Quantum dynamics of crystals of molecular nanomagnets inside a resonant cavity

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It is shown that crystals of molecular nanomagnets exhibit enhanced magnetic relaxation when placed inside a resonant cavity. Strong dependence of the magnetization curve on the geometry of the cavity has been observed, providing evidence of the coherent microwave radiation by the crystals. A similar dependence has been found for a crystal placed between Fabry-Perot superconducting mirrors. These observations open the possibility of building a nanomagnetic microwave laser pumped by the magnetic field.

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Many fascinating magnetic effects occur at the boundary between classical and quantum physics of the angular momentum. They have been intensively investigated, both theoretically and experimentally, over the last two decades. The discovery of high-spin molecular nanomagnets has given a strong boost to that field. The most carefully studied nanomagnets are Mn_{12} and Fe_{8} molecular clusters. Both have spin 10, which is twenty times the spin of electron. Such a large angular momentum is almost classical. Still crystals of Mn_{12} and Fe_{8} exhibit spectacular magnetic effects related to the quantization and quantum tunneling of the angular momentum. The current great interest of physicists to these systems was ignited by the discovery of the quantum stepwise magnetization curve in Mn_{12}-acetate, see Fig. 1. It has the following simple explanation. The Mn_{12} cluster has a tetragonal symmetry. In the magnetic field $H_z$ applied along the tetragonal axis, it is described by the Hamiltonian

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

where $S = 10$, $D \approx 0.55$ K, $A \approx 1.2 \times 10^{-3}$ K, $g \approx 1.94$, and $\mathcal{H}'$ contains small terms that do not commute with $S_z$. If one neglects $\mathcal{H}'$, then, in a zero field, the ground state of the cluster is double degenerate. The two energy minima correspond to the spin looking up or down along the Z-axis. They are separated by the magnetic anisotropy barrier $U \approx 65$ K. At a non-zero field, the trivial algebra of Eq. 1 yields that the $m$ and $m'$ eigenvalues of $S_z$ come to resonance at

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

see Fig. 2. At $H_z \neq H_{mm'}$ transitions between negative and positive $m$ occur due to the thermal activation over the anisotropy barrier in Fig. 3. However, at $H_z = H_{mm'}$, the transitions are combinations of thermal activation and quantum tunneling. Thus, for $H_z = H_{mm'}$ the anisotropy barrier is effectively reduced by tunneling and the magnetic relaxation towards the direction of the field is faster than at $H_z \neq H_{mm'}$. This picture, first established by magnetic measurements, has been confirmed by the careful EPR study of spin levels in Mn_{12}-acetate.

The EPR experiments have demonstrated noticeable resonant absorption of electromagnetic radiation by molecular magnets. Most recently, it has been suggested that a crystal of magnetic molecules can also be a powerful source of coherent microwave radiation. The radiation can be produced during the relaxation of the crystal towards the minimum of the magnetic energy. In this paper we provide first experimental support to this suggestion by demonstrating strong interaction between the Mn_{12}-crystal and a microwave cavity. Our intention was to test whether placing the crystal inside a resonant cavity would result in any change in the magnetization curve. Before showing the experimental data, let us discuss why the detection of such an effect would constitute the evidence of the coherent radiation inside the cavity.

Consider a crystal of Mn_{12}-acetate magnetized in the negative Z-direction. At $|H_z| < < 10$ T the distance $E_1$...
between \( m = -10 \) and \( m = -9 \) levels in Fig. 2 is about 14 K. Thus, at \( T << E_1 \), most of the molecules are occupying the \( m = -10 \) level. The occupation numbers of the excited states scale as \( \exp(-E/T) \) where \( E \) is the energy distance from \( m = -10 \). In the absence of a very large transverse field, quantum tunneling from \( m = -10 \) in Mn\(_{12}\) has a negligibly low probability. The thermodynamic equilibrium is achieved either through thermal activation or through thermally assisted quantum tunneling from excited states. The activation of molecules to the excited states is believed to be due to the absorption of phonons. At \( T << E_1 \) the rate of phonon-induced transitions from \( m = -10 \) to \( m = -9 \) for the Hamiltonian of Eq. (3) is given by 16

\[
\Gamma_{\text{phonon}} = \frac{\hbar S \omega_1^2}{12\pi \rho c_s} \exp\left( -\frac{\hbar \omega_1}{T} \right),
\]

where \( \omega_1 = E_1/\hbar \) is the frequency of the phonon (\( f_1 = \omega_1/2\pi \approx 300 \text{ GHz} \)), \( \rho \sim 1.8 \text{ g/cm}^3 \) is the mass density of the crystal, and \( c_s \sim 10^5 \text{ cm/s} \) is the speed of the transverse sound. At 2 K Eq. (3) yields \( \Gamma_{\text{phonon}} \sim 5 \times 10^5 \text{s}^{-1} \).

