Experimental Evidence of a Haldane Gap in an $S=2$ Quasi-Linear-Chain Antiferromagnet

G. E. Granroth and M. W. Meisel
Department of Physics and Center for Ultralow Temperature Research, University of Florida, 215 Williamson Hall, P.O. Box 118440, Gainesville, Florida 32611-8440

M. Chaparala
National High Magnetic Field Laboratory, Florida State University, 1800 E. Paul Dirac Drive, Tallahassee, Florida 32306-3016

Th. Jolicœur
Service de Physique Théorique, Commissariat à l'Energie Atomique, Saclay, F-91191 Gif-sur-Yvette, France

B. H. Ward and D. R. Talham
Department of Chemistry, University of Florida, 200 Leigh Hall, P.O. Box 117200, Gainesville, Florida 32611-7200
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The magnetic susceptibility of the $S = 2$ quasi-linear-chain Heisenberg antiferromagnet (2,2′-bipyridine)trichloromanganese(III) has been measured from 1.8 to 300 K with the magnetic field H parallel and perpendicular to the chains. The analyzed data yield $g \approx 2$ and $J \approx 35$ K. The magnetization M has been studied at 30 mK and 1.4 K in H up to 16 T. No evidence of long-range order is observed. Depending on crystal orientation, $M \approx 0$ at 30 mK until a critical field is achieved ($H_{c\parallel} = 1.2 \pm 0.2$ T and $H_{c\perp} = 1.8 \pm 0.2$ T), where M increases continuously as H is increased. These results are interpreted as evidence of a Haldane gap. [S0031-9007(96)00903-9]

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Ever since Haldane's prediction in 1983 [1,2], a significant amount of experimental and theoretical effort has been focused on understanding the difference between half-integer and integer spin linear chain Heisenberg antiferromagnets. These endeavors established the presence of the Haldane gap Δ in $S = 1$ systems, where $\Delta_{S=1}/J = 0.41$ and J (> 0) is the nearest-neighbor exchange energy. Experimentally, $[Ni(C_2H_8N_2)_2NO_2][ClO_4]$ [3], known as NENP, has received considerable attention since $J \approx 45$ K is sufficiently large to access the Haldane phase with a variety of probes. Along with inelastic neutron scattering [4–6] and high magnetic field ESR [7,8] studies, magnetization investigations of single crystals of NENP at temperatures significantly below the gap have explicitly demonstrated the presence of $\Delta_{S=1}$ consistent with Haldane's description [9–11]. Recently, several numerical studies have been performed on $S = 2$ antiferromagnetic quantum spin chains, and the results yield $\Delta_{S=2}/J = 0.08$ [12], 0.055 ± 0.015 [13], 0.05 [14], 0.085 ± 0.005 [15], and 0.049 ± 0.018 [16]. In addition, Schollwöck and Jolicœur [15] have studied the phase diagram of the $S = 2$ spin chain Hamiltonian that includes single-ion (D) and exchange (η) anisotropies. Such a Hamiltonian, with the addition of rhombic anisotropy, E term, is

$$\mathcal{H} = J\sum_i (S_i^x S_{i+1}^x + S_i^y S_{i+1}^y + \eta S_i^z S_{i+1}^z) + D\sum_i (S_i^z)^2 + E\sum_i [(S_i^x)^2 - (S_i^y)^2]. \quad (1)$$

For $E = 0$, $\eta = 1$, and $D > 0$, the analysis of Schollwöck and Jolicœur indicates the Haldane phase is maintained only for $D/J \leq 0.04 \pm 0.02$. For larger positive D values, a gapless phase with XY character separates the Haldane phase from a gapped phase with a singlet ground state. For large negative values of D, long-range ferromagnetic or antiferromagnetic order is established, depending on the sign of η. From their phase diagram, Schollwöck and Jolicœur [15] conclude that it is unlikely to find real $S = 2$ materials that achieve the Haldane state. Nevertheless, attempts to find appropriate $S = 2$ systems have been reported, and, as predicted, these materials appear to experience a transition to a long-range ordered state before reaching the Haldane phase [17,18].

