Local Magnetic Properties of a Monolayer of Mn$_{12}$ Single Molecule Magnets

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The magnetic properties of a monolayer of Mn$_{12}$ single molecule magnets grafted onto a Si substrate have been investigated using depth-controlled $\beta$-detected nuclear magnetic resonance. A low energy beam of spin polarized radioactive $^8$Li was used to probe the local static magnetic field distribution near the Mn$_{12}$ monolayer in the Si substrate. The resonance linewidth varies strongly as a function of implantation depth as a result of the magnetic dipolar fields generated by the Mn$_{12}$ electronic magnetic moments. The temperature dependence of the linewidth indicates that the magnetic properties of the Mn$_{12}$ moments in this low dimensional configuration differ from bulk Mn$_{12}$.

Single molecule magnets (SMMs)$^1$ are molecules which contain a small number of magnetic ions with large magnetic interactions between them ($J \sim 10 - 100$ K). The magnetic cores of each molecule are surrounded by organic or inorganic ligands. Since the molecules are magnetically isolated, they form at low temperature a lattice of very weakly interacting spins. Practical application of SMMs as molecular scale units for information storage$^2$ or “qubits” for quantum computation$^3$ requires addressing individual molecules, which may be realized in principle by depositing a monolayer of molecules on a suitable substrate. Methods to deposit suitably derivatized Mn$_{12}$-type clusters on gold$^8$ and Si$^{12,13}$ have been developed recently, opening up exciting possibilities for applications of SMMs for information storage on a single molecule and for the investigation of the quantum behavior of isolated spins, such as quantum tunnelling of the magnetization (QTM)$^{11,12,13}$, topological quantum phase interference$^{14,15}$, and quantum coherence$^{16,20,21}$. Unfortunately, the small quantity of magnetic material in the case of a monolayer (or sub-monolayer$^{11}$) implies that it is virtually impossible to accurately determine magnetic properties with conventional bulk techniques, such as SQUID magnetometry or conventional nuclear magnetic resonance (NMR). However, a new technique, namely depth-resolved $\beta$-detected NMR ($\beta$-NMR), which has $\sim 10^{13}$ orders of magnitude higher sensitivity compared to conventional NMR, is well-suited for studying such systems.$^{22,23,24,25,26}$

In this paper we report $\beta$-NMR measurements of the magnetic moment of Mn$_{12}$ molecules which are grafted as a monolayer on a Si substrate. The experiments were performed using a low energy beam of highly polarized radioactive $^8$Li, implanted into the Si substrate just below the Mn$_{12}$ monolayer. The strength and distribution of the magnetic dipolar fields from the Mn$_{12}$ moments determines the shape of the $^8$Li NMR resonance. Interestingly, the temperature dependence of the signal deviates significantly from the measured magnetization for bulk Mn$_{12}$. This is evidence that the interactions characterizing Mn$_{12}$ in this 2D configuration are different from the bulk.

Magnetic resonance techniques have been used extensively to study the magnetic properties of SMMs in the bulk. In particular, conventional NMR$^{27,28,29,30,31}$ and muon spin relaxation$^{27,28,32,33}$ (μSR) have been used to measure the molecular spin dynamics in both the thermally activated regime as well as the quantum tunneling regime. $\beta$-NMR is a closely related technique, where one measures the nuclear magnetic resonance and relaxation of $^8$Li, a spin $I = 2$ nucleus with a small electric quadrupole moment $Q = +31$ m$b$ and gyromagnetic ratio $\gamma = 6.301$ MHz/T. The radioactive $^8$Li$^+$ beam is produced at the isotope separator and accelerator (ISAC) at TRIUMF. It is then polarized using a collinear optical pumping method, and implanted into the sample. Since the implantation energy can be varied between 0.9 – 28 keV, corresponding to an average implantation depth in Si of 1 – 250 nm, depth resolved $\beta$-NMR measurements are possible. As in any form of NMR, the time evolution of the nuclear polarization is the quan-
tity of interest. It can be measured through the $\beta$-decay asymmetry, where an electron is emitted preferentially opposite to the direction of the nuclear polarization at the time of decay [34] and detected by appropriately positioned scintillation counters. As noted above, this method of detection is dramatically more sensitive than conventional NMR and makes $\beta$-NMR suitable for studies of ultra-thin films and nano-structures [22 23]. The nuclear resonance in a static magnetic field, $H_0 = H_0 \hat{z}$, can be detected by measuring the time averaged nuclear polarization along $\hat{z}$, $p_z(\nu)$, as a function of the frequency $\nu$ of a small ($\sim 1$ G) oscillating perpendicular magnetic field, $H_1(t) = H_1 \cos(2\pi \nu t) \hat{z}$. A loss of polarization occurs when $\nu$ matches the Larmor frequency of the nuclear spins of the $^8$Li, a value that is given by the product of $\gamma$ and the local field it experiences. Hence, the position and shape of the resonance(s) signals provide detailed information on the distribution of static local magnetic fields.

