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Ferromagnetic Ordering and Simultaneous Fast Magnetization Tunneling in a Ni_4 Single-Molecule Magnet

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Low-temperature heat capacity and oriented single-crystal field-cooled and zero-field-cooled magnetization data for the single-molecule magnet $[\mathrm{Ni(hmp)(dmb)Cl}]_4$ are presented that indicate the presence of ferromagnetic ordering at ~300 mK, which has little effect on the magnetization relaxation rates.

The discovery of single-molecule magnets (SMMs) has allowed for a detailed study of quantum effects such as ground-state tunneling of the direction of magnetization,[1−3] exchange bias,[4,5] and spin−spin cross-relaxation effects[6] associated with nanomagnetic materials. This is due to the fact that SMMs are monodisperse in nature (i.e., they have the same size, shape, and anisotropy).[7,8] A SMM can be magnetized as a result of having a large spin ground state (S) that experiences considerable Ising-type axial magnetoanisotropy (D), giving rise to a potential energy barrier ($|D|S_z^2$) between the "spin-up" and "spin-down" states.[7−10]

SMMs have been proposed as potential candidates for quantum computation. However, one of the major challenges in implementing these molecular systems is the ability to control tunneling decoherence below the blocking temperature (T_B) of a SMM. Spin decoherence arises from a number of sources including nuclear hyperfine interactions, intermolecular dipolar interactions, spin−spin relaxation, and magnetic ordering. Magnetic ordering has been observed in a number of molecular nanomagnets[11−13] and has been shown to strongly affect tunneling rates and observed magnetic behavior.

Specific heat measurements are an invaluable tool for studying the physical properties of crystalline materials. The heat capacity is extremely sensitive to crystallographic and magnetic phase transitions and can lead to insight regarding long- and short-range ordering and the nature of the ordering. One difficulty in employing the heat capacity to study SMMs is that these complicated molecules (many atoms) make it difficult to separate the magnetic portion of the heat capacity from the lattice contribution. Even at low temperatures (< 1 K), lattice and Schottky contributions can be appreciable.

Here we present the heat capacity and oriented single-crystal magnetization hysteresis data for $[\mathrm{Ni(hmp)(dmb)Cl}]_4$ ($\mathrm{Ni_4^{dmb}}$),[5,14] where hmp^- is the anion of 2-(hydroxymethyl)pyridine and dmb is 3,3′-dimethyl-1-butanol, which show that this interesting system displays both ferromagnetic ordering and fast magnetization tunneling below its blocking

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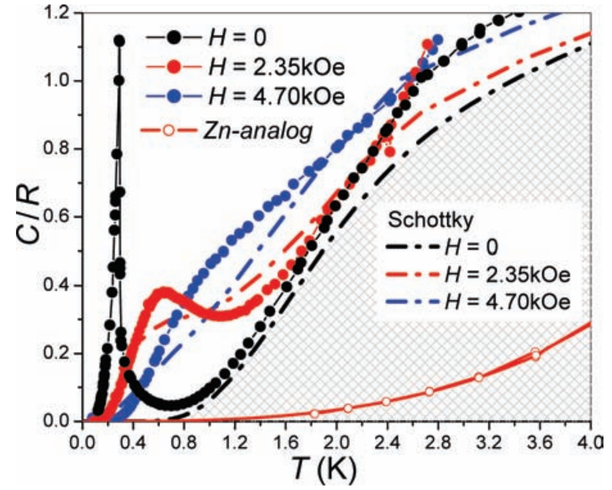

Figure 1. C_p vs T plot for $[Ni(hmp)(dmb)Cl]_4$ in a zero applied field and with applied fields of 2.35 and 4.70 kOe, with calculated Schottky distributions.

temperature. Ni_4^{dmb} is an attractive system for several reasons. First, the Ni_4^{dmb} molecule crystallizes in the high-symmetry $I4_1/a$ tetragonal space group with only one crystallographically independent molecule in the unit cell with S_4 site symmetry. Second, the large aliphatic substituent on the dmb alcohol ligand provides substantial electronic insulation between neighboring Ni_4^{dmb} molecules. Third, there are no solvate molecules in the crystal. Solvate disorder has been shown to give rise to microenvironments within the crystal lattice that can detrimentally impact the ability to precisely interpret experimental data.