In this Letter, we report the first evidence of the presence of the Haldane gap in an $S = 2$ chain antiferromagnet. The magnetic properties of (2,2′-bipyridine)trichloromanganese(III), $MnCl_3$(bipy), where bipy represents (2,2′-bipyridine), $C_{10}H_8N_2$, were first reported by Goodwin and Sylva [19] down to 118 K in 1967, and the crystal structure was published by Perlepes *et al.* [20] in 1991. The system consists of a quasilinear chain of Mn^{3+} ($S = 2$) ions in $MnCl_2$(bipy) units, asymmetrically connected by bridging Cl^- ions (Fig. 1). The Mn^{3+} coordination is a distorted octahedron where the Mn-Cl bonds along the chain axis (Mn1-Cl1 = 2.51 Å and Mn1-Cl1′ = 2.71 Å) are longer than those in the equatorial plane (2.24 Å) [20]. Axial elongation results in singly occupied dz^2 orbitals and a value of $D < 0$ [21,22]. The Mn-Mn intrachain distance is 4.83 Å, and the strongest Mn-Mn interactions are through overlap of the metal dz^2 orbitals with the chlorine bridge. The

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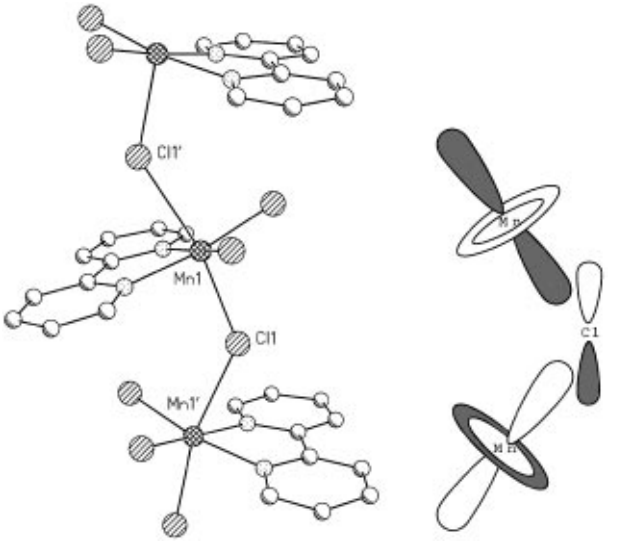

FIG. 1. Left: The crystal structure of $MnCl_3$(bipy) is shown. The important bond distances and angles are given in the text. Note a slight corrugation of the line connecting successive Mn^{3+} ions. Right: Magnetic orbital scheme showing the Mn-Cl-Mn intrachain overlap.

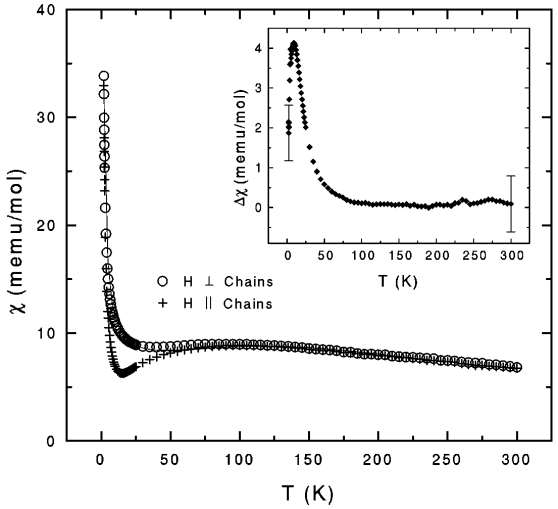

FIG. 2. The magnetic susceptibility $\chi(T)$ measured in a magnetic field of 0.1 T applied perpendicular (O) and parallel (+) to the chains. The solid line indicates a fit of the data by Eq. (2) as explained in the text. The inset shows $\Delta\chi(T) = \chi_{\perp}(T) - \chi_{\parallel}(T)$, where typical uncertainty limits are indicated at high and low temperatures.

