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Quantum fluctuations and long-range order in molecular magnets

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ABSTRACT

We review our studies of the effect of transverse fields on the susceptibility and magnetization of single crystals of the prototype single molecule magnet (SMM), Mn_{12}-acetate, and of a new high-symmetry variant, Mn_{12}-acetate–MeOH. SMM single crystals can exhibit long range ferromagnetic order associated with intermolecular dipole interactions. Transverse fields increase quantum spin fluctuation and quantum tunneling of the magnetization suppressing long range order. However, we have found that suppression of the Curie temperature by a transverse field in Mn_{12}-acetate is far more rapid than predicted by the Transverse-Field Ising Ferromagnetic Model (TFIFM). It appears that solvent disorder in Mn_{12}-acetate that results in an intrinsic distribution of small discrete tilts of the molecular magnetic easy axis from the global easy axis of the crystal ($\approx \pm 1°$) gives rise to a distribution of random-fields that further suppresses long-range order. Semiquantitative agreement with the predictions of a Random-Field Ising Ferromagnet Model is found. Subsequent susceptibility studies we have conducted of the high symmetry Mn_{12} variant, Mn_{12}-acetate–MeOH, with the same spin structure and similar lattice constants but without the same solvent disorder as Mn_{12}-acetate, agrees with the TFIFM. An important implication of our studies is that long-range order in these two chemically very similar SMMs are described by distinct physical models.

1. Introduction

The single molecule magnets (SMMs) are metalorganic compounds composed of transition-metal ions and organic ligand molecules. At low temperature, each molecule has a large ground-state spin and a strong uniaxial anisotropy, leading to Ising-like behavior, with its spin oriented either up or down along the easy axis. The molecules form van der Waals crystals and the intermolecular exchange interactions between molecules are typically quite small. This has led to the commonly used approximation that the large spins on each molecule are independent and do not interact with one another. Indeed, much of early research on SMMs did not consider intermolecular interactions or collective phenomena. Such studies include the famous observation of quantum tunneling of magnetization in Mn_{12}-acetate [1], and the study of Berry phase oscillations in Fe_8 [2]. However, the molecules do interact with each other and the dominant interaction is often magnetic dipolar interaction and, while the strength of the intermolecular dipole interactions is much less than the scale of the anisotropy energy of the molecules, there are quite notable effects of intermolecular interactions. This has lead to a renewed interest in studies of collective phenomena due to dipolar interactions in SMM single crystals [3–6].

For spins on an ordered lattice, dipolar interactions lead to long range order with a ferromagnetic or antiferromagnetic ground state that depends on the lattice structure and sample shape. In several SMMs, finite temperature transitions to a dipolar ferromagnetic state have been observed or predicted theoretically [3,7–12]. In Mn_{12}-acetate, a transition to dipolar ferromagnetism was inferred from neutron scattering experiments by Luis et al. [3]. This finding was supported by Monte Carlo simulations [11]. Calculations based on the Mean Field Approximation (MFA) by Garanin and Chudnovsky [12] and Millis et al. [9] have predicted the existence of an ordered state in elongated crystals of Mn_{12}-acetate at low temperature. Our measurements of the longitudinal magnetization and susceptibility of Mn_{12}-acetate are consistent with the occurrence of a transition to dipolar ferromagnetism at finite temperature [4]. In our experiments we apply transverse fields to induce quantum fluctuations (i.e. increase the rate of quantum tunneling of magnetization) and study the interplay between intermolecular interactions and quantum fluctuations by observing the field dependence of the magnetic susceptibility [4,6].

In this article we review our experimental and theoretical studies of interactions and long-range order in molecular magnets. In Section 2, we introduce the molecular magnets that we study. In Sec-

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tion 3 we discuss our experimental setup and results. In the following section we present our theoretical model. In Section 5 we present a comparison between theoretical calculations and experimental data. And, finally, we present our conclusions and perspectives.

2. Single molecule magnets

2.1. Mn_{12}-acetate

One of most studied SMMs is Mn_{12}-acetate, $[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4] \cdot 2CH_3CO_2H \cdot 4H_2O$. Each Mn_{12} molecule behaves as a nanomagnet with spin $S = 10$ oriented along the crystallographic c axis by a strong uniaxial magnetic anisotropy $DS^2 = 65$ K, where D is the first order uniaxial anisotropy constant. Mn_{12}-acetate crystallizes in a body centered tetragonal lattice (space group $I\bar{4}$) with unit cell parameters at 83 K of $a = b = 17.1668(3)$ Å, $c = 12.2545(3)$ Å, molecules per unit cell $(Z) = 2$, $V = 3611.39$ Å^3 [13]. The magnetic centers are well separated by the organic ligands and intermolecular exchange is small compared to the intermolecular magnetic dipole interactions [14], $E_{dip} = (g\mu_B)^2S^2/(a^2c) \sim 0.08$ K, which is one order of magnitude larger than intramolecular hyperfine interactions. In the absence of applied fields, magnetic ordering with a Curie temperature of about 0.9 K [12,9] has been predicted.

2.2. Mn_{12}-acetate–MeOH

Mn_{12}-ac–MeOH, $[Mn_{12}O_{12}(O_2CMe)_{16}(MeOH)_4] \cdot MeOH$, is a new high-symmetry variant of the original SMM Mn_{12}-ac. Each molecule in Mn_{12}-ac–MeOH has the same ground state spin of $S = 10$ and similar anisotropy of $DS^2 = 66.7$ K as the molecules in original Mn_{12}-ac. Mn_{12}-ac–MeOH also crystallizes in the space group $I\bar{4}$ with unit cell parameters at 173 K of $a = b = 17.3500(18)$ Å, $c = 11.9971(17)$ Å, $Z = 2$, $V = 3611.4$ Å^3. [15–17]. All the parameters are nearly identical to Mn_{12}-acetate.

