Resonant photon absorption and hole burning in Cr$_7$Ni antiferromagnetic rings

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Presented are magnetization measurements on a crystal of Cr$_7$Ni antiferromagnetic rings. Irradiation with microwaves at frequencies between 1 and 10 GHz leads to observation of very narrow resonant photon absorption lines which are mainly broadened by hyperfine interactions. A two-pulse hole burning technique allowed us to estimate the characteristic energy diffusion time.

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Magnetic molecules are currently considered among the most promising electron spin based quantum systems for the storing and processing of quantum information. For this purpose, ferromagnetic and antiferromagnetic systems have attracted an increasing interest. In the latter case the quantum hardware is thought of as a collection of coupled molecules, each corresponding to a different qubit. The main advantages would arise from the fact that they are extremely small and almost identical, allowing to obtain, in a single measurement, statistical averages of a larger number of qubits. The magnetic properties can be modelled with an outstanding degree of accuracy. And most importantly, the desired physical properties can be engineered chemically.

Recently, the suitability of Cr-based antiferromagnetic molecular rings for the qubit implementation has been proposed. The substitution of one metal ion in a Cr-based molecular ring with dominant antiferromagnetic couplings allowed to engineer its level structure and ground-state degeneracy. A Cr$_7$Ni molecular ring was characterized by means of low-temperature specific heat and torque-magnetometry measurements, thus determining the microscopic parameters of the corresponding spin Hamiltonian. The energy spectrum and the heat and torque-magnetometry measurements, thus characterized by means of low-temperature specific heat [6, 7, 10].

The measurements were made in a dilution cryostat using a 20 µm sized single crystal of Cr$_7$Ni. The magnetic probe was a micro-SQUID array equipped with three coils allowing to apply a field in any direction and with sweep rates up to 10 T/s. The electromagnetic radiation was generated by a frequency synthesizer (Anritsu MG3694A) triggered with a nanosecond pulse generator. This setup allows to vary continuously the frequency from 0.1 Hz to 20 GHz, with pulse lengths form ~1 ns to continuous radiation. Using a 50 µm sized gold radio frequency (RF) loop, the RF radiation was directed in a plane perpendicular to the applied field [11]. The electromagnet was converted into a microwave power of the generator could be varied from 0 to 20 dBm (10$^{-11}$ to 10$^{-1}$ W). The sample absorbs only a small fraction of the generator power. This fraction is however proportional to the microwave power of the generator.

Fig. 1a shows magnetization versus applied field curves for several field sweep rates at a cryostat temperature of 0.04 K. The magnetization loops exhibit a clear hysteresis which is characteristic for the phonon-bottleneck regime with a spin-phonon relaxation time to the cryostat of a few seconds [21]. In order to quantify the out-of-equilibrium effect, Fig. 1b presents the same data as in Fig. 1a but the magnetization $M$ is converted into a spin temperature $T_S$ using the equation:

$$M(T_S)/M_0 = \tanh(g\mu_B S \mu_0 H/k_B T_S)$$

with $S = 1/2$ and $g = 2.1$ [9]. Fig. 1b shows clearly a strong adiabatic cooling when sweeping the field down to zero field. Note that this cooling mechanism might be
used before qubit operations to reach extremely low temperatures even at relatively high cryostat temperatures. High frequency noise from the RF-loop around the sample leads to spin temperatures at 1 T being higher than the cryostat temperature.

Fig. 2 shows magnetization curves $M(H)$ in the quasi-static regime with a field sweep rate slow enough (0.00014 T/s) to keep the system at equilibrium. During the field sweep, RF pulses were applied to the sample with a pulse length of 1 $\mu$s and a period of 4 s between each pulse. Depending on the RF frequency, clear dips are observed which result from resonant absorptions of photons associated with spin transitions between the quantum numbers $m_s = 1/2$ and $-1/2$. After each pulse, the magnetization relaxes back to the equilibrium magnetization (see the fine structure in the inset of Fig. 2).

Typical relaxation measurements at a constant applied field after RF pulses of different durations are shown in Fig. 3. The relaxation is exponential with the rate independent of the pulse length. Detailed studies showed that the relaxation rate is dominated by the phonon-bottleneck regime, that is the spin-phonon relaxation time to the cryostat.

