

Testing the radiation emanating from the molecular nanomagnet Fe_8 during magnetization reversals

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In the molecular nanomagnet Fe_8 tunneling can occur from a metastable state to an excited state followed by a transition to the ground state. This transition is accompanied by an energy release with an equivalent frequency of 109.5 GHz. We constructed an experimental setup to measure whether this energy is released thermally or in the form of electromagnetic radiation. Contrary to a previous publication we find no evidence for release of electromagnetic radiation and place an upper limit of 5% on the total radiative energy released during the transition. The transitions between the first and second excited states to the ground state are consistent with a release of thermal energy alone. We also observe that the energy release extends for a longer time for the second excited state than for the first excited state.

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While investigating the Fe_8 molecular magnet Shafir and Keren [1] made a serendipitous observation: tunneling events were accompanied by a jump in the temperature of a thermometer placed far from the sample and attached directly to the mixing chamber of a dilution refrigerator (DR). When the line of sight between the thermometer and sample was blocked, the tunneling signal remained, but the temperature jumps disappeared. This led to the conclusion that energy bursts accompany the tunneling event and arrive at the thermometer in the form of electromagnetic radiation as was suggested theoretically [2]. In order to block the line of sight the DR had to warm up and cool down again. Therefore, the test experiment was not done simultaneously with the main experiment. Here we revisit the same phenomena, but with an experimental setup designed to detect photons in the microwave range, and with a test experiment done simultaneously with the photon detection.

At low temperature, the molecules are described by the Hamiltonian

$$\mathcal{H} = -DS_z^2 + g\mu_B S_z H + \mathcal{H}',$$

where $S = 10$ is the spin, $D = 0.292K$ is the anisotropy parameter, H is the applied magnetic field, μ_B is the Bohr magneton, $g \approx 2$ is the gyromagnetic factor, and \mathcal{H}' does not commute with S_z and is responsible for tunneling between spin projection states m [3,4]. When the field is strong ($\sim \mp 1$ T) only the $m = \pm S$ are populated. When the field is swept across zero and changes sign, the $m = \pm S$ state becomes metastable. At matching fields, which are separated by 0.225 T [5,6], quantum tunneling of magnetization (QTM) can take place from $m = \pm S$ to an $m' = \mp(S - n)$ state, where $n = 0, 1, 2, \dots$ is an excited state index. For $n > 0$, the excited m' state decays spontaneously to the ground state $\mp S$ and energy is emitted. For $n = 1$ this energy corresponds to a frequency of 109.5 GHz or wavelength of 2.7 mm, and for $n = 2$ it corresponds to a frequency of 195 GHz.

We tested several single crystals, each weighing roughly 20 mg. They were synthesized according to [7] and oriented visually according to their facets. The experiment is performed below 0.2 K in order to have temperature-independent

quantum tunneling [5,6]. Figure 1 depicts the experimental setup, which is located inside the inner vacuum chamber of the DR. The cooling of the sample and all detectors is provided via copper cold fingers attached to the mixing chamber (MC) of the DR. The magnetization is measured using a Hall sensor array placed at the center of a magnet. The array is made of Hall bars of dimensions $100 \times 100 \mu\text{m}^2$ with $100\text{-}\mu\text{m}$ intervals; the active layer in these sensors is a two-dimensional electron gas formed at the interface of the GaAs-AlGaAs heterostructure. The surface of the Hall sensor is parallel to the applied field. Consequently, the effect of the applied field on the sensor is minimal and determined only by the ability to align the array surface and field. The sample with the Hall sensor is located in the middle of a copper cylinder, which acts as a wave guide and is also thermally linked to the MC.

Two bolometers are located at both ends of the cylinder. The bolometer configuration is also shown in Fig. 1. The bolometers are made of a RuO_2 thermistor attached to absorbing sheets. The thermistor is a standard LakeShore RX-202A with typical temperature-dependent resistance. The thermistor is soldered from both sides to the copper sheets and copper General Electric (GE)-varnish coated wires are soldered to the sheets. The thermistors are biased by an ac current of 10 nA and their voltage is measured with a lock-in amplifier.

The absorbing sheets consisted of two copper plates $11 \text{ mm} \times 4 \text{ mm} \times 35 \mu\text{m}$ in size, with a gap between them. The RuO_2 thermistor is bridging the gap. A thermally isolating layer of glass epoxy FR-4 is placed under the absorbing sheets. The bolometers are mounted on a printed circuit board and have a weak thermal link to the MC.

