Electron Paramagnetic Resonance Linewidths and Lineshapes for the Molecular Magnets Fe$_8$ and Mn$_{12}$

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Abstract

We study theoretically Electron Paramagnetic Resonance (EPR) linewidths for single crystals of the molecular magnets Fe$_8$ and Mn$_{12}$ as functions of energy eigenstates $M_s$, frequency, and temperature when a magnetic field along the easy axis is swept at fixed excitation frequency. This work was motivated by recent EPR experiments. To calculate the linewidths, we use density-matrix equations, including dipolar interactions and distributions of the uniaxial anisotropy parameter $D$ and the Landé $g$ factor. Our calculated linewidths agree well with the experimental data. We also examine the lineshapes of the EPR spectra due to local rotations of the magnetic anisotropy axes caused by defects in samples. Our preliminary results predict that this
effect leads to asymmetry in the EPR spectra.

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Molecular magnets such as Mn$_{12}^1$ and Fe$_8^2$ have recently drawn much attention because of the macroscopic quantum tunneling of their magnetizations at low temperatures$^3$ and their possible applications to quantum computing.$^4$ These materials consist of many identical clusters (see Fig. 1) with the same magnetic properties and characteristic energies. Each cluster has many different species of ions and atoms, with a total spin angular momentum in the ground state of $S=10$. The clusters have strong crystal-field anisotropy and, thus, a well-defined easy axis, and the magnetic interaction between different clusters is weak.

Recently, multi-frequency Electron Paramagnetic Resonance (EPR) measurements$^5-7$ on single-crystals of the molecular magnets Fe$_8$ and Mn$_{12}$ showed interesting results in the linewidths as functions of the energy level $M_s$, excitation frequency, and temperature when a magnetic field along the easy axis was swept with the excitation frequency fixed. Figures 2(a) and (b) show the experimental linewidths as a function of the value of $M_s$ from which the spin system is excited. For example, $M_s=5$ in Fig. 2(a) denotes the transition $M_s=5\rightarrow4$. The experimental results are that (i) the linewidths are about 200 G to 1400 G at $T=10$ K for Fe$_8$ [Figs. 2(a) and (b)], and about 1000 G to 2000 G at $T=25$ K for Mn$_{12}$; (ii) the linewidths increase non-linearly as a function of the absolute value of the energy eigenstate $M_s$ [Figs. 2(a) and (b)]; (iii) the linewidths attain a minimum at $M_s=1$ and $M_s=0$ [Fig. 2(a)]; (iv) the linewidths decrease with increasing frequency (compare the linewidth for $M_s=5$ in Fig. 2(a) with that in Fig. 2(b)).

In this paper, we present the theoretical EPR linewidths for single crystals of Fe$_8$ and Mn$_{12}$, using density-matrix equations with the assumption that the uniaxial crystal-field anisotropy parameter $D$ and the Landé $g$ factor are randomly distributed around their mean values (“$D$-strain” and “$g$-strain” effects$^8$) due to possible random defects and impurities in the samples. We find that the calculated linewidths$^9$ agree well with recent experimental data$^6,9$ as functions of the energy level $M_s$ and the frequency. We also briefly consider the effect of the temperature on the linewidths. Finally we present a preliminary analysis of how local rotations of the magnetic anisotropy axes, caused by defects in the samples, affect the lineshapes.
To obtain the linewidths for Fe$_8$, we consider a single-spin system with $S=10$ in a weak oscillating transverse field. We choose the easy axis to be the $z$-axis. Since the Fe$_8$ clusters have an approximate $D_2$ symmetry, the lowest-order ground-state single-spin Hamiltonian is

$$\mathcal{H}_0 = -DS_z^2 - E(S_x^2 - S_y^2) - g\mu_B H_z S_z,$$

where $D=0.288 k_B$ and the transverse anisotropy parameter, $E=0.043 k_B$. Here $S_\alpha$ is the $\alpha$-th component of the spin operator, $g$ is the Landé $g$-factor ($\approx 2$), $\mu_B$ is the Bohr magneton, and $H_z$ is the longitudinal static applied field. When $H_z$ is large enough, the eigenvalue of $S_z$, $M_s$, is a good quantum number. Next we introduce an interaction $V(t)=V_0 \cos(\omega t)$ between the spin system and an oscillating transverse field $H_x$ with angular frequency $\omega \equiv 2\pi f$, where $V_0 \propto H_x S_x$. We treat $V(t)$ as a small perturbation to $\mathcal{H}_0$. The interaction between the spin system and the surrounding environment can be understood by density-matrix equations.

