Local Spin Anisotropy Effects upon the Magnetization and Specific Heat of Dimer Magnets

Dmitri V. Efremov1,* and Richard A. Klemm2,†

1Institut für Theoretische Physik, Technische Universität Dresden, 01062 Dresden, Germany
2Department of Physics, Kansas State University, Manhattan, KS 66506 USA

(Dated: March 23, 2022)

We present an exactly solvable model of equal spin $s_1$ dimer single molecule magnets. The spins within each dimer interact via the Heisenberg and the most general quadratic global and local (single-ion) anisotropic spin interactions, and with the magnetic induction $\mathbf{B}$. For antiferromagnetic couplings and $s_1 > 1/2$, the low temperature $T$ magnetization $\mathbf{M}(\mathbf{B})$ exhibits $2s_1$ steps of universal height and midpoint slope, the $s$th step of which occurs at the non-universal level-crossing magnetic induction $B_{s,s}^{lc}(\theta, \phi)$, where $\theta, \phi$ define the direction of $\mathbf{B}$. The specific heat $C_V$ exhibits zeroes as $T \to 0$ at these $B_{s,s}^{lc}(\theta, \phi)$ values, which are equally surrounded by universal peak pairs as $T \to 0$. The non-universal $B_{s,s}^{lc}(\theta, \phi)$ values lead to a rich variety of magnetization plateau behavior, the structure and anisotropy of which depend upon the various global and local anisotropic spin interaction energies. We solve the model exactly for $s_1 = 1/2$, 1, and 5/2, and present $\mathbf{M}(\mathbf{B})$ and $C_V(\mathbf{B})$ curves at low $T$ for these cases. For weakly anisotropic dimers, rather simple analytic formulas for $\mathbf{M}(\mathbf{B})$ and $C_V(\mathbf{B})$ at arbitrary $s_1$ accurately fit the exact solutions at sufficiently low $T$ or large $B$. An expression for $B_{s,s}^{lc}(\theta, \phi)$ accurate to second order in the four independent anisotropy energies is derived. Our results are discussed with regard to existing experiments on $s_1 = 5/2$ Fe$_2$ dimers, suggesting further experiments on single crystals of these and some $s_1 = 9/2$ [Mn$_4$]$_2$ dimers are warranted.

PACS numbers: 05.20.-y, 75.10.Hk, 75.75.+a, 05.45.-a

INTRODUCTION

Single molecule magnets (SMM’s) have been under intense study recently, due to their potential uses in magnetic storage and quantum computing.1–3 The materials consist of insulating crystalline arrays of identical SMM’s 1-3 nm in size, each containing two or more magnetic ions. Since the magnetic ions in each SMM are surrounded by non-magnetic ligands, the intermolecular magnetic interactions are usually negligible. Although the most commonly studied SMM’s are the high-spin Mn$_{12}$ and Fe$_{8}$,1–5 such SMM’s contain a variety of ferromagnetic (FM) and antiferromagnetic (AFM) intramolecular interactions, rendering unique fits to a variety of experiments difficult.6

In addition, there have been many studies of AFM Fe$_n$ ring compounds, where $n = 6, 8, 10, 12$, etc.7–10 In these studies, analyses of inelastic neutron diffraction data and the magnetic induction $\mathbf{B}$ dependence of the low-temperature $T$ specific heat and magnetization steps were made, using the isotropic Heisenberg near-neighbor exchange interaction, the Zeeman interaction, and various near-neighbor spin anisotropy interactions.7–10 However, the rings were so complicated that analyses of the data using those simple models were inaccessible to present day computers.8, 9 Thus, those authors used either simulations or phenomenological fits to a first-order perturbation expansion with different spin anisotropy values for each global ring spin value.8–10

