Magnon Spin Resonance in the Haldane Spin Chains of $Ni(C_2H_8N_2)NO_2ClO_4$

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We present a high-frequency electron spin resonance study of the magnetic transitions occurring between excited states in a Haldane spin system. We show that these transitions are induced between the low-energy magnon states, which develop at the boundary ($q \approx \pi$) of the Brillouin zone. Our study provides therefore the first evidence that, in the Haldane phase, the excitations associated with the quantum gaps correspond actually to a $s=1$ magnetic state.

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According to the Haldane conjecture [1], the ground state (GS) of isotropic antiferromagnetic (AF) chains of integer spins is disordered and nonmagnetic (the GS is actually defined as an $s=0$ state). The low-energy spectrum of such a system exhibits very peculiar properties. The corresponding excitations result from a triplet state and, unlike the half-integer spin case, a quantum gap is expected to open in the dispersion curve. This gap should occur at the boundary of the Brillouin zone $q=\pi/a$ (hereafter the lattice parameter is $a=1$). All these properties have been proved by experimental investigations, in particular on the compound NENP [$Ni(C_2H_8N_2)NO_2ClO_4$], which is a good realization of a Haldane spin system [2]. However, concerning these excitations around $q=\pi$, there remains an important prediction to be checked: Since the triplet state is defined as an $s=1$ state, magnetic "$\Delta m=1$" transitions should be allowed between the different components of the triplet state. At the zone center ($q=0$), the fluctuation spectrum results from two-particle excitations [3]. The gap at $q=0$ is therefore predicted to be twice the value of the quantum gap [4].

Magnetic transitions can be probed by the electron spin resonance (ESR) technique. In that case, the absorption of energy is realized without momentum (q) transfer: The required condition is therefore $\Delta q=0$. As a consequence, if the transitions are induced from the GS, they correspond to $q=0$ excitations. However, if they are induced between excited states they can be produced anywhere in the Brillouin zone. In Haldane spins chains, ESR measurements were carried out for the first time by Date and Kindo [5], at the fixed frequency $\omega=47$ GHz. In NENP an ESR signal was clearly observed for **H** applied perpendicular to the chain axis **b**. However, no signal was detected for **H** parallel to **b**. It was suggested [5] that for that direction, no resonance can be seen because it is dramatically broadened by a spin-wave continuum occurring, at $q=0$, in the same frequency range. To explain the data, an energy-level diagram (ELD) describing the field dependence of the resulting excitations at $q=0$ was given. Surprisingly, it appears to be comparable—although not identical—to the $q=\pi$ ELD determined by neutron inelastic scattering (NIS) measurements [6]. This analysis contradicts the theoretical prediction that the gap at $q=0$ should be twice the gap at $q=\pi$ [3].

In the present work, we report an ESR investigation on NENP performed in a wide frequency range between 160 and 1000 GHz and in high field, up to $H=17$ T. For **H** perpendicular to **b** we have observed a resonance which compares well with the 47-GHz signal of Date and Kindo [5]. However, we also observed resonances for **H** *parallel* to the chain axis **b**. We could follow all these signals at field values very close to and larger than the critical fields H_c, at which the spin system is expected to undergo a phase transition. In this Letter, we limit the discussion to data obtained for $H<H_c$, i.e., *in the Haldane phase* [1]. A new analysis is presented, which rules out definitively the basic contradiction mentioned above about the energy gaps. It also provides the first experimental evidence that the lowest excitations (at $q=\pi$) in a Haldane spin chain correspond actually to an $s=1$ *magnetic* state.

Our measurements were performed on pure NENP single crystals, the structure of which belongs to the orthorhombic system defined with orthogonal axes $(a,c,b) \equiv (x,y,z)$. The magnetic chains are made of Ni^{2+} ions disposed along the b axis [2]. The recorded signals as shown in Fig. 1 are the derivative of the absorption of the unpolarized light delivered by a CO_2 optically pumped far-infrared waveguide laser. The ESR spectrometer has been described elsewhere [7]. The samples were in the Faraday configuration, i.e., with the wave vector of the radiation parallel to the external magnetic field **H**.

