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Microwave absorption and magnetization tunneling in Mn_{12}-acetate molecular clusters

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In this paper we study the effect of microwave absorption on the quantum relaxation rate of Mn_{12} molecular clusters. We have determined first the resonant frequencies of a microwave resonator containing a single crystal of Mn_{12}-Acetate and measured initial isothermal magnetization curves while microwave power was put into the resonator. We have found that the tunneling rate changes one order of magnitude for certain frequencies. This suggests that the microwave shaking of the nuclear spin and molecular vibrational degrees of freedom is responsible for the huge increasing of the tunneling rate.

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Physical properties of molecular clusters have been studied intensively in the past as a function of temperature and applied magnetic field.[1–8] The numerous experiments performed on Mn_{12}-acetate and Fe_8 clusters, together with the work of many theorists,[9–15] have very much improved the field of spin tunneling to now become a well defined arena to test new ideas and perform new experiments. 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 a one-to-one correlation between experimental results and theory. New theoretical suggestions and experimental results have recently appeared, making these systems very much attractive not only for basic research but also for applications in the field of microwave detection and generation. It has been theoretically suggested that the molecular clusters may emit microwave power in their staircase demagnetization process,[16] and it has been experimentally observed that the magnetization process of Mn_{12} single crystals occurs faster when they are placed inside a microwave resonator or between two superconducting Fabry-Perot mirrors.[17]

In this paper we show data for the case when a Mn_{12}-acetate single crystal is placed inside a microwave resonator which has resonant modes below 20 GHz. The microwave power was generated using Hewlett Packard HP83621 synthesized sweepers whose performances were accomplished when they were a part of 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. The nominal radiation power was 25 dBm, and the power reaching the resonator through the coaxial cable was measured to be about -15 dBm. In this work we used a resonant loop of 5.42-mm diameter which was made up of five coils of 0.1 mm thick 99.9%-pure copper wire. The coaxial cable and the resonator-Mn_{12} set up were inside an MPMS superconducting quantum interference device (SQUID) magnetometer. The ac magnetic field associated with the microwave radiation was perpendicular to the dc magnetic field applied in a parallel direction to the easy anisotropy axis of the molecule. The sample was surrounded by a helium gas bath used as a thermal contact between the magnetic sample and the resonator. The temperature constancy of the helium gas bath during the magnetic measurements was better than 2 mK.

Mn_{12}-acetate is a high-spin ($S=10$) molecular magnet that behaves as a superparamagnet above its blocking temperature $T_B \approx 3$ K, following the Curie-Weiss law $M \propto 1/T$. This yields a $1/T^2$ dependence for the thermal derivative of the magnetic moment, dM/dT, so that M shows the steepest variation as temperature decreases close to T_B. Below this temperature, the sample exhibits magnetic hysteresis and the values of the tunneling resonant fields are in full coincidence with those previously reported.[1–6]

Figure 1 presents the magnetic moment for the Mn_{12} single crystal in the superparamagnetic regime as a function of the frequency of the microwave radiation. The temperature of the thermal bath was kept constant at $T=5$ K during the whole process. The measurement of each point took 10 sec. We see that the magnetization of the Mn_{12} single crystals shows sharp peaks for certain frequency values, while between these peaks the magnetization is constant with an accuracy better than 0.01%. We also found that, while the positions of the peaks were not affected by the power of the microwave radiation, their intensity increased (for nominal power up to 10 dBm) and depended on the frequency as well. The average full width at half maximum (FWHM) of these peaks is of the order of 0.2 GHz.