Here we focus on the simpler cases of equal spin $s_1 = s_2$ magnetic dimers, for which the full spin anisotropy effects can be evaluated analytically, investigated in detail numerically, and compared with experiment. AFM dimers with $s_1 = 1/2, 3/2, [11–14]$ and various forms of Fe$_2$ with $s_1 = 5/2$ were studied recently.15–20 Several Fe$_2$ dimers and effective $s_1 = 9/2$ dimers of the type [Mn$_4$]$_2, [21, 22]$ have magnetic interactions weak enough that their effects can be probed at $T \approx 1K$ with presently available $\mathbf{B}$. A comparison of our results with magnetization $\mathbf{M}$ versus $\mathbf{B}$ step data on a Fe$_2$ dimer strongly suggests a substantial presence of local spin anisotropy.17

The paper is organized as follows. In Section II, we present the model in the crystal representation and given exact formulas for the matrix elements. The general thermodynamics are presented in Section II, along with the universal behavior of the $\mathbf{M}(\mathbf{B})$ and $C_V(\mathbf{B})$ behavior associated with the energy level crossing. In Section IV, we solve the model exactly for $s_1 = 1/2$, giving analytic expressions for the magnetization and specific heat. In Section V, we discuss the exact solution for $s_1 = 1$, present the equations from which the eigenvalues are readily obtained, and give numerical examples of the low-$T$ magnetization and specific heat curves. In Section VI, we present numerical examples of the low-$T s_1 = 5/2$ magnetization and specific heat curves. In section VII, we rotate to the induction representation, and give the eigenstates to first order in the anisotropy energies. These are used to obtain asymptotic expressions for the magnetization and specific heat for arbitrary $s_1$ that are highly accurate at sufficiently low $T$ and/or large $B$. In addition, analytic formulas for the magnetic inductions at which the level crossings occur are provided, accurate to sec-
ond order in the anisotropy energies. Finally, in Section VIII we discuss our results with regard to experiments on Fe₂ dimers.

**THE MODEL IN THE CRYSTAL REPRESENTATION**

We represent the \( s_1 = s_2 \) dimer quantum states, \( |\psi_s^m\rangle \) in terms of the global (total) spin and magnetic quantum numbers \( s \) and \( m \), where \( S = S_1 + S_2 \) and \( S_z = S \cdot \hat{z} \) satisfy \( S^2 |\psi_s^m\rangle = s(s + 1) |\psi_s^m\rangle \) and \( S_z |\psi_s^m\rangle = m |\psi_s^m\rangle \), where \( s = 0, 1, \ldots, 2s_1 \), \( m = -s, \ldots, s \), and we set \( \hbar = 1 \). We also have \( S_{\pm} |\psi_s^m\rangle = A_s^{z} |\psi_s^{m\pm 1}\rangle \), where \( S_{\pm} = S_x \pm i S_y \)

\[
A_s^m = \sqrt{(s-m)(s+m+1)}. \tag{1}
\]

For an arbitrary \( B \), we assume the Hamiltonian has the form

\[
\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_a + \mathcal{H}_b + \mathcal{H}_d + \mathcal{H}_c,
\]

contains the Heisenberg exchange and Zeeman interactions, the gyromagnetic ratio \( \gamma = g \mu_B \), where \( g \approx 2 \) and \( \mu_B \) is the Bohr magneton. The global axial and azimuthal anisotropy terms

\[
\mathcal{H}_b = -J_b S_z^2 \tag{3}
\]

and

\[
\mathcal{H}_d = -J_d (S_x^2 - S_y^2), \tag{4}
\]

respectively, only involve components of \( S \), but have been the main anisotropy terms discussed in the SMM literature,[5, 21] so we have included them for comparison. Such terms have been commonly studied as an effective Hamiltonian for a singlet orbital ground state, in which the tensor global spin interaction with a fixed spin quantum number \( s \) has the form \( A \cdot S \cdot \hat{S} \), resulting in the principal axes \( x, y \) and \( z \).[23] For a dimer, we take \( \hat{S} \) to be diagonal in the orientation pictured in Fig. 1. Then

\[
J = -(\Lambda_{xx} + \Lambda_{yy})/2, \quad J_0 = -\Lambda_{zz} + (\Lambda_{xx} + \Lambda_{yy})/2, \quad J_d = (\Lambda_{yy} - \Lambda_{xx})/2.
\]

