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Electromagnetic radiation emanating from the molecular nanomagnet Fe_8

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Photons emitted by transition between the discrete levels of single molecular magnets might obey the elementary condition for Dicke's super-radiance. We investigate this possibility in the Fe_8 molecule where magnetization jumps are known to occur at discrete magnetic-field values. We found energy bursts each time the molecule undergoes a magnetization jump, confirming their quantum nature. A series of tests indicated that photons carry out the energy and that indeed these photons obey the elementary conditions for super-radiance.

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In recent years, the interest in single molecule magnets (SMM) has grown widely, mostly because of their quantum tunneling of the magnetization (QTM).[1] Some of the future potential applications of SMM are in quantum computation,[2,3] as multibit magnetic memory,[4] as an essential part in spintronics,[5] and as an MRI contrast.[6] More recently the interaction between SMM and radiation was investigated. Experiments using external microwave sources have been carried out on Fe_8 in which the absorption and its relation to the magnetization curve were studied.[7–12]

In addition, it was proposed in theoretical works that single-molecule magnets could be used to generate Dicke's super-radiance (SR).[13–18] In this radiative process, a short intense pulse of light emanates from a molecular system due to interactions via the electromagnetic field. For super-radiance the photon wavelength must be similar to the sample size.[19] Following these works, Tejada *et al.*[20,21] reported that during magnetization avalanches of the molecular magnet Mn_{12}, radiation was released. In the same year, Bal *et al.*[22] were also looking for this phenomenon, but with the additional possibility of being able to analyze the radiation frequency. However, they could only place an experimental upper bound on SR emission from Mn_{12}. As far as we know, no attempt has been made to measure the energy bursts from Fe_8 molecule.

Here we report the experimental detection of radiation emission from Fe_8. These molecules have spin $S=10$ and high magnetic anisotropy that corresponds to a 27 K energy barrier between spin projection $S_z=\pm 10$ and $S_z=0$, in zero external field. These molecules show QTM at regularly spaced steps in the hysteresis loop.[23]

The magnetization is measured using a Faraday force magnetometer as depicted in Fig. 1. The design of the magnetometer was dictated by a different experiment concerning H nuclear magnetic resonance during field sweep; this experiment will be presented elsewhere. The main objective in the design was to avoid having any metallic parts next to the sample. The phenomenon described here was discovered by accident. The Faraday force magnetometer is mounted in the inner vacuum chamber of a dilution refrigerator (DR), equipped with a main superconducting magnet that produces the field H, and two oppositely wound superconducting magnets that produce a field gradient.

The sample is grown by the method described in Ref. 24 and is 20 mm^3. It is oriented with its easy axis parallel to the magnetic field H and mounted on the small load-sensing device. The device is made of two parallel plates variable capacitor. The movable plate is suspended by two pairs of orthogonal crossed 0.2 mm diameter phosphor bronze wires attached to it with epoxy. The static plate was mounted on an epoxy screw, for adjusting the initial capacity C_0. When the sample is subjected to a spatially varying magnetic field B, it will experience a force $\mathbf{F}=M_z(\partial B_z/\partial z)\hat{z}$. This force is balanced by the wires. The displacement of the plate is proportional to $\mathbf{F}$ and can be detected as a capacitance C change. The total capacitance response is then given by

$$\frac{1}{C_0}-\frac{1}{C}=aM_z\frac{\partial B_z}{\partial z},$$

where a is a constant that depends on the elastic properties of the wires. This design is discussed further in Sakakibara *et al.*[25]

The sample is glued to poly-chloro-trifluoro-ethylene (PCTFE), a fluorocarbon-based polymer, which has no H atoms and is suitable for cryogenic applications. The bottom

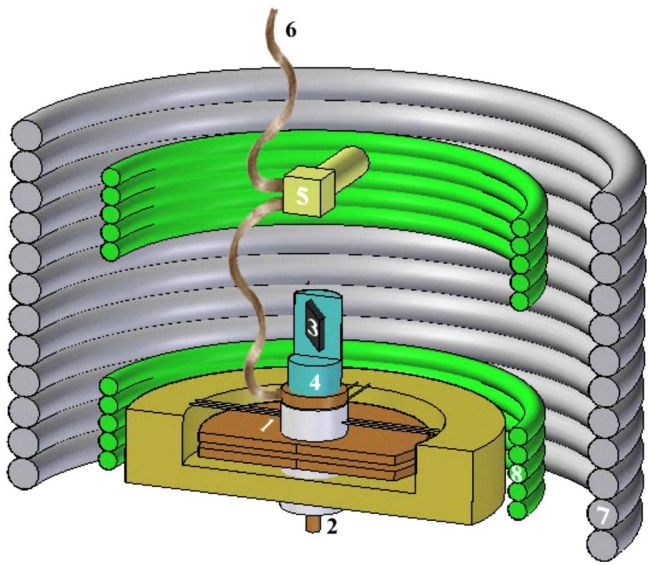

FIG. 1. (Color online) Cross sectional view of the Faraday balance with: (1) movable plate of the capacitor, (2) screw for capacitor's fixed plate height adjustment, (3) sample, (4) PCTFE, (5) gold plated casing of the thermometer, (6) thermal link to the DR mixing chamber, (7) main coil, (8) and gradient coils.

