

Field-induced commensurate long-range order in the Haldane-gap system $\text{Ni}(\text{C}_5\text{H}_{14}\text{N}_2)_2\text{N}_3(\text{ClO}_4)$

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(received 23 April 2001; accepted in final form 29 June 2001)

PACS. 75.10.Jm – Quantized spin models.

PACS. 75.30.Kz – Magnetic phase boundaries (including magnetic transitions, metamagnetism, etc.).

PACS. 75.40.-s – Critical-point effects, specific heats, short-range order.

Abstract. – High-field neutron diffraction studies of the new quantum-disordered $S = 1$ linear-chain antiferromagnet $\text{Ni}(\text{C}_5\text{H}_{14}\text{N}_2)_2\text{N}_3(\text{ClO}_4)$ (NDMAZ) are reported. At $T = 70$ mK, at a critical field $H_c = 13.4$ T applied along the [013] direction, a phase transition to a commensurate Néel-like ordered state is observed. The results are discussed in the context of existing theories of quantum phase transitions in Haldane-gap antiferromagnets, and in comparison with previous studies of the related system $\text{Ni}(\text{C}_5\text{H}_{14}\text{N}_2)_2\text{N}_3(\text{PF}_6)$ (NDMAP).

Introduction. – One of the most exciting recent developments in experimental studies of one-dimensional (1D) magnets was the observation of a field-induced quantum phase transitions in two new quasi-1D $S = 1$ antiferromagnets (AFs) $\text{Ni}(\text{C}_5\text{H}_{14}\text{N}_2)_2\text{N}_3(\text{ClO}_4)$ (NDMAZ) [1] and $\text{Ni}(\text{C}_5\text{H}_{14}\text{N}_2)_2\text{N}_3(\text{PF}_6)$ (NDMAP) [2,3]. In the absence of an external magnetic field the ground state of such systems is a non-magnetic singlet. Long-range magnetic order is totally destroyed by quantum spin fluctuations even at $T = 0$: spin correlations are short range, and decay exponentially on a length scale of a few lattice repeats [4]. The main feature of the magnetic excitation spectrum is the so-called Haldane energy gap Δ [4]. Such magnetically disordered systems may be described as “quantum spin liquids”. The effect of the magnetic field is to suppress zero-point fluctuations, and restore a gapless spectrum. The result is a quantum phase transition at a certain critical field $H_c \sim \Delta/(g\mu_B)$, to a Néel-like state with long-range staggered magnetic order, that may be characterized as a “spin solid” [5–10]. The transition is driven by a complete softening of one member of the Haldane excitation triplet, subject to Zeeman splitting in an external field, and was shown to be equivalent to

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Bose condensation in one dimension [6, 11]. While the high-field transition was predicted theoretically some time ago, NDMAZ ($\Delta \approx 1.7$ meV) [1, 12] and NDMAP ($\Delta \approx 0.5$ meV) [2, 13–17] were the first systems where it was actually observed and investigated by means of magnetization, magnetic resonance, and specific heat measurements. For many “veteran” Haldane-gap materials, such as Y_2BaNiO_5 ($\Delta \approx 9$ meV [18]), the critical field values are prohibitively high. In other well-studied compounds, such as $\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_2\text{NO}_2(\text{ClO}_4)$ (NENP, $\Delta \approx 1$ meV [19]), the transition does not occur at all, and is replaced by a broad crossover phenomenon, due to certain structural features [20–22].