For **H**$\parallel$**a** or **H**$\parallel$**c**, the ESR lines observed below H_c, at $T=4.2$ K, display rather symmetric line shapes [see Figs. 1(a) and 1(b)]. The peak-to-peak linewidth ΔH is narrow, of the order of 0.3 T (≈ 0.4 K). For **H**$\parallel$**b**, two ESR signals could be detected between 0 and 10 T for a given

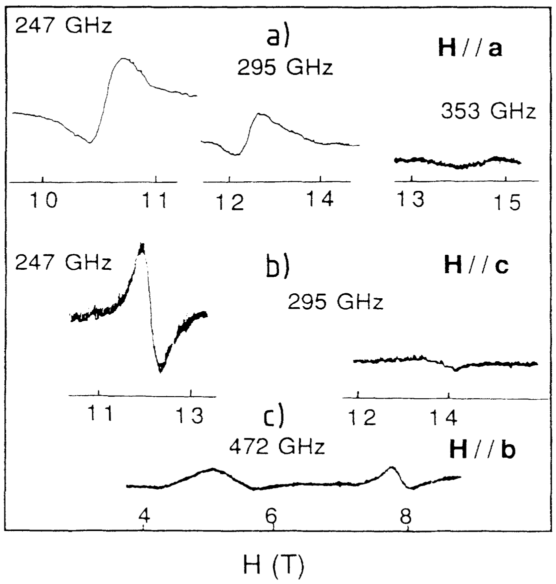

FIG. 1. Examples of ESR signals observed for different field directions in NENP.

frequency. As shown in Fig. 1(c), the line observed at high field ($H \approx 8$ T) is symmetric and narrow ($\Delta H \approx 0.4$ K) while the low-field ($H \approx 5.3$ T) signal is less symmetric and much broader ($\Delta H \approx 1.4$ K). For all these resonances, the linewidth is observed to increase dramatically as $H \rightarrow H_c$, while the corresponding peak-to-peak intensity (h) vanishes: The present ESR signals observed in the Haldane phase ($H < H_c$) disappear at the critical field H_c.

Our study, performed at different frequencies, allows a rather complete determination of the ELD associated with these ESR lines. Our results disagree quantitatively with the $q=0$ diagram of Ref. [5]. We show in Fig. 2 that they agree very well with the $q=\pi$ ELD, known for NENP [6]. In Figs. 2(a) and 2(b) the NIS results for **H**∥**b** and **H**∥**a** are represented by open dots. The full lines are theoretical predictions—to be discussed below—describing the field dependence of the quantum gaps E_G^a ($a=x,y,z$), observed at $q=\pi$ in NENP. They are obtained from a fitting procedure through the NIS data, where the only adjustable parameter is the gyromagnetic ratio g_a. For **H**∥**b** and **H**∥**a**, we obtain $g_z \approx 2.11 \pm 0.06$ and $g_x \approx 2.13 \pm 0.06$, respectively. These curves predict the critical fields—the field at which the low-energy gap cancels—to occur at $H_c^z \approx 10$ T and $H_c^x \approx 14$ T [8]. Each double-headed arrow represents an observed ESR transition: The length of the arrow measures the resonant frequency and the arrow is positioned at the resonant field determined experimentally. For **H**∥**c** [Fig. 2(c)], the diagram is built in a different manner, since no neutron data are available. For this field direction, the energy gap $E_G^y = 13.6$ K can be considered to be field independent. The arrows are therefore positioned with

