Gadolinium as a single atom catalyst in a single molecule magnet

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Endohedral fullerenes are perfect nanolaboratories for the study of magnetism. The substitution of a diamagnetic scandium atom in Dy2ScN@C80 with gadolinium decreases the stability of a given magnetization and demonstrates Gd to act as a single atom catalyst that accelerates the reaching of thermal equilibrium. X-ray magnetic circular dichroism at the M4,5 edges of Gd and Dy shows that the Gd magnetic moment follows the sum of the external and the dipolar magnetic field of the two Dy ions and compared to Dy2ScN@C80 a lower exchange barrier is found between the ferromagnetic and the antiferromagnetic Dy configuration. The Arrhenius equilibration barrier as obtained from superconducting quantum interference device magnetometry is more than one order of magnitude larger, though a much smaller prefactor imposes faster equilibration in Dy2GdN@C80. This sheds light on the importance of the angular momentum balance in magnetic relaxation.

A catalyst accelerates the approach of thermal equilibrium without being consumed by this process. In the classical picture it lowers the kinetic barrier between two states A and B, where the transition rates are described by Boltzmann factors comprising the barrier, the energy difference between A and B, and by a prefactor reminiscent to the attempt frequency. The concept of a catalyst may as well be applied for the case of single molecule magnets that were prepared in a state outside thermal equilibrium towards which they decay with certain rates. From the temperature dependence of these rates Arrhenius barriers and attempt frequencies may be inferred. The exponential prefactors in the kinetics reflect the energy landscape where a process runs. In the present case the 4f electron spins of a single gadolinium atom are shown to catalyze magnetic transition rates dramatically.

Single molecule magnets (SMM’s) display hysteresis, i.e. maintain non-equilibrium magnetization for a measurably long period of time [13]. After the discovery of single ion molecule magnets [4] the lanthanide magnetochromistry got a significant boost, where new strategies for the improvement were developed [5–7]. With these ideas on rational design magnetic hysteresis of single molecules at 60 K [8] and even above liquid nitrogen temperatures [9] is reached by now. Endohedral fullerenes provide a versatile environment to encapsulate different diamagnetic and paramagnetic ions [10, 11]. First magnetic studies were performed on Gd@C82 [12] and it took 17 more years until SMM behaviour in endohedral fullerenes was found with DySc2N@C80 [13]. In the following many different C80 mixed dysprosium-lanthanide nitride clusters have been synthesized and magnetically characterized [14–16]. As in other radical bridged lanthanide complexes [17] dysprosium ion pairs appear to form excellent SMM’s [18]. For the case of Dy2ScN@C80 the particularly long zero field lifetime of the magnetization was attributed to exchange protection of two Kramers ions [19]. Heterometallic clusterfullerenes require more effort for synthesis and separation, and only recently an endeavour of implementing three different rare earth atoms inside C80 combined single atom magnetism and luminescence [20]. If more than one paramagnetic atomic species is involved, element specific methods such as x-ray magnetic circular dichroism (XMCD) [21] give unprecedented insight into the magnetic ordering of heteroatomic clusters [22–24].

Here we investigate the interplay between two Dy and one Gd ion in a 1 nm carbon cage. The substitution of scandium with gadolinium decreases the excitation gap between the ferro- and antiferromagnetically coupled Dy doublets. Although the kinetic barrier increases, the prefactor dictates a lower magnetization lifetime in Dy2GdN@C80. This strong change in magnetization dynamics indicates Gd to break the spin flip protection symmetries which are found in Dy2ScN@C80 and exhibits the role of the Gd angular momentum in the change of magnetisation.

Dy2GdN@C80 endofullerenes were produced by arc-discharge synthesis using the corresponding metals [10, 11]. The subsequent separation by high pressure liquid chromatography resulted in a sample of 95 % purity with 5% Dy3N@C80 contamination as inferred from time of flight mass-spectrometry [25]. The Dy3N@C80 content does not affect the conclusions of this paper. The magnetization measurements were performed by x-ray magnetic circular dichroism (XMCD) and SQUID magnetometry. XMCD was performed at the X-Treme beamline of the Swiss light source (SLS) [26] on a sample obtained after spray coating of a toluene solution of the molecules on an aluminum substrate. The total elec-
tron yield was normalized by the secondary electron current from a gold mesh in the x-ray beam before it hits the sample and by the x-ray absorption cross section of gold. The SQUID magnetometer was a Quantum Design (QD) MPMS3 Vibrating Sample Magnetometer (VSM), where we performed magnetization experiments in external magnetic fields up to 7 T and temperatures down to 1.55 K. For the SQUID measurements, the toluene solution was drop-cast into a QD polypropylene powder sample holder. A temperature independent diamagnetic background of $-5.8 \times 10^{-8}$ Am²/T was inferred from temperature dependent magnetization measurements. From the paramagnetic saturation at 2 K and 7 T, $m_{sat}$ of 2.17 × 10⁻⁶ Am² and a maximum magnetic moment of 17 $\mu_B$ an ensemble of 1.4 × 10¹⁶ molecules with a mass of 33 $\mu_B$ is inferred. (The saturation magnetic moment of 17 $\mu_B$ being the sum of two non-collinear Dy $J_z=15/2$ and one collinear Gd $J_z=7/2$ moment.)

