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Giant magnetisation step in Fe$_2$: Molecular nanomagnets in the weak exchange limit

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Abstract – We investigate a Fe$_2$ molecular nanomagnet that displays a giant, field-induced step in its magnetisation curve. Detailed magnetisation and magnetic torque investigations demonstrate that in this Fe$_2$ system the single-ion anisotropy is dominant over the isotropic exchange coupling. Accurate spin Hamiltonian parameter values and tensor orientations are obtained. The theoretical analysis reveals that this system is a very promising candidate for the direct observation of the Néel vector tunnel splitting in weakly coupled molecular nanomagnets.

Two decades of research on Molecular Nanomagnets (MNM) have demonstrated that these systems display a rich variety of fascinating quantum phenomena, including quantum tunneling of the magnetisation [1,2], quantum tunneling of the Néel vector, [3] and quantum coherence [4,5]. The vast majority of detailed physical investigations were performed on systems where the isotropic exchange interaction is strong compared to other interactions in the system, such as single-ion anisotropies, non-Heisenberg spin-spin interactions, or the Zeeman interaction. Consequently, the total spin $S_T$ is a reasonably good quantum number, and the influence of mixing between total-spin states on the low-temperature physics can be dealt with by introducing higher-order terms in the single-spin Hamiltonian, which describes the system in the space of the ground spin multiplet (giant spin approximation) [6].

However, recently, cases have been reported where the single-spin Hamiltonian completely fails to capture the essential low-temperature physics. For example, in Mn$_6$ single-molecule magnets, the magnetisation relaxation was found to proceed via excited spin multiplets under the influence of the single-ion anisotropy [7]. Furthermore, a weakly coupled Dy$_3$ trimer was recently reported to possess a ground doublet with peculiar chirality and slow magnetisation dynamics originating from the first-excited state [8]. Hence, it can be expected that in MNM, featuring exchange interactions that are weak compared to the single-ion anisotropies, fascinating new physics may be observed. A further recent example of molecular nanomagnets in the weak-exchange limit is a star-shaped tetranuclear vanadium(III) cluster [9].

Here we present a comprehensive investigation of the magnetic properties of a dimeric compound consisting of two highly anisotropic Fe$^{2+}$ ($S = 2$) ions that are weakly exchange-coupled (fig. 1), including magnetic-susceptibility, magnetisation, and torque measurements. In an external field, the system undergoes a single spin state transition from an antiparallel to a parallel spin arrangement. Interestingly, our theoretical analysis revealed that the ground and low-lying first-excited states of the system correspond to the Néel states ($|↑↓ + ↓↑⟩$) and ($|↑↓ − ↓↑⟩$) with a tunnel splitting of 83MHz at zero field, with the sublattice magnetic moment classically very well localised due to the large single-ion anisotropy. This makes this system a prime candidate to
investigate Néel vector tunneling in the weak-exchange limit.

Figure 1 depicts the crystal structure of the compound [Fe(3-bpp)(NCS)$_2$(bipy)], where bipy = 4,4′-bipyridine, and 3-bpp = 2,6-bis(pyrazol-3-yl)pyridine [10]. In the lattice, there is a close contact between the iron ion of one molecule and a sulfur atom of the nearest neighbour molecule. The Fe…S distance is much larger (3.755 Å) than typical Fe-S covalent bond lengths, which the Cambridge Structure database (11/2010) reports to be 1.92 Å to 2.81 Å, with an average of 2.28(7) Å. However, this contact will prove crucially important for the magnetic properties. The next nearest neighbors are much further away, and the molecules therefore form Fe$_2$ magnetic dimers in the solid. Susceptibility and magnetisation measurements were performed on a Quantum Design MPMS XL7 magnetometer. Torque measurements at $T > 1.5$ K and $B < 10$ T were performed with a home-built CuBe cantilever torque magnetometer, while measurements at higher fields and lower temperatures were performed at the Grenoble High Magnetic Field Laboratory, by using a CuBe torque magnetometer inserted into a dilution fridge in magnet M9. Curves recorded at ±θ were averaged to eliminate field inhomogeneity effects [11].

The magnetic susceptibility, recorded on a powder sample of Fe$_2$, shows a maximum as a function of temperature, characteristic of antiferromagnetic exchange interactions (fig. 2(a)). Antiferromagnetic coupling between two $S = 2$ centers is expected to give rise to a series of total spin levels, with $S_T = 0,1,2,3,4$, whose energies are $E \propto S_T(S_T + 1)$. An applied magnetic field stabilises states with higher $S_T$, leading to successive $\Delta S = +1$ spin state crossings at regular field intervals [12]. However, the magnetisation curve (fig. 2(b)) recorded on a single crystal of Fe$_2$ displays a single step from $M \approx 0$ to $M = 8.8$ $\mu_B$, at $B = 3.4$ T. The change in magnetisation appears to indicate a transition from $M_S = 0$ to $M_S = -4$ (with $g = 2.2$).