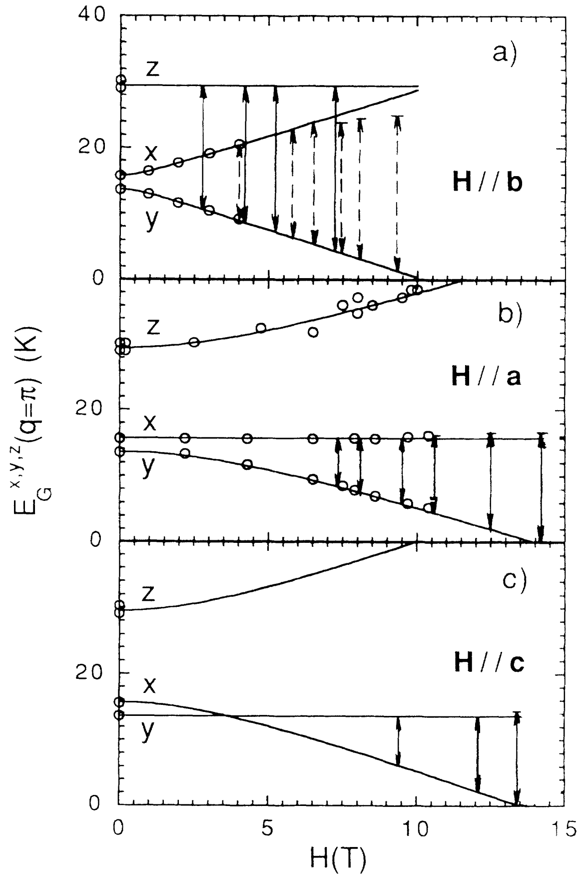

FIG. 2. Comparison between the observed ESR transitions (double arrows) and the $q=\pi$ ELD as a function of H, for different field directions. The dots are the NIS data of Ref. [6] and the lines are obtained from Eq. (2) (see text). The solid and dashed arrows correspond to "$\Delta m=1$" and "$\Delta m=2$" transitions, respectively.

respect to this value. The branch $E_G^y(H)$ is determined with these ESR transitions, yielding $g_y \approx 2.38 \pm 0.20$ and $H_c^y \approx 13.5$ T [8]. In Fig. 2(c), the branch $E_G^z(H)$ also corresponds to this value of g_y. Except very near the critical fields where small (but actual) precursor deviations are observed, the agreement between the different sets of data—neutron *and* ESR—and the theory is remarkable. In NENP, the magnetic coupling is not fully isotropic. The degeneracy of the $s=1$ triplet state of the $q \approx \pi$ excitations is removed completely by small orthorhombic anisotropies, which yield the three distinct quantum gaps E_G^a. Another consequence is that the states associated with the $q \approx \pi$ excitations are formed by a combination of the three possible magnetic states $|+1\rangle$, $|0\rangle$, and $|-1\rangle$. As a result of this state mixing, "$\Delta m=2$" transitions, in principle forbidden, become allowed. The results shown for **H**∥**b** give clear evidence of this fact. In Fig. 1(c), the two signals observed in low and high fields correspond to "$\Delta m=1$" and "$\Delta m=2$" transitions, respectively. In Fig. 2(a), the "$\Delta m=2$" transitions are shown by the dashed arrows. The remarkable agreement obtained here, together with the fact that in Haldane spin chains the low-energy spectrum is defined as an $s=1$ state—then allowing "$\Delta m=1$" (and possibly "$\Delta m=2$") transitions—leads to the definitive conclusion that the reported ESR transitions are induced between $S=1$ excited states located around $q=\pi$ in the Brillouin zone.

To complete the analysis, let us consider the effect of the field on the dispersion of the excitation spectrum, around $q=\pi$. In the absence of available experimental results, we refer again to the theoretical description used above and we obtain the curves shown in Fig. 3(a). In that figure the field is chosen to be parallel to **b**, as an example. Figure 3(a) describes the q dependence of the excitations for $H=5.3$ T [this is the value of the resonant field of the low-field signal in Fig. 1(c)]. For that field direction, only the $E^y(q)$ and $E^x(q)$ branches are affected by H. They are shifted, but in such a way that they remain almost *parallel*. The possible "$\Delta m=1$" and "$\Delta m=2$" ESR transitions—in agreement with the required condition $\Delta q=0$—are represented by double arrows. For "$\Delta m=2$," the length of the arrows, i.e., the resonant frequency, is about the same in the whole narrow q range considered in the figure. This behavior explains why, at low temperature, the ESR lines can be symmetric and narrow, since, in that case, the contributions to the signals come mainly from the low-energy excitations. At higher temperature, the q range to be considered extends beyond this interval where the dispersion curves are expected to collapse into a single line. In that case, the ESR lines become broader and less symmetric (an actual fact). A similar situation describes the "$\Delta m=1$" transition (the low-field signal) of Fig. 1(c), since the dispersion curves for $E^z(q)$ and $E^y(q)$ are seen in Fig. 3(a) not to be parallel.