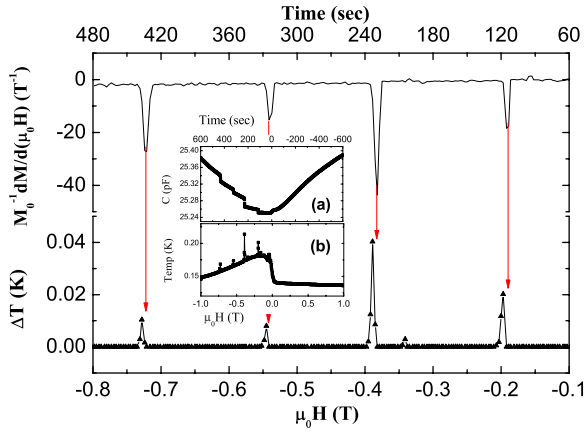

FIG. 2. (Color online) Normalized derivative of the magnetization extracted from the capacitance (see text) and temperature spikes vs magnetic field swept from positive to negative. The changes in the magnetization are followed by an increase in the temperature indicating release of energy. Raw date is in the inset: (a) capacitance (which represents magnetization) and (b) temperature vs magnetic field swept from positive to negative. Steps in the capacitance indicate QTM in the sample.

of the PCTFE is connected by a thermal link to the DR mixing chamber which produces the cooling and to the movable plate. Approximately 2 cm above the sample, on the thermal link, there is a calibrated thermometer (RuO_2 R2200) in a gold plated casing. It is important to mention that the sample is in vacuum with no exchange gas, and therefore its temperature T is not exactly the same as the temperature of the thermometer. However, this is not a problem in our experiment since below 400 mK the magnetization jumps of Fe_8 are temperature independent.[26] Finally, when needed a copper cover can be added which blocks the line of sight between the sample and the thermometer.

In the experiment we apply a field of +1 T and wait until thermal equilibrium is reached. We then record the capacitance, temperature, and field value as the field is swept from +1 T to −1 T at a rate of 0.1 T/min. The capacitance vs the applied magnetic field (and time) is shown in inset (a) of Fig. 2. When the field is positive the capacitance is a smooth function of the field. This is because the spins are at their ground state for all positive fields and have nowhere to tunnel to. Once the field becomes negative, clear jumps in the capacitance are observed, indicating jumps in the magnetization that are taking place as the magnetization is tunneling between states. In inset (b) of Fig. 2 we show the temperature reading of the thermometer. For positive field the temperature is quite stable. At zero field there is a big and broad increase in the temperature. This is caused by an eddy currents developing in the copper wires due to the change in the sweep rate during the transition from positive to negative field. At negative fields there is a mild decline in the temperature accompanied by clear temperature spikes.

In principle, C should have been constant for $H>0$ since the magnetization is constant. However, in a DR it is difficult to place the sample in the center of the main magnet, and the gradient has some field dependence. The measurements at $H>0$ could be used to calibrate the field gradient. A simpler approach is to present

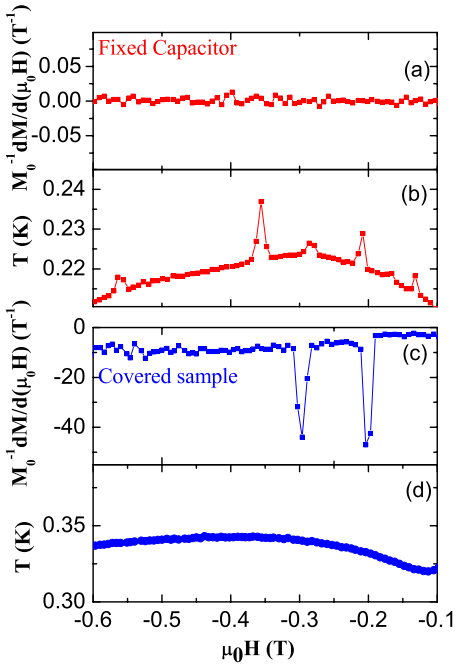

FIG. 3. (Color online) Test cases: The capacitance (a) and temperature (b) vs magnetic field swept from positive to negative with jammed capacitor. The rise in the temperature indicates the change in the magnetization. The normalized derivative of the magnetization (c) and temperature (d) vs magnetic field (same sweeping direction) with covered sample. The change in the magnetization is not followed this time by an increase in the temperature.

