Coexistence of one- and three-dimensional excitations in a quasi-one-dimensional $S=1$ Heisenberg antiferromagnet

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Electron-spin resonance (ESR) measurements at high frequency and high magnetic field are performed on the quasi-one-dimensional (1D) $S=1$ Heisenberg antiferromagnet, $Ni(C_5H_{14}N_2)_2N_3(PF_6)$ that exhibits a field-induced long-range ordering (LRO) at low temperatures. In the Haldane disordered phase, the ESR signals we observed are well described as originating from the transitions within the first excited triplet of a single chain. In the LRO phase, we observed two ESR branches, one of which is assigned to an antiferromagnetic resonance mode, and the other to a 1D excitation that persists in the LRO phase. [S0163-1829(99)02037-8]

When the exchange interactions between spins are restricted to lower dimensions, magnetic materials exhibit fascinating properties. Mesoscopic magnetism appearing in zero-dimension (0D) has attracted much attention from condensed-matter physicists. There has been a renewed interest in 1D Heisenberg antiferromagnet (HAF) stimulated by Haldane's conjecture.[1] According to this conjecture, a 1D HAF with integer spin quantum number (S) has an energy gap (Haldane gap) between the singlet ground state and the first excited one, while the corresponding system with half-odd-integer S has no gap in the excitation spectrum. This conjecture has been tested both theoretically and experimentally. Now, it is widely accepted that the Haldane gap does exist in $S=1$ 1D Heisenberg antiferromagnetic systems.

The magnetic excitation spectra in $S=1$ 1D HAF's have been studied by neutron inelastic scattering[2–6] and electron-spin resonance[7–11] (ESR) techniques. These measurements showed that the first excited state is a triplet whose energy is minimum at wave vector (q) equals π. When magnetic anisotropy terms such as $D\Sigma_i(S_i^z)^2$ and $E\Sigma_i\{(S_i^x)^2-(S_i^y)^2\}$ are present, this triplet splits into three nondegenerate states. On applying an external magnetic field, these states Zeeman split and the ESR transitions within the triplet levels have been observed.[7–11] Surprisingly, the ESR transitions from the singlet ground state to the excited triplet which are forbidden from the momentum conservation law have also been observed in the quasi-1D $S=1$ HAF's, $Ni(C_2H_8N_2)_2NO_2(ClO_4)$ (NENP) (Refs. 8,10,11) and $Ni(C_3H_{10}N_2)_2NO_2(ClO_4)$ (NINO).[10,11] Two theories[12,13] were presented to explain these unexpected ESR transitions. They invoked a staggered magnetic field caused by a staggered inclination of the octahedra surrounding Ni^{2+} ions. This staggered magnetic field mixes the state at $q=0$ with that at $q=\pi$, thereby making the transitions from the ground state to the excited triplet possible. A polarization analysis of the ESR absorption in NINO (Ref. 14) has confirmed the theoretical prediction.

Recently, Honda *et al.*[15] have reported the observation of a field-induced long-range magnetic ordering in the quasi-1D $S=1$ HAF, $Ni(C_5H_{14}N_2)_2N_3(PF_6)$ (NDMAP). From a heat-capacity measurement on a single-crystal sample of NDMAP, these authors have constructed the magnetic field (H) versus temperature (T) phase diagram which is reproduced in Fig. 1. It would be interesting to study the magnetic excitation in the field-induced long-range ordered (LRO) phase of an $S=1$ quasi-1D HAF. In this paper, we report the observation of an antiferromagnetic resonance (AFMR) mode in the LRO phase. We also observed an ESR signal in the LRO phase which can be explained as originating from a 1D excitation.

First, we summarize the crystal and magnetic properties of NDMAP. This compound crystallizes in the orthorhombic system with the lattice constants $a=18.046$ Å, $b=8.7050$ Å, and $c=6.139$ Å.[16] Ni^{2+} ions are bridged by azido ions along the c axis making an antiferromagnetic chain along this direction.[16] These chains are weakly coupled via intervening PF_6 counter anions. All the Ni sites in NDMAP are crystallographically equivalent. This means that the staggered field is absent in this compound. The magnetic parameters are obtained from the susceptibility measurement as follows:[15] $J/k_B=30.0$ K, $D/J=0.3$, $g_{\parallel}=2.10$, and $g_{\perp}=2.17$. Here, J is the intrachain exchange interaction constant and $g_{\parallel}$ and $g_{\perp}$ are the g values parallel and perpendicular to the chain c axis, respectively. The anisotropy in the susceptibility due to

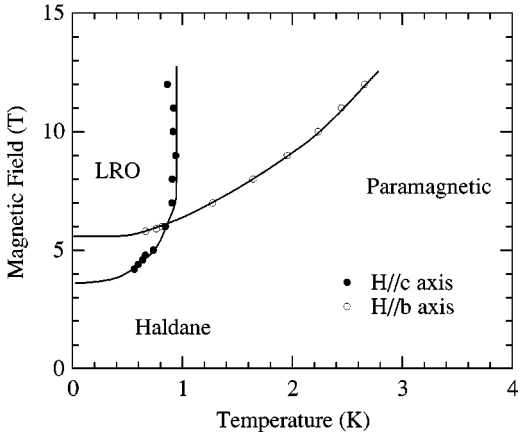

FIG. 1. The magnetic field versus temperature phase diagram of $Ni(C_5H_{14}N_2)_2N_3(PF_6)$ determined from the heat-capacity measurement.The phase boundary curve separating the long-range ordered (LRO) phase from the disordered phases (Haldane and paramagnetic) is anisotropic. The figure is from Ref. 15.

