Single crystal EPR determination of the spin Hamiltonian parameters for Fe₈ molecular clusters

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Abstract

We use a multi-high-frequency resonant cavity technique to obtain EPR spectra for single crystal samples of the biaxial molecular magnet Fe₈[(tacn)₆O₂(OH)₁₂]Br₈·9H₂O (Fe₈). By performing measurements at many closely spaced frequencies, we are able to extrapolate data back to zero magnetic field and, thereby, obtain accurate estimates of the zero-field splittings. Furthermore, from the (low-) field dependence of these splittings, with the magnetic field parallel to the easy axis, we can directly measure the *g_z*-value. Measurements performed with the magnetic field parallel to the intermediate and hard axes may be used to constrain further the Hamiltonian parameters. Our results are in broad agreement with recent inelastic neutron scattering data. In addition, analysis of individual resonances (which we can assign to known transitions) reveals a pronounced *M_S* dependence of the resonance line widths. Furthermore, the line positions exhibit complex (again *M_S* dependent) temperature dependences that cannot be reconciled with the standard spin Hamiltonian. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Recent advances in magnetic recording and sensing technologies (e.g. computer hard disk drives) have been possible due to the scalability of magnetic devices to smaller and smaller dimensions. Once the sizes of magnetic devices reach the nanoscale (< 100 nm), previously unimportant quantum effects will radically affect functionality. Furthermore, scalability will become a problem since, for a device to perform a specific task, its (quantum) structure must be precisely known. The limit to precise artificial manufacture of reproducibly functioning ‘magnetic quantum dots’, using conventional lithography followed by etching, is rapidly approaching. To overcome this problem, chemists have been able to synthesize large magnetic molecules that, when combined to form crystals, behave like assemblies of identical magnetic ions in identical environments,

each with a giant spin ground state [1–10]. This novel approach will likely lead to new technologies and exciting new scientific challenges [5].

Examples of molecular magnets that have received considerable recent interest are the uniaxial [Mn₁₂-O₁₂(CH₃COO)₁₆(H₂O)₄]·2CH₃COOH·4H₂O (Mn₁₂) system [1–6], and the biaxial [Fe₈(tacn)₆O₂(OH)₁₂]Br₈·9H₂O (Fe₈) system [7,8]. Both of these molecules (Mn₁₂ and Fe₈) exhibit spin *S* = 10 ground states and, at low temperatures, both systems possess the ability for their magnetic moments to quantum tunnel coherently through their respective anisotropy barriers [5,11–18]. This phenomenon, which has aroused great interest, is still not well understood. In this study, we utilize a high-resolution electron paramagnetic resonance (EPR) technique to probe the quantum energy level (Hamiltonian) structure of the Fe₈ system.

To lowest order, the spin Hamiltonian for the biaxial Fe₈ system is given by:

$$H_0 = DS_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2) + \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \hat{\mathbf{S}} \quad (1)$$

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where D ($\sim -0.2 \text{ cm}^{-1}$) is the uniaxial spin–spin coupling parameter, E ($\sim -0.03 \text{ cm}^{-1}$) characterizes the magnetic anisotropy in the plane perpendicular to the magnetic easy (z) axis, $\hat{S}$ is the vector spin operator and $\hat{S}_x$, $\hat{S}_y$ and $\hat{S}_z$ represent projections along the hard, intermediate and easy axes respectively; g is the Landé tensor, and $\mathbf{B}$ is the applied magnetic field vector [16]. Inelastic neutron scattering [19] and high-frequency EPR studies [8,20] of powder samples have shown the need to include higher-order terms (fourth-order in the spin operators) in the above Hamiltonian; these terms are important, because they may provide clues as to the mechanism of the quantum tunneling phenomenon. However, the neutron and EPR studies published to date do not agree on the magnitudes of the higher-order Hamiltonian terms, or even on the exact D and E parameters [8,19–22].

