Characterization of the $S = 9$ excited state in Fe$_8$Br$_8$ by Electron Paramagnetic Resonance

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High Frequency electron paramagnetic resonance has been used to observe the magnetic dipole, $\Delta M_1 = \pm 1$, transitions in the $S = 9$ excited state of the single molecule magnet Fe$_8$Br$_8$. A Boltzmann analysis of the measured intensities locates it at 24 ± 2 K above the $S = 10$ ground state, while the line positions yield its magnetic parameters $D = -0.27$ K, $E = \pm 0.05$ K, and $B_4^0 = -1.3 \times 10^{-6}$ K. $D$ is thus smaller by 8% and $E$ larger by 7% than for $S = 10$. The anisotropy barrier for $S = 9$ is estimated as 22 K, which is 25% smaller than that for $S = 10$ (29 K). These data also help assign the spin exchange constants (J’s) and thus provide a basis for improved electronic structure calculations of Fe$_8$Br$_8$.

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I. INTRODUCTION

Single molecule magnets (SMM’s), defined as compounds where a magnetic domain can, in principle, be reduced to a single molecule$^{1,2}$, have recently been of high theoretical and experimental interest due to their novel properties and potential applications. These properties and potential applications include quantum tunneling of their magnetization (QTM)$^{3,4,5,6}$, whose detailed mechanism is still not fully understood, molecular memory devices$^{7,8}$, and elements of quantum computers$^{9}$. One of the best characterized SMM’s is $[\text{C}_6\text{H}_{15}\text{N}_3\text{H}_6\text{Fe}_8(\mu_3-\text{O})_2(\mu_2-\text{OH})_{12}]\text{Br}_7(\text{H}_2\text{O})\text{Br}_8\text{H}_2\text{O}$, abbreviated Fe$_8$Br$_8$$^{10,11}$, whose main spin-bearing skeleton is shown in Fig. 1.

Studies by magnetization$^{12}$, neutron scattering$^{13,14}$, electron paramagnetic resonance (EPR)$^{15,16,17,18,19,20,21}$, and NMR$^{22}$ techniques have established that the ground state has a spin value $S = 10$. Figure 1 shows a schematic of the spin configuration of the Fe$^{3+}$ ($S = 5/2$) ions. At temperatures below 1 K, the magnetization relaxation takes places via QTM$^{23}$. While a great deal of progress has been made in understanding the nature of QTM in Fe$_8$Br$_8$, many questions still remain unclear. For example, the magnitudes of calculated tunneling rates are much lower than the observed values$^{24}$. Secondly, there is a lack of data on the nature and magnitude of the spin-exchange constants, J’s, between the eight Fe$^{3+}$ ions in the Fe$_8$Br$_8$ core. The best estimates come from the temperature dependence of the $dc$ magnetic susceptibility, $\chi_{dc}$.$^{12,24}$. The $\chi_{dc}$ could be fitted by several sets of J’s. One of the criteria of such a procedure is the prediction of the proper spin $S$ value of the ground state, together with the location of the excited states, in particular the $S = 9$ state. The $\chi_{dc}$ fit yielded at least two sets of J’s, but the set providing the better fit yielded the position of the $S = 9$ state to be less than 0.5 cm$^{-1}$ above the ground state.$^{12}$ The other set predicted the $S = 9$ state at greater than 25 cm$^{-1}$ (36 K) above the ground state. Clearly, from the point of view of understanding the magnetic structure of Fe$_8$Br$_8$, it is important to experimentally determine the location of the excited states, in particular the $S = 9$ manifold.

FIG. 1: Schematic representation of Fe$_8$Br$_8$$^{12}$. The arrows represent spin orientations of the Fe$^{3+}$ ions in the $S = 10$ ground state. The organic ligands and the eight Br$^-$ anions have been omitted for clarity. Each Fe$^{3+}$ has $S = 5/2$, thus the ground state can be seen as $S = 6 \times 5/2 - 2 \times 5/2 = 10$. 

