Massive triplet excitations in a magnetized anisotropic Haldane spin chain

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Inelastic neutron scattering experiments on the Haldane-gap quantum antiferromagnet $Ni(C_5D_{14}N_2)_2N_3(PF_6)$ 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 reopening of the spin gap is clearly observed. In the high-field Néel-ordered state the spectrum is dominated by three distinct excitation branches. A theoretical model consistently describing the experimental data is proposed.

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Understanding the profound effects of perturbations on critical phases of matter is a central challenge in condensed matter physics. The characteristic nonlinear responses underlie natural phenomena and are the basis for countless technical applications. They are also of great fundamental significance because the corresponding critical exponents delineate universality classes for interacting many body systems. Quasi-one-dimensional systems exhibit a range of critical phases, and their simplicity enables advanced dialogue between theory and experiments.[1,2] Here we examine the effect of a symmetry-breaking perturbation on the critical "magnetized" state of the isotropic antiferromagnetic (AF) $S=1$ chain.[3] While the zero field valence bond solid ground state is rather robust,[3,4] a large magnetic field can close the singlet-triplet energy gap Δ and produce an extended "Luttinger spin liquid" critical phase for $H>H_c=\Delta/g\mu_B$.[5–9] Theory predicts that axially asymmetric magnetic anisotropy is a relevant perturbation that reduces the extended critical phase to a *single critical point*.[6–8] It is also expected to have a profound effect on the nature of magnetic excitations for $H>H_c$.

Only recently did experiments that could probe the high field behavior of $S=1$ chains become technically feasible. This was in part due to the discovery of the very useful model material $Ni(C_5D_{14}N_2)_2N_3(PF_6)$ (NDMAP),[10] where various techniques[10–12] 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 axially asymmetric (AA) geometry in the *thermally disordered* phase: at $H>H_c$, but at temperatures high enough to destroy long-range Néel order.[13] Somewhat unexpectedly the spectrum retains a considerable quasielastic (gapless) component at $H>H_c$. The theoretically predicted suppression of criticality and reopening of the gap[6,7] was not observed. At the time, this behavior was not fully understood, though several intriguing explanations were put forward.[13] One attributed the phenomenon to the 1D diffusion of thermally excited classical solitons, while another drew parallels with the incommensurate Luttinger liquid state expected in the axially symmetric (AS) geometry. To clarify the nature of the high-field state in the AA geometry, we carried out a new series of measurements at considerably lower temperatures and in higher magnetic fields, overcoming any finite-T effects. The spin dynamics is found to be qualitatively different from that previously seen at elevated temperatures. The new data allow a direct 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 coaligned by neutron diffraction to produce a sample of total mass 1.4 g and a mosaic spread of 3°. NDMAP crystallizes in the orthorhombic space group *Pnmn*. The $S=1$ AF spin chains, formed by Ni^{2+} ions bridged by azidogroups, run along the crystallographic c axis. The anisotropy (hard) axis of the Ni^{2+} ions forms an angle of about 16° with the chain direction. 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.[12] 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 measurements were performed at $T=30$ mK in fields of up to 11 T applied along the crystallographic a axis.

The first series of experiments was performed at the SPINS three-axis cold-neutron spectrometer installed at the NIST Center for High Resolution Neutron Scattering (CHRNS). 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 background was measured away from the 1D AF zone-center, at $(0,k,0.35)$ and $(0,k,0.65)$.

Typical data are shown in Fig. 1. A similar scan previously measured in zero field (Fig. 3 in Ref. 12) clearly shows