Figure 1 displays polycrystalline heat capacity $[C_p(T)]$ data for Ni_4^{dmb} with applied magnetic fields of 0, 2.35, and 4.70 kOe in the temperature range 0.04−4.5 K. A very sharp λ peak is clearly evident in the H = 0 trace at ~300 mK, corresponding well to transitions previously reported for alternating-current (ac) and direct-current (dc) magnetic measurements.[5,14,15] The phase transition in the heat capacity disappears when a magnetic field is applied, indicating a Zeeman energy larger than the ordering energy. As shown below, we find the ordering to vanish with applied magnetic field values over ~170 Oe.

To isolate the magnetic portion of the heat capacity, the lattice contribution of the heat capacity was evaluated by subtraction of the heat capacity data collected for the analogous diamagnetic Zn_4^{dmb} complex (Figure S1 in the Supporting Information) and the Schottky contribution was calculated from single-molecule spin levels simulated based on the spin Hamiltonian parameters extracted from magnetic data (Figures S2 and S3 in the Supporting Information). Essentially, the lattice energy at very low temperatures is negligible because the number of available phonon modes is significantly quenched. Also, the Schottky data suggest that only the ground state (M_s = ±4) is populated in the temperature range of the phase transition, and thus the observed peak in the zero-field C_p vs T data below 0.7 K is attributable to the ground-state doublet.

The magnetic entropy gain was evaluated by integrating $H = 0$ C_p data with respect to ln T below T_c (0−0.7 K; Figure S4 in the Supporting Information). The resulting calculation yielded a value of ~0.38R, which is less than the expected value of $R\ln(2) = 0.69R$ for an $S = 4$ spin system in its $M_s = \pm 4$ ground state (R = gas constant). The small value of ΔS = 0.38R, below T_c, arises because of the low coordination number (z = 4) of the crystal diamond structure and spin frustration characteristic of dipolar Ising systems, which in conjunction prevent easy attainment of the ferromagnetic 3D long-range ordering.

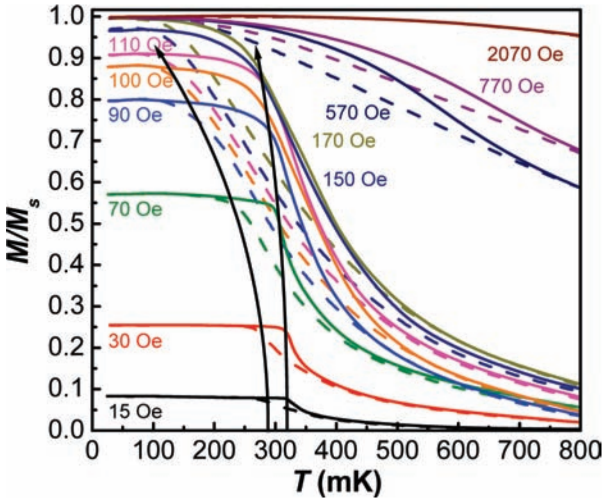

Figure 2. ZFC (continuous lines) and FC (dashed lines) magnetization curves for different magnetic field values (from 15 to 2070 Oe) in the temperature range 20−800 mK. The sharp transition at ~300 mK corresponds to ferromagnetic coupling due to intermolecular exchange interactions.

In order to study more closely the field effects on the ferromagnetic ordering in the system, oriented single-crystal magnetization measurements were performed. Zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves collected with applied magnetic fields of 15−2070 Oe along the easy magnetic axis are presented in Figure 2. The sample was cooled from 1 K down to 20 mK in the absence of an applied field (ZFC). A longitudinal magnetic field is then applied, and the temperature is raised to 1 K again at a rate of ~3 K/min (continuous lines in Figure 2). When the same applied field is maintained, the temperature is then cycled back down to 20 mK (FC; dashed lines in Figure 2). In the measurement obtained with an applied magnetic field of H = 15 Oe (black curves in Figure 2), the results reveal that, immediately after application of the applied field, the sample reaches a finite magnetization value that remains constant until the temperature reaches a critical value of $T_c \sim 300$ mK. At higher temperatures, the magnetization decreases inversely proportional to the temperature, $M = f(1/T)$ (superparamagnetic regime), indicative of ferromagnetic ordering, with a transition temperature that is in very good agreement with the specific heat measurements and previous ac and dc magnetization measurements.[5,14,15] We associate the observed hysteretic behavior between the ZFC and FC measurements with different distributions of dipolar fields felt by the molecules during the two processes. The distribution is broader in the FC process because of temperature-mediated disorder within the system. As a consequence, fewer molecules lie within the tunneling window and, thus, the tunneling-mediated ordering process is lengthened. Conversely, in the ZFC case, the individual magnetic moments are fully polarized as the system approaches the transition temperature. The ferromagnetic ordering transition is broadened and

