Zeeman levels with exotic field dependence
in the high field phase of a $S = 1$ Heisenberg antiferromagnetic chain

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We have performed electron spin resonance measurements over a wide frequency and magnetic field range on a single crystal of the $S = 1$ quasi-one-dimensional Heisenberg antiferromagnet Ni(C$_5$H$_{14}$N$_2$)$_2$N$_4$(PF$_6$). We observed gapped excitation branches above the critical field ($H_c$) where the Haldane gap closes. These branches are analyzed by a phenomenological field-theory using complex-field $\phi^4$ model. A satisfactory agreement between experiment and theory is obtained.

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Recently, field-induced phenomena in quantum spin systems have attracted considerable interest. These include magnetization plateaus [1, 2, 3] and field-induced long-range order (LRO) [4, 5, 6]. Gapped one-dimensional (1D) spin systems subject to an external magnetic field strong enough to close the gap are driven into a new phase. When the system has XY or Heisenberg symmetry, this phase is critical and its low-energy physics is described by the Tomonaga-Luttinger liquid [7], whose elementary excitations are of the particle-hole type (spinon pairs). The high-energy physics which cannot be described using this picture has been recently investigated experimentally [8, 9, 10] as well as theoretically [11].

One-dimensional Heisenberg antiferromagnets (HAFs) with integer spin are typically gapped and have a disordered spin liquid singlet ground state [12]. The first excited state is a triplet and one of the Zeeman-split triplet branches goes down in magnetic field. At some critical field $H_c$ the gap closes, a qualitatively new ground state emerges and magnetism recovers. Above $H_c$, a LRO is expected to occur in quasi-1D integer-spin HAFs owing to interchain interaction. Such a field-induced LRO in the $S = 1$ quasi-1D HAF was found recently by specific heat measurements on a single crystal of Ni(C$_5$H$_{14}$N$_2$)$_2$N$_4$(PF$_6$), abbreviated NDMAP. Figure 1 shows the magnetic field versus temperature phase diagram of NDMAP. The regions below and above the boundary denoted as $H_{LRO}(T)$ correspond to the Haldane disordered phase, and to the LRO phase, respectively. The critical field $H_c$ in the present paper is defined as $H_{LRO}$ extrapolated to $T = 0$.

Quite recently, three distinct excitation branches were observed in inelastic neutron scattering (INS) experiments on NDMAP in the LRO phase above $H_c$ for $H \parallel a$, and a satisfactory description within a phenomenological field theory was obtained [6]. This observation is remarkable because one would expect two branches from the conventional spin-wave theory.

Electron spin resonance (ESR) is one of the powerful methods to investigate magnetic excitations, especially at low energies with a much better energy resolution than INS. In Ref. [13] we observed ESR signals in a single crystal of NDMAP and interpreted the results as the coexistence of 1D and 3D excitations, because no satisfactory description was available above $H_c$ at that time.

In the present paper we extend the ESR study of NDMAP to a much wider frequency range from which we obtain new results. A nontrivial field dependence of the resonance modes, very different from that expected from a conventional spin-wave theory, is observed. We compare the experimental results with model calculations based on the field theory used in the analysis of the recent INS experiments [6], and obtain a good agreement with the theory.

First we summarize the crystal and magnetic properties of NDMAP. This compound crystallizes in the or-
Figure 2 shows a typical example of ESR spectra observed for $H \parallel a$ and $H \parallel c$. The signal at about 13.5 T for $H \parallel a$ comes from the LRO phase. In Fig. 3(a), the resonance frequencies for $H \parallel a$ as a function of magnetic field are shown with solid circles. We also plot with solid squares the gap energies obtained from the recent INS measurements at 30 mK. In the figure, the vertical broken line and the vertical dotted line denote the $T = 0$ critical field $H_c$ and the boundary field $H_{\text{LRO}}$ between the disordered and LRO phases at 1.5 K, respectively. It is obvious that the slope of the branches changes at $H_c$ and not at $H_{\text{LRO}}$. It should be remarked that a similar change of slope was observed in the quasi-1D material NENC and in the 3D weakly coupled dimer system TiCuCl$_3$.