Mn-Cl-Mn bond angle of 135° is consistent with antiferromagnetic exchange [23]. Furthermore, the closest Mn-Mn distance between chains is 7.96 Å, and since no ligands bridge the chains, interchain exchange J' is expected to be small. Following published procedures [20], a total of four batches of the material have been prepared. Two attempts provided powderlike material and the other two runs resulted in samples of microcrystals with a typical size of 90 μm × 0.4 mm × 0.9 mm. The material was identified using combustion and single crystal x-ray analyses.

The temperature dependence of the magnetic susceptibility, $\chi(T)$, of approximately 2.4 mg of 90 oriented single crystals was studied from 1.8 to 300 K in a static magnetic field of 0.1 T using a commercial SQUID magnetometer (Fig. 2). The single crystals were glued to weighing paper, using clear fingernail polish, before being placed in a gelcap which was held in a straw. Although we could not measure the background of this system independently, a similar arrangement was constructed, sans sample, and measured. This background contribution has been subtracted from the data reported in Fig. 2, where the data points at 300 K are independent of orientation and are normalized to the average value measured on powdered specimens, weighing nominally 30 mg. The normalization was preformed to correct for a small discrepancy between the measured and actual backgrounds. Ultimately, our $\chi(T = 300\ \mathrm{K})$ value is consistent with the one reported previously [19].

The $\chi(T)$ results (Fig. 2) show a broad peak near 100 K, anisotropy for $T < 80$ K, a strong upturn at the lowest temperatures, but no indication of long-range order. While the broad peak is the expected behavior for linear chain Heisenberg antiferromagnets, the Curie-like increase at low temperatures may be associated with impurities. The anisotropy is such that $\chi_{\perp} > \chi_{\parallel}$, which is in contrast to the Cr^{2+} compounds [17,18] where $\chi_{\perp} < \chi_{\parallel}$. Since no explicit expressions exist for $\chi(T)$ of an $S = 2$ linear chain Heisenberg antiferromagnet over a broad temperature range that include anisotropy terms, we have fit the data of Fig. 2 by

$$\chi(T) = \chi(0) + \frac{C}{T} + \chi_{\mathrm{LCHA}}(S = 2, g, J, T), \quad (2)$$

where $\chi_{\mathrm{LCHA}}(S = 2, g, J, T)$ represents the $S = 2$ linear chain Heisenberg antiferromagnetic calculations of Weng [24], as parametrized by Hiller *et al.* [25]. Since the expression for $\chi_{\mathrm{LCHA}}(S = 2, g, J, T)$ is not expected to be valid when significant anisotropy is present or in a region where a gapped phase might exist (i.e., $T < J$), the fitting procedure focused primarily on the region $T > 80$ K, with the exception that the Curie constant C was adjusted to the low temperature data. The results of the fit, shown by the solid line in Fig. 2, yield $\chi(0) = 0.0 \pm 0.5$ memu/mol, $C = 47.5 \pm 0.5$ memu K/mol, $J = 34.8 \pm 1.6$ K, and $g = 2.04 \pm 0.04$. The Curie constant could be explained by a small concentration of impurity spins. However, we want to be careful about making this assignment and trying to subtract this "Curie tail." For example, as previously mentioned, we know that $\chi_{\mathrm{LCHA}}(S = 2, g, J, T)$ is an inadequate description of $\chi(T)$ in this region. Nevertheless, it is noteworthy that various attempts to subtract a reasonable Curie-like contribution always give $\chi(T) \to 0$ as $T \to 0$. To further explore the nature of the magnetic signal at the lowest temperatures, standard 9 GHz ESR

was performed on a packet of five oriented crystals from 4 to 60 K. The observed signal is consistent with a concentration of approximately $(0.05 \pm 0.03)\%$ Mn^{2+} spins ($S = 5/2$, $g = 2$) that follow a Curie temperature dependence. The signal may also contain contributions from trace amounts (at the ppm level) of $S = 3/2$ and $S = 1/2$ extrinsic impurities. However, since the concentration of ESR visible spins is more than an order of magnitude smaller than needed to explain the static susceptibility data, we consider isolated Mn^{3+} ions not in the chain environment and $S = 1$ end-chain spins [13,15] as the most likely source of the low temperature behavior.

