

**Magnetic deflagration in the molecular magnet
Mn12-ac**

by

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Abstract

Magnetic deflagration in in the molecular magnet $\text{Mn}_{12}\text{-ac}$, “Magnetic Deflagration”

by

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In 1995, Paulsen and Park [1, 2] observed abrupt spontaneous reversals of the magnetization in crystals of the molecular magnet $\text{Mn}_{12}\text{-ac}$, which they dubbed “magnetic avalanches”. They suggested that the magnetic avalanches were a thermal runaway process where the reversing spins release heat stimulating further relaxation. Various exotic phenomena were proposed as an alternative explanations [3]. In 2005, Suzuki et al. [4] established that this spontaneous magnetic relaxation occurs as a “front” separating regions of opposing magnetization that propagates at a constant speed through the crystal. They suggested that this propagating front is analogous to a flame in chemical deflagration and introduced the thermal relaxation process, magnetic deflagration. The analysis presented there was limited by lack of data. A more thorough comparison with the theory would require the ability to trigger avalanches in a more controlled way rather than wait for their spontaneous occurrence.

The work presented in this thesis is a continuation of the program initiated by Suzuki [4, 5]. Significant progress experimental progress has been made allowing us to trigger avalanches over a wide range of conditions. The magnetization dynamics and the ignition temperatures are studied in detail using an array of micro-sized Hall sensors and Germanium thermometers. In addition, we report the existence of a new species of avalanches consisting only of the fast-relaxing isomers of $\text{Mn}_{12}\text{-ac}$, the so-called “minor species”. We explore avalanches of both species, as well as

the interaction between them. Finally, a detailed analysis is performed to compare the experiment with the theory of magnetic deflagration [6]. We find the theory of magnetic deflagration to be consistent with the data and extract values for the key physical quantities: the thermal diffusivity and avalanche front temperatures. Agreement between our predicted values and an independent measurement of these quantities would provide compelling verification of the theory.

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It takes a certain amount of audacious self-confidence to imagine that one can make even a small a contribution to the greatest edifice of mankind, science. To the extent that I posses this trait I owe to my grandfather, Robert A. Schaller, to whom I dedicate this thesis. He was a true American and an inspiration of self-reliance and initiative to his family.

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Chapter 1

Introduction

1.1 Introduction

Chemical combustion is an exothermic reaction, which takes place along a front that travels through the material changing the initial unreacted material ahead of the front into reaction products, or ash, behind. The reacting agents release energy as they form a stable chemical compound. This energy heats the nearby unreacted agents, which in turn increases their reaction rates and a self-sustaining thermal runaway process ensues.

There are two physical parameters governing the speed at which the reaction front progresses through the material: the chemical reaction rate, and the rate at which heat spreads away from the front [7]. As a thermal process, local equilibrium must be established at time scales much less than the reaction rate. This allows the reaction rate to be quantified with an Arrhenius law,

$$\Gamma = \Gamma_0 \exp(-U/k_B T), \quad (1.1)$$

where U is the activation energy of the chemical reaction and T is the local temperature at the front.¹ In addition, one can distinguish between two classes of combustion, namely deflagration and detonation, by the mechanism by which heat is transported from the reacted to the unreacted regions in the material. For deflagration, the heat diffuses away from the front, which limits the speed to less than the speed of sound in a particular material. In detonation, the heat is transported as a super-sonic shock (compression) wave, and generally requires a more energetic reaction.

Because the conditions for heat diffusion are substantially easier to satisfy than those required for a shock wave, deflagration is the more common process. In fact, the conditions for deflagration is so easily satisfied that analogous processes are frequently realized in other contexts that do *not* involve chemical energy and span many orders

¹The basis for the Arrhenius law is quite general. The assumption of local equilibrium implies that the metastable reactants are in a Maxwell-Boltzmann distribution. If the reactants attain the activation energy, U , which they do with a probability $\propto \exp(-U/k_B T)$, they react.

of magnitude in energy. A standard astrophysical example of deflagration is the burning of carbon in supernovae [8] where nuclear energy substitutes for the chemical (electronic) energy in the reaction. As an exotic high-energy example, deflagration has been proposed as the mechanism for the burning of a neutron star into strange matter [9]. It has even been used to describe the production of gravitational waves resulting from a vacuum phase transition in the early universe [10].

As perhaps the lowest energy realization, “magnetic deflagration” has recently been invoked to account for the magnetic avalanches, or abrupt magnetization reversals, that often occur in crystals of molecular magnets [1, 2, 4, 6]. Here, Zeeman energy is released when metastable spins opposing an applied magnetic field are flipped in the direction of the field, producing a deflagration front that travels through the crystal at subsonic speed. Because this process involves such low energies, it is non-destructive leaving the crystals intact for repeated measurements; this is clearly an advantage if one intends to subject the model to precise experimental confirmation. In addition, the “activation energy” U can be tuned with an applied external field. With these attributes in mind, magnetic deflagration holds promise to be the cleanest and best tested manifestation of deflagration surpassing even its chemical namesake.

In addition, magnetic deflagration contains aspects of interest to physicists which have yet to be seen in any other manifestation of deflagration. Molecular magnets are known to exhibit enhanced relaxation rates due to quantum tunneling [11, 12]. There is the prospect of studying “quantum magnetic deflagration”, for which there is already evidence [13, 14, 15].

In this thesis, we subject the theory of magnetic deflagration to rigorous experimental test. We find the theory to be consistent with the experimental data. However, the lack of measurements of the thermal diffusivity and the flame temperatures make the results presented somewhat inconclusive. By applying the theory, we are able to predict a range of values for these quantities. More compelling confirmation will

then come from an independent measurement of either the flame temperature or the thermal diffusivity, or preferably both.

In what remains of this chapter, the molecular magnet $\text{Mn}_{12}\text{-ac}$ is introduced and a brief history of the magnetic avalanches (deflagration) is given.

In chapter 2, the experimental details employed to obtain data relevant to the avalanches are discussed. In particular, we describe the method of igniting avalanches as well as characterizing the ignition conditions. The magnetization dynamics and avalanche speeds are measured with an array of Hall sensors, which are also described here. By cooling the crystal in a small external magnetic field, the amount of magnetization that reverses during an avalanche can be tuned. This chapter concludes with a description of the field cooling process used to prepare the initial magnetization of the avalanche.

It is well known that roughly 5% of the molecules in crystals of $\text{Mn}_{12}\text{-ac}$ are a fast-relaxing isomer (“minor species”) of the primary isomer (“major species”). In Chapter 3, we present a method used to magnetically partition the crystal with the major and minor species aligned anti-parallel to one another. This magnetic preparation allows us to make a direct measurement of the dipolar fields due to major species by exploiting the faster relaxation rates of the major species. The magnetic preparation also allows us to study avalanches of exclusively on species or the other. In Chapter 4, we present data for avalanches involving the only the major or minor species. In addition, the interaction between the major and minor species is investigated revealing the catalytic behavior of the minor species.

Chapter 5 contains details on the avalanche data (avalanche speeds, dynamics, and ignition temperatures) obtained with a wide variety of magnetic preparations.

In Chapter 6, a quantitative analysis is performed for the avalanche speeds using the results of Garanin and Chudnovsky [6]. As a measure of the validity of the theory of magnetic deflagration, predictions for both the thermal diffusivity and flame

temperatures are extracted.

The thesis is concluded in Chapter 7 with an outline for future studies of magnetic deflagration in molecular magnets.

1.1.1 Note on nomenclature and units

We abuse the language differentiating magnetic avalanches with magnetic deflagration fronts. The qualitative success of the theory of magnetic deflagration seems to justify treating them as one and the same even at this early stage of study. In the remainder of this thesis, we will use the terms “avalanche”, “deflagration”, and “front” more or less interchangeably. Any distinction will hopefully be clear in context.

All energies (unless otherwise stated) are given in units of J/k_B , which is conventional in the field of molecular magnets. This choice leads to two relevant quantities having peculiar units: the heat capacity and the thermal conductivity. The heat capacity per molecule is then dimensionless and the thermal conductivity has units m^2/s .

1.2 Mn₁₂-ac

Mn₁₂-ac, $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4] \cdot 2CH_3COOH \cdot 4H_2O$, is the prototypical molecular magnet composed of 12 Mn atoms strongly coupled to form a superparamagnetic cluster at low temperatures [16, 17]. A schematic of the molecule is shown in Figure 1.1. Of the 12 Mn atoms, eight are Mn^{3+} with spin $S = 2$ and four are Mn^{4+} with spin $S = 3/2$. These Mn atoms are antiferromagnetically coupled via oxygen-mediated superexchange and form a small ferrimagnet with net spin $S = 10$. Surrounding this magnetic core are groups of non-magnetic ligands (Acetic acid and water).

For convenience to the experimenter, these molecules are usually grown and studied in a crystal. In particular, the crystals are body-centered tetragonals with lattice dimensions $a = b = 1.73$ nm and $c = 1.21$ nm [16]. Although each molecule has

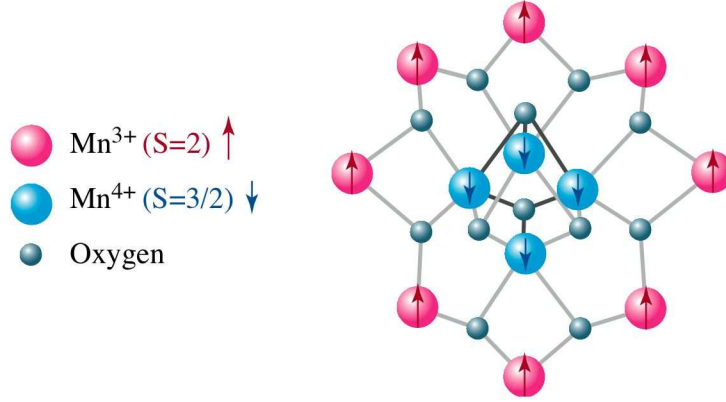


Figure 1.1: Schematic representation of Mn₁₂-ac. The Mn atoms with different oxidation states couple antiferromagnetically to form a spin $S = 10$ ferrimagnet.

a large magnetic moment ($10g\mu_B$), the magnetic interaction (dipole-dipole and exchange) between molecules in the crystal is generally assumed to be negligible due to the large, insulating, organic ligands.²

Like the lattice, the Mn₁₂ magnetic core also has tetragonal (S_4) symmetry. Due to the intramolecular geometry and magnetic interactions, there is a large magnetic anisotropy [17]. The magnetic properties of each molecule in the crystal can be modeled with the effective spin Hamiltonian [21, 22, 23, 24, 25]

$$\mathcal{H} = -DS_z^2 - AS_z^4 - g\mu_B S_z B_z + \mathcal{H}_\perp, \quad (1.2)$$

where $D = 0.548$ K and $A = 1.17 \times 10^{-3}$ K define the magnetic anisotropy along the c axis. $g = 1.94$ and B_z is the total magnetic field at the molecule along the c axis. $\mathcal{H}_\perp$ is a small symmetry breaking term required for transitions between the $S_z = -10, -9, \dots, 9, 10$ states. The fact that absence of magnetic interaction between neighboring molecules allows us to write Eq. 1.2 for a single representative spin. It also allows magnetization experiments on crystals of roughly 10^{17} molecules to be treated as a measurement on an ensemble of identical spins.

²Recent work has called into question this assumption [19, 20], which is discussed briefly in section 3.1

The anisotropy makes the z (c) axis the preferred direction for the magnetic moment of each molecule and, therefore, the magnetization of the crystal. It also creates an energy barrier, U , against the reversal of each spin. At zero magnetic field ($B_z = 0$) the energy barrier is about 60 K, and there are two equivalent stable states, $S_z = -10$ and $S_z = 10$. U can be adjusted with the application of an external magnetic field, which also breaks the degeneracy of the ground states. Figure 1.2 illustrates two cases: $B_z = 0$ and $B_z = +2.0$ T. Certain non-zero values of the field B_z bring energy levels into back to degeneracy³, i.e., the energy levels are said to “cross”. The fields at which the energy level crossings occur are commonly called “resonant fields” since it is at these fields that the effects of resonant quantum tunneling may be very pronounced. Figure 1.2 (b) shows the energies and fields at which these level crossings occur. The effect of tunneling at the level crossings may be incorporated statistically by effectively reducing the barrier, U . The prominent effects of tunneling, for which molecular magnets are famous, will be discussed shortly.

1.2.1 Magnetization and hysteresis curves

Magnetization experiments are performed at non-zero temperatures on crystals containing a large number of spins. We can therefore expect to use statistical mechanics to understand the results of real experiments. In equilibrium, the probability for a spin to occupy a particular energy level E_n at temperature T is given by the Maxwell-Boltzmann distribution

$$P(E_n) = \frac{e^{-E_n/T}}{Z}, \quad (1.3)$$

where $Z = \sum_n \exp(-E_n/T)$. If the magnetic field, B_z , is changed, the symmetry between the two ground states $S_z = \pm 10$ is broken, creating a true ground state and a metastable ground state. Some time is required to establish a new equilibrium

³Neglecting the small symmetry-breaking terms $\mathcal{H}$ which make the level crossings, “avoided level crossings”.

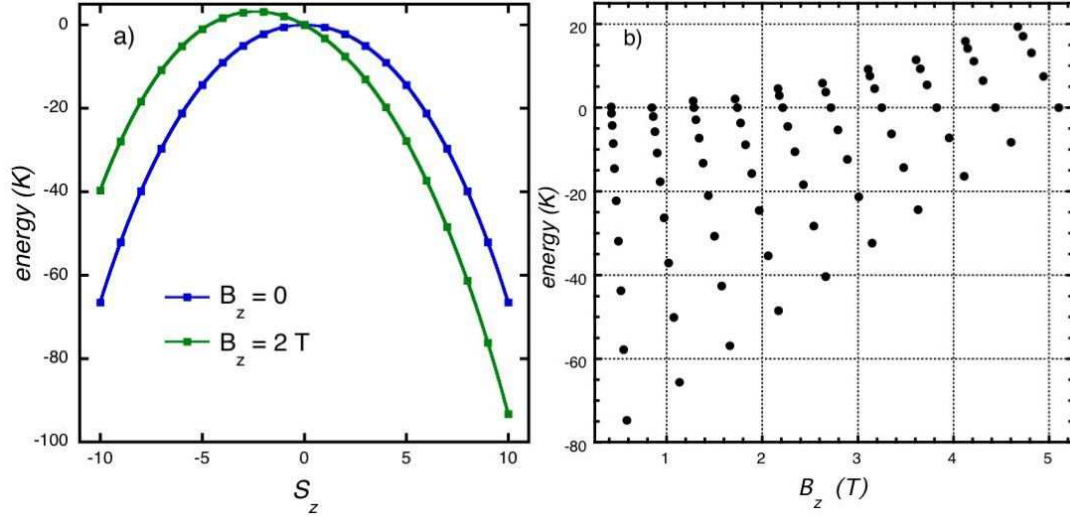


Figure 1.2: (a) Schematic representation for the $S = 10$ energy levels of Mn₁₂-ac for two values of the magnetic field: $B_z = 0$ and $B_z = 2$ T. The squares represent the available 21 energy levels. The solid lines are drawn as visual aids. (b) Energy level crossings. Filled circles denote the energy of a level crossing for a particular field.

distribution. In order for this to occur, spins must depopulate the now metastable energy levels. The difference between the highest accessible energy level and the metastable ground state is the barrier, U . The rate that spins can leave the metastable “well” is proportional to the probability that it will occupy an energy level at the top of the barrier in favor of the metastable ground state. The probability is $P \sim \exp[-U/T]$. The rate of decay from the metastable state is therefore

$$\Gamma = \Gamma_0 e^{-U/T}, \quad (1.4)$$

where Γ_0 is an experimentally determined prefactor with dimensions s^{-1} . Γ is commonly referred to as the relaxation rate, an allusion to the process of relaxing from an excited state to the ground state. For Mn₁₂-ac, the barrier U is calculated from Eq. 1.2 and $\Gamma_0 = 3.6 \times 10^7 \text{ s}^{-1}$ [39].

When the rate of change for the external field is slow compared to the relaxation rate, the crystal behaves as a paramagnet, i.e., the magnetization responds to an external magnetic field in a manner consistent with a Curie-Weiss law. This condition

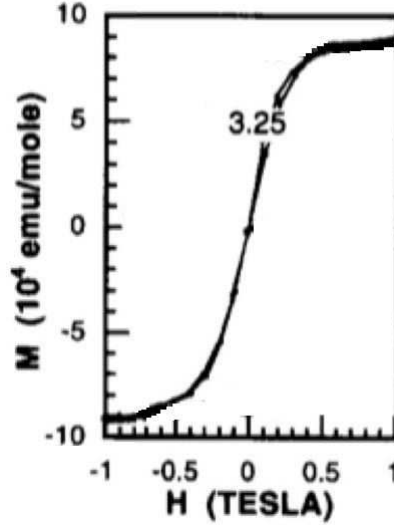


Figure 1.3: Magnetization, M_z , versus applied field, $\mu_0 H_z$ on single crystals of Mn₁₂-ac with an external sweep rate of 0.3 mT/s. If the field changes slowly with respect to the relaxation rate (Eq. 1.4), the magnetization follows an equilibrium Curie-Weiss law. This magnetization curve taken at 3.25 K reflects this behavior. (Data taken from Ref. [1])

is most easily satisfied at high temperatures where the relaxation rate is high. Figure 1.3 shows the paramagnetic behavior of Mn₁₂-ac.⁴ At 3.25 K and an external field sweep rate of 0.3 mT/s, the magnetization curve shows the behavior we expect of an equilibrium paramagnet.

At low temperatures, however, the time required for the spins to establish equilibrium becomes long compared to the time the external experimental parameters can be varied. In this case, the spins can remain in a non-equilibrium distribution for long periods of time and hysteretic effects can appear in the magnetization curves. Figure 1.4 shows magnetization curves taken with an external field sweep rate of ± 10 mT/s for several temperatures below 3.25 K. Since the relaxation rate decreases dramatically as the temperature is decreased, the magnetization curves show the non-equilibrium, metastable behavior characterized by hysteresis.

In order to observe metastability, the relaxation rate (Eq. 1.4) must be slower

⁴This data was cropped from a Figure taken from Ref. [1]. The full data reported there is shown below in Figure 1.7.

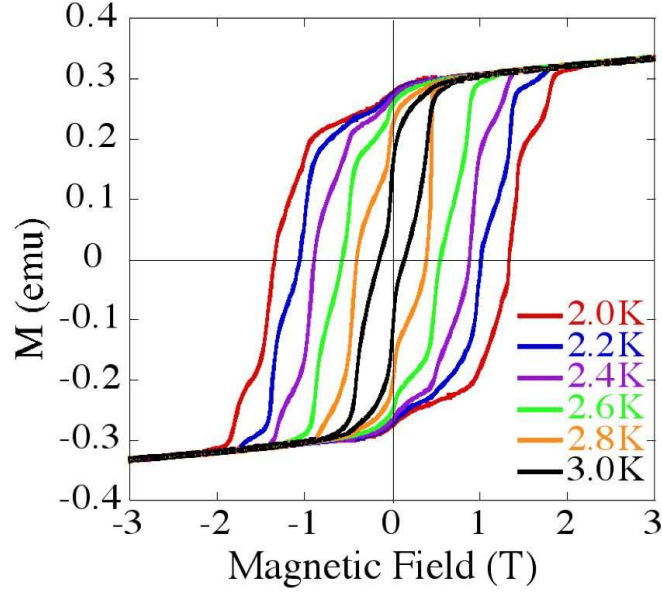


Figure 1.4: Magnetization, M_z , versus applied field, $\mu_0 H_z$ at low temperatures with and field sweep rate of ± 10 mT/s. Lower temperatures lead to larger coercive fields. (Data taken from Ref. [11].)

than the time required to perform the measurement. The “blocking temperature” can be defined as the temperature required to make the relaxation time less than the measurement time. In other words, above the blocking temperature, the spins are considered “unblocked” and the magnetization is in equilibrium with the external field. Figure 1.5 illustrates a method of determining the blocking temperature in Mn₁₂-ac. The filled circles are magnetization measurements taken as the sample is cooled from a high temperature in the presence of an external field, $\mu_0 H_z = 10$ mT. Above 3 K, the magnetization is in equilibrium with the field and shows the expected paramagnetic behavior. As the sample sample is cooled, the magnetization increases until about 3 K, at which point the relaxation rate becomes slower than the rate at which the temperature is decreased. Therefore, the blocking temperature is ≈ 3 K, with an applied field of 10 mT.

Although it is not commonly referred to in the literature, we may also define

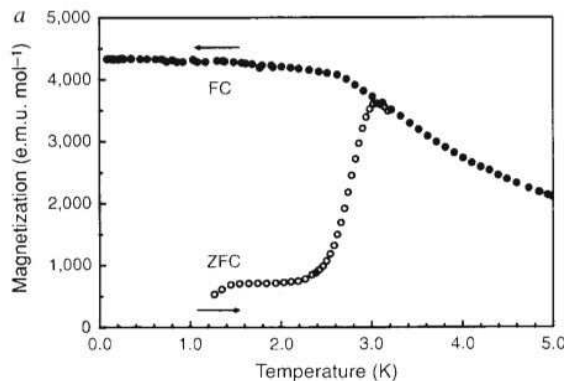


Figure 1.5: Magnetization as a function of temperature to determine the blocking temperature. The filled circles are magnetization taken as the sample is cooled with an applied field of 10 mT. The open circles are taken after the sample was cooled in zero field, a 10 mT field applied, and the temperature was increased. (Data from Ref. [17].)

a “blocking field” in analogy to the blocking temperature.⁵ In this case, an external field, H , lowers the barrier, U , which increases the rate of relaxation from the metastable state. The blocking field is then defined as the external field required to increase the relaxation rate such that the magnetization is in equilibrium with the external field. Generally speaking, lower temperatures require higher fields (lower barriers) to unblock the spins as illustrated clearly in Fig. 1.4.

Again, Figure 1.4 shows magnetization curves (data from Ref. [11]) taken at various low temperatures where the relaxation time is long compared to the sweep rate of the applied magnetic field (± 10 mT/s). As the temperature decreases, the blocking field required to reverse the magnetization increases. In addition to larger blocking fields, new features appear in this hysteresis curve as the temperature is decreased. There are periodic changes in the rate at which the magnetization relaxes as a function of the applied field. From this behavior, one can deduce that the

⁵In ferromagnets, the analogue of the blocking temperature is the Curie temperature; and the analogue of the blocking field is the coercive field. The term “coercive field” has been applied to molecular magnets in the same manner in which “blocking field” is used here. This usage is avoided here since it confuses the superparamagnetic (non-ferromagnetic) behavior of molecular magnets.

magnetic moments are tunneling at resonant fields.

Assuming for the moment that we do not know Eq. 1.2 or its parameters, we may deduce an effective Hamiltonian to describe a spin S_z of Mn₁₂-ac and the location of these tunneling resonances

$$\mathcal{H} = -D_{eff}S_z^2 - g\mu_0B_zS_z. \quad (1.5)$$

This is the minimal Hamiltonian capturing the bi-stability of S_z broken by B_z , where D_{eff} is the yet to be determined anisotropy coefficient. A simple calculation reveals that energy level crossings occur at $B_z = 0$ and every $\Delta B_z = D_{eff}/g\mu_B$ thereafter. Judging from Figure 1.4, the spacing between the steps in the hysteresis curves is approximately 0.45 T. Attributing these steps to energy level crossings implies that $D_{eff} \approx 0.60$ K and $g = 2$.⁶ The observation of these equally spaced steps provided the first evidence for macroscopic quantum tunneling of the magnetization [11, 12].

The approximate Hamiltonian, Eq. 1.5, eventually fails to describe measurements performed at lower temperatures and higher fields. Figure 1.6 shows a hysteresis curve taken at 300 mK with an external sweep rate of ± 10 mT/s.⁷ The steps are striking; however, attributing the location of the steps to resonant tunneling at energy level crossings requires the full Hamiltonian, Eq. 1.2. As will be seen, understanding the details of the magnetic avalanches also require the full Hamiltonian.

1.2.2 Minor species

In all crystals of Mn₁₂-ac, approximately 95% of the molecules are of the type described above. The remaining 5% are defect fast-relaxing molecules, which are an isomer of the “major species” [26]. Like a molecule of the major species, the “minor species” molecules form a rigid spin $S = 10$ at low temperatures. The magnetic relaxation rate of the minor species can also be described with an Arrhenius law (Eq. 1.4);

⁶This assumes $B_z = \mu_0 H_z$.