A peak around 30 cm\(^{-1}\) has been reported in the far infrared spectrum\(^{25}\), but it was not established whether it was a normal molecular vibration involving metal ions, or a transition to the \(S = 9\) level from the \(S = 10\) ground state. Moreover this peak was not observed for the closely similar compound \(\text{Fe}_8\text{Br}_4(\text{ClO}_4)_4\), whose spin Hamiltonian (Eq. 1), parameters are known to be close to those of \(\text{Fe}_8\text{Br}_8\).  

The magnetic properties of the ground state of \(\text{Fe}_8\text{Br}_8\) have been well described by the following spin Hamiltonian, with \(S = 10\):\(^{11,15,16,17,18,19,20,21,25,26,27}\)

\[
\hat{H} = \mu_B \vec{\vec{g}} \cdot \vec{S} + D S_z^2 + E (S_x^2 - S_y^2) + B_1' O_1^x + B_2' O_2^x + B_3' O_3^x. \tag{1}
\]

where the first term is the Zeeman interaction, \(D\) represents the usual zero-field, uniaxial anisotropy parameter, and \(E\) the second order rhombic anisotropy. The fourth order terms are given by: \(O_1^x = 3S_z^2 - [30S(S+1) - 25]S_x^2 - 6S(S + 1) + 3S_z^4\) \(O_2^x = 1/4[7S_x^4 - S(S+1) - 5](S_x^2 + S_y^2) + (S_x^2 + S_y^2)(7S_z^2 - S(S+1) - 5)\), and \(O_3^x = 1/2(S_x^4 + S_y^4)\).

Here, we report on an EPR detection of the \(S = 9\) state of \(\text{Fe}_8\text{Br}_8\), and preliminary evaluation of its spin Hamiltonian parameters as defined in Eq. 1. We observe a series of peaks, called \(\beta\) transitions, which we assign to an \(S = 9\) excited state of \(\text{Fe}_8\text{Br}_8\). From the temperature variation of the line intensities, we establish that the \(S = 9\) manifold lies at 24 \(\pm\) 2 K above the \(S = 10\) ground state, in contrast to the suggestion of \(> 36\) K from susceptibility analysis.\(^{12}\)

Section II below describes the single crystal preparation and the EPR instrumentation. The results obtained, and their analysis, are presented in section III, with the discussion presented in section IV, and the main conclusions presented in section V.

### II. Experimental

\([\text{C}_8\text{H}_{15}\text{N}_3]_6\text{Fe}_8(\mu_3-\text{O})_2(\mu_2-\text{OH})_2\text{Br}_7(\text{H}_2\text{O})\text{Br}_8\text{H}_2\text{O}\) (Fe\(_8\text{Br}_8\)) was synthesized following the procedure of Weighardt.\(^{10}\) Relatively large \(2 \text{ mm} \times 2 \text{ mm} \times 0.5 \text{ mm}\), optical quality single crystals were prepared by slow evaporation. The crystals were aligned with the Zeeman field applied along the easy axis of magnetization by sight, to within a few degrees.\(^{10}\) The final orientation was confirmed by EPR splittings, being the extremum for the canonical orientations. The EPR measurements were made using a variable frequency (44 - 200 GHz), cavity based, high sensitivity spectrometer described earlier.\(^{15,16,28}\) The main component of the spectrometer is a millimeterwave vector network analyzer (MVNA), a phase-sensitive, fully sweepable, superheterodyne source-detection system. A variable flow cryostat situated within the bore of an 17 T superconducting solenoid allows for temperatures down to 1.5 K, with an accuracy of \(\pm 0.01\) K. The high sensitivity of the MVNA technique (10\(^9\) spins G\(^{-1}\) s\(^{-1}\)) allows for observation of the low level transitions of the \(\text{Fe}_8\text{Br}_8\) ground and excited states in a single crystal, and for angular variation studies, as described earlier.\(^{6,15,21}\)

