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Resonant microwave power absorption and relaxation of the energy levels of the molecular nanomagnet Fe_8 using superconducting quantum interference device-based magnetometry

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Energy levels and saturation of molecular nanomagnet Fe_8 crystals were investigated using a 95 and 141 GHz electron paramagnetic resonance (EPR) technique based on a standard superconducting quantum interference device (SQUID) magnetometer. The technique provides *quantitative* determination of the dc magnetic moment as a function of microwave power, magnetic field, and temperature. [DOI: 10.1063/1.2011793]

Single molecule magnets (SMMs) are of interest as potential components in high density memory storage, quantum computing,[1] and, due to high frequency resonances at low or no applied magnetic field, spintronics devices: Such as spin-based oscillators and signal processors.[2] Knowledge of the spin Hamiltonian parameters are generally obtained by high-field electron paramagnetic resonance (HFEPR) and neutron scattering measurements.[3–7] Current experimental interest are dynamic quantities such as the relaxation of the spins along the longitudinal axis, τ_1, which is a measure of the time for energy to be transferred from the spins to the phonons, and the transverse relaxation τ_2 which is a measure of the time that individual moments contributing to the transverse magnetization remain in phase. At low temperatures, when the magnetic heat capacity $C_m \gg$ lattice heat capacity C_{ph}, a phonon blockade may arise limiting the heat flow from the phonons to the cryostat.[8–11] We define τ_{ph} as the time constant characterizing the transfer of energy from the phonons to the cryostat, and τ_b as the time constant characterizing the energy transfer from the combined system of electron spins and phonons to the cryostat.[8,9] At high temperatures, when $C_m \ll C_{ph}, \tau_b$ becomes equal to τ_1.[8,9] Recently, efforts have been made to measure these dynamical quantities by micro-(superconducting quantum interference device) SQUID based magnetometry and micro-Hall magnetometry in the presence of microwave radiation, as well as by standard high-field EPR spectroscopy.[12–17] We use another new technique that is based on a standard commercial SQUID magnetometer coupled with high-power microwave energy generated by a klystron. This SQUID-based EPR technique was previously used to study DPPH and cupric sulfate pentahydrate, both simple $S=1/2$ paramagnetic systems.[18,19] Here we apply this technique to a high spin $S=10$ system to obtain qualitative data on τ_b as a function of temperature, field, and magnetic quantum state M_s (where M_s denotes the component of angular momentum along the easy axis of magnetization) as well as to determine a lower bound on τ_2. We study $[Fe_8O_2(OH)_{12}(1,4,7\text{-triazacyclononane})_6]Br_8 \cdot 9H_2O$, or Fe_8, which has been well characterized.[3–7,10,12–17,20–22] These studies have determined that the ground state is $S=10$. There are $2S+1$ M_s energy levels $(-10,-9,\cdots 9, 10)$. The energy as a function of moment angle is generally modeled as a double-well potential with the 10 negative M_s levels on one side and the 10 positive M_s on the other. The height of this barrier has been shown by ac susceptibility measurements to be about 22 K.[20,21]

A detailed description of the apparatus is given in Ref. 18. Briefly, we used a commercial SQUID magnetometer capable of field sweeps from 0 to 7 T and temperature sweeps of 1.8–400 K to obtain the magnetic moment. A 400 mW klystron operating at 95 GHz or a 141 GHz (100 mW) klystron generates the microwaves. The sample consisted of a single crystal (~ 3 mm^3 grown by the typical method)[23] with the high symmetry magnetic axis aligned approximately parallel to the applied dc magnetic field. The alignment was confirmed by comparison with powder spectra and iterative rotations to find the peak turning points.