⁷Data taken from [5]

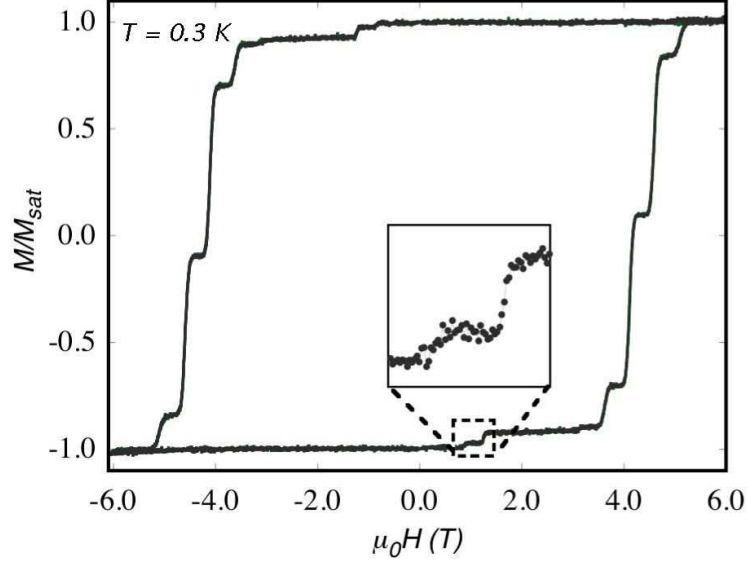


Figure 1.6: Magnetization, M_z , versus applied field, $\mu_0 H_z$ at 300 mK with and field sweep rate of ± 10 mT/s. The data around ± 1 T shows a small amount of relaxation due to the minor species of Mn₁₂-ac. (Data taken from Ref. [5].)

however the minor species has a reduced energy barrier of ≈ 42 K at zero field as well as greatly increased prefactor $\Gamma_0 = 4.5 \times 10^9 \text{ s}^{-1}$ [27]. Subsequently, the relaxation rate of the minor species is significantly faster than the major species.

The different relaxation rates are evident in magnetization curves. Figure 1.6 shows a hysteresis loop for a single crystal of Mn₁₂-ac taken at 0.3 K with an external field sweep rate of ± 10 mT/s. Starting from zero field, the total magnetization is constant as the field is increased to ≈ 0.90 T. Small steps (relaxation) are observed in the magnetization at 0.90 and 1.28 T. These steps are due to resonant relaxation of the minor species molecules. Above 1.5 T, all minor species molecules have reversed and no further change in the total magnetization is seen until ≈ 3 T, at which point the major species begins to relax. Between 3.1 and 5.3 T, evenly spaced steps are observed due to tunneling of the major species. Above 5.3 T, all the major species molecules have reversed and the crystal is completely magnetized. This demonstrates the difference in the blocking fields for the major and minor species; ≈ 5 T and ≈ 1

T respectively.

The steps in the hysteresis curve due to the minor species are also an indication that an effective Hamiltonian can be introduced to describe the minor species molecules as well,

$$\mathcal{H} = -D^{minor} S_z^2 - g\mu_B S_z B_z + \mathcal{H}_\perp, \quad (1.6)$$

where D^{minor} can be deduced from the spacing between the resonances, $D^{minor} = g\mu\Delta B_z \approx 0.49$ K [34].⁸

Although the presence of the minor species is occasionally a nuisance, they can be useful under certain circumstances. In Ref. [35], the resonance fields of the minor species were used to make a direct measurement of the dipolar field due to the major species, which we describe in Chapter 3. The presence of the minor species was found to have a significant effect on magnetic avalanches, which will be discussed in Chapter 4.

1.3 Magnetic avalanches

When performing magnetization curves at low temperatures on single crystals of Mn₁₂-ac, Paulsen and Park [1] occasionally observed an abrupt (< 10 ms) complete reversal of the magnetization. These are clearly seen in Figure 1.7 as the vertical lines in the hysteresis curves. A thermometer was mounted near the sample and the magnetization was measured with a SQUID magnetometer. The temperature and magnetization as a function of time were recorded as a function of time during an avalanche. The responses for an avalanche are shown in Figure 1.8. The magnetic change occurred faster than could be resolved with the magnetometer they employed. The thermometer recorded a temperature of 1.3 K shortly after (250 ms) after the avalanche. Paulsen and Park suggested that the temperature within the crystal may

⁸Again we have assumed $B_z = \mu_0 H_z$.

actually be much larger since the thermal mass of the $\text{Mn}_{12}\text{-ac}$ is small compared to the thermal mass of the thermometer.

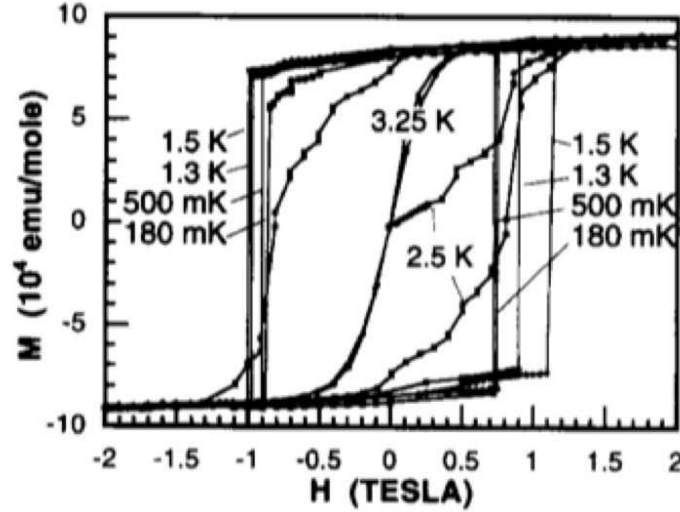


Figure 1.7: Magnetization, M_z , versus applied field, $\mu_0 H_z$ on single crystals of $\text{Mn}_{12}\text{-ac}$ with an external sweep rate of 0.3 mT/s. If the field changes slowly with respect to the relaxation rate (Eq. 1.4), the magnetization follows an equilibrium Curie-Weiss law. The magnetization curve at 3.25 K reflects this behavior. (Data taken from Ref. [1])

They suggested that the magnetization reversal was the result of a thermal runaway produced by the heat released by the relaxing spins. Assuming that no heat escaped the crystal in the time scale of the reversal, and using the measured value of the specific heat from Ref. [18], they calculated that the temperature must increase to approximately 12 K. The thermal nature of the avalanches was confirmed by a series of experiments measuring a temperature rise due to heat released by the avalanche [28, 29, 30, 31]).

Although a number of exotic explanations for the avalanches were proposed and explored [3], the measurements of Suzuki et al. [4] asserted magnetic deflagration as the leading explanation. The magnetization dynamics were measured during spontaneously occurring avalanches using an array of Hall sensors placed along the length of a single crystal (details below). Suzuki et al. discovered that the magnetization re-

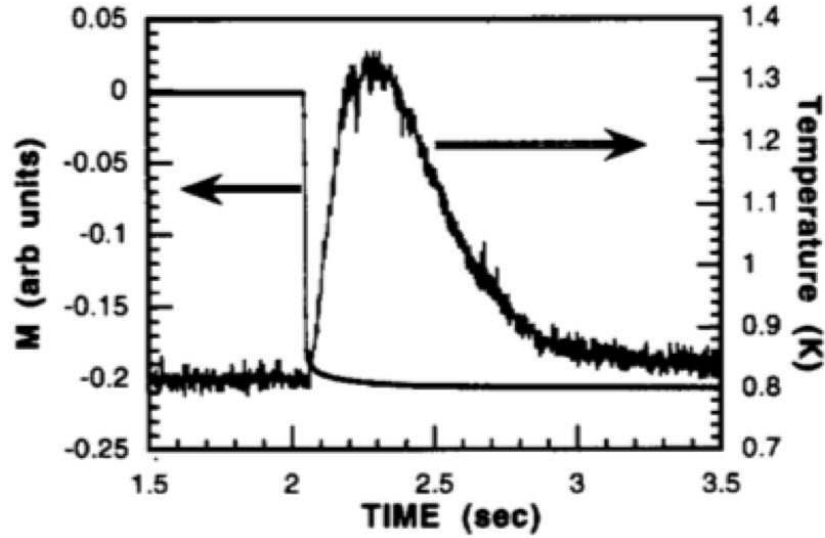


Figure 1.8: Magnetization and temperature as a function of time during an avalanche. (Data taken from Ref. [1])

versal during an avalanche occurs as propagating front separating regions of opposing magnetization. The front travels through the crystal at a constant speed of roughly 10 m/s. Combined with the fact that heat is released during an avalanche, they suggested that the traveling magnetization front is analogous to a chemical deflagration front.

Shortly after the results of Suzuki et al., Hernández-Mínguez et al. [13] reported the results of an intriguing avalanche study focused on the behavior near the resonant fields of $\text{Mn}_{12}\text{-ac}$. They employed an surface acoustic wave (SAW) generator to trigger the avalanches. Like Paulsen et al., they used a SQUID magnetometer to measure the total magnetization change during an avalanche with approximately 0.1 ms resolution. Assuming that the magnetization reversal observed was the same traveling front reported by Suzuki et al., they deduced the front speed from the total time of the magnetization change and the measured length of the crystal. The ability to ignite avalanches controllably allowed them to study the avalanche speed as a function of applied field. Indeed, they found that the relaxation rate increases

near the resonance fields, which they interpreted as an enhanced deflagration speed introducing the notion of “quantum magnetic deflagration”.

The results of Hernández-Mínguez et al. are intriguing; however, there are several aspects of the measurement which prevent it from being compelling evidence for quantum magnetic deflagration. In particular, at the high temperature (2 K) and the sweep rates (30 mT/s) used, the relaxation of magnetization near resonant fields *prior* to the ignition of an avalanche is possible. As we will demonstrate in Chapters 4 and 5, the relaxation of magnetization prior to the ignition of an avalanche leads to slower avalanche speeds and which produces an apparent maxima in the speeds just before the resonant fields. Therefore, precise control over the sample magnetization prior to the ignition of the avalanche must be exercised in order to study the effects of quantum tunneling on the avalanche dynamics.

In 2007, Garanin and Chudnovsky [6] developed a comprehensive theory of magnetic deflagration. In particular, they introduced the two fundamental aspects of magnetic deflagration, which are encapsulated in the following equations:⁹

$$C \frac{\partial T}{\partial t} - \nabla \cdot k \nabla T = -\langle E \rangle \frac{\partial n}{\partial t} \quad (1.7)$$

$$\frac{\partial n}{\partial t} = -\Gamma n. \quad (1.8)$$

Equation 1.7 describes the flow of heat through the solid with the relaxing spins, $\frac{\partial n}{\partial t}$, as a source of heat. k is the thermal conductivity and C is the heat capacity. Equation 1.8 describes the thermal relaxation of the spin density, n . $\langle E \rangle$ is the average amount of heat released per molecule when its spin relaxes to the stable state. For a single relaxing molecule, the energy change from the metastable to stable state is easily calculated from Eq. 1.2 as $\Delta E = 2g\mu_B S B_z$. However, since not all spins necessarily relax during an avalanche, the average energy released per molecule must

⁹This form of Eq. 1.8 assumes the equilibrium value of n is zero, which is appropriate for all avalanches reported herein.

be introduced

$$\langle E \rangle = 2g\mu_B S \left(\frac{\Delta M}{2M_s} \right) B_z, \quad (1.9)$$

where M_s is the saturation magnetization and $\Delta M = |M_z - M_s|$ is the change from initial to final magnetization. The parameter $\Delta M/2M_s$ ranges from 0 to 1.

Since both k and C are functions of temperature, Eqs. 1.7, 1.8 are coupled, nonlinear differential equations, which make them very difficult to solve in general. There is a fortunate set of circumstances, both experimental and theoretical, that allow for an easy application of Eqs. 1.7, 1.8 to magnetic avalanches in $\text{Mn}_{12}\text{-ac}$.

Measuring the avalanche speed is the most accessible way to study avalanches experimentally. This is evidenced by the number of publications primarily dedicated to the speeds [4, 13, 14, 41, 15]. There also exists a simple approximation to Eqs. 1.7, 1.8 to handle quasi-one-dimensional propagating avalanche speed [6]

$$v = \sqrt{\frac{4k_B T_f \kappa \Gamma(B, T_f)}{U(B)}}, \quad (1.10)$$

where κ is the thermal diffusivity.¹⁰ A few criteria for this approximation to hold are worth enumerating here. A more detailed discussion will follow in Chapter 6.

Avalanches occur in crystals, which occupy three-dimensional space. There is evidence that avalanches ignite at single point in the crystal and propagate out as a (nearly) spherical front [41]. This suggests that in order for the deflagration front to be treated as a one-dimensional wave, attention must be restricted to the region sufficiently far from the point of ignition. As a heuristic guide, the front speed should be measured at a distance from the ignition point no closer than the width of the crystal. This condition is satisfied for all avalanches reported herein.

Eq. 1.10 also requires the assumption that the relaxation rate of the spins at the highest temperature, $\Gamma(U, T_f)$, is significantly slower than the rate that heat traverses

¹⁰The factor $\sqrt{4}$ is not appropriate for $\text{Mn}_{12}\text{-ac}$. An explanation appears later in the text.

the interface width, κ/δ^2 , where δ is the magnetic interface width. This condition may also be satisfied if $U/k_B T_f \gg 1$ (see Eq. 1.4).

1.3.1 Suzuki et al. in detail

Since the work reported in this thesis is essentially a continuation of the program initiated by Suzuki, it is worthwhile to discuss the measurements of Ref. [4] in more detail.

A single crystal was attached to an array of Hall sensors, which was aligned with the c axis. Both Hall sensor array and crystal were immersed in liquid ^3He at 250 mK. An external field was applied parallel to the c axis of the crystal and the magnetization was recorded with each Hall sensor. Figure 1.9 shows a magnetization curve taken at low temperature (data taken from Ref. [4]). At ± 4 T, avalanches occur spontaneously for this particular crystal. The inset shows data taken with higher temporal resolution.

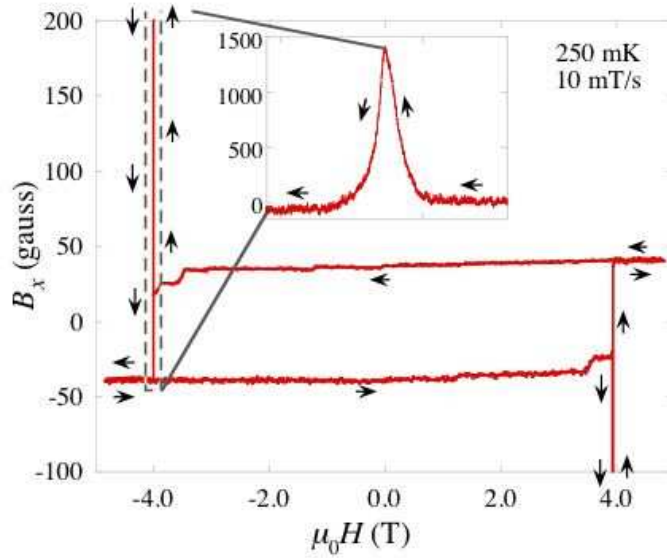


Figure 1.9: Magnetization versus external field. The anomalous behavior at ± 4 T is due to avalanches. The inset shows the magnetization measured by one Hall sensor during an avalanche taken with higher temporal resolution. (Data taken from Ref. [4].)

The avalanche progresses through the crystal in a similar fashion to that of a domain wall in a ferromagnet ¹¹. There is an interface separating regions of opposing magnetization, which produces a large transverse magnetic field, B_x , near the front. With the measurement arrangement employed, the Hall sensors are sensitive to the B_x produced by the transient front.

Figure 1.10 shows the response recorded on seven equally spaced Hall sensors in the array as a function of time. Each sensor records nearly the same peak displaced in time. The peak corresponds to the avalanche arriving at that particular sensor. By recording the arrival times at each sensor along with the sensor positions, the speed of the avalanche can be deduced. The inset of Figure 1.10 is a plot of Hall sensor positions with respect to the arrival times. The slope of a linear fit yields the avalanche speed.

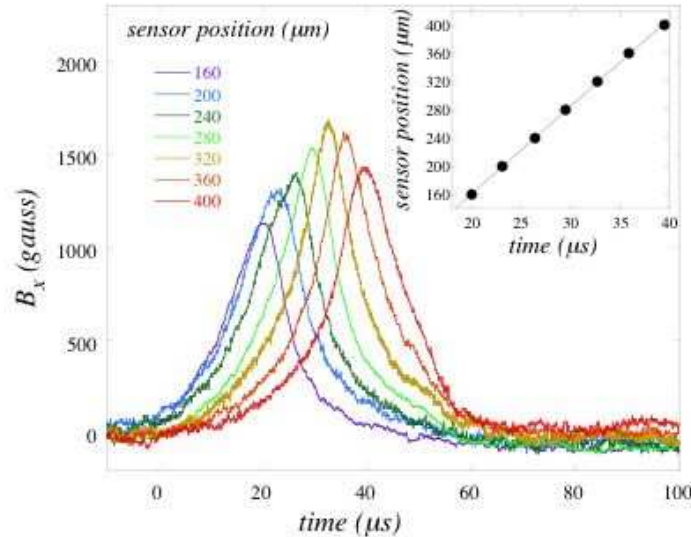


Figure 1.10: Magnetization as a function of time as measured by seven equally spaced Hall sensors. The arrival of the avalanche front is registered as a peak at a particular Hall sensor. The inset is a plot of the avalanche arrival times with respect to the sensor position. The avalanche speed is deduced from a linear fit. (Data taken from Ref. [4].)

¹¹ $\text{Mn}_{12}\text{-ac}$ is a superparamagnet at the temperatures greater than ≈ 3 K, which are produced during an avalanche. This precludes the possibility of a ferromagnetic domain wall.

Figure 1.11 (a) is a schematic depiction of the field lines produced during an avalanche. The avalanche front separates regions of the crystal with opposing magnetizations. Consequently, a field with a large quadrupole moment is produced. The Hall sensors detect the transverse field (B_x) produced by the front. Figure 1.11 (b) shows the data from which the field line schematic is deduced.

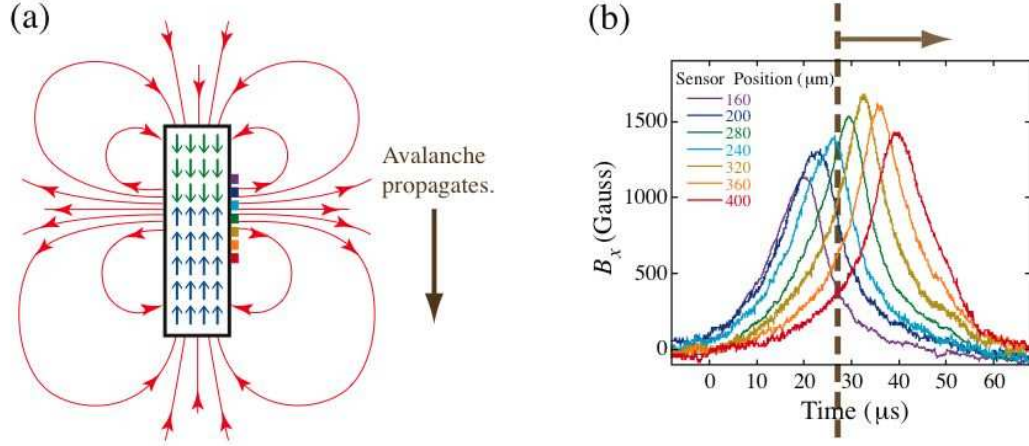


Figure 1.11: (a) A schematic depiction of the field lines producing the peaks registered on each Hall sensor. (b) The vertical dashed line marks the time at which the field lines are considered. (Data taken from Ref. [5])

The speeds were recorded for avalanches on three crystals with similar dimensions. The results are shown in Figure 1.12. Since the measurement protocol used in that experiment amounted to simply sweeping the external field and recording any spontaneous avalanches, the scope of the data is limited.

The results of Suzuki et al. offered a strong argument for the correctness of magnetic deflagration. Equally importantly, the method employed to measure the avalanche dynamics proved robust and reliable; interpreting the Hall sensor peaks could not be more transparent. The only obvious feature of the measuring scheme missing is the lack of a controllable mechanism for triggering the avalanche. In order to determine the success of the theory of deflagration or the role played by quantum tunneling in the avalanche process, a method of reliably triggering avalanches

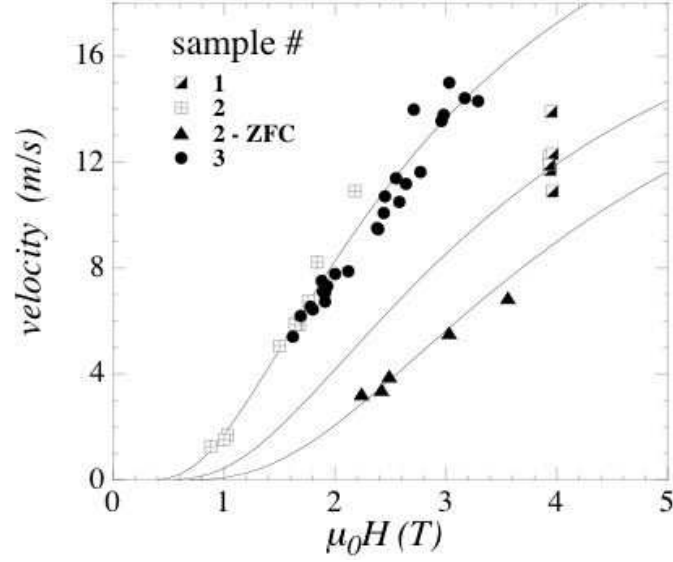


Figure 1.12: Speeds for avalanches recorded at various fields and initial magnetizations. (Data taken from Ref. [4])

at a predetermined field must be introduced. In Ref. [15], this lack of a trigger was alleviated with a simple constantan wire. Used as a heater, the controllable triggering of avalanches was demonstrated, as well as a characterization of the trigger conditions, i.e., ignition temperature. We exercise this control and explore magnetic avalanche/deflagration physics in the remainder of this thesis.

Chapter 2

Experimental procedure

2.1 Generic conditions

The work presented in this thesis is essentially a continuation of the program initiated by Suzuki in Ref. [4, 5]. As such, we follow a similar scheme for studying the avalanche dynamics with an array of Hall sensors, which is detailed in the thesis Ref. [5]. We recapitulate the scheme here with less detail.

All measurements were performed in a commercial Oxford ^3He cryostat with a base temperature of 250 mK. Surrounding the sample space is a 14 T superconducting magnet. The samples, Hall sensors, heater, and thermometers were all immersed in liquid ^3He . For all data reported herein, the c axis of the crystal is aligned parallel to the applied magnetic field, with an estimated accuracy of better than 3° . We follow convention and denote this as the z direction as illustrated in Figure 2.1.

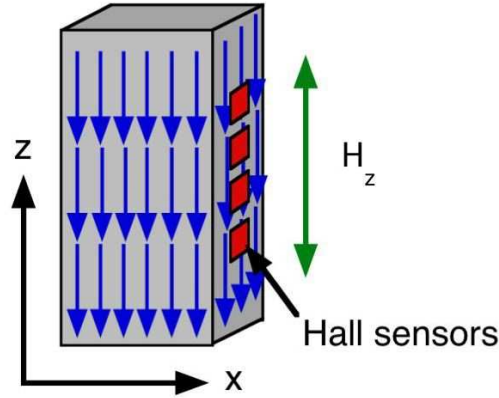


Figure 2.1: Schematic of the $\text{Mn}_{12}\text{-ac}$ crystal alignment with respect to the external field. The long arrows represent the magnetic moment of each molecule.

2.2 Magnetic data acquisition

The magnetization dynamics were studied with an array of custom Hall sensors.¹ Each Hall sensor in the array has a sensing area of $30 \times 30 \mu\text{m}^2$, and are spaced from

¹The Hall sensor array and germanium thermometer were supplied by the group of E. Zeldov at the Weizmann Institute of Science, Rehovot Israel.

one another by 80 μm center to center. The avalanche signal on a particular Hall sensor is recorded with one channel of a four-input digital oscilloscope.² The array has eleven sensors, but there are only eight inputs to two oscilloscopes. One Hall sensor must be recorded by both sensors in order to synchronize the data. Therefore, at most seven sensors could be measured at once in this experiment. We find that as few as four sensors can be used to reliably and precisely measure the avalanche dynamics. Before it reaches the oscilloscopes, the signal is amplified with a single stage IC instrumentation amplifier with a gain of 100.³

An excitation current ranging from 33 to 66 μA was used for the Hall sensors. The magnetization of the crystal produces a signal on the Hall sensor, which is proportional to the excitation current. During an avalanche, there is also an EMF induced by the changing magnetization, which is independent of the size of the excitation current.⁴ The excitation current is chosen to overwhelm the signal due to the EMF.

