Excited-state *X*-band EPR in a molecular cluster nanomagnet

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The *X*-band excited-state electron paramagnetic resonance (EPR) spectra of Mn_{12}-acetate nanomagnet crystals has been measured. Three lines belonging to the $m=-1 \leftrightarrow 0$ transition at $H_C = 600$ G and to the $m=0 \leftrightarrow -1$ and $m=-2 \leftrightarrow -1$ high-field transitions at 7800 and 9200 G, respectively, were detected below 50 K in agreement with the energy level scheme obtained from high-field EPR. The lines are rather broad. T_2 is shorter than 30 ns and $T_1 T_2 < 10^{-15}$ s². Similarly broad excited-state EPR spectra were also observed in a Fe(8) single crystal.

It is by now well established[1,2] that the Mn_{12}-acetate[3] spin cluster nanomagnet (the complete chemical formula is $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4] \cdot 2CH_3COOH \cdot 4H_2O$) offers the possibility to study the transition from simple molecular paramagnetism to bulk ferromagnetism. The magnetic properties of the cluster can be described by a single microscopic degree of freedom, i.e., its total spin $S=10$. At low temperatures the molecular spin magnetization can coherently tunnel through the Ising-type magnetic anisotropy barrier between the two opposite directions corresponding to two equivalent potential wells. The spin energy levels of Mn_{12}-acetate have been extensively studied in recent years by ac magnetization[4] studies, high-field electron paramagnetic resonance (EPR) (Refs. 5 and 6), and inelastic neutron diffraction[7] measurements.

However, to the best of our knowledge, there has been so far no report of any data on the direct measurements of the electronic spin relaxation behavior. The study of spin dynamics in Mn_{12}-acetate has so far almost exclusively been conducted with ac-susceptibility measurements,[8,9] which probe the overall dynamics of the entire magnetic cluster magnetization and not any particular spin state. In these ac-susceptibility measurements, it has been found that the correlation time for reorientation of the cluster magnetization is surprisingly long at low temperatures obeying the Arrhenius law $\tau = \tau_0 \exp(E_A/kT)$ with an activation energy $E_A = 64$ K and $\tau_0 \approx 10^{-7}$ s. At low temperatures the magnetization of the entire spin cluster tunnels through the magnetic anisotropy barrier instead of climbing over the barrier as evidenced from the magnetic field dependence of the relaxation time $\tau(H)$, which shows narrow minima whenever the spin energy levels E_m and E_m in the two nonequivalent potential wells match. Hernandez *et al.*[10] assumed that tunneling is driven by a transverse field alone, while Fort *et al.*[11] suggested that a fourth-order term $\mathcal{H}_{in-plane}$ is necessary to reproduce the experimental temperature dependence of the relaxation time τ. While the overall behavior of the cluster dynamics at low temperatures is by now relatively well understood, the details of the electronic spin relaxation are far from being completely clear. For instance, in Mn_{12}-acetate a recent measurement of the dispersion of the real and imaginary parts of the ac magnetic susceptibility[12] between 8 and 20 K showed a much higher activation energy $E_A = 160$ K and a much smaller prefactor $\tau_0 = 10^{-9}$ s.

The most direct way of testing the spin dynamics of Mn_{12}-acetate is the measurement of the electron spin-spin (T_2) and spin-lattice (T_1) relaxation times or the electron paramagnetic resonance linewidth using pulsed or cw EPR. Due to experimental limitations (e.g., serious phase distortions of the signal), the determination of the relaxation times via the measurement of the EPR linewidths in recent high-field cw EPR experiments[5,6] was found to be rather unreliable. These phase distortions are absent in the *X*-band EPR (~ 10 GHz). But so far it has been considered that because of its large magnetic anisotropy Mn_{12}-acetate is EPR silent in the *X* band.[13] This is so as the first EPR experiments in Mn_{12}-acetate failed to yield an *X*-band EPR spectrum at room temperature. We show in this paper that Mn_{12}-acetate is not EPR silent in the *X* band and that valuable information about the spin dynamics of Mn_{12}-acetate can be obtained from the excited-state *X*-band EPR at low temperatures.