### III. Results

Figure 2 (bottom panel) shows a typical EPR spectrum of \(\text{Fe}_8\text{Br}_8\) at 131 GHz with the Zeeman field applied along the easy axis of an \(\text{Fe}_8\text{Br}_8\) single crystal at 35 K. The spectrum consists of a series of strong peaks \(\alpha_{-10}, \alpha_{-9}, \alpha_{-8}\), etc; the subscripts represent the spin projection quantum number, \(M_s\), corresponding to the level from which the EPR absorption transition originates, in the \(S = 10\) ground state following the convention introduced earlier.\(^{11,16,17}\) The \(\alpha\) transitions have been very

![FIG. 2: EPR spectrum of Fe\(_8\)Br\(_8\) at 131 GHz and 35 K with the zeeman field applied along the easy axis (bottom panel), along with the energy level diagram corresponding to the S = 10 spin system (top panel). The S = 10 energy level diagram has been constructed through the spin Hamiltonian parameters of Caciuffo et al.\(^{13}\). The single-headed arrow at 0.8 tesla designates the expected position where a \(\beta\) transition would appear if the \(\beta\) transitions originated from an \(S = 10\) state.](image-url)
well analyzed earlier \cite{11,16,17}, and have been shown to arise
from the magnetic dipole ($\Delta M_s = \pm 1$) transitions within
the 21 $M_s$ levels of the $S = 10$ multiplet. The specific
peak assignment is indicated in the top panel for the $\alpha$
transitions. In addition to the $\alpha$ resonances, there are ad-
ditional peaks present in Fig. 2 that are labelled as the $\beta$
transitions and are the focus of the current investigation.

Our analysis procedure consisted of three steps: (a) to
ascertain that the $\beta$ transitions are from an excited
state, (b) to determine the spin multiplicity of this ex-
cited state, and (c) to deduce the spin Hamiltonian pa-
rameters for the $\beta$ spin system and its energy position
relative to the ground state ($S = 10$).

Direct evidence that the $\beta$ transitions originate from
a thermally populated excited state is provided by the
temperature dependence of their intensities. Figure 3
shows spectra at 5, 15, and 35 K, respectively, giving
clear experimental evidence that the $\beta$ transitions arise
from a thermally populated excited state, because their
intensities rapidly decrease as the temperature is lowered.

In order to quantitatively measure the intensities of
the $\beta$ peaks as a function of temperature, the spectra of
the ground and excited states needed to be separated.
The separation was accomplished by using a Gaussian
fit for each individual peak. The validity of Gaussian
fits, especially for the low field transitions, has been pre-
viously established\cite{12}. The criterion for the goodness
of the fit was that the sum of the $\alpha$ and $\beta$ transitions
mirrors the experimental data quite well by visual inspection
and also by minimizing the remaining intensity obtained
by subtracting the Gaussian fits from the experimental
spectra. This remaining intensity was within the ex-
perimental noise in our separation procedure. Each Gaussian
fit was then summed to yield a separated $S = 10$
spectrum. The spectra were then separated by subtracting
the Gaussian fits of the $\alpha$ peaks from the experimental
spectra. These Gaussian fits were then summed, giving a
separated $S = 10$ spectrum. The remaining $\beta$ peaks were
then fit with Gaussian functions, and summed, yielding a
separated $S = 9$ spectrum. We verified that these sep-
.arated spectra agreed well with the experimental data by
taking the sum of the $\alpha$ and $\beta$ spectra and comparing it
with experiment, as shown in Fig. 4(a).

Figure 3 also shows the relative decrease in the inten-
sity of the separated excited state ($\beta$) spectra in relation
to the $S = 10$ spectra as the temperature is decreased.
The spectral envelope present in the $S = 10$ spectra at
5, 15, and 35 K is generally evident in the corresponding
excited state spectra, though the relative intensities are
modified slightly due to differing matrix elements in the
transition probabilities, $P_{nm} \propto |< \psi_n | S_{\pm} | \psi_m >|^2$, of
the two spin systems, given by Eq. 2:

$$P \propto [S \times (S + 1) - M_s \times (M_s + 1)].$$  

(2)

In order to analyze the intensity of the $\beta$ peaks we
normalized their intensities. The normalization process
involved dividing the intensity of a $\beta$ peak, with a given