This set of data may be interpreted in the scope of the dissipation and absorption of microwaves inside the resonator. The microwave frequencies whose values coincide with those of the corresponding resonant frequencies are filtered by the resonator. The rest of the frequencies are reflected and go all the way back through the coaxial cable. This point was

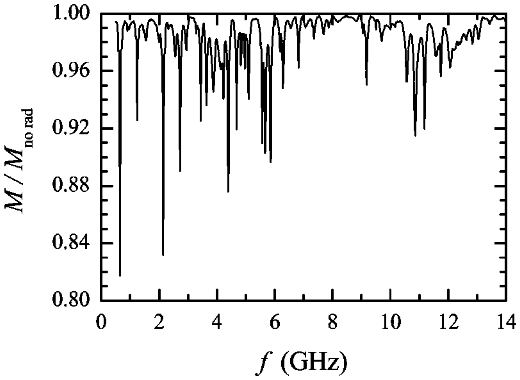

FIG. 1. Magnetization of the Mn_{12}-acetate sample inside the copper resonant loop as a function of the frequency of a-25 dBm microwave radiation. The magnetic moment was recorded with a magnetic field $\mu_0 H = 0.3$ T, when the thermal bath was at 5 K.

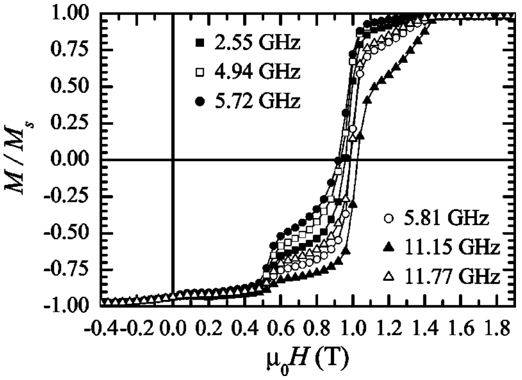

FIG. 2. Isothermal magnetization curves of the Mn_{12}-acetate sample inside the copper resonant loop obtained at 2 K for different microwave frequencies that produced the same amount of dissipated power.

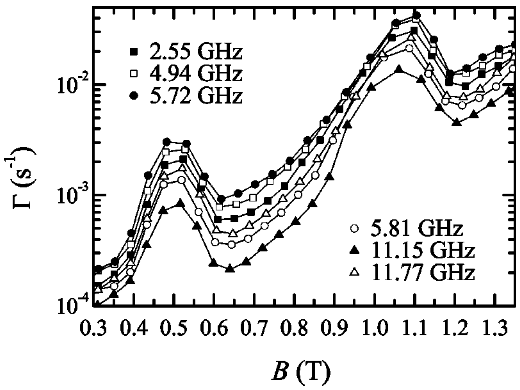

FIG. 3. Magnetic relaxation rates of the Mn_{12}-acetate sample inside the copper resonant loop calculated from the differential susceptibility dM/dH derived from Fig. 2.

verified by analyzing the reflection coefficient measured with the HP8510C network analyzer. For each resonant frequency, standing waves are formed in the resonator that live a certain time t according to the quality factor Q, which may be estimated at each frequency as the ratio between the frequency at the resonance and the FWHM of that resonance. This time is the characteristic decay time of the energy stored at each resonant mode and ranges from 10^{-8} to 10^{-7} s for the different magnetization peaks. A part of this energy will dissipate as heat in the surface of the copper resonator, due to the electrical currents induced, and another part will be directly absorbed by the magnetic sample.

The energy absorbed by the magnetic molecules can be due to molecular, mostly vibrational levels, hyperfine and electronic spin transitions. As a result of all these effects, the magnetization of the sample changes and the intensity of the change is related to the amount of energy delivered to the sample at each mode. Similar results have been obtained using different microwave resonators as coaxial cavities and superconducting coils,[18] suggesting that strong temperature dependent magnetic materials as the molecular clusters in their superparamagnetic regime can be used as spectroscopy bolometers.

