Electron Paramagnetic Resonance Linewidths and Lineshapes for the Molecular Magnets Fe_8 and Mn_{12}

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Abstract

We study theoretically Electron Paramagentic 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 temperatures³ 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) measurements⁵⁻⁷ on single-crystals of the molecular magnets Fe₈ and Mn₁₂ 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 \rightarrow 4. The experimental results are that (i) the linewidths are about 200 G to 1400 G at T=10 K for Fe₈ [Figs. 2(a) and (b)], and about 1000 G to 2000 G at T=25 K for Mn₁₂; (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 Fe₈ 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" effects⁸) due to possible random defects and impurities in the samples. We find that the calculated linewidths⁹ 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 Fe₈, 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 Fe₈ clusters have an approximate D_2 symmetry, the lowest-order ground-state single-spin Hamiltonian is¹⁰

$$\mathcal{H}_0 = -DS_z^2 - E(S_x^2 - S_y^2) - g\mu_B H_z S_z , \qquad (1)$$

where $D=0.288k_B$ and the transverse anisotropy parameter, $E=0.043k_B$.⁶ Here S_{α} is the α -th component of the spin operator, g is the Landé g-factor (≈ 2), μ_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.¹¹

We consider the case that the frequency ω 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 $M_s - 1$:¹¹

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

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

$$H_{\text{res}} \equiv \frac{\hbar \omega - D(2M_s - 1)}{g\mu_B}.$$
(3)

Here \mathcal{E}_{M_s} is the energy of the level M_s , $\tilde{V} \equiv |\langle M_s|V_0|M_s-1\rangle|$, $\rho(t)$ 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 rate¹² 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 $0.288k_B$ and 2.00, with standard deviations σ_D and σ_g , respectively. Then we calculate the average power absorption at a fixed frequency and T=10 K by integrating over Eq. (2) using Mathematica¹³ to obtain the linewidth as a function of M_s . The lineshapes depend on the magnitudes of σ_D and σ_g , compared to the natural linewidth determined by γ_{M_s+1,M_s} . If σ_D and σ_g are much larger than (comparable to) the natural linewidth, then the lineshape is Gaussian (Lorentzian). At intermediate values of σ_D and σ_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. (3)].^{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. 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 ($k_BT \ll \hbar \omega$) 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 σ_D , σ_g , and the effective distance between neighboring dipoles, d, within an experimentally acceptable range

in order to fit the experimental data.

For the Fe₈ 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 $Hamiltonian^{10}$

$$\mathcal{H}_0 = -DS_z^2 - CS_z^4 - g\mu_B H_z S_z \tag{4}$$

with $D=0.55k_B$, $C=1.17 \times 10^{-3}k_B$, and $g=1.94.^{14}$ 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 Fe₈ 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 θ from the crystal c axis. The angle θ is assumed to have a Gaussian distribution about zero with a small standard deviation. Hereafter a, b, and c denote the crystal axes, while c, c, and c 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 θ from the c axis. Then the single-spin Hamiltonian, in terms of the spin operators along the magnetic anisotropy axes, becomes

$$\mathcal{H} = -DS_z^2 - g\mu_B H S_z \cos\theta + g\mu_B H S_x \sin\theta. \tag{5}$$

For simplicity, we drop the fourth-order anisotropy terms. We also set $\psi = 90^{\circ}$, where ψ is

the third of the Euler angles defined in literature, 15 which does not affect the eigenvalues of \mathcal{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 θ 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 θ , 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 ($M_s=3\rightarrow 2,\ M_s=2\rightarrow 1$) 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 θ . 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 Fe₈ and Mn₁₂. 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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FIGURES

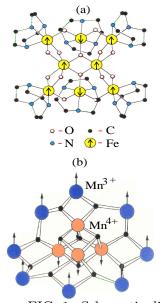


FIG. 1. Schematic diagram of the magnetic core of (a) the Fe₈ cluster and (b) the Mn₁₂ cluster. Each Fe₈ cluster has D₂ symmetry, while each Mn₁₂ cluster has tetragonal symmetry. Both clusters have ground-state spin S=10 (for Fe₈, $S=(6-2)\times 5/2$, and for Mn₁₂, $S=8\times 2-4\times 3/2$).

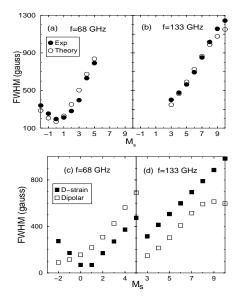
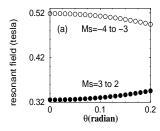


FIG. 2. (a) and (b) Experimental (filled circles) and theoretical (open circles) Full Width at Half Maximum (FWHM) vs M_s for different frequencies at T=10 K for Fe₈. (c) and (d) Line broadening due to the D-strain (filled squares) and dipolar interactions (open squares) for (a) and (b), respectively. Here $\vec{H} \parallel \hat{z}$. The fit is best when the standard deviation of D is 0.01D and the effective distance between dipoles is 12 Å.



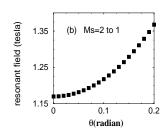


FIG. 3. The resonant field vs θ for the transitions (a) $M_s = -4 \rightarrow -3$ and $M_s = 3 \rightarrow 2$, and (b) $M_s = 2 \rightarrow 1$ at f = 66.135 GHz for $\vec{H} \parallel \hat{c}$. Each curve is symmetric about $\theta = 0$.