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig3.png}
\caption{Temperature dependence of EPR spectra of Fe$_8$Br$_8$, for $B \parallel z$ at 131 GHz and 5, 15, and 35 K.}
\end{figure}

$M_s$ value, by the corresponding $\alpha$ peak with the same $M_s$
value. This enabled us to ignore instrumental effects and
spectral envelope changes with temperature. At 5 K, the
$\beta$ peaks are barely discernable from the noise level of
the spectrum. At 10 K, however, they increase in intensity
enough to emerge from the $\alpha$ transitions. The decreasing
intensity of the $\beta$ peaks, upon lowering temperature,
unambiguously designate the $\beta$ peaks as being due to a
thermally populated excited state.

Once it was concluded that the $\beta$ peaks originated
from an excited state, the spin multiplicity of the ex-
cited state needed to be determined. The presence of
an excited state (with perhaps $S = 9$) close to the
ground state of Fe$_8$Br$_8$ has been previously inferred from
magnetic susceptibility\cite{12}, and mentioned in subsequent
$\mu$SR\cite{24}, EPR\cite{25}, and neutron diffraction studies\cite{29}, with-
out any evidence for its location or multiplicity. Herein,
the spin multiplicity of the excited state has been de-
termined by two independent methods. First, by the
location of the leading peak ($\beta_{-9}$) in the set of peaks
assigned to the $S = 9$ state. Figure 3 shows an experi-
mental spectrum taken at 131 GHz and 35 K. As is evi-
The location of the first $S = 9$ peak was provided by Caciuffo et al. Additional, more quantitative support, that the spin Hamiltonian parameters are very different from those for the ground state, is strong evidence that the excited state is indeed $S = 9$, for the excited state, as anticipated theoretically. This lack of a $\beta_{-10}$ transition, barring spin Hamiltonian parameters being very different from those for the ground state, is strong evidence that the excited state is $S = 9$. The location of the first $\beta$ peak is consistent with slightly modified spin Hamiltonian parameters and a spin multiplicity of $S = 9$ for the excited state, as anticipated theoretically.

Additional, more quantitative support, that the spin $S$ of this excited state is indeed $S = 9$ was provided by computer simulations which were run using SIM. The procedure was first checked for the $S = 10$ state for which the parameters are known. The simulations for the $S = 10$ state were performed with the spin Hamiltonian parameters previously determined by Caciuffo et al. using neutron scattering. A typical comparison is shown in Fig. 4(a). The simulated spectra for the $S = 10$ ground state were in close agreement with our experimental results, thereby validating the simulation procedure.

The $\beta$ transitions were then accurately simulated for the three frequencies utilized (110, 131, and 155 GHz), using the spin Hamiltonian parameters obtained in the present study. A field-frequency plot is shown in Fig. 4(b). Quite good agreement can be seen between the simulated curves (continuous lines) and the observed peak positions. A more explicit and quantitative comparison is shown in Table I, using the measured data for 131 GHz. The D parameter decreases in magnitude by 8%, $-0.27 \pm 0.015$ K, $\mathcal{B}_1^0 = 1.3 \times 10^{-6}$ K,$\mathcal{B}_1^4 = 0$ K, $\mathcal{B}_1^4 = 0$ K.

![Experimental, resummed $\alpha$ and $\beta$, separated $S = 9$, and separated $S = 10$ spectra at 35 K and 131 GHz for B $\parallel z$. (b) Separated spectra at 15 K, (c) and at 5 K.](image)

**Fig. 4:** (a) Experimental, resummed $\alpha$ and $\beta$, separated $S = 9$, and separated $S = 10$ spectra at 35 K and 131 GHz for B $\parallel z$. (b) Separated spectra at 15 K, (c) and at 5 K.