We studied the *X*-band EPR of Mn_{12}-acetate single crystals in the excited states close to the top of the energy barrier. The range of temperatures covered was between 50 and 4 K. The splitting of the Mn_{12}-acetate spin cluster excited states in an external magnetic field is shown in Fig. 1. It can be seen that in the *X* band ($\nu_L = 9.7$ GHz) at around 600 G there should be a low-field allowed $\Delta m = \pm 1$ transition between the thermally populated $m=-1$ and $m=0$ levels [we assign this as the low-field (LF) transition]. The same two levels are again split by the same amount at a magnetic field of about 7900 G, but this time with the $m=-1$ level being higher in energy (HF1 transition). Still another transition, which also falls into our *X*-band EPR observation window, is the lower transition between $m=-1$ and $m=-2$ (HF2 transition), which is predicted to occur around 9000 G. We have observed all three transitions and studied their linewidths as a function of temperature and crystal orientation.

Black needlelike Mn_{12}-acetate single crystals prepared by the standard procedure[3] were selected and glued together with their long (*c* axes) parallel to each other, simulating a quasisingle crystal. The *c* axis is the four-fold axis of this
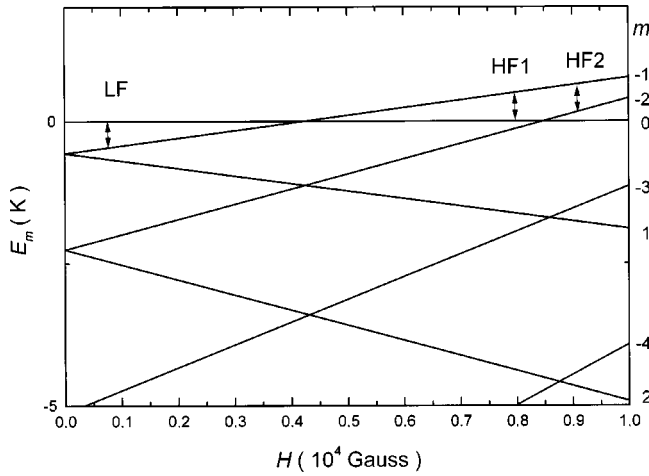
FIG. 1. Part of the energy level diagram of a Mn$_{12}$-acetate ($S = 10$) cluster as a function of the external magnetic field [Eq. (1)]. The arrows indicate the $\Delta m = \pm 1$ transitions that could be observed already in the X-band ESR experiment for $H \| c$. For the calculation of the energy level scheme, we have used the parameters of Barra *et al.* (Ref. 6).

FIG. 2. (a) X-band excited-state ESR spectra of Mn$_{12}$-acetate for $H \| c$ at $T = 16$ K. (b) X-band excited-state ESR spectra of a Fe(8) single crystal at $T = 50$ K. A weak peak at 1.8 kG seen in Mn$_{12}$-acetate comes from the Cr^{2+} signal of our dielectric resonator.

material, which has an overall tetragonal symmetry.[3] About 30 single crystals were needed in order to detect the weak excited-state EPR signals at low temperatures. The estimated error in the misorientation of the crystals within the bunch was smaller than $10°$. After the single crystals were glued together, they were sealed under vacuum in order to avoid further degradation of the sample with aging. All the EPR measurements were made with a Bruker E 580 spectrometer (which could be run in the pulsed as well as in the cw regime) equipped with an Oxford cryogenics liquid-helium cryostat. Temperature stability was better than ± 0.1 K.

At room temperature Mn$_{12}$-acetate exhibits only a weak broad peak around $g \approx 2$, which we ascribe to the degraded part of the sample. The same line was observed also in high-field EPR experiments[5,6] and will not be discussed further. The glue had no EPR signal as checked in an independent measurement. On cooling the sample below 50 K, three new lines emerged for $H \| c$ at about 600, 7500, and 9200 G [Fig. 2(a)]. These three lines were assigned as the LF, HF1, HF2 lines, respectively, as shown in Fig. 1. It is interesting to note that similar excited-state single-crystal X-band EPR spectra were also observed at 50 K in the $S = 10$ octanuclear iron molecular cluster Fe(8) [Fig. 2(b)], which also has a spin ground state $S = 10$ and an Ising-type magnetic anisotropy similar to the one in Mn$_{12}$-acetate.[14,15]

A strong argument for assigning the observed signals to excited-state X-band EPR transitions is the temperature dependence of their intensities. For all three lines we observe a broad intensity maximum around 22 K. Below this temperature the signal rapidly decreases with decreasing temperature. Such a behavior is characteristic for signals from an excited state. The intensity of the $m = -1 \leftrightarrow 0$ transition follows the $1/T$ temperature dependence of the electronic susceptibility at high temperatures, but at low temperatures it obeys a thermally activated behavior. Fitting the temperature dependence of the intensity of the LF line at $H \| c$ (Fig. 3), we