Using a single crystal Si cantilever magnetometer [26] mounted in the mixing chamber of a commercial dilution refrigerator, the magnetization of several different single crystals has been studied at 30 ± 5 mK and 1.4 ± 0.2 K in magnetic fields up to 16 T. Typical results at 30 mK are shown in Fig. 3, where the data were taken on two single crystals with approximate mass of 200 μg. A weak temperature independent diamagnetic background and a small constant magnetization consistent with the saturation of impurity spins have been subtracted [27]. The two crystals were held together on the cantilever using a trace amount of vacuum grease. The data taken at 1.4 K are consistent with the results reported in Fig. 2 and magnetization data taken at 2 K with the SQUID magnetometer to be detailed elsewhere. The results at 30 mK (Fig. 3) clearly indicate the presence of a nonmagnetic state at the lowest fields, and the continuous onset of a magnetic state for fields above a critical field, H_c, which depends on crystal orientation, namely, $H_{c\|} = 1.2 \pm 0.2$ T and $H_{c\perp} = 1.8 \pm 0.2$ T. Furthermore, no discontinuities, hysteresis, or other unexplainable anomalies [27] were observed in M vs H traces up to 16 T at either 30 mK (inset of Fig. 3) or 1.4 K.

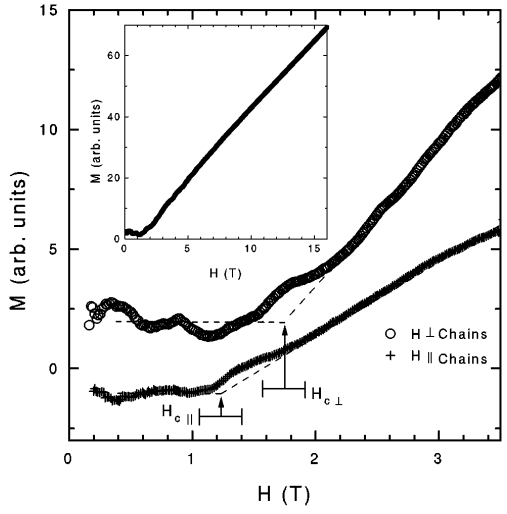

FIG. 3. $M(H)$ at 30 mK for the field applied perpendicular (O) and parallel (+) to the chains of two single crystals with total mass $\approx$200 μg, where both traces are offset vertically from zero for clarity. The arrows identify $H_{c\perp}$ and $H_{c\|}$ with their respective uncertainties. The inset shows a more complete view of the $H\perp$ chain data.