**TABLE I:** Experimental and simulated peak positions at 131 GHz for the $S = 9$ state, for B $\parallel z$, using $D = -0.27$ K, $E = \pm 0.05$ K, $\mathcal{B}_1^0 = 1.3 \times 10^{-6}$ K, $\mathcal{B}_1^4 = 0$ K, $\mathcal{B}_1^4 = 0$ K.

| Transition $M_s \rightarrow M_{s+1}$ | Experiment (tesla) | Simulation (tesla) |
|----------------------------------|-------------------|-------------------|
| $-9 \rightarrow -8, \beta_{-9}$  | 1.2082            | 1.2282            |
| $-8 \rightarrow -7, \beta_{-8}$  | 1.6208            | 1.6400            |
| $-7 \rightarrow -6, \beta_{-7}$  | 2.0409            | 2.0608            |
| $-6 \rightarrow -5, \beta_{-6}$  | 2.4610            | 2.4691            |
| $-5 \rightarrow -4, \beta_{-5}$  | 2.8679            | 2.8727            |
| $-4 \rightarrow -3, \beta_{-4}$  | 3.2659            | 3.2760            |
| $-3 \rightarrow -2, \beta_{-3}$  | 3.6394            | 3.6721            |
| $-2 \rightarrow -1, \beta_{-2}$  | 4.0312            | 4.0585            |
| $-1 \rightarrow 0, \beta_{-1}$   | 4.4126            | 4.4571            |

![Experimental and simulated EPR spectra of Fe$_8$Br$_8$, for B $\parallel z$ at 35 K and 131 GHz.](image)

**Fig. 5:** Experimental and simulated EPR spectra of Fe$_8$Br$_8$, for B $\parallel z$ at 35 K and 131 GHz.

Linewidths were not an optimized parameter in the
FIG. 6: Frequency dependence of the first eight $\beta$ transitions in FeBr$_8$ with B || z. The solid lines portray the frequency dependence given by the spin Hamiltonian parameters determined in this work, whereas the solid squares are the observed field positions.

Simulations, though the relative intensities matched the experimental data well. Therefore, the simulated spectrum presented in this work is the sum of the $S = 10$ and $S = 9$ separated spectra using peak positions generated by SIM$^{30}$, the agreement between the experimental and simulated spectra, as shown in Fig. 6 can be seen to be quite satisfactory, thereby supporting the parameter assignment. We are thus able to assign the full experimental spectrum to transitions in the $S = 10$ multiplet ($\alpha$'s) and the $S = 9$ multiplet ($\beta$'s), as shown in Figure 2.

Once the spin Hamiltonian parameters had been determined, the relative intensities of the $\alpha$ and $\beta$ transitions were used, at temperatures from 5 to 35 K, to determine the location of the $S = 9$ state above the ground state. The intensity of a specific peak between given $M_s$ and $M_{s+1}$ states, is proportional to the population difference between the $M_s$ and $M_{s+1}$ states and the transition probability, $P$, as given in Eq. 1:

$$I \propto P(N_{M_s} - N_{M_{s+1}})/Z. \quad (3)$$

Therefore, assuming very similar partition functions and $D$ values for the two states, the intensity ratio between two transitions of the same $M_s$ states in the $S = 9$ and $S = 10$ manifolds, respectively, is given by Eq. 2:

$$I_9/I_{10} = (P_9/P_{10})\exp(-\Delta E_{10-9}/kT), \quad (4)$$

where $k$ is the Boltzmann constant and $\Delta E_{10-9}$ is the energy difference between given $M_s$ states in the $S = 10$ and $S = 9$ manifolds. The areas of the Gaussian fits, for a given $M_s$ to $M_{s+1}$ transition, were factored by their transition probabilities, in both the $S = 9$ and $S = 10$ manifolds, in order to determine their ratios. Due to the fact that each $\beta$ transition is normalized to its corresponding $\alpha$ transition, the ratio of intensities should be constant, regardless of the specific $M_s$ pair, for any given temperature.

A Boltzmann analysis of the intensity ratios is shown in Fig. 7b. The ratios of intensities of the $\beta$ to $\alpha$ transitions were compared at 5, 15, 20, 25, 30 and 35 K, and plotted vs. inverse temperature ($T^{-1}$). The slope yields the energy difference (18 K) between a given $M_s$ state and the corresponding $M_s$ state. Therefore, the energy difference between the $M_s = 10$ and $M_s = 9$ in zero field (5.46 K) must be added to the energy.