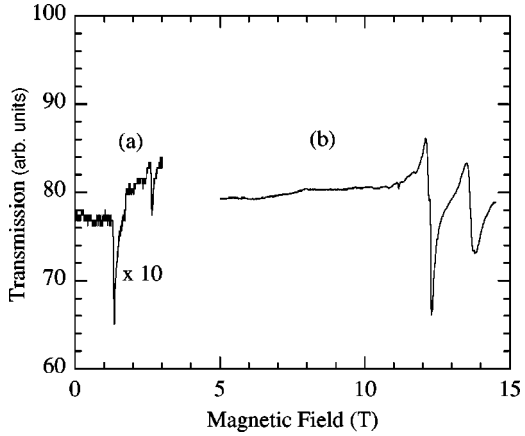

FIG. 2. An example of ESR spectrum obtained in (a) the Haldane disordered phase at the frequency (ν) of 144.47 GHz, and in (b) the LRO phase at $\nu = 329.63$ GHz. All these spectra were taken at 1.7 K.

the E term was so small that we were unable to determine its value.

The single crystals of NDMAP were grown in the same manner as that described before.[15] The ESR measurements were performed using a millimeter vector network analyzer with extension up to about 700 GHz from the *AB* millimeter, France and a superconducting magnet up to 20 T from the Oxford Instruments, UK. At the low-frequency range below 100 GHz, we used a homemade spectrometer with a Gunn oscillator.[17] Because the lowest temperature available with our spectrometer is about 1.7 K, all the measurements were done with H perpendicular to the chain c axis ($H \| b$ axis).

Figure 2 shows an example of ESR spectrum observed in (a) the Haldane disordered phase, and in (b) the LRO phase, respectively. The absorption intensity in (a) is much weaker than that in (b). This is easily understood if one remembers that the ESR signals in (a) originate from the transitions within the excited triplet. In this case, the absorption intensity depends much on temperature[7,9,10] and is very weak at low temperatures below the temperature corresponding to the Haldane gap.

First, we discuss the ESR signals observed in the Haldane disordered phase. We plot in Fig. 3 the position of the ESR signals in the frequency (ν)–magnetic-field plane. We interpret these ESR signals as arising from the transitions within the excited triplet. The magnetic-field dependence of the first excited triplet has been studied theoretically.[18–20] From the perturbation theory, Golinelli *et al.*[20] have obtained the following result when H is applied parallel to the x axis,

$$\Delta^{\pm} = \frac{1}{2}\{\Delta_z + \Delta_y \pm [(\Delta_z - \Delta_y)^2 + g_{\perp}^2 \mu_B^2 H^2]^{1/2}\}, \qquad (1)$$

where Δ_y and Δ_z are the gap energies in zero field and μ_B is the Bohr magneton. We have another mode Δ_x ($\Delta_y < \Delta_x < \Delta_z$) whose energy is independent of H. The gap energies Δ_x, Δ_y, and Δ_z are related to the single-ion anisotropy constants D and E as given by Eqs. (2.11) and (3.1) in Ref. 20. The ESR transitions from the Δ_y to Δ_x and Δ_z levels and that from the Δ_x to Δ_z levels are possible because of the presence of the D and E terms. We found that the experimental condition ($H \| b$) corresponds to the case of $H \| x$. A good fit between theory and experiment is obtained with $E/k_B = 0.14$ K using the value of D obtained before.[15]

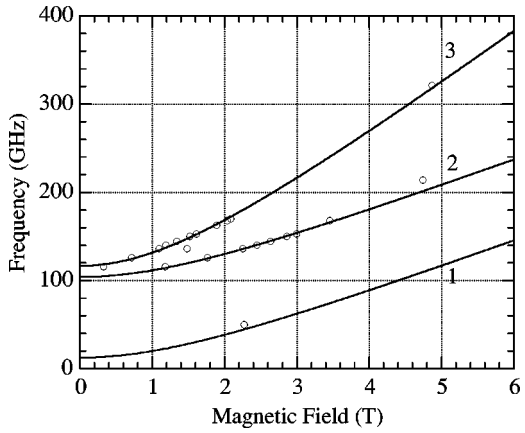

FIG. 3. The magnetic field versus frequency plot of the ESR signals observed in the Haldane disordered phase. Curves labeled 1 through 3 are the theoretical ones discussed in the text.