In addition, ultralow-temperature torque measurements (fig. 3(a)) also reveal the presence of a single step, with a subsequent monotonic increase towards higher fields. The angle dependence of the inflection point characterising the torque step as a function of angle (fig. 3(c)) is clearly different from the usually observed $B_c \propto \cos^2 \theta - 1$ behaviour [13]. Measurement of the magnetic torque as a function of angle at $B = 2$ T and two different temperatures reveal an intriguing change of sign of the torque signal with
temperature (fig. 4(a)). Measurements at higher fields ($B = 8$ T) showed conventional $\sin \theta \cos \theta$ behaviour at high temperatures ($15$ K) [13], while those at $1.8$ K display a very unusual shape (fig. 4(b)). Clearly, these results are different from those of the major fraction of molecular nanomagnets, which are the result of strong isotropic exchange interactions in addition to weak to moderate single-ion anisotropies. In fact, the exchange interaction in Fe$_2$ is expected to be weak, because of the long Fe-S distance, while the single-ion anisotropy of Fe$^{2+}$ is expected to be large [14].

The description of the system is simplified by the presence of a crystallographic inversion center between the two iron ions, which forces the single-ion anisotropy of the two ions to be equal and collinear, and precludes the presence of antisymmetric exchange interactions [15]. A suitable spin Hamiltonian is therefore [16]:

$$\mathcal{H} = -J \mathbf{S}_1 \cdot \mathbf{S}_2 + D (\mathbf{S}_1^2 + \mathbf{S}_2^2) + g \mu_B \mathbf{B} \cdot (\mathbf{S}_1 + \mathbf{S}_2)$$  \hspace{1cm} (1)

with $J$ the isotropic exchange interaction strength and $D$ the second-order axial single-ion anisotropy. Note that this is the same Hamiltonian that is typically used to describe molecular nanomagnets, and it is only the relative values of $J$ and $D$ that cause the profound change in the physical behaviour. Excellent fits of all the experimental data were obtained for $J = -1.74(6)$ cm$^{-1}$, $D = -8.5(4)$ cm$^{-1}$, and $g = 2.23(5)$. The $J$ value was obtained from the susceptibility and single-crystal magnetisation measurements, while torque measurements afforded the sign, magnitude and direction of the $D$ tensor. Detailed angle-dependent torque measurements revealed that the easy axis direction is very close ($\pm 10$ deg) to the crystallographic $a$-axis (fig. 1). The fit of the single-crystal magnetisation data (fig. 2(b)) improved when assuming the presence of $3.5\%$ uncoupled $S = 2$ impurity. This is not unreasonable for the present compound, given that there is no significant covalent bonding between the two Fe$^{2+}$ complexes, that form the magnetic dimer. Also, the ellipsoids of the bridging sulfur atoms in the crystal structure (fig. 1) are slightly elongated, which is consistent with the presence of a small degree of static disorder. Any positional disorder will lead to breaking of the Fe...S contact and the corresponding magnetic interaction. Note that the step in the experimental ultralow-temperature torque data (fig. 3(a)) is broader than in the simulation (fig. 3(b)). This non-thermal broadening is attributed to the presence of distributions in the spin Hamiltonian parameters, and a small misorientation of the single crystal. This is also the cause for the small systematic deviation between the calculated and observed crossing fields (fig. 3(c)).

The sign of the torque value at $B = 2$ T going from $1.8$ to $15$ K is due to population of an excited state with a larger magnetic moment and an opposite effective $D$ value. Such a sign change of the anisotropy was previously found in the Mn$_{3\times3}$ grid [17]. It is now also clear that the unusual low-temperature angle dependence of the torque at $B = 8$ T (fig. 4(b)) is due to the extreme angle dependence of the crossing field $B_c$, which causes the applied field of $B = 8$ T to be above or below $B_c$, depending on angle.

Figure 5(a) gives the energy level diagram as a function of applied field $B_0$ along the easy axis of the single-ion anisotropy. The lowest two states are essentially the symmetric and antisymmetric combinations of the $|m_S, m_{S_z}| = |22\rangle$ and $|2 - 2\rangle$ states with small admixtures of $|\pm 1 \pm 1\rangle$, where both states have total $M_S$ values of $M_S = 0$. These two states can be viewed as the tunnel-split superpositions of the Néel states. The next lowest

**Fig. 4:** (Color online) Measured (symbols) and calculated (lines) torque curves as a function of angle $\theta$ between easy axis and external magnetic field at $1.8$ (○) and $15$ K (□) in the ac-plane at an external field of (a) $2$ tesla, (b) $8$ tesla.