FIG. 7: (a) Temperature Dependence of the intensity of the -8 to -7 transition in the $S = 9$ state, $I_a$, normalized to the -8 to -7 transition in the $S = 10$ state, $I_{10}$. The curve joining the experimental points is a guide to the eye. (b) Boltzmann analysis of the normalized intensities of the $S = 9$ spin state. The slope yields the excitation energy as $18 \pm 2$ K between level with the same $M_s$ values in the $S = 10$ and $S = 9$ manifolds. Addition of the zero field splitting between the $M_s = -10$ and $M_s = -9$ levels (5.5 K) leads to the location of the $S = 9$ state at $24 \pm 2$ K above the ground state.
obtained from the Boltzmann analysis, yielding an energy difference $\Delta$ of 24 $\pm$ 2 K (16.7 $\pm$ 1.5 cm$^{-1}$). Figure 5 shows a schematic of the energy levels in zero field for the $S = 10$ and $S = 9$ manifolds based on the present study. Clearly, the higher $M_s$ levels of the $S = 9$ state overlap with the lower $M_s$ levels of the $S = 10$ state, indicating at least a partial breakdown of the single spin model.

IV. DISCUSSION

Our determination that the $S = 9$ manifold in Fe$_8$Br$_8$ is located 24 $\pm$ 2 K above the $S = 10$ ground state is in contrast to earlier suggestions based on magnetic susceptibility ($> 36$ K$^{-1}$). The four central Fe$^{3+}$ ions in the Fe$_8$Br$_8$ core $(\text{Fe}_1^{3+}, \text{Fe}_2^{3+}, \text{Fe}_3^{3+}, \text{and Fe}_4^{3+})$ (as shown in Fig. 1) can be described as that of a butterfly configuration. All magnetic coupling interactions, $J$, between Fe$^{3+}$ ions in Fe$_8$Br$_8$ have been determined to be antiferromagnetic. Therefore, the magnitude of these coupling constants dictates both the location and spin topology of the $S = 9$ excited state.

As mentioned in the Introduction, a detailed analysis of the $dc$ magnetic susceptibility data led Delfs et al. to two reasonable sets of exchange parameters; (a) $J_{1-2} = 20$ cm$^{-1}$, $J_{1-3} = 120$ cm$^{-1}$, $J_{1-5} = 15$ cm$^{-1}$, and $J_{3-5} = 35$ cm$^{-1}$, and (b) $J_{1-2} = 102$ cm$^{-1}$, $J_{1-3} = 120$ cm$^{-1}$, $J_{1-5} = 15$ cm$^{-1}$, and $J_{3-5} = 35$ cm$^{-1}$. While set (b) provided a much better fit to the experimental data, it predicted the position of the first excited state, $S = 9$, at less than 0.5 cm$^{-1}$ above the $S = 10$ ground state. We do note, however, that Delfs et al. did not include any zero field splitting terms in their susceptibility analysis. Nevertheless, this same basic configuration of exchange constants has been recently supported by detailed symmetry-based calculations by Raghu et al. Though the magnitudes of the coupling constants calculated by these authors are different from those of Delfs, the dominance of the $J_{1-3}$ interaction over other magnetic couplings remains consistent. The present study supports the essential correctness of set (a).

The coupling set (a) of Delfs et al. and the best set of Raghu et al., both show that $J_{1-3}$ dominates the exchange interactions. The perturbation leading to the $S = 9$ excited state must result from the smallest difference in $J$’s acting on the same ion or symmetrically equivalent set of Fe$^{3+}$ ions. Thus it seems reasonable to deduce that this perturbation does not involve $J_{1-3}$, hence the butterfly core $(\text{Fe}_1, \text{Fe}_2, \text{Fe}_3, \text{Fe}_4)$, but rather the Fe’s on the corners of the cluster $(\text{Fe}_5, \text{Fe}_6, \text{Fe}_7, \text{Fe}_8)$ via some linear combination of their wavefunctions.

