}$$

The zero-temperature limit of Γ_α may be defined by crystalline defects, end-chain spins, staggered magnetization, or other possible effects. In any event, this contribution will allow the low-temperature behavior of $1/T_1$, Eq. (6), to appear as an $\exp(-\Delta/T)$ form rather than as $\exp(-2\Delta/T)$.[25,26] The results obtained by Fujiwara *et al.*[9] certainly suggest the necessity of this term. Furthermore, since Γ_α is related to the magnetic effects, it may depend explicitly on magnetic field. This effect is supported by the work of Regnault *et al.*[5] who found a magnetic-field dependence of the form $\{1+\beta(H/H_c)^2\}$, where β is a fitting parameter. Of course, care must be taken when using this functional form since staggered magnetization effects may cause H_c to be ill defined.[11,12] Our attempts to use this form did not adequately reproduce the trends that we observed (Fig. 1). On the other hand, our data seem to reflect a magnetic-field dependence given by $\{1+H/H_0\}^2$, where $H_0=33$ $T=k_B|J|/(g\mu_B)$ when $|J|=46$ K and $g=2.1$.

The question of the temperature dependence of the Haldane gap has been investigated theoretically[26,29,30] and experimentally.[10,28,31] For our analysis, we will take $\Delta_\alpha(H,T)$ to be given as

$$\Delta_\alpha(H,T)=\Delta_\alpha(H,0)+\sqrt{\delta\Delta_\alpha(H,0)T}\exp(-\Delta_\alpha(H,0)/T), \tag{9}$$

where δ is the adjustable parameter. A value of $\delta=2\pi$ is expected theoretically,[26] while $\delta=0.11$ was obtained from neutron-scattering work using NINAZ.[28]

Given the above preamble, we are ready to use Eq. (6) to fit the T_1 data shown in Fig. 1. The results of the fit are shown in Fig. 1 with $\Gamma_{\alpha,1}/\Delta_\alpha(H,0)=\Gamma_{\alpha,2}/\Delta_\alpha(H,0)=\delta=0.1$, and $A'_x=A'_y=A'_z/100=1800$. With the exception of the $H(\|b)=3.46$ T data, all the trends in the data are qualitatively reproduced, especially the ''bump'' in the $H(\|b)=7.56$ T data. In the present analysis, this ''bump'' feature is only possible if the gaps are temperature dependent. Once a small but finite δ value is included in the analysis, then a subtle interplay exists between this parameter and the $\Gamma_{\alpha,1}$ and $\Gamma_{\alpha,2}$ values. The values of these last two parameters allow $\Gamma_\alpha(H,T)$ to meet the constraints established in other experiments.[5,9,10,21] Finally, although the result $A'_x=A'_y$ is not unexpected, we do not have an explanation for A'_z being two orders of magnitude larger. This large size of A'_z is needed to reproduce the high-temperature dependence of the

$H\|a$ and $H\|c$ results. Consequently, other factors like the staggered magnetization or phonon interactions might influence the size of this value.

It is noteworthy that other analysis procedures do not provide a qualitative description of our data. For example, summing over q values for different choices of $S(q,\omega)$ does not improve the trends provided by the present work. In addition, the $q=0$ limit analysis which is applicable to $AgVP_2S_6$ (Ref. 17) does not describe the data shown in Fig. 1. On the other hand, the high-temperature data ($1/T<0.025$ K^{-1}) shown in Fig. 1 have the temperature dependence given by Eq. (4), namely $1/T_1 \propto \chi T$, assuming that $\chi''_\alpha(q,\omega_N)$ is proportion proportional to the static susceptibility $\chi(T)=M(T)/H$, see Fig. 2. Contrarily, using the same assumption, the $1/T_1 \propto \chi T$ behavior, which may be expected in the Haldane phase,[16,26,32] is not reflected in the data for $T<40$ K, which is also close to $|J|$.

In summary, the magnetic-field, temperature, and crystal orientation dependence of our T_1 measurements on naturally occurring ^{13}C in NENP can be explained when using values of the Haldane gaps measured by other techniques. In addition, our data in a magnetic field of 7.56 T oriented along the axis of the Ni chains can only be explained if a temperature-dependent Haldane gap is used. Additional work is needed to clarify the role of the staggered magnetization and the role of phonon interactions in the relaxation process, especially at intermediate temperatures.

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*Present address: Department of Physics and Astronomy, University of North Carolina, Chapel Hill, NC 27599-3255.

†Present address: Department of Physics, University of Florida, 215 Williamson Hall, P.O. Box 118440, Gainesville, FL 32611-8440.

‡Present address: Institute for Solid State Physics, University of Tokyo, Roppongi 7-22-1, Minato-ku, Tokyo 106, Japan.

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