These results indicate no evidence for three-dimensional long-range magnetic order to 30 mK, where either hysteresis or a spin-flop transition should have been detectable. In addition, the presence of a critical field, marking a transition from a nonmagnetic to a magnetic state, for both crystal orientations is incompatible with the existence of long-range order or the presence of a gapless phase [15]. Consequently, the spins are in either a Haldane or large D/J phase. However, as discussed earlier, the crystal structure indicates that the single-ion anisotropy should be small compared to J. Ergo, we conclude the critical fields are related to a Haldane gap, where anisotropy in H_c is related to a small $D \neq 0$ [Eq. (1)]. For the present discussion, we will assume any rhombic anisotropy [i.e., the last term in Eq. (1)] to be negligible, and we follow the type of analysis that has been applied successfully to NENP [11,28]. In other words, for $D = 0$, the singlet ground state is separated from the first excited states, which form a degenerate triplet, by the Haldane gap $\Delta_{S=2}$ (Fig. 4). The presence of $D \neq 0$ causes the singlet ground state to shift and the triplet to split, with the estimates of the resultant energy gaps given by $\Delta_\perp = \Delta_{S=2} - 2D$ and $\Delta_\| = \Delta_{S=2} + 4D$ as shown in Fig. 4 [28]. Finally, application of an external magnetic field causes the $|1, \pm 1\rangle$ state to split, where the $|1, -1\rangle$ level crosses the ground state at a critical magnetic field given by $g_\| \mu_B H_{c\|} = \Delta_\perp$ and $g_\perp \mu_B H_{c\perp} = \sqrt{\Delta_\perp \Delta_\|}$ [28,29]. Taking $g_\|$ and $g_\perp = 2.04 \pm 0.04$, we obtain $D = 0.3 \pm 0.1$ K and $\Delta_{S=2} = 2.3 \pm 0.8$ K. With these values and $J = 34.8 \pm 1.6$ K, we may obtain $D/J = 0.010 \pm 0.003$ and $\Delta_{S=2}/J = 0.07 \pm 0.02$, which agree well with the numerical work [12–16]. It is interesting to note the sign of D, obtained from the analysis of the critical fields, conflicts with the sign predicted by the crystal structure. However, both the numerical work and this experimental estimate should include an E term. In addition, the quasilinear (i.e., "corrugated") nature of the Mn chains (Fig. 1) may generate additional energy shifts and magnetic field dependences [30,31]. Finally, we comment that these additional effects may give rise to the anisotropy in $\chi(T < 80$ K), see Fig. 2, which remains unexplained.

In summary, our magnetic studies of the $S = 2$ quasi-linear-chain Heisenberg antiferromagnetic system $MnCl_3$(bipy) indicate the absence of any long-range order down to 30 mK. At the same time no magnetization is observed at 30 mK until a critical magnetic field is achieved in either orientation ($H_{c\|} = 1.2 \pm 0.2$ T and $H_{c\perp} = 1.8 \pm 0.2$ T), after which a net magnetization evolves continuously as the field is increased. These results are interpreted as evidence of a Haldane gap $\Delta_{S=2}$ and indicate experimentally that $\Delta_{S=2}/J = 0.07 \pm 0.02$, which is in good agreement with the numerical results.

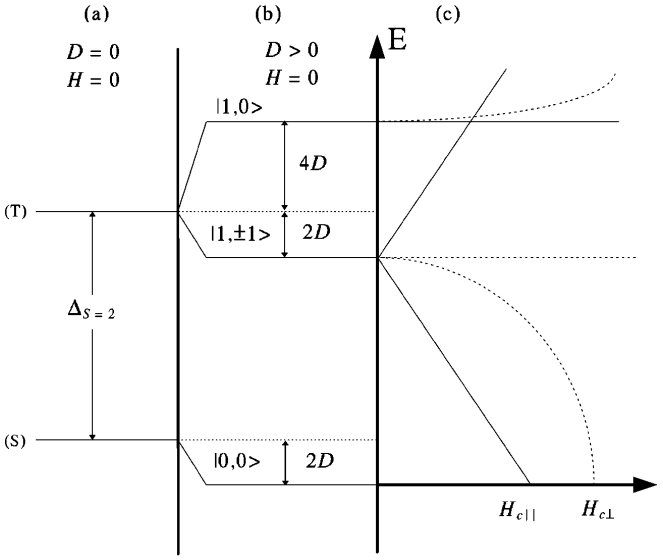

FIG. 4. The energy levels for the singlet (S) ground state and the first excited triplet (T) state are shown schematically for $E = 0$ [Eq. (1)]: (a) for $D = 0$ and (b) for $D > 0$. In (c), the horizontal axis is the externally applied magnetic field. The field dependence of the states are shown schematically for $H\|$ chains (solid lines) and $H\perp$ chains (broken lines). The crossing of the $|1, -1\rangle$ triplet state with the singlet ground state defines H_c.

Additional experiments are needed to clarify the gap values and to understand the detailed role of the anisotropy present in this system.

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