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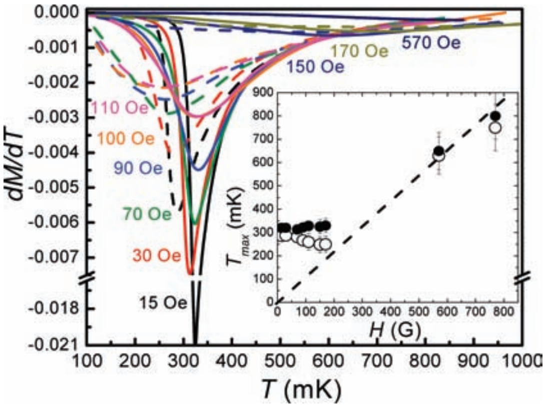

Figure 3. Derivatives of the ZFC (continues lines) and FC (dashed lines) magnetization curves presented in Figure 2. The inset shows the behavior of the temperature of the peak as a function of the applied field. The plateau below 170 Oe is associated with a ferromagnetic ordering of the molecular spins within the sample below ~300 mK.

shifted to lower temperatures by application of successively larger longitudinal magnetic fields and is completely eliminated in fields greater than ~170 Oe, when the Zeeman interaction energy becomes greater than the intermolecular coupling energy. This is clearly observed in Figure 3, where the temperature derivatives of the ZFC and FC magnetization curves are presented. The inset shows the behavior of the transition temperature as a function of the applied field. The plateau below ~170 Oe represents the critical temperature of the ferromagnetic transition (~300 mK). Interestingly, the ferromagnetic ordering in this regime is promoted by the fast quantum tunneling relaxation rate exhibited by Ni_4^{dmb}.[5] Note that, in an ordered system, coupled molecules are expected to tunnel simultaneously. The statistical probability of this occurring is much less than that for a single-molecule tunneling because of greater *inertia* and, thus, should drastically reduce tunneling relaxation rates. However, the tunneling rates[5] in this system seem relatively unaffected by the ferromagnetic ordering event.

The single-molecule tunneling window is principally governed by the magnitude of the tunnel splitting associated with the quantum superposition between opposite-spin projections ("spin-up" and "spin-down") and can be modulated by application of a magnetic field. The energy associated with tunneling windows for individual molecules can be significantly affected by intermolecular interactions, thus decreasing the number of molecules available for tunneling. This should lead to a significant reduction of the relaxation rates. However, phonon-mediated tunneling transitions between the ground spin states of the molecules could account for the elevated tunneling rates observed in this ordered system. This could occur even if molecules are out of the tunneling window due to exchange-bias effects. *Direct* phonon-mediated transitions between the $M_s = \pm4$ states will have a high probability in the Ni_4 system because of its low spin ($S = 4$) and intrinsic fourth-order transverse anisotropy (i.e., $S_+^4 + S_-^4$), which is imposed by tetragonal crystal symmetry and facilitates phonon transitions between M_s states differing by multiples of ±4. In addition, when the wavelength of the generated phonons is larger than the separation between molecules, molecules can simultaneously relax, accompanied by a coherent emission of phonons.[16] This may explain the high relaxation rates observed in this system. Note that the observation of an *increase* in the relaxation rates due to *collective* photon-mediated processes has been previously suggested.[17,18]

The Ni_4^{dmb} complex has proven be a benchmark system and has been paramount to the study of SMMs because of its unique physical properties. The long-range ferromagnetic ordering in this system appears to have little effect on the exhibited tunneling rates. As stated above, magnetic ordering, in conjunction with fast magnetization tunneling, is counterintuitive. In an attempt to better understand the exhibited physical properties of this system, we have initialized more in-depth single-crystal magnetization studies to probe the field and temperature dependences of the magnetic ordering and magnetization tunneling rates. Furthermore, we have initiated in-depth heat capacity and single-crystal magnetization studies on a series of Ni_4 SMMs that differ in their peripheral alcohol ligand. It has been shown that changing the peripheral ligands in the Ni_4 series of molecules modulates ordering temperatures and the nature of the ordering (i.e., antiferromagnetic or ferromagnetic) and has a significant effect on the tunneling rates. It is our hope that, in studying this interesting series of Ni_4 SMMs, we may shed new light on the study of SMMs and their exhibited quantum behavior.

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Supporting Information Available: Additional heat capacity and magnetization data. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 749872 contains crystallographic data that can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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