Propagation of Avalanches in Mn_{12}-acetate: Magnetic Deflagration

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Local time-resolved measurements of fast reversal of the magnetization of single crystals of Mn_{12}-acetate indicate that the magnetization avalanche spreads as a narrow interface that propagates through the crystal at a constant velocity that is roughly two orders of magnitude smaller than the speed of sound. We argue that this phenomenon is closely analogous to the propagation of a flame front (deflagration) through a flammable chemical substance.

Mn_{12}-acetate (hereafter Mn_{12}-ac) is a prototypical molecular magnet composed of magnetic molecules, \([\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4]\cdot2\text{CH}_3\text{COOH}-4\text{H}_2\text{O}\), with cores consisting of twelve Mn atoms strongly coupled by exchange to form superparamagnetic clusters of spin \(S = 10\) at low temperatures. Arranged in a centered tetragonal lattice, the spin of the Mn_{12} clusters is subject to strong magnetic anisotropy along the symmetry axis (the c-axis of the crystal). Below the blocking temperature of \(\approx 3.5\) K, the crystal exhibits remarkable staircase magnetic hysteresis due to resonant quantum spin tunneling between energy levels on opposite sides of the anisotropy barrier corresponding to different spin projections, as illustrated in Fig. 1(a). This and other interesting properties of Mn_{12}-ac have been intensively studied in the last decade (see Refs. 3,4,5,6 for reviews).

It has been known for some time\(^7\) that Mn_{12}-ac crystals exhibit an abrupt reversal of their magnetic moment under certain conditions. This phenomenon, also observed in other molecular magnets, has been attributed to a thermal runaway (avalanche) in which the initial relaxation of the magnetization toward the direction of the field results in the release of heat that further accelerates the magnetic relaxation. Direct measurements of the heat emitted by Mn_{12}-ac crystals\(^3\) as well as measurements of the magnetization reversal in pulsed magnetic fields\(^2\) have confirmed the thermal nature of the avalanches. More recently, the electromagnetic signal associated with avalanches was detected\(^10,11\) and it was argued that if the radiation is of thermal origin it would indicate a significant increase in the temperature of the crystal. This has not been confirmed by direct bulk measurements of the temperature using a thermometer. Evidence has been obtained\(^9\) that the avalanche may not be a uniform process throughout the sample. No clear understanding of the avalanche process has emerged to date.

In this Letter we report local time-resolved measurements of fast magnetization reversal (avalanches) in monosize single crystals of Mn_{12}-ac. We show that a magnetic avalanche takes the form of a thin interface between regions of opposite magnetization which propagates throughout the crystal with a constant field-dependent speed ranging from 1 to 15 m/s. We demonstrate that this phenomenon is closely analogous to the propagation of a flame front (deflagration) through a flammable chemical substance.

Microscopic arrays of Hall bars were used to measure the magnetization of three single crystals of Mn_{12}-ac with dimensions: sample 1, 0.29 \(\times\) 0.29 \(\times\) 0.64 mm\(^3\); sample 2, 0.28 \(\times\) 0.28 \(\times\) 1.44 mm\(^3\); sample 3, 0.24 \(\times\) 0.24 \(\times\) 1.02 mm\(^3\). Eleven Hall bars of dimensions 10 \(\times\) 10 \(\mu\)m\(^2\) with 30 \(\mu\)m intervals were used for sample 1, and 30 \(\times\) 30 \(\mu\)m\(^2\) with 130 \(\mu\)m intervals for samples 2 and 3.

Using an excitation current of 2 \(\mu\)A, the Hall bar signal was amplified by a factor of 1200, and detected and recorded by several digital scopes and a data acquisition card. In order to ensure proper synchronization, one channel of each scope was anchored to the same signal. The Hall sensor and amplifier introduced combined delays of up to 3 \(\mu\)s. A magnetic field was applied in the \(z\)-direction along the crystal easy axis (see Fig. 1), lowering (raising) the energy of the states corresponding to spin projections along (opposite to) the field direction. The Hall sensors were aligned to detect the magnetic induction of the sample in the \(x\)-direction. \(B_x\) is proportional to the spatial derivative of \(M_z\) in the region near the sensor. For a uniform magnetization in the \(z\)-direction, \(B_x\) scales with the temperature using a thermometer. Evidence has been obtained\(^9\) that the avalanche may not be a uniform process throughout the sample. No clear understanding of the avalanche process has emerged to date.

FIG. 1: (a) The potential energy function in a longitudinal magnetic field; (b) Schematic diagram of a sample mounted on an array of Hall sensors used to detect \(B_z\). The magnetization is relatively uniform for quasi-equilibrium conditions; pronounced non-uniformity in magnetization during an avalanche generates large values of \(B_z\).
derives from the gradient at the sample ends, which is proportional to $M_z$ itself. During an avalanche, there is a large contribution to $B_x$ from the local region corresponding to the avalanche front, where $\partial M_z/\partial z$ is large.