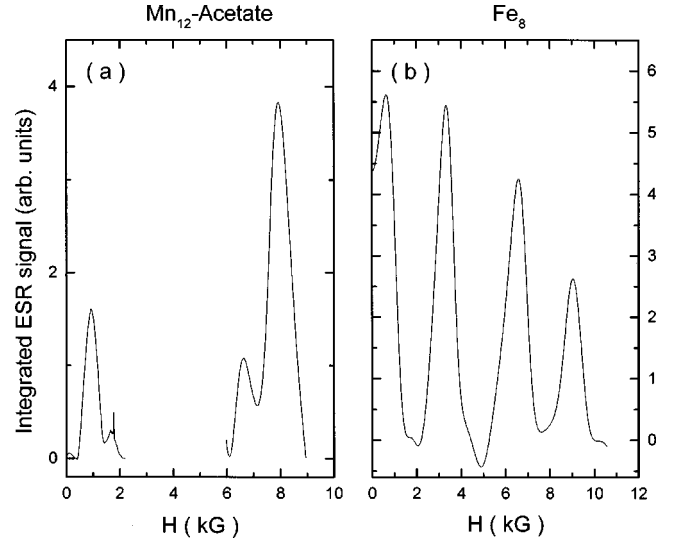obtained $D = 0.397$ cm^{-1} and $B = 4.2 \times 10^{-4}$ cm^{-1}, which is in good agreement with previously published results.[6] The barrier evaluated from

$$\mathcal{H}_0 = -D S_Z^2 - B S_Z^4 - g \mu_B H \cos \theta S_Z \tag{1}$$

is here about 64 K. Here θ is the angle between the magnetic field and the direction of the easy axis.

The center of the LF line is at 582 G at $T = 30$ K, while the those of the HF1 and HF2 transition lines were found at 7807 and 9360 G, respectively. Ascribing the lines LF1,
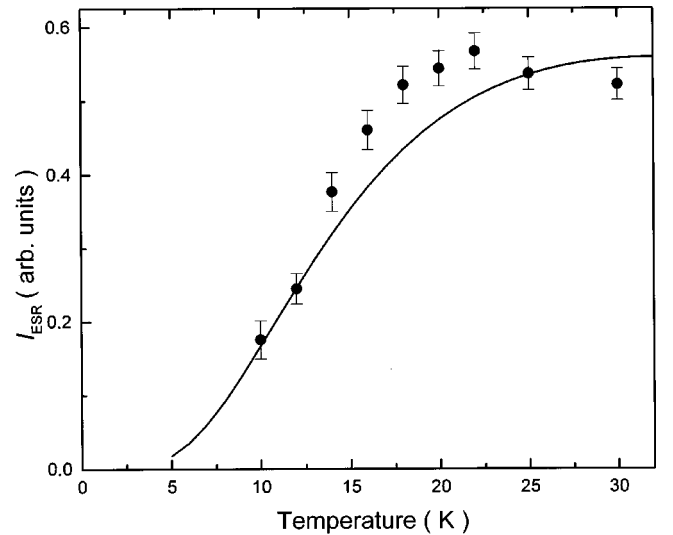

FIG. 3. Temperature dependence of the intensity of the LF excited-state ESR line in the X band in a Mn$_{12}$-acetate quasisingle crystal showing a broad maximum around 22 K. The solid line represents the calculated temperature dependence of the ESR intensity of the $m = -1 \leftrightarrow 0$ transition using $D = 0.397$ cm^{-1} and $B = 4.2 \times 10^{-4}$ cm^{-1}.
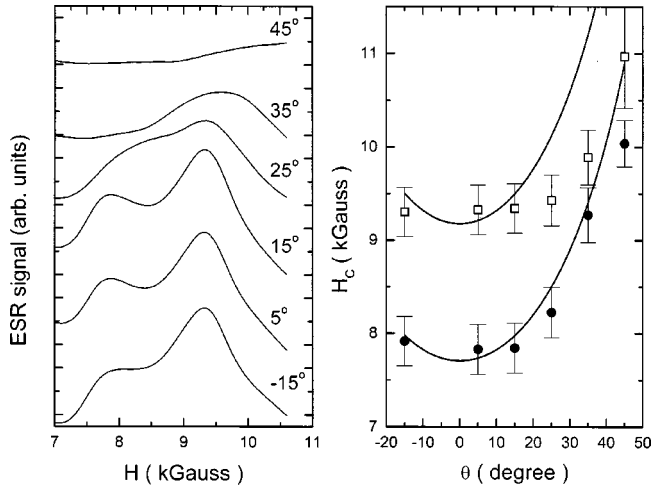
FIG. 4. (a) HF1 and HF2 X-band ESR spectra as a function of the orientation θ of the pseudocrystal in the external magnetic field and (b) the angular (θ) dependence of the positions of the HF1 and HF2 ESR lines.