Between one of the bolometers and the sample there is a combination of two filters making a 80–180-GHz bandpass. The high pass is a “thick grill filter” based on waveguide cutoff [8] and the low pass is based on a mesh grid [9]. We will refer to this bolometer and filter combination as the “open” side. The other bolometer is totally blocked from radiation by a thick aluminum plate. The blocked side serves as the test experiment; the radiation is to be detected by the open bolometer only. The bandpass filter was tested at room temperature, using a Spacek Labs GW-110-10 Gunn oscillator source operating at 110 GHz and a DW-2P broadband detector.

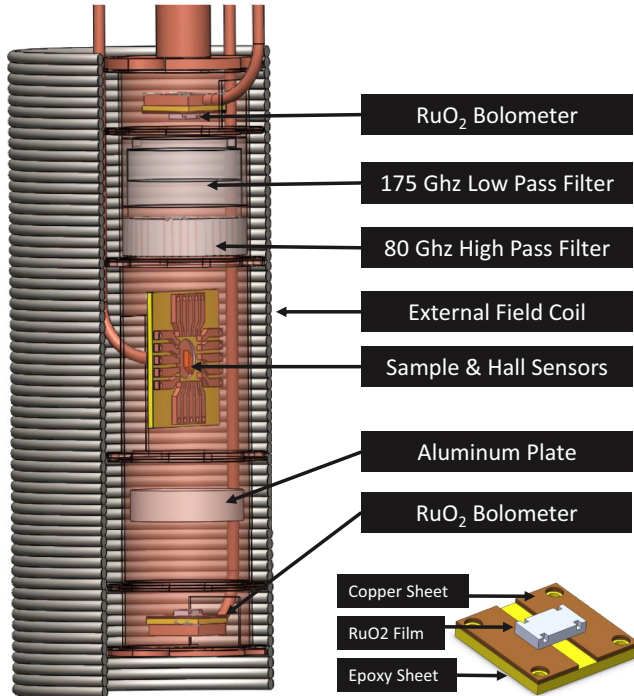


FIG. 1. (Color online) Experimental setup showing the Hall sensors responsible for the magnetization measurements, the bolometers with filters which detect photons, the magnet, and the cold fingers linked to the mixing chamber.

We test the response of the bolometers to a pulse of radiation *in situ* by replacing the Fe_8 sample with two Fairchild LED56 diodes that are pointing in both directions of the cylinder. The diodes are thermally connected directly to the 1-K pot of the DR for better cooling power. The diode bias power is selected so as to give a similar energy pulse to the bolometers as a tunneling event with the Fe_8 sample (see below). In Fig. 2 we plot the open and blocked bolometer voltage as a function of time after energizing the diodes. The solid line indicates the voltage across the diodes as a function of time. The bolometer voltage is proportional to the temperature of the thermistor and therefore to the power deposited. The temperature of the bolometer which is open to radiation increases as soon as the diode power is turned on. Two seconds later, the thermal energy from the diodes reaches both bolometers simultaneously. The instantaneous increase of the open bolometer voltage is the most significant indication of radiation. This increase is detected with a signal-to-noise ratio (SNR) of 100 in amplitude (see the blue trace in Fig. 2) and an even larger SNR in time by the temporal separation between the early and late pulses.

We also test the ability of the two bolometers to detect thermal energy. The inset of Fig. 2 shows the case when the sample area is heated by a resistor. The power and duration of this heat pulse are again similar to that produced by the Fe_8 sample (see below). In this case the temperature of both bolometers increases simultaneously to equal temperature. Therefore, by subtracting the voltage of the bolometers, and focusing on the early time before thermal energy arrives to the bolometers, we obtain the signal of electromagnetic radiation

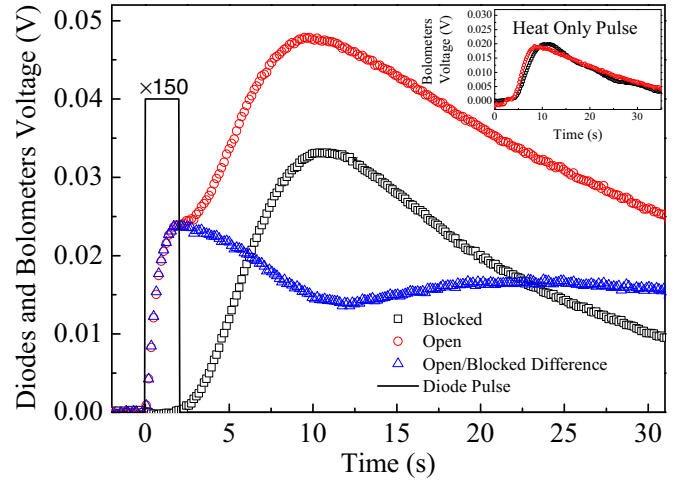


FIG. 2. (Color online) The response of the bolometers to a test radiation and thermal energy pulses. The solid line is the voltage pulse applied to the light emitting diodes. The red and green symbols show the voltage developed across the open and blocked bolometers as their temperature increases due to the radiative pulse from the diodes. The blue symbols show the voltage difference. The difference within the first second represents a detection of a photon signal. Inset: The same experiment but with an input of thermal energy into the sample using a biased resistor.