$$\frac{2}{\Delta C}\frac{dC}{d\mu_0 H} = \frac{1}{M_0}\frac{dM}{d\mu_0 H},$$

where ΔC is the difference in capacitance between $H=0$ and $H=1T$, and M_0 is the saturation magnetization. This quantity is significant only at the jumps. We also subtracted from T a polynomial fit to the mild temperature decline for negative fields. The resulting $(1/M_0)dM/d\mu_0 H$ and ΔT are shown in Fig. 2. It is now clear that the thermal spikes of a few tens of milli-Kelvin occur about 1 s after the capacitance (magnetization) jumps, and that every magnetization jump is accompanied by a thermal spike. The thermal spikes begin at the lowest field where tunneling is taking place, indicating that they involve transitions between the lowest-lying states of the molecular spin. This is a very different situation from Mn_{12} where the energy bursts are believed to be due to transitions between high-lying states.[20] Finally, in Fe_8, the bursts take place in a region where tunneling is temperature independent. This should make their analysis much simpler.

A priori, there could be many reasons for the thermal spikes. The first that comes to mind is heating from the moving part of the capacitor. To disqualify this possibility we jammed the movable capacitor plate by raising the lower plate until they touch each other, and repeated the measurement. The results are presented in Figs. 3(a) and 3(b). Because the capacitors' plates were jammed, there is no change in the capacitance, but the spikes in the temperature are still present.

Another source of heating could be phonons. Since the entire system is in vacuum, the energy could reach the thermometer only via the copper wire thermal link. To check this possibility we performed two experiments. First, we moved the thermometer to a separate copper wire, thermally linked directly to the mixing chamber, but not to the sample. We confirmed that the results presented in Fig. 2 are reproducible in this configuration (not shown). Second, we blocked the line of sight between sample and thermometer by covering the sample with a copper cylinder. The results are depicted in Figs. 3(c) and 3(d). The steps in the capacitance are still seen, although not all of them and they are somewhat broader for a reason that is not clear to us. Perhaps the force acting on the sample causes it to fracture after many field and thermal cycles. In contrast, the jumps in the temperature disappeared completely. The last two experiments confirmed that the cause of the temperature spikes is electromagnetic radiation and not phonons.

A question that should be asked is how come this phenomenon has not been seen before. We believe that all the experiments with Fe_8 used exchange gas or liquid as a cooler, and not a thermal link. In the former case, the radiation emitted from the sample is hard to detect. Moreover, most experiments have been done with small crystals to prevent avalanches, so the radiation was weak.

Next we identify the energy levels that participate in the transitions. The main part of the Hamiltonian is given by

$$\mathcal{H} = DS_z^2 + E(S_x^2 - S_y^2) + g\mu_B H_z S_z, \tag{1}$$

where z is the direction of the large uniaxial anisotropy, S_x, S_y, and S_z are the three components of the total spin operator, $D/k_B = -0.292$ K and $E/k_B = 0.046$ K are the axial and the rhombic anisotropy parameter, respectively (k_B is the Boltzmann factor), μ_B is the Bohr magneton, and the last term of the Hamiltonian describes the Zeeman energy associated with an applied field H.[27,28] The energy as a function of field and corresponding level quantum number m is shown in Fig. 4.[23] In the inset, a zoom view of the avoided level crossing taking place at $\mu_0 H = -0.4$ T is presented. There are two possible transitions. The first possibility, suggested in the original SR theory, is that the photon is emitted by transition between the avoided levels as indicated by the vertical arrow in the inset of Fig. 4. The photon energy in this case equals that of the tunnel splitting which is 10^{-6} K.[23] The second possibility is that photons are emitted due to transition between states with the same sign of their quantum number m as indicated by the solid arrows in the main panel of Fig. 4.[20,22] In the case of Mn_{12} these were high-lying thermally excited states such as $m=1$ to $m=2$. In the experiment presented here these must be low-lying states. In this case the photon energy is ~5 K. The difference in photon energy expected from these two possibilities is huge and can easily be distinguished.

To determine the energy released by the sample we have to convert the size of the thermal spikes to the energy detected by the resistor. For this purpose, we measured the energy needed to change the temperature of the thermometer by the same amount as in Fig. 2, when the energy is injected directly into it. The temperature is determined by four-wire resistance measurement, with very low current of 0.7 μA. Changing the current to 10 μA for 0.5 s and immediately after measuring it with 0.7 μA produced a spike similar to the ones shown in Fig. 2. The energy needed to produce these thermal spikes is 0.25 μA.