A direct evidence of long-range AF order above H_c can only be obtained in neutron diffraction experiments. Recently, such measurements were performed for NDMAP, and brought valuable insight into the nature of the transition and the high-field phase [3]. It was found that long-range ordering can be either 3-dimensional or 2-dimensional, depending on the direction of the applied field, but always commensurate with the underlying crystal lattice. This study was enabled by the rather small value of the gap energy and hence the critical field ($H_c \sim 5$ T) in this material. Performing a similar neutron diffraction investigation of NDMAZ is crucial to establish the universal nature of the observed behavior, but is, unfortunately, much more challenging from the technical point of view. In NDMAZ the Haldane excitation triplet is split by single-ion anisotropy: $\Delta_x = 1.61$ meV, $\Delta_y = 1.76$ meV and $\Delta_z = 2.8$ meV for excitations polarized along the a , b and c crystallographic axes, respectively [1, 23]. The spin chains in NDMAZ are parallel to the c -axis. In the presence of anisotropy the critical field depends on sample orientation and is given by $H_c^\alpha = \sqrt{\Delta_\beta \Delta_\gamma} / g\mu_B$. The expected values are $H_c^\perp \approx 18$ T for $\mathbf{H} \perp \mathbf{c}$ and $H_c^z \approx 12$ T for $\mathbf{H} \parallel \mathbf{c}$. Even the lower critical field, for $\mathbf{H} \parallel \mathbf{c}$, is not easy (though possible) to achieve in a neutron scattering experiment: for low-temperature studies the current limit is about 14.5 T. Sadly, an experimental geometry with $\mathbf{H} \parallel \mathbf{c}$ cannot be realized. The softening of the Haldane-gap excitation occurs at the 1D AF zone-center, *i.e.*, at a momentum transfer $q_\parallel = \pi/c$ along the chain axis. It is at this position that magnetic Bragg reflections, characteristic of the ordered high-field phase, are expected to appear. However, the scattering plane accessible when using a split-coil cryomagnet is perpendicular to the field direction. To enable a π/c transfer along the chains the sample must thus be mounted with the c -axis as closely in the horizontal plane as possible, which pushes the critical field up, towards its maximum value of 18 T. In the present paper we report the first neutron scattering observation of field-induced long-range ordering in NDMAZ that was achieved by using the most powerful split-coil magnet available, and by mounting the sample with the chain axis at a small angle relative to the field direction to minimize H_c , yet sufficiently tilted to enable momentum transfers of π/c along the chains.

Experimental procedures. – The crystal structure of NDMAZ (fig. 1) is monoclinic, space group $C2$, with lattice constants $a = 18.898$ Å, $b = 8.171$ Å, $c = 6.111$ Å and $\beta = 98.27^\circ$ [24]. The magnetism is due to $S = 1$ Ni^{2+} ions that are bridged by azido groups and form distinct chains propagating along the c crystallographic axis. Unlike in NDMAP, where the Ni sites form a body-centered lattice [25], in NDMAZ the arrangement of spin carriers is c -face centered. In the present study we used a 0.5 g fully deuterated sample that was found to contain two single-crystal twins of roughly equal volume, sharing the b and c axes, and having the a axes 16.5 degrees away from each other. The mosaic spread of each of the two crystallites was found to be 0.4° .

The measurements were carried out at the E4 2-axis diffractometer installed at the Hahn-Meitner-Institute, Germany, using a neutron beam of wavelength $\lambda = 2.44$ Å. The sample was mounted in a 14.5 T split-coil cryomagnet with the [013] real-space axis vertical, *i.e.*, parallel to the field direction. The angle between the direction of magnetic field and the chain

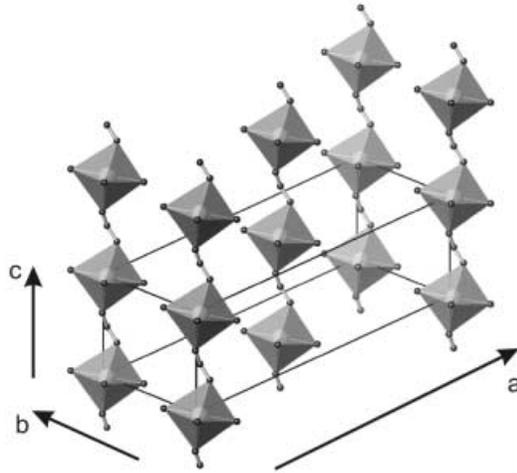


Fig. 1 – A schematic view of the antiferromagnetic spin chains in the NDMAZ crystal structure. Only NiN_6 octahedra (grey) and N-atoms (black) are shown.

axis was $\phi = 24^\circ$. All measurements were carried out at $T = 70$ mK, achieved by using a ^3He - ^4He dilution refrigerator magnet insert. Nuclear Bragg reflections originating from the two members of the twinned crystal could be easily identified except along the $(h, 0, 0)$ reciprocal-space direction where they exactly overlap.

Results. – At $T = 70$ mK, in magnetic fields exceeding $H_c \approx 13.4$ T new Bragg reflections were detected in both crystallites at $(h, \frac{2n+1}{2}, \frac{2m+1}{2})$ (h, m, n integer) reciprocal space positions. Figure 2 shows scans across the $(0, 1.5, -0.5)$ reciprocal-space point taken above and below the critical field. The shaded areas represent experimental resolution, as measured on the $(4, 0, 0)$ nuclear Bragg reflection, that corresponds to almost the same momentum transfer as $(0, 1.5, -0.5)$. Gaussian fits to the data show that the observed width of the magnetic peaks is resolution-limited in both directions. The measured field dependence of the $(0, 1.5, -0.5)$ peak intensity is shown in fig. 3. The solid line represents a power law fit to the data, that gives an estimate for the critical field $H_c = 13.1(4)$ T and the order parameter critical index $\beta = 0.21$.