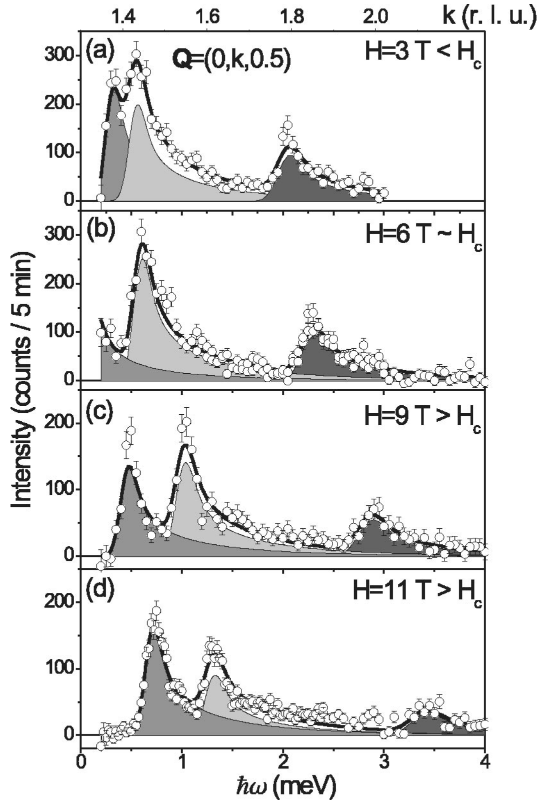

FIG. 1. A series of constant-$q_{\parallel}$ scans measured in NDMAP at $T=30$ mK for different values of magnetic field applied along the a axis (symbols). The lines are fits to a simple single-mode cross section function as described in the text.

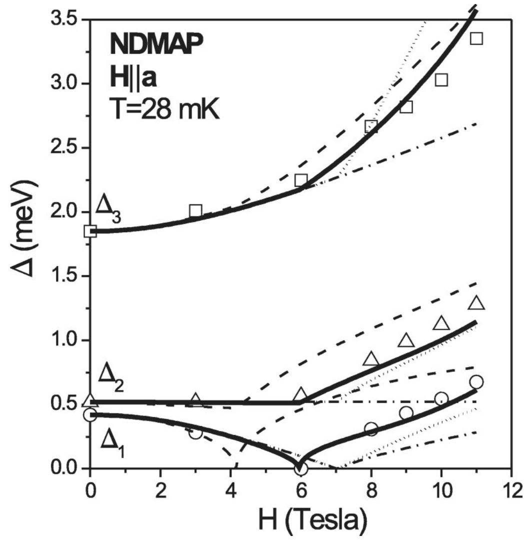

FIG. 2. Measured field dependence of the gap energies in NDMAP at $T=30$ mK and H applied along the crystallographic a axis (open symbols). Dashed, dash-dot, and dotted lines show predictions of the models proposed in Refs. 6, 7, and 15, respectively. The solid lines are the best fit to the data using the model (1).

two peaks at roughly 0.47 and 1.9 meV energy transfer, respectively. The data plotted in Fig. 1(a) 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 the gap in the lowest mode vanishes to within experimental error, as illustrated in Fig. 1(b). At the same time, long-range AF order sets in.[11] The main result of the present experiments is the observation that for $T=30$ mK and $H>H_c$ the gap in the lowest mode reopens and increases with field [Figs. 1(c), 1d]. In the ordered state the spectrum at $q_{\parallel}=\pi$ thus contains three distinct sharp excitation branches.

The 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.[12] The cross section was numerically convoluted with the spectrometer resolution function. The adjustable parameters at each field were the gaps and intensities for each mode. In Fig. 1 the partial contributions of the three branches are shown as shaded areas. The measured field dependence of the gap energies is plotted in Fig. 2.

To study the wave vector dependence, additional measurements were performed using the Disk Chopper Spectrometer (DCS) at NIST 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 $H=0$, $H=6$ T, and $H=10$ T are visualized in the false-color and contour plots in Fig. 3, and correspond to a typical counting time of 20 hs. They are to be compared to similar three-axis data measured previously at $T=2$ K and shown in Fig. 2 of Ref. 13. 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. 13 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 $T=2$ K (Ref. 13) and is based on a Fermion representation of excitations in *isotropic* Haldane spin chains. The new data show that this model does not apply in the AA geometry of the present experiment: the spectrum is truly gapped and has no intrinsic incommensurate features. Due to the weakness of in-plane anisotropy in NDMAP, the discrepancy cannot be attributed to the difference in experimental geometry ($\mathbf{H}\|a$ here vs $\mathbf{H}\|b$ in Ref. 13). The quasielastic scattering at $T=2$ K, $H>H_c$ is thus to be attributed to a diffusion of thermally excited topological solitons,[13] and its anomalous q width is due to the T-dependent soliton density.[14]