In this study, we report multiple high-frequency (20 to 200 GHz), high-sensitivity EPR measurements on a single Fe_8 crystal. The $(2S+1)$ -fold quantum energy level structure associated with the large molecular moment S necessitates spectroscopies spanning a wide frequency range. Furthermore, the large zero-field splittings demand the use of frequencies and magnetic fields considerably higher than those typically used by the majority of EPR spectroscopists. Extrapolation of the frequency dependence of transitions to zero-field (for any orientation of the field) allows us to determine directly and accurately (to within 0.5%) the first five zero-field splittings, which are in good agreement with the neutron studies [19]. The dependence of these splittings on the applied field strength, and its orientation with respect to the crystal, enable us to identify (to within 1°) the easy, intermediate and hard magnetic axes. Subsequent analysis of EPR spectra for the field parallel to the easy axis yields a value for g_z that is

appreciably different than the value assumed in recent high-field powder EPR studies by Barra et al. [20]. Frequency-dependent data obtained for a field applied along the hard and intermediate axes further constrain the g -tensor and spin Hamiltonian parameters.

2. Experimental

The high degree of sensitivity required for single crystal measurements is achieved using a resonant cavity perturbation technique in combination with a broad band millimeter-wave network analyzer exhibiting an exceptionally good signal-to-noise ratio; the details of this technique are described elsewhere [23,24]. Temperature control was achieved using a variable flow cryostat situated within the bore of an 8 T superconducting solenoid. Single Fe_8 crystals were grown using standard techniques. One of these samples was mounted on a sapphire wedge allowing for accurate and reproducible control of the sample orientation relative to the externally applied dc field; all measurements were performed in the standard EPR configuration with the ac excitation field transverse to the dc field.

3. Results and discussion

Fig. 1 shows typical EPR spectra obtained with the field approximately parallel to the easy (upper trace) and intermediate (lower trace) magnetic axes of a single crystal measuring less than $1 \times 1 \times 0.2 \text{ mm}^3$. The high quality of these data illustrate the extraordinary sensitivity of our technique. The easy axis spectra are relatively simple, showing a single series of more-or-less evenly spaced resonances. Starting at low fields, the easy axis resonances correspond to the $M_S = -10 \rightarrow -9$, $-9 \rightarrow -8$, etc. transitions. The diminishing intensity with increasing field is due to the reduced thermal population of the lower $|M_S|$ levels, and an M_S dependence of the transition probabilities accounts for the fact that the $M_S = -9 \rightarrow -8$ transition is stronger than the $M_S = -10 \rightarrow -9$ transition. The intermediate axis spectra are considerably more complex, showing several branches — a high-field branch that moves to higher fields with increasing frequency, and a lower-field branch of broader resonances that move to lower fields with increasing frequency. The multiple branches are a consequence of the strong mixing between levels for this orientation, leading to many more allowed transitions.

Considerably more insight into the field dependence of the quantum energy level structure of Fe_8 is obtained when we repeat the measurements in Fig. 1 at many closely spaced frequencies. Fig. 2 shows the frequency dependence of EPR transitions obtained with the mag-

Fig. 1. Upper panel: typical spectra obtained with the magnetic field applied approximately parallel to the easy axis; the temperature is 10 K in each case. Lower panel: typical spectra obtained with the magnetic field applied approximately parallel to the intermediate axis; the temperature is 3 K in each case.

Fig. 2. Frequency dependence of the first five EPR transitions (M_S values indicated in the figure) observed with the magnetic field applied approximately parallel to the easy axis. We obtain the g_z value from the slopes of linear fits to the data.