In Fig. 1 is the magnetization as a function of magnetic field of an Fe_8 crystal in the absence (squares) and presence (stars) of microwave irradiation at 95 GHz at a cooling bath temperature of $T_b=4$ K. The exact sample temperature is not known but it is expected to be greater than T_b. Dips in the

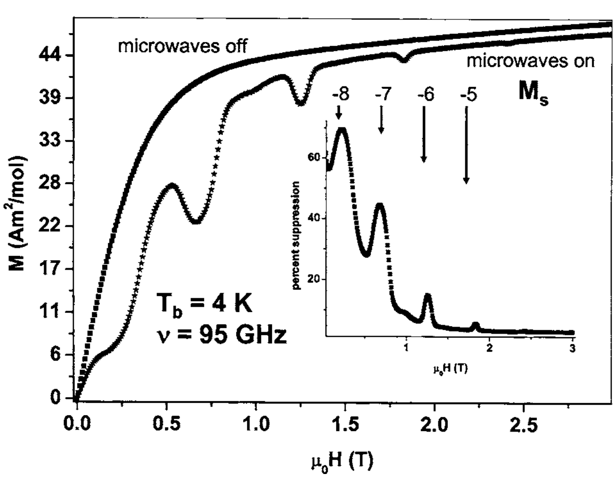

FIG. 1. Magnetization of a single aligned crystal of Fe_8 with $\sim H \| z$ as a function of magnetic field and microwave irradiation. The inset shows the percent of suppression as a function of swept field.

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magnetization are spaced at regular intervals. These dips correspond to resonant absorption of the microwave power at magnetic fields corresponding to the eigenstates of the standard spin Hamiltonian.[3–7,19] The lack of return to the baseline is attributed to nonresonant microwave heating.

The inset to Fig. 1 shows the suppression of the magnetization expressed in percent $(1-\mathrm{M}_{\mathrm{on}}/\mathrm{M}_{\mathrm{off}})\times 100$, where M_{on} and M_{off} are the z axis magnetization in the presence and absence of microwave irradiation, respectively. These peaks are assigned to the $S=10$ ground state and labeled with numbers representing the M_s from which the spins are excited by the $\Delta M_s=1$ transition; i.e., $M_s=-8$ represents the transition from $\mathrm{M_s}=-8$ to -7. Some deviations of the peak positions from the published spin Hamiltonian values are observed.[3–7,19] These are attributed to small misalignments and temperature dependent line-shifts from the buildup of internal dipolar fields.[7] These data represent *quantitative values of the magnetization without recourse to normalization* as function of M_s, magnetic field, and known microwave irradiation power for these high spin systems. The microwave irradiation power is known within only a factor of two to four.[18]

For a linearly polarized electromagnetic rf field and a system at thermal equilibrium the power absorbed P_a (in W/mol) in a transition between a lower and upper state is $P_a=(\frac{1}{2})\omega\chi''\mu_0 H_1{}^2, \omega$ is the angular frequency in rad/s,χ'' is the imaginary component of the transverse susceptibility in $\mathrm{m}^3/\mathrm{mol}$, and H_1 is the magnitude of the magnetic component of the oscillating field in A/m, which is proportional to the square root of the microwave power. For an $S=1/2$ system and in conjunction with the classical Bloch solutions for τ_1 it can be shown that $P_a=\chi_0\mu_0 H^2(1-M_{\mathrm{on}}/M_{\mathrm{off}})\tau_1{}^{-1}$, where χ_0 is the molar dc susceptibility in $\mathrm{m}^3/\mathrm{mol}$.[9,11,18] Hence, for a $S=1/2$ system by measuring the percent suppression and P_a in the low power linear region one can explicitly determine the energy transfer time as outlined in Refs. 11 and 18. However, for higher spin systems a quantum mechanical approach is essential and the absorbed power in W,P_{abs}, for a transition between states M_s and M_s-1 can be written:[9]

$$\mathbf{P}_{\mathrm{abs}}=\tfrac{1}{8}(N_i-N_j)(\pi\hbar\omega)(\gamma\mu_0\mathbf{H}_1)^2\{\mathbf{J}(\mathbf{J}+1)-\mathbf{M}_s(\mathbf{M}_s-1)\}f_{(\omega)} \tag{1}$$

where N_i and N_j are, respectively, the populations of the lower and upper states, J is the total angular momentum and $f_{(\omega)}$ is a shape function in seconds. Equation (1) predicts that power absorption should be: Linear with $H_1{}^2$ when $N_i \gg Nj$; nonlinear with $H_1{}^2$ as N_j populates and ΔN becomes a complex function of $H_1{}^2$; approach zero as N_j approaches N_i; and strongly M_s dependent. The population difference ΔN is a function of temperature, magnetic field strength, and a balance between the upward transition rate induced by the H_1 field and the downward relaxation rate τ_b. The τ_b is dependent on the M_s of the relaxing spin levels,[24] as well as the factors outlined in the introduction. At low temperatures in the presence of a phonon blockade the temperature of the sample may be a function of the microwave power complicating the ΔN term. At higher temperatures the excited states such as $S=9$ which is 24 K above the ground state would need to be considered.[6]

