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Resonant experiments in magnetism: superradiance and magnetic spectroscopy

J. Tejada*, R. Amigó, J.M. Hernandez, A. García-Santiago

Departament de Física Fonamental, Universitat de Barcelona, Fonamental Avda. Diagonal 647, Barcelona 08028, Spain

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Abstract

We discuss the use of high-spin molecular clusters combined with microwave resonators to generate coherent microwave radiation and measure its frequency and power. The staircase demagnetization energy in molecular magnets may appear as coherent emission of microwave power forming geometry-dependent standing waves in the resonator. We observed that the equilibrium magnetization of these materials is strongly affected by the microwave radiation injected into the resonator and also studied the influence of selective microwave absorption on spin tunneling.

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Keywords: Spin tunneling; Molecular magnets; Microwaves

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1. Introduction

The discovery of high-spin molecular nanomagnets has open a new window to study the phenomena occurring at the boundary between classical and quantum physics of the angular momentum. The most carefully studied molecular magnets are Mn_{12} [1–5] and Fe_8 [6–9]. The main advantage of working with molecular magnets is that we know well the spin Hamiltonian ruling classical and quantum magnetic properties of these systems and it is possible to get one-to-one correlation between experimental results and theory. For example, the Mn_{12} cluster has a tetragonal symmetry and is described by the Hamiltonian

$$H = -DS_z^2 - AS_z^4 - \mu_B g H_z S_z + H', \qquad (1)$$

where z is the easy anisotropy axis of the crystal, $D = 0.65\,\mathrm{K}$ is the longitudinal anisotropy, $A = 1.2 \times 10^{-3}\,\mathrm{K}$, S is the spin operator ($S = 10$), $\mathbf{H}$ is the longitudinal magnetic field, $g = 1.94$ is the g-factor and H' contains small terms that do not commute with S_z.

At non-zero field, the trivial algebra of Eq. (1) yields that the spin levels m and m' at the two potential wells associated to the uniaxial anisotropy term come to resonance at

$$H_z = H_{mm'} = -(m + m')\frac{D}{g\mu_B}\left[1 + \frac{A}{D}(m^2 + m'^2)\right]. \qquad (2)$$

That is, at $H \neq H_{mm'}$ transitions between negative and positive m occur due to thermal transitions over the anisotropy barrier, while at $H = H_{mm'}$ the transitions are combinations of thermal activation and quantum tunneling [10–14]. EPR experiments [4,5,8,15–18] have also established that the spin levels of molecular magnets show strong absorption of microwave radiation in the range of tens to few hundred gigahertz. Most recently, it has been suggested that a crystal of molecular cluster can also be a powerful source of coherent radiation [19].

In this paper, we show results for molecular clusters placed in between two Fabry–Perot superconductor mirrors exhibiting enhanced magnetic relaxation. In a second set of experiments we injected external microwave radiation in microwave resonators containing, in a well-determined place, a single crystal of Mn_{12} and we

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*Corresponding author. Tel.: +34-93-402-1155; fax: +34-93-402-1149.

E-mail address: antonio@ubxlab.com, jtejada@ubxlab.com (J. Tejada).

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observed peaks in the equilibrium magnetization at the resonant frequencies of the resonator. An enormous enhancement of the tunneling probability was also observed for certain frequencies.

2. Magnetic spectroscopy

We will start with the experiments when a single crystal of Mn_{12} molecular cluster is placed inside a microwave resonator and radiation power is externally introduced. The microwave power was generated using Hewlett-Packard HP83621 and the energy absorption was measured by a HP8510C network analyzer system. In the experiments shown here we swept the radiation from 0.1 to 20 GHz in steps of 0.02 GHz. We checked at room temperature that the nominal radiation power was 25 dB m and that reaching the resonator through the coaxial cable was −15 dB m. We will show results for the case of two five-turn resonant loops: the first one made up of 0.1-mm-thick 99.9%-pure copper wire with a diameter of 5.42 mm (resonator 1), and the second one made up of 0.015-mm-thick superconductor niobium–titanium alloy with a diameter of 3.09 mm (resonator 2). The coaxial cable and the resonator-Mn_{12} setup (RMS) were placed inside an MPMS SQUID magnetometer. The temperature constancy of the helium gas bath surrounding the RMS during the magnetic measurements was better than 0.002 K.

