Electromagnetic radiation produced by avalanches in the magnetization reversal of Mn$_{12}$-Acetate

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Abstract

Electromagnetic radiation produced by avalanches in the magnetization reversal of Mn$_{12}$-Acetate has been measured. Short bursts of radiation have been detected, with intensity significantly exceeding the intensity of the black-body radiation from the sample. The model based upon superradiance from inversely populated spin levels has been suggested.

PACS numbers: 75.50.Xx, 42.50.Fx, 07.57.Hm
Populations of spin levels in molecular nanomagnets can be easily manipulated by the magnetic field. For systems studied to date the distances between the levels may go up to 0.5 THz. Sources and detectors in this frequency range are scarce. Meantime the electromagnetic radiation in the range $0.1 - 0.5$ THz is considered to be best for detecting small tumors and for security screening at the airports\textsuperscript{1}. In this Letter we report experimental studies of the electromagnetic radiation from Mn$_{12}$-Acetate, performed with the help of an InSb bolometer inside a SQUID magnetometer. Magnetic clusters Mn$_{12}$-Ac have spin $S = 10$ and high magnetic anisotropy that corresponds to a 66 K energy barrier between spin-up and spin-down states in zero field. The clusters form a centered tetragonal crystal lattice inside which they weakly interact through magnetic dipolar forces. At low temperature, due to the high anisotropy, a crystal of Mn$_{12}$-Ac, can be prepared in a metastable spin state\textsuperscript{2}. The crystals exhibit extraordinary staircase magnetic hysteresis\textsuperscript{3} explained by resonant quantum spin tunneling. It also has been known for some time\textsuperscript{4} that at low temperature and high field-sweep rate, sufficiently large crystals exhibit an abrupt reversal of the magnetic moment. This effect has been attributed to a thermal avalanche in which the initial relaxation of the magnetization towards the direction of the field results in the release of heat that further accelerates relaxation. Direct measurements of the heat emission by Mn$_{12}$-Ac crystals\textsuperscript{5}, as well measurements of the magnetic relaxation in pulse fields\textsuperscript{6}, supported this conjecture. The avalanches have long been considered as undesirable events that prevent experimentalists from studying spin tunneling in large crystals. Our interest to avalanches was motivated by the fact that they create a large inverse population of spin energy levels.

The experimental setup is schematically presented in Figure 1. The sample was prepared by assembling together 20 single crystals of Mn$_{12}$-Ac of total volume $V \approx 22 \text{ mm}^3$. The conventional composition, lattice structure, and magnetic properties of the crystals have been confirmed by chemical, infrared, X-ray diffraction methods, and by SQUID magnetometry. The crystals were glued together with their c-axes parallel to each other within a maximum five-degree misalignment. The assembly was placed inside a cylindrical waveguide, 5 mm in diameter, with the c-axis approximately parallel to the axis of the guide. The InSb bolometer was positioned inside the waveguide, 13 cm above the sample located at the center of the measuring area of the SQUID magnetometer. The cooling agent was helium gas maintained at 1.8 K at the locations of the sample and the bolometer. Before conducting measurements of the sample, we placed the bolometer inside the measuring area of the magnetometer and
obtained the dependence of the resistance of the bolometer on temperature and the magnetic field. The voltage drop on the bolometer measured at a constant current goes down when it absorbs radiation. The spectral bandwidth of the commercial InSb bolometer is 60 GHz - 3 THz, and the response time when illuminated is less than 1 \( \mu s \) in the kelvin temperature range. To calibrate the bolometer response to the radiation, we used a heater that delivered measured heat pulses to the sample. The temperature of the sample was monitored by a thermometer in a thermal contact with the sample.