In Fig. 2 we plot the percent of magnetic suppression as a function of incident microwave power for the $M_s=-8$, $-7,-6,-5$ transitions. Despite the complications of heating

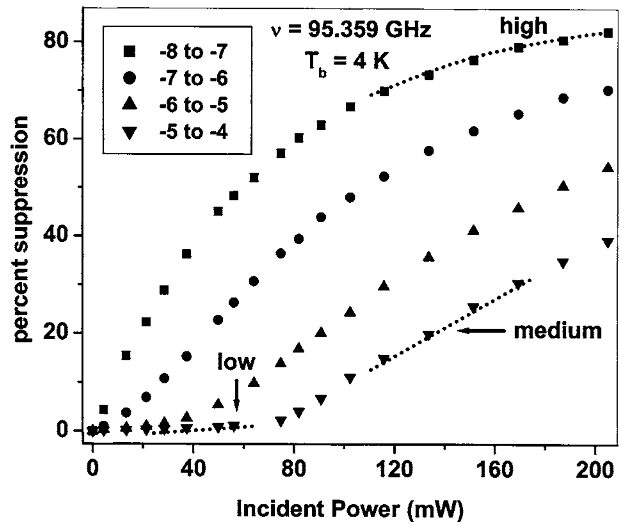

FIG. 2. The percent of suppression as a function of magnetic quantum number and microwave power at bath temperature of 4 K and 95 GHz.

from a phonon blockade these data can be qualitatively examined in the light of Eq. (1). There are three relaxation regimes, as marked (the dotted lines are guides for the eyes): Low and medium power linear regimes $(N_i>N_j)$ and a high-power $(N_i\sim N_j)$ nonlinear regime. For higher energy levels the system becomes more difficult to saturate. Suppression of the magnetic moment by 80% is attainable under these conditions for the $M_s=-8$ to -7 transition. This value is considerably larger than the $<5\%$ suppression expected if the two levels are completely saturated $(N_i=N_j)$. Upper excited states must then be populated. The transition from the low to medium power linear regimes is attributed to the transition from mostly photon generated transitions and relaxation between two levels to photon excitation followed by phonon-assisted processes over many levels. These data show P_{abs} is not a simple product of a two level resonance and the ΔN term in Eq. (1) is a complicated function of many energy levels.

In Fig. 3 we plot the percent suppression as a function of magnetic field for microwave irradiation of 141 GHz at 4 K (stars) and 10 K (solid line). A temperature-dependent low-

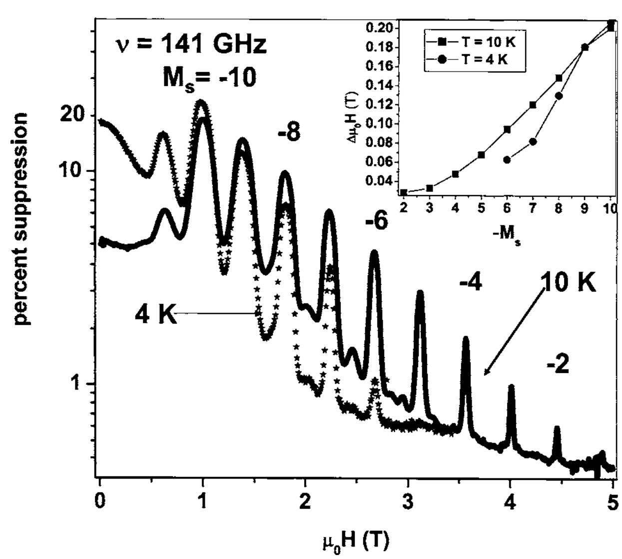

FIG. 3. A semilog plot of the percent of suppression as a function of swept field at two bath temperatures, 4 (stars) and 10 K (line), and microwave irradiation. The inset shows the $\Delta H_{1/2}$ as a function of M_s.