netic field applied at an angle $\theta = 9^\circ$ away from the magnetic easy axis in the easy/hard plane of the sample. From these measurements, one sees that the field dependence is dominated by the linear Zeeman term in Eq. (1), i.e. the transitions show an almost linear dependence on field. By extrapolating data back to zero field, we directly obtain the first five zero-field splittings with unprecedented accuracy ($< \pm 0.5\%$): 3.796, 3.419, 2.995, 2.582, and 2.135 cm^{-1} . This method for obtaining the zero-field splittings is quite different than the method employed by Barra and coworkers [8,20], which relies on fitting high-frequency/field spectra with up to eight adjustable parameters. By extrapolating our data very carefully to zero field, we obtain the zero-field splittings without any dependence on, for example, the g tensor. Indeed, the values we obtain here are in good agreement with recent neutron measurements [19], as shown in Table 1, thus restoring confidence in the high-frequency EPR technique as a viable means for obtaining the Hamiltonian parameters for molecular magnets such as Fe_8 and Mn_{12} .

In the low-field limit, and as a first approximation, one expects the Zeeman term in Eq. (1) to give rise to a linear dependence of each transition energy on the z -component of the magnetic field strength, i.e. the field component parallel to the easy axis. Fig. 3 shows the average linear slopes (normalized so as to correspond to a g -value) of the first three transitions ($M_S = -10 \rightarrow$

Fig. 3. A plot of the slopes of the data in Fig. 2 (average of first three transitions) versus the angle ψ between the magnetic field and one of the crystal edges; the field was rotated in the easy/hard plane.

-9 , $-9 \rightarrow -8$, and $-8 \rightarrow -7$) versus the angle ψ between the applied magnetic field and one of the crystal edges; the field was rotated in the easy/hard plane. From this data, it is apparent that the magnetic easy axis ($\theta = 0^\circ$) is oriented at an angle $\psi = 24^\circ$. Furthermore, the apparent g_z value for this orientation is 2.043 ± 0.014 . As a first approximation (Eq. (1)), the g -value obtained from the slopes in Fig. 2, when the field is applied exactly along the easy axis ($\psi = 24^\circ$, $\theta = 0^\circ$), should correspond exactly to the g_z value. However, the biaxial anisotropy term $E(\hat{S}_x^2 - \hat{S}_y^2)$ in Eq. (1) gives rise to weak off-diagonal elements that also depend on the z -component of the magnetic field. We have performed simulations to ascertain the influence of these off-diagonal Zeeman terms using the accepted value for E (0.032 cm^{-1}), and a value of $g_z = 2$. These simulations are shown in Fig. 4; note the apparent g_z value at $\theta = 6^\circ$ of 2.008. Taking this into consideration, we obtain a revised g_z value of 2.035 ± 0.014 , which is appreciably higher than the value deduced by Barra et al. [20] and which may also account for discrepancies between the Hamiltonian parameters they deduce and those obtained from inelastic neutron scattering measurements [19].

In Fig. 5, we show data obtained with the magnetic field close to the intermediate axis (5° away, or $\theta = 85^\circ$). The field dependence of the transitions for this orientation is complicated due to the competing Zeeman and $D\hat{S}_z^2$ terms in the Hamiltonian. However, this

Table 1

Comparisons between the zero-field splittings obtained from this study, and those calculated from the Hamiltonian parameters reported by Caciuffo et al. [19] and Barra et al. [20]

Transition	$-10 \rightarrow -9$ (cm^{-1})	$-9 \rightarrow -8$ (cm^{-1})	$-8 \rightarrow -7$ (cm^{-1})	$-7 \rightarrow -6$ (cm^{-1})	$-6 \rightarrow -5$ (cm^{-1})
This study	3.796	3.419	2.995	2.582	2.135
Caciuffo et al. [19]	3.763	3.373	2.973	2.559	2.143
Barra et al. [20]	3.722	3.342	2.945	2.546	2.218

complexity is precisely what is needed to constrain further the Hamiltonian parameters — especially the fourth-order terms; the considerable mixing and repul-

Fig. 4. Simulations of the apparent g_z values for the first five transitions as a function of the angle θ between the applied magnetic field and the easy axis. The $E(\hat{S}_x^2 - \hat{S}_y^2)$ term in Eq. (1) gives rise to an apparent $g_z = 2.008$ (at $\theta = 0^\circ$) in spite of the fact that the simulation assumes a value of $g_z = 2.000$.