The experiments reported here were performed on two different samples. Sample 1 was prepared using a three-step process[12]: 1) grafting of methyl ester of 10-undecanoic acid on a H-terminated Si(100) substrate, 2) hydrolysis of the ester group, and 3) ligand exchange between $[\text{Mn}_{112}\text{O}_{12}(\text{OAc})_{16}(\text{H}_2\text{O})_{14}]^+\cdot\text{H}_2\text{O}-2\text{AcOH}$ and the grafted undecanoic acid to anchor the Mn$_{112}$ SMMs to the organic layer. A schematic of sample 1 is shown in Fig. 1(a). Sample 2 is an identically prepared Si substrate, i.e. following step 1 only. It is used as a control sample in order to confirm that the effects measured in 1 are solely due to the Mn$_{112}$. The samples were mounted in an ultra high vacuum (UHV) environment on a cold finger cryostat. The resonance lines of $^8$Li were measured at various temperatures and implantation energies in both samples in an external magnetic field $H_0 = 6.55$ Tesla, perpendicular to the Si surface.

The $\beta$-NMR spectra were measured by implanting the $^8$Li beam at different energies in the Si substrate below the Mn$_{112}$ monolayer. An example of the stopping profile of the implanted $^8$Li at two different energies is shown in Fig. 1(a). At $E = 1$ keV, where most of the $^8$Li stop within 10 nm of the Si surface, the dipolar field from the Mn$_{112}$ moments is large, as illustrated in Fig. 1(b). However, at $E = 28$ keV the average $^8$Li implantation depth is $\sim 250$ nm, and the dipolar field at this depth is negligible; hence, the local field experienced by the $^8$Li is simply the applied uniform $H_0$. As a result the measured resonance line at 1 keV is significantly broadened compared to that measured at 28 keV, as clearly seen in Fig. 1(c) at $T = 3.2$ K. Furthermore, the resonance measured in sample 2 at $E = 28$ keV and $T = 3.2$ K is identical to that measured in sample 1 under the same conditions, and the broadening observed in sample 2 is much smaller at $E = 1$ keV. This demonstrates that low energy $\beta$-NMR spectroscopy is sensitive to the magnetization of the Mn$_{112}$ monolayer. In particular, the $^8$Li nuclei implanted into sample 1 at low $E$, and hence stopping close to the Mn$_{112}$ molecules, experience a large distribution of magnetic fields, which is attributed to the dipolar fields from the Mn$_{112}$ monolayer.

The observed resonance broadening, depicted in Fig. 1(c), can be described in terms of dipolar fields from the Mn$_{112}$ moments ($m = m\hat{z}$, which are preferentially aligned by $H_0$. For discussion purposes, let us start by assuming that the Mn$_{112}$ moments are arranged in a 2 dimensional square lattice with a lattice constant $a$ at
$z = -z_0$, where the Si substrate surface is assumed to be at $z = 0$. The $z$ component of the total dipolar field, experienced by a $^8$Li at $\mathbf{R} = x\hat{x} + y\hat{y} + z\hat{z}$, due to moments $m_i$ at $\mathbf{R}_i = X_i\hat{x} + Y_i\hat{y} + z_0\hat{z}$ is

