Origin of the fast magnetization tunneling in the single-molecule magnet [Ni(hmp)(t-BuEtOH)Cl]$_4$

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We present high-frequency angle-dependent EPR data for crystals of [Ni$_x$Zn$_{1-x}$](hmp)(t-BuEtOH)Cl]$_4$ ($x$=1 and 0.02). The $x$=1 complex behaves as a single-molecule magnet at low temperatures, displaying hysteresis and exceptionally fast magnetization tunneling. We show that this behavior is related to a fourth-order transverse crystal-field interaction, which produces a significant tunnel splitting ($\sim$10 MHz) of the ground state of this $S$=4 system. The magnitude of the fourth-order anisotropy, and the dominant axial term ($D$), can be related to the single-ion interactions ($D_i$ and $E_i$) at the individual Ni$^{II}$ sites, as determined for the $x$=0.02 crystals. © 2005 American Institute of Physics. [DOI: 10.1063/1.1845871]

Single-molecule magnets (SMMs) provide a molecular, or “bottom-up,” route to magnetic nanostructures. They typically consist of a core of magnetically coupled transition metal ions, resulting in a well-defined giant spin ground state. Their main attraction is an intrinsic bistability, which is realized via a significant negative (easy-axis) magnetocrystalline anisotropy [see Eq. (1)]. This bistability has aroused significant interest in terms of the use of SMMs in future molecular devices. Unlike mesoscale magnetic particles of much larger dimensions, SMMs straddle the interface between classical and quantum behavior, displaying both superparamagnetic-like behavior, and magnetic quantum tunneling (MQT) at low temperatures. Furthermore, they offer all of the advantages of molecular chemistry, e.g., purity, solubility in various solvents, a well-defined periphery of organic ligands, a crystalline assembly of monodisperse units, etc. When grown as crystals, the magnetic unit is monodisperse—each molecule in the crystal has the same spin, orientation, magnetic anisotropy, and structure, etc. Thus, bulk probes of SMM crystals enable fundamental studies of properties intrinsic to individual magnetic nanostructures.

We have recently synthesized a family of SMMs based on tetranuclear nickel clusters having the general formula [Ni(hmp)(ROH)X]$_4$, where R=CH$_3$, C$_2$H$_5$, etc., and X=Cl or Br,$^3$ and hmp$^-$ is the monoanion of 2-hydroxy-methylpyridine. Low-temperature ($\leq$1 K) magnetization studies have demonstrated that each of these Ni$_4$ complexes exhibits MQT,$^2$ albeit the temperature-independent MQT rate is exceptionally fast (too fast to measure). In this article, we focus on the [Ni(hmp)(t-BuEtOH)Cl]$_4$ member of this family, where t-BuEtOH is 3,3-dimethyl-1-butanol. Previous electron paramagnetic resonance (EPR) studies have confirmed the expected $S$=4 ground state, as well as showing that it possesses an easy-axis-type anisotropy,$^3$ i.e., a negative axial crystal-field parameter ($D=\pm 0.600$ cm$^{-1}$). Our motivation for studying the R=t-BuEtOH complex stems partly from its high symmetry ($S_d$). More importantly, however, crystals of this complex contain no solvate molecules. As recent studies of Mn$_{12}$-acetate have shown, solvent molecules can have a pronounced influence on the quantum properties of SMMs.$^3$ The Ni$_4$ SMMs offer no exception. EPR spectra for the R=CH$_3$ and C$_2$H$_5$ Ni$_4$ complexes consist of extremely broad absorption peaks, with multiple fine structures, making detailed analysis rather difficult.$^4$ In contrast, EPR spectra for the t-BuEtOH complex exhibit very sharp lines (see Fig. 1 and Ref. 4).

The effective spin Hamiltonian for an isolated Ni$_4$ SMM is

$$\hat{H} = D \hat{S}_z^2 + g \mu_B B \cdot \hat{S} + \hat{O}_4 + \hat{H}',$$

(1)

