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Magnetic Response of Mn(III)F(salen) at Low Temperatures

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The low temperature magnetic response of Mn(III)F(salen), salen = $H_{14}C_{16}N_2O_2$, an $S = 2$ linear-chain system, has been studied. Using a single crystal with the field applied perpendicular to the chain direction, torque magnetometry, down to 20 mK and up to 18 T, revealed a feature at 3.8 T when $T \leq 400$ mK. ESR (≈ 200 GHz) studies, using single crystals at 4 K and in 5 T, have not detected any signal. In 10 mT, the temperature dependence of the susceptibility of powder-like samples can be reasonably fit when $J/k_B = 50$ K and $g = 2$. In addition, these data are unchanged for $P \leq 1.0$ GPa. Using a randomly-oriented, powder-like, deuterated (12 of 14 H replaced by D) sample of 2.2 g at 270 mK, neutron scattering data, acquired with the Cold Neutron Chopper Spectrometer at the Spallation Neutron Source, show several well defined excitations that may be from the zero-field energy levels of antiferromagnetic $S = 2$ spins with $g = 2$, $J/k_B = 50$ K, $D/k_B = 2.8$ K, and $E/k_B = 0.5$ K.

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1. Introduction

Linear-chain, integer-spin antiferromagnets, commonly known as Haldane systems, have a storied history in the field of quantum spins, with $S = 1$ materials receiving the most attention [1]. The $S = 2$ systems have received less consideration for several reasons, including a smaller Haldane gap, since $\Delta_{S=1} = 0.41J$ and $\Delta_{S=2} = 0.09J$, where J is the nearest-neighbor exchange energy [2]. Due to a report suggesting Mn(III)F(salen) is an $S = 2$ Haldane system with $J/k_B = 50$ K and no evidence of long-range order down to 2 K [3], we have studied the magnetic response of single-crystals at low temperatures and in high magnetic fields.

2. Experimental results

Using a single crystal with the field applied perpendicular to the chain direction, torque magnetometry, down to 20 mK and up to 18 T, revealed a reproducible feature in the response of a torque magnetometer [4], Fig. 1. In addition, neutron scattering data acquired with a randomly-oriented, powder-like, deuterated (12 of 14 H replaced by D) sample of 2.2 g at 270 mK and obtained with the CNCS (Cold Neutron Chopper Spectrometer) at the SNS (Spallation Neutron Source) show several well defined excitations, Fig. 2. Finally, EPR studies near 200 GHz have not identified a response from single crystals at 4 K and in 5 T, and the low-field (10 mT), high-temperature (up to 300 K) magnetic susceptibility, $\chi(T)$, of randomly oriented microcrystals is unchanged for $P < 1.0$ GPa.

3. Discussion and summary

Our $\chi(T)$ results can be simulated with $J/k_B \approx 50$ K [5], which is close to the value reported by Birk *et al.* [3]. Following the analysis used with Mn(III)Cl_3(bipy), an $S = 2$ Haldane system [6, 7], our magnetometry results indicate the possible presence of a critical field of 3.8 T. Assuming $\Delta_{S=2} = 0.09J$ and $g = 2$, this field yields $J/k_B = 53$ K. Recently, high-field EPR work [8] was used to determine the single-ion anisotropies D and E in Mn(III)Cl_3(bipy), where two zero-field modes with energies $\propto J(D \pm E)$ were detected. If MnF(III)F(salen) behaves in a similar fashion and taking $J/k_B = 50$ K from our $\chi(T)$ data, the features at 4.5 meV and 5.4 meV in Fig. 2 suggest $D/k_B = 2.8$ K and $E/k_B = 0.5$ K for $g = 2$.

It is too early to determine if Mn(III)F(salen) is an "even" Haldane system or an XY material [9, 10]. The local environments of the Mn are complicated, with three distinct Mn per unit cell in a –1–2–3–3–2–1– chain motif where three different bridging Mn–F–Mn angles are present [3]. Our characterization of this interesting material continues.