Crystals are attached to the Hall sensor array with Apiezon M grease, as depicted schematically in Figure 2.1. Stycast 2850 epoxy, silicone grease, Eicosane wax, and paratone oil were also used to mount the crystal with indistinguishable results.

In this configuration, the Hall sensors measure the magnetic induction in the x direction, B_x . When the crystal is uniformly magnetized, as depicted schematically in Figure 2.1, it produces a field approximately that of a magnetic dipole. Therefore, the sensors located near the end of the crystal record the largest B_x . Any inhomogeneity in the magnetization, M_z , changes the dipolar field due to the crystal and is measurable on the Hall sensors as a change in B_x . For instance, the inhomogeneous magnetization of an avalanche produces a transient quadrupole moment, as shown in Figure 1.11. The precise dependence of B_x on the magnetization M_z is detailed in Appendix A and Ref. [5].

²Tektronix TDS 2014.

³Burr-Brown INA 105.

⁴This EMF can be measured on a Hall sensor during an avalanche when the excitation current is zero.

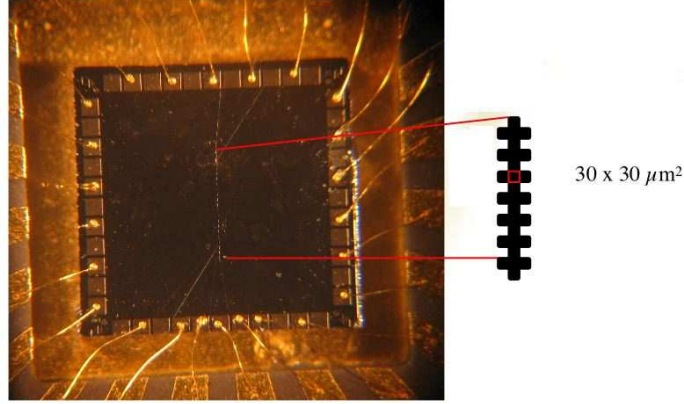


Figure 2.2: A picture of a Hall sensor array used for measuring the magnetization dynamics during an avalanche. Typically, the dimensions of a single sensor are $30 \times 30 \mu\text{m}^2$, with $50 \times 50 \mu\text{m}^2$ spacing.

2.3 Heater and ignition temperature data acquisition

In order to trigger the avalanches, we use a simple twisted constantan wire positioned near the crystal, as shown in Fig. 2.3. The entire crystal, a portion of the heater, and a significant portion of the Hall sensor array (or thermometer) were encased in Apiezon M grease to ensure good thermal contact between the crystal and the heater. Passing a current (typically $\sim 10 \text{ mA}$) through the wires warms the crystal with an estimated 0.1 mW to 1.0 mW . This leads to an increase of the sample temperature at a rate of about 10 K/s . The avalanche dynamics occur on a time scale of roughly $100 \mu\text{s}$. This implies that the heater can increase the temperature during an avalanche by approximately 1 mK , which will be shown later to be a negligible increase with respect to the avalanche dynamics. Therefore, the output of the heater constitutes “slow” heating. The temperature increases slowly until the an avalanche ignites. The temperature at which the avalanche ignites is denoted as the “ignition temperature”, T_{ig} .

The output of the heater and the ignition temperature for the avalanches were

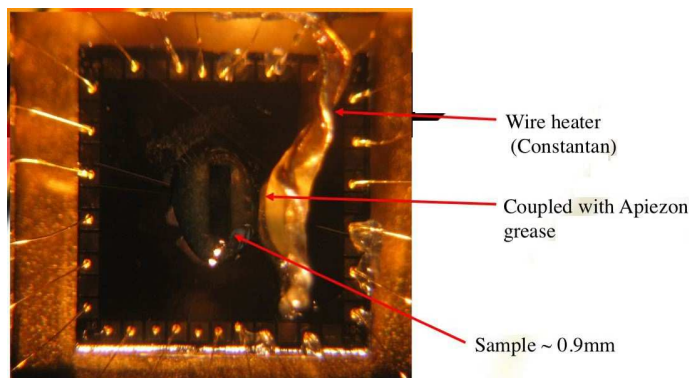


Figure 2.3: Picture of the Hall sensor array, crystal, grease, and Constantan wire heater assembly. Typically, the sample is encased completely with grease to make sufficient contact with the heater; however, a portion of the grease was removed for this picture so that the sample was not obscured.

measured with a custom germanium thin film resistance thermometer. The construction and geometry of the thermometer was constructed to mimic the layout of the Hall sensor array, which allowed for easy switching between thermal and magnetic measurements.⁵ A thin film of germanium was deposited by e-gun evaporation through shim masks onto heated GaAs substrates in vacuum. The sensing area of the thermometer is $40 \times 100 \mu\text{m}^2$. However, since the thermal conductance between the Ge and the GaAs substrate is much higher than the thermal conductance between the Ge and the crystal, regardless of the mounting material, the thermal mass of the thermometer quite large. As will be discussed later, this does not affect the interpretation of the ignition temperature data. It does prevent an accurate measurement of the heat released by the relatively small crystal.

A four-wire measurement with an excitation current of $10 \mu\text{A}$ was used to measure the resistance. Figure 2.4 also shows the calibration curve for the resistive thermometer, which shows typical behavior for a semiconductor above approximately 1 K. Below 1K, there is a deviation from the expected behavior, which is an indication

⁵The Ge thermometer was originally intended and designed for use as an array similar to the Hall sensor array with the hope of spatially resolving the temperature profile generated by an avalanche. This line of investigation was abandoned due to the high thermal conductivity between the individual thermometers in the array.

that self-heating is preventing the thermometer from following the ^3He bath temperature. This heating could be reduced by decreasing the excitation current through the thermometer; however, this limited the signal required to measure the response due to the avalanche (see Chapter 4). Therefore, the resolution of temperatures below 1 K was sacrificed.

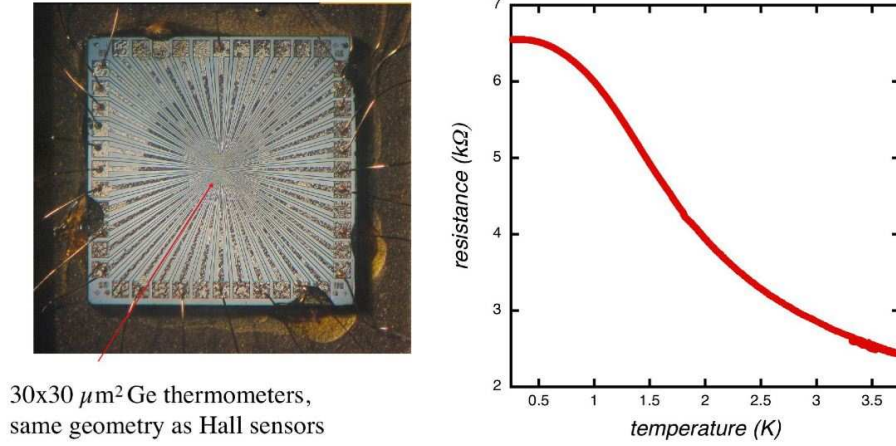


Figure 2.4: A picture of the germanium thermometer along with the calibration using an excitation current of approximately $10 \mu\text{A}$. The decrease in slope below 1 K is likely due to heating and ultimately limits the thermometer resolution.

The signal of the thermometer was amplified with a single IC instrumentation amplifier with a gain of ten, and then recorded with the two digital oscilloscopes. Two oscilloscopes were used to record the temperature profile with two different time scales.

2.4 Magnetic preparation for avalanche

We would like to trigger avalanches under the widest range of conditions possible for two reasons. First, this would serve as a demonstration of the tunable nature of magnetic deflagration. In other words, it would showcase one of the advantages for studying deflagration in its magnetic incarnation. Second, by exploring a large volume in the parameter space we can subject the theory of magnetic deflagration to

a rigorous test.

Prior to the ignition of an avalanche, the sample must be prepared with a metastable magnetization. As discussed in section 1.2.1, this requires the temperature to be less than the blocking temperature. At sufficiently low temperatures, the relaxation rate is slow enough to allow the field to be changed without affecting the magnetization. Since the blocking field increases as the temperature is decreased, it is desirable to cool the sample to the lowest temperature available.⁶ The base temperature of the ^3He cryostat is 250 mK. At this temperature, the blocking field is greater than 3.0 T. All avalanches reported here were prepared at the base temperature and triggered at a field below 3.0 T.

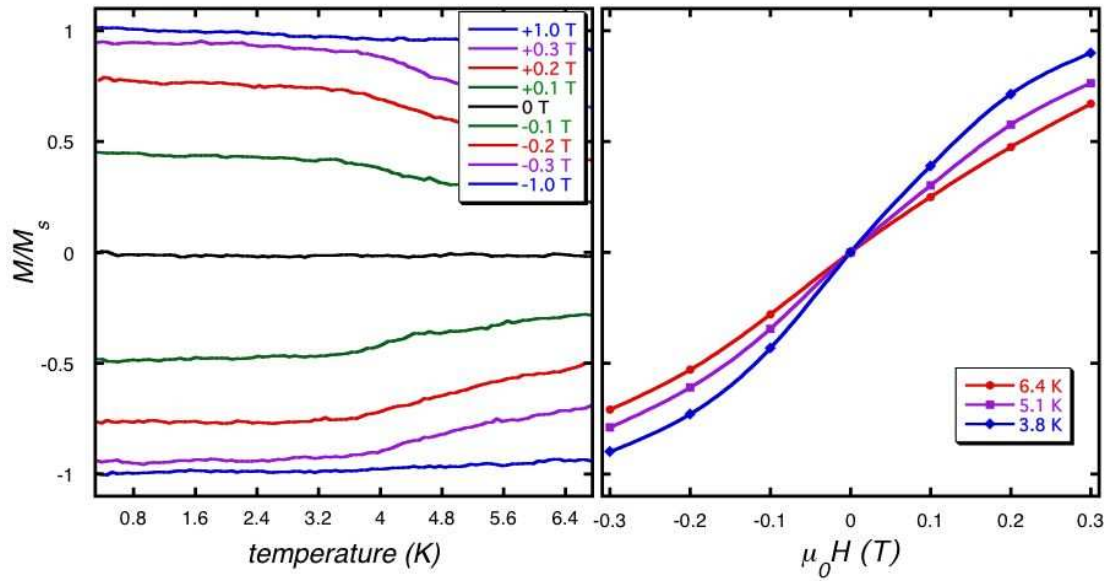


Figure 2.5: (a) The magnetization, M_z , as a function of temperature for various external fields. M_s is defined as the magnetization with all the spins aligned in the positive direction. At the blocking temperature (≈ 3.5 K) the magnetization remains unchanged as the temperature decreases. (b) M_z as a function of external field for three temperatures above the blocking temperature.

In addition to controlling the field at which the avalanche is triggered, the initial magnetization may be controlled precisely as well. By cooling the sample from a high

⁶Below approximately 0.5 K, little increase in the blocking field is observed and the relaxation rate is dominated by quantum tunneling rather than thermal processes.

temperature (above the blocking temperature) in the presence of various external fields, the sample can be “frozen” with an arbitrary magnetization. Figure 2.5 (a) shows the magnetization as a function of temperature for nine different cooling fields. At high temperatures, the spins are unblocked and behavior characteristic of a paramagnet is observed, i.e., the magnetization decreases as the temperature increases. Around 3.5 K, the magnetization stops changing as the temperature is reduced and no further changes are seen down to the base temperature.⁷ Figure 2.5 (b) show the magnetization as a function of external field for three different temperatures above the blocking temperature. Again, this is characteristic behavior of a paramagnet, with the slope (susceptibility) increasing as the temperature is decreased.

Judging from Figure 2.5, cooling the sample in ± 0.3 T is nearly sufficient to saturate the magnetization at low temperatures. Any intermediate value, $-M_s \leq M_z \leq M_s$, may be prepared by cooling at an intermediate field, $-0.3 \text{ T} \leq \mu_0 H_z \leq 0.3 \text{ T}$. The M_z recorded in Fig. 2.5 should be understood as the total magnetization due to each species of molecule, $M_z = M_z^{major} + M_z^{minor}$. And therefore, M_s is the total saturation magnetization, $M_s = M_s^{major} + M_s^{minor}$.

With the temperature at the base temperature of ≈ 0.3 K, the external field is adjusted to a predetermined value, creating a metastable condition, and an avalanche is triggered. With this field-cooling method for preparing the initial magnetization, M_z , an avalanche may be prepared with nearly any combination of external field and metastable magnetization, provided the external field is below the blocking field. As will be discussed in detail in Chapter 5, the amount of magnetization that reverses during an avalanche is $\Delta M = M_z - M_s$. This may be thought of as the “fuel” available for burning in chemical deflagration. Also in Chapter 5, we will tune both parameters (H_z and ΔM) and explore the results.

For an external field of approximately $|\mu_0 H_z| \leq 1.25 \text{ T}$, the minor species may

⁷There is a small change in the magnetization between 3.5 K and approximately 1.0 K due to the minor species.

also contribute to the fuel, ΔM . Therefore, the M_z due to the minor species must also be accounted for at these low fields unless precautions are taken to prevent their relaxation during the avalanche. In Chapter 3 we describe a method used to magnetically partition the sample such that the major and minor species molecules are anti-parallel. This allows avalanches of exclusively one species or the other to be studied. In the Chapter 4, we study the interaction and interplay between the minor and major species during an avalanche.

Chapter 3

Dipolar field of $\text{Mn}_{12}\text{-ac}$

Some recent work has focused on circumstances where the assumption of independent spins breaks down in crystals of molecular magnets. Ferromagnetic ordering due to magnetic dipole-dipole interactions has been demonstrated experimentally by Evangelisti et al. [36] in the high-spin molecular magnet Fe_{17} . Based on neutron scattering experiments, Luis et al. [19] have claimed that Mn_{12} -ac also orders ferromagnetically provided a large transverse field is applied to reduce the magnetic barrier and increase the relaxation rate. Recent detailed calculations by Garanin and Chudnovsky [20] indicate that dipolar ferromagnetism in a transverse field should indeed be found in Mn_{12} -ac below a Curie temperature $T_c \sim 0.8$ K. A careful determination of the dipolar field is therefore crucial for such studies.

No data reported here were taken under such circumstances (large transverse fields of ~ 3 T [19]), which are thought to be required for long range ferromagnetic ordering in Mn_{12} -ac. However, the dipolar field is found to have a significant effect on the propagation of avalanches. In other words, the assumption that $B_z = \mu_0 H_z$ in Eq. 1.2 fails and must be replaced with $B_z = \mu_0(H_z + M_z)$, where M_z is the magnetization of the crystal accounting for the dipolar fields. In addition, the methods employed here to determine M_z can also be used to study avalanches of either major or minor species as will be discussed extensively in Chapter 4. For these reasons, we include a detailed account of the determination of the dipolar fields.¹

3.1 Magnetic partition

Using a simple protocol similar to one described in Ref. [34], the difference in the blocking fields of the major and minor species allows one to magnetically partition the crystal with three distinct preparations:

¹In general, M_z is inhomogeneous throughout the crystal with the strongest deviations from the mean, $\langle M_z \rangle$, near the edges. We recapitulate the experiment performed to measure the average magnetization, $\langle M_z \rangle$, in crystals of Mn_{12} -ac. From here, we drop the distinction and assume the $M_z = \langle M_z \rangle$.

1. $M_z^{major} = 0$ and $M_z^{minor} = -M_s^{minor}$. Major species spins are random, resulting in zero magnetization, while the minor species are aligned. Starting with an unmagnetized (zero-field-cooled) crystal, and maintaining the temperature at 300 mK: a magnetic field of -2 T is applied which is sufficient to completely magnetize the minor species while leaving the major species spins unchanged; sweeping the field back to zero yields a sample with minor species spins aligned and major species spins random with zero net magnetization.
2. $M_z^{major} = -M_s^{major}$ and $M_z^{minor} = -M_s^{minor}$. Major and minor species spins are aligned in the same direction. A larger magnetic field of -6.0 T is applied along the c-axis of the crystal, sufficient to magnetize both species; reducing the magnetic field to zero yields a sample with major species and minor species spins aligned in the same direction.
3. $M_z^{major} = M_s^{major}$ and $M_z^{minor} = -M_s^{minor}$. Major and minor species spins are aligned in opposite directions. This magnetic preparation is described schematically in Figure 3.1. Starting with the spins aligned in same direction (Fig. 3.1(a)), the magnetic field is ramped to -2 T in the direction opposite to the magnetization, reversing the direction of the minor species spins while leaving the major species spins unchanged, as shown in (Fig. 3.1(b)). Reducing the field back to zero, (Fig. 3.1(c)), yields a sample in which the minor and major species are magnetized in opposite directions.

3.2 Measurement of dipolar field

With the sample prepared according to these three methods, a hysteresis curve may be performed involving only the relaxation of the minor species provided the magnitude of the external field remains well below the major species blocking field, i.e., $|\mu_0 H_z| \leq 2.0$. Under these circumstances, the major species remains “frozen”.

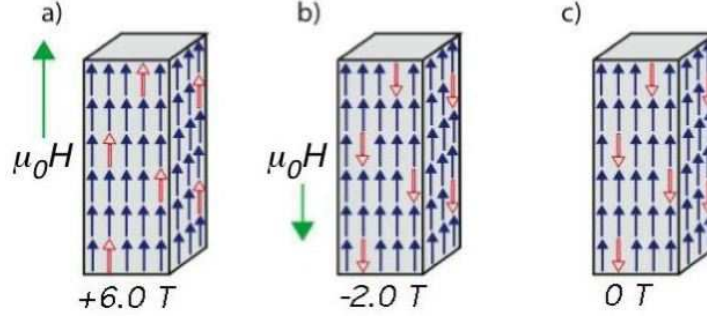


Figure 3.1: Schematic of the procedure used to prepare $\text{Mn}_{12}\text{-ac}$ with minor and major species magnetized in opposite directions. (a) First, a +6 T field is applied to align all spins. (b) Then, a -2 T field is applied, reversing the magnetization of the minor species. (c) Finally, the field is returned to zero, leaving the major and minor species spins anti-parallel.

Fig. 3.2 (a) shows hysteresis curves for the minor species taken at 0.3 K and an external field sweep rate of 5 mT/s for the three different magnetic preparations. The curves are normalized by M_{sat} , the saturation value of the minor species. The minor species hysteresis curves exhibit a steps as the major species. However, the smaller anisotropy leads to a smaller spacing between steps. Fig. 3.2 (b) shows the derivative of the magnetization curve, which is useful for determining the location and widths of the tunneling resonances.

It is clear that the externally applied magnetic field corresponding to the tunneling resonances depends on the direction of the magnetization of the major species. The circles of Fig. 3.2 are data taken with the net magnetization of the major species equal to zero. Fully magnetizing the major species in the positive direction shifts the location of the tunneling resonance fields by ≈ -0.05 T, as indicated by the triangles. Here the dipolar field adds to the external field to satisfy the resonance condition. The squares are data taken with the major species magnetized fully in the negative direction with a consequent shift in the resonance field of $\approx +0.05$ T. In this case, the external field is larger to offset the dipolar field in the opposite direction. A close determination of the shift corresponding to the dipolar field associated with full

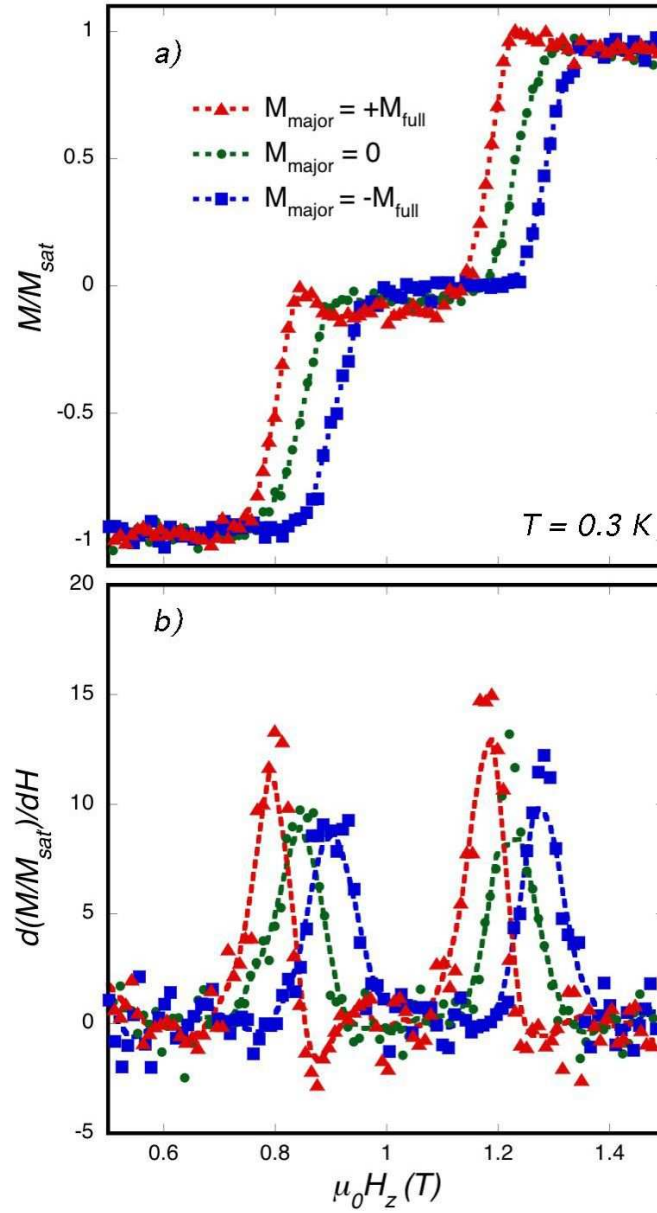


Figure 3.2: (a) Magnetization of the minor species as a function of external magnetic field swept at +5 mT/s with the major species magnetization prepared following the three protocols described in the text. The triangles (squares) are data taken with the major species aligned in the positive (negative) direction. The circles are data taken with the minor species randomly oriented to yield zero magnetization. (b) The derivative of the curves shown in frame (a).

magnetization of the major species of $\text{Mn}_{12}\text{-ac}$ yields 51.5 ± 8.5 mT. The dipolar fields of a completely magnetized crystal of $\text{Mn}_{12}\text{-ac}$ calculated in Ref. [6] was found to be 52.6 mT, in excellent agreement with this data.

Further evidence is provided by measurements of magnetic avalanches and will be discussed in Chapter 4. We can therefore no longer make the assumption $B_z = \mu_0 H_z$, which neglects the field due to the sample magnetization, M_z . For all field dependent quantities calculated in the thesis, the effect of the sample magnetization is accounted for with $B_z = \mu_0(H_z + M_z)$.

Chapter 4

Major, minor, and combined avalanches

As described above, all single crystals of $\text{Mn}_{12}\text{-ac}$ contain two species of molecules. The major species described comprises roughly 95% of the crystal relaxes slowly and is well described with the effective Hamiltonian, Eq. 1.2. The remaining molecules are the fast-relaxing minor species and may be described approximately with Eq. 1.6. By following the partitioning protocol described in Chapter 3, avalanches of exclusively either major or minor species may be studied; so-called “major avalanches” and “minor avalanches”, respectively. In addition, both species may be allowed to relax during a so-called “combined avalanche”. It is found that the minor species can act as a “catalyst” for the major species in close analogy with catalysts in chemical combustion. In other words, the presence of the minor species acts to simultaneously lower the ignition threshold and increase the avalanche speed. This is analogous to a chemical catalyst acting to increase a chemical reaction rate, thereby deepening the connection between chemical and magnetic deflagration. We postpone the quantitative analysis of each type of avalanche until Chapter 6.

4.1 Magnetic preparation

The sample is first cooled in an external field sufficient to completely magnetize the sample ($|\mu_0 H_z| \geq 0.3 \text{ T}$) as described in section 2.4. For all avalanches reported in this chapter, the initial magnetization was prepared in a large cooling field. Then, following the protocol described in section 3.1, the crystal is prepared with three distinct magnetic partitions involving the minor and major species. This, in turn, allows for three classes of avalanches, which are depicted schematically in Figure 4.1. The long filled arrows represent the major species and the short open arrows represent the minor species. The external field H_z is depicted by the long filled arrow outside the crystal.

