Massive triplet excitations in a magnetized anisotropic Haldane spin chain.

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Inelastic neutron scattering experiments on the Haldane-gap quantum antiferromagnet Ni(C5D14N2)2N3(PF6) are performed at mK temperatures in magnetic fields of almost twice the critical field \( H_c \) applied perpendicular to the spin chains. Above \( H_c \) a re-opening of the spin gap is clearly observed. In the high-field Néel-ordered state the spectrum is dominated by three distinct long-lived excitation branches. Several field-theoretical models are tested in a quantitative comparison with the experimental data.

One-dimensional (1D) integer-spin antiferromagnets (AFs) are famous for having a disordered “spin liquid” ground state and an energy gap \( \Delta \sim \exp(-\pi S) \) in the excitation spectrum. Elementary excitations are a triplet of massive (gapped) long-lived “magnons”. An external magnetic field modulates the magnon energies by virtue of Zeeman effect. At a certain critical field \( H_c \) the gap in one of the branches approaches zero. The result is a condensation of magnons and the emergence of a qualitatively new ground state. Theory predicts that in an axially asymmetric (AS) Heisenberg or XY-like scenarios the emergence of a new ground state actually is, depends on the symmetry of the problem. Theory predicts that in an axially symmetric (AS) Heisenberg or XY-like scenarios the high-field phase is a gapless “Luttinger spin liquid” with quasi-long-range order and a diffuse continuum of excitations (no sharp magnons). The high-field phase in the axially asymmetric (AA) case is expected to be totally different. Here the ground state should have true long-range Néel order (“spin solid”). A simple boson description predicts a re-opening of the gap at \( H > H_c \), and implies the restoration of a single-particle excitation spectrum. Is this state then similar to a classical easy-plane AF in a field, that also features long-range order and sharp gapped spin waves?

Recently only did experiments which are the key to understanding the high-field behavior, become technically feasible. This was in part due to the discovery of the very useful model material Ni(C5D14N2)2N3(PF6) (NDMAP) where various techniques confirmed a quantum phase transition at an easily accessible critical field of \( H_c \approx 6 \) T. Inelastic neutron studies were carried out in the AA geometry in the thermally-disordered phase: at \( H > H_c \), but at temperatures high enough to destroy long-range Néel order. Somewhat unexpectedly, it was found that as the Haldane gap closes at \( H_c \), the spectrum retains a considerable quasielastic (gapless) component at higher fields. The theoretically predicted reopening of the gap was thus not observed. At the time, this behavior was not fully understood, though several intriguing explanations were put forward. One attributed the phenomenon to the 1D diffusion of thermally excited classical solitons, while another drew parallels with the incommensurate Luttinger liquid state in the AS geometry. To better understand this issue, we carried out a new series of measurements at considerably lower temperatures and in higher magnetic fields, overcoming any finite-\( T \) effects to directly probe the ground state properties. The spin dynamics in this regime was found to be qualitatively different from that previously seen at elevated temperatures. The new data allow a quantitative comparison with several quantum field-theoretical models, while emphasizing dramatic differences between the high-field phase and a classical magnet.

Five newly-grown deuterated NDMAP single crystals were co-aligned by neutron diffraction to produce a sample of total mass \( 1.4 \) g and a mosaic spread of \( 3^\circ \). NDMAP crystallizes in the orthorhombic space group \( Pnma \). The \( S = 1 \) AF spin chains, formed by \( \text{Ni}^{2+} \) ions bridged by azido-groups, run along the crystallographic \( c \) axis, and \( (a, b) \) is the magnetic easy plane. In zero field the Haldane gap energies were previously determined to be \( \Delta_x = 0.42 \) meV, \( \Delta_y = 0.52 \) meV, and \( \Delta_z = 1.89 \) meV. In our experiments the sample was mounted with the \( a \) axis vertical, and the data were collected in the \( (0, k, l) \) reciprocal-space plane. The sample environment was a cryomagnet with a dilution refrigerator. The measurements were performed at \( T = 30 \) mK in magnetic fields of up to \( 11 \) T applied along the crystallographic \( a \) axis.

The first series of experiments was performed at the SPINS 3-axis cold-neutron spectrometer installed at the
FIG. 1: A series of constant-$q_\parallel$ scans measured in NDMAP at $T = 30$ mK for different values of magnetic field applied along the $a$ axis (symbols). The lines are fits to a simple single-mode cross section function as described in the text.