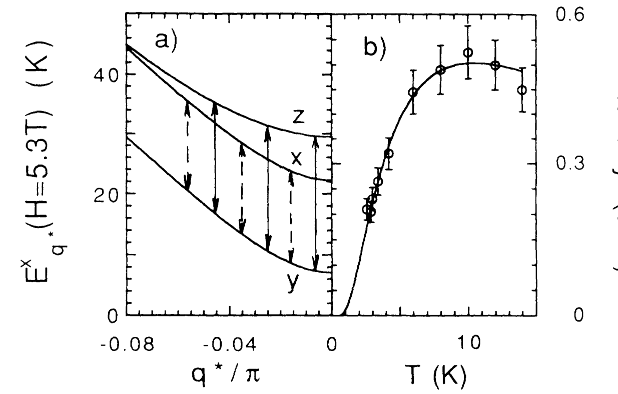

FIG. 3. (a) Dispersion of the excitations around $q=\pi$ ($q^*=q-\pi$) for a field $H=5.3$ T applied along **b**. The lines are given by Eq. (2). The solid and dashed double arrows give examples of expected "$\Delta m=1$" and "$\Delta m=2$" transitions, for the ESR condition $\Delta q=0$. (b) Temperature dependence of the integrated intensity $I\approx h\Delta H^2$ for the ESR signal observed for **H**‖**a** at $H=10.7$ T ($\omega=247$ GHz$=11.8$ K). The line is the prediction for transitions between excited states (see text).

The Hamiltonian which describes the properties of the magnetic chains of NENP is

$$H=\sum_i J\mathbf{S}_i\cdot\mathbf{S}_{i+1}+DS_i^{z2}+E(S_i^{x2}-S_i^{y2})+\mu_B\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S}_i\,, \tag{1}$$

where the first term with $J\approx 50$ K is the Heisenberg contribution and the last term, the Zeeman coupling. A numerical evaluation of the effect of an anisotropy on the isotropic quantum gap was given by Sakai and Takahashi [4]. According to these authors, the effect of D [with $E=0$ in Eq. (1)] yields a splitting of the isotropic gap ($E_G^0\approx 0.4J$) into a doublet and a singlet state, with respective energies E^z ($>E_G^0$) and E^{xy} ($<E_G^0$). A second anisotropy such as E in (1) can be assumed to have a similar effect as D. In that case, we can predict the XY doublet to be split and the singlet to be slightly shifted, yielding three distinct gaps, as observed in NENP, with $E_G^z>E_G^x>E_G^y$. Applying to this second effect the same quantitative dependences as established in Ref. [4] for a single anisotropy, we obtain from the experimental results ($E_G^z=29$ K, $E_G^x=15.7$ K, $E_G^y=13.6$ K) the following evaluations: $D\approx 8$ K and $E\approx 0.5$ K. In NENP, D as defined in Eq. (1), is seen to be positive. It is worth emphasizing that our analysis is in complete agreement with this result. This is not the case for the localized spin-cluster model presented in [5], which unreasonably requires $D<0$.