Figure 2A shows the magnetization curve obtained by sweeping the magnetic field between \(-2 \) T and 2 T at 1.8 K. For the sweep rate between 5 mT/s and 27 mT/s the avalanches reproducibly occur at \( B \approx \pm 1.4 \) T. At the time of the avalanche, the temperature of the crystals jumped by about 2 K, from 1.8 K to 3.8 K. Figure 2B shows two bursts of the radiation measured by the InSb bolometer during the total magnetization cycle at the field-sweep rate of 27 mT/s. These bursts have been observed in hundreds of hysteresis cycles and are completely reproducible in terms of their position and height. They coincide precisely with the occurrence of the avalanches. The time dependence of the burst is blown in Fig. 2C. Each burst is characterized by a steep decrease of the voltage drop on the bolometer within a time of the order of 0.03 s. It is followed by the slow increase of the voltage towards the noise level, which we interpreted as a thermal equilibration of the system. A similar equilibration has been observed after supplying a heat pulse to the sample. However, the short radiation burst preceding the equilibration appears to be a unique signature of the magnetization avalanche. The total magnetic energy released in the avalanche was \( B \Delta M \sim 2 \) mJ. Experimenting with heat pulses, we found that four times this energy (resulting in the 12 K temperature of the sample) was required to produce the bolometer signal of the level of the radiation burst from the avalanche.

The spin Hamiltonian of Mn12-Ac molecular cluster in the magnetic field applied along the c-axis, is

\[
\mathcal{H} = -DS_z^2 - FS_z^4 - bS_z + \mathcal{H}',
\]

where \( S \) is the spin of the cluster, \( D = 0.55 \) K and \( F = 1.1 \times 10^{-3} \) K are uniaxial anisotropy constants, \( b = g\mu_B B \) is the reduced magnetic field (with \( B \) being the actual field, \( g = 1.94 \) being the gyromagnetic factor, and \( \mu_B \) being the Bohr magneton), and \( \mathcal{H}' \) contains smaller terms that do not commute with \( S_z \) (see for details Ref.2). The energy
levels of (1) are given by

\[ E_m = -Dm^2 - Fm^4 - bm, \]  

with \( m \) being the magnetic quantum number for the spin of the molecule \( S \). At \( b = kD \), with \( k = 0, \pm 1, \pm 2, ... \), the levels \( m \) and \( m' \) satisfying \( m + m' = -k \) are nearly degenerate, as is illustrated in Figure 3 for \( k = 3 \). This resonance approximately corresponds to the field at which the avalanches have been observed.

For an individual molecule the rate of the spontaneous decay from the level \( m \) to the level \( m + 1 \) with the emission of light is

