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Observation of a level crossing in a molecular nanomagnet using implanted muons

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Abstract

We have observed an electronic energy level crossing in a molecular nanomagnet (MNM) using muon spin relaxation. This effect, not observed previously despite several muon studies of MNM systems, provides further evidence that the spin relaxation of the implanted muon is sensitive to the dynamics of the electronic spin. Our measurements on a broken ring MNM \([\text{H}_2\text{N}^\text{Bu}^\text{t}][\text{Cr}_8\text{CdF}_9(\text{O}_2\text{CC}(\text{CH}_3)_3)_{18}],\) which contains eight Cr ions, show clear evidence for the \(S = 0 \rightarrow S = 1\) transition that takes place at \(B_c = 2.3\) T. The crossing is observed as a resonance-like dip in the average positron asymmetry and also in the muon spin relaxation rate, which shows a sharp increase in magnitude at the transition and a peak centred within the \(S = 1\) regime.

(Some figures in this article are in colour only in the electronic version)

Molecular nanomagnets (MNMs) [1] comprise clusters of transition metal ions. Strong exchange coupling between these ions within a single molecule results in each molecule possessing a ground state described by a total spin eigenvalue \(S\). Excited states will possess other values of \(S\) and the splitting of these levels in an applied magnetic field often leads to level crossings in which an excited spin state in zero field becomes the new ground state at fields above the field at which a crossing occurs. MNMs have been widely studied in recent years, most recently in anticipation of their possible deployment as elements of quantum computers [2], although much interest also centres on the quantum tunnelling of the magnetization (QTM) which can take place when magnetic energy levels are at resonance [1]. When implanted muons were first used to probe the spin dynamics in these systems, it was hoped that they would be sensitive to level crossings. However, early studies failed to observe any signature of such crossings [3] and, despite the possible observation of effects ascribed to a matching of the MNM electronic energy level splitting with that of the muon hyperfine levels [4] and the observation of crossings in broadly related systems [5], the observation of a crossing in an MNM has remained elusive until now. Here we demonstrate that muons can be sensitive to the electronic energy level crossings in MNMs. Our measurements on a broken ring system, made using the new HIFI spectrometer at the ISIS facility, demonstrate the effect of the level crossing on the integrated positron asymmetry and on the muon spin relaxation rate.

The material measured in this study is related to the octonuclear system \([\text{Cr}_8\text{F}_8(\text{O}_2\text{CC}(\text{CH}_3)_3)_{16}]\) [6]. This material has a \(S = 0\) ground state due to antiferromagnetic coupling \((\mu_{\text{Cr,Cr}} \approx 16.9\) K) between the eight nearest neighbour Cr\(^{3+}\) \((s = 3/2)\) spins. In contrast, the broken ring system \(\text{Cr}_8\text{Cd}[7]\) (full formula \([\text{H}_2\text{N}^\text{Bu}^\text{t}][\text{Cr}_8\text{CdF}_9(\text{O}_2\text{CC}(\text{CH}_3)_3)_{18}])\), shown
The application of magnetic fields of up to 29 T with a full width at half maximum of approximately 0.4 T. Increasing the temperature causes the resonance to broaden in an asymmetric fashion and shifts the minimum to a slightly higher field of 2.35 T.

Another method of examining the resonance is to fit the time-differential spectra to the functional form

\[ A(t) = A_{\text{rel}} e^{-\lambda t} + A_{\text{bg}}, \tag{1} \]

where \( A_{\text{rel}} \) is the relaxing amplitude and \( A_{\text{bg}} \) is the background contribution, which we expect to be highly field dependent due to the effect of the magnetic field on the incoming muons and outgoing positrons due to the Lorentz force. The amplitude \( A_{\text{rel}} \) was held fixed throughout the fitting procedure and the extracted relaxation rate \( \lambda \), measured at 70 mK, is shown in figure 2(b). The relaxation rate is seen to increase sharply around \( B_c \) and peak at \( B = 2.54 \) T. Note that the peak is observed well within the \( S = 1 \) regime. (The origin of the apparent broad, low-amplitude peak in the low-field region is unclear, although this most likely represents a background contribution to the relaxation.)

Our previous study of MNM systems [12] identified the mechanism through which the muon spin is relaxed in these materials. Specifically, measurements on Cr₈ and on the related \( S = 1 \) MNM system Cr₇Mn showed that the muon spin ensemble is relaxed by static nuclear magnetism in \( S = 0 \) systems such as Cr₈ and by the large electronic spin in \( S \neq 0 \) MNMs such as Cr₇Mn. Moreover, a large difference in relaxation rates between protonated and deuterated samples demonstrates that the proton fluctuations are largely responsible for the dephasing of the large MNM electronic spin that we detect with muons at low temperatures.

It is likely, therefore, that for our level crossing measurement of Cr₈Cd, the channels through which the muon spins are relaxed change quite dramatically from weak nuclear relaxation in the \( S = 0 \) regime to strong electronic relaxation upon traversing the level crossing to the \( S = 1 \) regime above \( B_c \). Although it is probable that the fluctuation rate of the net moment of a molecule is symmetrically peaked about the crossing, the...
Figure 2. (a) Average asymmetry (corrected for background) as a function of applied magnetic field measured at 70 mK and 20 K. Resonance-like minima are observed at the level crossing.

(b) Relaxation rate $\lambda$ at 70 mK resulting from fitting the measured spectra to equation (1). The peak is displaced to slightly higher fields than the level crossing.

The effective coupling of the muon to the electronic spins on the molecule is likely to be smoothly turned on upon crossing into the $S = 1$ regime and this may cause the peak in the muon response to be shifted to slightly higher fields, as we observe. Another possibility for the shift is that the electronic fluctuation rate lies outside the muon time window close to the transition, but slows above the crossing causing the maximum in $\lambda$, as it descends into the regime in which the muon is sensitive.

In conclusion, muon spin relaxation has been shown to be sensitive to the level crossing in the molecular nanomagnet Cr$_8$Cd. This opens up possibilities for its use in probing such crossings in other systems. Future work will involve examining the crossings between two $S \neq 0$ states in order to further examine the nature of the coupling of the muon to the molecules.

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