FIG. 5. Temperature dependence of the peak-to-peak ESR linewidths (a) LF line and (b) HF line.

HF1, and HF2 to the transitions (Fig. 1) between $m = -1$ and $m = 0$, $m = 0$, and $m = -1$ and $m = -2$ and $m = -1$, respectively, we calculated D from the position of the line, i.e., $h\nu = E_0 - E_{-1}$. The calculated values of $D = 0.39$ cm^{-1} and $B = 5.5 \times 10^{-4}$ cm^{-1} provide additional support to the assignment of the observed lines to the excited-state EPR signal. The calculated parameters are in satisfactory agreement with the ones obtained from the temperature dependence of the intensity.

The assignment of the observed spectra to excited-state ESR lines is fully consistent with the strong angular dependence of the peak positions. Figure 4(a) shows a part of the observed angular dependence. The signals are clearly present when the external magnetic field is parallel to the crystal c axis, i.e., the axis of the uniaxial magnetic anisotropy, but are not found in our observation window when the magnetic field is applied perpendicularly to the c axis. As can be seen from Fig. 4(a), the high-field lines, present at $\theta = 0$, quickly disappear from the X-band observation window as θ is increased. The observed angular dependence of the positions of two high-field lines agrees [Fig. 4(b)] rather well with the angular dependence predicted on the basis of the previously determined magnetic anisotropy parameters: $D = 0.39$ cm^{-1} and $B = 7.6 \times 10^{-4}$ cm^{-1}.

The temperature dependence of the peak-to-peak width of the LF and HF2 lines is shown in Fig. 5. For the HF2 line the width increases from ~ 0.5 kG at 4 K to more than 0.9 kG at 55 K. The temperature dependence is not smooth, and a near saturation is seen around 25 K which is followed by a second increase of the width at higher temperatures. The width of the LF line, on the other hand, rapidly increases with increasing temperature from 0.38 kG between 4 and 20 K and then saturates at a value ~ 0.5 kG.

Spin dynamics could be in principle most directly probed by measuring the spin-spin (T_2) or spin-lattice (T_1) relaxation times. We have tried to measure the relaxation times using pulsed EPR techniques (two-pulse-echo decay sequence for T_2 and inversion recovery pulse sequence for T_1
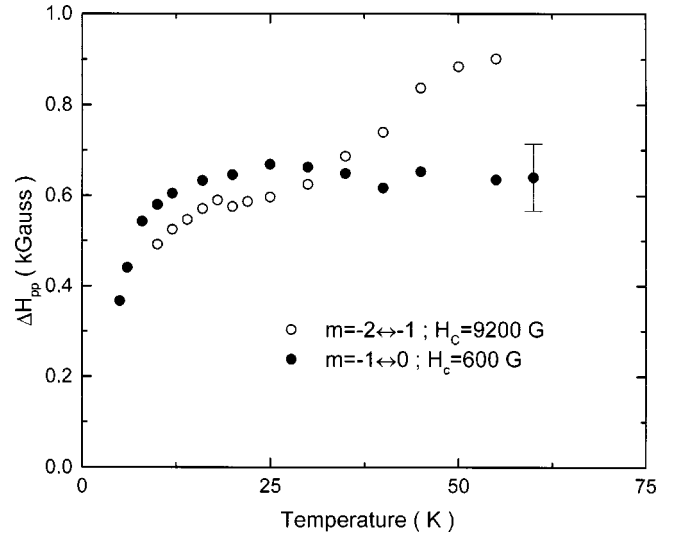
measurements). However, no free induction decay (FID) or spin echo was observed on a Bruker pulsed E 580 X-band EPR spectrometer operating at 9.7 GHz. This means that the upper limit for the T_2 as well as for the spin memory time T_M is about 30–50 ns, i.e., so short that the free induction decay and spin echo decay are already within the dead time of our spectrometer.