The single crystals of NDMAP were grown in the same manner as that described in Ref. 4. The ESR measurements were performed using a millimeter vector network analyzer with extensions up to about 700 GHz from the AB Millimeter, France and a superconducting magnet up to 16 T from the Oxford Instruments, UK. We performed the ESR measurements in $H \parallel a$ and $H \parallel c$ geometries at the lowest temperature available with our spectrometer (1.5 K). Faraday and Voigt configurations were used for $H \parallel a$ and $H \parallel c$, respectively. As shown in Fig. 1, the external magnetic field of $\approx 9$ T for $H \parallel a$ brings the system into the LRO phase at 1.5 K.

From the analysis of the magnetic susceptibility data, the following values are obtained [5]: $J/k_B = 30.0$ K, $D/J = 0.3$, $g_l = 2.10$ and $g_\perp = 2.17$, where $J$ is the intrachain exchange interaction constant and $g_l$ and $g_\perp$ are the $g$ values parallel and perpendicular to the chain, respectively. From the INS measurements done on single crystals of deuterated NDMAP [13], the following parameters were determined: $J = 2.85 \text{ meV}(= 33.1 \text{ K})$, $J'_x = 3.5 \times 10^{-4} \text{ meV}(= 4.1 \times 10^{-3} \text{ K})$, $J'_y = 1.8 \times 10^{-3} \text{ meV}(= 2.1 \times 10^{-2} \text{ K})$ and $D = 0.70 \text{ meV}(= 8.1 \text{ K})$, where $J'_x$ and $J'_y$ are the interchain exchange interactions along the $a$ and $b$ axes, respectively.

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terms of a complex triplet field $\phi = A + iB$ which is assumed to be small, $|\phi| \ll 1$. For a dimerized $S = \frac{1}{2}$ system, the field $\phi$ describes the dimer wave function $|\phi\rangle = (1 - |\phi|^2)^{1/2}|s\rangle + \sum_{\alpha=x,y,z} \phi_i(t_\alpha)$, where $|s\rangle$ and $|t_\alpha\rangle$ are the singlet and three triplet states of the dimer; it is a continuum analog of the bond-boson description used in [13]. The uniform and staggered magnetization are given by $M = (\phi^* \times \phi)$ and $L = (\phi^* + \phi)(1 - |\phi|^2)$, respectively. The effective Lagrangian density in the continuum limit has the following form:

$$\mathcal{L} = \hbar (A \cdot \partial_t B - B \cdot \partial_t A) - (1/2) v^2 (\partial_t A)^2$$

$$- \sum_\alpha \{ m_\alpha A_\alpha^2 + \tilde{m}_\alpha B_\alpha^2 \} + 2H \cdot (A \times B) \quad (1)$$

$$- \lambda (A^2)^2 - \lambda_1 (A^2B^2) - \lambda_2 (A \cdot B)^2.$$

This model, though derived for dimerized $S = \frac{1}{2}$ chains, may also be used for other gapped 1D systems which are in the same universality class, particularly for $S = 1$ Hal-dane chains. In this case, the quantities $m_\alpha$, $\tilde{m}_\alpha$, and $\lambda_i$ should be treated as phenomenological parameters; the direct microscopic justification of this model for $S = 1$ chains is the subject of ongoing work. The spatial derivatives of $B$ are omitted in (1) because they appear only in terms which are of the fourth order in $A$ and $B$. By integrating out the “slave” $B$-field one obtains an effective real-field $\varphi^4$-type theory similar to that of Affleck [21]; actually, Affleck’s theory may be viewed as a special case of (1) with isotropic $\tilde{m}_\alpha = \tilde{m}$ and with simplified interaction term $\lambda_{1,2} = 0$. Another special case $m_\alpha = \tilde{m}_{\alpha}$ leads to the spectra which for $H < H_c$ exactly coincide with those obtained in the approach of Tsvelik [22] who has proposed an effective theory involving three massive Majorana fields, and also with the perturbative formulas of Refs. [23]. If one additionally assumes the simplified interaction potential $\lambda_{1,2} = 0$, the theory becomes equivalent to that of Mitra and Halperin [14] who postulated a bosonic Lagrangian to match Tsvelik’s results for the field dependence of the gaps below $H_c$.