Major avalanches The major avalanche preparation is shown in Figure 4.1 A, where only the major species is anti-parallel to the applied field. Therefore, only the

major species spins are metastable and relax during the avalanche.

Minor avalanches The minor avalanche preparation is shown in Figure 4.1 B. Only the minor species is metastable and relaxes during the avalanche.

Combined avalanches Figure 4.1 C shows the magnetic preparation for combined avalanches. Here, both species of spins are metastable and relax during the avalanche.

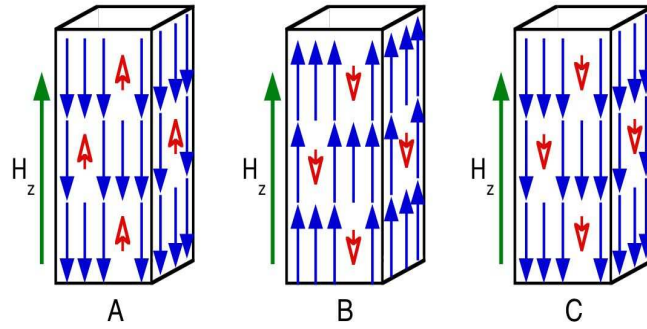


Figure 4.1: Schematic crystal for the three different classes of avalanches: A) “Major avalanches”; only the major species reverses. B) “Minor avalanches”; only the minor species reverses. C) “Combined avalanches”; both species reverse during avalanche. The long arrows represent the major species molecules and the short open arrows represent the minor species.

The field was swept at a constant rate of ± 5 mT/s until the desired field was reached. At this point, the avalanche was triggered by manually activating the heater. After the heater was activated, a delay of as much as 0.5 s occurred until the temperature was high enough to trigger the avalanche. Under these circumstances, the accuracy with which the external field could be determined was approximately ± 5 mT.

When triggering avalanches involving the minor species (either minor or combined avalanches), careful attention must be paid to the magnetization due to each species, $M_z = M_z^{major} + M_z^{minor}$. To facilitate the discussion, we introduce the parameter ΔM^{minor} to account for the amount of metastable minor species magnetization

reversing during an avalanche,

$$\Delta M^{minor} \equiv |M_z^{minor} - M_s^{minor}|, \quad (4.1)$$

where M_s^{minor} is the saturation magnetization due to the minor species. At the sweep rates (± 5 mT/s) and base temperatures (0.3 K) typically used here, the minor species magnetization begins to stabilize as the field is increased to $|\mu_0 H_z| \approx 0.8$ T, as demonstrated in Figure 3.2, before the avalanche is triggered. It is completely stabilized by about 1.2 T. For minor (or combined) avalanches triggered below 0.8 T, no magnetization has stabilized and therefore $\Delta M^{minor} = 2M_s^{minor}$. For minor (or combined) avalanches triggered between 0.8 T and 1.2 T, approximately half of the minor species spins have stabilized resulting in $\Delta M^{minor} = M_s^{minor}$. Finally, for avalanches triggered above 1.2 T, all minor species molecules have relaxed and $\Delta M^{minor} = 0$.

Sweeping the field at a faster rate would decrease the amount of minor species relaxation at lower fields [34]; however, this would also lead to greater imprecision in the determination of the external field. In the following chapter, we describe avalanches triggered after the field was fixed and stabilized. This reduced the error in the determination of the applied field to $< \pm 0.5$ mT. This could not be used here, however, since fixing the field would cause additional relaxation of the minor species prior to the ignition of the avalanche.

All avalanches reported in this chapter involving the major species have an initial major magnetization, $M_z^{major} = -M_s^{major}$. We also introduce a parameter to characterize the available “fuel” burned in avalanches involving the major species,

$$\Delta M^{major} \equiv |M_z^{major} - M_s^{major}|, \quad (4.2)$$

where M_s^{major} is the saturation magnetization due to the major species. Again, all major (and combined) avalanches triggered in this chapter have $\Delta M^{major} = 2M_s^{major}$.

4.2 Major avalanches

With the sample suitably prepared as described above, avalanches were triggered by applying a constant current through the heater. Figure 4.2 shows the thermometer response for a major avalanche.¹ The heater was turned on at 0.03 s, and the subsequent slow rise in temperature from $t \approx 0.03$ s to $t \approx 0.11$ s reflects the gradual heating of the entire sample in response to the power provided by the heater (which remains on). The sharp rise in temperature at $t \approx 0.11$ s signals the sudden release of heat (see Eq. 1.9) associated with the ignition of an avalanche. The temperature at which this occurs is denoted as the ignition temperature. The inset of Figure 4.2 shows the same signal recorded on the second oscilloscope with higher time resolution. The ignition temperature was determined from these data.

The maximum temperature (approximately 1.4 K for this major avalanche) depends on the energy released during the avalanche. In principle, the heat capacity of Mn₁₂-ac could be deduced from a measurement of this peak temperature since the internal energy released (Eq. 1.9) can be precisely determined. However, a number of factors preclude the extraction of such information from the peak temperature recorded during the avalanches reported here. An ideal thermometer has negligible thermal mass (heat capacitance) compared to the sample which is measured. As discussed in Chapter 2, the thermal mass of the thermometer is actually quite large due to the high thermal conductance between the Ge and the GaAs substrate. In addition, the thermal mass of the grease (addenda) is also expected to be large, as one may deduce visually from the picture of the mounting conditions in Figure 2.3. Finally, the thermal conductance between the crystal and the ³He bath is large. A reliable measurement of the maximum temperature reached during an avalanche would require these all these quantities to be minimized and precisely measured. Possible

¹The noise at low temperatures is exaggerated by two factors: self-heating in the thermometer that limits the low temperature resolution; and noise associated with digitizing (continuous) data acquired by the oscilloscopes.

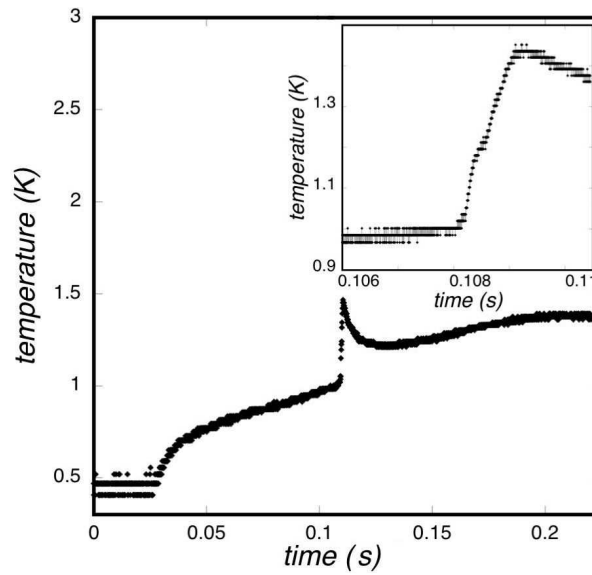


Figure 4.2: Temperature profile for a major avalanche triggered at 0.83 T, with a change of magnetization $\Delta M = 2M_s^{major}$. The temperature rise starting at 0.03 s is due to the heater. The sudden increase in temperature at 0.11 s is due to heat released during an avalanche. The inset shows the temperature profile due to the avalanche with higher time resolution. For this major avalanche, the ignition temperature is ≈ 1 K.

future measurements of this peak temperature will be discussed in Chapter 7.

Measurements were repeated several times at a given field, and were reproducible within a given run. Although, the ignition temperature was reproducible within a given experimental run, it varied by as much as 0.25 K from one run to another. This is most likely due to uncontrolled thermal gradients that were different depending on the thermal connection between the thermometer and the sample. For example, the thickness of the layer of Apiezon M grease was perforce different for different runs. It may also be due to sample geometry (shape and size) which allows the heat generated by the avalanche to leave the crystal more or less easily. Because of the uncontrolled features of the ignition temperature data, we do not explore the quantitative modeling of igniting avalanches, which also must be postponed for future measurements. Nonetheless, we will find the dependence of the ignition temperatures on parameters such as the external field to be consistent with the theory of deflagration.

In separate experimental runs for similar sized $\text{Mn}_{12}\text{-ac}$ crystals, the magnetization dynamics were measured with the Hall sensor array.² Figure 4.3 (a) shows the output of the six Hall sensors for an avalanche triggered at 0.90 T. The speed of the deflagration front was deduced from measurements of the arrival time of the peak at each sensor as shown in Figure 4.3 (b).

Figure 4.4 shows typical major avalanche ignition temperatures and speeds triggered at various external fields. As a reminder, all these avalanches involve complete major species magnetization reversal during, i.e., $\Delta M = 2M_s^{major}$. We postpone the detailed analysis and comparison with the theory of magnetic deflagration until Chapter 6; however, we expect that the avalanche data can largely be understood with the help of the relaxation rate (Eq. 1.4).

Consider first the ignition temperature. After current is passed through the heater, the crystal slowly heats until the temperature approaches the blocking temperature,

²A different crystal with similar dimensions was used in order to avoid potential crystal degradation from thermally cycling.

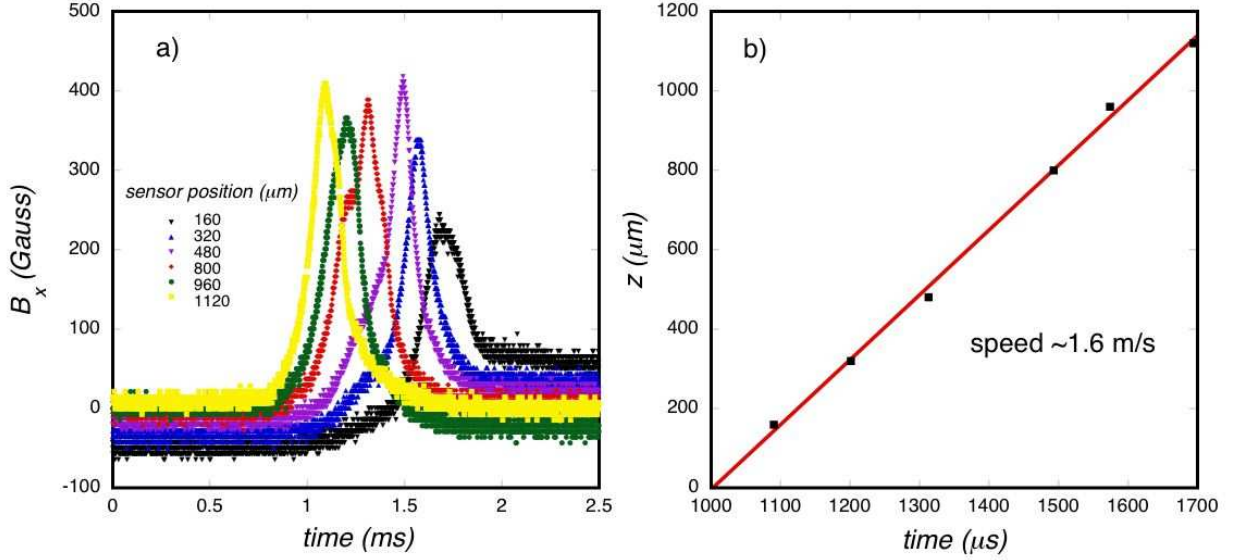


Figure 4.3: (a) The time response of six Hall sensors placed along the length of the crystal, for a major avalanche triggered at 0.90 T with $\Delta M = 2M_s^{major}$. The peak indicates the arrival of the magnetization interface (avalanche front). (b) A plot of the Hall sensor position as a function of the avalanche front arrival time. Applying a linear fit allows the speed to be deduced.

at which point the spins reverse and an avalanche occurs. Increasing the external field lowers the barrier, which in turn lowers the ignition threshold. This decreased ignition threshold is evidenced by lower ignition temperatures at higher fields, as shown in Figure 4.4 (a).

Similar behavior is evident in the avalanche speeds. Once an avalanche is ignited, the speed of the front must be related to the rate at which the metastable spins at the deflagration front *react*, which is also controlled by Eq. 1.4. Again, larger fields lead to a lower barrier. This is reflected as increased speeds at higher fields, as shown in Figure 4.4 (b).

Since it is well known that $\text{Mn}_{12}\text{-ac}$ shows significant enhancement of the relaxation rate at resonant fields, it may not be surprising to see non-monotonic behavior of the ignition temperatures and speeds as a function of field. Indeed, there are a series of minima in the ignition temperatures at 0.45 T, 0.90 T, and 1.35 T, which

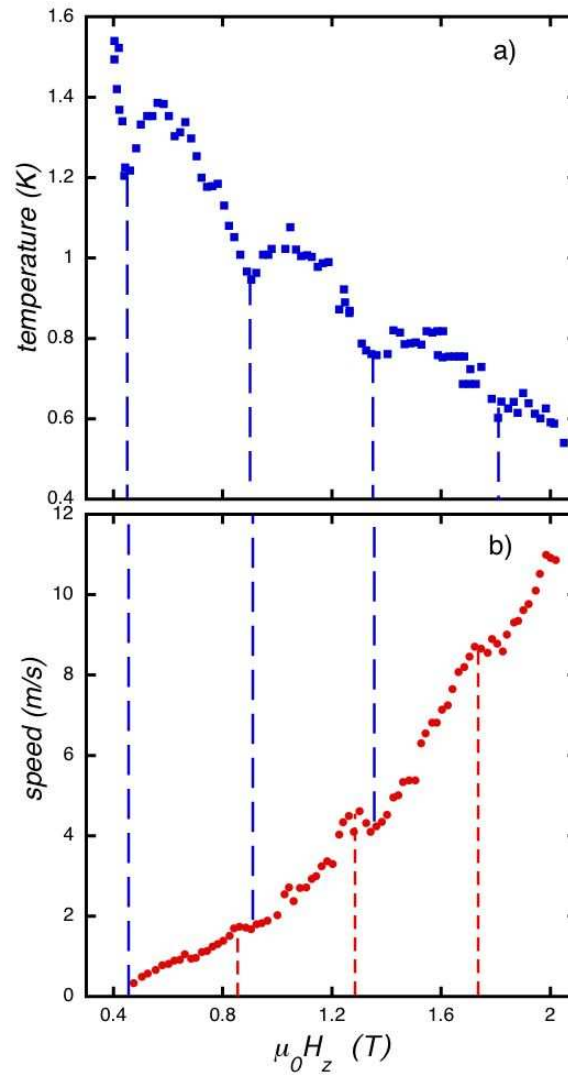


Figure 4.4: (a) Ignition temperatures and (b) speeds for major species avalanches with $\Delta M = 2M_s^{major}$, i.e., full major species magnetization reversal during the avalanche. Vertical dashed lines indicate the location of the relevant energy level crossings. The particular level crossings are illustrated in Fig. 4.5

presumably are due to the reduction of the barrier by tunneling. These fields are indicated in Figure 4.4 (a) with vertical dashed blue lines. Curiously, there is no corresponding enhancement in the avalanche speeds at these fields. There are, however, small maxima in the avalanche speeds at the fields: 0.85 T, 1.28 T, and 1.72 T. This may seem puzzling at first glance. However, it actually presents an additional qualitative confirmation for the theory of magnetic deflagration.

If tunneling enhancement of the relaxation rate is to occur, it must occur at a field where an energy level crossing occurs. Figure 4.5 shows the locations of the energy level crossings for $\text{Mn}_{12}\text{-ac}$ major species. As discussed in section 1.2.1, tunneling at a particular energy level occurs only for a particular range of temperatures. Tunneling at high energy levels requires high temperatures. Therefore, the active energy levels seen for the avalanche speeds and ignition temperatures act as a crude thermometer for each process. As will be discussed in detail in Chapter 6 the temperature of the sample near the front is expected to be at least 4 K, while the ignition temperatures are measured to be approximately 1 K. Figure 4.5 shows the active level crossings for the avalanche ignition and the avalanche front as blue and red circles, respectively.³ In addition, the behavior of the spins must become classical as temperature increases, i.e., the effects of the tunneling must disappear. Therefore, effects of tunneling on the low ignition temperatures is more pronounced than the high temperature avalanche front speeds.

In Chapter 5, the major avalanche speeds will be examined more thoroughly. We now turn our attention to the physics of minor avalanches.

³Five active (red) level crossings are depicted for the avalanche speeds even though Fig. 4.4 (b) only shows three. The data in Chapter 5 provides evidence for the remaining two active level crossings.

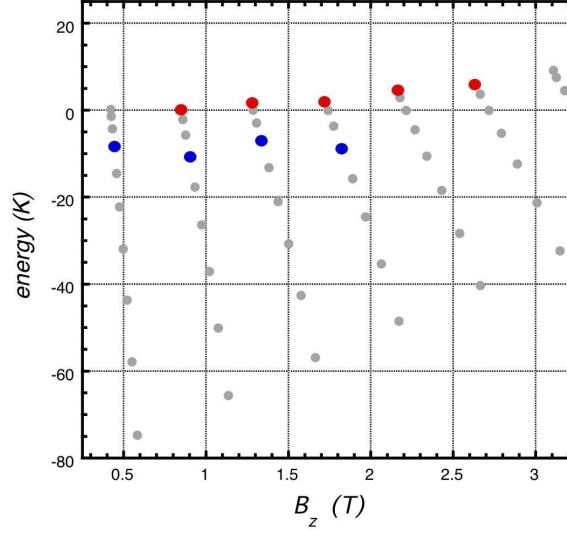


Figure 4.5: Energy level crossings as a function of field, B_z , for $\text{Mn}_{12}\text{-ac}$ major species. The level crossings active in the ignition process are indicated with blue circles. Those active in the avalanche propagation (speed) are indicated with red circles. The higher energy levels involved in the avalanche propagation reflect the higher temperatures involved.

4.3 Minor avalanches

Since the minor species makes up such a small portion of the crystal, the average heat released (Eq. 1.9) by a minor avalanche is only 5% of that of a corresponding major avalanche. It is somewhat surprising then that the minor species can independently sustain an avalanche unaided by the major species. Nevertheless, avalanches consisting of only the minor species do occur. Moreover, the minor avalanche speeds are significantly larger than those of the major avalanches. In this section, we discuss minor avalanches prepared as described in Chapter 3 and section 4.1.

For comparison, the temperature profiles and avalanche speeds are shown with those of the major avalanches taken on the same crystal at the same field. Figure 4.6 shows the thermometer response for a (a) major and (b) minor avalanche recorded on the same crystal; both taken at $\mu_0 H_z = 0.83$ T. Two aspects of the minor avalanche profile immediately stand out: the significantly lower ignition and the lower peak

temperatures. We will say more about the ignition temperatures in a moment. The lower peak temperature is a direct consequence of the reduced heat release.

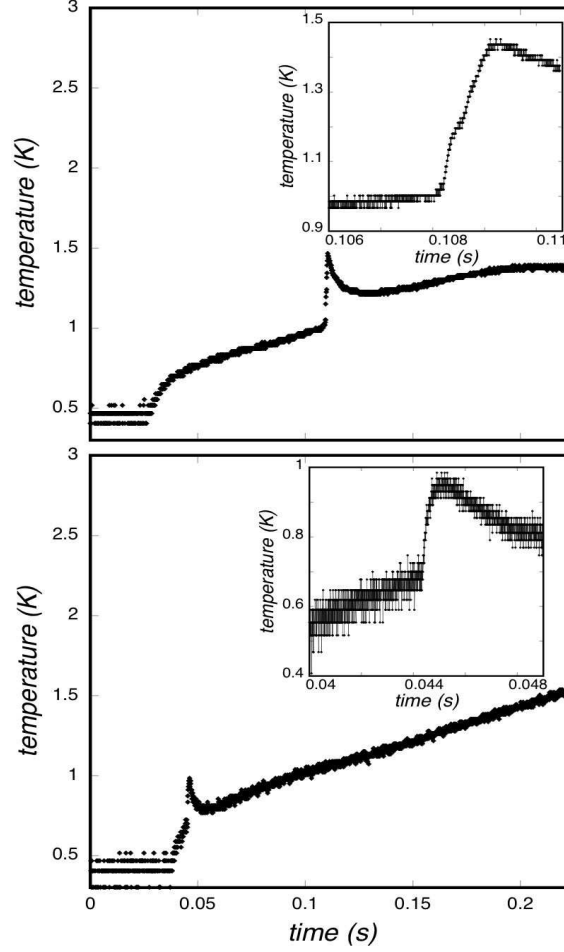


Figure 4.6: Temperature recorded by thermometer in contact with crystal during the triggering of an avalanche. (a) Major avalanche triggered at 0.83 T. The heater is turned on at 0.03 s and the temperature begins to increase slowly. The abrupt rise in temperature at 0.11 s is due to heat released by the avalanche. The inset shows data taken at the ignition temperature with higher resolution for the same avalanche. (b) Minor avalanche triggered at 0.83 T.

Figure 4.7 shows the magnetic signals due to a (a) major and (b) minor avalanche recorded on the same crystal; both taken at $\mu_0 H_z = 0.90$ T. Because of the significantly smaller signal produced by the minor avalanche, signal averaging was applied to remove high frequency noise. The result is shown in the inset. The ratio of the minor peak amplitude to that of the major peak is about 0.04, in reasonable agreement

with the expected ratio of minor species to major species in the sample, ≈ 0.05 .

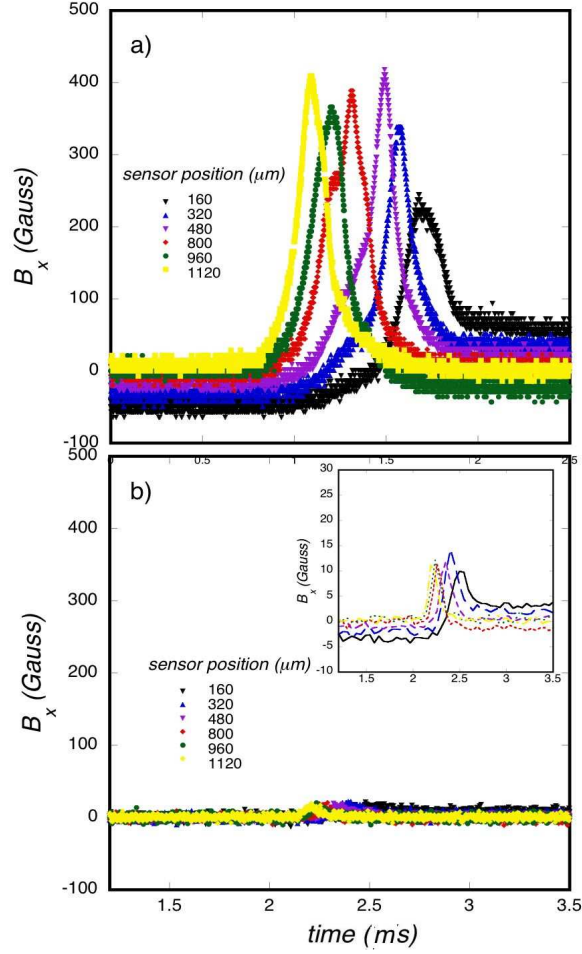


Figure 4.7: Signals recorded by six Hall sensors in contact with the crystal during an avalanche. (a) Major species triggered at 0.9T. The velocity of the avalanche is determined by recording the arrival time of the peak at each of the six sensors. (b) Minor species avalanche triggered at 0.9T. The inset shows the output of each sensor with the high frequency noise averaged out.

A comparison of the speeds and ignition temperatures for the major and minor avalanches is shown in Figure 4.8. Again, we let the respective relaxation rates, given by Eq. 1.4, guide our intuition. At 0.83 T, the barrier U of major species (calculated from Eq. 1.2) is 56 K, compared to $U = 39$ K for the minor species (calculated from Eq. 1.6). The lower barrier of the minor species should result in both lower ignition temperatures as well as increased speeds for the minor avalanches. Both of these

expectations are confirmed by Figure 4.8.

At first glance one may mistakenly attribute the apparent minima in the minor ignition temperatures to quantum tunneling reduction of the barrier, in a similar fashion as the major avalanches; but this is not the case. The minor ignition temperature minima are actually due to the loss of magnetization prior to the ignition of the avalanche. To make this clear, the inset of Figure 4.8 (a) shows a quarter of the minor species hysteresis curve taken with the major species magnetized in the positive direction as discussed in section 3.1. As the field is swept at +5 mT/s across the minor species resonance fields at 0.79 T and 1.20 T, a portion of the metastable magnetization stabilized thus removing *fuel* available for deflagration. The vertical black lines drawn on Fig. 4.8 indicate the center of the minor species resonance fields. For fields below 0.74 T, the entire minor species magnetization reverses during an avalanche, i.e., $\Delta M = 2M_s^{minor}$. However, for those triggered above 0.85 T and less than 1.15 T, only about half the magnetization reverses during the avalanche, i.e., $\Delta M = M_s^{minor}$. Finally, for fields above 1.20 T, all the minor species magnetization has stabilized, precluding the possibility of igniting an avalanche.