We also attempted to measure the spin-lattice relaxation time T_1 using the cw signal saturation method. It was found that even with microwave powers up to $P = 200$ mW the signals still increased as $P^{1/2}$ and thus spin-lattice relaxation times could not be determined. Since the intensity maximum is expected at $\gamma^2 H_1^2 T_1 T_2 = 1$, this demonstrates that $T_1 T_2 < 10^{-15}$ s^2.

There are several possible origins for the rather large width of the observed excited-state ESR lines: homogeneous broadening due to electron dipole-dipole interactions or spin-phonon interactions and inhomogeneous broadening due to anisotropic hyperfine interactions with the Mn nuclei, g-factor anisotropy broadening, misorientation of the crystals, or distribution of demagnetizing fields. Let us now qualitatively discuss these possibilities point by point.

If the observed lines would be homogeneously broadened due to electron-electron dipolar interactions, then $T_2 = 1/\pi\gamma\Delta H_{1/2}$. If the total linewidth were due to dipolar broadening then the linewidth gives us a T_2 of 0.1 ns and the bound on $T_1 T_2 < 10^{-15}$ s^2 would give a T_1 shorter than 10^{-5} s consistent with the NMR results. If on the other hand the homogeneous broadening were due to spin-phonon interactions, then $T_2 \approx T_1 \approx 0.1$ ns. This is much shorter than the value of the electronic spin-lattice relaxation time $T_1 = 10^{-7}$ s derived from the proton NMR T_1 data.[16] To check on that we performed an estimate of the maximum dipolar linewidths from the known crystal and electronic structure of Mn$_{12}$-acetate. It should be remembered that the Mn$_{12}$-acetate spin cluster contains four Mn^{IV} ($S = 3/2$) and eight Mn^{III} ($S = 2$) paramagnetic ions and that the $S = 10$ ground state is the result of competing antiferromagnetic Mn^{IV}-Mn^{III},

Mn^{IV}-Mn^{IV}, and Mn^{III}-Mn^{III} pair interactions between these 12 ions. The resulting width is of the order of 10^2 G and is somewhat smaller than the observed width. We can therefore conclude that a rather significant contribution to the linewidth is of electronic dipolar origin, i.e., of homogeneous nature. This agrees with the fact that no spin-echo signal could be observed and that the lines could not be saturated even at rather high microwave powers. This contribution should be exchange narrowed at low temperatures, thus explaining a part of the observed temperature dependence of the linewidth.

Another contribution is due to inhomogeneous broadening. The inhomogeneous part of the broadening should be responsible for the fact that the high-field lines are broader than the low-field lines. This can be due to g-factor anisotropy or distribution of demagnetizing fields due to a distribution of crystal shapes. This last contribution is not only field, but also temperature dependent, as it is proportional to the sample magnetization. Each of this contributions can be estimated to be of the order of at least 100 G. Additional support for the absence of the hyperfine interactions as a source of line broadening in Mn_{12}-acetate is obtained from the fact that in this temperature range the EPR linewidths of Mn_{12}-acetate and Fe(8) are almost identical even though in Fe(8) hyperfine interactions are absent (Fig. 2). This is due to the fact that neither Fe nor oxygen nuclei have a sufficiently large fraction of magnetic isotopes in natural abundance.

In summary, we have detected and analyzed the excited-state X-band EPR spectra in Mn_{12}-acetate. In the range between 60 and 4 K, three lines at $H_C \sim 600$, 7800, and 9200 G were observed, with center positions in accordance with the energy scheme obtained in high-field EPR experiments. The angular variation of the line positions and the temperature dependence of the line intensities confirm their assignments to the respective transitions. The cw linewidths vary between 400 and 1000 G, and are strongly temperature dependent. From the saturation behavior and the absence of the electron spin echo or FID, one finds that the electronic T_2 is shorter than 30 ns and that $T_1 T_2 < 10^{-15}$ s^2. A significant source of line broadening is of homogeneous nature and due to electron-electron dipolar interactions. The inhomogeneous contribution to the line broadening seems to be due to the distribution of demagnetizing fields as a result of the distribution of crystal shapes as well as g-factor anisotropy.

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