Influence of thermal coupling on spin avalanches in Mn$_{12}$-acetate

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The effect of thermal coupling on spin avalanches in Mn$_{12}$-acetate has been probed using a single crystal assembly. Time-resolved, synchronized measurements of magnetization and temperature are reported. Unusually low avalanche trigger fields occur when thermal coupling to the bath is weak. A temperature rise observed at zero magnetic field is attributed to a change in magnetostatic energy.

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Over the past decade there has been much interest in single molecule magnets due to their macroscopic quantum behaviour. Mn$_{12}$O$_{12}$(CH$_3$COO)$_{16}$(H$_2$O)$_4$, abbreviated to Mn$_{12}$-acetate or Mn$_{12}$, is one of the most studied single molecule magnets to date. Strong uniaxial anisotropy and a large spin ($S = 10$) enable macroscopic quantum tunneling (MQT), in which the spin can reverse its direction by tunneling through the anisotropy barrier. In bulk crystals of Mn$_{12}$ such tunneling events can be observed as steps in the magnetization curve, which occur at regular intervals in the external magnetic field $B_n = nB_0$, where $n$ is an integer and $B_0 = 0.46$ T.\(^5\)\(^6\)\(^7\) Recently, however, much attention has focused on spin avalanches, in which the entire ensemble of spins reverses very rapidly.\(^8\) Spin avalanches are generally accepted to be thermal phenomena, driven by the cooperative process of spin-phonon relaxation.\(^9\)\(^10\) They occur only when the sample is sufficiently large that phonons emitted by the reversing spins cannot escape to the bath. The most recent research has shown that avalanches propagate through the crystal at constant velocity—a classical phenomenon dubbed “magnetic deflagration.”\(^8\)

In this Brief Report we study the influence of thermal coupling to a heat bath on spin avalanches in a single crystal assembly of Mn$_{12}$. We report measurements of the magnetic hysteresis curve by superconducting quantum interference device (SQUID) magnetometry and time-resolved, synchronized measurements of the sample temperature and magnetization, using a pickup coil. The effect of thermal coupling on the trigger field is discussed. We also study a temperature rise at zero magnetic field that is not associated with avalanches. Similar temperature rises have been observed by other researchers.\(^9\)\(^10\)\(^11\) but have never been satisfactorily explained.

The experiments described in this Brief Report were performed on an assembly of single crystals of Mn$_{12}$-acetate grown according to the procedure described by Lis.\(^12\) Each crystal had a length $\sim$ 2 mm and a cross sectional area $\sim 0.5 \times 0.5$ mm$^2$. The long dimension is known to correspond to the $c$-axis. Hence, we were able to glue 35 crystals together using G.E. varnish to create an assembly of mass $m = 21$ mg with the $c$-axes aligned to within $\sim 5^\circ$.

We began by measuring two sets of magnetic hysteresis curves using a commercial SQUID magnetometer. In the first set, the sample was strongly coupled to the bath via a constant flow of helium exchange gas. In the second set, the thermal coupling was weakened by enclosing the sample in an evacuated glass tube. For both sets the sample was mounted with the $c$-axis parallel to the external magnetic field to within $\sim 5^\circ$.

For the first set of measurements we initially cooled the sample to 1.8 K with the external magnetic field set to zero. By ramping the field slowly to 2 T we found the saturation moment to be 0.95 mJ T$^{-1}$. We then measured a series of hysteresis curves at different temperatures, each time sweeping from $+2$ T to $-2$ T and back at a rate of 3 mT s$^{-1}$. Avalanches were consistently observed for $T \leq 2.4$ K, but the field values at which they were triggered were not completely reproducible, giving rise to asymmetric hysteresis curves [Fig. 1(a)]. In addition, the trigger fields did not always correspond to the resonance fields $B_n$. This is in contrast to previous measurements made on similar-sized assemblies of single crystals at similar temperatures but in agreement with measurements made on individual single crystals at lower temperatures.\(^13\)\(^14\) Above 2.4 K, the avalanches disappeared and MQT steps were recovered. Above 3.6 K, the magnetization curve became non-hysteretic.

For the second set of measurements the thermal coupling was weakened by enclosing the sample in an evacuated glass tube that functioned as a shield against the flow of helium exchange gas. It was necessary to reduce the sample volume by $\sim 20\%$ in order to fit it inside the tube. This reduced the mass from 21 to 17 mg and the saturation moment from 0.95 to 0.77 mJ T$^{-1}$. The rest of the experiments described in this Brief Report were conducted on the diminished sample.