In Fig. 1 we show the equilibrium magnetization for the Mn_{12} single crystal inside resonator 1 (RMS1) in the superparamagnetic regime as a function of the frequency of the microwave radiation. It is clear that there are frequencies at which the magnetization shows sharp peaks, while between these peaks the magnetization is constant within an accuracy better than 0.01%. The results for Mn_{12} inside resonator 2 (RMS2) are similar, see Fig. 2, but the magnetization peaks occur at different frequency values. We checked for both resonators that while the positions of the peaks were not affected by the power of the microwave radiation, their intensities increase with the power of the radiation and also depend on the frequency. The average full-width at half-maximum (FWHM) of these peaks is of the order of 0.2 GHz. We also verified that the peaks coincide, within an accuracy of hundred megahertz, with those recorded for the reflection coefficient measured with the HP8510C network analyzer at room temperature. This shift may be attributed to the change of the magnetic susceptibility of the Mn_{12} crystal from 5 to 300 K. It can be concluded, therefore, that the gravity center of the magnetization peaks coincides with the frequency of the different resonant modes of the RMS. The reproducibility of all these data was checked by performing the same measurements several times.

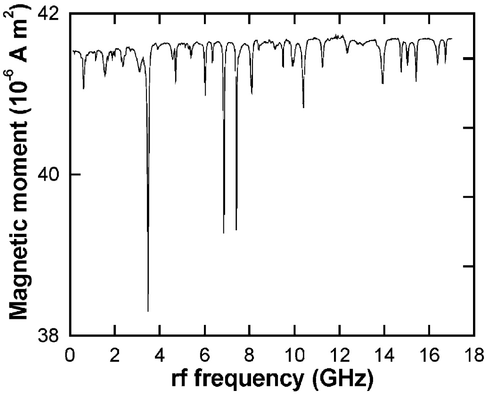

Fig. 1. Equilibrium magnetization of RMS1 at 5 K when a magnetic field of 3 kOe was applied on.

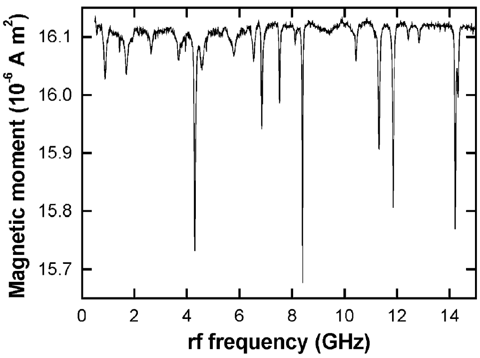

Fig. 2. Equilibrium magnetization of RMS2 at 5 K when a magnetic field of 3 kOe was applied on.

The figure of merit, Q, for each peak, estimated as the ratio between the frequency at the maximum of the peak, f, and the FWHM ranges between 100 and 300 for the different resonant peaks. Standing waves are then formed at the resonance frequencies and live a certain time of about 10^{-8} s. These standing waves are consequently depositing energy into the resonator during the 10 s that takes each magnetic measurement. This energy is partially dissipated at the surface of the copper wires and partially absorbed by the molecular cluster. The frequencies that do not match the different resonant modes of the device are reflected and do not produce any variation in the magnetization of the magnetic material. The energy dissipated at the surface of the copper wires introduces heat into the device and contributes therefore to the magnetization change. The energy absorbed by the sample will also change the equilibrium magnetization of the sample via modification of both the phonon spectrum, when the energy is absorbed by molecular vibration levels, or the magnetic relaxation, when the energy is absorbed by hyperfine nuclear levels.