Taking \( |J_d/J| \ll 1 \) and \( |J_0/J| \ll 1 \) still leaves \( J_d/J_0 \) unrestricted. The single-ion axial and azimuthal anisotropy terms,\n
\[
\mathcal{H}_a = -J_a \sum_{i=1}^{2} S_{iz}^2, \tag{5}
\]

and

\[
\mathcal{H}_c = -J_c \sum_{i=1}^{2} (S_{ix}^2 - S_{iy}^2), \tag{6}
\]

respectively, arise from spin-orbit interactions of the local crystal field with the individual spins. These terms have usually been neglected in the SMM literature, but have been studied with regard to complexes containing a single magnetic ion, such as Ni²⁺,[23] and with regard to clusters of larger numbers of identical magnetic ions.[23, 24]

The local axial and azimuthally anisotropic exchange interactions

\[
\mathcal{H}_f = -J_f S_{1z} S_{2z}, \tag{7}
\]

\[
\mathcal{H}_c = -J_c (S_{1x} S_{2x} - S_{1y} S_{2y}), \tag{8}
\]

satisfy

\[
2\mathcal{H}_f/J_f = \mathcal{H}_b / J_0 - \mathcal{H}_a / J_a, \tag{9}
\]

\[
2\mathcal{H}_c/J_c = \mathcal{H}_d / J_0 - \mathcal{H}_c / J_c, \tag{10}
\]

so we need only include either \( \mathcal{H}_a \) or \( \mathcal{H}_f \) and \( \mathcal{H}_c \) or \( \mathcal{H}_e \), respectively.[23] That is, if we stick to the Hamiltonian \( \mathcal{H}_c \), we may incorporate the effects of \( \mathcal{H}_f \) and \( \mathcal{H}_e \) by letting \( J_0 \to J_0 + J_f/2 \), \( J_a \to J_a - J_f/2 \), and \( J_d \to J_d + J_c/2 \), \( J_e \to J_e - J_c/2 \), respectively. Since \( \mathcal{H}_a \) and \( \mathcal{H}_c \) describe the axial and azimuthal anisotropy each single ion attains from its surrounding environment, they are the physically relevant local anisotropy interactions.

For the case of Fe₂,[15] a constituent of the high-spin SMM Fe₈ and the AFM Fe₈ rings,[4, 8, 9] the exchange between the Fe⁺³ \( s_1 = 5/2 \) spins occurs via two oxygen ions, and these four ions essentially lie in the same \((xz)\) plane.[15, 18] We set the \( z \) axis parallel to the dimer axis, as pictured in Fig. 1. Since the quantization axis is along the dimer axis, which is fixed in a crystal, we denote this representation as the crystal representation.

We generally expect each of the \( J_j \) for \( j = a, b, d, e \) to satisfy \( |J_j/J| \ll 1 \), but there are not generally any other restrictions upon the various magnitudes of the \( J_j \). Since all dimers known to date have predominantly AFM couplings \( (J < 0) \), and also because their magnetizations and specific heats are particularly interesting, we shall only consider AFM dimers. In addition, since no studies on unequal-spin dimers have been reported to our knowledge, we shall only treat the equal-spin \( s_1 = s_2 \) case.

We note that for equal spin dimers, the group symmetry of the dimer environment is \( C_{2v} \), so that Dzialoshinskii-Moriya interactions do not arise.[23] Hence, our Hamiltonian \( \mathcal{H} \) is the most general quadratic anisotropic spin Hamiltonian of an equal-spin dimer.