The samples were immersed in liquid $^3$He; most of the data were obtained at the base temperature of 250 mK. The few points measured at 400 and 650 mK were found to lie on the same curve within the scatter of the data, indicating that the temperature dependence is weak. A longitudinal magnetic field (parallel to the easy axis) was swept back and forth through the hysteresis loop to $\pm 6$ T until an avalanche was triggered. As reported in an earlier paper, avalanches occur in a stochastic way at 0.25 K both at resonant magnetic fields (where energy levels on opposite side of the barrier match, see Fig. 1) and away from resonance. Avalanches were also found for sample 2 for zero field-cooled conditions, where the sample starts from zero magnetization (instead of full saturation).

Figure 2 shows an avalanche for sample 1. Steps due to quantum tunneling of the magnetization were observed, with a magnetization that was almost uniform throughout the sample, until an avalanche occurred, as shown in the inset. During the avalanche the Hall bar recorded a large peak in $B_x$, signaling the abrupt onset of a highly non-uniform magnetization.

For a field sweep rate of 10 mT/s and temperature 0.25 K, Fig. 3 shows an avalanche triggered at 4 T and recorded for sample 1 by seven of the eleven sensors placed in sequential positions near the center of the sample. The avalanche was triggered above the top-most sensor and traveled downward (see Fig. 1). $B_x$ displays the largest peak at the center due to the finite size of the sample. The inset shows the sensor position as a function of the time at which the sensor registered the peak amplitude. The slope of the straight line drawn through these points yields a constant velocity of 12 m/s for this avalanche.

Figure 4 summarizes the data obtained for the velocity of propagation of avalanches versus longitudinal magnetic field at which the avalanches occurred. ZFC denotes data obtained for sample 2 cooled in zero field, thus starting from zero magnetization and ending in full magnetization, $\Delta M/2M_{sat} = 0.5$; $\Delta M/2M_{sat} = 1$ for sample 3 and the remaining sample 2 data; for sample 4, $\Delta M/2M_{sat}$ varied around 0.7. From top to bottom, the curves are fits to the data for $\Delta M/2M_{sat} = 1, 0.7$ and 0.5 (see text).
can occur. Smaller velocities are obtained for avalanches in sample 2 when starting from the zero-field-cooled condition. Avalanches for sample 1 were obtained only at relatively high magnetic fields in the vicinity of 4 T; the velocities for this sample range in value and do not appear to be consistent with data for the other two samples.

Interestingly, as shown in Fig. 5, an approximate collapse is obtained for all the data when plotted as a function of $g\mu_B HS(\Delta M/M_{sat})$, the energy per molecule released during an avalanche. Thus, avalanches require the release of a threshold energy, above which they propagate with a speed that appears to be a linear function of the energy for the range investigated in these experiments.

Our observations cannot be attributed to magnetization reversal associated with domain wall motion, since there is no long-range order in our system. Some insight can be obtained by noting that, from a thermodynamic point of view, a crystal of Mn$_{12}$ molecules placed in a magnetic field opposite to the magnetic moment is equivalent to a metastable (flammable) chemical substance. In our case, the role of the chemical energy stored in a molecule is played by the difference in the Zeeman energy, $\Delta E = 2g\mu_B HS$, for states of the Mn$_{12}$-ac molecule that correspond to $S$ parallel and antiparallel to $H$; here $g = 1.94$ is the gyromagnetic factor and $\mu_B$ is the Bohr magneton. For Mn$_{12}$-ac in a field of a few Tesla, $\Delta E$ is below 0.01 eV, as is the energy barrier, $U(H)$, between spin-up and spin-down states due to the magnetic anisotropy. Thus, for the avalanches in Mn$_{12}$-ac, $\Delta E$ and $U$ are two orders of magnitude smaller than typical energies of chemical reactions. However, our temperature range is also more than two orders of magnitude below room temperature, making the analogy rather close.

A well-known mechanism for the release of energy by a metastable chemical substance is combustion or slow burning, technically referred to as deflagration. It occurs as a flame of finite width, $\delta$, propagates at a constant speed, $v$, small compared to the speed of sound. The parameter $\delta$ is determined by the distance, $\delta \sim \sqrt{\kappa \tau}$, through which the heat diffuses during the time of the “chemical reaction” $\tau$. In our case

$$\tau(H) = \tau_0 \exp \left[ \frac{U(H)}{k_B T_f} \right],$$

where $\tau_0 \sim 10^{-7}$ s is the attempt time and $T_f$ is the temperature of the flame. The dynamics of the flame are governed by the thermal diffusivity, $\kappa$, which obeys:

$$\frac{\partial T}{\partial t} = \kappa \nabla^2 T.$$ \hspace{1cm} (2)

For $\kappa$ independent of $T$, substituting $T = T(x - vt)$ at $x > vt$, one obtains $T = T_f \exp [-v(x - vt)/\kappa]$ in front of the interface, which yields $v\delta = \kappa$. An interface thickness that is at most the distance between sensors, $\delta \sim 30 \mu m$, and the experimentally measured velocities of the order of $1 - 15$ m/s, yield an upper bound on $\kappa$ in the range $10^{-5}$ m$^2$/s to $10^{-4}$ m$^2$/s, consistent with heat pulse experiments.