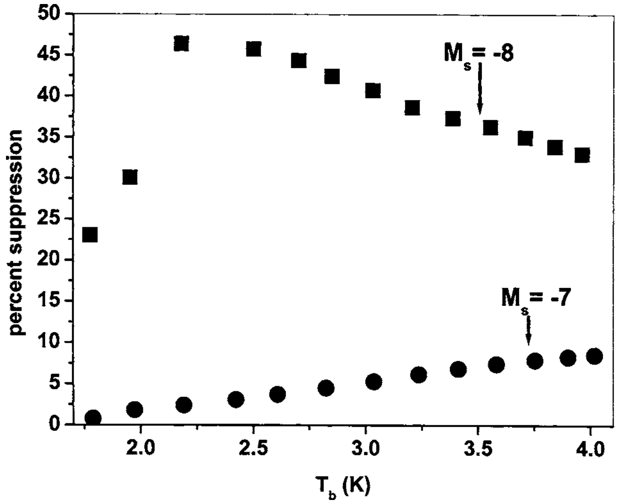

FIG. 4. The dependence of the percent of suppression on the bath temperature for the $M_s=-8$ and -7 transitions with resonant microwave stimulation at medium power.

field peak <1 T is present. We find that this peak is enhanced in powder spectra and thus attribute it to sample dependent impurities or conformations of Fe_8 resulting from solvent loss. The appearance of a peak at zero field is attributed to nonresonant heating, in good bath conditions, i.e., liquid helium, it is diminished. At 4 K, only the lower states $M_s=-10$ to -6 are sufficiently populated to allow power transfer. At 10 K, thermal population of the excited levels produces additional maxima in the field sweep corresponding to EPR $\Delta M_s=1$ resonances over the range of $M_s=-10$ to -2. In the inset of Fig. 3 we show the width at half-height, $\Delta H_{1/2}$, at 10 K (circles) and 4 K (triangles) as a function of M_s. In agreement with conventional EPR work,[6,7] the linewidths decrease rapidly as a function of $|M_s|$. Linewidths found by this method are about 35% broader at 10 K than those determined by conventional EPR.[6,7] It is currently unclear why. Small misalignments and sample degradation can dramatically increase linewidths. One can estimate a lower bound on the coherence times from the linewidths such that $\tau_2 \sim 2/(\gamma \Delta H_{1/2})$, i.e., for the $M_s=-3$ transition the lower bound to τ_2 is 3×10^{-10} s , in rough agreement with conventional EPR results.[4–7]

Figure 4 shows the temperature dependence of the percent suppression of the magnetization of the $M_s=-8$ and -7 transitions. The $M_s=-7$ level shows a monotonic increase whereas the $M_s=-8$ level shows a clear maximum in the percent saturation at ~ 2.3 K. We attribute this, at least partly, to thermal population of these states (N_i) increasing as the temperature increases, allowing more power absorption [see Eq. (1)] and hence more suppression of M_z. When the Boltzmann distribution has sufficiently populated the $M_s=-8$ state such that thermal population is not dominating power transfer, when the bath temperature is $T_b \sim 2.5$ K, the percent suppression begins to decrease. The decrease in percent suppression and thus τ_b with increased temperature is typical of the main EPR spin lattice relaxation processes.[9,18] The large magnitude of the magnetization suppression indicates significant population of upper excited states.[25] At these low temperatures, nonresonant heating and phonon blockades resulting in large resonant heating and can be invoked. However, measurements also show anomalous large suppression at 35 K. At high temperatures the phonons should be in equilibrium with the bath, and other mechanisms may be involved; for instance, cross relaxation.[26,27]

We find this method to be a useful complement to the micro-SQUID and micro-Hall based techniques, in that it is (a) based on a standard SQUID-magnetometer, hence a quantitative method, (b) is a bulk technique, as opposed to a micro-crystal methodology and (c) easily used over a broad range of temperatures and fields (d) and for $S=1/2$ systems explicit determination of τ_1 can be obtained.[11,18]

