Determination of the magnetic anisotropy axes of single-molecule magnets

W. Wernsdorfer¹, N. E. Chakov², and G. Christou²

¹Lab. L. Nédé, associé à l’UJF, CNRS, BP 166, 38042 Grenoble Cedex 9, France
²Dept. of Chemistry, Univ. of Florida, Gainesville, Florida 32611-7200, USA

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Simple methods are presented allowing the determination of the magnetic anisotropy axes of a crystal of a single-molecule magnet (SMM). These methods are used to determine an upper bound of the easy axis tilts in a standard Mn₁₂−Ac crystal. The values obtained in the present study are significantly smaller than those reported in recent high frequency electron paramagnetic resonance (HF-EPR) studies which suggest distributions of hard-axes tilts.

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Single-molecule magnets (SMMs) are among the smallest nanomagnets that exhibit magnetization hysteresis, a classical property of macroscopic magnets. They straddle the interface between classical and quantum mechanical behavior because they also display quantum tunneling of magnetization and quantum phase interference. These methods have allowed us to estimate an upper bound for standard and deuterated Mn₁₂−Ac SMM with hard-axes tilts. The molecules comprise several magnetic ions, whose spins are coupled by strong exchange interactions to give a large effective spin. The molecules are regularly assembled within large crystals, with all the molecules often having the same orientation. Hence, macroscopic measurements can give direct access to single molecule properties.

An important tool to tune the quantum properties is the application of transverse fields. In particular, the tunnel splitting can be tuned by a transverse field. The transverse component increases in general the tunnel rate via the transverse to the easy axis of magnetization. This method is more sensitive but for angles close to the easy plane of magnetization. The positions of the tunnel resonances are only slightly affected by a small misalignment angle. This method is therefore not very sensitive.

A second, very similar method consists of measuring hysteresis loops as a function of the angle of the applied field. Typical results for angles close to the easy axis of magnetization are presented in Fig. 4 showing faster relaxation for larger misalignment angles. This behavior can be understood by separating the applied field into two components, one parallel and the other transverse to the easy axis of magnetization. The transverse component increases in general the tunnel rate via the transverse to the easy axis. This method is more sensitive than the first one, but is often not very convenient.

A third method is shown in Fig. 2. Let’s call (x, y, z) the coordinate system of the magnetic anisotropy of a SMM where the easy axis of magnetization is along z. Another coordinate system (x′, y′, z′) is rotated by two misalignment angles (θ, φ) with respect to (x, y, z). The purpose of the method is to find the misalignment angles. For the sake of simplicity, the following discussion is in two dimensions. A generalization to three dimensions is straightforward and is discussed below. The two reduced coordinate systems (x, z) and (x′, z′) are misaligned by θ (Fig. 2). The method consists of sweeping the applied field H along z′ in the presence of a constant transverse field Hᵗ applied along x′. The latter can be decomposed into Hᵗₓ and Hᵗᶻ along x and z, respectively (Fig. 2).

Hᵗₓ modifies the tunnel rates of the spin system whereas Hᵗᶻ shifts all resonance positions by the quantity...
FIG. 1: (Online color) (a) Positive part of the hysteresis loop of a single crystal of Mn$_{12}$–Ac for several misalignment angles. The magnetization $M$ along the $c$–axis of the crystal is normalized by its saturation value $M_s$. The steps are due to resonant tunneling between the spin ground state with the quantum number $m = -10$ and excited state $m = 4, 3, \ldots, 0$. No clear difference is observed between the misalignment angles of 0 and 1°. (b) Similar hysteresis loops but for angles close to the hard plane (along the $a$–axis of the crystal).

$$H_{z'}^{\text{shift}} = H_{\text{tr}} \tan(\theta).$$

Fig. 2 exhibits a typical measurement for Mn$_{12}$–Ac for a misalignment angle of $\theta = 0.1^\circ$ and $H_{\text{tr}} = \pm 4.1$ T leading to $H_{z'}^{\text{shift}} \approx \pm 0.007$ T. The latter can be measured easily, thereby allowing a field alignment much better than $0.1^\circ$.