only. This signal is also depicted in Fig. 2 by a blue curve. It decays slowly since the cooling powers of the two bolometers are different due to different distances from the mixing chamber. The early time signal, up to $\sim 4s$, demonstrates that we can clearly detect electromagnetic radiation emitted from the diodes using our experimental setup.

In the experiment with Fe_8 , the molecules are polarized by applying a magnetic field of ± 1 T in the \hat{z} direction. Afterward, the magnetic field is swept to ∓ 1 T. The sweep is done at different sweep rates. During the sweep we record the Hall voltages, the external field, and the bolometer voltage. The normalized magnetization M/M_0 is given by the Hall voltage divided by the voltage at $H = 1$ T. We found that, depending on the sweep rate, magnetization reversal can occur in two different ways: a continuous reversal with multiple steps at matching fields or a fast abrupt reversal, in avalanche form, as shown in Fig. 3. We look for electromagnetic radiation in both cases. In the avalanche process, a large amount of heat is released and a clear tunneling front is present [10]. Without an avalanche, the temperature of the sample is expected to remain low compared to the energy barrier. In this case, a unique quantum of energy should be emitted in the tunneling process.

The results of our experiment in the case of an avalanche are shown in Fig. 4. The sweep rate is 1.67 mT/s. The left ordinate is the bolometer voltage. The right ordinate is the normalized magnetization M/M_0 . The bottom abscissa shows the field values, and the top abscissa shows the time. When the external field is at a matching value a QTM occurs followed by a rise of the bolometer voltage. However, there is no observable difference in the rise time or voltage amplitude between the opened and the blocked bolometer. The bolometer voltage starts to rise 2 s after the avalanche. This is a time

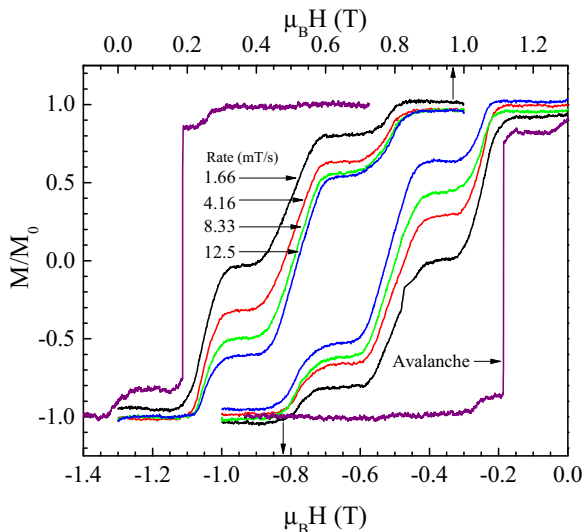


FIG. 3. (Color online) Fe₈ hysteresis loops with multistep magnetization jumps, at different sweep rates, and a hysteresis loop with an avalanche. The fields for the positive sweep rates are given by the bottom abscissa, and those for the negative sweep rates are given by the top abscissa.

interval similar to the diode experiment and is due to thermal energy arriving at the bolometer. We therefore conclude that no significant photon contribution in the band between 70 and 180 GHz is detected when an avalanche is taking place.

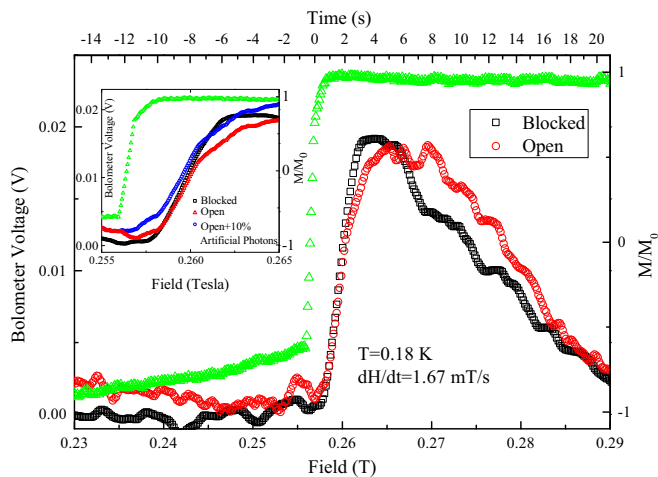


FIG. 4. (Color online) Magnetization and energy emission measurements done simultaneously on an Fe₈ molecular magnet after an avalanche. The left ordinate is the open and closed bolometer voltage, which is proportional to their temperature. The right ordinate is the normalized magnetization. No difference between the two bolometers is detected within the experimental sensitivity. The experimental sensitivity is demonstrated in the inset. The photon signal was copied from the first 4 s of the open bolometer in Fig. 2, normalized to 10% of the closed bolometer, and added to the open bolometer. A clear difference between open and closed bolometers can be seen. We thus set the experimental sensitivity of photons to 5% of the thermal (phonon) energy.