The ground state as proposed in Figure 1 is confirmed by x-ray magnetic circular dichroism. The XMCD for Dy and Gd is shown in the bottom of Figure 1(a). Sum rule analysis [28–30] reveals effective saturation magnetic moments of Gd³⁺ and Dy³⁺ in Dy₂ScN@C₈₀ [25]. The Dy effective magnetic moment at saturation of 4.5±0.1 $\mu_B$ compares well with the value in DySc₂N@C₈₀ [13]. The moment of Gd gets 5.8±0.1 $\mu_B$. It is smaller than the expectation for a free, collinear Gd ion as also observed in other Gd molecular magnet systems [31].

The magnetization curves of Gd and Dy are shown in Figure 2(b). For endohedral Gd it deviates from a Brillouin function with $g = 2$ and $J = 7/2$. This certifies endohedral Gd not to behave as a free ion but that it is subject to magnetic interaction with the two Dy ions. Compared to the free ion, the relative magnetization of Gd in Dy₂GdN@C₈₀ is largest at a field of about 0.2 T, which is close to the field imposed by the two Dy ions in the ferro ground states.

The above statements are substantiated with the implementation of a pseudospin model to the level scheme in Figure 1(d) [25]. The solid lines in Figure 2(b) are the best fit, where the access to the individual magnetisation curves of Dy and Gd improves the reliability of the extracted parameters significantly. The magnetic moment of Dy gets 8.8 $\mu_B$ and is in line with that of Dy₂ScN@C₈₀ [19], while that of Gd gets 6.9 $\mu_B$. The parameter $B_D$ [25] that describes the splitting of the Gd states due to the Dy dipolar fields is 0.24 T, which is close to the value of 0.2 T of a moment of 10 $\mu_B$ at a Dy-Gd distance of 0.36 nm. This affirms that in zero field the Gd magnetism is governed by the dipolar fields of the two Dy ions and that possible exchange interaction between Dy and Gd must be much smaller. Finally, the excitation energy or gap between the lowest ferromagnetically and the lowest antiferromagnetically coupled states $U_g$ is determined from comparison of the data to the model. In Dy₂GdN@C₈₀ it decreases, compared to Dy₂ScN@C₈₀ from 9 to 0.1±0.8 $k_B$ K. This $U_g$ value points to zero field degeneracy of the four possible Dy spin configurations.
Figure 2. (a) Top: X-ray absorption spectrum $I_{\text{tot}}$ vs. photon energy of Dy$_2$GdN@C$_{80}$ (green line). The intensity ratio between Gd and Dy is in line with the 1:2 stoichiometry. Maximum electron yield 106 pA. Middle: Background subtracted x-ray absorption spectra $I(c^+)$ and $I(c^-)$ for both x-ray helicities with the maxima of the Gd and Dy intensities normalized to 1. External field 6.5 T, parallel to the x-ray incidence. Bottom: X-ray magnetic circular dichroism (XMCD) $I(c^+) - I(c^-)$. (b) Field dependent XMCD of Dy (up-triangle, light blue) and Gd (down-triangle, yellow). Brillouin function $B_{7/2}$ (dashed line) corresponding to $g = 2$, $J = 7/2$, $T = 1.95 \, \text{K}$, representing the magnetization of free Gd. The solid lines are fits of the element specific magnetisation curves to an extended pseudospin model [23]. (c) Differences between XMCD(Gd) and $B_{7/2}$ (black disks), and XMCD(Dy) (black squares). The solid lines are obtained from the fit results in (b). The peak of XMCD(Gd) - $B_{7/2}$ indicates the B-field of the Dy ions at the Gd site.

Figure 3. Comparison of the magnetization of Dy$_2$GdN@C$_{80}$ (green line) and Dy$_2$ScN@C$_{80}$ (black line) normalized with the corresponding saturation values $m_{\text{sat}} = m(7 \, \text{T}, 2 \, \text{K})$. (a) At 10 K both molecules show paramagnetic behaviour, where the initial slope of the normalized magnetization of Dy$_2$GdN@C$_{80}$ is a factor of 0.8 smaller than that of Dy$_2$ScN@C$_{80}$. (b) At 1.8 K with a field scan rate of 5.3 mT/s Dy$_2$GdN@C$_{80}$ shows a small hysteresis of 68 mT $m_{\text{sat}}$, while Dy$_2$ScN@C$_{80}$ displays a large hysteresis with an area of 3190 mT m$_{\text{sat}}$. The inset zooms the hysteresis of Dy$_2$GdN@C$_{80}$ with the axes $m/m_{\text{sat}}$ and $\mu_0 H(T)$. Black arrows indicate the field scan directions.