For the following discussion of the observed low-T properties it is crucial to note that at $T=30$ mK the spin chains are antiferromagnetically ordered at $H>H_c$,[11] with a static staggered magnetization along the b axis, as large as $1\mu_{\rm B}$ per site at $H=11$ T. Clearly, interchain coupling is needed to stabilize order at a nonzero temperature. However, in the AA

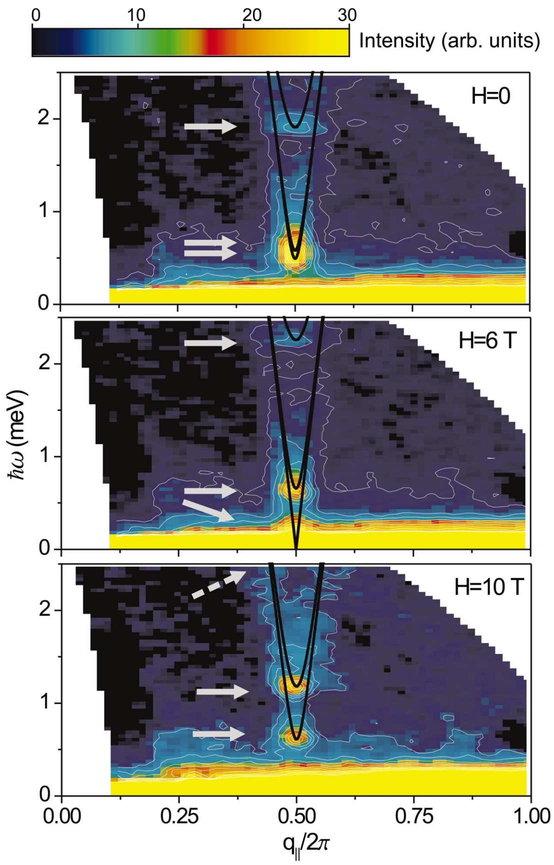

FIG. 3. (Color) Inelastic spectra measured in NDMAP using the Disk Chopper spectrometer for several applied fields. The range of the false-color scale in the lower panel is 0 to 15 arb. units. Contour lines are drawn with 3 arb. units steps in all panels. Arrows indicate the gap energies for the different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

geometry, even an *isolated* chain orders for $H>H_c$ at $T=0$, the system being equivalent to the (1+1)-dimensional Ising-model.[6] Since interchain interactions in NDMAP are very weak,[12] 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 $\boldsymbol{L}$ around its equilibrium direction. As a consequence, in SWT there are only two sharp excitation branches, polarized perpendicular to the $\boldsymbol{L}$. 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 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 semiclassical 1D magnet.[14]