In order to generalize the above method to a three dimensional alignment, it is convenient to choose two orthogonal planes. Firstly, the projection of the easy axis into one plane is measured. Then, the orthogonal plane is rotated so that it contains the easy axis projection. Finally, it is sufficient to apply again the above method in this orthogonal plane in order to find the easy axis. The final result can be checked by sweeping the field along the easy axis in the presence of a constant transverse field.

No net shifts of the resonance fields should be observed when comparing both parts of the hysteresis loops.

It is also important to note that the above method works in the thermally activated regime and even above the blocking temperature. In particular, only small transverse fields are needed at higher temperatures. For easy plane anisotropies and more complex anisotropies, analogues versions can be figured out easily.

We use here our methods to determine an upper bound of the easy axis tilts in a standard Mn$_{12}$–Ac crystal.
FIG. 4: (Online color) (a and b) Normalized magnetization along the c−axis of the crystal versus applied field along the c−axis for several constant transverse fields $H_{tr}$. Although the transverse fields increase the tunnel rates, no significant broadening of the resonance fields is observed.

We first align our fields with respect to the easy axis of Mn$_{12}$−Ac using the above methods. We measure then all tunnel transitions as a function of transverse field (Fig. 4) and study their widths $\sigma$. Fig. 5 presents the first derivative of the magnetization $dM/dH$ for the zero field resonance for several transverse fields. We defined the resonance width $\sigma$ as the half-width-at-half-maximum, in accordance with Ref. [17, 18, 19]. Fig. 6 presents $\sigma$ as a function of a transverse field showing a minimum of the width at about 4 T. Recent HF-EPR studies [17, 18, 19] suggested that there are distributions of hard-axes tilts with widths of 1.7° and 1.3° for standard and deuterated Mn$_{12}$−Ac, respectively. Fig. 6 shows the expected width of the zero field resonance supposing that it is only due to the distribution of hard-axes tilts. Our results suggest an upper bound of 0.5°. The actual hard-axes tilts might be much smaller because we expect a dipolar broadening of the resonance lines of about 0.03 T. In addition, higher order tunneling transitions induced by dipolar and small superexchange interactions might further broaden the resonance transition [22]. We therefore believe that the hard-axes tilts should not exceed about 0.2°.

This result is confirmed by the second method. An upper bound for the hard-axis tilts is given by the angle needed to get a hysteresis loop that reaches $|M/M_s| = 0.5$. We find $\theta = 89.6°$ (Fig. 1b), that is an upper bound of 0.4° for the hard-axis tilts. The actual value might be much smaller because we neglect here multi-body tunnel effects [22] that should be rather strong due to the high transverse fields.

We also applied our methods to the Mn$_{12}$−BrAc SMM and could not confirm the hard-axes tilts of 7.3° suggested by del Barco et al. [20]. Our results showed that the hard-axes tilts in Mn$_{12}$−BrAc might be even smaller than in Mn$_{12}$−Ac.

Finally, we speculate about the origin of the line widths observed in the EPR studies [17, 18, 19]. We suggest that the observed fine structures are due to the presence of fast relaxing species having a smaller magnetic anisotropy and are tilted with respect to the c−axis by about 10° [23]. These species are coupled via dipolar interactions to the normal ones leading to multi-body effects (cross relaxations) [22] that might broaden the lines. Such an interpretation is supported by the fact that Mn$_{12}$−BrAc does not show anormalous EPR line width broadening [32] because it hardly has fast relaxing species.

In conclusion, we have presented three methods that allow the determination of the magnetic anisotropy axes of a crystal of a single-molecule magnet (SMM). The precise field alignments are necessary when studying quantitatively resonant tunneling of magnetizations in spin systems like SMMs.
FIG. 6: (Online color) Half-width-at-half-maximum $\sigma$ versus transverse field for the zero field resonance.

[21] The position of the resonances should increase roughly by the factor of $\cos(\theta) \approx 1$ for small angles $\theta$.
[31] Several authors have pointed out that in the Mn$_{12}$ carboxylate family different isomeric forms give rise to different relaxation rates. This was first observed in Mn$_{12}$-ac$_{11}$, Mn$_{12}$-ac$_{24}$, and Mn$_{12}$-ac$_{28}$ and has been studied in detail in detail. We found that a minor species of Mn$_{12}$-ac$_{23}$, randomly distributed in the crystal, exhibits a faster relaxation rate which becomes temperature independent below 0.3 K.