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

With the help of Eq. (1) one finds that at \( k = 3 \) the frequencies of the corresponding radiation are between \( f \approx 80 \text{ GHz} \) for the \( m = 1 \rightarrow m = 2 \) transition and \( f \approx 350 \text{ GHz} \) for the \( m = 9 \rightarrow m = 10 \) transition, that is, in the range of the InSb bolometer. The corresponding wavelengths are between 3.8 mm for the \( m = 1 \rightarrow m = 2 \) transition and 0.85 mm for the \( m = 9 \rightarrow m = 10 \) transition. At \( k = 3 \) and \( m = 1 \) the rate \( \Gamma_1 \) of Eq. (3) is of the order of \( 10^{-7} \text{ s}^{-1} \), that is, the lifetime of the corresponding excited state with respect to the photon emission is of the order of one year. Other individual magnetic dipole transitions in Mn\(_{12}\)-Ac have similarly low rates. However, as first noticed by Dicke\(^8\), \( N_m \) dipoles confined within a volume of size \( d \) which is small compared to the wavelength of the radiation \( \lambda \), cannot radiate independently. At \( d < \lambda \) a spontaneous phase locking of the atomic dipoles occurs that results in the coherent radiation burst with the power \( P_{SR} \propto N_m^2 \) emitted within a time of the order of \( \tau_{SR} \sim 1/N_m\Gamma_m \). This phenomenon, known as the superradiance or superfluorescence, has been widely observed in gases on increasing the concentration of the gas confined within a volume of dimensions \( d < \lambda \) (see reviews\(^9\)). In our case the condition \( d < \lambda \) is fulfilled at least for the first few transitions starting from \( m = 1 \). For \( m = 1 \) the superradiance rate would then be \( \Gamma_{SR} = 1/\tau_{SR} = N_1\Gamma_1 \), where \( N_1 \sim N \exp(-U_{eff}/T) \) is the population of the \( m = 1 \) level, \( N \) is the total number of Mn\(_{12}\)-Ac molecules available for the relaxation and \( U_{eff} \) is the effective energy barrier between the two wells shown in Fig. 3. For our sample, \( N \sim 6 \times 10^{18} \) and \( U_{eff} \approx 47 \text{ K} \). The latter corresponds to the distance from \( m = -10 \) to the \( m = -4, 1 \) resonance that dominates the magnetic relaxation at \( k \approx 3 \) and \( T = 3.8 \text{ K} \). Correspondingly, \( \exp(-U_{eff}/T) \sim 4 \times 10^{-6} \) and \( N_1 \sim 2 \times 10^{13} \). The rate of the electromagnetic decay of the
\[ m = 1 \text{ state then increases from } \Gamma_1 \sim 10^{-7} \text{s}^{-1} \text{ to } \Gamma_{SR} = N_1 \Gamma_1 \sim 2 \times 10^6 \text{s}^{-1}. \] The total duration of the relaxation due to the continuous supply of the population of the \( m = 1 \) level is given by \[ \tau = \tau_{SR} \exp(U_{eff}/T) \sim 0.1 \text{s}, \] which is in a remarkable agreement with experiment.

In our model the relaxation from the upper levels in the right well in Fig. 3 is dominated by the emission of photons, while at the lower levels it must switch to the emission of phonons due to the violation of the condition \( d < \lambda \) at the bottom of the well. This condition is one of the two basic requirements for the superradiance to occur. The other condition is that \( \Gamma_{SR} \) exceeds the rate of decoherence of the phases of the magnetic dipoles. In our case this decoherence is provided by spin-phonon transitions at a rate \( \Gamma_{phon} < 10^6 \text{s}^{-1}. \) Remarkably, the superradiance rate computed above, \( \Gamma_{SR} \sim 2 \times 10^6 \text{s}^{-1}, \) indeed, exceeds the phonon rate. Given the fact that our model also provides the correct duration of the avalanche, this is hardly a coincidence. It is, therefore, conceivable that the magnetization avalanche is an electromagnetic phenomenon to the same degree as it is a phonon runaway. This conjecture is supported by the experimental fact that avalanches only occur when the total number of molecules in a crystal assembly exceeds a critical value, \( N \sim 10^{18}, \) needed to ignite superradiance.

The work at the University of Barcelona has been supported by the European Commission through Contract No. IST-2001-33186 and by the Spanish Government through Contract No. MAT-2002-03144. The work of E.M.C. has been supported by the U.S. National Science Foundation through Grant No. EIA-0310517.

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FIG. 1: Experimental setup.
FIG. 2: (A) Hysteresis curve of the 20-crystal sample of Mn$_{12}$-Ac at $T = 1.8$ K and the field-sweep rate of 27 mT/s. Avalanches in the magnetization reversal reproducibly occur at $B \approx \pm 1.4$ T; (B) Variation of the voltage drop on the InSb bolometer as a function of the magnetic field. The radiation bursts detected by the bolometer coincide with the magnetization reversal; (C) Time dependence of the bolometer voltage for one of the radiation bursts seen in Fig. 2B.
FIG. 3: Spin levels of Mn$_{12}$-Ac in the magnetic field corresponding to the third resonance, $k = 3$. The horizontal axis represents the magnetic quantum number $m$. Arrows show the relaxation path from the initial state magnetized in the negative $z$-direction to the final state magnetized in the positive $z$-direction.