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[1] M. N. Leuenberger, D. Loss, Nature (London) **410**, 789 (2001).
[2] W. H. Rippard, M. R. Pufall, S. Kaka, S. E. Russek, and T. J. Silva, Phys. Rev. Lett. **92**, 027201 (2004).
[3] R. Caciuffo, G. Amoretti, A. Murani, R. Sessoli, A. Caneschi, and D. Gatteschi, Phys. Rev. Lett. **81**, 4744 (1998).
[4] A. L. Barra, D. Gatteschi, and R. Sessoli, Chem.-Eur. J. **6**, 1608 (2000).
[5] S. Maccagnano, R. Achey, E. Negusse, A. Lussier, M. M. Mola, S. Hill, and N. S. Dalal, Polyhedron **20**, 1441 (2001).
[6] D. Zipse, J. M. North, N. S. Dalal, S. Hill, and R. S. Edwards, Phys. Rev. B **68**, 184408 (2003).
[7] K. Park, M. A. Novotny, N. S. Dalal, S. Hill, and P. A. Rikvold, Phys. Rev. B **65**, 014426 (2002); S. Hill, S. Maccagnano, Kyungwha Park, R. M. Achey, J. M. North, and N. S. Dalal, *ibid.* **65**, 224410 (2002); S. Hill, R. S. Edwards, S. I. Jones, N. S. Dalal, and J. M. North, Phys. Rev. Lett. **90**, 217204 (2003).
[8] P. L. Scott and C. D. Jeffries, Phys. Rev. **127**, 32 (1962).
[9] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Dover, New York, 1986), Chap. 10.
[10] I. Chiorescu, W. Wernsdorfer, A. Muller, H. Bogge, and B. Barbara, Phys. Rev. Lett. **84**, 3454 (2000).
[11] G. A. Candela and R. E. Mundy, J. Chem. Phys. **46**, 47 (1966).
[12] L. Sorace, W. Wernsdorfer, C. Thirion, A.-L. Barra, M. Pacchioni, D. Mailly, and B. Barbara, Phys. Rev. B **68**, 220407 (2003).
[13] W. Wernsdorfer, A. Muller, D. Mailly, and B. Barbara, Europhys. Lett. **66**, 861 (2004).
[14] E. Del Barco, A. D. Kent, E. C. Yang, and D. N. Hendrickson, Phys. Rev. Lett. **93**, 157202 (2004).
[15] M. Bal, J. R. Friedman, Y. Suzuki, K. Mertes, E. M. Rumberger, D. N. Hendrickson, Y. Myasoedov, H. Shtrikman, N. Avraham, and E. Zeldov, Phys. Rev. B **70**, 100408 (2004).
[16] K. Petukhov, W. Wernsdorfer, A. L. Barra, cond-mat/0502175 (2005).
[17] S. Hill, R. S. Edwards, N. Aliaga-Alcalde, and G. Christou, Science **303**, 2033 (2004).
[18] B. Cage and S. Russek, Rev. Sci. Instrum. **75**, 4401 (2004).
[19] B. Cage, S. Russek, D. Zipse, and N. Dalal, J. Appl. Phys. **97**, 10M507 (2005).
[20] C. Delfs, D. Gatteschi, L. Pardi, R. Sessoli, K. Weighardt, and D. Hanke, Inorg. Chem. **32**, 3099 (1993).
[21] A. L. Barra, P. Debrunner, D. Gatteschi, Ch. E. Schulz, and R. Sessoli, Europhys. Lett. **35**, 133 (1996).
[22] A. Mukhhin, B. Gorshunov, M. Dressel, C. Sangregario, and D. Gatteschi, Phys. Rev. B **62**, 3022 (2000).
[23] K. Wieghardt, K. Pohl, L. Jibril, and G. Huttner, Angew. Chem., Int. Ed. Engl. **23**, 77 (1984).
[24] M. N. Leuenberger and D. Loss, Phys. Rev. B **61**, 12200 (2000).
[25] With the probe immersed in liquid helium and a Cernox thermometer mounted next to a 2 mg sample reading 4.3 K the $M_s=-8$ transition can be heated to a spin temperature of 10 K. Nonresonant heating in this configuration is found to be very small.
[26] N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, Phys. Rev. **114**, 445 (1959).
[27] We note that a simultaneous transition between four neighboring Fe_8 molecules a,b,c,d that conserves energy and populates an excited state is possible. For instance, the cw pump of -8 to -7 produces excess population in the -7 levels: This excess could be relieved by $a=-7$ to -6 $=13$ D, $b=c=-7$ to $-8=-15$ D and $d=-9$ to $-8=17$ D, $a+b+c+d=0$ and the -6 level has been populated.