The solid lines in Figs. 3(a) and (b) represent the best fit of the calculated energy gaps at $q = \pi$ to the experimental data. This fit is obtained using the following set of model parameters (all values in meV): $m_a = 0.5$, $m_b = 0.8$, $m_c = 5.29$, $\tilde{m}_a = 0.353$, $\tilde{m}_b = 0.342$, $\tilde{m}_c = 0.647$, $\lambda = 1$, $\lambda_1 = -\lambda_2 = 0.13$. We obviously see a change in slope of each excited branch and reopening the energy gap of the lowest branch at $H_c$. Below $H_c \simeq 5.5$ T in Fig. 3(a), three excitation branches are in a good agreement with the neutron data. The ESR transitions from the ground to the excited states at $q = \pi$ are forbidden because no staggered component exists in the ground state of this compound. In both figures, the ESR resonance points only appear near $H_c$, because these correspond to the transition between the excited states and the intensity is related to the population of the excited states at 1.5 K. The thin broken line in each figure indicates the transition between the lowest two magnon branches at $q = \pi$. For those temperature-induced transitions, the agreement between experiment and calculation is satisfactory for $H \parallel a$ and is not good for $H \parallel c$. Above $H_c$, the calculated branches are close to the experimental data near $H_c$, but deviate from them at high fields. This is probably because the theory is applicable only for the state with a small staggered order and thus only for fields which are not too far above $H_c$.

In these calculations, we have taken into account the tilting of the crystal field axis of the Ni$^{2+}$ ions from the crystallographic $c$ axis. The tilting angle is 15.9°. In Fig. 3(b), a change in slope at about 7 T observed in the A and B branches are reproduced in the calculation. Because of the tilting of the crystal field axis, the external magnetic field applied parallel to the $c$ axis mixes the wave functions of A and B branches. The origin of this change in slope is different from that of the changes visible near the critical field. The observed ESR line below $H_c$ in Fig. 3(b) deviates from the expected thin broken line, although a satisfactory agreement is obtained for
$H \parallel a$; the reason for this discrepancy is not clear at present. For $H \parallel c$, we did not observe ESR signals corresponding to the lowest calculated mode above $H_c$; we believe this is caused by a strong damping of the lowest magnon mode due to the interaction with domain walls, because our measurement was done at a high temperature. A similar problem arose in INS measurements in the $H \parallel a$ geometry done at 2 K where the lowest magnon mode appeared to be quasielastic, and only after lowering the temperature to 30 mK the mode was successfully observed. The damping should be much stronger in the $H \parallel c$ geometry, due to the lower energy and respectively higher density of domain walls.

Remarkably, the observed field dependence of the ESR modes for both geometries is very different from that expected from a conventional spin-wave theory. Indeed, in a conventional (classical) antiferromagnet with easy-plane anisotropy $D$ and external magnetic field $H$ applied in the easy plane, there are two resonance modes with the energies $\varepsilon_1 = g\mu_B H$ and $\varepsilon_2 = 2S\sqrt{D|J|}$. For $H$ perpendicular to the easy plane, one would classically expect to see one field-dependent resonance mode with the energy $\varepsilon_x' = \sqrt{(g\mu_B H)^2 + \varepsilon_z^2}$, the energy of the other mode being zero. We have observed and described theoretically completely different behaviors above $H_c$ for both directions: in the $H \parallel a$ case (in-plane geometry) the energies of all modes increase approximately as $g\mu_B H$, and for $H \parallel c$ we observe the (avoided) crossing of two modes whose energies behave roughly as $g\mu_B H$ and $2g\mu_B H$.

In conclusion, we have performed ESR measurements on a single crystal of the $S=1$ quasi-one-dimensional Heisenberg antiferromagnet NDMAP and observed ESR spectra corresponding to the gapped state above the critical field where the Haldane gap closes. For $H \parallel a$ our ESR data above $H_c$, taken at $T = 1.5$ K, agree very well with those from inelastic neutron scattering obtained at much lower temperature, and the observed resonances are not affected by the boundary of the long-range-ordered phase at $H \simeq 9$ T. For $H \parallel c$ we observed a change in slope of the ESR line resulting from an avoided crossing between the two modes having nontrivial slopes $H$ and $2H$. The observed field dependence of the magnon modes for both geometries $H \parallel a$ and $H \parallel c$ is very different from that expected from a conventional spin-wave theory. Model calculations based on the phenomenological field-theoretical approach have reproduced all the features of the observation and a satisfactory quantitative agreement between theory and experiment is obtained.

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