These two absorptions are possible due to the high AC magnetic field associated with the resonant modes which compares very well to the usual AC fields in EPR experiments. This field may be calculated as $H^2_{AC} \approx 8\pi E/V$, where V is the volume of the resonator, $E = QP/2\pi f$ is the energy stored within, Q is the quality factor of the RMS, and P is the time-averaged power loss [20]. Using typical values involved in our experiments, we obtained $H_{AC} \approx 1$ Oe, which compares fairly well to the usual AC fields in EPR experiments [21], so that we should expect to have quantum transitions between levels whose spacing matches the energy of the photons.

3. Resonant spin tunneling

In this section we will describe the experiments performed to study the influence of the microwave absorption on the spin tunneling in Mn_{12}-acetate in the blocked state. The experiments were performed as follows: first we cooled the RMS2 down to 2 K, saturated the magnetization of the Mn_{12} single crystal in a magnetic field of 3 T, and then measured the demagnetization process until −3 T while injecting microwave radiation into the resonator. The frequencies of the radiation power were selected to produce all of them the same variation in the equilibrium magnetization of the Mn_{12}-acetate at 5 K. The low temperature isothermal demagnetization curves for some of these microwave frequencies are shown in Fig. 3.

From these data it is clear that the $M(H)$ values depend on both the microwave frequency and the applied magnetic field, suggesting that the pure thermal heating associated to the microwave power dissipation in the walls of the resonator is not the only source to explain the variation of the blocked magnetization.

Fig. 4 shows the differential susceptibility dM/dH calculated from the curves shown in Fig. 3. From the relative variation of the relaxation rate, which is proportional to dM/dH, for the different microwave frequencies we see that there are two contributions: a first one which is independent of the magnetic field and can be associated to the absorption of the microwave radiation by the molecular vibrational modes, and a second one which is field dependent and may be due to the microwave radiation absorption by either the hyperfine or the electronic spin levels. That is, the experimentally detected huge variation in the tunneling rates for the different microwave frequencies might be then well interpreted considering the hyperfine coupling between the electronic and nuclear spins. The simultaneous co-flipping via tunnel effect of both electronic and nuclear spins is governed by certain selection rules [21–25] and, consequently, the acceleration of the dynamics of the nuclear spins by the external AC field associated to the microwave power can significantly increase the tunneling rate.

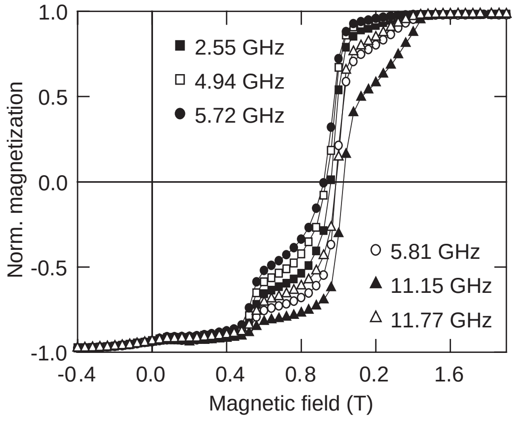

Fig. 3. Isothermal magnetization curves of RMS2 at 2 K for different microwave frequencies that produced the same amount of dissipated power in the RMS.

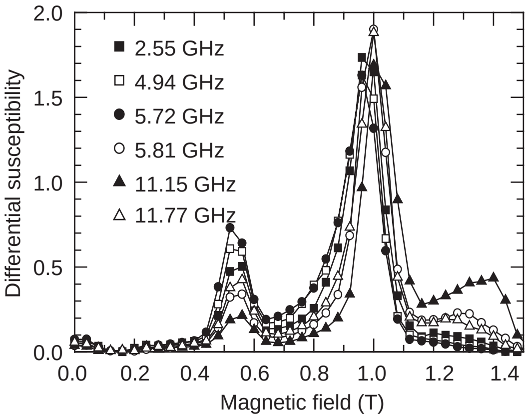

Fig. 4. Differential susceptibility curves of RMS2 at 2 K.

