Experimental Report

Proposal: **4-01-1395** **Council:** 4/2014

Title: Magnetic excitations in S = 2 quasi-one-dimensional Heisenberg antiferromagnets

This proposal is a new proposal

Researh Area: Chemistry

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Samples: C16H14F1Mn1N2O2
C24H44Dy1N1O8Pt2S8
C24H44Er1N1O8Pt2S8
C24H44N1O8Pt2S8Y1
C18.5H21F1Mn1N2O5
C19H20F1Mn1N2O2

Instrument	Req. Days	All. Days	From	To
IN6	0	3	19/09/2014	22/09/2014

Abstract:

Haldane's conjecture of a spin-gap in the magnetic excitation spectrum for one-dimensional integer spin Heisenberg antiferromagnets, has during recent years increased the interest in well-suited materials with S = 2, since the proposed gap still remains elusive for such systems. We have synthesized a series of S = 2 quasi-one-dimensional Heisenberg antiferromagnets, and through chemical manipulations optimized the structure of these, in order to make them as promising candidates as possible for the observation of the Haldane gap. Furthermore, preliminary inelastic neutron scattering data have revealed the presence of several magnetic excitations in one member of the series, and we wish to clarify the nature of these by studying the members of the series that set the outer limits in terms of intrachain magnetic exchange interaction and interchain separation.

The conjecture made by Haldane, on the gapped ground state of integer spin one-dimensional Heisenberg antiferromagnets [1,2], has experimentally been verified for many $S = 1$ systems [3]. However, for $S = 2$ chains, the gap remains elusive [4,5]. The gap size for $S = 2$ systems is predicted to be only 8 % of the exchange coupling constant J, while being approximately 41 % of J for $S = 1$ systems. Strong intrachain exchange interactions is therefore a prerequisite for a gap size sufficiently large to be observable. This, along with the strict requirement of the absence of three-dimensional magnetic ordering at low temperatures, leaves only very few well-suited $S = 2$ systems [6].

The system *catena*-Mn(F)(salen), as recently published by our group [7], is a promising candidate for an $S = 2$ Haldane system. Magnetic susceptibility measurements clearly indicate the absence of three-dimensional long range magnetic ordering, and fitting of the susceptibility results in $J = 4.7$ meV. Consequently a gap size of $\Delta_{S=2} \sim 0.4$ meV is expected. Taking into account the local anisotropy of the high-spin manganese(III) ion, the effect of which is to split the triplet state, two transitions should be spectroscopically observable using INS, namely $|0,0\rangle \rightarrow |1,\pm1\rangle$ and $|0,0\rangle \rightarrow |1,0\rangle$. Approximately 2 grams of a polycrystalline powder sample of *catena*-Mn(F)(salen) was measured on IN6 at various temperatures and two different incident neutron wavelengths, $\lambda_i = 5.12$ Å and $\lambda_i = 4.14$ Å

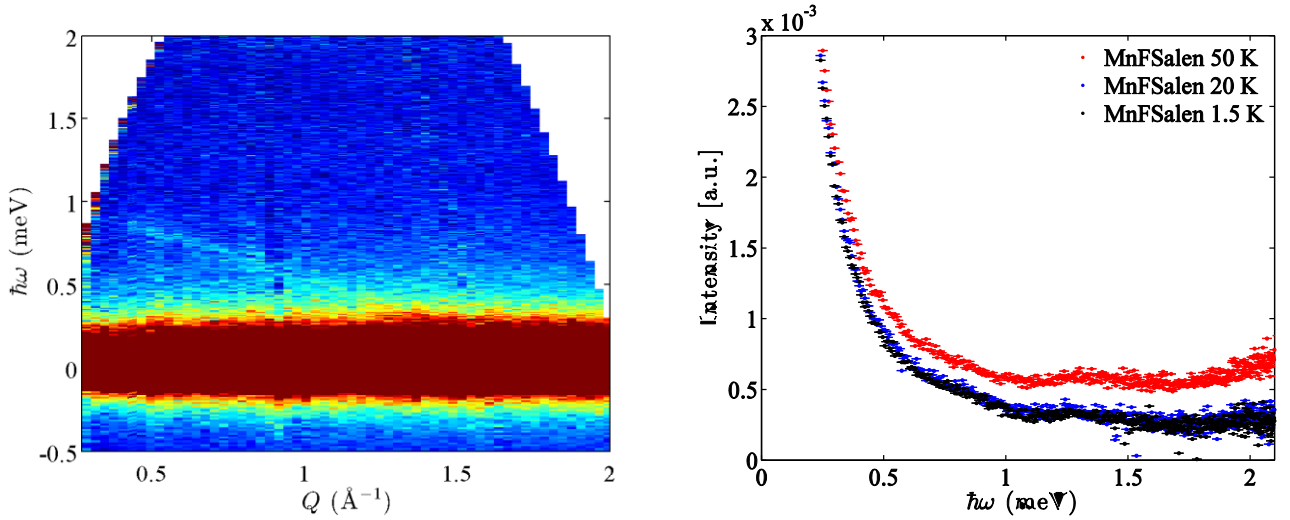

Figure 1. Left: $S(\boldsymbol{Q},\omega)$ plot for *catena*-Mn(F)(salen) at $T = 1.5$ K and $\lambda_i = 5.12$ Å. **Right:** INS spectra for *catena*-Mn(F)(salen) obtained with $\lambda_i = 5.12$ Å at the indicated temperatures (integration over full available Q-range).

