Half-ordered state in the anisotropic Haldane-gap antiferromagnet Ni(C₅D₁₄N₂)₂N₃(PF₆).

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Neutron diffraction experiments performed on the Haldane gap material Ni(C₅D₁₄N₂)₂N₃(PF₆) in high magnetic fields applied at an angle to the principal anisotropy axes reveal two consecutive field-induced phase transitions. The low-field phase is the gapped Haldane state, while at high fields the system exhibits 3-dimensional long-range Néel order. In a peculiar phase found at intermediate fields only half of all the spin chains participate in the long-range ordering, while the other half remains disordered and gapped.

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High-field phase transitions in quantum antiferromagnets (AFs) have recently drawn a great deal of attention. Of particular interest is field-induced spin freezing exhibited by many quantum spin liquids. The massive triplet of low-lying S = 1 gap excitations (magnons) in such systems is subject to Zeeman splitting by external magnetic fields. A soft-mode quantum phase transition occurs when the gap for one member of the triplet is driven to zero. The result is a Bose condensation of magnons. In the presence of magnetic anisotropy and weak inter-chain interactions, always found in real materials, the magnetized high-field phase is a Néel-like state with AF long-range order. The phase transition itself and the peculiarities of the high-field phase have been studied experimentally in several model materials including the Haldane-gap antiferromagnets NDMAP (Ni(C₅H₁₄N₂)₂N₃(PF₆)) and NDMAZ (Ni(C₅H₁₄N₂)₂N₃(ClO₄)) and the bond-alternating S = 1 chain NTENP (Ni(N,N′-bis(3-aminopropyl)propane-1,3-diamine(μ-NO₂))₂ClO₄) and dimer systems such as TiCuCl₆ and Cs₃Cr₂Br₉.

It has been long established that magnetic anisotropy, which is particularly important for S = 1 materials, has a strong impact on the phase transition. The value of the critical field H_c depends on the relative orientation of the applied field and the anisotropy tensor. A very interesting case is that of NDMAP. This compound features two equivalent sets of Haldane spin chains with non-collinear local anisotropy axes. To date, all experiments were performed in magnetic fields applied along the principal axes of the orthorhombic crystal structure that are also the macroscopic magnetic anisotropy axes. In these geometries all tilts of the local anisotropy axes relative to the field direction are the same for the two chain types. In the present study we investigate a less symmetric scenario, in which the magnetic field is applied in a general direction relative to the crystal axes. We find two consecutive field-induced transitions from the quantum-disordered spin liquid to ordered Néel phase, with a novel “half-ordered” phase in-between.

