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# Torque-detected ESR of a tetrairon(III) single molecule magnet

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ABSTRACT

Single-crystal studies on anisotropic ESR-active materials can be conveniently carried out using torque-detected (TD) ESR, a novel technique which brings to ESR the sensitivity typical of torque magnetometry (TM). This method, which is easily operated in high magnetic fields and in a wide range of frequencies, was applied to investigate magnetic anisotropy in crystals of a tetrairon(III) single-molecule magnet with an $S = 5$ ground state. TDESR was supported by TM measurements carried out in situ and provided an accurate estimate of the second-order axial anisotropy parameter $D$ and of the longitudinal fourth-order contribution $B_4^0$. The results were validated through a parallel angle-resolved investigation by traditional high-frequency ESR on the same material.



## 1. Introduction

Magnetic anisotropy is an essential ingredient of the behavior of many magnetic materials, including molecules known as Single Molecule Magnets (SMMs). In these materials, an axial Ising-type anisotropy produces an energy barrier to magnetic moment reversal and results in slow magnetic relaxation at low temperatures ($T$) [1]. Transverse anisotropy components also play a key role in causing tunneling through the barrier in a strongly field- and symmetry-dependent fashion [2]. To date the most powerful method to investigate magnetic anisotropy in SMMs is electron spin resonance (ESR) operated at high frequencies and in high fields (HFESR) to fully reveal the fine structure of the ground spin state [3–6]. Sensitivity and accessible frequency ranges are crucial parameters for HFESR. Cavity perturbation techniques can be used to detect magnetic resonance transitions on single crystal samples at frequencies up to 700 GHz, but these spectrometers are limited to discrete frequencies or very narrow frequency ranges [7,8]. On the other hand, broad band methods, such as frequency domain magnetic resonance spectroscopy (FDMRS) [9–11] suffer from their low sensitivity. Indeed, measurements performed on single crystals of SMMs using FDMRS are very rare, and only studies on single-crystal mosaics have been published [12,13].

As an alternative, magnetic resonance transitions can be detected by measuring magnetization changes induced by the absorption of radiation [10], a technique introduced more than 40 years ago [14]. To this aim, different magnetic sensors were used to probe the effect of microwave irradiation off and on resonance, including SQUIDs [15], micro-SQUIDs [16], and Hall bars [17,18]. SQUIDs and micro-SQUIDs are highly sensitive but they have a slow response time and, in addition, cannot be operated in very high magnetic field (above 8 T for SQUIDs and much less for micro-SQUIDs). On the contrary, Hall bars are highly sensitive and have a fast response time. In any case, use of these setups was so far limited to either single frequencies or very narrow frequency ranges.

We have now combined our experience in FDMRS and torque magnetometry to develop a novel tool for magnetic characterization which has been named torque-detected ESR (TDESR). Technical details have been already presented elsewhere [19]. Torque magnetometry (TM) measures the mechanical couple experienced by a magnetic sample in a homogeneous magnetic field (**H**) due to the noncollinearity between **H** and the magnetization (**M**), i.e. due to the presence of transverse magnetization [20]. When the sample has a permanent magnetic moment, the torque signal allows measuring the magnetization directly. For a paramagnet, the appearance of a transverse magnetization is a consequence of magnetic anisotropy. In a paramagnetic molecule with $N$ thermally accessible spin states, the component of the torque signal along a given axis $\alpha$ is:

$$\tau_\alpha = \frac{\sum_{i=1}^{N} \tau_{i,\alpha} \exp(-E_i/k_B T)}{\sum_{i=1}^{N} \exp(-E_i/k_B T)} \quad (1)$$

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where $E_i$ is the energy of the $i$th spin state (in general, a function of the spin Hamiltonian parameters and of the applied magnetic field), $k_B$ is the Boltzmann constant and:

$$\tau_{i,\alpha} = -\left(\frac{\partial E_i}{\partial \theta_\alpha}\right)_{\mathbf{H}} \quad (2)$$

is the contribution provided to the torque by the $i$th state. Here, $\theta_\alpha$ is the angle used to describe the rotation of the sample around the $\alpha$-axis. Resonant absorption of microwave (MW) radiation changes the population of the states with respect to Boltzmann distribution in a way which depends on the transition probabilities, on the MW power, and on the spin–lattice relaxation time. It consequently leads to a change in the torque signal, which can be used to detect magnetic resonance transitions. The torque signal was measured here by using a highly sensitive CuBe cantilever, which enables studying very small single crystals. The cantilever response is fast compared with commercial SQUIDs, and the device can be operated up to high magnetic fields and in a broad frequency range. Furthermore, the MW radiation has virtually no effect on the measured torque values off resonance. Finally, conventional torque measurements performed in advance on the crystal of interest "in situ" provide an initial estimate of the magnitude and orientation of the anisotropy tensor. As a disadvantage, the torque signal – and consequently the sensitivity of TDESR – is strongly dependent upon the applied field direction because all torque components vanish whenever the field lies along a principal magnetic direction [20]. Under these special conditions the technique cannot be used. However, by properly adjusting the field orientation, TDESR can be made several orders of magnitude more sensitive than FDMRS.

We herein present a combined study by TM, TDESR and HFESR on a single crystal of $[Fe_4(L)_2(dpm)_6]$ (**1**) where Hdpm is 2,2,6,6-tetramethyl-3,5-heptanedione (also known as dipivaloylmethane) and $H_3L$ is the tripodal ligand (*R*,*S*)-2-hydroxymethyl-2-(2-methyl-butoxymethyl)propane-1,3-diol [21]. Among SMMs of the $Fe_4$ family, this particular derivative was chosen because it exhibits very narrow lines in the HFESR spectra recorded on a powder sample [21]. Moreover, all molecules in the crystal are magnetically equivalent and iso-oriented, a most favorable situation for single-crystal studies (see below).