All together, 5 inequivalent magnetic reflections were observed in the high-field phase on the $(h, 1.5, -0.5)$ reciprocal-space rod. For NDMAZ it was previously possible to measure the absolute values of magnetic Bragg intensities and deduce the spin structure in the high-field phase, through a calibration against measured nuclear peak intensities [3]. For technical reasons such analysis was impossible in the present experiment. The sample was aligned at room temperature outside the cryostat. Even if this alignment was perfect, an additional misalignment of the order 1–2 degrees was unavoidable when inserting the sample into the well of the cryomagnet and cooling to base temperature. As a result, the $(0, 1, 3)$ reciprocal-space plane of the sample was slightly misaligned with the horizontal scattering plane. The 14.5 T magnet (unlike the 9 T magnet used for NDMAZ) could not be tilted to compensate for this effect. Under these circumstances the absolute intensities of Bragg reflections measured in rocking curves are unreliable, since some of the peaks can, in fact, be outside the scattering plane, and are only picked up by the non-zero vertical angular acceptance of the detector.

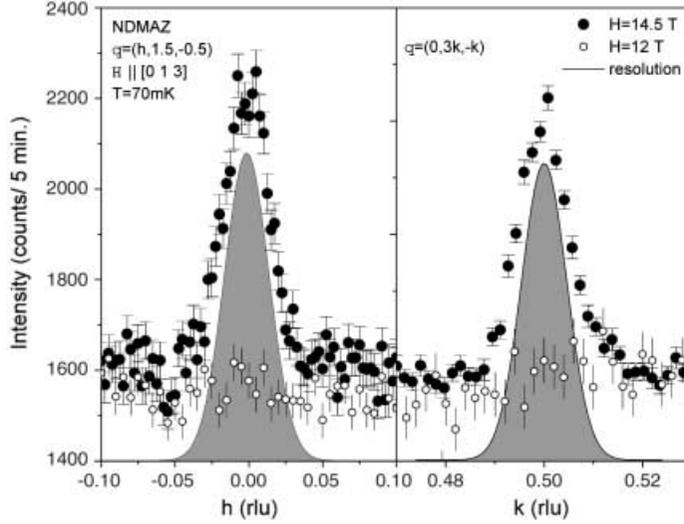


Fig. 2 – h - (left) and k -scans (right) across the $(0, 1.5, -0.5)$ reciprocal-space point in a deuterated NDMAZ sample at $T = 70$ mK for magnetic fields above (solid circles) and below (open circles) the critical field $H_c = 13.4$ T. The field is applied along the $[0, 1, 3]$ direction. Shaded areas represent the measured experimental wave vector resolution.

Discussion. – Despite the obvious limitations imposed on the measurements by the technical aspects of the experiment, the results presented above contain important information pertaining to the nature of the high-field phase in NDMAZ. The principal result of this work is that the magnetic Bragg reflections, characteristic of the high-field state, are detected at strictly commensurate positions. Similar behavior was previously seen in NDMAP [3]. Theoretical studies of isolated Haldane spin chains in applied field suggested a potential for incommensurate ordering [6, 9]. In particular, the longitudinal part of the real-space correlation function for a single chain at $H > H_c$ contains a cos-term with a built-in periodicity that depends on $(H - H_c)$ (eq. 2.8 in ref. [9]). This incommensurability is in many ways similar to that in $S = 1/2$ -systems in applied fields [26, 27], and can be understood from a fermion mapping of the Heisenberg Hamiltonian [5–7]. The reason why incommensurate ordering does not actually occur lies in the power law prefactor to the cos-term: it decays rapidly with distance, and the Fourier transform of the spin correlation function does not contain any singularities or even local maxima at incommensurate wave vectors [8, 28].

