Antiferromagnetic ordering in MnF(salen)

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Abstract
Antiferromagnetic order at \( T_N = 23 \) K has been identified in Mn(III)F(salen), salen = \( \text{H}_2\text{C}_{16}\text{N}_2\text{O}_2 \), an \( S = 2 \) linear-chain system. Using single crystals, specific heat studies performed in magnetic fields up to 9 T revealed the presence of a field-independent cusp at the same temperature where \(^1\text{H} \) NMR studies conducted at 42 MHz observed dramatic changes in the spin-lattice relaxation time, \( T_1 \), and in the linewidths. Low-field (less than 0.1 T) magnetic susceptibility studies of single crystals and randomly-arranged microcrystalline samples reveal subtle features associated with the transition.

Keywords: antiferromagnetism, low-dimensional magnetism, magnetic spin chains, specific heat, NMR

(Some figures may appear in colour only in the online journal)

1. Introduction

After Haldane identified significant differences in the magnetic behavior of integer and half-interger, Heisenberg, antiferromagnetic spins in one-dimension [1, 2], some time elapsed before Ni(C\(_2\)H\(_8\)N\(_2\))\(_2\)NO\(_2\)(ClO\(_4\)), commonly referred to as NENP, emerged as a model \( S = 1 \) system [3] exhibiting no evidence of long-range ordering down to at least 4 mK [4, 5]. With a wide-range of work reported on \( S = 1 \) Haldane systems [6], the challenge of finding an \( S = 2 \) Haldane system was reportedly resolved with the identification of \( \text{MnCl}_3(\text{bpy}) \), bpy = \( \text{C}_10\text{H}_8\text{N}_2 \) (2,2'-bipyridine) [7, 8], as a Haldane gapped system with nearest-neighbor interaction \( J \approx 35 \) K and no long-range order down to 30 mK [9]. However, high-field magnetization [10] and EPR studies [11] of as-grown microcrystalline samples at low temperature, \( T = 1.3 \) K, provided evidence of a spin-flop transition and the presence of antiferromagnetic resonance (AFMR) modes. Recently with the use of single crystals, long-range antiferromagnetic ordering has been identified in \( \text{MnCl}_3(\text{bpy}) \) near 11 K [12, 13].

Although other candidate \( S = 2 \) linear-chain materials have been identified [6, 14–19], these systems possess long-range ordering, and evidence of a gapped quantum spin liquid state just above the ordering was not detected in \( \text{CrCl}_2 \) [19]. In parallel with these experimental studies, theoretical activity to extend and explore the quantum spin properties of antiferromagnetic \( S = 2 \) spins in one-dimension is topical and intense [20–27].

Recently, a new \( S = 2 \) linear-chain system, MnF(salen), salen = \( \text{H}_2\text{C}_{10}\text{N}_2\text{O}_2 \), was synthesized, and the low-field, high-temperature magnetic properties were fit with \( J/k_B \approx 46 \) K, while no evidence of a magnetic transition was detected down to 1.8 K [28]. The linear chains are formed when high-spin Mn(III) ions, equatorially coordinated to two oxygen and two nitrogen donor atoms from the salen ligand, are bridged through axial positions by fluoride ions. The electronic structure of the title compound [28] and a review of magnetic...
exchange via fluoride ion bridges [29] have been reported. The initial report by Birk et al [28] motivated a suite of studies, including torque magnetometry and EPR on single crystals and neutron scattering on a partially deuterated, as-grown, microcrystalline powder-like sample, and a brief report of the resulting data sets has been published elsewhere [30]. During the course of this work [30], specific heat and \(^1H\) NMR investigations were initiated, and both experiments provided unambiguous evidence of long-range antiferromagnetic order at \(T_N = 23\) K. The purpose of this paper is to present these data sets and the corresponding analyzes, which, when combined with additional studies of the low-field magnetic response, provide insight into the nature of the magnetic transition.

2. Experimental details and results

2.1. Material preparation

All chemical reagents were purchased from Sigma-Aldrich, Alfa Aesar, or Tokyo Chemical Industry (TCI) Company and used without further purification. Using the facilities at the University of Florida, the samples of MnF(salen) were synthesized as described elsewhere [28]. The identity and purity of the compound were confirmed by x-ray diffraction and FT-IR spectroscopy.

2.2. Specific heat

The specific heat studies used the facilities located at P. J. Šafárik University and were made with several single crystal samples. In the temperature range between 0.38 K and 40 K, a commercial system (quantum design PPMS) equipped with a \(^3He\) insert was used while employing the relaxation method technique. Two independent measurements were made, where the first used one single crystal of mass 0.8 mg (sample 1) and the second one employed two crystals of total mass 0.67 mg (sample 2), and these data are shown in figure 1. Below 1 K, the experiment was conducted in a \(^3He\)-\(^4He\) dilution refrigerator (Air Liquide Minidil) using a 2.1 mg single crystal. The sample was attached using Apiezon N vacuum grease to the home-made calorimeter consisting of a sapphire substrate, which also supported a thin-layer RuO\(_2\) thermometer and a resistive heater. The RuO\(_2\) thermometer was calibrated against a commercial (Scientific Instruments (SI)) RuO\(_2\)-based thermometer. The magnetoresistance changes of the SI thermometer were included using a known correction from the literature [31]. The specific heat was measured down to 60 mK by standard dual-slope and heat-pulse methods [32], which are similar to the ones used in PPMS instrument.