In order to have any effect due to the electromagnetic radiation, the absorption of photons must have the rate comparable to the rate of the absorption of phonons. This can be achieved in the EPR experiment in which the sample is placed in the ac magnetic field \( H_{ac} \) oscillating at frequency \( f_1 \). The rate of the absorption of photons in the EPR setup is given by 17

\[
\Gamma_{\text{photon}} = k \frac{S g^2 \mu_B^2}{\hbar} H_{ac}^2 F(\omega),
\]

where \( k \) is a numerical factor of order one that depends on the polarization of photons and \( F(\omega) \) is the shape function of the resonance. In the case of the Lorentzian line of the width \( \Delta \omega \), the shape function is given by

\[
F(\omega) = \frac{1}{\pi} \frac{\Delta \omega}{(\omega - \omega_1)^2 + (\omega - \omega_1)^2}.
\]

It reduces to the Delta-function \( \delta(\omega - \omega_1) \) for \( \Delta \omega \rightarrow 0 \). At a finite width, the maximal EPR rate is achieved at \( \omega = \omega_1 \) and is given by \( \Gamma_{\text{photon}} \sim g\mu_B S H_{ac}^2/\hbar \Delta H \), where \( \Delta H \) is the field width of the line, \( \hbar \Delta \omega = g\mu_B \Delta H \). In Mn\(_{12}\), \( \Delta H \) is of order of 400 Oe. Consequently, at \( H_{ac} \sim 1 \text{ Oe} \) the rate of the absorption of EPR photons becomes comparable to the phonon rate of Eq. (3) and the microwave power delivered to the Mn\(_{12}\) crystal can significantly alter the magnetic relaxation.

In our experiments no external ac magnetic field has been used. The crystal of Mn\(_{12}\)-acetate was simply placed inside a resonant cavity and the magnetization curve has been measured. Let us assume for the moment that only thermal photons are available for the transitions between, e.g., \( m = -10 \) and \( m = -9 \) levels. The wavelength of these photons is comparable to the dimensions of the cavity. Their magnetic field can be then estimated from \( H_{ac}^2/8\pi \sim (\hbar \omega_1)/V \exp(-\hbar \omega_1/T) \), where \( V \sim 5 \times 10^{-2} \text{cm}^3 \) is the volume of the cavity. This gives \( H_{ac} \sim 3 \times 10^{-8} \text{ Oe} \), as compared to \( H_{ac} \sim 1 \text{ Oe} \) needed to beat the phonon rate in the EPR experiment at \( \Delta H \sim 400 \text{ Oe} \). Thus at 2 K thermal photons inside the cavity excite Mn\(_{12}\) molecules at a rate that is fifteen orders of magnitude lower than the phonon rate. This is mainly due to the fact that at any temperature each cubic centimeter of a solid contains \( (c/c_m)^3 \sim 10^{15} \) times more thermal phonons than thermal photons. At \( T = 2 \text{ K} \) our cavity would have \( 10^{-3} \) average number of thermal photons of energy \( E_1 \). Consequently, the cavity should play absolutely no role in the magnetic relaxation unless it occasionally acquires a very large number of non-thermal photons. If all these photons have the same phase, their effect will be equivalent to the effect of the ac magnetic field in the EPR experiment and may become comparable to the effect of the phonons.

Single crystals of Mn\(_{12}\)-acetate have been grown with the average length and diameter of about 2 mm and 0.2 mm respectively. The elongation of the crystals was along the c-axis. The conventional composition and the structure of the crystals have been established by chemical, infrared, and X-ray diffraction techniques. In addition, the dc and ac magnetometry of the crystals have been performed. The same values of the blocking temperature and resonance fields, as previously reported, have been found.

In constructing resonant cavities we followed the procedures described in Refs. 21, 22. Five cylindrical cavities of different diameter and adjustable length were constructed using 99.99% purity copper. Two diameters were used: 1.6 mm and 3.2 mm. The length of the cavity was controlled with the help of the same-purity copper rod connected to the upper surface of the cavity. The micrometer stepping motor control system was used that had the spatial resolution of 1 \( \mu \text{m} \). The inner lateral and
FIG. 3: (A) Demagnetization curves, $M(H)$, of Mn$_{12}$-acetate crystal at $T = 2.0$ K inside the resonant cavity of diameter 1.6 mm for five different lengths of the cavity: $L = 21.0$ mm (black), $L = 20.9$ mm (red), $L = 20.1$ mm (green), $L = 19.8$ mm (dark blue), and $L = 19.5$ mm (light blue); (B) $dM/dH$ for the curves shown in (A).

planar surfaces of the cavity were polished to a roughness of less than 10 $\mu$m to achieve the quality factor between $Q = 10^3$ and $Q = 10^4$. The crystals were fixed in a vertical position at the bottom of the cavities, with the c-axis axis of the crystal parallel to the cylindrical axis of the cavity. The grease of high thermal conductivity was used to attach the crystal to the bottom of the cavity. The cavity containing the crystal was immersed in a helium gas inside the MPMS SQUID magnetometer. The upper moving surface made the cavity not hermetic, thus allowing the exchange of helium with the outside reservoir. The temperature inside and outside the cavity was monitored by carbon thermometers.