The crystal structure of NDMAP (orthorhombic space group Pnma, a = 18.046 Å, b = 8.705 Å, and c = 6.139 Å) was described in detail in Ref. The S = 1 chains run along the crystallographic c axis. The in-chain exchange constant is J = 2.6 meV. Inter-chain interactions are much weaker: |J₁/J| < 10⁻⁵. Magnetic anisotropy is predominantly of single-ion easy-plane type with D/J ≈ 0.25. In addition, there is a weak in-plane anisotropy term, and the degeneracy of Hal-
dane triplet is fully lifted. The gap energies for excitations polarized along the principal anisotropy axes $x$, $y$ and $z$ are $\Delta_x = 0.42(3)$ meV, $\Delta_y = 0.52(6)$ meV, and $\Delta_z = 1.9(1)$ meV.\footnote{The anisotropy axes are determined by the geometry of the corresponding Ni$^{2+}$ coordination octahedra and, as mentioned above, do not exactly coincide with crystallographic directions. Instead, the $x$ and $z$ axes of the NiN$_6$ octahedra are in the $(a, c)$ crystallographic plane, but tilted by $\alpha \approx 16^\circ$ relative to the $a$ and $c$ axes, respectively. There are two types of chains related by symmetry, and the corresponding tilt directions are opposite. Within each set of chains the Ni$^{2+}$-sites form a simple orthorhombic Bravais lattice. On the other hand, the two sets of chains are displaced by $(0, 0.5, 0.5)$ relative to each other. The overall lattice of Ni$^{2+}$ ions is thus a body-centered one. Due to this geometric frustration, the two sets of antiferromagnetic spin chains are magnetically decoupled at the Mean Field level. The main features of the crystal structure of NDMAP are illustrated in Fig. 1.\footnote{Our new neutron diffraction experiments were performed on a fully deuterated single crystal NDMAP sample of approximate mass 100 mg. The data were taken on the D23 lifting-counter diffractometer at Institut Laue-Langevin. Sample environment was a vertical-field cryomagnet with a dilution refrigerator insert. The data were taken at $T \sim 35$ mK in magnetic fields up to 6 T. Unfortunately, there was no possibility to rotate the sample in situ during the experiment. Re-mounting the sample to explore several orientations was not an option either, as the crystals are known to shatter and deteriorate rapidly during cooling/heating cycles. For this reason only one experimental geometry was realized, with the magnetic field applied at an angle $\psi = 14.2^\circ$ to the $c$ axis, in the $(a, c)$ crystallographic plane, as shown in Fig. 1.\footnote{For one set of spin chains that we will refer to as “type A”, the field was thus almost exactly parallel to the main anisotropy axis, the corresponding angle being $\phi_B = \alpha - \psi = 1.8^\circ$. For type-B chains the angle between the field direction and the local Ni$^{2+}$ anisotropy axes was considerably larger, $\phi_B = \alpha + \psi = 30.2^\circ$.} In the geometry of the present experiment two distinct anomalies are detected at $H_c^{(1)} = 3.4$ T and $H_c^{(2)} = 4.1$ T. Below $H_c^{(1)}$ there is no antiferromagnetic Bragg scattering in NDMAP that retains its singlet ground state. At $H_c^{(1)}$ antiferromagnetic Bragg reflections simultaneously appear at both $(0, 0.5, 0.5)$ and $(1, 0.5, 0.5)$ reciprocal-space positions. These two peaks remain of roughly equal intensity in the field range $H_c^{(1)} < H < H_c^{(2)}$. Above the 2nd transition at $H_c^{(2)}$ the intensity of the $(0, 0.5, 0.5)$ peak starts to increase more rapidly. In contrast, the $(1, 0.5, 0.5)$ peak intensity flattens out and even decreases slightly. Typical scan across the two magnetic Bragg reflection collected at $H = 6$ T are shown in the insets in Fig. 2.\footnote{Though a detailed determination of the magnetic structure has not been performed, a survey of several magnetic Bragg peaks at $H = 6$ T revealed a consistent intensity pattern. It was found that $(h+k+l)$-even reflections are considerably stronger than the $(h + k + l)$-odd ones. Within each of these reflection classes the intensity is a smooth function of wave vector transfer, typical of the combined effects of the magnetic form factor and neutron polarization factors. Such behavior is consistent with an almost-collinear antiferromagnetic spin arrangement on a body-centered lattice, which was previously shown to be realized in NDMAP in high magnetic fields applied strictly along the high-symmetry crystallographic directions.\footnote{The field-dependent behavior observed in the present study is in stark contrast that previously seen for $H||c$ (i.e., $\phi_A = \phi_B$), where only a single transition was detected. The unusual two-stage transition can be understood in the framework of a simple model first proposed by I. Harada.\footnote{The key idea is that long-range ordering occurs in each set of spin chains independently.}}\footnote{The critical fields for an individual spin chain in an arbitrarily directed magnetic field can be estimated using perturbation theory.\footnote{Though clearly oversimplified, for a magnetic field applied parallel to any of the}}}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Main panels: field dependence of two magnetic Bragg peak intensities measured in NDMAP at $T = 35$ mK. The magnetic field is applied in the $(a, c)$ crystallographic plane at an angle $14.2^\circ$ to the $c$ axis. The solid lines are as described in the text. Insets: $h$-scans across the two magnetic Bragg peaks at $H = 6$ T.}
\end{figure}
principal anisotropy axes this method is known to give the same values of \( H_c \) as more sophisticated calculations based on the quantum non-linear sigma-model or mapping to Majorana fermions. For a field in the \((x, z)\) plane applied at an angle \( \phi \) to the magnetic easy axis \( z \), the perturbative result for \( H_c \) is:

\[
\mu_B H_c = \sqrt{\frac{\Delta_x \Delta_y \Delta_z}{g_x^2 \Delta_x \sin^2 \phi + g_y^2 \Delta_y \cos^2 \phi}}. \tag{1}
\]

In this formula \( g_x \) and \( g_y \) are components of the Ni\(^{2+} \) gyromagnetic tensor. Making use of the previously measured gyromagnetic ratios\(^3\) for the geometry of the present experiment one gets \( H_c = 3.8 \) T and \( H_c = 4.3 \) T for type-A and type-B chains, respectively. While somewhat larger than the measured values, these two fields can be associated with the two observed ordering transitions at \( H_c^{(1)} \) and \( H_c^{(2)} \).