2.3. NMR

The \(^1H\) NMR studies were performed with standard four-phase cycling Fourier-transform spin-echo techniques using a spectrometer and probe built at UCLA. The sample holder was constructed from teflon and brass, and the coil was wound from teflon-coated wire. The choice of these materials effectively reduced extraneous proton signals to an undetectable level. The circuit was bottom-tuned using fixed matching and tuning elements, and the magnetic field set to the \(^1H\) resonance condition (989.4 mT at 42.130 MHz) using an electromagnet. The sample was cooled in a variable-temperature insert placed in a bucket dewar with its tail between the magnet pole-faces. The experiments were initiated with a single crystal of mass 5.1 mg, with the field aligned orthogonal to the chains axis. Subsequently, a randomly-oriented, as-grown microcrystalline sample was loaded, and several points were acquired to confirm the strong changes in the vicinity of the transition.

The temperature dependence of the spin-lattice relaxation rate, \(\tau_1^{-1}\), is shown in figure 2. These data exhibit a relatively weak variation with \(\tau_1^{-1} \sim 100\) s\(^{-1}\) down to about 80 K. Further cooling leads to a monotonic increase of almost 2 orders of magnitude before precipitously dropping by many orders of magnitude below \(T = 23\) K. The increase over the range 23 K < \(T \approx 80\) K signals the onset of antiferromagnetic correlations and the associated slowing of the fluctuating field. The drop in \(T_1^{-1}\) below 23 K is accompanied by a loss of signal intensity associated with the discontinuous onset of line-broadening, most of which is outside the spectrometer operating bandwidth of order 100 kHz. The data were collected while cooling and warming and no hysteresis was detected.

In figure 3, two spectra, characteristic of temperatures above and below the ordering temperature, are shown. For \(T > T_N\), the linewidth was approximately 50 kHz and exhibited unresolved features that presumably result from inequivalent
hyperfine couplings and internuclear spin–spin couplings. For $T < T_N$, the spectrum is much too broad for the pulse conditions ($p_1(\pi/2) = 1.1 \mu s$, refocusing pulse $p_2 = 0.7 \mu s$). Thus, the full spectrum for the low-temperature phase was constructed from a sum of field-swept spectra recorded at 5 mT intervals. Since the proton gyromagnetic ratio is $\gamma = 42.577 \text{ MHz T}^{-1}$, the equivalent steps in frequency correspond to slightly larger than 200 kHz, and therefore some spectral distortions are certainly present. Nevertheless, in the data, there is a center of symmetry about the unshifted position. Furthermore, the broadening was observed to onset discontinuously, indicative of a first-order transition, and the overall symmetry of the lineshape is consistent with commensurate magnetic ordering. The overall scale of the broadening ($\pm 2$ MHz) is consistent with direct dipolar electron-nuclear spin coupling, when assuming ordered moments of order 1–2 $\mu_B$ and a closest $^{1}H$-Mn distance of 3 Å.

Returning to the nuclear spin-lattice relaxation, a temperature-independent result is expected in the case $k_BT \gg zJ$ [33, 34], where the hyperfine-field fluctuations predominantly originate with electronic spin $T_2$ processes determined by the exchange interaction $J$ and $z$ is the number of nearest neighbors. The relaxation rate in this limit can be estimated as

$$T_{1}^{-1} = \frac{1}{2} \gamma^2 \frac{h^2}{\omega_{c}},$$

(1)

with $\omega_c$ a characteristic frequency for the spectral density, given by \(\omega_c^2 = J^2 z(S + 1)/\hbar^2\). To within geometric factors of order unity, the effective mean-square field for electron-nuclear dipolar coupling is

$$h^2 = \frac{2\pi \hbar \gamma}{3} \omega_c S(S + 1) \sum_i \langle r_i^6 \rangle,$$

(2)

where the sum is over the proton-Mn distances for the $i$th Mn site. If we take the characteristic distance as 4 Å, the result is $T_{1}^{-1} \sim 10 \text{ s}^{-1}$, which is about an order of magnitude smaller than observed. Presumably the discrepancy arises from a combination of properly estimating the geometric factors, the field orientation, and/or the sum.