Before placing crystals inside the cavities the magnetic signal from the crystals and from the cavities have been measured independently. The signal from the crystal was always two orders of magnitude greater than the paramagnetic signal from the cavity. We then proceeded to the measurements of crystals inside the cavities. The system was first saturated by a 5 T field applied along the c-axis of the crystal. Then the field was swept in the opposite direction at the rate 40 Oe/s. Very similar behavior has been found in all of the cavities. Typical demagnetization curves from Mn$_{12}$-acetate crystals inside a resonant cavity are shown in Fig. 3B. The dependence of the relaxation rate, $\Gamma = |M(H) - M_{eq}(H)|^{-1}(dM/dH)$ (with $M_{eq}$ being equilibrium magnetization), on the length of the cavity at two resonance fields is shown in Fig. 4.

In a separate set of experiments we placed the Mn$_{12}$-acetate crystal between two Fabry-Perot superconducting mirrors. The mirrors were prepared using method described in Ref. 24. The 200 nm YBaCuO layers were deposited by pulsed laser deposition on a 1 $\mu$m SrTiO$_3$ substrate. Their superconducting properties below 90 K were verified by magnetic measurements. The magnitude of the diamagnetic signal from the mirrors was found to be comparable to the magnitude of the signal from the crystal, but independent from the distance between the mirrors. The demagnetization curves from the Fabry-Perot setup are shown in Fig. 5. The diamagnetic signal from the superconductors was subtracted from the total signal to obtain Fig. 5B. The dependence of $dM/dH$ on the distance between the mirrors at $H_z = 0$ is shown in Fig. 6.

The experimental data clearly demonstrate the dependence of the magnetic relaxation in Mn$_{12}$-acetate crystals on the geometry of the cavity. We have verified that this phenomenon appears only in cavities of high quality factor. Could it be due to effects unrelated to the electromagnetic properties of the cavity? The first thing that comes to mind is that in the confined geometry the cooling of the crystals by the flow of helium could be not perfect. The rate of thermally assisted quantum tunneling in Mn$_{12}$ depends on temperature exponentially. Thus, fluctuations in the hermetic properties of the cavity could, in principle, result in a significant change of the relaxation rate. For that reason we carefully monitored temperature inside the cavity. The temperature variation was found not to exceed 0.3%. Such small fluctuations of temperature cannot account for any measurable change in the relaxation rate. All data on the dependence of the rate on the length of the cavity and the magnetic
field were reproducible within a 6% experimental error. Strong dependence of the relaxation rate on the geometry of the confinement was also observed in a Mn_{12}-acetate crystal placed between superconducting mirrors, that is, when the helium gas circulated freely around the crystal. We, therefore, concluded that the observed phenomenon had nothing to do with thermal effects and was, in fact, due to the microwave properties of the cavity.

As has been discussed above, in order to affect the magnetic relaxation of a Mn_{12} crystal, the number of coherent photons in the cavity must be very large compared to the number of thermal photons. There is only one source of these photons, it is the crystal itself. To change the orientation of the magnetic moment, the molecule must first go up the staircase of spin levels and then go down (see Fig. 2). Thus, the magnetic relaxation in the crystal creates massive inversed population of the energy levels. These excited states decay via emission of phonons or photons. Without a cavity, the corresponding magnetic-dipole photon transitions would have a negligible probability compared to the probability of phonon transitions. Consequently, the relaxation towards thermal equilibrium would occur via the emission of phonons. Inside the cavity, however, a maser effect can take place if some of the frequencies of the emitted photons coincide with resonances of the cavity. The photon emitted by one molecule remains in the cavity and stimulates the emission of photons by other molecules. The shortest wavelength, \( \lambda \), of a photon corresponds to the transition from \( m = 9 \) to \( m = 10 \). For Mn_{12} at \( H = 0 \) it is about 1 mm. The wavelengths of photons emitted in other transitions are longer. Consequently, for a crystal of size 2 mm, the phase of the emitted photons is the same for a macroscopically large number of molecules, \( N = N_{SR} \sim (\lambda/2)^3 \). In that case the emission of photons by different molecules becomes correlated and the superradiance may occur [4].