The spin Hamiltonian parameters determined for the $S = 9$ state provide some insight to the origin of the anisotropy of the cluster. The $S = 9$ parameters are slightly different from those of the $S = 10$ ground state. The 7% larger $E$ value for $S = 9$ is in accord with increased transverse distortion in the Fe$_8$ structure. The decrease in $D$ with decreasing magnetic moment indicates that the anisotropy present in the Fe$_8$Br$_8$ core has some dipolar contribution rather than arising purely from a spin-orbit interaction. Similarly, the change in sign of the $B^0_{12}$ term indicates that $B^0_{12}$ originates from many-body interactions between Fe$^{3+}$ ions, and not from a collective sum of individual $B^0_{ij}$ terms. This argument is in line with the fact that a $B_3$ term needs an effective interaction involving at least four spins. Alternatively, this significant change in $B^0_{12}$ may be a result of the breakdown of the single spin model, as has been proposed by Katsnelson et al. in connection with Mn$_{12}$-Acetate. Additional, detailed angular variation studies are underway for precise measurement and understanding of these questions.

The anisotropy barrier, estimated from $D$ and $E$ values for the $S = 9$ manifold is 22 K, as compared to that for the $S = 10$ ground state (29 K).

V. CONCLUSIONS

Using variable frequency, high-field, EPR measurements on single crystals of Fe$_8$Br$_8$, we have detected a set of transitions, labelled as $\beta$, which have been conclusively assigned to the $S = 9$ spin multiplet, located at an energy $\Delta = 24 \pm 2$ K ($17 \pm 1.5$ cm$^{-1}$) above the ground $(S = 10)$ state. The spin Hamiltonian parameters have been determined to a good accuracy, and differ from those of the $S = 10$ state: $D$ is smaller by 8%, while $E$ is larger by 7%. These parameters yield the anisotropy barrier ($\sim$ DS$_z^2 \sim 22$ K), about 25% smaller than for $S = 10$. $B^0_{12}$ for $S = 9$ also shows a dramatic change, the sign is opposite to that for the $S = 10$ state. Although electronic structure calculations have been reported for Fe$_8$Br$_8$, there has been little definitive

![FIG. 8: Schematic for the energy levels of both the $S = 10$ and the $S = 9$ states in zero magnetic field. $S = 9$ is located at an energy $\Delta = 24 \pm 2$ K as marked.](Image)
data on excited states. The results of the present study should serve as sensitive basis for more refined theoretical modelling of the bonding and magnetic properties of these materials.

