Polyhedron 29 (2010) 2462–2464

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Pressure dependence of the magnetization in Mn_7 single-molecule magnets

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ARTICLE INFO

Article history:
Received 5 February 2010
Accepted 19 May 2010
Available online 27 May 2010

Keywords:
Pressure dependence
Single-molecule magnet
Magnetism

ABSTRACT

Single-molecule magnet (SMM) clusters of Mn_7 can have ground states of $S = 11$ or $S = 16$, depending upon the local symmetry of the clusters. The possibility of inducing a switching of the spin ground state configuration as a function of pressure was investigated by measuring the temperature dependence of the magnetic susceptibility, $\chi_M(3\ K \leqslant T \leqslant 40\ K)$, using a home-made resonant coil magnetometer operated near 6 MHz and equipped with a pressure cell capable of producing $P \lesssim 2.5$ GPa. The results indicate the ground states of both materials are robust in the temperature–pressure–frequency parameter space that was probed.

1. Introduction

Functional materials that change electronic states with the application of external stimuli are being actively researched due to their technological implications. While there are numerous examples of materials that change their magnetic moment under light, pressure, or thermal treatment [1], as well as studies of single-molecule magnets (SMMs) under pressure [2–4], to date there are no reports of switching the net ground state magnetic moment of SMMs with pressure. Such SMMs having a large ground state spin have been shown to be of great interest for both fundamental and applied scientific research [5,6].

Recently, Stamatatos et al. reported that disk-like clusters of Mn_7 can have either $S = 11$ or $S = 16$ ground states, depending upon the local symmetry of the magnetic molecules [7,8]. For these Mn_7 clusters (Fig. 1), the six circumferential spins are all coupled ferromagnetically, but the central spin has alternating ferromagnetic and antiferromagnetic superexchange interactions with the exterior spins as the hexagram is traversed, giving rise to the sensitivity of the ground state to structural perturbations.

Since changes to the central spin orientation were previously induced by modifying the geometry with different ligands [7,8], we hypothesized that external mechanical stress might yield a similar result. Presently, we have seen no clear changes in magnetization with the application of pressures up to 2.3 GPa over a temperature range of $3\ K \leqslant T \leqslant 40\ K$ while using a resonant coil operating near 6 MHz. Herein we report the methodology of the high pressure magnetization studies, as well as data from the Mn_7 clusters as a function pressure.

2. Experimental details

2.1. Synthesis and characterization

The powder samples were made using the same procedure as reported by Stamatatos et al. [7,8]. The $S = 11$ material, $[Na(MeOH)_3][Mn_7(N_3)_6(mda)_6]_n$ (**1**), was produced by reacting $Mn(ClO_4)_2 \cdot 6H_2O$, N-methyldiethanolamine ($mdaH_2$), NaN_3, and NEt_3 in a 1:2:1:2 molar ratio in N,N-dimethylformamide (DMF)/MeOH to give a dark-red solution that, upon layering with Et_2O, gave dark-red crystals of $S = 11$ powder. Using a similar preparative procedure, but employing triethanolamine ($teaH_3$) instead of $mdaH_2$, gave the $S = 16$ compound $Na[Mn_7(N_3)_6(teaH)_6]_n$ (**2**).

2.2. Magnetic measurements

Using Stycast 1266 epoxy, powder samples were sealed in 2.5 mm diameter × 4.3 mm long detector coils wound using 63.5 μm diameter copper wire. A single coil-sample ensemble was mounted in a high pressure, self-clamping piston cell [9] using a 50/50 mixture of isoamyl alcohol (ACS reagent grade) and 99+% *n*-pentane as the pressure medium. The hydrostatic pressures were calibrated at room temperature, although slight variations in pressure can occur at low temperature [9,10]. The superconducting transition of Pb [11] was measured to verify the protocol resulted in pressure being reproducibly applied to the coil-sample ensemble.

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doi:10.1016/j.poly.2010.05.013

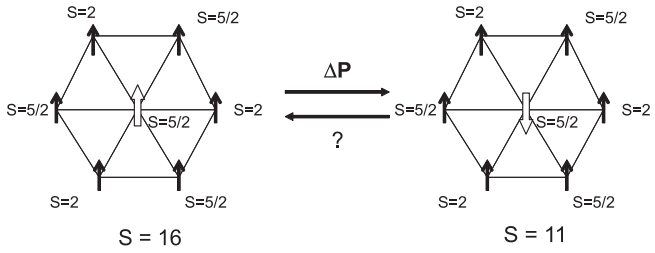

Fig. 1. Schematic of the hypothesized ground state switching of the Mn_7 SMM with changes in pressure. The central spin has both ferromagnetic and antiferromagnetic coupling to the external spins, making the relative orientation susceptible to subtle changes in the geometry of the molecule.