In NDMAP, depending on the field direction, the high-field phase was found to be ordered in either 2 or 3 dimensions [3]. For NDMAZ, at least in the geometry of the present experiment, it appears that above H_c the system is in true 3D AF ordered state. The observed Bragg reflections are resolution-limited along the $(1, 0, 0)$ and $(0, 3, -1)$ directions. While it is conceivable that the peaks can be broadened or even rod-like along the $[0, 1, 3]$ direction, such a coincidence seems unlikely. Moreover, there are intrinsic physical reasons for NDMAZ to prefer a 3D ordered state at high fields. In NDMAP the signature of 2D ordering are Bragg rods along the $(1, 0, 0)$ direction that represent the absence of static spin correlations along the a -axis, while 2D ordering occurs within the (b, c) planes [3]. This, in turn, is a consequence of extremely weak magnetic interactions along the 18 \AA crystallographic a -axis, and substantial inter-chain coupling within each (b, c) -plane [17]. The coupling between (b, c) planes in NDMAP is also highly frustrated, due to the body-centered structure. In NDMAZ

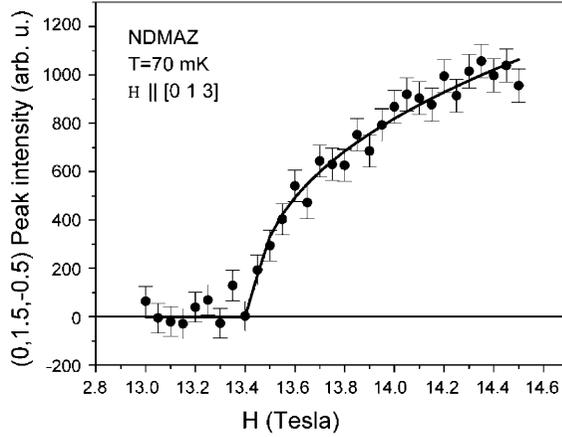


Fig. 3 – Measured field dependence of the $(0, 1.5, -0.5)$ magnetic Bragg peak intensity in NDMAZ at $T = 70$ mK. The solid line is a power law fit to the data, as described in the text.

the structure within each plane is quite similar to that in NDMAZ, and similar inter-chain interaction strengths along the b -axis can be expected. The crucial difference between the two structures lies in the interactions between Ni^{2+} sites from adjacent planes. Indeed, the monoclinic distortion in NDMAZ partially lifts the geometric frustration of the face-centered arrangement of the Ni ions. In addition, the distance between nearest-neighbor Ni-Ni sites from adjacent planes in NDMAZ is smaller than that in NDMAZ, which favors more potent inter-plane interactions. Future high-resolution inelastic neutron scattering studies will be required to fully resolve the issue of inter-chain coupling in the NDMAZ material.

The measured value $H_c = 13.4$ T for $\mathbf{H} \parallel [013]$ in NDMAZ is in reasonable agreement with the previously measured Haldane gap energies [23]. Indeed, for the axially symmetric case, with a magnetic field applied at an angle ϕ to the anisotropy axis, $\mu_B H_c = \Delta_z \Delta_\perp / \sqrt{g_z^2 \Delta_z^2 \cos^2 \phi + g_\perp^2 \Delta_z \Delta_\perp \sin^2 \phi}$ [3]. In this formula $g_z = 2.11$ and $g_\perp = 2.21$ are components of the Ni^{2+} gyromagnetic tensor along and perpendicular to the anisotropy axis, respectively [29]. For the geometry realized in the present experiment $\phi = 24^\circ$ and the formula gives $H_c = 13.8$ T. Note that inter-chain interactions always reduce the gap energy at the 3D AF zone-center, which should lead to smaller actual critical field values than given by the above equation.

The observed value of the critical index $\beta = 0.21$ for NDMAZ is similar to that found in NDMAZ and is also consistent with theoretical expectations. For a field applied at an angle to the anisotropy axis, the direction of ordered moment in the high-field phase is predetermined. On the one hand, it is the Haldane gap excitation polarized transverse to the applied field that softens at H_c and the resulting ordered moment must also be normal to \mathbf{H} , *i.e.*, be confined to the $(0, 1, 3)$ plane. On the other hand, it can be expected to lie in the magnetic easy plane $(0, 0, 1)$. The moment is thus necessarily aligned along the a -axis, and we are dealing with an Ising-type transition. In fact, for an isolated chain, the transition at H_c is expected to fall in the 1+1-dimensional Ising universality class, with H taking the role of temperature [6] and $\beta = 0.125$. For NDMAZ however, inter-chain interactions along the b -axis can be considered substantial, and 3D Ising behavior, with $\beta \approx 0.31$, may be expected. The measured critical exponent falls in between these two values and may be a signature of a dimensional crossover regime.

