LOW TEMPERATURE MICROWAVE EMISSION FROM
MOLECULAR CLUSTERS

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ABSTRACT. We investigate the experimental detection of the electromagnetic
radiation generated in the fast magnetization reversal in Mn_{12}–acetate at low
temperatures. In our experiments we used large single crystals and assemblies
of several small single crystals of Mn_{12}–acetate placed inside a cylindrical
stainless steel waveguide in which an InSb hot electron device was also placed
to detect the radiation. All this was set inside a SQUID magnetometer that
allowed to change the magnetic field and measure the magnetic moment and
the temperature of the sample as the InSb detected simultaneously the radia-
tion emitted from the molecular magnets. Our data show a sequential process
in which the fast inversion of the magnetic moment first occurs, then the radi-
ation is detected by the InSb device, and finally the temperature of the sample
increases during 15 ms to subsequently recover its original value in several
hundreds of milliseconds.

Molecular clusters are nanomagnets showing important phenomena associated
to their magnetic anisotropy and the possibility to tune their quantum mechan-
ical properties by applying a magnetic field. The discovery of the resonant spin
tunneling between the degenerate spin levels at both sides of the anisotropy en-
ergy barrier [1, 2] was the first sign that quantum mechanics can reveal itself in
these magnetic units made of several hundreds of atoms. Since then, near thou-
sand papers on molecular magnets have been published [3]. Very recently a new
field combining molecular magnets, magnetization studies, cavities and electro-
magnetic radiation has attracted the attention of different groups. The most recent
works on this particular topic deal with the absorption and emission of microwaves
[4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15]. In this letter we report low temperature
experimental studies of the detection of microwave emission of Mn_{12} single crystals
inside a cylindrical waveguide. This work follows that published very recently [13],
focusing now on the time sequence of the reversal of the magnetic moment, the
emission of radiation and the heat release in the sample on the millisecond scale.

In Figure 1 we show the details of our experimental setup. Two kinds of samples
were investigated. In some experiments, the sample was made by assembling to-
gether several tens of oriented single crystals of Mn_{12}–acetate with a total volume
around 20 mm³. In some others, we used only one large single crystal having a
magnetic moment \( M \) close to one third of that of the assemblies of crystals \( (M \sim 1 \) emu). An InSb hot electron device, with a spectral bandwidth of 60 GHz – 3 THz,
was used to detect the electromagnetic radiation possibly emitted by the sample.
Both the sample and the detector were placed inside a stainless steel cylindrical
waveguide and the whole assembly was inserted in a commercial rf-SQUID (Superconducting QUantum Interference Device) magnetometer that allowed to change the temperature, $T$, and the magnetic field intensity, $H$, of the experiment. The distance, $d$, between the sample and the detector ranged from 8 to 20 cm.

In our experiments we measured simultaneously the magnetic moment and the temperature of the sample, $M$ and $T_s$, and the voltage drop at the detector, $V_{InSb}$. $M$ was measured using either the rf-SQUID magnetometer, with a time resolution of 20 s, or a 30-turn, 4-mm-diameter copper detection coil, with a time resolution of 10 $\mu$s. $T_s$ was measured by an attached ruthenium oxide thermometer with a time resolution of 2 ms at $T = 4.2$ K. $V_{InSb}$ was measured as a function of temperature and magnetic field. The experimental resolution time for the voltage drop at the InSb device was about 1 ms. The thermometer and the detector were calibrated at the different temperature and magnetic field values of the experiment. The easy axis of the crystals and the applied magnetic field were checked to be parallel to the axis of the waveguide and the magnetic properties of different sets of crystals were measured with the rf-SQUID magnetometer.

We swept the applied magnetic field up and down between -2 T and 2 T with a sweeping rate $dH/dt = 30$ mT/s for different experimental temperatures. Prior to all these experiments, we characterized both crystallographically and magnetically (we performed dc and ac measurements to get the resonant field values and the blocking temperature) all the crystals used in our experiments to confirm that the materials were only made of pure single Mn$_{12}$–acetate phase. The most important result is that the total magnetic moment reverses orientation at one of the different resonant fields, depending on temperature. That is, instead of observing only regular steps associated to resonant spin tunneling, single large jumps are seen at
Figure 2. Temporal evolution of $T_s$ (right scale) and $dM/dt$ (left scale) around the magnetic field value at which the magnetization reversal occurs, for an individual single crystal (upper panel) and an assembly of single crystals (lower panel) ($T = 2.0$ K).

Figure 3. Magnification at short times of the temporal dependence of $T_s$ (right scale) and $dM/dt$ (left scale) around the magnetic field value at which the magnetization reversal occurs, for an individual single crystal (upper panel) and an assembly of single crystals (lower panel) ($T = 2.0$ K).

the different resonances. For instance, for the experiments carried out at $T = 2.0$ K, the inversion of the total magnetic moment $M$ occurs at $H = 1.38$ T, while at $T = 2.6$ K it does occur at $H = 0.98$ T.