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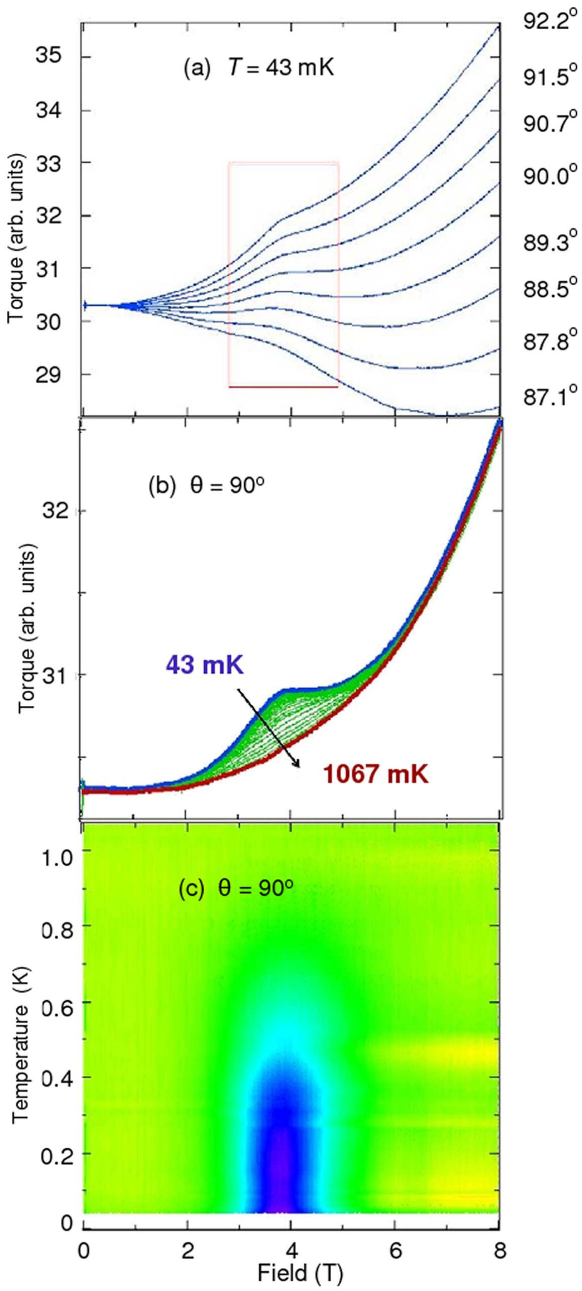

Fig. 1. The temperature and magnetic field responses of the torque magnetometer, (a) for various orientations of the field with the chain axis at 43 mK, where the values of the angle θ are given and $\theta = 90°$ is the angle between the magnetic field and the magnetic easy-axis, where the detected torque was null below 2 T, and (b) with fixed orientation and different temperatures. Panel (c) shows the weak (green) to strong (blue to pink) response as a color gradient, indicating the presence of a critical field, $H_{C1} = 3.8$ T.

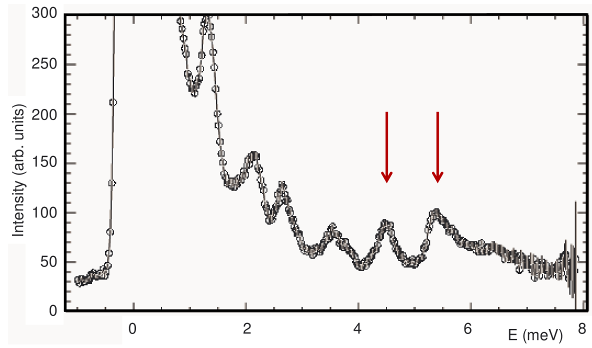

Fig. 2. The intensity versus energy obtained at 270 mK, for 0.9 $\text{Å}^{-1} \leq Q \leq 1.2\ \text{Å}^{-1}$ at an incident energy of 10 meV. The red arrows indicate the modes used in the analysis, see text.

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