where $\hat{S}$ is the spin angular momentum operator with components $\hat{S}_x$, $\hat{S}_y$, and $\hat{S}_z$; $g$ is the Landé g factor and $B$ is the applied field strength; $\hat{O}_4$ denotes fourth-order crystal-field terms; and $\hat{H}'$ describes additional perturbations such as hyperfine and intermolecular interactions.$^1$ MQT is caused by terms in the Hamiltonian which do not commute with the dominant $D \hat{S}_z^2$ interaction, e.g., terms containing $\hat{S}_x$ and $\hat{S}_y$. The rhombic term, $E(\hat{S}_x^2 - \hat{S}_y^2)$, is symmetry forbidden. Thus, the leading term in the crystal field that could cause MQT would be the fourth-order $B_4^2(\hat{S}_z^4 - 4 \hat{S}_x^2 \hat{S}_y^2)$ interaction. We note that this operator connects states differing in $m_z$ (projection of $S$ along $z$) by $\pm 4$ in second order of perturbation theory. Consequently, it is quite effective at causing tunneling between the $m_z=\pm 4$ ground states. While its effects are rather weak at low fields, causing tunnel splittings of order 10 MHz (see below), the interaction becomes zeroth order in the presence of a large transverse field ($g \mu_B B > DS$). In this way, angle-dependent hard-plane EPR experiments can be used to determine both the symmetry of the dominant

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resistance sensor using a combination of heaters and cold helium gas flow.

Figure 1(a) displays the microwave transmission through the cavity at a temperature of 10 K and a frequency of 101.2 GHz for the $x=1$ complex; in this experiment, the magnetic field was rotated in the hard [$xy$ or $(100)/(010)$] plane of the crystal. The data in Fig. 1(a) correspond to the case where the field is applied $23\degree$ away from one of the edges of the square base of the pyramidal sample [$x$ or $y$ direction, see inset to (b)], corresponding to the hard axis of the crystal ($\phi=0$). The sharp minima in transmission correspond to EPR absorptions; these resonances have been labeled according to the scheme described in Ref. 6. The splitting of the highest field peak (also weakly visible in the 4.5 T peak) is caused by a weak disorder associated with the t-BuEtOH ligand which gives rise to microenvironments with slightly different $D$ values ($-0.660$ cm$^{-1}$ and $-0.577$ cm$^{-1}$). This disorder, which sets in below a structural transition at 46 K, has been confirmed via specific heat and x-ray measurements.

Figure 1(b) displays a gray-scale contour plot of the absorption intensity, as a function of the magnetic field strength and its orientation ($\phi$) within the hard plane. Immediately apparent is the fourfold behavior of the peak position shifts. The maxima occur when the field is along the hard directions ($\phi=0^\circ$, $90^\circ$, etc.); the minima correspond to the medium axes, which are in between the hard directions ($\phi=45^\circ$, $135^\circ$, etc.). The hard directions ($\phi=0^\circ$, $90^\circ$, etc.) are located at $-23^\circ$ (or $+23^\circ$) and $67^\circ$ (or $-67^\circ$) away from the crystallographic (100) and (010) directions. The fourfold line shifts are caused by the fourth-order $B_2^4(S_{z1}^4-S_{z2}^4)$ interaction in Eq. (1). Superimposed on the absorption maxima (darker regions) in Fig. 1(b) are fits (white curves) to the data. The fourfold shifts are produced for all peaks (including $\beta'$) with just a single parameter, $B_2^4=4\times10^{-4}$ cm$^{-1}$. In addition, the hard-plane $g$ factors ($g_x=g_y=2.23$) may be obtained from the average peak positions. The satellite peak ($\beta''$) between 3.15 and 3.3 T, which is only seen for angles close to $\phi =0^\circ$, is a double-quantum transition [all others in Fig. 1(b) are $\Delta m_z=1$]. This transition is only allowed when there is a significant microwave $H_1$-field component parallel to the applied dc field $H_0$. It turns out that the relative orientations of $H_1$ and $H_0$ vary upon rotation of the cavity such that they are approximately parallel for $\phi=0$ and $180^\circ$, and perpendicular for $\phi=90$ and $270^\circ$. Spectra obtained at different $\phi$ angles were normalized to the intensity of $\alpha4$; hence, $\beta'$ vanishes in the vicinity of $\phi=90^\circ$, i.e., the twofold nature of this peak is an instrumental artifact and not connected to any intrinsic twofold symmetry of the sample. Finally, we note that the obtained large fourth-order $B_2^4$term results in a 10 MHz tunnel splitting between the $m_z=\pm 4$ ground states, thus explaining the fast magnetization tunneling in this system.