For \( B = B(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \), we have

\[
\mathcal{H}_0 |\psi_s^m\rangle = E_s^m |\psi_s^m\rangle + \delta E \sum_{\sigma = \pm 1} e^{-i\sigma \phi} A_s^{m\sigma} |\psi_s^{m + \sigma}\rangle, \tag{11}
\]

\[
\mathcal{H}_b |\psi_s^m\rangle = -J_b m^2 |\psi_s^m\rangle, \tag{12}
\]

and

\[
\mathcal{H}_d |\psi_s^m\rangle = -J_d \sum_{\sigma = \pm 1} F_s^{m\sigma} |\psi_s^{m + 2\sigma}\rangle, \tag{13}
\]

where
FIG. 1: Sketch of an Fe₂ dimer, with two bridging O⁻² ions (O). Ligands (not pictured) are attached to the Fe⁺³ ions (Fe). The arrows signify spins.

\[ E_s^m = -J_s(s+1)/2 - mb \cos \theta, \]  
\[ \delta E = -\frac{1}{2} b \sin \theta, \]  
\[ b = \gamma B. \]  
\[ F_x^s = A_x^s A_x^{1+s}. \]  
\[ \mathcal{H}_a \text{ and } \mathcal{H}_c \text{ contain the individual spin operators } S_{iz} \text{ and } S_{iz}^{1/2} \text{ for } i = 1, 2. \]  
\[ \mathcal{H}_x \text{ and } \mathcal{H}_y \text{ allow transitions satisfying } \Delta s = 0, \Delta m = 0, \pm 2. \]  
\[ \Delta \mathcal{H}_z \text{ allows transitions } \Delta s = 0, \pm 2, \Delta m = 0, \pm 2. \]  
\[ H_{s,s_1}^{m,\sigma} = D_{s+(\sigma'+1)/2,s_1}^m D_{s+(3\sigma'+1)/2,s_1}^m, \]  
\[ K_{s,s_1}^{\sigma,\sigma'} = C_{s+(\sigma'-1)/2,s_1}^s C_{s-(3\sigma'+1)/2,s_1}^s, \]  
\[ L_{s,s_1}^x = 2F_s^s \alpha_{s,s_1}, \]  
\[ \alpha_{s,s_1} = \frac{3s(s+1) - 4s_1(s_1+1) - 3}{(2s-1)(2s+3)}. \]  

We note that \( \alpha_{s,s_1} = 1 - \gamma_{s,s_1}^2 - \gamma_{s,s_1+1}^2 \) and that Eq. (29) holds for \( s \geq 0 \). Equations (18) and (19) allow for an exact solution to the most general Hamiltonian of arbitrary order in the individual spin operators. In all previous treatments of more complicated spin systems with similar anisotropy interactions, it was only possible to obtain numerical solutions, and therefore the full anisotropy of the magnetization and specific heat was not calculated.[23, 24] The operations of \( \mathcal{H}_0, \mathcal{H}_b \) and \( \mathcal{H}_d \) satisfy the selection rules \( \Delta s = 0, \Delta m = 0, \pm 1, \pm 2 \).

**GENERAL THERMODYNAMICS**

In order to obtain the thermodynamic properties, we first calculate the canonical partition function, \( Z = \text{Tr} \exp(-\beta \mathcal{H}) \). Since \( \mathcal{H} \) is not diagonal in the \( (s,m) \) representation, we must construct the wave function from all possible spin states. We then write

\[ Z = \text{Tr}(\Psi_{s_1} e^{-\beta \mathcal{H}} | \Psi_{s_1} \rangle), \]  
where \( | \Psi_{s_1} \rangle \) is constructed from the \( \{ | \psi_s^m \rangle \} \) basis as

\[ | \Psi_{s_1} \rangle = | \psi_{s_1}^m \rangle, | \psi_{s_1}^{m-1} \rangle, \ldots, | \psi_1^0 \rangle, | \psi_0^{-1} \rangle, | \psi_0^0 \rangle \],

where \( \beta = 1/(k_B T) \) and \( k_B \) is Boltzmann’s constant.