**Fig. 5:** (Color online) (a) Energy level diagram calculated using simulation parameters given in the text. The inset shows the splitting between the lowest two states, which both have $M_S = 0$. (b) Tunneling action and spin expectation values of the lowest two states as a function of $D/J$, calculated for $S_i = 2$ dimers. The dashed line indicates the situation for Fe$_2$. (c) Energy splitting $\Delta_T$ between the lowest two states as a function of magnetic field transverse to the single-ion easy axis, calculated from the spin Hamiltonian parameters derived for Fe$_2$. The dashed line indicates the $^1$H Larmor frequency as a function of field.
state is the pure $| -2 - 2 \rangle$ state, with $M_z = -4$, which crosses the ground state at $B_c = 3.38$ T for fields applied parallel to the easy axis. As a consequence of this energy level structure, it is possible to induce a large change of the magnetisation, as the system goes from $| \uparrow \downarrow \pm \downarrow \rangle$ to $| \uparrow \uparrow \rangle$ on application of a modest magnetic field. Figure 5(b) shows the spin expectation value for the two lowest spin states as a function of $D/J$ for $S = 2$ dimers. As $D/J$ decreases, the two lowest states evolve from superpositions of the Néel states into an $S = 0$ ground state and an $S = 1$ excited state, indicating that the strong-exchange approximation becomes increasingly valid. The value of $D/J$ for Fe$^{3+}$-based systems is typically $D/J \approx 0.01$ [3], which places them firmly in the strong-exchange regime. The low-energy structure of Fe$_2$ is similar to that found for [Mn$_4$]$_2$ dimers [18], but without the additional complication of the slow magnetisation dynamics and quantum tunneling. Furthermore, both $J$ and $D$ are an order of magnitude larger in Fe$_2$ than in [Mn$_4$]$_2$, making the former more robust to the influence of thermal fluctuations.

Interestingly, the splitting between the lowest two spin levels in an applied transverse field $B_z$ is not constant (fig. 5(c)), but shows an oscillatory behaviour, reminiscent of Fe$_8$ [19], or the Fe$_{18}$ antiferromagnetic ring [3]. In antiferromagnetic systems, this periodic quenching of the tunnel splitting has been attributed to quantum phase interference resulting from the quantum tunneling of the Néel vector [3,20]. This scenario is characterised by two parameters, the zero-field tunnel splitting $\Delta_0$, and the degree to which the Néel vector is localised in space, usually expressed as the tunnel action $S_0$. In the weak-exchange limit, these parameters are semi-classically given by [21]

$$\Delta_0 = \frac{2^{3/2} s^{3/2} N(D(D + J))^{3/4}}{\sqrt{\pi(J + 2D)}} \exp(-S_0/h)$$

$$S_0/h = 2NS\log\left(\frac{D}{J} + \sqrt{1 + D/J}\right).$$

The much larger single-ion anisotropy of Fe$^{2+}$ ($S = 2$) compared to Fe$^{3+}$ ($S = \frac{5}{2}$), results in a significantly higher ($S_0/h = 12.35$) tunnel action in (Fe$^{2+}$)$_2$ than for Fe$^{3+}$-based systems reported to date, with a maximum value for (Fe$^{3+}$)$_{18}$ of $S_0/h = 5.9$ [3]. Figure 5(b) shows how the tunnel action varies with the ratio of $D/J$. While it is the number of ions $N$ that is the main contributor to the large tunnel action in (Fe$^{3+}$)$_{18}$, this role is played by the large single-ion anisotropy $D$ in Fe$^{2+}$. Hence Fe$^{2+}$ explores the validity of the Néel vector tunneling scenario in the weak-exchange regime, in other words, in a completely different region of parameter space. Here the Néel vector is limited to one of the two spins.

The tunnel splitting, extracted by direct diagonalisation of the spin Hamiltonian matrix, is large enough ($\Delta_0 = 83$ MHz) to expect tunneling processes to be coherent, given that coherence times in molecular nanomagnets were recently shown to be in the microsecond range [4,5]. Whilst the tunnel splitting is too small to be detected by torque magnetometry, or specific-heat measurements, it lies in the experimentally very accessible radiofrequency region, suggesting that direct observation of the tunnel splitting oscillation as a function of transverse field may be possible in Fe$_2$. Direct electron spin resonance observation may be possible, but the calculated $\langle ES|S_{x,y,z}|GS\rangle$ matrix elements are all rather small, and independent of strength and orientation of the magnetic field. Here, GS and ES are the ground state $| \uparrow \downarrow \pm \downarrow \rangle$ and excited state $| \uparrow \downarrow \pm \downarrow \rangle$, respectively. A promising method to observe the tunnel splitting $\Delta$ may be to investigate the proton NMR spin-lattice relaxation rate, $T_1^{-1}$ as a function of transverse field. At the magnetic field $B_{cr}$ (fig. 5(c)), where $\gamma_N B_{cr} = \Delta$, an increase in $T_1^{-1}$ is expected due to the cross-relaxation between the electron spin and proton spin, as observed for antiferromagnetic rings, such as Cr$_8$, at field-induced level crossings [22]. It is interesting to note that the proposed experiments are only possible because $\Delta \approx \gamma_N B$ at moderate fields (fig. 5(c)).

In conclusion, we have investigated an Fe$^{2+}$ dimer, which is characterised by weak-exchange and strong single-ion anisotropy. We have demonstrated that its magnetic properties differ substantially from strong-exchange systems, including the observation of a giant magnetisation step. We propose that the Néel vector tunneling may be observed in this system.

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