Although the two compounds have similar lattice parameters, spin and anisotropy, there are some crucial differences relevant to this study, which originate from the organic ligand and solvent molecules that form the local molecular environment. In Mn_{12}-ac–MeOH, the four terminal water molecules of Mn_{12}-ac are replaced by terminal methanol molecules, the two acetic acid and four water solvent molecules are replaced by only one methanol that resides on a symmetry element making the overall structure highly symmetric and leading the crystal to retain the molecular S_4 symmetry [16]. In a perfect crystal, every molecule's easy axis lies along the crystal c-axis. However, in Mn_{12}-ac, each molecule is surrounded by four acetic acid solvent molecules. Each acetic acid can form only one OH···O hydrogen-bond with the two Mn_{12} molecules it lies between. Thus each Mn_{12} molecule can have n $(n = 0 - 4)$ hydrogen-bonds around it, which results in six different isomers [18], and three different easy axis tilts (the molecules easy-axis forms an angle with the crystal c-axis). So although the molecule itself has S_4 symmetry, the Mn_{12}-ac does not retain this symmetry in a crystal. As explained in detail later, in the absence of an applied magnetic field these small tilts of the magnetic easy axis of Mn_{12}-ac molecules have negligible effect on the magnetic properties. However, when a field is applied these small tilts can play an important role.

3. Experiment

3.1. Sample preparation and measurement techniques

Measurements of the longitudinal magnetization and susceptibility were performed on three Mn_{12}-ac–MeOH single crystals of dimensions $\sim 0.2 \times 0.2 \times 0.95$ mm^3, $0.085 \times 0.085 \times 0.68$ mm^3, and $0.075 \times 0.075 \times 0.85$ mm^3 (samples A, B and C, respectively) and three Mn_{12}-ac crystals of dimensions $\sim 0.4 \times 0.4 \times 2.17$ mm^3, $\sim 0.4 \times 0.4 \times 2.4$ mm^3 and $0.3 \times 0.3 \times 1.85$ mm^3 (crystals D, E and F, respectively). Details on sample preparation and handling are described on Refs. [4,6]. A Hall sensor, (active area 20×100 μm^2) was placed at the end of the crystal and used to measure the magnetization, M_z, along the easy direction (c-axis) of the crystal (see the bottom inset of Fig. 1). All measurements were taken between 0.5 and 6 K in a ^{3}He refrigerator in a 3D vector superconducting magnet. A small longitudinal field, H_z, was swept along the sample's easy axis at rates between 1×10^{-5} T/s and 6.7×10^{-3} T/s, in the presence of a series of fixed transverse fields $H_\perp$ applied in the y direction. For details on measurement setup and techniques see Refs. [4,6].

3.2. Measurement of the equilibrium susceptibility

Due to the anisotropy barrier, magnetic hysteresis occurs below a blocking temperature T_B, of approximately 3 K in zero field. This precludes measurements of equilibrium properties at temperatures where magnetic ordering is predicted. Therefore, our approach was to measure the magnetic susceptibilities above the blocking temperature and deduce the nature of the magnetic interactions from fits to the Curie–Weiss law. Hence, to measure the susceptibility, we need to make sure that the sample has achieved equilibrium before we can obtain a valid measurement. The factors that determine whether the measurement is taken at equilibrium are the longitudinal field sweep rate α, the temperature T and the transverse field $H_\perp$. However, T and $H_\perp$ are also parameters affecting the susceptibility; this leaves α as the only control parameter that can be adjusted to reach equilibrium. At low temperature, for a given $H_\perp$, the relaxation time gets longer; hence, we need to keep α small enough that the experimental time scale is larger than the relaxation rate. In order to establish the range of experimental conditions in which it is possible to measure the equilibrium susceptibility we first determine the blocking temperature T_B as a function of transverse field.

In the main panel of Fig. 1, the magnetization of Mn_{12}-ac–MeOH (Sample C) in the absence of transverse magnetic field is shown for temperatures below 1 K. The steps in the magnetization occur due to faster spin-reversal due to resonant tunneling of magnetization

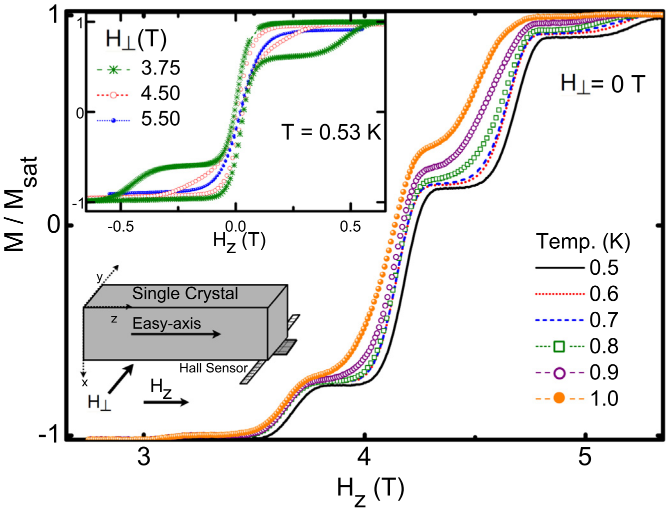

Fig. 1. Normalized magnetization of Mn_{12}-ac–MeOH as a function of longitudinal magnetic field, H_z, in zero transverse field at several temperatures below 1 K. The sweep rate of H_z in the main panel and the top inset is 1.67 mT/s. Top inset: magnetization vs. H_z at $T = 0.53$ K for different $H_\perp$. Bottom inset: Schematic diagram of the sample, the Hall sensor and magnetic fields. Reprinted from Ref. [6] (©APS).