The minor avalanche speeds also exhibit behavior that should not be confused with quantum enhancement of the avalanche speed. The apparent peak in the minor avalanche speeds occurs at a *lower* field than the minor species tunneling resonance. As the field is increased nearing the minor species resonance near 0.79 T, a portion of the minor species magnetization stabilizes prior to the ignition of the avalanche. This loss of magnetization is equivalent to the loss of fuel available to burn in chemical deflagration, which leads to slower speeds, as will be demonstrated in Chapter 5.

It is worth noting that a similar quantum enhancement of the avalanche speed may be present in the minor avalanches as for the major avalanches; however, it must be overwhelmed by the (detrimental) effects of the pre-ignition loss of magnetization. In order to observe the quantum enhancement of avalanche speeds in either species

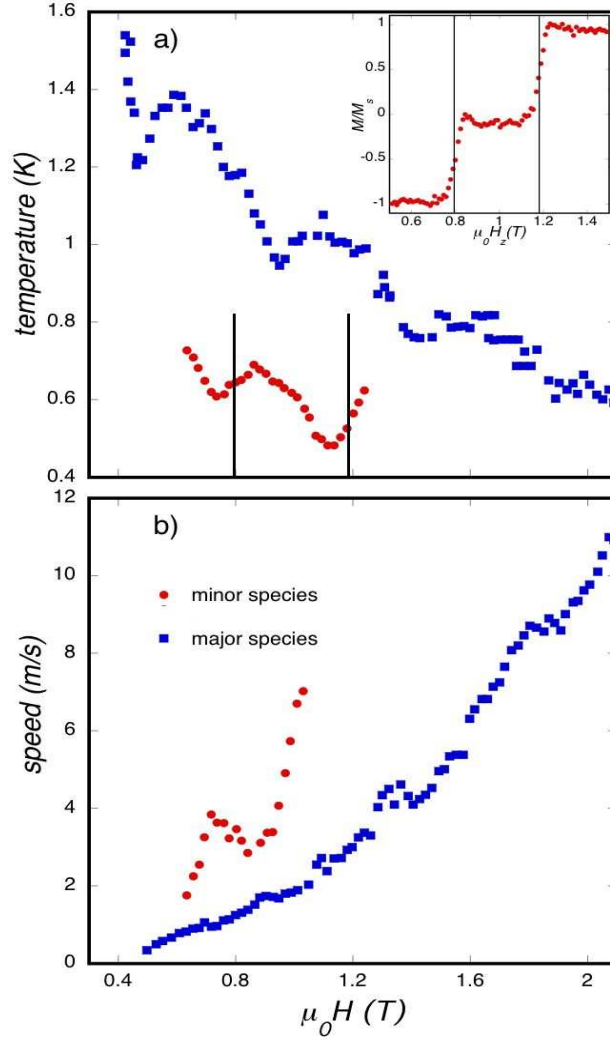


Figure 4.8: Comparison of major and minor avalanche (a) ignition temperatures and (b) front speeds. The inset shows a portion of the hysteresis curve for the minor species. M_s is defined as the full magnetization of the minor species molecules. The vertical lines are drawn at the center of the tunneling resonances for the minor species. The decrease of the speed and increase of the ignition temperature are due to the loss of metastable magnetization prior to the ignition of the avalanche, as explained in the text. The avalanche speeds below 0.75 T involve the full reversal of the minor species magnetization during the avalanche, i.e., $\Delta M = 2M_s^{minor}$. Those above 0.85 T are for avalanches with $\Delta M = M_s^{minor}$.

of avalanche, one must create conditions that eliminate the pre-ignition losses, e.g., lower base temperatures or faster sweep rates for the external field. In Ref. [34], the relaxation of the minor species was studied at various sweep rates at 60 mK. A sweep rate of 680 mT/s leads to a negligible amount of relaxation below 1.2 T. These conditions would be appropriate for minor avalanche studies focusing on the behavior near the resonant fields.

4.4 Combined avalanches

Combined avalanches were triggered with both the major and minor species reversing magnetization during the avalanche (see Fig. 4.1 C). Figure 4.9 shows data for the time-dependence of the temperature and the local magnetization for such an avalanche triggered at 0.90 T. The speeds and ignition temperatures were recorded on the same crystals for which data are shown in Figs. 4.6 and 4.7.

A few aspects stand out immediately in these data. In Figure 4.9 (a), there are two peaks on each Hall sensor rather than one. Consider, for instance, the Hall sensor shown with yellow data points. The first small peak occurs around 1 ms followed by a large peak at 1.5 ms. The first peak due to the relaxation of the minor species, while the major species relaxes later as indicated by the large peak. In Figure 4.9 (b), the peak temperature is approximately the same as the peak temperature due to a major avalanche triggered at the same field (as shown in Fig. 4.2). However, the ignition temperature is much closer to that of a minor avalanche (4.6 (b)). These data suggest that the presence of the metastable minor species acts as a “catalyst” for the major species in close analogy with the behavior of a catalyst in a chemical reaction.

Evidence for interpreting the minor species as a catalyst for the major species is provided by Fig. 4.10, which compares the avalanche data of the major avalanches

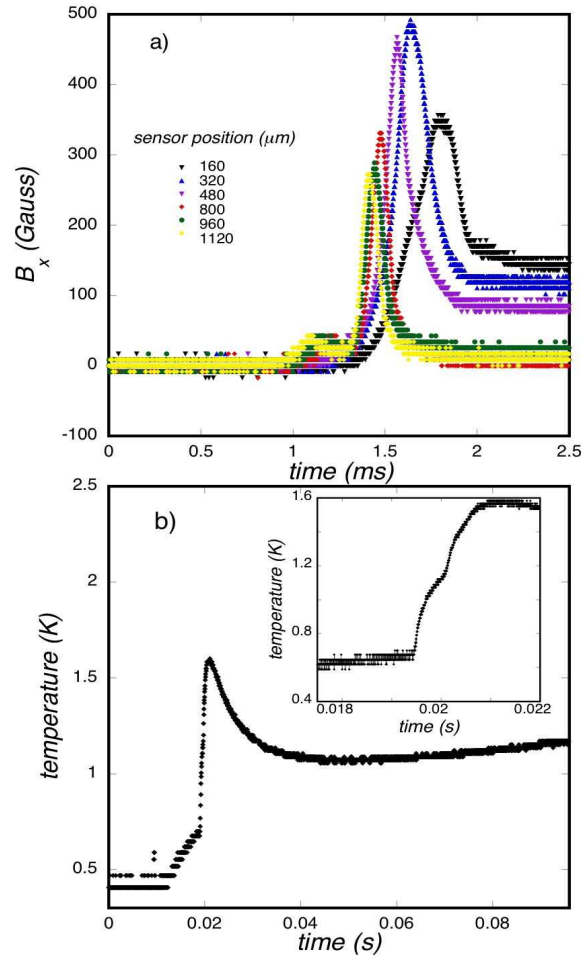


Figure 4.9: Avalanche dynamics for a combined avalanche triggered at 0.90 T. (a) Hall sensor responses and (b) temperature profile. Again, the inset displays the temperature data at ignition with greater resolution.

with those of the combined avalanches.⁴ The presence of the minor species in the combined avalanches significantly lowers the ignition threshold as well as increasing the avalanche speed. In fact, as will be shown shortly (in Fig. 4.12 (b)) the ignition temperature for the combined avalanches is nearly identical to that of the minor avalanches.

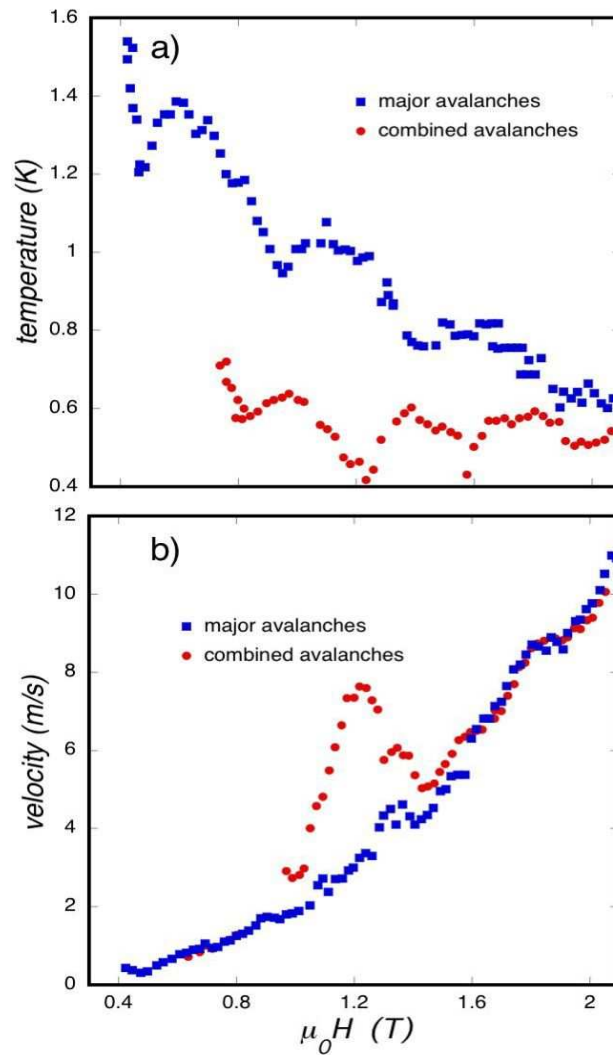


Figure 4.10: A comparison between major and combined avalanches. (a) Ignition temperatures. (b) Avalanche speeds.

Further evidence is provided by Figure 4.11, which shows the separation of the

⁴For this sample, the combined avalanches triggered below 0.95T avalanches ignited too close to the middle of the sample to resolve a speed reliably.

two species as reflected in the temperature profiles. At low fields, the two species do not relax simultaneously during an avalanche. For this crystal, at roughly 0.73 T the minor species relaxes prior to and independently of the major species. The precise field at which this occurs varies from crystal to crystal. Presumably, below this critical field, the heat released by the minor species is insufficient, or diffuses away too quickly to ignite the major species. The speeds and ignition temperatures for the combined avalanches shown in Fig. 4.10 are only for fields higher than those where the separation of the two species occurs.

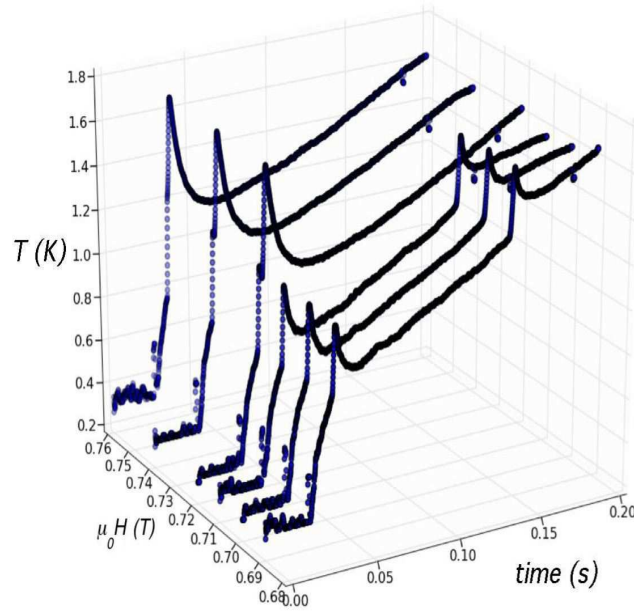


Figure 4.11: Temperature profiles for combined avalanches triggered at low fields. For this crystal, fields below 0.73 T are insufficient for the minor species to ignite an avalanche of the major species.

As said above, the ignition temperature of the combined avalanches are as low as the minor avalanches. In addition, they have a nearly identical dependence on the external field; both show similar minima due to loss of minor species magnetization prior to the ignition of the avalanche. However, a close look at the minor avalanche ignition temperatures in Figure 4.8 (a) and those of the combined avalanches in Figure

4.10 (a) reveals that the minima occur at different fields. In the following section, we make the analogy with a catalyst more complete by accounting for the shifts in the resonant fields between the minor and the combined avalanches.

4.5 Effects of major species dipolar field

The shift in the minor species' resonant fields can be explained by a careful accounting of the dipolar field due to the major species. Figure 4.12 (a) are the minor species magnetization curves discussed in section 3.1. It shows a quarter of the hysteresis curve for the minor species taken for three different magnetizations of the *major* species. The red triangles are data taken with major species completely magnetized in the negative direction. In other words, for fields less than +0.8 T, the major and minor species are parallel and both are aligned opposite to the applied field. The blue triangles are data taken with the major species magnetized in the positive direction, and thus anti-parallel to the minor species. Finally, the green circles are data taken with major species at zero magnetization, i.e., with an equal number of major species spins in the positive and negative directions. All curves were taken for the same conditions as were used when preparing the avalanches. Namely, the temperature was 0.3 K and the external field sweep rate was 5 mT/s. The shift of the minor species resonance field by $\mu_0 M_z^{major} = \pm 51.5$ mT relative to the middle curve is a direct measure of the dipolar field, M_z , due to the major species fully magnetized in one direction and the other. This internal field must be subtracted or added to the external field to obtain the total field, $B_z = \mu_0(H_z + M_z^{major})$.

The shift due to major species magnetization is also reflected in the ignition temperatures and avalanche velocities shown in Figs. 4.12 (b) and (c). Figure 4.12 (b) shows the ignition temperatures for the combined (blue triangles) and minor (red triangles) avalanches. Likewise, Fig. 4.12 (c) is a comparison between the avalanche speeds. In both (b) and (c), the minima and maxima due to the loss of minor species

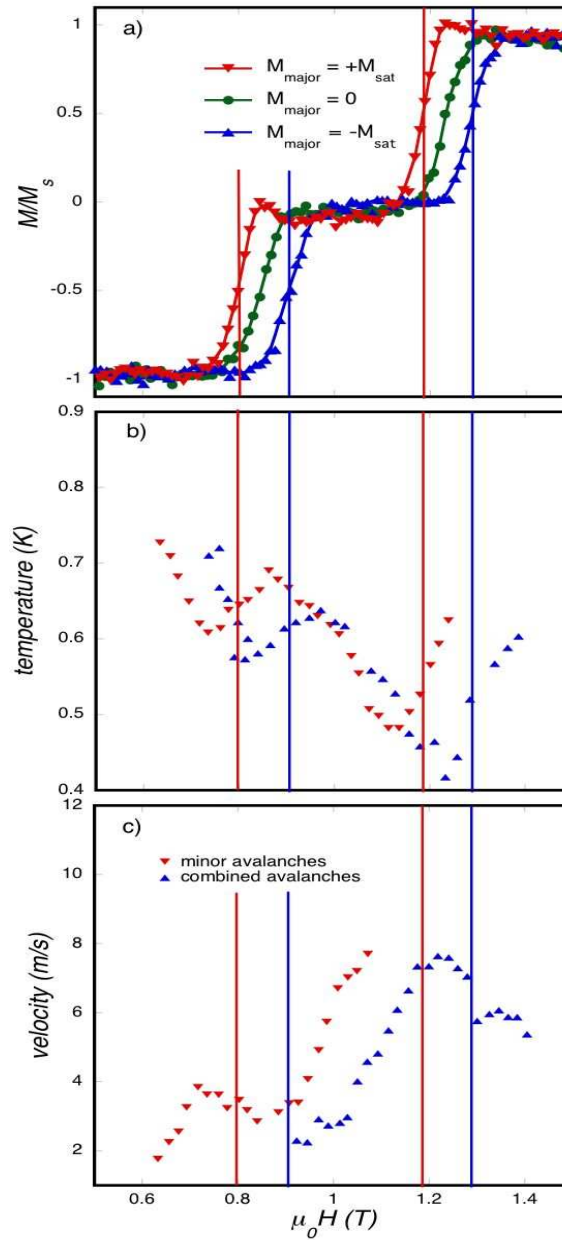


Figure 4.12: (a) A portion of the hysteresis curve is shown for minor species, with the major species prepared in three different magnetizations: $\pm M_{\text{sat}}$ and 0. M_s is defined as the magnetization due to the minor species when completely aligned. The shift of the resonance fields by ≈ 0.05 T from the zero field case is due to the dipole field of the major species. The structure of the (b) ignition temperatures and (c) speeds of the minor and combined avalanches also reflects this minor species resonance field shift.

magnetization appear, but are displaced by ≈ 100 mT from one another. Prior to the ignition of minor avalanches, the major species is anti-parallel contributing an additional $\mu_0 M_z^{major} \approx 50$ mT to the effective magnetic field applied to the minor species. The minor species resonant behavior shifts -50 mT from the applied field accordingly. Prior to the ignition of combined avalanches, the major and minor species are parallel. As a catalyst, the characteristics of the minor species controls the behavior of the combined avalanches, therefore, the effective field on the minor species is shifted $+50$ mT. Again, both circumstances are consistent with shift of the minor species resonances shown in Figure 4.12 (a) and discussed in section 3.1.

In following chapter, we focus on major avalanches and study the magnetization dynamics in detail. We will return to minor and combined avalanches briefly in Chapter 6.

Chapter 5

Tuning deflagration conditions

There are two parameters under experimental control when performing magnetic avalanche studies on $\text{Mn}_{12}\text{-ac}$: the external magnetic field and the initial magnetization, i.e., the metastable spin density (the available “fuel”). Varying the external magnetic field affects both the barrier against spin reversal as well as the temperature produced by the reversing spins, T_f . The variation of the metastable spin density affects primarily the energy released, $\langle E \rangle$, and therefore, T_f . By varying these parameters independently, we are able to explore the wide ranging conditions in which avalanches may be triggered. In particular, we explore three classes of avalanche preparations.

Fixed M_z (class I) This class contains those avalanches triggered at various external fields, but with fixed initial magnetizations. For these avalanches, both U and T_f vary.

Fixed H_z (class II) This second class contains avalanches triggered at a fixed external field, but with various initial magnetizations. Avalanches of this class differ primarily through T_f , with U varying only through the (presumably) small effects of the internal fields.¹

Fixed $\langle E \rangle$ (class III) The final class contains avalanches triggered with various initial magnetizations and external fields, such that the average energy released, $\langle E \rangle$, is fixed while U varies. These avalanches are particularly interesting since fixing $\langle E \rangle$ leads to essentially the same T_f for all.²

In this chapter, we present data on the magnetic dynamics for these three classes of avalanche preparations.

In the previous chapters, no mention was made of the spatial widths of the peaks recorded on the Hall sensors for an avalanche. The reason for this exclusion was

¹We will argue in Chapter 6 that although H_z is fixed for these avalanches, U is not. Therefore, the internal inhomogeneous fields produced by the avalanche front itself have a significant effect on U .

²Neglecting the small field dependence of the heat capacity, as discussed in Chapter 6.

practical. The precision with which the magnetic interface widths can be determined is limited by the number of sensors available and the spacing between them. In this chapter, we improve the precision of the width measurement by measuring an avalanche three times at each field for a particular crystal.

Another aspect that went unexplored in previous works is the dependence of the avalanche dynamics on the crystal dimensions. In general, one expects the heat to escape the crystal faster as the cross section decreases. This leads to lower temperatures and therefore, lower deflagration front speeds. Eventually, for small enough crystals, deflagration must become impossible. In this chapter, we explore avalanches in crystals with various dimensions to determine if avalanches have the expected dependence on the cross section.

In Chapter 6, the wide variety of avalanche conditions reported here will allow us to make a thorough comparison with the theory of deflagration.

Finally, only major avalanches will be discussed in this chapter. Therefore, we will drop the superscript designating the species of the magnetization and use only “ M_z ”.

5.1 Setup and magnetic preparation

In this chapter, we present avalanche data taken on four different crystals with dimensions $1.20 \times 0.10 \times 0.10 \text{ mm}^3$, $0.80 \times 0.15 \times 0.15 \text{ mm}^3$, $1.00 \times 0.20 \times 0.20 \text{ mm}^3$, and $1.00 \times 0.25 \times 0.25 \text{ mm}^3$, labeled as crystal A, B, C, and D, respectively. Detailed data is reported on crystal C. Although the absolute values of the avalanche speeds differed for different crystals (discussed in detail below), similar behavior was obtained for all crystals as a function of the experimental parameters, H_z and M_z .

Prior to triggering an avalanche, the sample must be prepared in a metastable magnetic state. The initial magnetization, M_z , was controlled by cooling the sample from $\approx 6 \text{ K}$ to below the blocking temperature in the presence of a small external

cooling field, as described in the section 2.4. With the sample well below the blocking temperature, the external field may be changed without changing the magnetization.

The field is increased to a large predetermined field $\geq +1.25$ T in order to avoid any complications involving the minor species. Once the field has stabilized (~ 1 min), a current is passed through the wire heater raising the temperature and triggering the avalanche. Avalanches were triggered at positive and negative fields; however, the data shown below is plotted with respect to $\mu_0 H$, where it should be understood as $|\mu_0 H|$. In Chapter 4, the field was swept at a constant rate (± 5 mT/s) while triggering an avalanche. This was required in order to accurately determine the loss of minor species magnetization prior to the ignition of the avalanche. In this chapter, we are only concerned with the major species. For fields below ~ 3.0 T at 0.3 K, a negligible amount of major species magnetization relaxes. Therefore, we can fix the field prior to ignition, which reduces the error in determining the applied field to approximately ± 0.5 mT.

In the previous chapter, we introduced the parameter $\Delta M = |M_z - M_s|$, where M_z is the initial magnetization and M_s is the magnetization with all spins aligned in the positive direction, to account for the metastable magnetization that reverses during an avalanche. The determination of M_z is shown in Figure 2.5. Determining ΔM from this field cooling data is fine in principle; however, it requires a precise accounting of the magnetization of both the major and minor species. Instead, we introduce a method of determining ΔM that is independent of the minor species magnetization.³ We measure ΔM directly as the change in magnetization during the avalanche. Since cooling the sample in zero field yields an un-magnetized sample, we use the change of magnetization during a zero-field-cooled (zfc) avalanche to define M_s as $M_s \equiv \Delta M_{zfc}$. Figure 5.1 shows an example of a zero-field-cooled avalanche. For convenience, we also introduce the parameter $\Delta M/2M_s$ as the dimensionless initial

³This assumes the avalanches are triggered above 1.2 T, which is appropriate for all reported in this chapter.

metastable magnetization density. As an example, cooling the sample in zero field leads to $M_z = 0$, or $\Delta M/2M_s = 0.5$.

We prepare the three classes of avalanches by varying the initial magnetization, M_z , and the external magnetic field H_z . Variation of H_z , tunes the barrier, U , as well as the average energy released per molecule during an avalanche,

$$\langle E \rangle = 2g\mu_B S B_z \left(\frac{\Delta M}{2M_s} \right), \quad (5.1)$$

where $B_z = \mu_0(H_z + M_z)$. Avalanches of class I are those with initial magnetization $M_z = -M_s$, i.e., $\Delta M/2M_{sat} = 1$, and variable H_z . Class II avalanches are triggered at a fixed external field, with various initial magnetizations. Finally, class III avalanches are triggered at various H_z and M_z , such that $\langle E \rangle$ remains constant.

5.1.1 Magnetization interface width

Figure 5.1 shows the time response of five equally spaced Hall sensors due to the occurrence of a zero-field-cooled avalanche. At time $t = 0$ ms, the magnetization is zero, as it must be for a zero-field-cooled sample. At $t \approx 0.32$ ms, the magnetization begins to reverse near the first sensor as the avalanche front approaches. At $t = 0.41$ ms, the signal on the first sensor is maximum indicating that the avalanche arrival at position $0 \mu\text{m}$. By $t = 0.65$ ms all spins have reversed and the sample is completely magnetized. The avalanche speed is deduced by plotting the arrival time of the peak at all the subsequent sensors.