The data taken with $\lambda_i = 5.12$ Å at $T = 1.5$ K is shown in the form of the $S(\boldsymbol{Q},\omega)$ plot in Figure 1 Left. A single low-intensity feature is observed in the range $Q = [0.3\ \text{Å}^{-1}, 1.1\ \text{Å}^{-1}]$ and $\hbar\omega = [0.5$ meV, 0.8 meV]. The feature is within the expected energy range, and show a dispersion in Q as expected. However, the feature seems to be independent of temperature, and a comparison between the INS spectra (integration over full available Q-range) at various temperatures reveals no significant differences between the spectrum at $T = 1.5$ K and those at higher temperatures (cf. Figure 1 Right). We therefore conclude that the observed feature is an artifact, its origin being unknown so far. A reason for the absence of magnetic excitations relating to the Haldane gap in the measured data could be a result of three-dimensional long-range magnetic ordering, even though magnetic susceptibility data suggest the absence of such. The crude diffraction data obtained from the INS measurements at $\lambda_i = 5.12$ Å at $T = 1.5$ K and $T = 50$ K is shown in Figure 2 Left, in terms of scattering intensity vs. Q (obtained by integration of the elastic line in the interval $\hbar\omega = [-0.05$ meV, 0.05 meV]). The two diffraction profiles look virtually identical, with no additional Bragg peaks being present in the low-temperature data. This supports the absence of three-dimensional long-range magnetic ordering in *catena*-Mn(F)(salen) in the studied temperature interval. In order to verify this result, beam time at the cold neutron powder diffractometer,

DMC, at Paul Scherrer Institut, Switzerland, has been allocated, and the experiment will be conducted in near future.

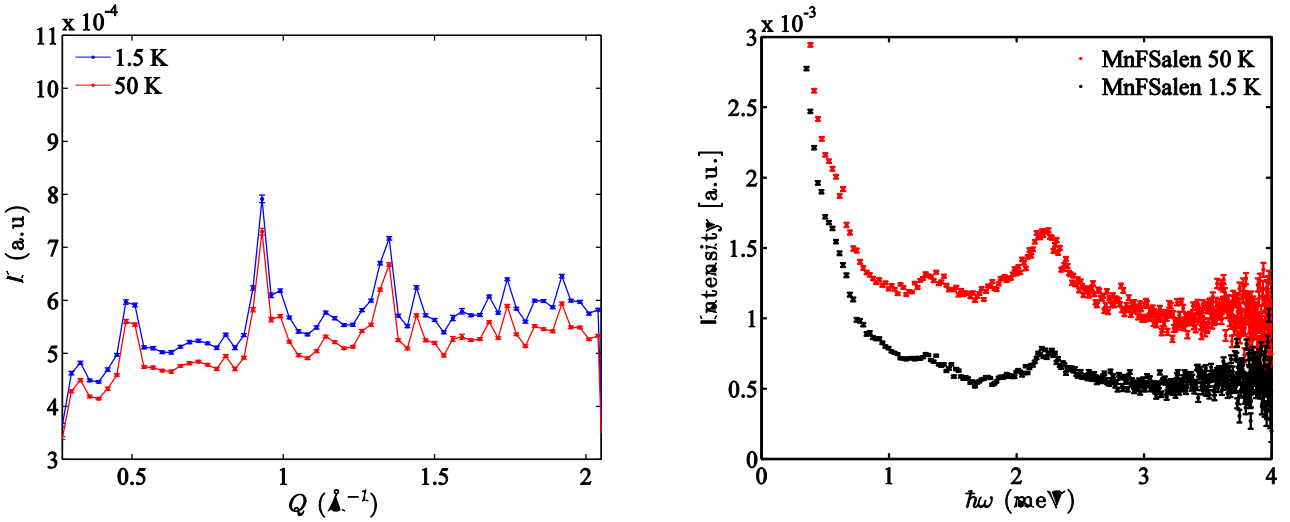

Figure 2. Left: Diffraction profile for *catena*-Mn(F)(salpn) at T = 1.5 K and T = 50 K, extracted from the data taken with λ_i = 5.12 Å. **Right:** INS spectra for *catena*-Mn(F)(salen) obtained with λ_i = 4.14 Å at the indicated temperatures (integration over full available Q-range).