Conclusion. – NDMAZ is the second Haldane-gap system where field-induced commensurate antiferromagnetic ordering is observed by means of neutron diffraction. The similarity of the behavior observed in NDMAZ and NDMAP suggests that it represents a generic trend for weakly coupled $S = 1$ quantum spin chains.

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We would like to thank S. M. SHAPIRO (BNL) for insightful discussions, and P. SMEIBIDL and S. KAUSCHE (HMI) for technical assistance. Work at Brookhaven National Laboratory was carried out under Contract No. DE-AC02-98CH10886, Division of Material Science, US Department of Energy. Work at RIKEN was supported in part by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Culture, Sports, Science and Technology.

REFERENCES

- [1] HONDA Z. *et al.*, *J. Phys. Condens. Matter*, **9** (1997) L83.
- [2] HONDA Z., ASAKAWA H. and KATSUMATA K., *Phys. Rev. Lett.*, **81** (1998) 2566.
- [3] CHEN Y. *et al.*, *Phys. Rev. Lett.*, **86** (2001) 1618.
- [4] HALDANE F. D. M., *Phys. Rev. Lett.*, **50** (1983) 1153.
- [5] AFFLECK I., *Phys. Rev. B*, **41** (1990) 6697.
- [6] AFFLECK I., *Phys. Rev. B*, **43** (1991) 3215.
- [7] TSVELIK A. M., *Phys. Rev. B*, **42** (1990) 10499.
- [8] SACHDEV S., SENTHIL T. and SHANKAR R., *Phys. Rev. B*, **50** (1994) 258.
- [9] YAJIMA M. and TAKAHASHI M., *J. Phys. Soc. Jpn.*, **63** (1994) 3634.
- [10] MITRA P. P. and HALPERIN B. I., *Phys. Rev. Lett.*, **72** (1994) 912.
- [11] NICOPOULUS V. N. and TSVELIK A. M., *Phys. Rev. B*, **44** (1991) 9385.
- [12] KODA A., KOBAYASHI T. C., AMAYA K. and YAMASHITA M., *J. Magn. & Magn. Mater.*, **196-197** (1999) 443; KOBAYASHI T. C. *et al.*, *J. Phys. Soc. Jpn.*, **70** (2001) 813.
- [13] HONDA Z., KATSUMATA K., HAGIWARA M. and TOKUNAGA M., *Phys. Rev. B*, **60** (1999) 9272.
- [14] HONDA Z. and KATSUMATA K., *J. Appl. Phys.*, **85** (1999) 6076.
- [15] HONDA Z., KATSUMATA K., NISHIYAMA Y. and HARADA I., *Phys. Rev. B*, **63** (2001) 064420.
- [16] HONDA Z., KATSUMATA K., HAGIWARA M. and TOKUNAGA M., *J. Appl. Phys.*, **87** (2000) 5896.
- [17] ZHELUDEV A. *et al.*, *Phys. Rev. B*, **63** (2001) 104410.
- [18] See reference lists in XU G. *et al.*, *Phys. Rev. B*, **54** (1996) R6827.
- [19] See reference list in REGNAULT L. P., ZALIZNYAK I., RENARD J. P. and VETTIER C., *Phys. Rev. B*, **50** (1994) 9174.
- [20] CHIBA M. *et al.*, *Phys. Rev. B*, **44** (1991) 2838.
- [21] KOBAYASHI T. *et al.*, *J. Phys. Soc. Jpn.*, **61** (1992) 1772.
- [22] ENDERLE M., REGNAULT L.-P., BROHOLM C., REICH D. H., ZALIZNYAK I., SIELING M. and L.ÜTHI B., unpublished (2000).
- [23] KOIKE Y. *et al.*, *J. Phys. Soc. Jpn.*, **69** (2000) 4034.
- [24] YAMASHITA M. *et al.*, *Synth. Met.*, **71** (1995) 1961.
- [25] MONFORT M., RIBAS J., SOLANS X., and FONT-BARDIA M., *Inorg. Chem.*, **35** (1996) 7633.
- [26] PYTTE E., *Phys. Rev.*, **10** (1974) 4637.
- [27] MÜLLER G., THOMAS H., PUGA M. W. and BECK H., *J. Phys. C*, **14** (1981) 3399.
- [28] ZALIZNYAK I. and SACHDEV S., private communication.
- [29] HONDA Z., KATSUMATA K. *et al.*, to be published.