Again, we measured hysteresis curves at a series of temperatures [Fig. 1(b)]. As before, spin avalanches were observed for $T \leq 2.4$ K. However, this time the trigger fields were lower and more reproducible, leading to symmetric hysteresis curves. In addition, the magnetic effect of thermal coupling on spin avalanches in Mn$_{12}$-acetate to Mn$_{12}$, is one of the most studied single molecule magnets to date. Strong uniaxial anisotropy and a large spin ($S = 10$) enable macroscopic quantum tunneling (MQT), in which the spin can reverse its direction by tunneling through the anisotropy barrier. In bulk crystals of Mn$_{12}$ such tunneling events can be observed as steps in the magnetization curve, which occur at regular intervals in the external magnetic field $B_n = nB_0$, where $n$ is an integer and $B_0 = 0.46$ T.\(^5\)\(^6\)\(^7\) Recently, however, much attention has focused on spin avalanches, in which the entire ensemble of spins reverses very rapidly.\(^8\) Spin avalanches are generally accepted to be thermal phenomena, driven by the cooperative process of spin-phonon relaxation.\(^9\)\(^10\) They occur only when the sample is sufficiently large that phonons emitted by the reversing spins cannot escape to the bath. The most recent research has shown that avalanches propagate through the crystal at constant velocity—a classical phenomenon dubbed “magnetic deflagration.”\(^8\)

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Again, we measured hysteresis curves at a series of temperatures [Fig. 1(b)]. As before, spin avalanches were observed for $T \leq 2.4$ K. However, this time the trigger fields were lower and more reproducible, leading to symmetric hysteresis curves. In addition, the magnetic
moment approached saturation more slowly leading to rounding of the avalanche steps as they approached saturation. Above 2.4 K no MQT was observed, in contrast to the multiple steps observed with the strongly coupled sample. Instead, the hysteresis curve became smoothly hysteretic. The loss of MQT in the weakly coupled sample suggests a strong rise in sample temperature due to spin-phonon relaxation. When thermal coupling to the bath is strong, heat is rapidly dissipated, but when the coupling is weak the heat cannot escape so quickly to the bath. It appears that the glass tube provides sufficient thermal isolation that sample heating causes the spin reversal mechanism to be dominated by thermal activation, rather than by MQT.

There are several reports in the literature of significant rises in the sample temperature during spin avalanches and MQT, with reported values ranging between 1 and 5 K. The spread is probably due to variations in sample size, field-sweep-rate, location of the thermometer, and thermal coupling between the sample and the bath. Here, we report time-resolved measurements of the temperature rise during avalanches in a weakly coupled sample. Our measurements were performed in a helium cryostat with a superconducting magnet. We placed the sample at the bottom of an open-ended glass tube that functioned as a weak thermal link to the bath. A multiturn coil was wound around the base of the tube to enable us to detect changes in the sample magnetization. The tube was then placed inside an evacuated copper sample holder with a vertical slit to minimize eddy currents, which was attached to the 1 K plate. We estimate that the c-axis of the crystal assembly was aligned parallel to the magnetic field to within $\sim 10^\circ$. A Cernox resistance thermometer was mounted directly on top of the sample using high thermal conductivity grease (Apiezon N). A low bias current of 5 nA was used to minimize self heating.

The sample was initially cooled to 1.6 K with the external magnetic field set to zero. We then swept the field at a rate of 24 mT s$^{-1}$ and used a VXI data acquisition board to record time-resolved signals from either the coil or the thermometer. Separate measurements were subsequently synchronized by aligning their trigger points. The temperature and magnetization measurements were both triggered from the thermometer signal, which was found to be highly reproducible on successive field sweeps. The rate of change of the sample magnetization $dM/dt$ was calibrated by measuring the constant voltage induced across the coil by the external field ramp $dB/dt$. This was done at high fields (between 2 T and 3.5 T) where the sample magnetization was saturated.