One can infer the spatial profile of the avalanche interface by plotting $B_x(z)$ at a particular time with respect to the Hall sensor position. For instance, Figure 5.1 (b) shows $B_x(z)$ at time $t = 0.41$ ms. We define the apparent magnetic interface width as twice the half-width measured when the avalanche is centered at the first Hall sensor. For the avalanche presented in Figure 5.1, the apparent full width at half maximum (FWHM) of B_x is $210 \mu\text{m}$. The precision with which this width can be determined at a particular instant of time is limited by the number and size of the Hall sensors

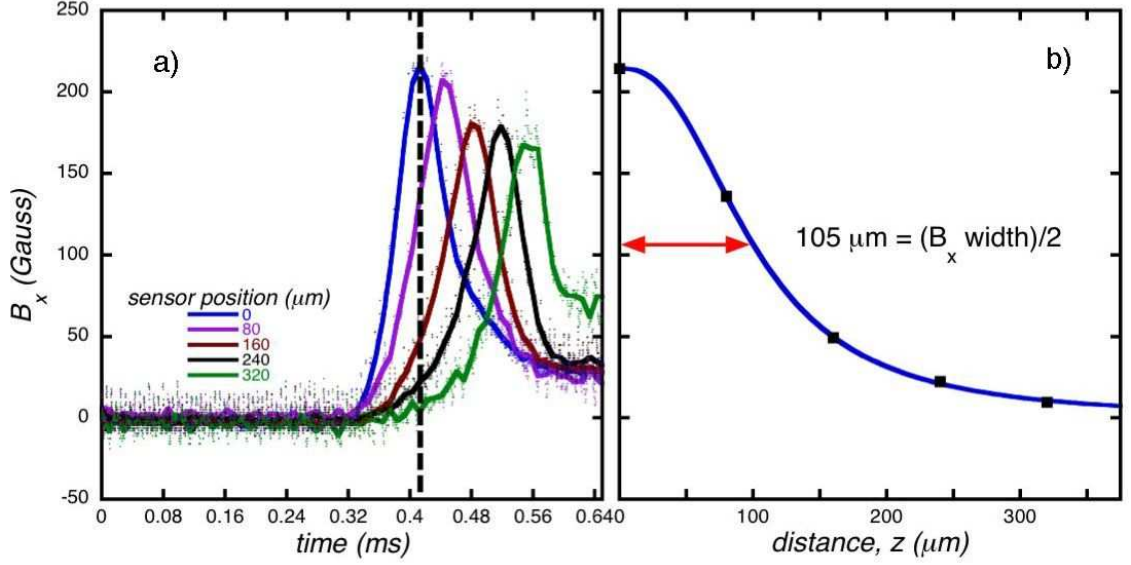


Figure 5.1: The time response of five equally spaced Hall sensors placed along the length of the crystal. The peak indicates the arrival of the magnetization interface (avalanche front). The inset shows the magnetic profile in space, $B_x(z)$ at time $t = 0.41$ ms.

used to measure the avalanche. This imprecision is reflected with the large error bars on the data, described in the following sections.

The apparent magnetic width of B_x as measured by the Hall sensors is *not* the actual width of the magnetization interface. The width of B_x is broadened by the cross section and geometry of a particular crystal. If one makes the assumption that the magnetization varies only in the direction of propagation (along the c -axis), then the transverse component of the induced field measured by the Hall sensors can be calculated numerically [42]. Under these circumstances, B_x recorded by the Hall sensors is proportional to the spatial gradient of the magnetization, i.e., $B_x \propto \partial M_z / \partial z$. The details of this calculation for the Hall sensor and crystal geometries used here are reported in Appendix 8.

In order to calculate the width of B_x , we must first assume a functional form for the magnetization interface, $\partial M_z / \partial z$. Fig. 5.2 (a) is an example of a calculated B_x assuming $\partial M_z / \partial z$ is a Gaussian [5]. Fig. 5.2 (b) shows the (nearly) linear relationship

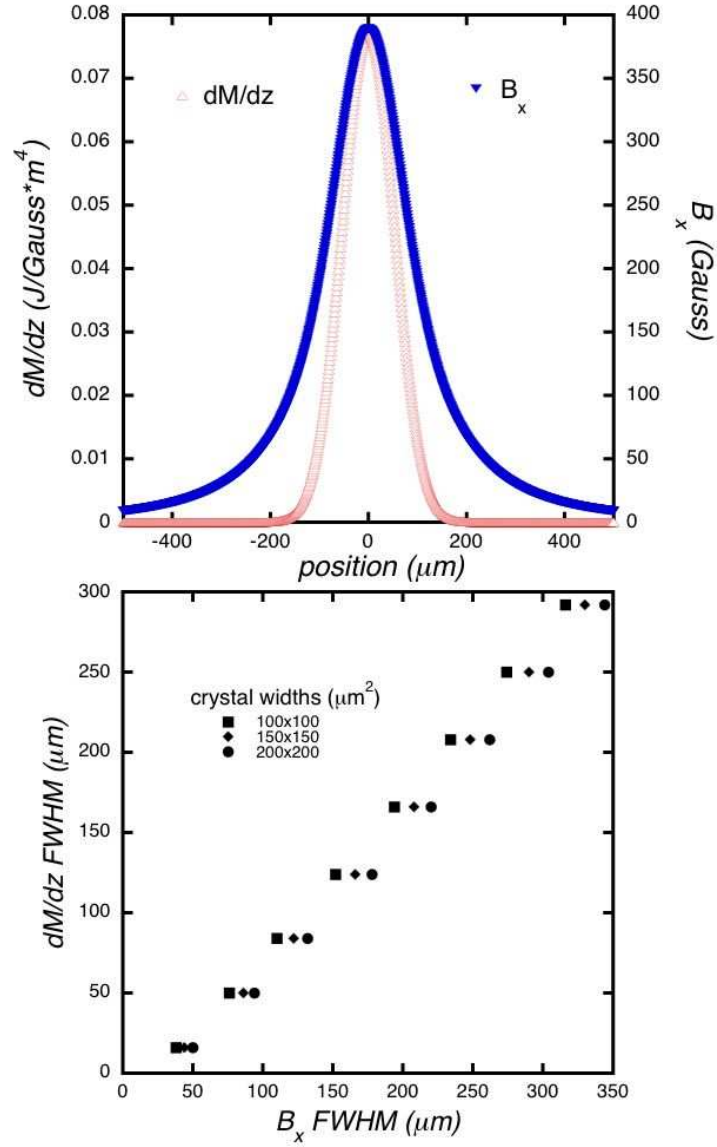


Figure 5.2: (a) The calculated transverse field $B_x(z)$ due to a particular magnetization interface, $\partial M_z(z)/\partial z$. (b) The linear relationship between the calculated width of B_x and actual magnetization interface width.

between B_x and $\partial M_z / \partial z$ calculated for three different crystal cross sections. Since the precise relationship depends on the assumptions for the magnetization interface, all widths shown below are the apparent widths of B_x as recorded on the Hall sensors.

Since $B_x \propto \partial M_z / \partial z$, a measurement of the amplitude of B_x during an avalanche can provide additional information about the magnetization interface width. For instance, if the change in magnetization, ∂M_z , is fixed, then the amplitude of B_x is inversely proportional to the interface width. We define the “ B_x^{max} ” as the maximum value of B_x recorded by a Hall sensor near the center of the crystal during an avalanche. For the avalanche depicted in Figure 5.1, the B_x^{max} is measured using the sensor at $z = 0$, with a value of $B_x^{max} = 215$ G.

Each data point in Figs. 5.3, 5.5, and 5.8 represents the average of three avalanche measurements taken on crystal A. The error bar drawn on each data point of these figures represents the calculated standard deviation of the three measurements.

5.2 Fixed M_z avalanches (class I)

The data reported for the major avalanches in Chapter 4 were all class I avalanches, for which $\Delta M / 2M_{sat} = 1$. We start here with more precise measurements of the same sort. As a reminder, the precision is improved here by fixing the field and waiting for it to stabilize prior to the ignition of the avalanche. It is also improved by repeating the measurement three times at each field.

Fig. 5.3 shows the results for class I avalanches triggered at various fields, all with the same initial metastable magnetization, $\Delta M / 2M_{sat} = 1$. Fig. 5.3 (a) shows the avalanche speeds calculated from the peak arrival times at the Hall sensors. The apparent magnetic widths are shown in Fig. 5.3 (b).

The speeds of the avalanches increase as the field is increased. This is expected since an increasing field both lowers the barrier and increases $\langle E \rangle$. There are maxima at fields corresponding to the tunneling resonances, which are denoted with vertical

dotted lines. The tunneling resonances occur at energy level crossings near the top of the barrier, as depicted in Figure 4.5. This tunneling enhancement of the avalanche speed is consistent with those reported for major avalanches in Chapter 4.⁴

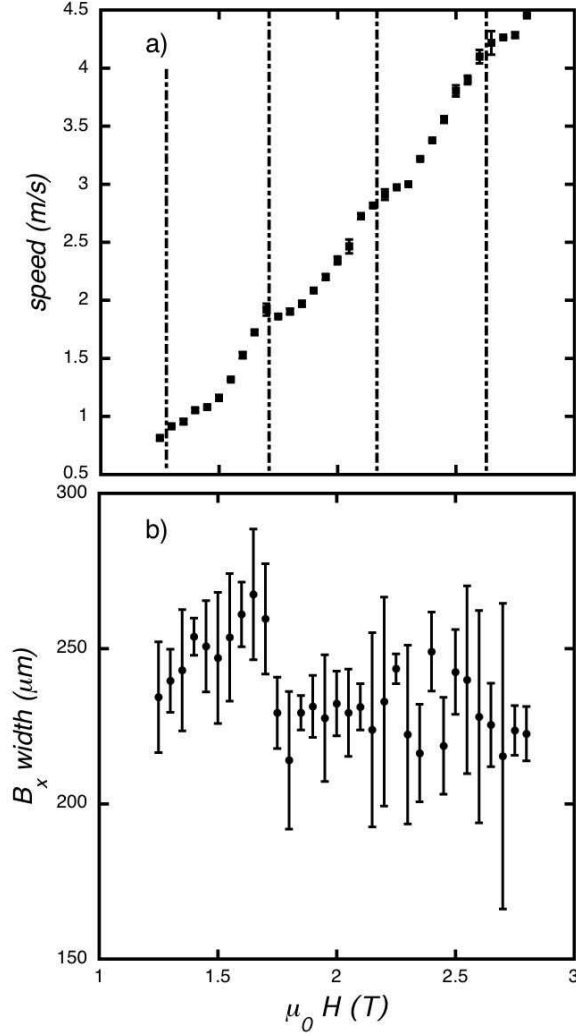


Figure 5.3: (a) Class I avalanche speeds and (b) B_x widths for crystal C with dimensions $1.0 \times 0.2 \times 0.2 \text{ mm}^3$. $\Delta M/2M_{sat} = 1$ for all.

It is interesting to compare the maximum speeds for this crystal C with those of Figure 4.4 (b). For instance, at 2.0 T, the speed of the avalanche for crystal C is reduced by a factor of five. The next section shows data for all four crystals A-D with

⁴Incidentally, it is also an indication that the flame temperatures are low enough to preserve the effective Hamiltonian, Eq. 1.2 and the rigid spin ($S = 10$) approximation.

similar variations in the maximum speed. Possible explanations for this variation will be given in Chapter 6. One interesting feature that each crystal has in common is the fact that the enhancement of the avalanche speed is approximately the same. A rough estimate from Figure 5.3 (a) gives approximately a 15% enhancement of the speed at the 1.72 T resonance. Examining Figure 4.4 (b) at the same resonance gives approximately 12%. We therefore expect that the flame temperatures are approximately the same, in spite of the fact that the speeds are so different. Further evidence supporting this conclusion will be given in Chapter 6.

The apparent magnetic interface widths are shown in 5.3 (b). No obvious dependence on the external field is evident. Aside from an apparent dip around 1.7 T, the magnetic width is nearly constant with an approximate value, 225 μm .

5.3 Fixed H_z avalanches (class II)

For the class I avalanches of the previous section, changing the field affects both the flame temperature as well as the barrier. This makes fitting the theory of deflagration to the data somewhat complicated. The motivation for studying class II avalanches is clear; triggering avalanches at a fixed field yields, approximately, a fixed barrier with only the available fuel, ΔM , varying. Although it will be shown in Chapter 6 that the barrier apparently does *not* remained fixed, the class II avalanches are interesting nonetheless, and offer insight into the effects of the internal fields produced by the avalanche front itself.

Figure 5.4 is the normalized change of magnetization during an avalanche, $\Delta M/2M_s$, as a function of the cooling field for crystal D. Like the results shown in Figure 2.5, the magnetization follows a Curie-Weiss law. This provides confirmation that the magnetization does not relax prior to the ignition of an avalanche. Similar results were obtained for all crystals.

Fig. 5.5 (a) and (b) show the speeds and apparent magnetic widths, respectively,

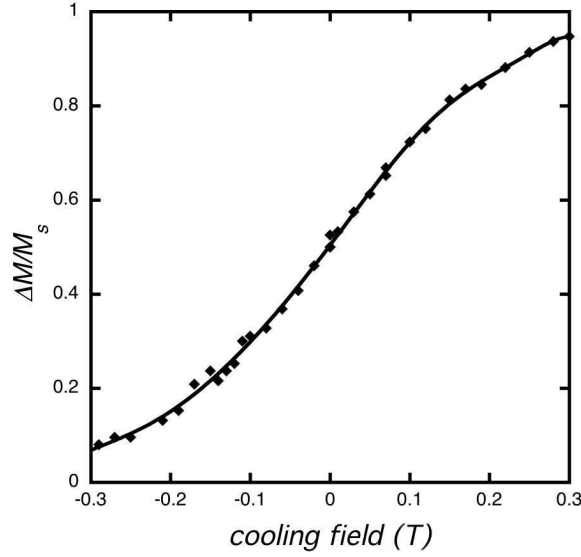


Figure 5.4: The normalized change of magnetization, $\Delta M/2M_s$, as a function of cooling field for crystal D. M_s is defined with the zero-field-cooled avalanche, $M_s \equiv \Delta M_{zfc}$.

for class II avalanches triggered at fixed values of the external field. In particular, data are shown for $\mu_0 H_z = 2.50$ T and $\mu_0 H_z = 2.20$ T. As $\Delta M/2M_s$ decreases, so does the speed. By keeping the field fixed and varying the initial magnetization, only $\langle E \rangle$ varies while U remains approximately fixed. Presumably, the avalanches with larger $\Delta M/2M_s$ have a higher flame temperatures and therefore, higher speeds.

The apparent magnetic interface widths are shown in 5.5 (b). Again, no obvious dependence on the external field is evident. The magnetic width is nearly constant with an approximate value, $225 \mu\text{m}$.

Figure 5.7 shows the values of B_x^{max} for crystal D, as a function of $\Delta M/2M_s$. B_{zfc} is defined as the maximum value of B_x recorded during a zero-field-cooled avalanche. Again, since precisely half the magnetization reverses during such an avalanche, it is sensible to normalize B_x^{max} with twice this value. Evidently, the amplitude is proportional to the change of magnetization, i.e., $B_x^{max} \propto \Delta M$. This gives further support to the fact that the magnetization interface widths are essentially constant.

In order to determine if there is any correlation between the crystal dimensions

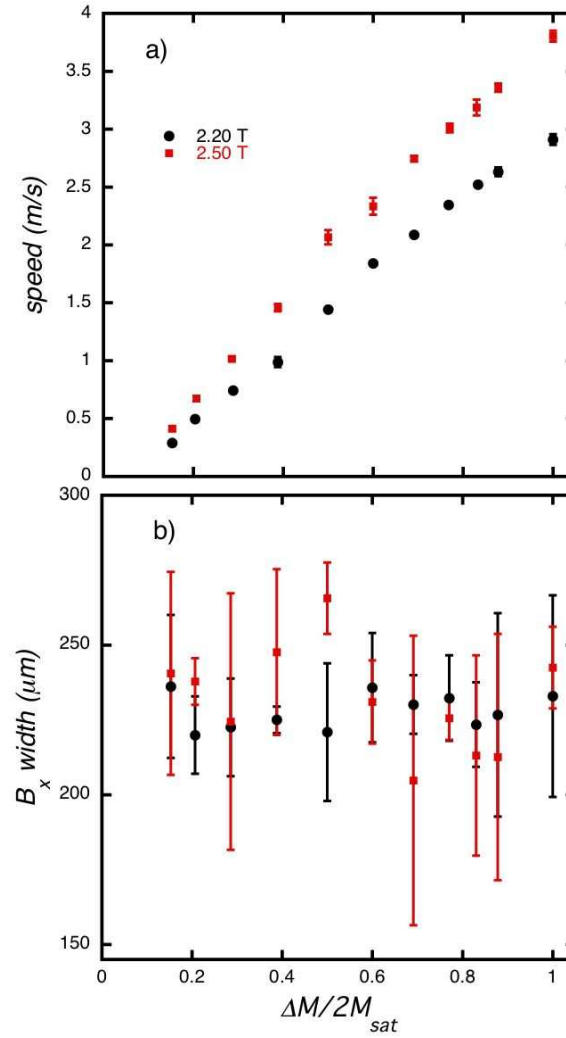


Figure 5.5: (a) Class II avalanche speeds and (b) B_x widths for crystal C with dimensions $1.0 \times 0.2 \times 0.2 \text{ mm}^3$. The field was fixed at 2.50 T and 2.20 T, while $\Delta M/2M_{sat}$ was varied between about 0.10 and 1.00.

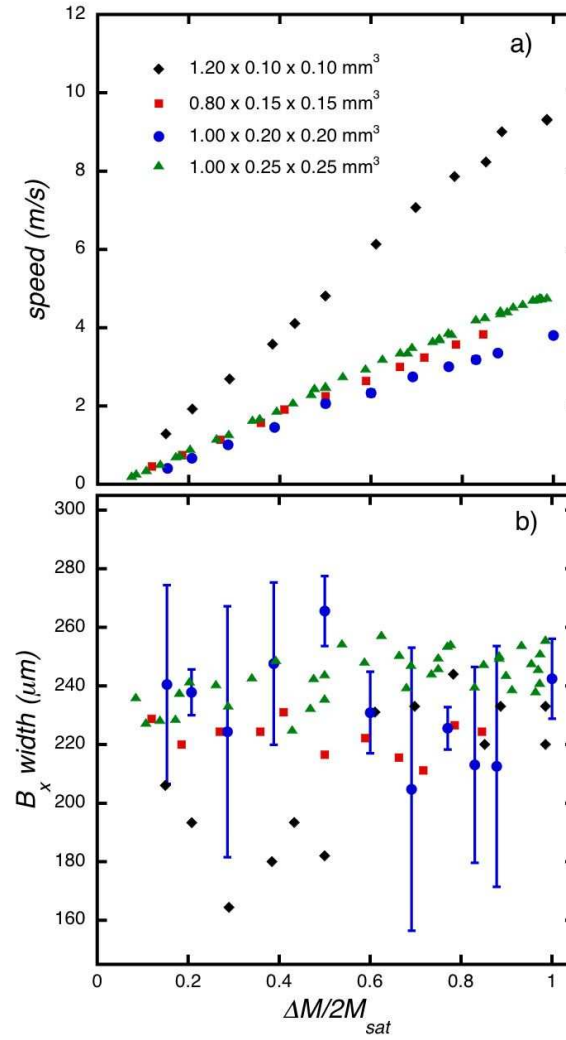


Figure 5.6: Data for class II avalanches triggered in four different crystals at $H_z = 2.5$ T for various initial magnetizations. (a) Avalanche speeds and (b) B_x widths.

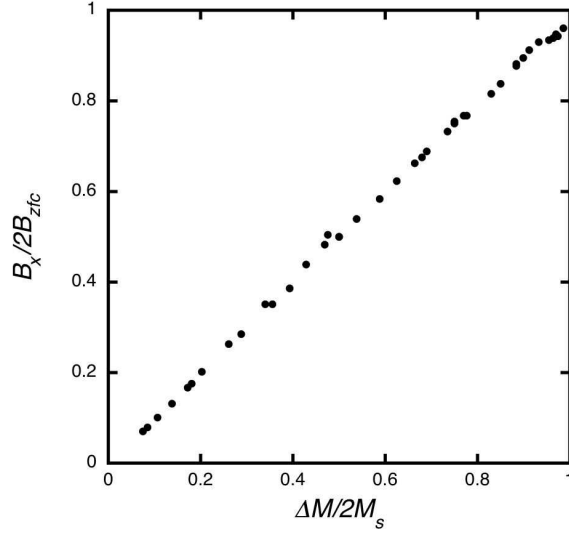


Figure 5.7: The normalized maximum B_x as a function of $\Delta M / 2M_s$ for crystal D. Here, B_x is the maximum transverse field recorded by the Hall sensor during an avalanche. The zero-field-cooled avalanche, B_{zfc} is used to normalize.

and the avalanche speed, we studied crystals with a wide range of cross sections. Fig. 5.6 compares the class II avalanche speeds and magnetic widths for all four crystals. We expect that the crystals with smaller cross sections should have lower speeds due to heat loss through the crystal surfaces. The speed of the avalanche does vary considerably from sample to sample; however, any dependence on the sample dimensions is not immediately obvious. This suggests that the heat loss through the surfaces of the crystal do not strongly influence the dynamics of the avalanche.

Figure 5.6 (b) shows the magnetic widths for all four crystals. There is a small increase in the width as the cross section of the crystal increases. Crystal A has the smallest cross section, 10^{-2} mm^2 , and a magnetic width of $\approx 200 \text{ } \mu\text{m}$. Crystal D has the largest cross section, $6.25 \times 10^{-2} \text{ mm}^2$, and a magnetic width of $\approx 240 \text{ } \mu\text{m}$. All crystals show a similar lack of dependence on the external field or initial magnetization.

5.4 Fixed $\langle E \rangle$ avalanches (class III)

Although they are tedious measurements to actually perform, class III avalanches are the easiest to fit with the theory of deflagration. By keeping the average energy released fixed, the flame temperature must also be approximately fixed. This assumes that the differences in the spin contribution to the heat capacity is negligible in the range of fields and temperatures reported here. Numerical calculation of the flame temperature in Chap. 6 support this approximation.

Fig. 5.8 (a) and (b) show the speeds and magnetic widths for class III avalanches triggered at various external fields. The initial magnetizations were also varied such that $\langle E \rangle$ remained approximately constant. Presumably, the temperature is also nearly constant for all avalanches so prepared. Therefore, the variation in avalanche speeds must be due to variation in the field-dependent barrier U . Again, the vertical dotted line drawn on Fig. 5.8 denotes the location of the resonant fields for $\text{Mn}_{12}\text{-ac}$ major species (red levels in Fig. 4.5).

Finally, for all avalanches reported here, the apparent magnetic widths show no obvious dependence on the external field, initial magnetization, or crystal cross section. All magnetic widths fluctuate from roughly 200 to 250 μm .

In the following chapter, we will apply the theory of magnetic deflagration to these avalanches. Since there are important physical parameters that have not been measured for $\text{Mn}_{12}\text{-ac}$, the variety of conditions in which avalanches have been triggered will be essential for conducting a sensible fit.

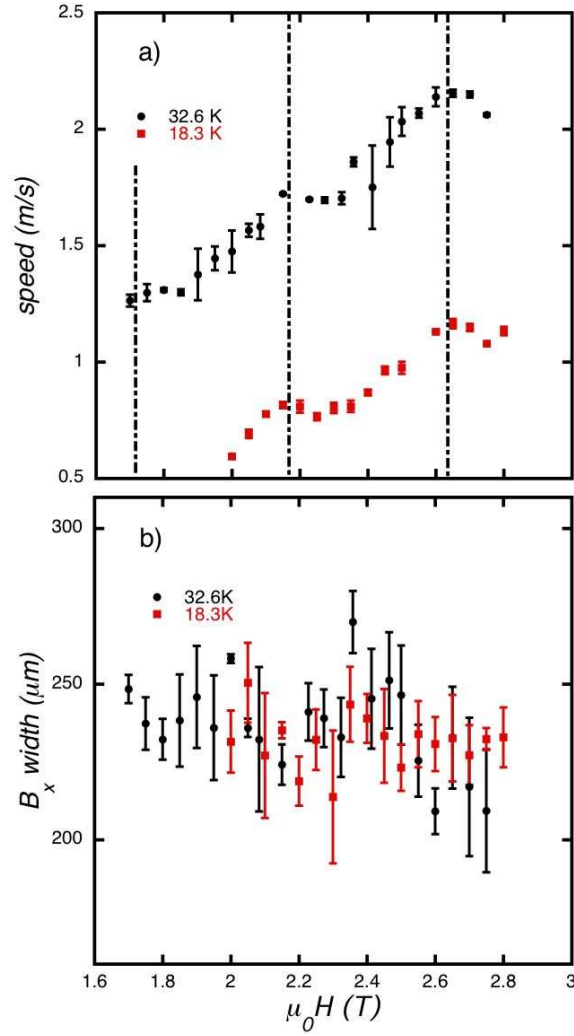


Figure 5.8: Data for $\langle E \rangle = 32.6\text{ K}$ and 18.3 K class III avalanches. (a) Avalanche speeds and (b) B_x widths for crystal C with dimensions $1.0 \times 0.2 \times 0.2\text{ mm}^3$. The vertical lines in (a) indicate the fields at which quantum tunneling occurs for the major species of $\text{Mn}_{12}\text{-ac}$.