The main purpose was to measure the field dependence of scattering at the 1D AF zone-center $l = 0.5$. Neutrons with a 3.7 meV fixed-final energy were used with a horizontally focusing analyzer and a BeO filter after the sample. Energy scans were performed on the $(0, k, 0.5)$ reciprocal-space rod. The wave vector transfer perpendicular to the chains was continuously adjusted to maintain the sample $c$ axis directed towards the analyzer for optimal wave vector resolution along the chains. The background (featureless and typically 4 counts/min) was measured away from the 1D AF zone-center, at $(0, k, 0.35)$ and $(0, k, 0.65)$. Typical background-subtracted data sets are shown in Fig. 1. A similar scan previously measured in zero field (Fig. 3 in Ref. [3]) clearly shows two peaks at roughly 0.47 mV and 1.9 meV energy transfer, respectively. The data plotted in Fig. 1 corresponds to $H = 3$ T, still well below $H_c \approx 6$ T. At this field the lower-energy peak is visibly split in two components. At $H = 6$ T $\approx H_c$ the gap in the lower mode vanishes altogether, to within experimental error, as illustrated in Fig. 1b. At the same time, long-range AF order sets in [8]. The main new result of the present study is the observation that at $T = 30$ mK at $H > H_c$ the gap in the lower mode re-opens and increases with field (Fig. 1c,d). In the ordered state the spectrum at $q_\parallel = \pi$ thus contains three distinct sharp excitation branches, just as in the low-field disordered phase.

The new 30 mK data clearly show that the quasielastic scattering previously observed at $H > H_c$ and $T = 2$ K is absent, and must therefore be a finite-$T$ effect. In the constant-$q$ scans collected at $T = 30$ mK all three peaks have resolution-limited widths at all fields. In fact, very good fits to the data (solid lines in Fig. 1) can be obtained using a simple model cross section that involves three excitations with a zero intrinsic energy width [9]. The cross section was numerically convoluted with the spectrometer resolution function, and the adjustable parameters at each field were the three gap energies and intensity prefactors for each mode. In Fig. 1 the partial contributions of the three branches are shown as shaded areas. The field dependence of the gap energies deduced from these fits is shown in Fig. 2 in open symbols.

To study the wave vector dependence of the dynamic structure factor additional measurements were performed using the Disk Chopper Spectrometer (DCS) at NIST.
representation of excitations in *isotropic* Haldane spin chains. The present data show that this model does not apply in highly anisotropic case of NDMAP: the spectrum is truly gapped and has no intrinsic incommensurate features. The quasielastic scattering at $T = 2 \, \text{K}$, $H > H_c$ is thus to be attributed to a diffusion of thermally excited topological solitons \[^{10}\], and its anomalous $q$-width is due to the $T$-dependent mean distance between solitons \[^{11}\].

For the following discussion of the observed low-$T$ properties it is crucial to note that at $T = 30 \, \text{mK}$ the spin chains are antiferromagnetically ordered at $H > H_c$ \[^{5}\], with a static staggered magnetization as large as $m \sim 1\mu_B$ per site at $H = 11 \, \text{T}$. Clearly, inter-chain coupling is needed to stabilize order at a non-zero temperature. However, in the AA geometry, even an *isolated* chain orders at $H > H_c$ at $T = 0$, the system being equivalent to the (1+1)-dimensional Ising-model \[^{3}\]. Since inter-chain interactions in NDMAP are very weak \[^{4}\], we can assume that a purely 1D problem is realized: long-range AF correlations are intrinsic to the 1D chains, and the sole role of residual 3D interactions is to maintain their stability at a finite temperature.

The conventional approach to describing spin excitations in ordered systems is the quasiclassical spin wave theory (SWT). In this model the magnons are *precessions* of staggered magnetization $\mathbf{m}$ around its equilibrium direction. As a consequence, in SWT there are only two sharp excitation branches, polarized perpendicular to the $\mathbf{m}$. In our case *three* sharp magnons are seen in the ordered state ($H > H_c$). At least one of the three branches must have the character of a ”longitudinal” magnon that is not a precession mode, but is polarized along the ordered moment. Thus, at $H > H_c$ quantum-mechanical effects remain crucial, and the SWT is inapplicable. Instead, the three observed excitation branches can be visualized as soliton-antisoliton breathers: the three massive bound states formed by the two types of topological defects allowed in an anisotropic semisclassical 1D magnet \[^{11}\]. In more detail our experiments can be understood in the frameworks of several field-theoretical models.