The rate of the emission of a photon increases by a factor \( N_{SR} \). This effect is much stronger for photons than for phonons because the wavelength of photons is \( (c/c_s) \times \) the wavelength of phonons of the same energy. Thus, the \( (c/c_s)^3 \) smallness of the phase space of photons in comparison with the phase space of phonons is compensated by the \( (c/c_s)^3 \times \) times greater \( N_{SR} \). Crystals used in our experiments contained about \( 1.6 \times 10^{16} \) Mn_{12} molecules, so that each magnetization step in Fig. 3 and Fig. 5 involved more than \( 10^{15} \) molecules. For \( Q \sim 3 \times 10^4 \) the 300-Ghz photons stay inside the cavity during \( t \sim 10 \) ns. The reabsorption of the radiation by the crystal requires \( \Gamma_{\text{photon}} t > 1 \). According to Eq. (4), our picture is self-consistent if during the 10 ns field sweep across the tunneling resonance of width \( \Delta H \sim 400 \) Oe the cavity was affecting the magnetic relaxation through \( 10^3 (\Delta H/\Delta h) \) microbursts of superradiance of duration 10 ns or less, each burst involving \( 10^{12} (\Delta h/\Delta H) \) molecules whose resonances were distributed within \( \Delta h < 1 \) Oe.

The effect of \( 10^{12} (\Delta h/\Delta H) \) coherent photons inside the cavity would be similar to the effect of the 1 Oe ac magnetic field in the EPR experiment. That is, the absorption of the photons increases the population of the levels with \( m > -10 \) in Fig. 3 as compared to their ther-
ternal population. Contrary to the EPR experiment, however, in our case the photons absorbed in the left well in Fig. 3 must be the same photons that are emitted in the right well. One can think about this process as the recycling of the emitted photons by the crystal after the number of photons in the cavity reaches the critical value. To affect the magnetic relaxation, one of the frequencies, $\omega$, of the emitted photons should satisfy two conditions. The first condition is that $\omega$ coincides with one of the distances between the spin levels in the metastable well (the left staircase in Fig. 3). It is fulfilled for certain values of the field $H_z = H_z^*$ which are uniquely determined by the spin Hamiltonian. If $A$ in Eq. (3) were zero, the fields $H_z$ would coincide with $H_{mm'}(A = 0) = H_n = n D / g \mu_B$. Because of $A \neq 0$, however, $H_z$ are different from $H_{mm'}$ of Eq. (2), except for $H_z = 0$. Nevertheless, due to the fact that $A << D$, the fields $H_z$ must group around $H_n$. The second condition is that the resonant frequency corresponding to $H_z = H_z^*$ also coincides with one of the resonances of the cavity. It is achieved by manipulating the length of the cylindrical cavity or the distance between superconducting mirrors in the Fabry-Perot setup.

Strong support to the above picture comes from the fact that the main period of oscillations of the relaxation rate on the distance between superconducting mirrors, (see Fig. 3) is about $0.5 \text{mm}$, which is one-half of the wavelength of the $300 \text{GHz}$ photons responsible for the transitions between $m = -10$ and $m = -9$ levels. This resonance is the most important one because almost all molecules initially occupy the $m = -10$ state. Exciting these molecules to the $m = -9$ level alone changes the effective energy barrier by $E_1 \approx 14 \text{K}$, thus increasing the relaxation rate by a factor $\exp(E_1 / T) \approx 10^3$. For cavities, the length-dependence of the relaxation rate is more complicated. Photons emitted in the magnetic dipole transitions should be in resonance with the TM modes of the cavity. The latter, for a cavity of radius $R$ and length $L$, satisfy

$$\omega_{mn}^2 = \frac{c^2 \kappa_{mn}}{R^2} + \frac{\pi^2 c^2 p^2}{L^2},$$

where $p = 1, 2, 3, \ldots$ and $x = \kappa_{mn}$ is the $n$-th zero of the Bessel function $J_n(x)$. Matching the spectrum of the spin levels of Mn$_{12}$-acetate with the spectrum of the cavity should be the way to explain the dependence of the magnetic relaxation on the length of the cavity. We have not succeeded in that task so far. Both spectra are rather dense. Their comparison is complicated by the distribution of energy levels due to dipolar and hyperfine fields, crystal imperfections, etc.

The main message that we want to disseminate is that the magnetic relaxation of molecular nanomagnets inside a resonant cavity differs from the magnetic relaxation outside the cavity. It seems impossible to understand this effect without invoking the superradiance. Our findings open the possibility of building a microwave laser pumped by the magnetic field. Measurements of microwave radiation from cavities containing crystals of molecular nanomagnets should be the next step in this direction.

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