Below \( H_c^{(1)} \) both types of spin chains are in a quantum-disordered gapped state. As the external field exceeds \( H_c^{(1)} \) at zero temperature, individual type-A chains acquire long-range Néel order. Weak interactions between type-A chains stabilize this ordered state at non-zero temperatures and ensure the existence of true 3-dimensional long-range static antiferromagnetic spin correlations. Nevertheless, considering that inter-chain interactions are very weak, in the field range \( H_c^{(1)} < H < H_c^{(2)} \) type-B chains must remain in the quantum-disordered gapped phase. The corresponding Ni\(^{2+} \) ions carry no static magnetization and do not participate in the long-range Néel order. This peculiar phase of NDMAP, where half the Haldane spin chains remain gapped while the other half participate in long-range anisotropic magnetic order can be described as “half-ordered” state. In this regime the only magnetized ions in NDMAP are located on type-A chains and form a simple Bravais lattice. As a consequence, \( (0, 0.5, 0.5) \) and \( (1, 0.5, 0.5) \) magnetic Bragg reflections have the same structure factor. Their intensities should differ only slightly due to slightly different form- and polarization-factors. These intensities are proportional to the square of the staggered magnetization on the A-sublattice: \( I_{(0, 0.5, 0.5)} \sim I_{(1, 0.5, 0.5)} \sim |m_A|^2 \).

The situation changes at \( H_c^{(2)} \) when the gap in type-B chains closes as well, and they too acquire static long-range AF spin correlations. Now static magnetic moments are located on both A- and B-sublattices and form a body-centered structure. In spite of geometric frustration, a definitive relative alignment between spins on the two sublattices is established via dipolar interactions and/or order-from-disorder fluctuation effects. The two magnetic Bragg peaks are then no longer equivalent. Assuming a collinear alignment of A- and B-type spins, their intensities are given by \( I_{(0, 0.5, 0.5)} \sim |m_A + m_B|^2 \) and \( I_{(1, 0.5, 0.5)} \sim |m_A - m_B|^2 \). As both staggered magnetizations increase with field, \( I_{(0, 0.5, 0.5)} \) increases rapidly and \( I_{(1, 0.5, 0.5)} \) levels off.

To construct a phenomenological semi-quantitative description we can assume that \( m_A = m_A^{(0)} |H/H_c^{(1)} - 1|^\beta \theta(H - H_c^{(1)}) + m_B^{(0)} |H/H_c^{(2)} - 1|^\beta \theta(H - H_c^{(2)}) \). Assuming that the ordered moments on the two chain subsets are collinear (and thus the corresponding polarization factors for neutron scattering intensities are equal), the expression for the measured Bragg intensities can be written as:

\[
I_{(0, 0.5, 0.5)} \propto \left[ m_A^{(0)} |H/H_c^{(1)} - 1|^\beta \theta(H - H_c^{(1)}) + m_B^{(0)} |H/H_c^{(2)} - 1|^\beta \theta(H - H_c^{(2)}) \right]^2, \tag{2a}
\]

\[
I_{(1, 0.5, 0.5)} \propto \left[ m_A^{(0)} |H/H_c^{(1)} - 1|^\beta \theta(H - H_c^{(1)}) - m_B^{(0)} |H/H_c^{(2)} - 1|^\beta \theta(H - H_c^{(2)}) \right]^2. \tag{2b}
\]

Fitting this form to the experimental data (solid lines in Fig. 2) yields the following parameters: \( H_c^{(1)} = 3.42(1) \) T, \( H_c^{(2)} = 4.07(1) \) T and \( \beta = 0.37(2) \) and \( m_A^{(0)}/m_B^{(0)} = 1.50(4) \). Overall, the experimentally measured field dependencies are rather well reproduced by the simple model.

The experimental observations of a two-stage transition and half-ordered state in NDMAP highlight several important aspects of field-induced spin freezing in highly anisotropic gap systems. First, the two-stage transition is a dramatic demonstration of the fact that gap energies and transition fields are influenced by local anisotropy parameters, rather than macroscopic magnetic anisotropy routinely measured with bulk methods. The second conclusion is that the principle driving force of the phase transition is the tendency of individual spin chains to form long-range Néel order at \( T = 0 \) in sufficiently strong fields. Inter-chain interactions are of course needed to stabilize this order in 3 dimensions at \( T > 0 \), but play only a minor role in determining the actual transition field at \( T \rightarrow 0 \). In future experiments it would be very interesting to investigate the angle-dependence of the tran-
sition fields in NDMAP in more detail.

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