Several field-theoretical models have been previously invoked to explain the field behavior quantitatively. The theory due to Affleck[6] is based on coarse graining the $O(3)$ nonlinear sigma model.[3] Its Lagrangian is that of an unconstrained *real* vector field $\boldsymbol{\varphi}$ with the φ^4-type interaction and three different masses Δ_α for the three field components. For $H>H_c$ the ground state has a nonzero staggered magnetization $\boldsymbol{L}=\langle\boldsymbol{\varphi}\rangle$ and a uniform magnetization $\boldsymbol{M}\propto\langle\boldsymbol{H}\times\boldsymbol{\varphi}\rangle$. This model captures the basic physics involved, but suffers from several serious drawbacks. In particular, for $\boldsymbol{H}\|\boldsymbol{e}_\alpha$, the predicted critical field $H_c^{(\alpha)}=\Delta_\alpha/(g\mu_B)$ and the behavior at $H\to H_c$ are inconsistent with established experimental[11,16–19] and theoretical[20] results. The prediction of Affleck's model, with the tilting of the anisotropy axes in NDMAP properly accounted for, are shown as dashed lines in Fig. 2. Another theory, due to Tsvelik,[7] stems from an integrable model of a $S=1$ chain and involves three Majorana fields with masses Δ_α. The critical field is given by $g\mu_B H_c^{(\alpha)}=\sqrt{\Delta_\beta\Delta_\gamma}$ and coincides with the perturbative formulas of Ref. 20. This model fits our NDMAP data better (dash-dot lines in Fig. 2), but a crucial qualitative inconsistency remains. The model fails to reproduce the behavior of two upper gaps at $H>H_c$, for which it predicts no change of slope at H_c. In yet another approach, Mitra and Halperin[15] have modified Affleck's theory by postulating the field-dependent part to be $\frac{1}{2}\Sigma_\alpha\{\partial_t\varphi_\alpha+\Sigma_{\beta\gamma}(\Delta_\gamma/\Delta_\alpha)^{1/2}\epsilon_{\alpha\beta\gamma}H_\beta\varphi_\gamma\}^2$, thus reproducing Tsvelik's results for the gap energies below H_c. At $H>H_c$ this theory does a much better job at reproducing the observed gap energies (dotted lines in Fig. 2). However, it still has one fundamental flaw: the staggered moment at $H>H_c$ is predicted to be parallel to the magnetic hard axis. This counterintuitive result is in contradiction with previous diffraction experiments on NDMAP,[11] that show an ordered moment along the b axis, i.e., in the easy plane.

We thus conclude that none of the established models provide a consistent description of the experimental data. Here we introduce an alternative approach, based on the model proposed in Ref. 21 for dimerized $S=1/2$ chains, known to be in the same universality class as $S=1$ Haldane chains. This Ginzburg-Landau-type theory is written in terms of a complex triplet field $\boldsymbol{\Phi}=\boldsymbol{A}+i\boldsymbol{B}$:

$$\mathcal{L}=\hbar(\boldsymbol{A}\cdot\partial_t\boldsymbol{B}-\boldsymbol{B}\cdot\partial_t\boldsymbol{A})-(1/2)v^2(\partial_x\boldsymbol{A})^2-\sum_\alpha\{m_\alpha\boldsymbol{A}_\alpha^2+\tilde{m}_\alpha B_\alpha^2\}+2\boldsymbol{H}\cdot(\boldsymbol{A}\times\boldsymbol{B})-\lambda(\boldsymbol{A}^2)^2-\lambda_1(\boldsymbol{A}^2\boldsymbol{B}^2)-\lambda_2(\boldsymbol{A}\cdot\boldsymbol{B})^2. \quad (1)$$

The uniform and staggered magnetization are written as $\boldsymbol{M}\propto(\boldsymbol{A}\times\boldsymbol{B})$ and $\boldsymbol{L}\propto\boldsymbol{A}(1-A^2-B^2)^{1/2}$, respectively. By integrating out the "slave" $\boldsymbol{B}$ field one obtains an effective φ^4-type theory which generalizes the models of Refs. 6,15. In fact, with $\lambda_{1,2}=0$, the special cases $\tilde{m}_\alpha=m_\alpha$ and $\tilde{m}_\alpha=\text{const}$ exactly correspond to the theories of Mitra and Halperin and Affleck, respectively. There are no particular reasons why either of these special cases should correspond to the actual Heisenberg $S=1$ chain with general single-ion anisotropy. The interaction constants $\tilde{m}_\alpha$ and m_α at the present stage may be treated as adjustable parameters to reproduce the measured masses $\Delta_\alpha=\sqrt{\tilde{m}_\alpha m_\alpha}$ at $H=0$ and the measured field dependencies. Very good fits are obtained with $\lambda_1/\lambda=0.35$, $\lambda_2=0$, $\tilde{m}_x/m_x=0.87$, $\tilde{m}_y/m_y=0.83$, and $\tilde{m}_z/m_z=0.35$ (solid lines in Fig. 2). The calculated staggered moment $\boldsymbol{L}$ at $H>H_c$ is directed along the b axis, in agreement with the experiment.[11]

