Experiment 1036 β -NMR Study of Single Molecule Magnets Mono-Layers

(Z. Salman, Oxford University and R. F. Kiefl, CIAR and UBC)

The use of nanoscale magnets for technological applications such as information storage or quantum computing requires monodisperse magnets that can be addressed individually. A major step towards achieving this goal came recently with the discovery of molecules that function as identical magnets, and the ability to deposit a monolayer of these molecules on a suitable substrate. At low temperatures these single molecule magnets (SMMs) exhibit fascinating quantum mechanical behaviour that dramatically effects macroscopic properties such as magnetization. These include the observation of quantum tunnelling of the magnetization (QTM), topological quantum phase interference, and quantum coherence. However, the small quantity of magnetic material present in a monolayer (or submonolayer) implies that it is virtually impossible to accurately determine their magnetic properties with conventional bulk techniques. However, depth-resolved β -detected NMR (β -NMR), which has $\approx 10^{13}$ orders of magnitude higher sensitivity compared to conventional NMR is well-suited for studying such systems



Fig. 1. (a) A schematic of sample **1** where the Mn₁₂ molecules are grafted on a Si substrate. The stopping profiles of ⁸Li in Si at E = 1 and 28 keV are also shown (purple and grey lines respectively). (b) The measured β -NMR spectra from sample **1** in an applied magnetic field $H_0 = 6.55$ Tesla at T = 3.2 K. The top spectrum is for E=1 keV and the bottom for E=28 keV. The solid lines are fits to the calculated resonance line-shape.

The experiments reported here were performed on two different samples. Sample 1 was prepared using a three-step process: 1) grafting of methyl ester of 10undecanoic acid on a H-terminated Si(100) substrate, 2) hydrolysis of the ester group, and 3) ligand exchange between $[Mn_{12}O_{12}-(OAc)_{16}(H_2O)_4]\cdot H_2O\cdot 2AcOH$ and the grafted undecanoic acid to anchor the Mn_{12} 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 steps 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_{12} . The resonance lines of ⁸Li were measured at various temperatures and implantation energies in both samples in an external magnetic field $H_0 = 6.55$ Tesla.

The β -NMR spectra were measured by implanting the ⁸Li beam at different energies in the Si substrate below the Mn_{12} monolayer. An example of the stopping profile of the implanted ⁸Li at two different energies is shown in Fig. 1(a). At E = 1 keV, where most of the ⁸Li stop within 10 nm of the surface of Si, the dipolar field from the Mn_{12} moments is large. However, at E = 28 keV the average ⁸Li implantation depth is ~ 250 nm, and the dipolar field at this depth is negligible; hence, the local field experienced by the ⁸Li is simply the applied uniform field 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(b) 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 β -NMR spectroscopy is sensitive to the magnetization of the Mn_{12} monolayer. In particular, the ⁸Li nuclei implanted into sample 1 at low E, and hence stop close to the Mn_{12} molecules, experience a large distribution of magnetic fields, which are attributed to the dipolar fields from the Mn_{12} monolaver.

The observed broadening of the resonance line at low implantation energies, compared to high implantation energy, enables the determination of functional form of the dipolar magnetic field from the Mn₁₂ moments experienced by the ⁸Li. This is found to follow a power law decaying function with power ~ -3 as expected from its dipolar nature. It also provides a measure of the size of the magnetic moment of individual Mn₁₂ molecules. The main finding of our study is that the temperature dependence of the size of magnetic moment on a Mn₁₂ molecules is dramatically different from bulk. In particular, at low temperatures (~ 3.2 K) the magnetic moment in the monolayer is estimated to be $5 - 12\mu_B$ compared to $20\mu_B$ in bulk.

Publications:

1. "Local Magnetic Properties of a Monolayer of Mn_{12} Single Molecule Magnets", submitted.

Conferences and Seminars:

1. Z. Salman: "The 10th International Conference on Molecule-Based Magnets (ICMM)", Victoria, B.C., Aug. 2006.

2. Z. Salman: Nuclear Magnetic Resonance Seminar, in the Technion - Haifa, Israel, Dec. 2006.