In a second set of experiments we studied the influence of the microwave absorption on the tunnelling rate of Mn_{12}-acetate at temperatures below T_B. We cooled the sample down to 2 K, saturated its magnetization in a magnetic field of 3 T, and measured the demagnetization process until -3 T while irradiating the sample inside the resonator. The isothermal magnetization data obtained for different microwave frequencies are shown in Fig. 2. For this experiment we selected those microwave frequencies that produced the same variation in the equilibrium magnetization of Mn_{12}-acetate at 5 K; that is, the microwave power dissipated in the resonator-Mn_{12} setup was the same for all the selected frequencies. This fact suggests that the microwave frequency dependence of the isothermal magnetization cannot be explained only in terms of the pure thermal heating associated with the microwave power dissipation in the resonator.

To check this point, we should estimate the maximum thermal heating at 2 K produced by the microwave power dissipation at the resonator-Mn_{12} setup at the different microwave frequencies of Fig. 2. However, this kind of measurement is pointless, for Mn_{12}-acetate is blocked at 2 K and so its magnetization is out of equilibrium. Instead we used a single crystal of a Fe_8 molecular magnet, which is superparamagnetic down to 1.5 K,[19] and measured the magnetization variation at 2 K for each microwave frequency. The thermal heating estimated for all the frequencies used corresponds to a maximum temperature variation in the sample of $\Delta T = 170 \pm 20$ mK. The uncertainty in the heating associated to the different microwave frequencies can therefore not explain by itself the huge differences observed in the isothermal magnetization curves.

Figure 3 shows the relaxation rate Γ calculated from the differential susceptibility dM/dH derived from the curves of Fig. 2. It is clear from the figure that the induced acceleration in the relaxation rate at the different microwaves frequencies depends strongly on the applied magnetic field. For example, if we look at the $M(H)$ curves corresponding to the frequencies of 5.72 and 11.15 GHz (topmost and lowest curves), we see that the ratio between the tunneling rates for these two frequencies goes from 4.60 at $H = 6.4$ kOe ($\Gamma \simeq 9.76 \times 10^{-4}$ and 2.12×10^{-4} s^{-1} for 5.72 and 11.15 GHz, respectively) down to 1.97 at $H = 9.9$ kOe ($\Gamma \simeq 1.77 \times 10^{-2}$ and 0.89×10^{-2} s^{-1} for 5.72 and 11.15 GHz, respectively). The relative variation of the relaxation rate for the different microwave frequencies suggests the presence of two contributions: a first one which is independent of the magnetic field and is due to the absorption of microwaves by the molecular vibrational modes, and a second one which is field dependent and is due to the microwave absorption by either the hyperfine or the electronic spin levels. The observed acceleration in the tunneling rates for the different microwave frequencies might be then interpreted by considering the hyperfine coupling between the electronic and nuclear spins. It has been shown[15,20–23] that the interaction between electronic and nuclear spins results in certain selection rules for the simultaneous coflipping of these spins via quantum tunneling. Since the low temperature dynamics of nuclear spins can be very slow, the acceleration of these dynamics by the external ac field associated with the microwave power can significantly increase the tunneling rate.

Our data actually suggest that tunneling is the most effective cause for explaining the entire demagnetization process in Mn_{12}. The experimental fact is that the demagnetization is accelerated by the microwave power not only at resonant fields, but at many different field intensities. The existence of a large distribution of tunneling splitting was first associated with dislocations[8,24] and hyperfine levels,[20,22–24] and very recently to a discrete form of disorder due to a distribution in the positions of solvent molecules around the periphery of the Mn_{12} core.[25–28] This manifests itself as the simultaneous tunneling from different spin states and could make it possible to have that large variation in the demagnetization process of Mn_{12} due to the absorption of microwave power.

We can conclude that the decoupling of the nuclear spin from the electronic spin may be the main cause of the large variation of the tunneling rate when the Mn_{12} sample is irradiated with microwaves. The measurement of the variation of the equilibrium magnetization with the microwave power suggests that it is possible to use these results as a new spectroscopic magnetic bolometer. Future experiments should also consider the possibility to use moderate microwave pulses to produce the population inversion in molecular magnets.

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