In Figure 2 we show the time dependence of $T_s$ and the time derivative of $M$, $dM/dt$, around the field value at which the magnetization reversal occurs for the cases of using a single crystal (upper panel) and an assembly of single crystals (lower panel). A short time magnification of Figure 2 is shown in Figure 3. For the case of the large single crystal, only one well defined magnetization reversal occurs (upper
Figure 4. Time variation of $V_{\text{InSb}}$ (right scale) and $T_s$ (left scale) due to the magnetization reversal at $T = 2.0$ K for an assembly of single crystals.

Figure 5. Time variation of $V_{\text{InSb}}$ (right scale) and $dM/dt$ (left scale) due to the magnetization reversal at $T = 2.4$ K for an assembly of single crystals.

panel), while several independent and sequential magnetization reversal are present in the case of the assembly of single crystals (lower panel). It is worth mentioning that in all cases the complete reversal of the total magnetic moment takes place in less than 3 ms. In fact, it takes longer when the temperature increases (e.g., 0.8 ms at $T = 1.8$ K and 2 ms at $T = 2.6$ K, for the case of the single crystal). The maximum variation of the temperature takes place in a time of a few milliseconds and a subsequent thermal relaxation of several hundreds of milliseconds follows to recover the initial temperature. The most interesting and intriguing results here are two: $T_s$ reaches a maximum value several milliseconds after the magnetization reversal occurs, and this value never goes above 4 K for the assembly of crystals and about 7 K for the large single crystal.

Figures 4 and 5 present the time dependence of the ac voltage signal of the detector, $V_{\text{InSb}}$, superimposed respectively to the time evolution of $T_s$ and $dM/dt$, respectively.
for the cases of the experiments carried out at $T = 2.0$ and 2.4 K using an assembly of single crystals. The voltage drop observed in the figures is made first of a fast signal of a few milliseconds duration and takes around 15 ms to recover its initial value. As in the previous figures, the initial time ($t = 0$) corresponds to a field value very close (the deviation is of the order of 0.01 Oe) to the magnetic field at which the first magnetisation reversal takes place. These phenomena are not detected above $T = 3.0$ K.

We also verified that warming the sample up to near 20 K by electric pulses of 100 ms through a ruthenium oxide heater in contact with the Mn$_{12}$ sample produces a single voltage drop at the detector of the same intensity and a time duration of hundreds of milliseconds. The voltage drop in this case is then different from the case of the magnetization reversal, as the detector does not register any fast pulse with a duration of a few milliseconds.

The Mn$_{12}$ molecules have total spin $S = 10$ and their magnetic properties are described by the spin Hamiltonian

$$\mathcal{H} = -DS_z^2 - FS_z^4 - g\mu_B H_z + \mathcal{H}',$$

where $D = 0.55$ K, $F = 1.2 \times 10^{-3}$ K, $g = 1.94$ and $\mathcal{H}'$ contains small terms that do not commute with $S_z$. The two energy minima corresponding to $m = \pm 10$ are separated by the so-called magnetic anisotropy barrier height $U = 65$ K. The $m$ and $m'$ eigenvalues of $S_z$ come to resonance at the field values

$$H_{m,m'} = n \frac{D}{g\mu_B} \left[ 1 + \frac{F}{D} \left( m^2 + m'^2 \right) \right],$$

where $m + m' = -n$. At $H_z \neq H_{m,m'}$, transitions between positive and negative $m$ occur due to thermal activation over the barrier height. However, at the resonance fields, $H_z = H_{m,m'}$, the transitions are combinations of thermal activation and quantum tunneling. At each resonant field the transition is mostly dominated by a pair $(m, m')$, which changes with the temperature of the sample. At the microscopic level, a Mn$_{12}$ molecule must be thus activated from the $m = -10$ level to the lowest $m$ from which tunnel becomes significant on the time scale of the experiment. The spin of the molecule then tunnels across the energy barrier and relaxes down the spin level staircase to the $m' = 10$ state, that is, towards the direction of the magnetic field. The corresponding energy difference between the $m = -10$ and the $m' = 10$ state is released in the form of phonons and photons. The phonon emission for the spin transition in one particular molecule is however much more probable than the corresponding photon emission. It has also been suggested that the total magnetization reversal due to spin-phonon avalanches is produced when the energy of the phonons released by many spin transitions cannot thermalise and cause the sample to warm up [10, 11, 12, 13, 14].