Figure 2(a) shows the changes in sample temperature and magnetization observed during an avalanche. The oscillation in the temperature signal is due to electrical pickup of the 50 Hz line voltage. A distribution of avalanche trigger fields was observed between 0.37 and 0.65 T, with a mean of 0.56 ± 0.09 T, which is close to $B_1$. The temperature rise was found to be quite reproducible, despite the spread in trigger fields, with a mean maximum temperature of 4.3 ± 0.1 K.

In order to compare the time-resolved avalanche measurements with our earlier SQUID measurements we integrated the calibrated signal $dM/dt$ and multiplied it by the sample volume to obtain the change in magnetic moment $\Delta \mu$. This yielded $\Delta \mu = 0.03 \text{ mJ T}^{-1}$ for all avalanches, regardless of the trigger field, which is a great deal smaller than the change in moment $\Delta \mu \approx 1.5 \text{ mJ T}^{-1}$ observed in the SQUID measurements on the weakly coupled sample. We believe the discrepancy to be due to the difference in timescale of the two measurements. As can be seen in Fig. 2(a), the spin reversal rate declines rapidly as the temperature rises, resulting in the termination of the avalanche after a few milliseconds. However, the SQUID measurements on the weakly coupled sample show that spin reversal continues over a much longer period of $\sim 100$ s at a rate $dM/dt < 2$
been aligned by their trigger points. Inset: small change in temperature and magnetization which have weakly coupled to the bath. (a) Main plots: spin avalanche measurements of magnetization and temperature on a sample at $B \approx 0$. Prior to this avalanche, a small rise in temperature occurs at $B \approx B_1$. These correspond approximately to $B_2$ and $B_3$. The trigger field was consistently higher than when the glass tube was evacuated [Fig. 3(b)], in agreement with our SQUID measurements. However, the change in magnetic moment $\Delta \mu$ was similar in both time-resolved experiments, suggesting that, in both cases, avalanches terminate long before full spin reversal is achieved. This is supported by the observation of two closely spaced bursts of spin reversal at the lowest trigger fields in the evacuated sample [inset in Fig. 3(b)].

We now report the results of a second time-resolved experiment, this time with the sample enclosed in a glass tube filled with helium exchange gas to improve the thermal coupling. The experimental conditions were identical to those of the previous experiment, except that we were unable to measure the sample temperature, due to the difficulty of sealing the glass tube around the sensor leads. Avalanches were observed at a variety of trigger fields between 0.91 and 1.42 T [Fig. 3(a)]. These correspond approximately to $B_2$ and $B_3$. The trigger field was consistently higher than when the glass tube was evacuated [Fig. 3(b)], in agreement with our SQUID measurements.

We determined the avalanche duration by fitting a Gaussian profile and taking the full width at half maximum. The duration was found to decrease exponentially as the trigger field increased, independent of thermal coupling to the bath [inset in Fig. 3(a)]. This is consistent with the recently proposed model of magnetic deflagration. A particularly interesting observation is that, in the evacuated sample, avalanches triggered at identical fields had identical spin-reversal patterns. Since the lack of smoothness is probably due to sample inhomogeneity resulting from the layers of varnish that bind the assembly, this suggests that avalanches propagate in a very reproducible manner.

In the final part of our report, we investigate the cause of the temperature rise at $B = 0$. The amount of heat generated is given by $\Delta Q = mc\Delta T$, where $m$ is the mass of the sample, $c$ is the specific heat capacity and $\Delta T$ is the observed temperature rise. Fominay et al. have measured the specific heat capacity of Mn$_{12}$ as a function of temperature at zero magnetic field. Using a polynomial fit to extrapolate their data to temperatures below 3 K we obtain $c = 0.8 \text{ J kg}^{-1} \text{K}^{-1}$ at $T = 1.6 \text{ K}$. The temperature rise was found to be very reproducible, with a maximum temperature of $2.2 \pm 0.05 \text{ K}$.

In addition to the above observations, we also observed occasional small signals before or after the main avalanche. Small temperature rises of $\sim 50 \text{ mK}$ were observed at $B \approx B_1$ [insets in Figs. 2(a) and 2(b)] and small changes in magnetization were observed close to $B \approx B_3$ and $B_4$. Because these signals were observed only occasionally, we were unable to synchronize temperature and magnetization measurements. Therefore, we cannot tell whether they were due to MQT or miniature avalanches involving parts of the sample in poor thermal contact with the rest. However, the duration of the magnetization signals (~ 100 ms) suggests that they are due to MQT rather than miniature avalanches, which in turn suggests that the main avalanche does not always result in full spin reversal.