Fig. 5. Frequency dependence of EPR transitions obtained with the magnetic field applied at an angle $\theta = 85^\circ$, i.e. close to the intermediate axis. The solid lines represent simulations of the data using Eq. (1).

Fig. 6. M_S dependence of the EPR line widths. The quadratic dependence may be used to estimate the width of the Gaussian distribution of D values.

Fig. 7. Temperature-dependent line shifts for transitions between various M_S levels (indicated in figure).

sion between levels (leading to many more allowed transitions) depends explicitly and sensitively on E and the other higher-order terms. The lines passing through the data in Fig. 5 have been generated from a preliminary simulation using Eq. (1). The D and E values were first obtained from a fit to the first five zero-field splittings, while the sample orientation ($\pm 5^\circ$) was varied to further optimize the fit to the data in Fig. 5. Our D and E values agree broadly with the neutron studies [19], though accurate comparisons cannot be made until fourth-order terms are included in our fitting routine.

Next we turn to the EPR line shapes and widths. The data in Fig. 1 suggest that the spin levels are inhomogeneously broadened, since a mixture of Gaussian and Lorentzian lineshapes provide the best fits to the data. A significant contribution to this broadening is likely due to a distribution in D and/or g values (strain), in addition to possible random dipolar or hyperfine fields; we note, a spread in D and/or g would not affect the zero field quantum tunneling resonance which has been shown to be Lorentzian in the Mn_{12} system by Friedman et al. [25]. To verify this, we plot the M_S dependence of the linewidths in Fig. 6, where M_S represents the spin projection of the level from which the transition was excited. From the M_S dependence, we conclude that D has a Gaussian distribution with a FWHM of approximately $3 \times 10^{-4} \text{ cm}^{-1}$, or 0.15%. We note that the linewidths show a marked quadratic dependence on M_S , in addition to a linear dependence, which may be attributable to a combination of D and g -strains.

Finally, in Fig. 7, we show the temperature dependence of data obtained with the magnetic field applied along the easy axis. The line positions for the first three transitions ($M_S = -10 \rightarrow -9$, $-9 \rightarrow -8$, and $-8 \rightarrow -7$) exhibit a pronounced, albeit complex, dependence on temperature. The $-10 \rightarrow -9$ transition shows a monotonic behavior, moving to higher fields with increasing temperature; the other two transitions move

initially to lower field then, above about 10 K, the resonances move back to higher field. These conflicting trends would seem to rule out any simple explanation such as temperature-dependent g , D or E values. We note that Mukhin et al. [26] have also observed different temperature dependences for the first two zero-field transitions in the Mn_{12} system ($M_S = -10 \rightarrow -9$, $-9 \rightarrow -8$), though only in the line widths. However, the present data show a very similar behavior to the mode contributions observed for the first three resonances in Mn_{12} by Mukhin et al. [26]. These mode contributions depend on the populations of levels, thus suggesting that (dipolar or exchange) interactions between Fe_8 molecules may be responsible for the line shifts observed in this study, something that has not been taken into consideration in Eq. (1).

4. Summary and conclusions

A multi-high-frequency EPR technique has been used to provide considerable insight into the quantum structure of the biaxial molecular magnet $\text{Fe}_8[(\text{tacn})_6\text{O}_2(\text{OH})_{12}]\text{Br}_8 \cdot 9\text{H}_2\text{O}$. Extrapolation of data to zero field enables accurate estimates of the zero-field splittings, and the field dependence of easy axis data has been used to determine the g_z -value; our results are in broad agreement with recent inelastic neutron scattering data. In addition, analysis of individual resonances reveals a pronounced M_S dependence of the resonance line widths. Furthermore, the line positions exhibit complex (again M_S dependent) temperature dependences that cannot be reconciled with the standard spin Hamiltonian.

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