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1. R. Sessoli, D. Gatteschi, A. Caneschi, and M.A. Novak, Nature (London) 365, 141 (1993).
2. M.A. Novak, R. Sessoli, A. Caneschi, and D. Gatteschi, J. Magn. Magn. Mater. 146, 211 (1995).
3. J.R. Friedman, M.P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. 76, 3830 (1996).
4. C. Sangregorio, T. Ohm, C. Paulsen, R. Sessoli, and D. Gatteschi, Phys. Rev. Lett. 78, 4645 (1997).
5. J.A.A.J. Perenboom, J.S. Brooks, S. Hill, T. Hathaway, and N.S. Dalal, Phys. Rev. B 58, 330 (1998).
6. S. Hill, R.S. Edwards, S.I. Jones, N.S. Dalal, and J.M. North, Phys. Rev. Lett. 90, 217204 (2003).
7. M.R. Cheesman, V.S. Oganesyan, R. Sessoli, D. Gatteschi, and A.J. Thompson, Chem. Comm. 17, 1677 (1997).
8. E.M. Chudnovsky and J. Tejada, Macroscopic Quantum Tunneling of the Magnetic Moment (Cambridge University Press, Cambridge, 1998).
9. M.N. Leuenberger and D. Loss, Nature 410, 789 (2001).
10. K. Weighardt, K. Pohl, I. Jibril, and G. Huttner, Angew. Chem. Int. Ed. Engl. 23, 77 (1984).
11. A.L. Barra, P. Debrunner, D. Gatteschi, C.E. Schulz, and R. Sessoli, Europhys. Lett. 35, 133 (1996).
12. C. Delfs, D. Gatteschi, L. Pardi, R. Sessoli, K. Weighardt, and D. Hanke, Inorg. Chem. 32, 3099 (1993).
13. R. Caciuffo, G. Amoretti, A. Murani, R. Sessoli, A. Caneschi, and D. Gatteschi, Phys. Rev. Lett. 81, 4744 (1998).
14. S. Carretta, E. Livioiti, G. Amoretti, R. Caciuffo, A. Caneschi, and D. Gatteschi, Phys. Rev. B 65, 052411 (2002).
15. S. Hill, J.A.A.J. Perenboom, N.S. Dalal, T. Hathaway, T. Stalcup, and J.S. Brooks, Phys. Rev. Lett. 80, 2453 (1998).
16. S. Maccagnano, R. Achey, E. Negusse, A. Lussier, M.M. Mola, S. Hill, and N.S. Dalal, Polyhedron 20, 1441 (2001).
17. A.L. Barra, D. Gatteschi, and R. Sessoli, Chem. Eur. J 6, 1608 (2000).
18. E. del Barco, J.M. Hernandez, J. Tejada, N. Biskup, R. Achey, I. Rutel, N.S. Dalal, and J.S. Brooks, Phys. Rev. B 62, 3018 (2000).
19. R. Blinc, P. Cveč, D. Arcon, N.S. Dalal, and R.M. Achey, Phys. Rev. B 63, 212401 (2001).
20. K. Park, M.A. Novotny, N.S. Dalal, S. Hill, and P.A. Rikvold Phys. Rev. B 65, 014426 (2002).
21. S. Hill, S. Maccagnano, K. Park, R.M. Achey, J.M. North, and N.S. Dalal, Phys. Rev. B 65, 224410 (2002).
22. Y. Furukawa, K. Kumagai, A. Lascialfari, S. Aldrovandi, F. Borsa, R. Sessoli, and D. Gatteschi, Phys. Rev. B 64, 094439 (2001).
23. W. Wernsdorfer and R. Sessoli, Science 284, 133 (1999).
24. A. Lascialfari, P. Carretta, D. Gatteschi, C. Sangregorio, J.S. Lord, and C.A. Scott, Physica B 289-290, 110 (2000).
25. A. Mukhin, B. Gorshunov, M. Dressel, C. Sangregorio, and D. Gatteschi, Phys. Rev. B 63, 214411 (2001).
26. A.L. Barra, F. Bencini, A. Caneschi, D. Gatteschi, C. Paulsen, C. Sangregorio, R. Sessoli, and L. Sorace, Chem. Phys. Chem 2 523 (2001).
27. A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions (Dover Publications, Inc., New York, 1986).
28. (a) S. Hill, N.S. Dalal, and J.S. Brooks, Appl. Mag. Reson. 16, 237 (1999); (b) M. Mola, S. Hill, P. Goy, and M. Gross Rev. Sci. Instrum. 71, 186 (2000).
29. Y. Pontillon, A. Caneschi, D. Gatteschi, R. Sessoli, E. Ressouche, J. Schweizer, and E. Lelievre-Berna, J. Am. Chem. Soc. 121, 5342 (1999).
30. Simulation software by Dr. H. Weihe; for more information see http://sophus.kiku.dk/software/epr/epr.html.
31. C. Raghu, I. Rudra, D. Sen, and S. Ramasesha, Phys. Rev. B 64, 064419 (2001).
32. M.I. Katsnelson, V.V. Dobrovitski, and B.N. Harmon, Phys. Rev. B 59, 6919 (1999).
33. J. Kortus, M.R. Pederson, C.S. Hellberg, S.N. Khanna, Eur. Phys. J. D 16, 177 (2001).
34. M.R. Pederson, J. Kortus, S.N. Khanna, J. Appl. Phys. 91, 7149 (2002).