To evaluate the trace, it is useful to diagonalize the \( \langle \mathcal{H} | \mathcal{H} | \Psi_{s_1} \rangle \) matrix. To do so, we let \( | \Psi_{s_1} \rangle = U | \Phi_{s_1} \rangle \), where

\[ | \Phi_{s_1} \rangle = (| \phi_{n_{s_1}} \rangle, | \phi_{n_{s_1}+1} \rangle, \ldots, | \phi_1 \rangle), \]  
and

\[ | \Phi_{s_1} \rangle = \left( | \phi_{n_{s_1}} \rangle, | \phi_{n_{s_1}+1} \rangle, \ldots, | \phi_1 \rangle \right), \]  
where \( \mathcal{U} \) is a unitary matrix of rank \( n_{s_1} = (2s_1 + 1)^2 \). Choosing \( \mathcal{U} \) to diagonalize \( \mathcal{H} \), we generally obtain \( \mathcal{H} | \phi_n \rangle = \epsilon_n | \phi_n \rangle \) and the partition function for a SMM dimer,

\[ Z = \sum_{n=1}^{n_{s_1}} \exp(-\beta \epsilon_n). \]
The specific heat \( C_V = k_B \beta^2 \frac{\partial^2 \ln Z}{\partial \beta^2} \) is then easily found at all \( T, B \),

\[
C_V = \frac{k_B \beta^2}{Z^2} \left[ Z \sum_{n=1}^{n_{s1}} \epsilon_n^2 e^{-\beta \epsilon_n} - \left( \sum_{n=1}^{n_{s1}} \epsilon_n e^{-\beta \epsilon_n} \right)^2 \right].
\]

(34)

It is easily seen from Eq. (34) that at the induction \( B_{s,s_1}^{lc} \), corresponding to the th level crossing in which \( \epsilon_s = \epsilon_{s-1}, C_V \to 0 \) as \( T \to 0 \). The magnetization requires \( \nabla_B(\epsilon_s) \) for each \( B \). As \( T \to 0 \), at most two eigenstates are relevant. For most \( B \) values, only one \( \epsilon_n \) is important. But near the th level-crossing induction \( B_{s,s_1}^{lc}(\theta, \phi) \) at which \( \epsilon_s = \epsilon_{s-1} \), two eigenstates are relevant. We then have

\[
C_V \left[ B_{s,s_1}^{lc}(\theta, \phi) \right] \quad \to \quad 0, \quad \text{as} \quad T \to 0.
\]

(36)

\[
C_V \left[ B_{s,s_1}^{lc}(\theta, \phi) \right] \cdot \frac{\partial C_V}{\partial \epsilon_n} \quad \to \quad \frac{c}{\cos c}, \quad \text{as} \quad T \to 0.
\]

(37)

\[
\frac{dM}{\gamma dB} \left[ B_{s,s_1}^{lc}(\theta, \phi) \right] = \frac{\beta \gamma}{4},
\]

(38)

\[
\text{where} \quad s = 1, \ldots, 2s_1 \quad \text{and} \quad c \approx 1.19967864 \quad \text{is the solution to} \quad \tan c = 1/c. \quad \text{The easiest way to obtain Eq. (39) is to first rotate the crystal so the quantization axis is along} \quad B, \quad \text{as discussed in Appendix B. We note that} \quad B_{s,s_1}^{lc}(\theta, \phi) \quad \text{depends upon} \quad s, s_1, \quad \text{and the direction of} \quad B \quad \text{when anisotropic interactions are present. Hence, the heights and midpoint slopes of the} \quad 2s_1 \quad M(B) \quad \text{steps are universal, but the step positions and hence their plateaus are not. Correspondingly, the} \quad 2s_1 \quad \text{positions of the} \quad C_V(B) \quad \text{zeros are non-universally spaced, but each zero is equally surrounded by two peaks of equal, universal height, the universal spacing between which is} \quad \propto T \quad \text{as} \quad T \to 0. \quad \text{Hence, the non-universal level-crossing inductions} \quad B_{s,s_1}^{lc}(\theta, \phi) \quad \text{fully determine the low-T thermodynamics of AFM dimers. In the next three sections, we consider the special cases of} \quad s_1 = 1/2, \quad 1 \quad \text{and} \quad 5/2. \quad \text{Then, in Section VII and Appendix D, we present out general expression for} \quad B_{s,s_1}^{lc}(\theta, \phi) \quad \text{accurate to second order in each of the} \quad J_j. \quad \text{We remark that a double peak in the low-T} \quad C_V(B) \quad \text{curve has been seen experimentally in a much more complicated FeB ring compound, and was attributed to level crossing.}\]