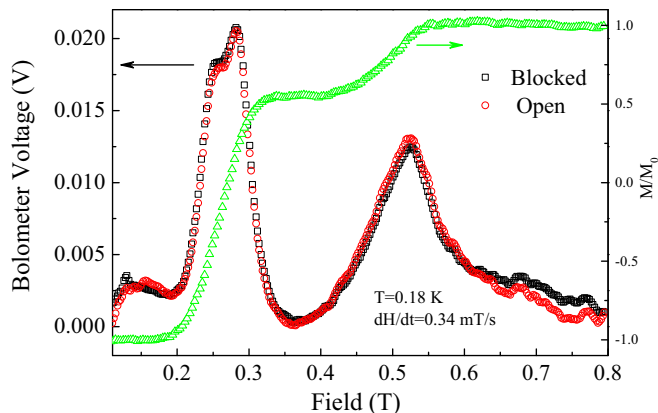


FIG. 5. (Color online) Magnetization and energy emission measurements done simultaneously on an avalanche free Fe₈ molecular magnet. The left ordinate is the open and closed bolometer voltage, which is proportional to their temperature. The right ordinate is the normalized magnetization. No difference between the two bolometers is detected within the experimental sensitivity. The second bolometer voltage peak decays more slowly than the first one, with no noticeable magnetization changes at fields approaching 1 T.

To place an upper limit on photon emission during the avalanche process, we copied the photon signal from the first 4 s of the diode experiment (blue curve in Fig. 2), scaled it to a range of fractions between 1 and 20% of the thermal energy signal recorded by the closed bolometer, and added it to the open bolometer signal. The goal was to assess the photon signal level that, if it was present, would clearly be temporally separate from, and of higher amplitude relative to the signal of, the closed bolometer. The case when the photon signal is scaled to 10% is shown in the inset of Fig. 4. This is a case in which the open bolometer voltage clearly precedes the closed one temporally and levels off at a higher amplitude. By varying the fraction between 1 and 20% and considering the noise, we found that we could place an upper limit of 5%. That is, no more than 5% of the energy emitted by the molecular magnet had been converted to light. If it did, we should have detected it.

The experimental results when an avalanche is absent are shown in Fig. 5. Here again we show the bolometer voltage, magnetization, field, and time as in Fig. 4. The sweep rate is 0.34 mT/s. Two clear transitions are observed in this experiment. Now the bolometer voltage raises over a longer time, reducing the rise time resolution. Therefore, detecting photons without an avalanche is harder and can only rely on pulse amplitudes. No amplitude difference is observed between open and closed bolometers for either of the magnetic transitions.

Thus, we do not observe electromagnetic radiation emanating from Fe₈ regardless of the sweep rate or transition index *n*. If the molecules do emit radiation, it consists of less than 5% of the total-energy release. This is the main finding of this work. A similar conclusion was drawn by Bal *et al.* regarding the Mn₁₂ molecular magnet [11].

However, it is interesting to notice that at the second transition it takes the bolometers more time (a longer field

interval) to cool down than at the first transition. This could have two possible explanations.

(1) The lifetime of the $n = 2$ excited state is longer than the $n = 1$ state. This possibility stands in contrast to lifetime measurements by Bahr *et al.* [12], although they were done at higher temperatures.

(2) As we sweep the field there are more transitions from the metastable state to $n = 3, 4 \dots$ excited states. As n increases the magnetization change becomes smaller but the energy released becomes larger. It is conceivable that we are unable to detect magnetically the higher transitions but can detect their energy release. More experiments are required to distinguish between the two possibilities.

To summarize, we reexamine the possibility that Fe_8 emits electromagnetic radiation after tunneling events using a specially designed experimental setup. Our results do not reproduce those reported earlier by Shafir and Keren [1]. We place an upper limit of 5% on the amount of energy released by radiation and conjecture that energy is released after tunneling in Fe_8 only in the form of thermal energy. This is important for understanding the role of phonons in the tunneling process.

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