The maximum total Zeeman magnetic energy, $E_{\text{mag}} \simeq 2M_{\text{sat}} H$, released is of the order of mJ. As stated above, the heating associated to the avalanche increases the temperature of the sample to circa, but not above, 4 K in the case of assemblies of single crystals and about 7 K when using only one large single crystal. This experimental fact has been verified in all the experiments carried out at different temperatures and with total inversion of the magnetic moment occurring at different magnetic fields. Most important, though, is the fact that the sample starts heating
once the total magnetic moment has reversed orientation. Moreover, the radiation
detection overlaps with the reversal of the magnetic moment and occurs also before
the temperature of the sample reaches its maximum value. We should however
take these experimental facts with precaution, because the resolution time of the
thermometer is of the order of several milliseconds. In any case, these data may also
suggest that thermal avalanches are not necessary to produce the total inversion
of the magnetic moment and the radiation emitted from the sample is coupled mostly
to the very fast magnetic reversal.

The fact that the magnetic reversal is accomplished first in a time of less than 3
ms at \( T = 2.0 \) K may be an indication that the tunneling process occurs from the
ground state \( (m = -10) \). This would open the possibility of having the phonon laser
effect, suggested very recently by Chudnovsky and Garanin \[20\], as the mechanism
inducing spin tunnelling. The inversion of the total magnetic moment of the sample
consists in this case in the coherent fast reversal of the magnetic moment of many
molecules by tunnelling caused by phonon vibrations. As a consequence, a huge
number of molecules is driven to one of the excited states \( m' \) of the right side of
the potential well before the occurrence of the staircase decay to the ground state
\( m' = 10 \).

We come now to the point of how to explain the detection of radiation by the
InSb in the absence of enough thermal black body radiation emitted by the set
of crystals. For an individual molecule, the rate of spontaneous decay from the
\( m \) level to the \( m + 1 \) level due to photons is much lower than that for phonons,
\( \frac{\Gamma_m^{\text{photons}}}{\Gamma_m^{\text{phonons}}} = \left( \frac{v}{c} \right)^3 \), where \( v \) and \( c \) are respectively the speeds of sound
and light in the material, as a consequence of their very different density of states
\[21\]. The detection of electromagnetic radiation imposes, therefore, the following
question: under which conditions may we expect to detect photons rather than
phonons?

A plausible explanation is that the detected electromagnetic radiation could be
superradiance. In his seminal paper published in 1954 \[22, 23, 24\], P. H. Dicke first
postulated that in the case of having a set of \( N \) quantum dipoles of the size of the
wavelength of the emitted photons, a spontaneous phase locking of the quantum
dipoles through the medium should occur, and a short burst of radiation, the so-
called superradiance, should be emitted. Superradiance emission from molecular
magnets has also been recently suggested theoretically as a result of the fast level
crossing \[12\]. In our experiments, the wavelength of the emitted photons between
the spin states \( m \) and \( m + 1 \) and the size of the set of magnetic quantum dipoles are
both of the order of a few mm. The number of molecules participating in the fast
magnetisation reversal ranges between \( 10^{18} \) and \( 10^{19} \) for large single crystals and
assemblies of small crystals, respectively. The typical value for the energy released
in such reversal is of the order of mJ. Consequently, the average power released is
of the order of 1 W. However, the power detected in our experiments ranges from
3.0 \( \mu \)W at 2.0 K to 0.2 \( \mu \)W at 2.6 K. In case this radiation should be superradiance,
the power would be \( P_{SR} = N_m \hbar \omega \Gamma_{SR} \), where \( N_m \) is the number of molecules at
level \( m \) contributing to radiation emission, \( \hbar \omega \) equals the energy difference between
levels \( m \) and \( m + 1 \), and \( \Gamma_{SR} = N_m \Gamma_m^{\text{photons}} \). Considering that \( \Gamma_m^{\text{photons}} \sim 10^{-7} \text{ s}^{-1} \)[13, 21], and using \( \omega \sim 100 \text{ GHz} \) and \( P_{SR} \sim 3 \mu \text{W} \) as measured in our experiments,
the number of molecules participating in the superradiance emission, \( N_m \), is of the
order of \( 10^{12} \), which is less than the number of molecules populating the excited
spin levels. The requirement that all the spins have the same transition frequencies clearly imposes a strong restriction on the power emitted as superradiance. The fact that the total duration of the emission of radiation, $\tau$, depends exponentially on the temperature of the sample explains that small variations in $T_s$ produce large variations in $\tau$.

To summarise, we have found that the fast reversal of the total magnetic moment of a set of Mn$_{12}$ single crystals is accompanied by the emission of electromagnetic radiation of less than 3 ms duration and a power of the order of $\mu$W at $T = 2.0$ K.

This work has been supported by the European Commission Contract No. IST-2001-33186 and by the Spanish Government Contract No. MAT-2002-03144. A. Hernández-Mínguez acknowledges financial support from Spanish MEC.

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