Chapter 6

Comparison with theory of magnetic deflagration

The wide variety of avalanche conditions reported in Chapter 5 allows us to make a thorough comparison with the theory of magnetic deflagration; however, we cannot claim precise confirmation without a more complete characterization of the physical properties of crystals of $\text{Mn}_{12}\text{-ac}$. Instead, by applying the theory to our data, we deduce values for two key quantities involved in the deflagration process: the flame temperature, T_f , and thermal diffusivity, κ . The validity of the theory must then be judged by the physical likelihood of these deduced quantities and, eventually, a direct measurement.

We deduce flame temperatures between 5 and 11 K, depending on the conditions in which the avalanche is triggered. Assuming the thermal diffusivity is temperature independent, we deduce values that vary significantly from crystal to crystal; ranging from approximately $\kappa = 10^{-5}$ to 10^{-4} m^2/s . This is consistent with the value of 10^{-5} m^2/s deduced from avalanche speeds in a similar fashion by Hernández-Mínguez et al. [14].

In addition, we argue that the internal, inhomogeneous field produced by the avalanche front has a significant effect on the speed of the front itself. We model this effect with a reduced effective barrier, U^* , that depends on the size of the transverse field, B_x^{max} (see section 5.3). As will be discussed below, the reduction of the barrier defies a simple classical analysis and may be a signal that quantum effects are important in the deflagration process for all values of H_z , not just those associated with the tunneling resonances.

As discussed in Chapter 1, the theory of magnetic deflagration is encapsulated in the two equations, which we repeat here for convenience

$$C \frac{\partial T}{\partial t} - \nabla \cdot k \nabla T = -\langle E \rangle \frac{\partial n}{\partial t} \quad (6.1)$$

$$\frac{\partial n}{\partial t} = -\Gamma n. \quad (6.2)$$

In Eq. 6.1, C is the heat capacity, k is the thermal conductivity, and $\langle E \rangle$ is the average

energy released per molecule. Since we've chosen all energies to be measured in units of J/k_B (or K), C is dimensionless and k has dimensions m²/s. In Eq. 6.2, n is the dimensionless metastable spin density, $\frac{\partial n}{\partial t}$ is its time derivative, and Γ is the Arrhenius relaxation rate (Eq. 1.4). From Eqs. 6.1 and 6.2 one can derive all quantities relevant to deflagration measurements, including the speeds of the fronts. However, they are in general very difficult (or impossible) to solve analytically. We must therefore turn to numerical solutions with conditions appropriate for the experiment or derive approximate analytical solutions. In section 6.1, we will explore the analytical results for the avalanche speeds. In section 6.2, we will explore a few aspects of the numerical solutions in support of the analytical results.

6.1 Analytical results

For all experimental data reported here the speed of the avalanche along the length of the crystal was constant. We also treat the avalanche as a planar front appropriately described as one dimensional motion. In this case, a simple expression can be used for the speed of the front [6]

$$v = \sqrt{\frac{3\kappa T_f \Gamma(B, T_f)}{U(B)}} \quad (6.3)$$

where T_f is the temperature at the front (flame temperature). κ is the thermal diffusivity, which relates the thermal conductivity and the heat capacity, $k = \kappa C$ and has dimensions m²/s. $U(B)$ is the field-dependent barrier with units K.

The importance of the dipolar fields in Mn₁₂-ac was demonstrated in Chapters 3 and 4, where it was shown to contribute as much as $\mu_0 M_z = \pm 52$ mT to the applied external field, H_z . We account for the initial magnetization, M_z , when calculating the various field dependent quantities using $B_z = \mu_0(H_z + M_z)$, where $-52 \text{ mT} \leq M_z \leq 52 \text{ mT}$ (see Figs. 2.5 and 5.4).

The barrier $U(B_z = \mu_0 H_z + \mu_0 M_z)$ is calculated from the effective spin Hamiltonian

(Eq. 1.2) as the energy difference between the metastable ground state and the highest energy level. We include only the effects due to B_z when calculating U ; however, the barrier is also expected to be reduced by the inhomogeneous field B_x produced by the front itself. The effects of B_x can be included in the calculation of U by including an additional Zeeman term in the effective Hamiltonian,

$$\mathcal{H} = -DS_z^2 - AS_z^4 - g\mu_B S_z B_z - g\mu_B S_x B_x + \mathcal{H}_\perp, \quad (6.4)$$

where $S_x = \sqrt{S^2 - S_z^2}$. In addition to reducing the classical barrier against reversal, B_x also increases the tunneling rate [25, 38]. For the moment we neglect the effects of B_x , but we will argue in favor of its inclusion shortly.

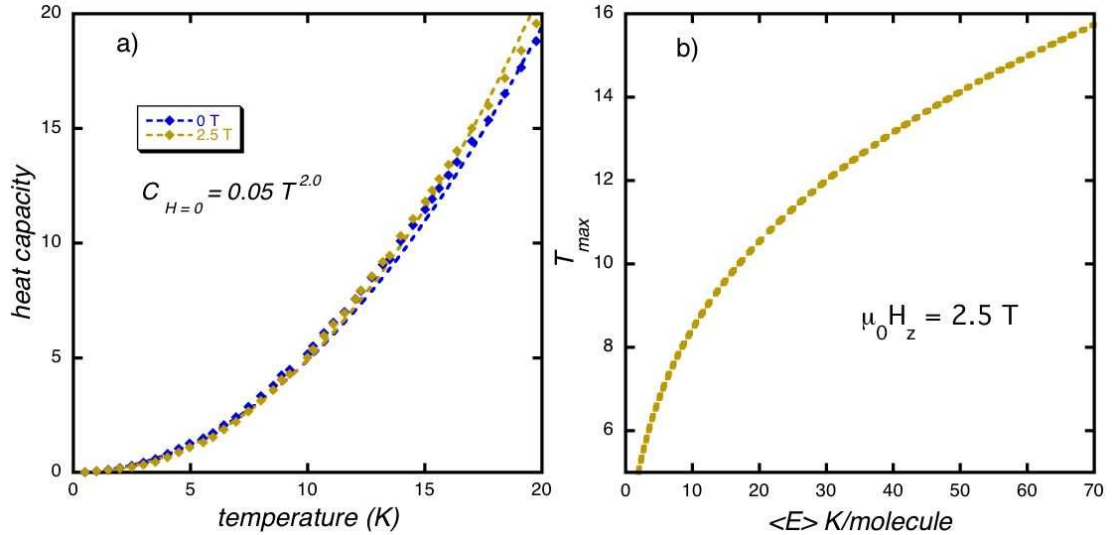


Figure 6.1: (a) Heat capacity as a function of temperature. Blue diamonds are the dimensionless heat capacity reported in Gomes et al. [39] for $\mu_0 H = 0 \text{ T}$. Gold diamonds are the calculated heat capacity at 2.5 T. (b) T_{max} calculated from the heat capacity as a function of average energy released per molecule.

The average magnetic energy released by the relaxing spins (Eq. 5.1) leads to an increase in the temperature near the front. The maximum possible temperature, T_{max} , is calculated using the experimental heat capacity reported by Gomes et al. in Ref. [39] and shown in Figure 6.1 (a) by gold diamonds.¹ The heat capacity of

¹Fitting the heat capacity to a power law yields $C \propto T^\alpha$, where $\alpha \approx 2$. In Ref. [6], the analytical

Mn₁₂-ac depends on the magnetic field. Therefore, we subtract the calculated zero-field spin (Schottky) contribution from the measured zero-field heat capacity from the experimental data. To this we add the calculated spin contribution at a specified field, B_z , for the total field dependent heat capacity $C_{tot}(B_z, T)$. The blue diamonds denote the heat capacity calculated as just described with an external field $\mu_0 H_z = 2.5$ T. The difference generated by including the spin contribution of the heat capacity is small, but we include it for completeness.

By equating the integral of this heat capacity to the average energy released per molecule, $\langle E \rangle$, we can calculate T_{max} as the upper limit of the integral

$$\langle E \rangle = \int_0^{T_{max}} dT C_{tot}(B_z, T). \quad (6.5)$$

We have assumed that the initial temperature is much less than T_{max} . In Chapter 4 the ignition temperatures for major avalanches triggered above 1 T are below 1 K. T_{max} is found to be between 7 and 18 K so this is a reasonable approximation. Including the effects of the dipolar fields on the heat capacity through the inclusion $\mu_0 M_z$ leads to a correction to T_{max} of less than 0.05 K. It is therefore neglected as well. T_{max} as a function of average energy released per molecule is plotted in Figure 6.1 (b).

Fig. 6.2 (a) is a plot of the avalanche speeds for crystal C from Chapter 5 with the three different preparations shown in Figs. 5.3, 5.5, and 5.8. Eq. 6.3 implies that the speeds should all fall on the same curve when plotted with respect to U/T_{max} (assuming a temperature-independent κ). Exponential behavior should be evident as a straight line when plotted on the semi-log plot. There are deviations, however, which are especially pronounced at high values of U/T_{max} . In particular, the class I avalanches with $\Delta M/2M_{sat} = 1$ (shown as filled diamonds) have the highest speeds.

We suggest that this is due to the overestimate of the barrier, which results from

expression for the front speed is found to be proportional to $\sqrt{\alpha + 1}$. For Mn₁₂-ac this leads to the factor of $\sqrt{3}$ in Eq. 6.3.

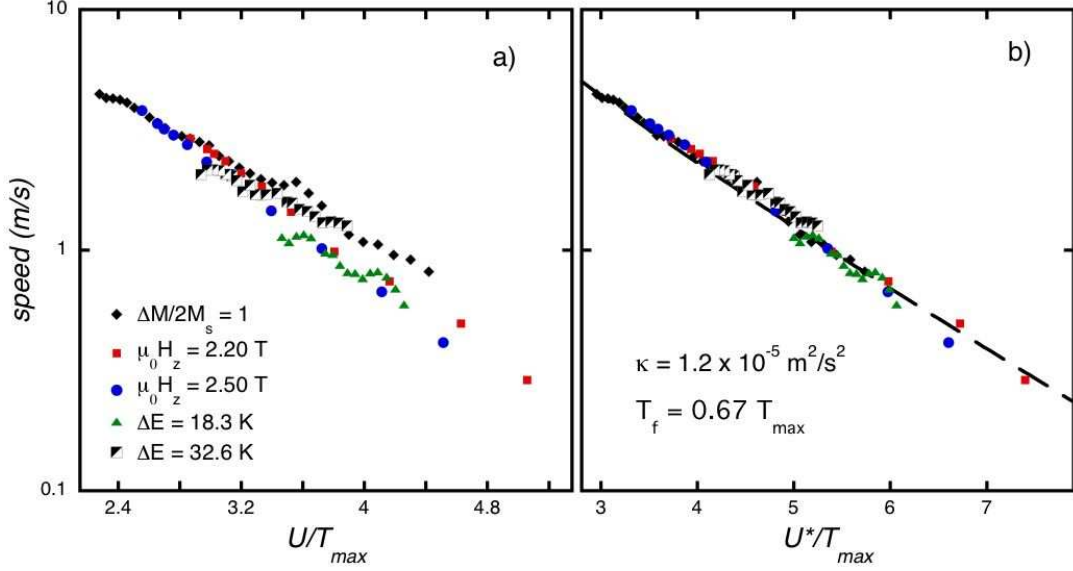


Figure 6.2: (a) Speeds vs. the calculated barriers and maximum temperatures. (b) The barrier is scaled using the change of magnetization, $U^* = (1 - \alpha \frac{\Delta M}{2M_s})U$, where $\alpha = 0.13 \pm 0.01$. A fit is applied using Eq. 6.3 yielding $\kappa = (1.2 \pm 0.2) \times 10^{-5} \text{ m}^2/\text{s}$ and $T_f = (0.67 \pm 0.02) \times T_{max}$.

neglecting the reduction due to the inhomogeneous $B_x(z)$ of the front itself.

It is unclear how to incorporate the effects of an inhomogeneous barrier, $U(z)$, into the analytical theory of magnetic deflagration (Eq. 6.3). Instead, we include the effects of B_x on the relaxation rate by introducing an effective barrier, U^*

$$U^* \equiv \left(1 - \alpha \frac{\Delta M}{2M_{sat}}\right) U, \quad (6.6)$$

where α is determined empirically to be 0.13 ± 0.01 . Although the scaling factor $\alpha \Delta M / 2M_{sat}$ explicitly contains M_z , it is used here to account for the size of B_x . This is verified by our experiment since we find that the maximum value of B_x , as measured by the Hall sensors due to an avalanche, is proportional to $\Delta M / 2M_{sat}$ (see Figure 5.7). Figure 6.2 (b) shows that the overestimate of the barrier can be corrected with the scaled barrier U^* , with the data apparently collapsed on a single curve.

Due to heat loss through the edges of the crystal, and heat diffusion ahead of the front, the flame temperature T_f must be less than T_{max} . We make the assumption that the T_f is proportional to T_{max} . We deduce both T_f and the diffusivity, κ , by

fitting the speeds with Eq. 6.3. The dashed line in Figure 6.2 (b) is the best fit with $T_f = (0.67 \pm 0.02) \times T_{max}$ and $\kappa = (1.2 \pm 0.2) \times 10^{-5} \text{ m}^2/\text{s}$. The uncertainty for T_f and κ is a result of the uncertainty of determining U^* .²

As confirmation for the deduced values of T_f , we reexamine the class II data from Figure 5.8 plotted with respect to U^* , as shown in Figure 6.3. Since T_f (and by assumption, T_{max}) is approximately constant for these avalanches, we can apply Eq. 6.3 to deduce T_f as a fitting parameter. Both curves in Figure 6.3 show non-monotonic behavior. The maxima in the speeds are due to a quantum tunneling reduction of the barrier. The fit is constrained to the lower speed avalanches away from the tunneling resonances, where the calculated barrier is likely to be more accurate. From these two fits we again find that $T_f = 0.67 \times T_{max}$.

All crystals show similar dependence on the barrier U^* and the flame temperature T_f . The dashed lines in Figure 6.4 are fits using Eq. 6.3, again treating κ and T_f as fitting parameters. For all crystals, $T_f \approx 0.67 \times T_{max}$. However, we find that the thermal diffusivity range from 1.2×10^{-5} to $8.7 \times 10^{-5} \text{ m}^2/\text{s}$ from crystal to crystal. This variation in κ accounts for the variation in avalanche speeds.

6.2 Numerical results

A brief numerical analysis is employed here to support the conjecture that $T_f < T_{max}$ even without loss of heat through the surfaces of the crystal.

Since the magnetic avalanche constitutes a wave traveling in one dimension at constant velocity, we may simplify the above equations. Let $T = T(z + vt)$ and $n = n(z + vt)$. This assumption reduces the partial to ordinary differential equations,

$$vT' - [kT']' = -v\Delta n' \quad (6.7)$$

$$n' = -\frac{\Gamma}{v}n, \quad (6.8)$$

²Note that, the scaling of U^* is insensitive to the choice of T_f or T_{max} since we assume they differ only by a constant factor.

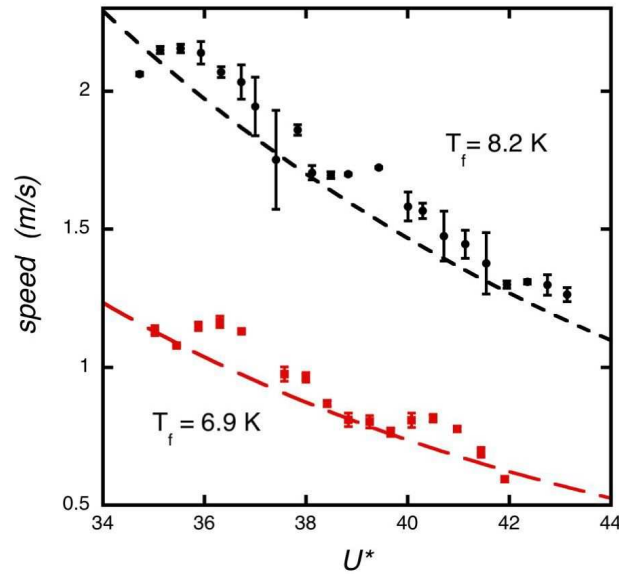


Figure 6.3: Avalanche speeds from Fig. 6 (a) plotted as a function of U^* . A fit using the analytical expression yields a value of the front temperature, $T_f \approx \frac{2}{3}T_{max}$.

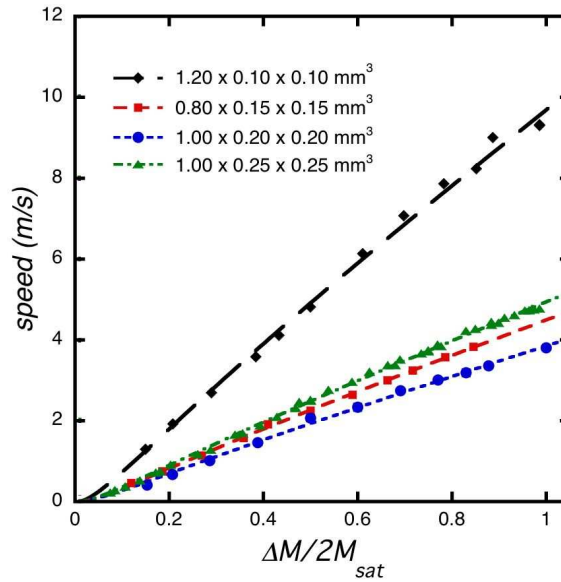


Figure 6.4: Class II avalanches triggered at $\mu_0 H_z = 2.50$ T. Fitting the speeds with Eq. 6.3 provides values of $T_f = 0.67 \times T_{max}$ and κ ranging from 1.2×10^{-5} to 8.7×10^{-5} m²/s.

where $' \equiv \frac{1}{v} \frac{\partial}{\partial t} = \frac{\partial}{\partial z}$. These coupled, non-linear, ordinary differential equations can be solved numerically to find all the avalanche speed consistent with the experimentally determined ΔE , U , and C given the appropriate boundary conditions. Since we are presently concerned with the determination of T_f , we take a more direct approach.

As shown in Appendix A, the signal measured a particular Hall sensor is proportional to $\partial M_z / \partial z$. Or in the language used in this section, it is proportional to $n'(z)$. n' can be numerically integrated directly to get $n(z)$. If we assume that the magnetic relaxation is thermal, i.e., deflagration, then these functions $n(z)$ and $n'(z)$ must satisfy Eq. 6.8. Therefore, the rate of relaxation can be deduced from Eq. 6.8 as $\Gamma = -vn'/n$. Assuming further that Γ is described by an Arrhenius law, Eq. 1.4, we arrive at an expression for the temperature profile

$$T(z) = \frac{-U^*}{\log \left[-\frac{v}{\Gamma_0} \frac{n'}{n} \right]}. \quad (6.9)$$

This approach of extracting $T(z)$ is analogous to finding the frequency of an oscillator given data on the position as a function of time and the expectation that it satisfies $\ddot{x} = -\omega^2 x$.

Figure 6.5 shows two different temperature profiles deduced from the same magnetization, $n(z)$. This approach is quite sensitive to the experimental noise, particularly away from the magnetization interface. We therefore use a numerical approximation to data actually measured for a particular avalanche. The numerically smoothed result for the magnetization profile is shown with the red squares in Figure 6.5. For a particular crystal, the width and shape of the magnetization interface is insensitive to the experimental parameters (within the uncertainty of our measurement protocol). We can then determine $T(z)$ for different avalanches by simply adjusting the speed, v , accordingly. Figure 6.5 shows the deduced temperature profiles for front speeds of 2.1 m²/s (black curve) and 5.2 m²/s (blue curve).

The precise values of $T(z)$ depend on the precision with which the interface may be determined. Since the experimental error in determining the interface width is

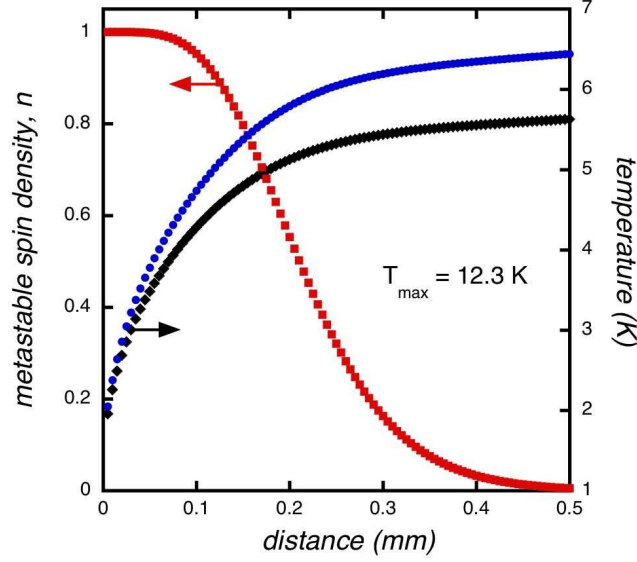


Figure 6.5: Temperature and magnetization in one dimension for an avalanche with $\mu_0 H_z = 2.5$ T, $\langle E \rangle = 32.6$ K, and $T_{max} = 12.3$ K. Note that the maximum temperatures reached are significantly less than T_{max} .

relatively large, we do not pursue this line of analysis further. We mention it here only as a curiosity in support of the conclusion that $T_f < T_{max}$.

6.3 Minor avalanche speeds

Presumably, we can use the same expression Eq. 6.3 for the minor avalanche speeds provided we use the appropriate values for $\Gamma(T_f, U)$. The minor species barrier, U , is calculated from the effective spin Hamiltonian Eq. 1.6. In addition, the prefactors differ by roughly two orders of magnitude; $4.5 \times 10^9 \text{ s}^{-1}$ for the minor species, and $3.6 \times 10^7 \text{ s}^{-1}$ for the major species. For some perspective, we compare the relaxation rates of the major and minor species at $\mu_0 H_z = 0.75$ T and $T_f = 3$ K. The minor species barrier is $U = 40$ K, while the major species barrier is $U \approx 57$ K. This leads to relaxation rates for the major and minor species of approximately 10^{-1} s^{-1} and 10^4 s^{-1} , respectively.

Fig. 6.6 (b) shows the measured speeds for the minor and major avalanches from

Chapter 4, along with the fits using Eq. 6.3. As a reminder, the maxima in the minor avalanche speeds near 0.7 T are *not* due to resonant tunneling during the avalanche. It is due to the loss of magnetization as the field is swept to the desired value. Therefore, we apply two separate fits to the minor avalanches. At low fields, all minor species molecules relax. Accordingly, the fit assumes $\Delta M/2M_s = 0.05$, i.e., only 5% of the total number of spins reverse during the avalanche. At higher fields, approximately half the minor spins have relaxed so $\Delta M/2M_s = 0.025$.

A single fit is applied to the major avalanches since all have $\Delta M/2M_s = 0.95$. The fit to the major avalanche speeds is performed treating the flame temperature and the thermal diffusivity as fitting parameters. We also used the reduced barrier U^* . We find that $T_f = 0.65 \times T_{max}$ and $\kappa = 2.4 \times 10^{-4} \text{ m}^2/\text{s}$, consistent with the speeds reported in section 6.1.

Since the minor avalanches were recorded for the same crystal, we do not expect the thermal diffusivity to change. We therefore fit the minor avalanche speeds with only one fitting parameter, borrowing the κ determined from the major avalanche speed fit. Again, we assume that $T_f \propto T_{max}$ and deduce the constant of proportionality from the fit. Unlike the major avalanches, a flame temperature of $T_f \approx T_{max}$ provides the best fit. This may be partially due to the fact that we do not use a scaled barrier U^* for the minor avalanches. An accurate determination of U^* for the minor avalanches is hindered by the dearth of extensive data for minor avalanche speeds.

The analysis of the combined avalanches is beyond the realm of Eq. 6.3. The quantitative description of combined avalanches thus awaits a more complete theory of magnetic deflagration allowing for two reacting agents.