Combining $v\delta = \kappa$ with $\delta \sim \sqrt{\kappa \tau}$, one obtains:

$$v \sim \frac{\delta}{\tau} \sim \sqrt{\kappa/\tau} = \left( \frac{\kappa}{\tau_0} \right)^{1/2} \exp \left[ \frac{-U(H)}{2k_B T_f} \right].$$ \hspace{1cm} (3)

The strongest dependence of $v$ on $H$ derives from the exponential, which contains the known dependence of the energy barrier, $U(H)$, on the magnetic field. Assuming that the temperature of the flame is proportional to the released magnetic energy density, $T_f = C_\chi \Delta M$, it is possible to fit all the data with a single value of the proportionality constant $C$, as shown in Fig. 4. The flame temperature obtained from these fits ranges from 8.5 K for an avalanche at 1 T to 26 K for an avalanche triggered at 4 T. We note that the prefactor obtained from the fit is consistent with the values of $\kappa$ and $\tau_0$ discussed earlier. Here we have used the simplest model of deflagration, a widely studied phenomenon that is known to be quite complex. This crude model captures the overall behavior, and yields parameters that are quite reasonable in size. A more complete theory is needed to account for the apparent data collapse of Fig. 5.

Recent bolometer measurements of the radiation generated by a magnetic avalanche gave puzzling results that can be understood within our model. One enigma was that the sample temperature measured by a thermometer directly following an avalanche was lower ($< 6$ K) than the temperature registered by the bolometer if one assumed thermal radiation. A second puzzle was that the reversal of the magnetization during the avalanche occurred on a much shorter time scale than the cooling of the sample following the avalanche. We suggest that the radiation observed during avalanches is generated by the narrow hot interface (flame) that propagates through the crystal. The temperature of the bulk of the crystal (including the “ash” left behind the interface) is always significantly lower than the temperature of the interface itself. The time of the magnetization reversal is determined by the time $t = 1/v$ needed for the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Velocity of propagation of avalanches versus energy released per molecule. The line is drawn to guide the eye.}
\end{figure}
interface to sweep the sample of length $l$. In our case $t \sim 0.1$ ms, while the time needed for the “ash” to reach equilibrium with the thermal bath can be much longer.

The strongest evidence that our observations are due to deflagration is the presence of a well defined propagating front requiring a threshold energy traveling at a subsonic velocity. The deflagration mechanism provides the condition needed for the avalanche to occur. This condition is the same as the condition needed to sustain the propagation of a flame through a chemical substance. It is well-known that deflagration of a flammable gas will not occur in a pipe of diameter, $d$, small compared to the width of the flame, $\delta$. In our case $\delta$ must be small compared to the diameter of the crystal. If this condition is not satisfied, the heat generated by the magnetization reversal diffuses mostly through the walls of the sample and cannot sustain the propagation of the interface. This explains why avalanches only occur in larger crystals with sufficiently large magnetization opposite to the direction of the field. The latter condition coincides with the condition of “flammability”\(^\text{19}\) needed to provide sufficient heating (that is, the large $T_d$) required for $\delta < d$. It is interesting to note in this connection that the few avalanches that were recorded around 1 T did not result in full reversal of the magnetization. At these low fields the conditions for ignition are marginally satisfied, and the “flame” is extinguished before the process of magnetization reversal has been completed. In addition to available magnetic energy (flammability), the conditions for ignition may also depend on the shape and quality of the crystal, which may account for differences observed for different samples.

Slow burning at a subsonic speed (deflagration) is governed by the linear process of thermal conductivity. In addition to deflagration, unstable chemical substances also exhibit detonation, which can be caused by instability of the flame or by direct initiation other than through deflagration.\(^\text{10}\) The initial stage of the detonation corresponds to a non-linear supersonic shock wave.\(^\text{15,18}\) Theory and experimental studies of advanced stages of detonation are lacking. Based on the close analogy between unstable chemical substances and molecular magnets, the latter may well exhibit “magnetic detonation” under the right conditions.

In conclusion, we have demonstrated that avalanches in the magnetization reversal of sufficiently large crystals of magnetic molecules are very similar to flame propagation (deflagration) through a metastable chemical substance. The analogy between the two systems derives from the magnetic bi-stability of molecular nanomagnets. Our observation of “magnetic deflagration” offers a potentially important new way to investigate the phenomenon of flame propagation (and, possibly detonation). In contrast to deflagration in flammable chemical substances, the analogous process of “magnetic deflagration” in molecular nanomagnets is non-destructive, reversible, and much easier to control.

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The prefactor of the exponential in Eq. [3] the second parameter required for the fits, differed by as much as 30% for different $\Delta M$, reflecting the fact that the prefactor is not well known within the theory. On the other hand, the exponential dependence is well captured by the model. 

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