$$H_z^q(z) = \sum_i \frac{\mu_0 m_i}{4\pi r_i^3} \left( \frac{3z^2}{r_i^2} - 1 \right), \quad (1)$$

where $r_i = |\mathbf{R} - \mathbf{R}_i|$. As we shall see below, it is useful for calculation purposes to parameterize the width of the dipolar field distribution experienced by a $^8$Li stopping at a depth $z$ with a reasonable analytical function. Simulations indicate that the dipolar fields from the Mn$_{12}$ monolayer decay in the Si according to a power law:

$$\Delta(z) = \Delta_0 \left( 1 + \frac{z}{z_0} \right)^{-\alpha}, \quad (2)$$

where $\Delta_0$ is the width of dipolar field distribution at the surface of the Si substrate ($z = 0$), $z_0$ is the distance between the monolayer and the Si surface and $\alpha$ is a parameter describing the decay of dipolar field in the substrate as a function of depth. Note that $\Delta_0$ is proportional to the magnetic moment $m$. In Fig. 2 we plot the results of the simulation for $\Delta$ as a function of distance from the plane of the monolayer (solid line). Near the Mn$_{12}$ moments $[(z + z_0) \ll a]$ the magnetic field is effectively that of the nearest moment and therefore $H_z^q(z)$ follows the asymptotic behavior for a dipolar field of a single moment, which agrees with Eq. (2) with $\alpha = 3.0$ (dotted line). The hatched area indicates the depth where $\alpha$ deviates from its asymptotic value.

In addition to the obvious broadening at low $E$, the observed line-shape also changes. At high $E$ [bottom of Fig. 1(c)] the line-shape fits well to a simple Lorentzian function, while at low $E$ [top of Fig. 1(c)] it has a different shape characterized by a sharp center and broad tails. The intrinsic resonance line-shape of $^8$Li in Si is that obtained at high implantation energy. Therefore, the low implantation energy line-shape may be simulated by calculating the broadening of the intrinsic line due to dipolar fields generated by the monolayer.

In the case for our Si substrates, where the roughness is 0.1 – 0.2 nm over an area of at least 200 × 200 nm$^2$, the simulations which assume a perfect flat substrate are still valid if the surface roughness is small ($\ll 1$ nm) within the area occupied by these neighbours. This is the case for our Si substrates.
due to the lack of knowledge of the exact structure of the grafted Mn$_{12}$ moments lattice on the surface, and therefore it is impossible to simulate the exact form of $n(B,z)$. However, this allows (at least qualitatively) an estimate of the size of dipolar fields as a function of depth. For each implantation energy we calculate a depth-averaged field distribution:

$$\langle n(B) \rangle = \int \rho(z) n(B,z) dz,$$

where $\rho(z)$ is the stopping distribution obtained using the TRIM.SP code [38, 39] to simulate the implantation profile of $^6$Li in Si. The final step in generating the line-shape is to convolute $\langle n(B) \rangle$ by the intrinsic Lorentzian line-shape, i.e. the line-shape obtained from the high $E$ measurement. Recall, this line-shape is identical to that obtained in sample 2, but it represents a more accurate in-situ reference to the low $E$ resonance since it can be measured at exactly the same experimental conditions (temperature, $H_1$, etc.). The calculated line-shape is used to fit the $\beta$-NMR spectra, e.g. the solid line in Fig. 1(c), where $\Delta_0$, $\alpha$ and $z_0$ are the fitting parameters.

The best fit of the resonance lines at the implantation energy of $E = 1$ keV and all temperatures is achieved with a common $\alpha = 3.0 \pm 0.1$ and $z_0 = 1.2 \pm 0.1$ nm, while $\Delta_0$ varies with temperature. In Fig. 3 we plot the fitted values of $\Delta_0$ as a function of temperature for both samples 1 (circles) and 2 (squares). At high temperatures the width $\Delta_0$ is small, $\sim 0.2$ mT, and is equal in both samples. However, in sample 1 it increases dramatically as the temperature is lowered below $\sim 100$ K reaching $\sim 1.1$ mT at $T = 3.2$ K, while it remains unchanged in sample 2. Clearly, this temperature dependent broadening is due to the Mn$_{12}$ magnetic moments at the surface of sample 1. The small $\Delta_0$ at high temperature in both samples is unrelated to the Mn$_{12}$ magnetic moments, but rather it is likely due to changes in the Si structure near the surface, caused by the grafted ligands and resulting in a small quadrupolar broadening [24, 40, 41].