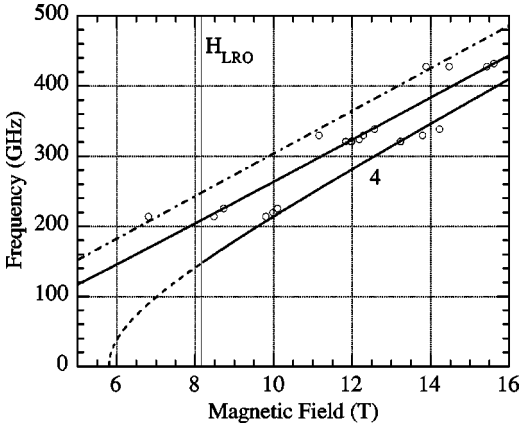

FIG. 4. The ESR signals observed in the LRO phase are plotted in the frequency (ν)–magnetic-field (H) plane. Dot-dashed line represents the ν-H relation expected for the electron paramagnetic resonance with $g = 2.17$, along which a weak signal is observed.

Next, we discuss the ESR signals observed in the LRO phase. The experimental points are shown in Fig. 4. These experimental points constitute two excitation branches. Here, H_{LRO} is the transition field from the disordered to the LRO phase at $T = 1.7$ K (Fig. 1). Since we expect an antiferromagnetic arrangement of spins to exist in the LRO phase, one of these two branches must be identified as an AFMR mode. Due to the single-ion anisotropy D (>0) term, spins in the LRO phase are confined to a plane perpendicular to the c axis. A small anisotropy coming from the single-ion E term determines the easy axis in this plane, provided that we neglect the effects of dipole-dipole interaction. Let us assign the branch labeled 4 to an AFMR mode. We found that our result is well fitted with the following formula proposed by Magariño *et al.*[21] to analyze the AFMR mode in the quasi-1D $S = 5/2$ HAF, $(CH_3)_4NMnCl_3$ (TMMC),

$$2\pi\nu/\gamma = g_{\perp}\mu_B\{(H - H_0)^2 - C\}^{1/2}, \qquad (2)$$

where, γ is the magnetomechanical ratio, H_0 is a constant which was introduced to include a quantum effect on the AFMR frequency,[21] and C is a constant. From a fitting of Eq.

(2) to the experiment, we get $H_0=2.0$ T and $C=14.5$ T^2. The value of H_0 obtained in NDMAP is larger than that in TMMC. This shows that the quantum fluctuation in the quasi-1D HAF becomes more prominent with decreasing S value. The constant C in Eq. (2) is given by $C=2H_EH_A$, where H_E and H_A are the exchange and anisotropy fields, respectively.[22] Using the value $J/k_B=30.0$ K determined before,[15] we get $H_A=0.18$ T ($g\mu_BH_A/k_B=0.26$ K). This value of H_A is not far from the E value obtained in the present experiment.

Finally, we discuss the ESR signals observed in the LRO phase which do not belong to branch 4 in Fig. 4. We note that these experimental points lie on branch 1 extrapolated from the low-field side (Fig. 3). Therefore, we interpret this ESR mode as originating from a 1D excitation persisting in the LRO phase. A possible explanation for this ESR transition to occur would be the following. It is shown theoretically that one of the excited triplet crosses the ground state at a critical field H_{c1}.[18–20] Above H_{c1} the ground-state energy at $q=0$ is almost field independent. One sees in Fig. 3 of Ref. 20 that the energy of the Δ_x state which is independent of H below H_{c1} begins to increase with H above it. Although no theory is available about the nature of the excited triplet above H_{c1}, we expect that the Δ_x state will have a $q=0$ component, because many energy levels are mixed at high fields. Then, we have an ESR transition from the ground state to the Δ_x state whose frequency increases with H. In this case, the $\nu-H$ relation of the ESR signal does not necessarily coincide with branch 1 extrapolated from the low-field side.The agreement between the theory and the experiment in the LRO phase should be considered as accidental. As was discussed by Affleck,[23] in the LRO phase of the quasi-1D $S=1$ HAF, $CsNiCl_3$, the massive triplet of the single chain splits up into two massless Goldstone modes and a massive longitudinal mode. In $CsNiCl_3$, the interchain coupling is strong enough to induce an LRO at a finite temperature even in zero field. We expect, however, that Affleck's prediction will apply to our case as well.

In conclusion, we have made ESR measurements on the quasi-1D $S=1$ HAF NDMAP which exhibits a field-induced long-range magnetic ordering at low temperatures. In the Haldane disordered phase, the ESR signals we observed are well described as originating from the transitions within the first excited triplet. In the LRO phase, we observed two ESR branches, one of which is assigned to an AFMR mode and the other to a 1D excitation which persists in the LRO phase. Clearly, more theoretical studies on the excitation spectra in $S=1$ 1D HAF's above H_{c1} are needed.

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