We consider the case that the frequency $\omega$ is fixed while $H_z$ is quasi-statically varied to induce a resonance. With the selection rule $\Delta M_s=\pm 1$, solving the density-matrix equations for the population change with time in the level $M_s$ due to $V(t)$, to first order in $V_0$ near resonance, provides the power absorption between the levels $M_s$ and $M_s - 1$:

$$\frac{d\mathcal{E}}{dt} = \frac{(\mathcal{E}_{M_s-1} - \mathcal{E}_{M_s})}{\hbar^2} \bar{V}^2 \Delta (\rho_{M_s,M_s-1} - \rho_{M_s-1,M_s-1}),$$

$$\Delta \equiv \frac{\hbar^2 \gamma_{M_s-1,M_s}}{(g\mu_B)^2 (H_z - H_{res})^2 + (\hbar \gamma_{M_s-1,M_s})^2},$$

$$H_{res} \equiv \frac{\hbar \omega - D(2M_s - 1)}{g\mu_B}.$$

Here $\mathcal{E}_{M_s}$ is the energy of the level $M_s$, $\bar{V} \equiv |\langle M_s | V_0 | M_s - 1 \rangle |$, $\rho(t)$ is the density matrix of the spin system. The subscripts represent eigenstates of the longitudinal part of $\mathcal{H}_0$, $\rho(t)_{m'm} = \langle m' | \rho(t) | m \rangle$, $\gamma_{m'm} = (W_m + W_{m'})/2$, $W_m = \sum_{k \neq m} W_{km}$, and $W_{km}$ is the transition rate from the $m$-th to the $k$-th eigenstate, $H_{res}$ is the resonant field, and $\hbar \gamma_{M_s-1,M_s}/g\mu_B$ gives a natural linewidth which is about 5 to 50 G at 10 K and increases as $M_s$ decreases. However, the experimentally observed linewidths are much larger than the natural linewidths and decrease as $M_s$ decreases [Figs. 2(a) and (b)].
To resolve these large discrepancies, we first assume that \( D \) and \( g \) are independent random variables with Gaussian distributions centered at 0.288\( k_B \) and 2.00, with standard deviations \( \sigma_D \) and \( \sigma_g \), respectively. Then we calculate the average power absorption at a fixed frequency and \( T=10 \) K by integrating over Eq. (2) using Mathematica\textsuperscript{13} to obtain the linewidth as a function of \( M_s \). The lineshapes depend on the magnitudes of \( \sigma_D \) and \( \sigma_g \), compared to the natural linewidth determined by \( \gamma (M_s+1,M_s) \). If \( \sigma_D \) and \( \sigma_g \) are much larger than (comparable to) the natural linewidth, then the lineshape is Gaussian (Lorentzian). At intermediate values of \( \sigma_D \) and \( \sigma_g \), the absorption lineshapes are neither Gaussian nor Lorentzian. Our numerical calculations show that the distribution in \( D \) narrows the linewidths linearly with decreasing absolute value of \( 2M_s-1 \) [Figs. 2(c) and (d)], with a slight rounding close to the linewidth minimum \( (M_s=1 \) and \( M_s=0) \) [Fig. 2(c)]. On the other hand, the distribution in \( g \) broadens the linewidths with decreasing \( M_s \) because the resonant field increases with decreasing \( M_s \) [see Eq. \textsuperscript{3}].\textsuperscript{5,9} For small-\( M_s \) transitions, the lineshapes are close to a Lorentzian because the natural linewidths are not very small compared to the measured linewidths.

Next, we consider the effect of the dipolar interactions between different clusters. (There is no distribution in cluster size.) The dipolar interactions narrow the linewidths as \( M_s \) decreases because the resonant field becomes stronger for smaller-\( M_s \) transitions, and the stronger resonant fields lead to a more polarized system [Figs. 2(c) and (d)]. The details of this effect on the linewidths at a fixed temperature were reported elsewhere.\textsuperscript{9} The dipolar interactions give rise to a temperature dependence of the linewidths and a shift in the positions of the resonance lines, because at low temperatures \( (k_B T \ll h\omega) \) high energy levels are not populated. Our study shows that a linewidth for a particular transition increases and then smoothly decreases with increasing temperature. The maximum linewidth as a function of temperature moves towards lower temperatures for larger-\( M_s \) transitions, which agrees with experiments.

The competition between \( D \)-strain, \( g \)-strain, and dipolar interactions determines the overall features of the linewidth, as a function of \( M_s \). We have varied \( \sigma_D, \sigma_g, \) and the effective distance between neighboring dipoles, \( d \), within an experimentally acceptable range
in order to fit the experimental data.

For the Fe$_8$ sample examined, the calculated linewidths agree well with the experimental data at the measured frequencies ($f = 68, 89, 109, 113, 133,$ and $141$ GHz) at $T=10$ K, using $\sigma_D \approx 0.01D$ and $d \approx 12$ Å. [Figs. 2(a) and (b)] As shown in Figs. 2(c) and (d), the $D$-strain effect and the dipolar interactions are equally important for the linewidths of the sample, while the $g$-strain does not contribute significantly (not shown).