For the field dependence of the quantum gaps two descriptions have been proposed, by Affleck [9] and Tsvelik [10]. Since the description of the latter author allows a very quantitative agreement with all the data (NIS *and* ESR) discussed here, we refer to that work. However, in Ref. [10], the description is given for only one anisotropy—i.e., for two gaps. To account explicitly for the presence of D and E in (1)—i.e., of three distinct gaps—we use the following expression:

$$E_q^{x/y}(H)=\{(g_z\mu_BH)^2+C^2q^{*2}+(E_G^{x2}+E_G^{y2})/2 \pm[(E_G^{x2}-E_G^{y2})^2/4+(g_z\mu_BH)^2(E_G^x+E_G^y)^2+4C^2q^{*2}(g_z\mu_BH)^2]^{1/2}\}^{1/2}\,, \tag{2}$$

which is given for **H** applied along z. In (2), $q^*=q-\pi$, μ_B is the Bohr magneton, and C is the excitation velocity, evaluated to be $C\approx 2.7J\approx 135$ K in Ref. [6]. For H applied in another crystal direction, the same expression can be used, after a circular permutation is performed in the indices x, y, and z. The curves shown in Figs. 2 and 3 are obtained from Eq. (2). According to our analysis, the ESR signals result from transitions between excited states, around $q=\pi$. Consequently, the integrated intensity $I \approx h\Delta H^2$ must be governed by the populations of the connected states. For the example shown in Fig. 3(b), which corresponds to the "$\Delta m = 1$" transition observed for **H**‖**a** at $H = 10.7$ T ($\omega = 247$ GHz $= 11.8$ K), the populations depend explicitly on $\exp[-E_G^x(H)/T]$ and $\exp[-E_G^y(H)/T]$, with $E_G^x(H) = 15.7$ K and $E_G^y(H) = 4.5$ K, according to Fig. 2(b). The solid line in Fig. 3(b) is the prediction for Boltzmann statistics fitted to the data.

For the discussion, we refer to the pioneering work of Haldane. In Ref. [1], the case of anisotropic (Ising-like) AF chains, which is characterized by a Néel GS, is considered in detail. It is shown that in the description of the (nonlinear) soliton excitations, additional degrees of freedom must be taken into account. These degrees of freedom result in drastic differences between half-integer and integer spin chains. In the latter case, the low-energy soliton excitation is an $s = 0$ singlet state. For chains of spins $s = 1$, it can be represented by the eigenvector $|\ldots\downarrow\uparrow 0\downarrow\uparrow\ldots\rangle$ where $\downarrow$, 0, and $\uparrow$ are the three possible states of each individual spin. When the system becomes isotropic the Haldane phase is achieved. The transition towards this phase can be viewed as a "condensation" —limited by instanton fluctuations—of such $s = 0$ soliton states. This picture is actually in agreement with the representation of the GS given for the Haldane phase: $|\mathrm{GS}\rangle = |00\uparrow\downarrow 0\uparrow\downarrow\uparrow 0\downarrow\rangle$ [11]. According to [1], the low-energy excitations for such a system correspond to $\Delta m = 1$ transitions from this GS. For this reason, they can be defined as "magnon" excitations. However, as for the solitons in the Néel phase, these excitations have additional degrees of freedom defined by the spin operator $s = 1$ [1]. The ESR technique provides a direct way for probing the spin state of these (nonlinear) magnons characterizing the Haldane phase.

In the present work, we have shown that in a Haldane system, the low-energy excitations (defined at $q = \pi$) correspond actually to an $s = 1$ magnetic state [1]. Our results also establish that the phase transitions occurring at H_c^a are actually driven by the magnon excitations at $q = \pi$, which have their additional spin in the state ($s = -1$, for instance) for which the Zeeman energy decreases with H.

Recently, different ESR lines have been observed in NENP [12]. Below H_c^a, they are seen only at low temperature, well below 4 K. These results do not contradict at all our analysis of excited states observed at much higher temperature, in the range $1.5 < T < 20$ K. We shall present a discussion of these important low-T data, which have definitely a different origin, in a subsequent paper, together with our results obtained for $H > H_c^a$.

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Note added.— After our work was submitted for publication, we received from I. Affleck, a preprint which develops a theory in complete agreement with the present experimental analysis.

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