Previously, the coils were used as elements of tank circuits whose resonances were driven by tunnel diode oscillators [12]; however, due to the delicate nature of this arrangement, a different approach was employed. For the present work, the detector coils were connected to an HP 8712C RF Network Analyzer to track the ~ 6 MHz resonance of the detector circuit while warming from 3 K to room temperature at ~0.5 K/min, from which we can extract the inductance and magnetic susceptibility. While it is possible to model the shape of the resonant peak in addition to the position, we chose the more conservative approach of only the latter due to the co-dependence of important circuit variables, as described in Appendix A.

3. Results and discussion

The results of the inductance measurements for Mn_7 ($S = 16$) (**2**) as a function of pressure are shown in Fig. 2. Changes in the inductance are clearly observed and can be assigned to the magnetic susceptibility of the sample, however no changes were seen with the application of pressure up to ~ 2.3 GPa. A similar null result as a function of pressure up to ~ 1.0 GPa was observed for the inductance measurements of Mn_7 ($S = 11$) (**1**), Fig. 3. In both cases, small

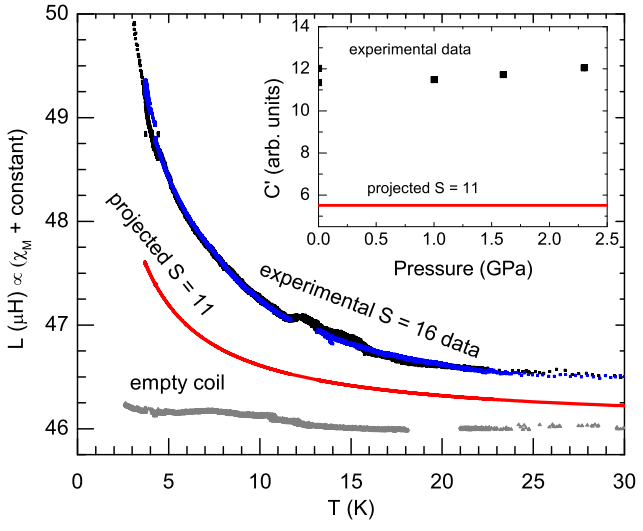

Fig. 2. Temperature dependence of the inductance as a function of pressure for the Mn_7 ($S = 16$) (**2**) powder. Chronologically, pressures of ~ 0.0 GPa, ~ 1.0 GPa, ~ 1.6 GPa, ~ 2.3 GPa, and again at ~ 0.0 GPa were applied. Only the data for the initial 0 GPa (black) and 2.3 GPa (blue) runs are shown, as all other data traces are indistinguishably different for the scale used in this figure. The data for the empty coil are shown along with the projected response if the sample was fully switched to an $S = 11$ state. The Curie constants extracted from fitting the data to a Curie law are shown in the inset. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

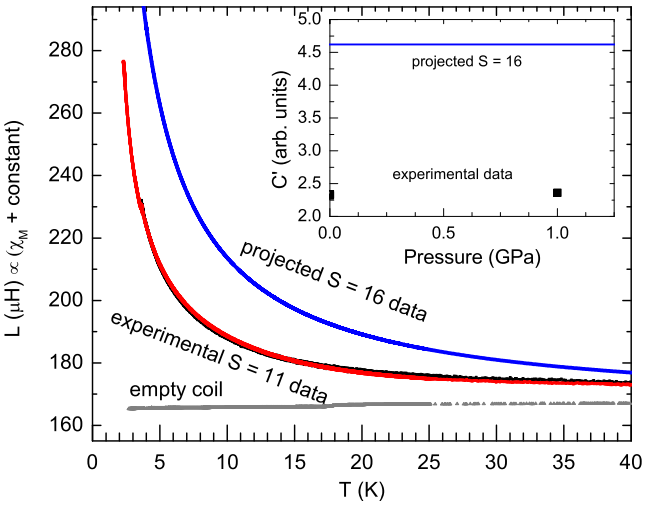

Fig. 3. Temperature dependence of the inductance as a function of pressure for the Mn_7 ($S = 11$) (**1**) powder. Chronologically, pressures of ~ 0.0 GPa, ~ 1.0 GPa, and again at ~ 0.0 GPa were applied. Only the data for the initial 0 GPa (black) and 1 GPa (red) are shown, as the data from the second 0 GPa run are indistinguishably different for the scale used in this figure. The data for the empty coil are shown along with the projected response if the sample was fully switched to an $S = 16$ state. The Curie constants extracted from fitting the data to a Curie law are shown in the inset. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

constant shifts of the inductance (~ 0.1 μH) resulting from perturbations of the circuit geometry have already been included for self-consistency where magnetic contributions are not detectable.