4. Coherent microwave radiation

Now we will describe the experiments performed without using the external microwave radiation power. Two superconductor Fabry–Perot mirrors were used as the resonator in these experiments and a Mn_{12} single crystal was placed between them. We also performed experiments using cylindrical cavities and the corresponding data are described in Ref. [26]. Each mirror consisted of a 200-nm-thick thin film of YBaCuO deposited by pulsed laser ablation onto a 1-μm-thick $SrTiO_3$ substrate. The superconducting properties were verified by DC and AC magnetic measurements below 90 K. The distance between the mirrors was changed by using a micrometric stepping motor control system having a spatial resolution of 1 μm.

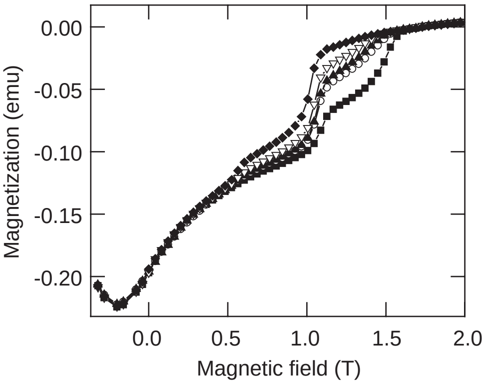

Fig. 5. Demagnetization curves of the Mn_{12}-acetate sample inside the Fabry–Perot setup at 2 K for five different distances between the superconducting mirrors ranging from 4.3 (*lowest curve*) to 6.0 mm (*topmost curve*).

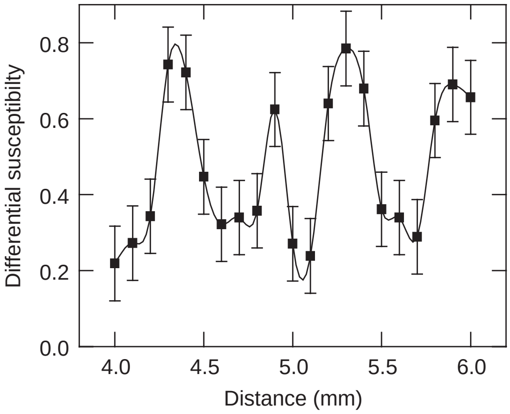

Fig. 6. Differential susceptibility of the Mn_{12}-acetate sample inside the Fabry–Perot setup at 2 K as a function of the distance between the superconducting mirrors.

Fig. 5 shows the demagnetization curves from the Fabry–Perot setup at 2 K, and the dependence of dM/dH on the distance between the mirrors at the zero field resonant field is shown in Fig. 6. We would like to make clear that in these experiments the Mn_{12} sample is also fully surrounded by the helium gas in the same manner as in the previous experiments and the common case of experiments carried out without using resonators.

The main result to explain here is the big changes in the relaxation rate observed at different distances between the superconductor mirrors. Several comments are in order:

(i) We verified that the magnetic signal due to the two mirrors does not depend on their mutual distance.
(ii) At zero field, the possible heating introduced by the magnetic field variation is very small and cannot therefore produce the observed variation in the magnetic relaxation.
(iii) Either phonons or photons (mostly microwave-like) can be emitted from the Mn_{12} sample during its staircase demagnetization process.
(iv) The phonon emisssion rate should not be modified changing the distance between the mirrors because the phonon wavelength is much smaller than the distance.
(v) The rate of emission of photons can be modified by the presence of the two mirrors when the photon wavelength matches the wavelength of a resonant mode.
(vi) For a Mn_{12} single crystal of 2 mm length, comparable to the wavelength of the emitted photons in the demagnetization staircase, the phase of emitted photons is the same for a macroscopically large number of molecules. In this case, the emission of photons can be correlated and superradiance may occur [19,27,28].
(vii) The main period of oscillations of the relaxation rate on the distance between the superconducting mirrors is about 0.5 mm, which is one-half of the wavelength of the 300 GHz photons responsible for the transitions between the $m = -10$ and -9 spin levels.

To conclude, we would like to mention that the combination of microwave resonators and molecular magnets suggests to use them as magnetic bolometers allowing also to perform a new magnetic spectroscopy. Our suggestion of superradiance emission should be checked by directly detecting the radiation.

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