The approach due to Affleck \[^{3}\] is based on coarse-graining the (1+1)-dimensional $O(3)$ non-linear sigma model (NLSM), to which, in turn, the $S = 1$ Heisenberg chain can be mapped \[^{1}\]. The resulting Lagrangian is that of an unconstrained *real* vector field $\varphi(x)$ with the $\varphi^4$-type interaction. Anisotropy is added by postulating separate masses $\Delta_n$ for the different components of this vector field. For $H > H_c$ the ground state has a non-zero staggered magnetization $\mathbf{L} = \langle \varphi \rangle$ and uniform magnetization $\mathbf{M} \propto \langle \mathbf{H} \times \varphi \rangle$. The $\varphi^4$-model captures the basic physics involved, but suffers from several drawbacks. In particular, the predicted value of the critical field for $\mathbf{H} | \mathbf{e}_n = g \mu_B H^{(n)} = \Delta_n$. This is inconsistent with established experimental \[^{8,12,13,14,15}\] and numerical \[^{16}\] results, as well as with simple arguments based on the

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**FIG. 3:** Inelastic spectra measured in NDMAP using the Disk Chopper spectrometer for several applied fields. The range of the false-color scale in the lower panel is 0 to 15 arb. u. Contour lines are drawn with 3 arb. u. steps in all panels. Arrows indicate the gap energies for the different excitation branches.

CHRNS. The data were collected using a fixed incident neutron energy of 4.5 meV. The sample was mounted with the $(b, c)$ plane horizontal, and the chain axis almost perpendicular to the incident beam. The background was measured separately, with the sample removed from the cryostat. The background-subtracted data collected at $H = 0$, $H = 6 \, \text{T}$ and $H = 10 \, \text{T}$ are visualized in the false-color and contour plots in Fig. 3 and correspond to a typical counting time of 20 hours. They are to be compared to similar 3-axis data measured previously at $T = 2 \, \text{K}$ and shown in Fig. 2 of Ref. \[^{10}\]. The new low-$T$ experiment shows that the excitations at $H > H_c$ have a simple relativistic (hyperbolic) dispersion relation, with a spin wave velocity equal to that at $H < H_c$ (see solid lines in Fig. 3). The “inverted” hyperbolic dispersion curves with “negative gaps” shown in solid lines in Fig. 3 of Ref. \[^{10}\] are clearly inconsistent with the new data. This latter dispersion form was proposed as one possible interpretation of the anomalous $q$-width of quasielastic scattering at $T = 2 \, \text{K}$ \[^{10}\] and is based on a Fermion
perturbation theory \cite{16, 17}. Another potential weakness is that at the mean field (MF) level \( M(H) \) and the lowest gap \( \Delta(H) \) come out to be \( \propto \sqrt{H - H_c^{(a)}} \), while a roughly linear behavior is seen experimentally and numerically. For NDMAP, the derivations of Ref. \cite{2} must be generalized to allow for an arbitrary field direction, since the anisotropy axis of the Ni\(^{2+}\) ions forms an angle of about 16° with the crystallographic c axis. The resulting predictions are shown in dashed lines in Fig. 2.

Another theory, due to Tsvelik \cite{4}, stems from the integrable \( SU(3) \) model of a \( S = 1 \) chain. It involves three Majorana fields with masses \( \Delta_\alpha \). The predicted critical fields \( g \mu_B H_c^{(a)} = \sqrt{\Delta_\beta \Delta_\gamma} \), coincide with the perturbative formulas of \cite{16, 17}. Again, incorporating an arbitrary field direction, and using the known parameters for NDMAP, we can directly compare the predicted gap energies (dash-dot lines in Fig. 2) to those measured in this work. Unlike the \( \varphi^4 \) model, Tsvelik’s approach predicts the linear behavior of \( M(H) \) and \( \Delta(H) \) near \( H_c \). The theory, however, fails to reproduce the two upper gaps at \( H > H_c \).

In the context of the present experiments we would like to introduce a different approach that is similar to the model proposed for dimerized \( S = 1/2 \) chains in Ref. \cite{15}. It is a Ginzburg-Landau-type theory written in terms of a complex triplet field \( \Phi(r) = A(r) + i B(r) \). The uniform and staggered magnetization are written as \( M \propto (A \times B) \) and \( L \propto A(1 - A^2 - B^2)^{1/2} \). Interaction terms \( (\Phi^* \cdot \Phi)^2 \) and \( (\Phi^* \times \Phi)^2 \) are naturally present in the model. Unlike the models discussed above, anisotropy enters the Lagrangian through two sets of masses, separately in the \( A \) and \( B \) “channels”:

\[
\sum_\alpha (m_\alpha A_\alpha^2 + \tilde{m}_\alpha B_\alpha^2).
\]