The inset of Fig. 3 presents the change of magnetization $\Delta M$ between the magnetization before and after the pulse as a function of the pulse length $w$. $\Delta M$ increases linearly with $w$ for short pulses of few tens of ns. It saturates for $w \approx 10 \mu$s and decrease for very long pulses because of cryostat heating effects. Non-resonant photon absorption is also observed for very long pulses.
The resonant photon absorption lines are often taken to estimate a lower bound on the decoherence time of a qubit. We therefore investigated in more detail the line width observed in Fig. 2. Fig. 4a presents a typical power dependence of the line width for continuous irradiation at 4.2 GHz. Resonant photon absorption is clear visible for a generator power larger than -60 dBm (1 nW). The line saturated at about -20 dBm (10 µW). Fig. 4b presents the absorption line for the pulsed technique (see Fig. 2) for several pulse lengths and a generator power of 15 dBm (32 mW). The resonant photon absorption is clearly visible for pulse lengths longer than 10 ns. Note that the pulse widths in Fig. 4a are nearly two times larger than those in Fig. 4b.

In order to shed light on the origin of the line width broadening, we developed a two pulse hole burning technique. The first pulse excites a fraction of spins that are in resonance during the pulse. In case of an inhomogeneous broadened line, the first pulse burns a hole into the line. Then, after a delay time \( t_d \) a second pulse of the same frequency is applied. For \( t_d = 0 \) the two pulses are equivalent to one long pulse that excites a certain amount of spins (dotted lines in Fig. 5). However, for non-zero delay times \( t_d \) the second pulse probes the evolution of spin excitation in the sample. For an inhomogeneous broadened line, the second pulse probes whether the burned hole of the first pulse evolved during the delay time. Fig. 5 shows the resulting magnetization variation \( \Delta M \) after two pulses as a function of delay time. It is shown that for \( t_d > 100 \text{ ns} \), \( \Delta M \) is clearly larger than for \( t_d = 0 \). This result suggests that the absorption lines in Figs. 2 and 4 are inhomogeneously broadened (at these time scales). The first pulse burns a hole into the line which starts to fill during the delay time. The filling time is clearly faster for an applied field in the center of the line (Fig. 5a) than at the border (Fig. 5b). It depends also on the pulse length: the longer the pulse length, the later starts the filling of the hole. Because the magnetization is relaxing back to equilibrium at a time scale much longer (phonon bottleneck regime), the hole filling can only be due to spins that are close to the resonance condition. Due to spin-spin interactions, the excited spin can give their energy to those spins, that is the energy diffuses from the excited spins to spins that are close to the resonance condition. The hole filling time is therefore dominated by spin-spin interactions and it can be called a energy diffusion time.

In our case of an assembly of identical spins, the line broadening is mainly due to dipolar and hyperfine interactions. The dipolar coupling energy can be estimated with \( E_{\text{dip}}/k_B \approx (g\mu_B S)^2/V \approx 0.1 \text{ mK} \) (S= 1/2 and \( V = 6.3 \text{ nm}^3 \)). The hyperfine coupling with the nuclear
spins can be obtained by considering the dipolar interaction of one Cr ion ($s = 3/2$) with the neighboring F nucleus having a nuclear spin $I = 1/2$. With $g_F = +5.26$ and the distance of $d = 0.2$ nm between F and Cr ions, the interaction energy is about 0.4 mK for each of the eight F nuclear spins. The hyperfine line broadening of all eight F nuclear spins is about 3 mK which corresponds to 5 mT, in good agreement with the observed line widths in Figs. 2 and 4. These line widths give a decoherence time of about 3 ns. Substantial reduction of the hyperfine broadening might be achieved by substituting the F ions with OH groups. The dipolar coupling can also be reduced by doping the crystal of Cr$_7$Ni molecules with Cr$_8$ molecules.

In conclusion, we presented magnetization measurements on a crystal of Cr$_7$Ni antiferromagnetic rings. Irradiation with microwaves at frequencies between 1 and 10 GHz leads to observation of very narrow resonant photon absorption lines which are broadened by spin-spin interactions. A two-pulse hole burning technique allowed us to estimate the characteristic energy diffusion time.

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