6.4 Discussion

The theory of magnetic deflagration is generally in good agreement with our data. The success, however, depends on the correctness of three deduced quantities: the

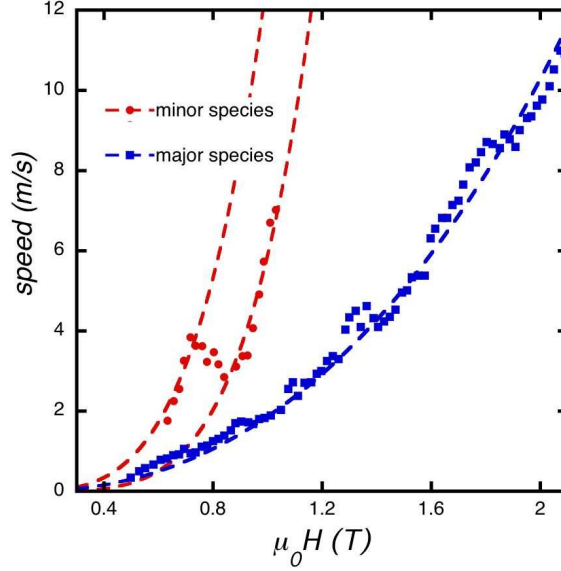


Figure 6.6: Major and minor avalanche speeds reported in Chapter 4. The dashed lines are fits to the speeds using Eq. 6.3.

flame temperature, T_f ; the thermal diffusivity, κ ; and the reduced barrier, U^* . We now discuss the physical likelihood of these deduced quantities.

The rate at which heat escapes the crystal during an avalanche must affect T_f . The rate of heat loss is controlled primarily by the crystal cross section, surface roughness of the crystal, and thermal mounting conditions. Variations in the mounting conditions inevitably occur (e.g., thickness of insulating grease), although an effort was made to ensure identical mounting conditions from crystal to crystal. Also, there were no obvious visible differences in surface quality of the crystals. The cross sections, however, were deliberately varied from $0.10 \times 0.10 \text{ mm}^2$ to $0.25 \times 0.25 \text{ mm}^2$ between the crystals. We expect that the crystals with smaller cross sections should have lower flame temperatures. According to Eq. 6.3, lower flame temperatures should lead to lower speeds. Fig. 6.4 reveals that the maximum speeds vary by approximately a factor of 2.5 from crystal to crystal, but without the expected dependence on cross section. This suggests that T_f is not significantly affected by the crystal dimensions. This is supported by the fact that the deduced T_f is approximately the same for all

four crystals. We therefore conclude that variations in the maximum speed are not due primarily to heat loss.

As stated in section 6.1, we find that κ must vary from crystal to crystal by nearly an order of magnitude to account for the variation in speeds. Ultimately, this prediction should be verified with an independent measurement; however, in general, the thermal diffusivity of dielectric crystals (like Mn₁₂-ac) at low temperatures is known to be strongly dependent on the defects, surface roughness, and dislocations in the crystal [40]. It should be noted that we have assumed a temperature independent κ , which is only correct over a narrow, low temperature range. The deduced values for κ must then be interpreted as average values over the temperature range of the avalanches (≈ 5 to 11 K). A discussion of the difficulties involved in measuring κ for Mn₁₂-ac are discussed in Chapter 7.

The fact that the reduced barrier given by the simple form of Eq. 6.6 provides such an effective scaling also presents a puzzle. We suggest that the scale factor of $\alpha\Delta M/2M_{sat}$ is due to the enhancement of the relaxation rate due to the transverse field, B_x , produced by the avalanche front. The reduced barrier can apparently be as low as 87% of the classically calculated barrier, U . A straightforward classical calculation implies that approximately a 4 kG transverse field is required to reduce the barrier to 0.87 U . The largest fields recorded by the Hall sensors during an avalanche are only ~ 0.5 kG, which suggests that classical reversal of the spin is insufficient to account for the enhanced relaxation rate and that quantum tunneling is also important (i.e., effectively reducing the barrier). However, the enhancement occurs at all fields, $\mu_0 H_z$, not just those fields which correspond to the tunneling resonances. Further work is required to determine the factors leading to the apparent reduction of the barrier, U .

6.4.1 Recapitulation of key assumptions and conclusions

For completeness, we briefly review a few of the key assumptions introduced to simplify the modeling of avalanche speeds.

One-dimensional planar front Eq. 6.3 describes the propagation of the a one-dimensional planar front moving with constant speed. There are instances where this is not the case [41], however this assumption seem reasonable for all data reported here.

$T_f \propto T_{\max}$ We have assumed that the flame temperature is proportional to the calculated maximum temperature. If the reduction of T_f is less than $T_{\max}$ due to heat loss through the surfaces of the crystal, this may not hold. The rate of heat loss across a boundary of a crystal is generally found to be proportional the temperature difference [40]. If this is rate is of the same order as the relaxation rate (Eq. 1.4) then our assumption of $T_f \propto T_{\max}$ will not hold.

Temperature independent κ It is well known that the thermal diffusivity generally decreases as the temperature decreases [40]; however, we have assumed it to be constant for fitting purposes. The deduced values of κ should then be treated as the average value over the range of temperatures 5 K to 11 K.

These assumptions allowed us to draw a number of interesting conclusions regarding the thermal diffusivity, the role of the inhomogeneous dipolar fields produced during an avalanche, and the flame temperature.

$\kappa \sim 10^{-5} \text{ m}^2/\text{s}$ to $10^{-4} \text{ m}^2/\text{s}$ We found that parameter primarily affecting the maximum speed of the avalanche front was the thermal diffusivity. In particular, we found that it may vary by nearly an order of magnitude from crystal to crystal. At low temperatures, such variation of κ in dielectrics like $\text{Mn}_{12}\text{-ac}$ is not uncommon [40].

Effective barrier U^* A temperature independent κ in Eq. 6.3 implies that all data should collapse on to the same curve when plotted with respect to U/T_f . This is not the case for the calculated U . However, the data do collapse if we accounting for the effects of the transient transverse field, B_x , on the barrier, U^* . Experimentally, we observed in Chapter 5 that $B_x^{max} \propto \Delta M/2M_s$. We therefore introduced the effective barrier, $U^* = (1 - \alpha \Delta M/2M_s)U$, where α is empirically determined to be 0.13.

$T_f = 0.67 T_{max}$ With the speeds for all avalanche preparations collapsed on a single curve as a function of U^*/T_{max} . By assuming $T_f \propto T_{max}$, we deduce the flame temperature to be $(0.67 \pm 0.02) \times T_{max}$. This is confirmed by a reexamination of the $\langle E \rangle$ (class III) avalanches, which all have essentially the same T_f . This allows T_f to deduced by fitting the data with Eq. 6.3 and using U^* . Using this method, we again find that $T_f \approx 0.67 \times T_{max}$.

Chapter 7

Conclusion and prospects

In this thesis, we have made a thorough investigation of magnetic avalanches in the molecular magnet $\text{Mn}_{12}\text{-ac}$. We have also argued that magnetic avalanches can be accurately described with the theory of magnetic deflagration. The qualitative success of magnetic deflagration seems indisputable. Particularly striking is the effect of the minor species in combined avalanches; which seems to fulfill the same role as that of a catalyst in chemical deflagration. By triggering avalanches with a wide variety of conditions, we were able to put the theory to a rigorous quantitative test as well. The result is that the theory of deflagration is consistent with data reported on magnetic avalanches reported here. However, the theory provides ample flexibility to fit the data. The flexibility comes from a lack of constraining measurements on the thermal diffusivity and the flame temperatures. In the absence of experimental data for these key physical quantities we instead deduced a range of values required to satisfy the theory. Therefore, compelling confirmation of the theory awaits an independent measurement for κ and T_f . In addition, we have argued that the effects of the internal inhomogeneous fields produced during an avalanche have a significant effect on the avalanche speed. It is unclear whether this effect can be explained purely classically or whether quantum tunneling is important.

If magnetic deflagration is to live up to the promise of being the most well characterized version of deflagration, more work must be done. We briefly discuss a few possibilities for future work.

7.1 Prospects

7.1.1 Thermal diffusivity

There are two obvious measurements that need to be performed in order to confirm the theory of magnetic deflagration: a measurement of thermal diffusivity and the flame temperature. We discuss a few aspects of the measurement of κ here, and T_f in the following section.

Since the thermal diffusivity and thermal conductivity, k , are related by $k = \kappa C$, where C is the heat capacity, one can also measure the thermal conductivity then deduce κ . A measurement of k is likely to be easier since it can be performed with a conventional steady state measurement involving two thermometers and a heater (for details see [40]). The sensitivity of a two thermometer one heater setup is limited by the contact thermal resistance. Since this is in series with the thermal path, it must be minimized. The deposition of gold on the surface of the crystal could provide sufficiently low contact resistance. A more serious limiting factor is the baseline conductance, K_{base} . It is determined as $K = P/\Delta T$ in the absence of the crystal, where P is the power applied with the heater, and ΔT is the temperature gradient across the crystal. We can give an estimate for how low K_{base} must be in order to measure a single crystal of Mn₁₂-ac according to our deduced values of κ .

Between 5 K and 10 K, the heat capacity is approximately $10^4 \text{ JK}^{-1}\text{m}^{-3}$ (see Figure 6.1 and Ref. [39]). The value for the diffusivity deduced was approximately $10^{-5} \text{ m}^2/\text{s}$. This implies a thermal conductivity of roughly $k \sim 10^{-1} \text{ WK}^{-1}\text{m}^{-1}$. A typical cross section of a single crystal is about 10^{-8} m^2 . The distance between the two thermometers should be comparable to the width of the magnetic interface, i.e., $\sim 10^{-4} \text{ m}$. This leads to a thermal conductance of $K \sim 10^{-5} \text{ W/K}$. The baseline thermal conductance of the measurement apparatus must be comparable, or ideally, much lower. This should present a challenging experiment to perform, since this is close to the lowest baseline thermal conductances reported in the literature [44]. The signal may be increased by measuring a number of crystals in parallel; however, a crucial measurement will be a study of single crystals to verify the variability of κ from crystal to crystal we predicted in Chapter 6.

7.1.2 Flame temperature and a novel heat capacity measurement

Some evidence for $T_f < T_{max}$ has already been seen some of our temperature profile data. Figure 7.1 is data for a major avalanche reported in Chapter 4. The avalanche begins releasing heat at 108 ms. Roughly 0.5 ms later—about the time it required for the avalanche pass the thermometer—a small kink in the temperature profile appears (denoted with a red arrow). The temperature then continues to rise until the maximum temperature is reached, followed by the slow return to the bath temperature. As a reminder, this kink cannot be due to the relaxation of the minor species since it was stabilized prior to the ignition of the avalanche.

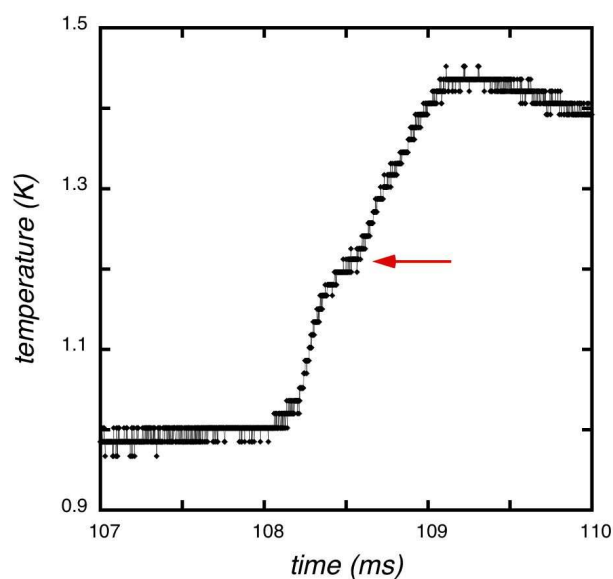


Figure 7.1: Temperature profile of a major avalanche reported in Chapter 4. Red arrow indicates possible measurement of $T_f < T_{max}$.

The shortcomings of our thermometer setup to determine the avalanche temperature profile were discussed in Chapter 4. They stem mostly from the fact that the heat capacitance (thermal mass) of the thermometer and addenda is larger than that of the crystal. An accurate determination of the temperature profile would require a small thermometer with a low thermally conductive path to the bath. Such ap-

paratuses are commonly used for heat capacity studies of small samples [43]. They typically involve a small resistive thermometer and heater deposited on a thin ($\sim 100 \mu\text{m}$) wafer of amorphous substrate with a low thermal conductivity. A measurement of the heat capacitance, C , involves a pulse of power applied with the the heater followed by monitoring of the temperature decay back to the bath temperature. Since the thermal conductance, K , of the substrate, leads, etc. can be characterized very accurately, a determination can be made from the data, $T(t) = T_0 \exp(-t/\tau)$, where $\tau = C/K$.

A temperature measurement of a magnetic avalanche on a similar apparatus would be interesting for two reasons. First, they are constructed with the aim of minimizing the thermal conductance as well as the addenda heat capacitance. This is an ideal setup for measuring T_f . Second, it presents an opportunity to perform a novel heat capacity experiment. The heat pulse could be provided internally by the magnetic energy, ΔE , of the reversing spins rather than an external heat pulse. This would provide a method of determining the heat capacity as a function of field as well as the initial magnetization.

7.1.3 Modeling combined avalanches

As stated in Chapter 6, no theory exists yet for magnetic deflagration involving two species of spins, i.e., combined avalanches. We state here the most likely starting point for such a study.

Since the two species of spins relax at different rates, we must include relaxation equations for each. An additional source due to the minor species must also be included in the heat diffusion equation. Eqs. 6.1 and 6.2 become

$$C \frac{\partial T}{\partial t} - \nabla \cdot k \nabla T = -\langle E_{maj} \rangle \frac{\partial n_{maj}}{\partial t} - \langle E_{min} \rangle \frac{\partial n_{min}}{\partial t} \quad (7.1)$$

$$\frac{\partial n_{maj}}{\partial t} = -\Gamma_{maj} n_{maj} \quad (7.2)$$

$$\frac{\partial n_{min}}{\partial t} = -\Gamma_{min} n_{min}. \quad (7.3)$$

It would be most interesting to explore the resulting analytical approximation to describe the speeds of these combined avalanches to be applied to the data of Chapter 4.

7.1.4 Magnetization interface widths

We have concentrated on modeling the avalanche speeds in this thesis, but there may be more to learn by a careful examination of the magnetization interface widths. The direct measurement of the B_x width is rather noisy; however, taken together with the linear dependence of the B_x amplitude on ΔM (Fig. 5.7) clearly suggest that the width, l_d , is essentially constant.¹ Garanin and Chudnovsky did not discuss the magnetization interface width for the magnetic deflagration front at length in Ref. [6]. They do, however, state that this width should approximately satisfy $l_d \sim \sqrt{\kappa/\Gamma}$. Assuming an Arrhenius relaxation rate, this becomes

$$l_d \sim \sqrt{\frac{\kappa}{\Gamma_0}} e^{U/2T_f} \quad (7.4)$$

The strong temperature dependence of l_d in this expression is not congruous with the data, unless the thermal diffusivity also has counter-balancing temperature dependence. If we assume for the moment that Eq. 7.5 holds, as well as an approximate expression for the front speed, $v \approx \sqrt{\kappa\Gamma_0} \exp(-U/2T_f)$, we may solve for the κ as

$$\kappa \approx v l_d. \quad (7.5)$$

Figure 7.2 shows the product of the measured front speeds and magnetic widths for crystal D plotted as a function of the calculated $T_f = 0.67 T_{max}$. Applying Eq. 7.5, we interpret this as the thermal diffusivity, κ . Applying a power law fit to the data gives $\kappa \sim 2.5 \times 10^{-7} T_f^{3.7} \text{ m}^2/\text{s}$. This is in violation of our intuition, which dictates that κ decreases as the temperature is increased. There are exceptional circumstances

¹Appendix A and Figure 5.2 show the linear relationship between the apparent width of B_x and the width of the magnetization interface, l_d .

where κ is found to be proportional to T^σ , where σ is positive [45, 40], but it would be very surprising in $\text{Mn}_{12}\text{-ac}$.

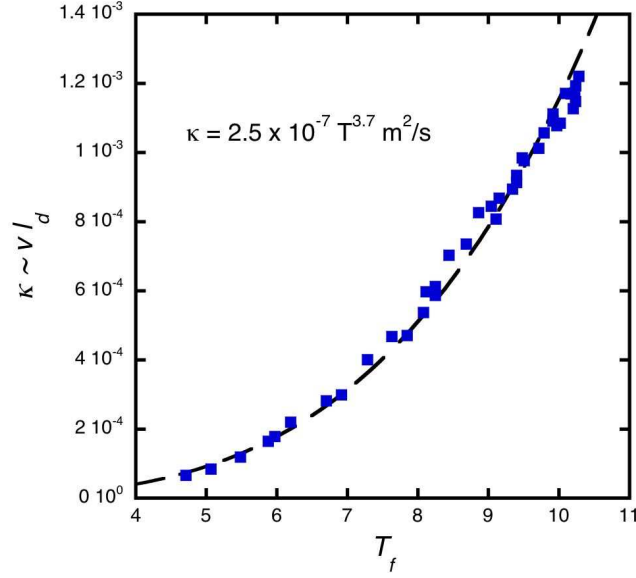


Figure 7.2: The product of the front speeds and apparent B_x width for crystal D (see Figure 5.6) plotted as a function of the calculated $T_f = 0.67 T_{max}$. According to Eq. 7.5, $\kappa \sim vl_d$. A power law fit is applied to the data giving $\kappa \sim 2.5 \times 10^{-7} T_f^{3.7} \text{ m}^2/\text{s}$.

Assuming the widths, l_d , to be constant, as the data suggest, there are a couple of conclusions to be drawn. The expression Eq. 7.5 may be too simplistic and inapplicable to the data presented here. Or, it may be correct according to the theory of deflagration, but is simply inapplicable to magnetic avalanches, which would imply a stark failure of the theory. Or, the theory of magnetic deflagration correctly describes all data here and we have applied it to make a surprising prediction for the thermal diffusivity. In any event, the conclusion awaits a more precise determination of the interface width along with the further theoretical work focusing on l_d .

7.2 Conclusion

This thesis is somewhat like a molecular magnet cooled below the blocking temperature. It is not the equilibrium state of the field, but rather a frozen snapshot of the

present state of affairs. We must conclude then that the study of magnetic avalanches is far from complete. This should be cause for optimism, for it leads to several obvious, and interesting, studies for the future.

Chapter 8

Appendix

We examine the transverse magnetic field detected by the Hall sensors in detail. Although this discussion is elementary, it is included for completeness.

In order to build the model, we start with a microscopic approach, but treating the magnetic molecules as classical objects. We use the static Maxwell's equations as our starting point

$$\nabla \cdot \mathbf{B} = 0 \quad (8.1)$$

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{J} \quad (8.2)$$

where $\mu_0 = 4\pi \times 10^{-7} \text{ N/A}^2$. $\mathbf{J}$ is treated as a fictitious current density producing the magnetic moment of the molecule. A general solution to Eqs. 8.1 and 8.2 involving localized current densities is given by the Biot-Savart law

$$\mathbf{B}(\mathbf{r}) = \frac{\mu_0}{4\pi} \int d^3r' \mathbf{J}(\mathbf{r}') \times \frac{(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3}. \quad (8.3)$$

Since $\frac{(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} = -\nabla \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} \right)$, we may rewrite Eq. 8.3 as

$$\mathbf{B}(\mathbf{r}) = \frac{\mu_0}{4\pi} \nabla \times \int d^3r' \frac{\mathbf{J}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (8.4)$$

We may now write an approximate expression for $\mathbf{B}(\mathbf{r})$ assuming the distance from the current distribution is much larger than its extent, i.e., $|\mathbf{r}| \gg |\mathbf{r}'|$ [46],

$$\mathbf{B}(\mathbf{r}) = \frac{\mu_0}{4\pi} \left[\frac{3\mathbf{n}(\mathbf{n} \cdot \mathbf{m}) - \mathbf{m}}{|\mathbf{r}|^3} \right], \quad (8.5)$$

where $\mathbf{m} \equiv \frac{1}{2} \int d^3r' \mathbf{r}' \times \mathbf{J}(\mathbf{r}')$ is the magnetic moment due to a single molecule. We may now introduce the continuous magnetization to describe the macroscopic crystal $\mathbf{M}(\mathbf{r}) \equiv \delta(\mathbf{r} - \mathbf{r}_m) \mathbf{m}$ with dimensions A/m. The field is then,

$$\mathbf{B}(\mathbf{r}) = \frac{\mu_0}{4\pi} \int d^3r' \left[\frac{3\mathbf{n}(\mathbf{n} \cdot \mathbf{M}(\mathbf{r} - \mathbf{r}')) - \mathbf{M}(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} \right]. \quad (8.6)$$

The c-axis of the crystal is assumed to lie along the z-axis of our coordinate system with the center at the origin. The avalanche propagates along the z axis. Considering the relatively low temperatures of the avalanches ($< 11 \text{ K}$) and the high magnetic

anisotropy, we restrict the vector magnetization $\mathbf{M}$ to M_z . We also assume that the magnetization varies only along z-axis. This is valid only if the avalanche ignites near the edge of the sample and sufficiently far from the Hall sensors such that the a planar front propagates at constant velocity. This is most frequently the case, but there are interesting exceptions when it is not [41]. Finally, we assume that the Hall sensors detect lay in the x-z plane and therefore detect only the x-component of the field. This simplifies Eq. 8.6

$$\mathbf{B}(\mathbf{r}) = \frac{\mu_0}{4\pi} \int d^3r' \left[\frac{3(x-x')(z-z')M_0(z')}{|\mathbf{r}-\mathbf{r}'|^5} \right]. \quad (8.7)$$

We assume the Hall sensors to lie parallel to the z-axis at $x = w/2 + \epsilon$, $y = 0$. One may then calculate the magnetic induction due the samples magnetization as [42]

$$B_x(w/2 + \epsilon, 0, z) = \frac{\mu_0}{4\pi} \int d^3x' M_z(z') f(\mathbf{x} - \mathbf{x}'), \quad (8.8)$$

where $f(\mathbf{x} - \mathbf{x}') = 3 \frac{(z-z')(x-x')}{|\mathbf{x}-\mathbf{x}'|^3}$. We may integrate over z' by parts giving

$$\begin{aligned} B_x(w/2 + \epsilon, 0, z) = & \frac{\mu_0}{4\pi} \left[M_z \int dx' \int dy' \left(\frac{w/2 + \epsilon - x'}{|\mathbf{x} - \mathbf{x}'|^{3/2}} \right) \right]_{-L/2}^{L/2} \\ & - \frac{\mu_0}{4\pi} \int dz' \frac{\partial M_z}{\partial z'} \int_{-w/2}^{w/2} dy' \int_{-w/2}^{w/2} dx' \left(\frac{w/2 + \epsilon - x'}{|\mathbf{x} - \mathbf{x}'|^{3/2}} \right). \end{aligned}$$

Since the magnetization of the sample is zero at the ends, the first term is on the right hand side of Eq. 2 is zero. Carrying out the remaining integrals over x' and y' yields

$$B_x(w/2 + \epsilon, 0, z) = \frac{\mu_0}{4\pi} \int dz' \left(\frac{\partial M_z(z')}{\partial z'} \right) F(z - z'), \quad (8.9)$$

where

$$\begin{aligned} F(z - z') = & -\log \left[\frac{w/2 + \sqrt{\epsilon^2 + (w/2)^2 + (z - z')^2}}{-w/2 + \sqrt{\epsilon^2 + (w/2)^2 + (z - z')^2}} \right] \\ & + \log \left[\frac{w/2 + \sqrt{(w + \epsilon)^2 + (w/2)^2 + (z - z')^2}}{-w/2 + \sqrt{(w + \epsilon)^2 + (w/2)^2 + (z - z')^2}} \right]. \end{aligned}$$

The magnetization is calculated from the magnetic moment of all the molecules in the unit cell divided by the volume. $\text{Mn}_{12}\text{-ac}$ is a body-centered tetragonal so there are two molecules per unit cell. Since the spin of a single molecule is $S = 10$, $|\mathbf{m}| = g10\mu_B$, where $\mu_B \approx 9.27 \times 10^{-24}$ J/T (or equivalently, Am^2). The unit cell volume is $V = 3.62 \times 10^{-27}$ m^3 [16, 17]. We then use $|\mathbf{M}(\mathbf{r})| \leq \frac{2 \times 10 g \mu_B}{V} = 9.9 \times 10^4$ J/Tm³ or A/m as the magnetization.

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