The crystal structure of **1**, as determined by single-crystal X-ray diffraction at 120(2) K [21], has monoclinic symmetry and belongs to space group $P2/n$ with $a = 17.0632(7)$, $b = 15.5838(7)$, $c = 19.5691(8)$ Å and $\beta = 110.600(1)^\circ$. The molecular structure viewed perpendicular to the metal plane and along the **b** crystal axis is shown in Fig. 1a and b, respectively. The system consists of four $Fe^{3+}$ ions ($s_i = 5/2$) that are antiferromagnetically coupled to give a ground total spin state of $S = 5$. Disregarding the 2-methyl-butoxymethyl residues on tripodal ligands, the molecule has approximate axial ($D_3$) symmetry along the normal to the metal plane (**n**), which is thus expected to be close to the unique (easy) magnetic axis of the system.

The crystallographic symmetry, however, is $C_2$ and the twofold axis is directed along the line joining Fe1 and Fe2, which is parallel to the **b** axis of the unit cell. Therefore, Fe1···Fe2 must represent a principal direction ($y$) for the second-order anisotropy tensor of the $S = 5$ state, the easy axis ($z$) and the third principal direction ($x$) being forced to lie in the **ac** plane. HFESR spectra recorded on a polycrystalline sample have been previously [21] used to determine the anisotropy parameters appearing in the spin Hamiltonian of Eq. (3) and gathered in Table 1 (entry 1):

$$\hat{H} = \mu_0 \mu_B g \hat{\mathbf{S}} \cdot \hat{\mathbf{H}} + D[\hat{S}_z^2 - S(S+1)/3] + E(\hat{S}_x^2 - \hat{S}_y^2) + B_4^0 \hat{O}_4^0 \quad (3)$$

In Eq. (3), $D$ and $E$ are the zero-field splitting parameters that describe second-order axial and rhombic components of anisotropy (the nonaxial molecular symmetry permits $E \neq 0$). $B_4^0$ is associated with the fourth-order axial operator [1]:

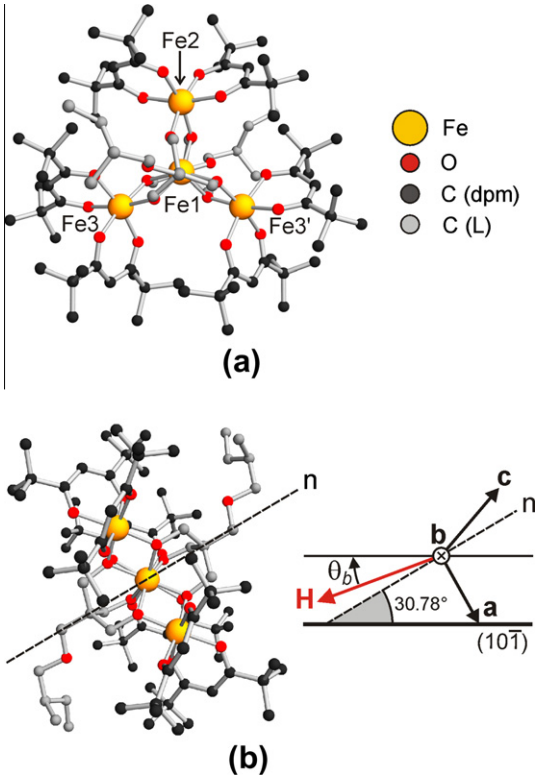


**Fig. 1.** Molecular structure of **1** viewed normal to the metal plane (a) and along the **b** axis (b). Metal centers Fe3 and Fe3′ are symmetry related through a crystallographic twofold axis directed along Fe1···Fe2. Hydrogen atoms and disorder effects on the alkyl substituents of tripodal ligands are omitted for clarity. Part (b) includes the unit cell axes (**a–c**) along with the normal to the metal plane (**n**, dashed line), the trace of the (1 0 $\bar{1}$) face of the crystal (bold line) and the definition of the angle $\theta_b$ used to describe the rotation of the crystal around the **b** axis. According to the crystal structure, at $\theta_b = 30.78^\circ$ the field lies along **n**.

$$\hat{O}_4^0 = 35\hat{S}_z^4 + [25 - 30S(S+1)]\hat{S}_z^2 + 3S^2(S+1)^2 - 6S(S+1) \quad (4)$$

The negative $D$ value and the small $|E/D|$ ratio (0.067) point to a dominant easy-axis anisotropy, as required for a SMM, while the positive $B_4^0$ value results in a "compressed" parabolic shape for the anisotropy barrier, as detailed in Ref. [22].

We have investigated a single crystal of **1** using TM to accurately determine the orientation of the easy magnetic axis, and subsequently using TDESR. Magnetic resonance transitions detected as a function of field and frequency have been used to extract the anisotropy parameters of the $S = 5$ ground state. In the third part of the work, we have studied a single-crystal sample by HFESR, applying the magnetic field along the easy axis and in the hard plane. The parameter sets obtained by the different techniques are in excellent agreement with each other and provide an accurate characterization of magnetic anisotropy in this SMM.

## 2. Experimental

Well-formed monoclinic crystals of **1** were prepared as described in Ref. [21]. The crystals grow as rod-like prisms developed along the [1 0 1] zone axis, with (0 1 0), ($\bar{1}$ 0 1), (0 $\bar{1}$ 0) and (1 0 $\bar{1}$) as main crystal faces. Technical details of the TDESR setup, which operates in the frequency range 30–1440 GHz (1–48 $cm^{-1}$) in fields up to 8 T and at temperatures down to 1.7 K, can be found elsewhere [19]. For the TM and TDESR measurements, a face-indexed single crystal of approximately 100 μg