For the sake of completeness, data was also taken with λ_i = 4.14 Å at T = 1.5 K and T = 50 K. These data revealed two features around $\hbar\omega$ = 1.3 meV and $\hbar\omega$ = 2.2 meV (cf. Figure 2 Right). However, from their T- and Q-dependence, the features are determined to be phononic in origin. Our failure to observe magnetic excitations relating to the Haldane gap in *catena*-Mn(F)(salen), can be a result of the powder averaging and/or the incoherent scattering from the hydrogen present in the sample. Attempts at growing sufficiently large single crystals of *catena*-Mn(F)(salen) are therefore ongoing.

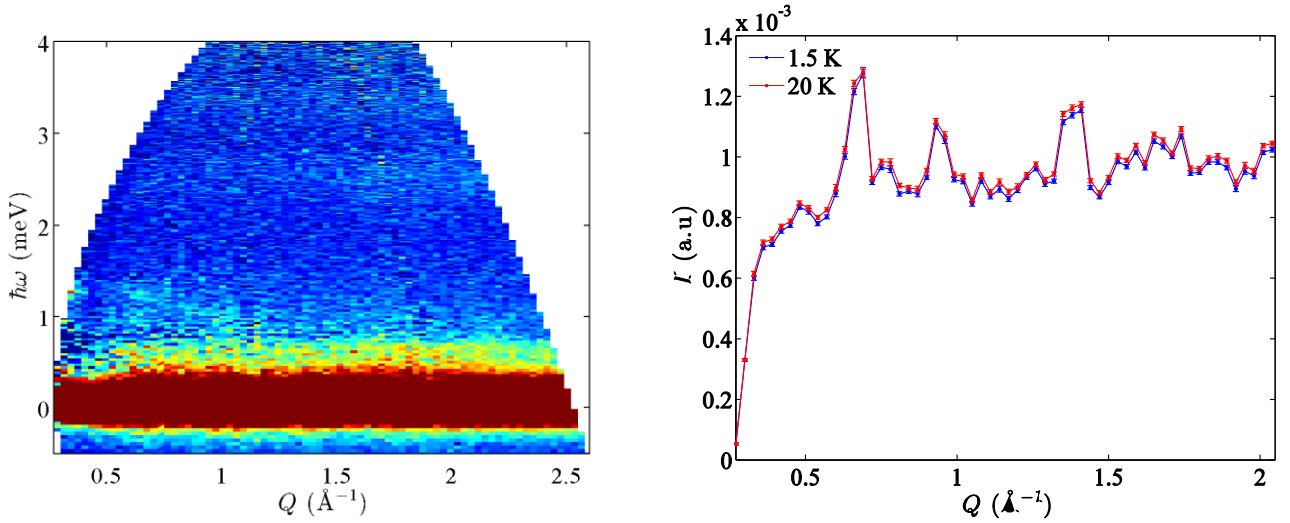

Figure 3. Left: $S(\boldsymbol{Q},\omega)$ plot for *catena*-Mn(F)(salpn) at T = 1.5 K and λ_i = 4.14 Å. **Right:** Diffraction profile for *catena*-Mn(F)(salpn) at T = 1.5 K and T = 20 K, extracted from the data taken with λ_i = 4.14 Å.

The related system *catena*-Mn(F)(salpn) contains more bent fluoride-bridges than the parent *catena*-Mn(F)(salen) chain. This results in weaker exchange coupling of J = 3.6 meV. Magnetic susceptibility data suggest that the system undergoes three-dimensional long-range magnetic ordering at $T \approx$ 12 K. Approximately 1.5 grams of a polycrystalline powder sample of *catena*-Mn(F)(salpn) was measured on IN6 with λ_i = 4.14 Å, in order to investigate the possible presence of spin waves in the material. The $S(\boldsymbol{Q},\omega)$ plot obtained at T = 1.5

K, does not reveal any magnetic excitations. Examination of the of the crude diffraction data obtained from the INS measurements (obtained by integration of the elastic line in the interval $\hbar\omega$ = [–0.05 meV, 0.05 meV]), surprisingly reveals two virtually identical diffraction profiles at T = 1.5 K and T = 20 K. Opposed to the magnetic susceptibility data, this suggests that *catena*-Mn(F)(salpn) does not undergo three-dimensional long-range magnetic ordering at temperatures down to 1.5 K. This issue will be addressed at the upcoming beam time at DMC, PSI.

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[1] F.D.M. Haldane, Phys. Lett. A 93 (1983) 464. [2] F.D.M. Haldane, Phys. Rev. Lett. 50 (1983) 1153. [3] M. Yamashita, T. Ishii, H. Matsuzaka, Coord. Chem. Rev. 198 (2000) 347. [4] U. Schollwöck, T. Jolicoeur, Europhys. Lett. 30 (1995) 493. [5] G.E. Granroth, M.W. Meisel, M. Chaparala, T. Jolicœur, B.H. Ward, D.R. Talham, Phys. Rev. Lett. 77 (1996) 1616. [6] M.B. Stone, G. Ehlers, G.E. Granroth, Phys. Rev. B 88 (2013) 104413. [7] T. Birk, K.S. Pedersen, S. Piligkos, C.A. Thuesen, H. Weihe, J. Bendix, Inorg. Chem. 50 (2011) 5312.