As discussed above, a measurement of $\Delta_0$, or more precisely the difference between the broadening in samples 1 and 2, as a function of temperature is equivalent to measuring the $z$ component of the effective magnetic moment ($m_z$) of a single Mn$_{12}$ molecule. As shown in Fig. 3 there is a sharp increase below $\sim 100$ K and saturation at low temperature. The increase of $m_z$ below 100 K is indicative of the gradual de-population of thermally activated states. The low temperature saturation occurs when most of the Mn$_{12}$ moments reside in their ground spin state in this 2D configuration and are aligned with the applied magnetic field. We compare the measured magnetization for the monolayer to that measured in a bulk Mn$_{12}$ sample at the same applied field (solid line in Fig. 3). The bulk magnetization was scaled to match the low temperature broadening. Clearly, there is a dramatic difference between our experimental results in the monolayer compared to that in the bulk. This difference is a strong indication that the magnetic properties of Mn$_{12}$ in the 2D configuration are significantly different from the bulk. Earlier studies suggest that the Mn$_{12}$ clusters in the monolayer remain intact [36]. Hence the difference is most probably due to changes in their electronic structure, which may be caused by distortions of the Mn$_{12}$ core in the monolayer due to the different local environment.

Several other points are noteworthy. No shift in the resonance frequency is observed. Simulations show that this is expected due to the randomness in the lattice which acts to reduce the shift to below experimental resolution ($< 0.05$ mT). In addition the value of $z_0 = 1.2 \pm 0.1$ nm, obtained from the fits, is in very good agreement with the thickness of the grafted layer ($\sim 1.1$ nm) measured using atomic force lithography [12]. Inspecting the resonance lines at different depths and $T = 3.2$ and 5 K shows that $\alpha$ (obtained from best fits using a common value of $\Delta_0$ and $z_0$ for each temperature) exhibits a strong dependence on the implantation depth (Fig. 4). As expected, we find that at low implantation depth (near the monolayer) $\alpha \approx 3$, with a large deviation at larger depths. The deviation from the asymptotic value $\alpha = 3.0$ begins to occur when the average implantation depth exceed $\sim 1$ nm. Compared with simulations of the dipolar fields of the Mn$_{12}$ moments on the Si substrate, this corresponds to $0.3 - 0.5$ a and allows a rough estimate of the average distance between neighbouring Mn$_{12}$ molecules of $a \approx 2 - 3.3$ nm, a reasonable value considering the size of Mn$_{12}$ molecules core [12]. Finally, using the extracted values of $a$ and $z_0$ to simulate the dipolar field to roughly estimate $\Delta_0$, we find that the low temperature average of $\Delta_0 \sim 1$ mT corresponds to a Mn$_{12}$ magnetic moment of $5\mu_B - 12\mu_B$, as expected.

**FIG. 4:** $\alpha$ as a function of implantation depth estimated from fitting the resonances at $T = 3.2$ K (circles) and 5 K (squares). The solid line is a guide to the eye and the dashed line represents the asymptotic value $\alpha = 3.0$ near the monolayer.
for an electronic magnetic moment with a large effective spin.

In conclusion, we used $\beta$-NMR of $^8$Li to measure the effective magnetic moment of a single Mn$_{12}$ molecule in a monolayer grafted on Si, demonstrating that the technique has the required sensitivity to investigate the magnetic properties of a sub-monolayer of magnetic molecules. The temperature dependence of the Mn$_{12}$ magnetic moment indicates that their magnetic properties and spin Hamiltonian are dramatically different from bulk. Since future practical applications of SMMs will undoubtedly require them to be fabricated in the form of monolayers, it is important to understand and thus control any modifications that result from depositing them on surfaces[42].

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