Besides avalanches, we also observed slower changes in the temperature and magnetization at $B = 0$ [Fig. 2(b)]. The change in magnetization at $B = 0$ is known to arise from thermally activated relaxation of a minority molecular species constituting about 5% of the sample. The relaxation rate of this species is much faster than that of the majority species because the anisotropy barrier is lower. However, the rate of change of the total magnetic moment is still slow compared to an avalanche, because thermal activation is a non-cooperative process. Over a period of 20 s, the change in magnetic moment was found to be $\Delta \mu = 0.06 \text{ mJT}^{-1}$, in good agreement with the SQUID measurements over a similar timescale. The kJT$^{-1}$ m$^{-3}$ s$^{-1}$ (close to the noise floor of the coil). This suggests that the majority of the spin reversal detected by the SQUID was due to thermal activation.

FIG. 2: (Color online). Time-resolved, synchronized measurements of magnetization and temperature on a sample weakly coupled to the bath. (a) Main plots: spin avalanche at $B = 0.65 \text{ T}$. The grey line is a guide to the eye. Upper inset: separate avalanche recorded over a longer time interval. Prior to this avalanche, a small rise in temperature occurs at $B \approx B_1$. Lower inset: distribution of trigger fields. (b) Step at $B = 0$. This plot comprises four separate measurements (two of temperature and two of magnetization) which have been aligned by their trigger points. Inset: small change in magnetization at $B \approx B_1$. 

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FIG. 3: (Color online). (a) Avalanches in sample with helium exchange gas (offset vertically for clarity). Inset: avalanche duration vs trigger field. Open circles: sample with exchange gas; closed circles: evacuated sample; solid line: exponential fit. (b) Avalanches in evacuated sample. Inset: two bursts of spin reversal are seen at the lowest trigger fields.

At $B = 0$, no work is done by the external magnetic field because $\int B \, d\mu = 0$. However, work can be done by the internal demagnetizing field $B_0 = -\mu_0 N \mu / V$, where $N$ is the demagnetizing factor, $\mu_0$ is the permeability of free space and $V$ is the volume of the sample. The magnetostatic energy $E_m = \int B_0 \, d\mu$ is given by

$$E_m = \frac{\mu_0 N \mu^2}{2V}. \quad (1)$$

Taking the sample to be approximately spherical we assume a demagnetizing factor $N = 1/3$. The total change in the magnetic moment between full saturation and the beginning of the avalanche is $\Delta \mu \approx 0.2 \text{ mT}^{-1}$. The amount of magnetostatic energy released is therefore $\Delta E_m \approx 10 \mu J$, in good agreement with $\Delta Q$.

In conclusion, we have compared avalanche measurements in samples with weak and strong thermal coupling to a heat bath and have shown that a decrease in thermal coupling leads to a reduction in trigger field. This supports the view that heating is an important factor in the triggering of avalanches. Time-resolved measurements of the sample magnetization have shown an exponential dependence of the avalanche duration on the trigger field, consistent with the model of magnetic deflagration. A comparison of time-resolved measurements with SQUID magnetometry measurements has shown that avalanches terminate long before saturation is reached. The elevated sample temperature following an avalanche allows spin reversal to continue via thermal activation.

In addition to our studies of spin avalanches, we have also observed significant heating at $B = 0$. This has been observed previously by other researchers, but no satisfactory explanation has been given. We attribute the temperature rise to a release of magnetostatic energy.

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17 Throughout this Brief Report, we use the symbol \( \mu \) for the magnetic moment of the sample and \( M \) for the magnetization (\( M = \mu/V \), where \( V \) is the sample volume).
18 The amplitude of the 50 Hz oscillation gets larger as the temperature increases because the sensor resistance decreases by an order of magnitude between 1.6 and 4.3 K. This causes the ratio of pickup voltage to sensor voltage to decrease.
19 The sample volume \( V = 5.5 \text{ mm}^3 \) was computed from the saturation moment \( \mu_S = 0.77 \text{ mJ T}^{-1} \) measured by SQUID magnetometry, using the known crystal structure and unit cell volume\(^{12} \) and the known spin \( S = 10 \) per molecule.
20 In the case of the double peaks observed at the lowest trigger fields, only the first peak was fitted.