Although the high pressure magnetometer developed for these experiments detected signals associated with the sample, no changes in the magnetic susceptibility due to the application of hydrostatic pressures were observed for either of the two Mn_7 clusters studied. These observations indicate the Mn_7 SMM ground states of (**1**) and (**2**) are robust in the temperature–pressure–frequency parameter space that was probed. Future studies using low frequency devices, such as SQUID-amplified magnetometers, and higher pressures may be warranted.

Acknowledgements

This work was supported, in part, by the National Science Foundation (NSF) via DMR-0701400 (MWM), CHE-0414555 and CHE-0910472 (GC), the National High Magnetic Field Laboratory (NHMFL) by a cooperative agreement connecting DMR-0654118 and the State of Florida, and the Research Experiences for Undergraduates (REU) Programs operated by the NHMFL and the UF Department of Physics, DMR-0851707. We also thank the UF Physics Instrument Shop for help with machining the pressure cell.

Appendix A. Analysis of resonant signal

The model for the magnetometer is an *RLC* circuit, where the simplest possible network that captures the character of the circuit has been chosen, Fig. A.1. A simple expression for the impedance magnitude of this circuit is

$$Z = \sqrt{\frac{\left(R^2 + (\omega L)^2\right)\left(\frac{1}{\omega C}\right)^2}{R^2 + \left(\omega L - \frac{1}{\omega C}\right)^2}} + \mathscr{A}\omega + \mathscr{B}, \tag{A.1}$$

where R is the resistance, L is the inductance, C is the capacitance, ω is the angular frequency, $\mathscr{A}$ is a linear background term, and $\mathscr{B}$ is a constant background term. The inductance, L, is assumed to have

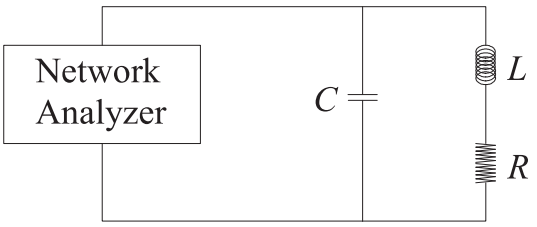

Fig. A.1. Circuit used for the analysis of the resonant response.

two contributions: the actual detector coil, L_{detector}, and an effective inductance coming from the coaxial cable and the rest of the circuit, L_{other}. Using Faraday's law for an ideal solenoid to find L_{detector}, the expression for the inductance can be written as

$$L = \mu_o(1\chi_M)N^2\frac{A}{\ell} + L_{\text{other}}, \tag{A.2}$$

where μ_o is the permittivity of free space, χ_M is the magnetic susceptibility of the sample, N is the number of turns in the coil, A is the cross-sectional area, and ℓ is the length of the coil. This equation can be rewritten as

$$L = A_{\text{cal}}\chi_M(T) + L_{\text{constant}}, \tag{A.3}$$

where A_{cal} is a calibration factor, L_{constant} contains both L_{other} and the temperature independent inductance of the coil, and the temperature dependences of the variables for the region of interest have been explicitly identified. In other words, only χ_M has an appreciable temperature dependence for $3\text{ K} \leqslant T \leqslant 40\text{ K}$. It is noteworthy that uncalibrated coils can still measure the susceptibility, but only in arbitrary units. The apparatus and analysis were tested by investigating the temperature dependence of the magnetic response of gadolinium sulfate octahydrate, $Gd_2(SO_4)_3{\cdot}8H_2O$ [13].

Although weak intermolecular interactions, small zero-field splittings, and other effects are present, the SQUID magnetometer $\chi_M(T \geqslant 2\text{ K})$ data of the Mn_7 materials [7,8][1] indicate that, to first order, the magnetic response of both (**1**) and (**2**) can be fit to a Curie Law, namely

$$L = \frac{C'}{T} + L_{\text{constant}}, \tag{A.4}$$

where ratios of C' for different pressures can be taken in order to detect changes of angular momentum in the sample. Independent of other effects, a change in the spin state from $S = 11$ to $S = 16$, or *vice versa*, will result in a clear change in the Curie-like contribution, and the magnitude of the resulting changes of inductance of the detection coil are within the resolution of the magnetometer.

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