For Mn$_{12}$, we perform a similar analysis as above, using the ground-state single-spin Hamiltonian$^{10}$

$$H_0 = -DS_z^2 - CS_z^4 - g\mu_B H S_z$$

with $D = 0.55k_B$, $C = 1.17 \times 10^{-3}k_B$, and $g = 1.94$. Detailed analysis can be found in the literature.$^9$ For this sample, the $D$-strain and $g$-strain effects play significant roles in the linewidths, while the dipolar interactions are not as important as for the Fe$_8$ sample.

Next we discuss how the distribution of the directions of the magnetic anisotropy axes of clusters affect the EPR lineshapes. Because of defects in the samples, each cluster sees a slightly different crystal field due to the surrounding clusters, compared to the situation in a perfect crystal. We assume that these slightly different crystal fields result in local rotations of the magnetic anisotropy axes of some of the clusters by an angle $\theta$ from the crystal $c$ axis. The angle $\theta$ is assumed to have a Gaussian distribution about zero with a small standard deviation. Hereafter $a$, $b$, and $c$ denote the crystal axes, while $x$, $y$, and $z$ denote the magnetic anisotropy axes of a single cluster.

As a preliminary study, we examine the lineshapes for Mn$_{12}$ when the magnetic field is applied along the $c$ axis and the magnetic anisotropy easy axis of a single cluster is tilted by $\theta$ from the $c$ axis. Then the single-spin Hamiltonian, in terms of the spin operators along the magnetic anisotropy axes, becomes

$$H = -DS_z^2 - g\mu_B H S_z \cos \theta + g\mu_B H S_x \sin \theta.$$  \hspace{1cm} (5)

For simplicity, we drop the fourth-order anisotropy terms. We also set $\psi = 90^\circ$, where $\psi$ is
the third of the Euler angles defined in literature,\textsuperscript{15} which does not affect the eigenvalues of $H$.

Because of the local rotations of the magnetic anisotropy axes, some of the clusters experience slightly different resonant fields than those aligned with the crystal $c$ axis. In contrast to the Gaussian distributions of the resonant field due to the distributions in $D$ and $g$, this effect gives rise to an asymmetry in the resonant field, which leads to an asymmetry in the EPR lineshapes. Assuming that $\theta$ is small, we treat the terms proportional to $\sin \theta$ as small perturbations to the rest of the terms in Eq. (5). Using second-order perturbation theory, we obtain the resonant fields as a function of $\theta$, shown in Fig. 3. Each curve in Fig. 3 is symmetric about $\theta=0$. Figure 3 shows that for transitions between $M_s$ and $M_s+1$ ($M_s=-4\rightarrow-3$) an asymmetry appears in the direction of decreasing field, while for transitions between $M_s$ and $M_s-1$ ($M_s=3\rightarrow2$, $M_s=2\rightarrow1$) the asymmetry is in the direction of increasing field. At the examined frequency ($f=66.135$ GHz) the asymmetry effect is more significant for the small-$M_s$ transitions. Based on the analytic form of the resonant field, we can obtain analytically the distribution of the resonant field at a particular frequency for transitions between the levels $M_s$ and $M_s \pm 1$, including Gaussian distributions of $D$, $g$, and $\theta$.\textsuperscript{16} For simplicity, we have neglected the effects of natural linewidths, dipolar interactions, and temperature on the EPR lineshapes.

In conclusion, we have examined the EPR linewidths as functions of $M_s$, frequency, and temperature for single crystals of the molecular magnets Fe\textsubscript{8} and Mn\textsubscript{12}. We found that the distribution in $D$ is important to explain the linewidths for both of the molecular magnets, and that the dipolar interactions are crucial to understand the temperature dependence of the linewidths. Our preliminary study of the EPR lineshapes shows that the distribution of the directions of the magnetic anisotropy axes of clusters provides an asymmetry in the EPR spectra.

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FIG. 1. Schematic diagram of the magnetic core of (a) the Fe$_8$ cluster and (b) the Mn$_{12}$ cluster. Each Fe$_8$ cluster has D$_2$ symmetry, while each Mn$_{12}$ cluster has tetragonal symmetry. Both clusters have ground-state spin $S = 10$ (for Fe$_8$, $S = (6 - 2) \times 5/2$, and for Mn$_{12}$, $S = 8 \times 2 - 4 \times 3/2$).
FIG. 2. (a) and (b) Experimental (filled circles) and theoretical (open circles) Full Width at Half Maximum (FWHM) vs $M_s$ for different frequencies at $T=10$ K for Fe$_8$. (c) and (d) Line broadening due to the $D$-strain (filled squares) and dipolar interactions (open squares) for (a) and (b), respectively. Here $\vec{H} \parallel \hat{z}$. The fit is best when the standard deviation of $D$ is 0.01$D$ and the effective distance between dipoles is 12 Å.

FIG. 3. The resonant field vs $\theta$ for the transitions (a) $M_s=-4\rightarrow-3$ and $M_s=3\rightarrow2$, and (b) $M_s=2\rightarrow1$ at $f=66.135$ GHz for $\vec{H} \parallel \hat{c}$. Each curve is symmetric about $\theta=0$. 

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