In summary, we have carried out a comprehensive experimental survey of the high field phase of an antiferromagnetic $S=1$ chain subject to symmetry-breaking anisotropy. For $H>H_c$ we find three gapped coherent modes, the gap vanishing only at the critical field $H=H_c$. Anisotropy is thus a relevant perturbation on the critical state of the isotropic model, and causes the gapless continuum to coalesce into three coherent modes. We have also introduced a phenomenological field theory that gives a consistent quantitative description of the observed behavior. The next experimental challenge will be to investigate the AS geometry, searching for manifestations of an extended quantum critical phase.

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[1] C. Broholm *et al.*, in *High Magnetic Fields Applications in Condensed Matter Physics and Spectroscopy*, edited by C. Berthier, L. P. Lévy, and G. Martinez (Springer-Verlag, Berlin, 2002).
[2] A. Zheludev, Appl. Phys. A: Mater Sci. Process **74**, S1–S5 Part 1 Suppl. S (2002).
[3] F.D.M. Haldane, Phys. Lett. **93A**, 464 (1983); Phys. Rev. Lett. **50**, 1153 (1983).
[4] I. Affleck, T. Kennedy, E.H. Lieb, and H. Takaki, Phys. Rev. Lett. **59**, 799 (1987).
[5] K. Katsumata, H. Hori, T. Takeuchi, M. Date, A. Yamagishi, and J.P. Renard, Phys. Rev. Lett. **63**, 86 (1989).
[6] I. Affleck, Phys. Rev. B **41**, 6697 (1990); **43**, 3215 (1991).
[7] A.M. Tsvelik, Phys. Rev. B **42**, 10 499 (1990).
[8] M. Takahashi and T. Sakai, J. Phys. Soc. Jpn. **60**, 760 (1991); M. Yajima and M. Takahashi, *ibid.* **63**, 3634 (1994).
[9] S. Sachdev, T. Senthil, and R. Shankar, Phys. Rev. B **50**, 258 (1994).
[10] Z. Honda, H. Asakawa, and K. Katsumata, Phys. Rev. Lett. **81**, 2566 (1998).
[11] Y. Chen, Z. Honda, A. Zheludev, C. Broholm, K. Katsumata, and S.M. Shapiro, Phys. Rev. Lett. **86**, 1618 (2001).
[12] A. Zheludev, Y. Chen, C. Broholm, Z. Honda, and K. Katsumata, Phys. Rev. B **63**, 104410 (2001).
[13] A. Zheludev, Z. Honda, Y. Chen, C. Broholm, and K. Katsumata, Phys. Rev. Lett. **88**, 077206 (2002).
[14] H.-J. Mikeska and M. Steiner, Adv. Phys. **40**, 191 (1991).
[15] P.P. Mitra and B.I. Halperin, Phys. Rev. Lett. **72**, 912 (1994).
[16] L.P. Regnault, I. Zaliznyak, J.P. Renard, and C. Vettier, Phys. Rev. B **50**, 9174 (1994).
[17] Z. Honda, K. Katsumata, H.A. Katori, K. Yamada, T. Ohishi, T. Manabe, and M. Yamashita, J. Phys.: Condens. Matter **9**, L83 (1997).
[18] Z. Honda, K. Katsumata, M. Hagiwara, and M. Tokunaga, Phys. Rev. B **60**, 9272 (1999).
[19] A. Zheludev, Z. Honda, K. Katsumata, R. Feyerherm, and K. Prokes, Europhys. Lett. **55**, 868 (2001).
[20] O. Golinelli, Th. Jolicoeur, and R. Lacaze, Phys. Rev. B **45**, 9798 (1992); J. Phys.: Condens. Matter **5**, 7847 (1993); L.-P. Regnault, I.A. Zaliznyak, and S.V. Meshkov, *ibid.* **5**, L677 (1993).
[21] A.K. Kolezhuk, Phys. Rev. B **53**, 318 (1996).