The smaller barrier $U_g$ between the ferro and the antiferro states is a hint that Gd may accelerate the approach of the Dy spin system to thermal equilibrium. In Figure 3 magnetization curves for the two molecules are displayed. At 10 K temperature both display paramagnetism with a characteristic thermal equilibrium curve. The relative zero field susceptibility of Dy$_2$GdN@C$_{80}$ is a factor of 0.81 smaller than for Dy$_2$ScN@C$_{80}$. This confirms that more magnetic states are available in Dy$_2$GdN@C$_{80}$. The additional states of the Gd ion interfere with the Dy$_2$ units and decrease the hysteresis of Dy$_2$ScN@C$_{80}$ at 1.8 K by a factor of 47 (see Figure 3(b) and supplementary materials [25]). Apparently, the exchange protection as it is operational in Dy$_2$ScN@C$_{80}$ breaks down if gadolinium sits in the same cage instead.
of scandium. This identifies Gd to soften the hysteresis, and makes it an option in engineering of single molecule magnets, if e.g. heat dissipation shall be minimized in high frequency applications.

For all molecules investigated so far, the ground state parameter $U_g$ of the molecules as determined from the magnetisation in thermal equilibrium was in line with the Arrhenius barrier $\Delta_{\text{eff}}$ from the decay of the magnetisation [19] [32]. In the following we will see that this is not the case for Dy$_2$GdN@C$_{80}$, and the discrepancy between $U_g$ and $\Delta_{\text{eff}}$ spots new light on the demagnetisation dynamics.

The fluctuation rates of the magnetic states are expressed in the kinetics that describe the approach to thermal equilibrium. Figure 4(a) shows an experiment where the magnetic moments of the molecules were saturated in a magnetic field, which is then ramped down to zero. The subsequent decay contains information on the ground state and the dynamics of the spin flips involved. The decay rate is not constant but decreases to a constant value. This behaviour is common to single molecule magnets [13] [17]. At 1.55 K and after two hours the decay rates of Dy$_2$ScN@C$_{80}$ and Dy$_2$GdN@C$_{80}$ are in the order of $10^{-4}$ s$^{-1}$, though the back-extrapolation of these rates to $t = t_0$ indicates that 60% of all Dy$_2$ScN@C$_{80}$ decayed with this rate, while it were 0.7 % only in the case of Dy$_2$GdN@C$_{80}$. For a quantification of the kinetics that describe the approach to thermal equilibrium we investigate the decay rates as a function of temperature. It is, however, difficult to determine decay rates below $10^{-3}$ m$_{\text{sat}}$, because of the relaxation of the magnet in the SQUID. In order to get a reliable value for the magnetic lifetime we evaluated the integral of the magnetization after reaching zero field at time $t_0$ that we like to call remanence time $T_0$:

$$T_0 = \int_{t_0}^{\infty} \frac{m(t)}{m_{\text{sat}}} \, dt,$$

where $T_0$ corresponds to the decay time $\tau$ of a single exponential $m(t - t_0) = m_{\text{sat}} \exp(-\chi(t - t_0)/\tau)$. The validity of using this remanence time to describe the decay of the magnetization is justified by the evaluation of the decay data of Dy$_2$ScN@C$_{80}$ (see Figure [3(b]), where a barrier $\Delta_{\text{eff}}/k_B$ of 9.0±0.2 K is found as compared to 8.5±0.5 K with the standard method [19] [25]. This barrier fits the dipole and exchange splitting in Dy$_2$ScN@C$_{80}$ as inferred from the equilibrium magnetization [19]. The Arrhenius slopes in Figure 4(b) indicate for Dy$_2$GdN@C$_{80}$ a larger barrier than for Dy$_2$ScN@C$_{80}$. The barrier $\Delta_{\text{eff}}$ of 15.1±0.4 K can not be understood with a decay path, where the lowest ferro-states are directly excited into the lowest antiferro-states, since $U_g$ is much lower. This suggests that the flip of the magnetization in a $|\bar{1}\rangle \rightarrow |\bar{1}\rangle$ transition involves excitation of the Gd 4f states. The high barrier is consistent with a picture where the Dy angular momentum change in a $|\bar{1}\rangle \rightarrow |\bar{1}\rangle$ transition can be temporarily stored in the Gd ions. Furthermore, the kinetics of the magnetization decay comprises a prefactor $\tau_0$ in $\tau(T) = \tau_0 \exp(\Delta_{\text{eff}}/k_B T)$. It is a factor of $4.1\pm0.8\times10^{-4}$ smaller in Dy$_2$GdN@C$_{80}$ as compared to Dy$_2$ScN@C$_{80}$. It includes, besides an attempt frequency, as well the quantum symmetry of the object [32]. Apparently, single Gd atoms break the symmetry that imposes the exchange protection in Dy$_2$ScN@C$_{80}$ and act as a reservoir for angular momentum that is involved in the flip of the magnetization.

In conclusion x-ray magnetic circular dichroism establishes non-collinear magnetism of the Dy ions and quasi collinear magnetism of Gd in Dy$_2$GdN@C$_{80}$. The ground state energy difference between the ferromagnetic and the antiferromagnetic Dy configuration decreases relative to Dy$_2$ScN@C$_{80}$. From temperature dependent magnetization decay measurements we however infer a higher kinetic barrier. The decrease of the prefactor for the description of the magnetic lifetime overcompensates the higher barrier and identifies Gd as a single atom catalyst for the decay of the magnetization in single molecule magnets.

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