By integrating out the \( B \)-field one obtains an effective \( \varphi^4 \)-type theory similar to that of Affleck. However, the Zeeman term \( H \cdot (\varphi \times \partial_t \varphi) \) of Ref. \cite{2} becomes replaced by the anisotropy-dependent expression \( \sum_{\alpha \beta \gamma} m_\alpha \epsilon_{\alpha \beta \gamma} H_{\alpha \beta} \partial_t A_\gamma \). Remarkably, this model includes Affleck’s theory as the special case \( \tilde{m}_\alpha = \text{const} \), and at the same time it reproduces the results of the Tsvelik’s theory for \( \Delta(H) \) and \( M(H) \) below \( H_c \) in another special case \( m_\gamma = \text{const} \). There are no particular reasons why either of these special cases should correspond to the actual Heisenberg \( S = 1 \) chain with single-ion anisotropy realized in NDMAP. The masses \( \tilde{m}_\alpha \) and \( m_\alpha \) at the present stage may be treated as adjustable parameters to reproduce the measured gap energies \( \Delta_\alpha = \sqrt{m_\alpha m_\alpha} \) at \( H = 0 \) and the measured field dependencies. Very good fits to our experimental data are obtained with \( \tilde{m}_z/m_x = 0.87 \), \( \tilde{m}_y/m_x = 0.83 \), and \( \tilde{m}_x/m_z = 0.35 \) (solid lines in Fig. 2). A detailed description of the application of this model to NDMAP will be reported elsewhere.

In summary, the present low-\( T \) study is a direct observation of several fundamental quantum-mechanical features predicted for anisotropic Haldane spin chains, and helps clarify the nature of the previously investigated finite-\( T \) spin dynamics. The next experimental challenge will be to investigate the AS geometry, searching for manifestations of the Luttinger spin liquid regime.

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[1] F. D. M. Haldane, Phys. Lett. **93A**, 464 (1983); Phys. Rev. Lett. **50**, 1153 (1983).
[2] K. Katsumata, H. Hori, T. Takeuchi, M. Date, A. Yamagishi, J. P. Renard, Phys. Rev. Lett. **63**, 86 (1989).
[3] I. Affleck, Phys. Rev. B **41**, 6697 (1990); Phys. Rev. B **43**, 3215 (1991).
[4] A. M. Tsvelik, Phys. Rev. B **42**, 10499 (1990).
[5] M. Takahashi and T. Sakai, J. Phys. Soc. Jpn. **60**, 760 (1991); M. Yajima and M. Takahashi, J. Phys. Soc. Jpn. **63**, 3634 (1994).
[6] T. S. S. Sachdev, T. Senthil, and R. Shankar, Phys. Rev. B **50**, 258 (1994).
[7] Z. Honda, H. Asakawa, and K. Katsumata, Phys. Rev. Lett. **81**, 2566 (1998).
[8] Y. Chen, Z. Honda, A. Zheludev, C. Broholm, K. Katsumata, and S. M. Shapiro, Phys. Rev. Lett. **86**, 1618 (2001).
[9] A. Zheludev, Y. Chen, C. Broholm, Z. Honda, and K. Katsumata, Phys. Rev. B **63**, 104410 (2001).
[10] A. Zheludev, Z. Honda, Y. Chen, C. Broholm, and K. Katsumata, Phys. Rev. Lett. **88**, 077206 (2002).
[11] H.-J. Mikeska and M. Steiner, Adv. Phys. **40**, 191 (1991).
[12] L. P. Regnault, I. Zaliznyak, J. P. Renard, and C. Vettier, Phys. Rev. B **50**, 9174 (1994).
[13] Z. Honda, K. Katsumata, H. A. Katori, K. Yamada, T. Ohishi, T. Manabe, and M. Yamashita, J. Phys.: Condens. Matter **9**, L83 (1997).
[14] Z. Honda, K. Katsumata, M. Hagiwara, and M. Tokunaga, Phys. Rev. B **60**, 9272 (1999).
[15] A. Zheludev and Z. Honda and K. Katsumata and R. Feyrer-herm and K. Prokes, Europhys. Lett., **55**, 868 (2001).
[16] O. Golineni, Th. Jolicoeur and R. Lacasse, Phys. Rev. B **45**, 9798 (1992); J. Phys.: Condens. Matter **5**, 7847 (1993).
[17] L.-P. Regnault, I. A. Zaliznyak, and S. V. Meshkov, J. Phys: Condens. Matter **5**, L677 (1993).
[18] A. K. Kolezhuk, Phys. Rev. B **53**, 318 (1996).