Figure 2(a) displays a series of EPR spectra for a doped [Ni$_{0.02}$Zn$_{0.98}$](t-BuEtOH)Cl$_4$ crystal at 2.5 K and 120 GHz. The field was rotated in the $xz$ plane: in the top trace, the field is oriented at $\theta=-34^\circ$ away from the hard plane; successive traces were taken in $2.5^\circ$ steps towards the hard plane. Figure 2(b) displays the angle dependence of the EPR peak positions for a full $360^\circ$ rotation of the sample.
Fig. 2. (a) EPR spectra for a doped [Ni$_{0.02}$Zn$_{0.98}$](hmp)$(t$-BuEtOH)$_4$Cl$_4$ crystal at 2.5 K and 120 GHz. The field was rotated in the $xz$ plane: in the top trace, the field is oriented at $\theta = -34^\circ$ away from the $z$ axis; successive traces were taken in 2.5° steps toward the $z$ axis. The inset shows the energy versus magnetic field diagram for $S=1$, for a field tilted 15° away from the easy axis; the levels are labeled in zero magnetic field ($|\pm 1\rangle_2$ and $|\pm 1\rangle_3$ correspond to symmetric and antisymmetric combinations of the $S=1$ states) and the arrow indicates the origin of the EPR transitions seen in the main figure. (b) Angle dependence of the EPR peak positions in (a) for a full 360° rotation of the sample (inset depicts the experimental geometry); the solid curves are fits to the data.

(inset depicts the experimental geometry). Due to the low concentration of Ni$^{II}$ in the sample, we can assume that the EPR spectra are dominated by NiZn$_4$(hmp)$_4$(t-BuEtOH)$_4$Cl$_4$ molecules having $S=1$. However, the Ni$^{II}$ ion can reside at four different sites on the molecule and, in general, the crystal-field tensor at each site will have a different orientation, albeit related by the symmetry group of the molecule. Indeed, this is the reason why one observes a pair of maxima either side of $\theta = 0^\circ$ and $180^\circ$ in Fig. 2(b); these maxima would coincide at $\theta = 0$ and $180^\circ$ if the Ni$^{II}$ crystal-field tensors were collinear and coincident with the full Ni$_4$ crystal-field tensor. Thus, these experiments indicate that the Ni$^{II}$ tensors are tilted with respect to the molecule. In fact, all of the peaks in Fig. 2 correspond to the same transition, as indicated by the $S=1$ energy level diagram [inset to Fig. 2(a)]. The four resonance branches originate from each of the four inequivalent Ni$^{II}$ sites. For the ideal experimental geometry, one should expect the two high-field branches to lie on top of each other. However, a slight sample misalignment lifts this degeneracy. Nevertheless, this is taken into consideration in our fitting procedure. Similar experiments performed in a plane parallel to the diagonals of the pyramidal sample (inclined 45° to the data in Fig. 2), reveal that the Ni$^{II}$ easy axes are tilted along the (100) and (010) directions, and inclined 15° away from the (001) direction. This likely explains why the hard directions for the Ni$_4$ molecule are found between these directions (see Fig. 1), i.e., along (100) and (010).

Frequency-dependent studies (not shown) performed with the field along one of the high symmetry directions provide access to the crystal-field parameters for the Ni$^{II}$ ions: $D_t = -5.27 \text{ cm}^{-1}$ and $E_d = \pm 1.2 \text{ cm}^{-1}$. A simple calculation, which assumes no tilting, enables a comparison between $D_t$ and the Ni$_4$ $D$ value: the negative $E$ value yields $D = -0.66 \text{ cm}^{-1}$; the positive $E$ value yields $D = -0.69 \text{ cm}^{-1}$. Such agreement (within 10%) is impressive, considering the approximate nature of the calculation. Armed with Ni$^{II}$ crystal-field parameters, one can also fit the angle-dependent data for NiZn$_4$(hmp)$_4$(t-BuEtOH)$_4$Cl$_4$ for each plane of rotation [i.e., solid curves in Fig. 2(b)]. As discussed above, our fitting procedure allows for misalignments between the actual and assumed rotation planes; indeed, such a misalignment of about 8° is the reason for the asymmetry between the heights of the maxima in Fig. 2(b). A full account of this analysis will be presented elsewhere. However, the easy-axis tilting and significant $E$ term associated with the Ni$^{II}$ ions provide a natural explanation for the significant $B_{i1}$ term and the fast magnetization relaxation for the Ni$_4$ system.

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10We note that, due to the relatively large size of the sample used in these studies, the microwave $H_1$ is not uniform over the sample. Therefore, there will always be weak components of $H_1$ both parallel and perpendicular to $H_0$. 

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