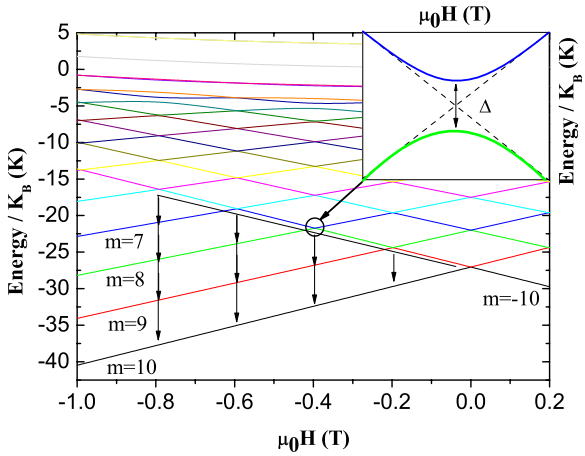

FIG. 4. (Color online) Zeeman diagram of the 21 levels of the $S=10$ manifold of Fe_8 as a function of the field applied along the easy axis and the quantum numbers m. The inset is a zoom on the level crossing, which, in fact, is an avoided crossing with energy split Δ (Ref. 23).

To estimate this energy theoretically we consider the possibility where by sweeping the field from positive to negative, the tunneling that is taking place at $\mu_0 H = -0.4$ T is from $m=-10$ to $m=8$, followed by a transition from $m=8$ to $m=9$ to $m=10$. Judging from the relative area of the magnetization derivative peaks in Fig. 2, about 0.4 of the total spins tunnel at this crossing. The expected energy release after the tunneling is twice 5 K (see Fig. 4) or 1.4×10^{-22} J. The 20 mm^3 sample, with 2 nm^3 unit cells,[24] has 10^{19} molecules. Therefore, the energy that was released is 0.6 mJ. Considering the distance between sample and thermometer and its cross section, the solid angle of the thermometer is 0.02 ± 0.004. Therefore, the energy that should reach it is 12 μJ. This is much closer to the estimated value discussed above than energy from avoided levels photon of 10^{-6} K. Therefore, it is clear that photons emitted by transitions between low lying states, and not avoided levels, are responsible for the thermal spikes.

Having established the energy carrier and the energy source we examine first the possibility of black body radiation. The temperature of the sample can increase after the magnetization steps but not too much since we see the consecutive step. An upper limit is 5 K where steps are no longer observed. At this temperature Stephan-Boltzmann law would predict a radiation power 2–3 orders of magnitude smaller than what is needed to produce our temperature spikes.

Next we consider the possibility of SR. The most important condition for SR is $\lambda > l$, where λ is the photon wavelength and l is the sample size of 2.7 mm in our case. λ for a 5 K photon is 3 mm. Therefore, this SR condition is obeyed. The second condition is that the transition rate will be bigger than any other decoherence rate of the molecular spins. The transition rate for a single molecule emitting a photon is[20]

$$\Gamma_1 = \frac{2g^2\mu_B^2}{3\hbar^4 c^3}(S-m)(S+m+1)(E_m - E_{m+1})^3. \quad (2)$$

For the $m=8$ to $m=9$ this gives $\Gamma_1 = 10^{-7}$ sec. In the SR case the minimal transition rate $\Gamma_{SR} = N\Gamma_1$, where N is the total number of molecules in the $m=8$ (without the thermal factor which exists in Mn_{12}). The maximum transition rate is $\Gamma_{SR} = N^4\Gamma_1/4$.[19] This gives $\Gamma_{SR} > 10^{11}$ sec^{-1}. Since there is no temperature dependence of the tunneling in Fe_8 below 400 mK it is believed that the source of dephasing is nuclear moments, and it is given by $\Gamma_{nuclear} \sim 10^8$ sec^{-1}.[29] Therefore, the second SR condition $\Gamma_{SR} \gg \Gamma_{nuclear}$ is also obeyed. Thus, it is conceivable that the transitions between low-lying states in Fe_8 are accompanied with SR of photons.

Finally, we consider the possibility of classical magnetic dipole radiation. It was shown in Ref. 13 that since this radiation is a collective phenomenon that conserves the total spin value, it is equivalent to SR, provided that the relaxation between levels occurs fast enough. Equation 18 in Ref. 13 relates the emitted power I to the second derivative of the magnetization projection by $I = \frac{2}{3c^3}(\frac{d^2 m_z}{dt^2})^2$, which could be approximated as $\frac{2}{3c^3}\frac{\Delta m_z^2}{\Delta t^4}$. Using this relation, our energy burst for the transition between say $m=8$ to $m=10$ can be viewed as dipole radiating classically for ~ 10 nsec. This time is much shorter than $1/\Gamma_1$ and closer to $1/\Gamma_{SR}$, hence the equivalence to SR.

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