2.4. Magnetometry

Two commercial magnetometers (quantum design MPMS-XL7), one at UCLA and the other at the University of Florida, were used. Previously, several batches, including the deuterated one, of as-grown, randomly arranged microcrystals provided a response similar to the data reported by Birk et al [28]. More specifically, the isothermal (1.8 K) magnetization of a polycrystalline sample at 5 T achieves a value $\sim 0.4 \mu_B$ [28], which is not consistent with long-range ferromagnetic order. Furthermore, when using the Padé approximations of quantum Monte Carlo simulations [35], the low-field magnetic susceptibility at high temperatures was well fit when $J = 50 \pm 2$ K for $g = 2$ [30]. After the discovery of the specific heat and NMR signatures of long-range antiferromagnetic ordering at $T_N = 23$ K, the magnetic susceptibility studies were extended to include a single crystal and zero-field-cooling (ZFC) versus field-cooling (FC) study of a fresh (less than one-month old) as-grown microcrystalline sample. The results shown in figure 4 indicate the single crystal sample possesses a subtle bump near 22 K when a field of 0.1 T is oriented nominally parallel to the chains. Although ZFC and FC studies using 10 mT failed to reveal any variation of the magnetic response for the microcrystalline sample, differences below 30 K were detectable when the FC cycle was repeated in 7 T while cooling from room temperature and subsequently collecting data while warming in 10 mT, figure 4. Finally, all samples possess a residual, temperature-dependent, batch-dependent, increasing signal below 30 K, and this contribution is presumably due to small amounts of isolated Mn(III) ions [28].

3. Discussion and summary

Firstly, the specific heat data reveal the presence of a small bump at $T_N = 23$ K, and this result is strikingly similar to the
K. The increase of $H$ contacts − heat as only a tiny portion of entropy is removed. Although between the planes generates a subtle anomaly in the specific to the strength of interlayer interaction, where weak-coupling results reported for another $S = 2$ quasi-linear chain material MnCl$_3$(bpy) [12]. More specifically, the entropy change in the vicinity of the transition is 48 mJ (K mol)$^{-1}$ or 0.4% of the total magnetic entropy of $R \ln(5) = 13.38$ J (K mol)$^{-1}$. In fact, a small value of the magnetic entropy removed at or below the ordering temperature is a signature of the low-dimensionality of the material since the majority of entropy is reduced by the low-dimensional short-range correlations at higher temperature. Other examples of this situation have been reported for the one-dimensional antiferromagnet (CH$_3$)$_2$MnMnCl$_3$, commonly known at TMMC [36], for the molecular magnet [Fe$^{6+}$(ΔFe$^{4+}$(A)(ox)$_2$(Phen)$_2$)$_2$]$_n$ [37], and the metal-organic framework Co$_4$(OH)$_2$(C$_{10}$H$_{16}$O$_4$)$_3$ [38]. Furthermore, the specific heat signature is not consistent with ferromagnetic ordering, because the reversal of the well-developed short-range correlations would provide a significantly larger jump at the transition, and the reverse case of ferromagnetic chains becoming antiferromagnetically ordered is an example [39].

For MnF(salen), the magnetic contribution can not be separated from the phonon contribution, so an accurate estimate of the total magnetic entropy removed below the ordering temperature is not possible. The only theoretical work, which evaluates the contribution of three-dimensional ordering to the specific heat at the Neél temperature, is reported for the two-dimensional square-lattice including interlayer interaction [40]. This theoretical work clearly shows how the entropy removed at the three-dimensional ordering transition is related to the strength of interlayer interaction, where weak-coupling between the planes generates a subtle anomaly in the specific heat as only a tiny portion of entropy is removed. Although not theoretically treated in the literature, this type of result experimentally extends to one-dimensional chains, as evidenced by the work on Cu(pyz)(NO$_3$)$_2$ [41]. Consequently, one can infer the perturbation preventing the occurrence of a Haldane state for $S = 2$ chains might be very weak. Additional theoretical consideration of this situation is warranted by the recent findings reported here for MnF(salen) and elsewhere for MnCl$_3$(bpy) [12].

Secondly, the NMR data from both single crystal and microcrystalline samples indicate a robust, first-order antiferromagnetic transition at $T_N = 23$ K. The increase of $T_1$ by almost two orders of magnitude as the temperature is decreased toward $T_N$ is consistent with the slowing of the moments due to increased correlations and the removal of entropy. The NMR data are unambiguously consistent with an antiferromagnetic transition, as a ferromagnetic transition entropy. The NMR data are unambiguously consistent with an antiferromagnetic transition, as a ferromagnetic transition would have dramatically shifted the central resonance [42]. The results indicate the importance of local probes, such as NMR and muon-spin rotation, that detect the formation of static moments and provide transition signatures commonly missed by standard magnetometry techniques. In addition, the difficulty of thermodynamically observing the transition of MnF(salen) is not caused by the competition between structural coherence and the magnetic correlation length [17].

Finally, all of the results suggest MnF(salen) is antiferromagnetically ordered below 23 K, where the interchain coupling is antiferromagnetic, leading to the conjectured spin arrangement shown in figure 5. This magnetic spin arrangement was discussed by Birk et al [28] and can be probed by neutron techniques when a suitable sample is available and awarded beam time.

6 Note the correction of a couple of typos in Birk et al, [27], where the labels Mn1 and Mn3 were switched in their figure 1, while the angles Mn1-F2-Mn2 and Mn2-F3-Mn3 were incorrectly given in the text and should be 150.43° and 151.72°, respectively.
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