\text{ANALYTIC RESULTS FOR SPIN 1/2}

Plots of \( C_V/k_B \) and \( M/\gamma \) versus \( \gamma B/|J| \) for the isotropic spin 1/2 dimer were given previously. For \( s_1 = 1/2 \) with an arbitrary \( B \) and \( J_j \) for \( j = a, b, d, c \), the rank 4 Hamiltonian matrix is block diagonal, since \( s = 0,1 \) is a good quantum number. The eigenvalues are given by

\[
\epsilon_1 = \frac{J_d}{2},
\]

(41)

\[
\epsilon_n = \frac{J_d}{2} - J + \lambda_n, \quad n = 2, 3, 4,
\]

(42)

\[
0 = \lambda_n^2 + 2\lambda_n J_b - \lambda_n \left[ J_d^2 - J_b^2 + \lambda_n^2 \right] - b^2 \sin^2 \theta [J_b - J_d \cos(2\phi)].
\]

(43)

For the special cases \( B||i \) for \( i = x, y, z \), the \( \lambda_n^i \) satisfy

\[
\lambda_n^x = 0, -J_b \pm F_z,
\]

(44)

\[
\lambda_n^{xy} = -2J_y, -J_y \pm F_x
\]

(45)

\[
F_i = \sqrt{b^2 + J_d^2},
\]

(46)

\[
J_{x,y,z} = (J_b - J_d)/2, \quad J_d
\]

(47)

\[
\Delta_x = \exp(-\beta J_{x,y}) \exp(-\beta J_y) + \exp(2\beta J_{x,y}),
\]

(50)

\[
\Delta_z = \exp(-\beta J_b) \exp(-\beta J_y) + 1,
\]

(51)

\[
\text{respectively. When the interactions are written in terms of the less physical} \quad J_d, \quad J_b, \quad \text{and} \quad J_c, \quad \text{then} \quad J_b \to J_b + J_f \quad \text{and} \quad J_d \to J_d + J_c/2, \quad \text{so that for} \quad s_1 = 1/2, \quad J_f \quad \text{and} \quad J_c \quad \text{merely renormalize} \quad J_b \quad \text{and} \quad J_d. \quad \text{Neither of the single-ion spin anisotropy terms} \quad H_a \quad \text{and} \quad H_c \quad \text{affect the thermodynamics for} \quad s_1 = 1/2. \quad \text{We note that} \quad M_b(J_d) = M_c(-J_d) \quad \text{for} \quad B, \quad \text{as expected from} \quad H_d = -J_d(S_x^2 - S_y^2) \quad \text{for} \quad H_d = -J_d(S_x^2 - S_y^2).
\]

\[
\text{From Eqs. (41), (42), (44), and (45), the single level crossing induction} \quad (s = 1) \quad \text{for} \quad \text{am} \quad s_1 = 1/2 \quad \text{dimer with} \quad B||i \quad \text{occurs at}
\]

\[
\gamma B_{1/2}^{lc} = \left\{ \sqrt{J_x^2 + J_b + J_d}, \quad B||\hat{x}, \quad \text{and} \quad B||\hat{z} \right\},
\]

(52)

\[
\text{provided that} \quad J + J_{xy,y} < 0 \quad \text{and} \quad J + J_b < 0, \quad \text{respectively.}
\]

\[
\text{To distinguish the different effects of the global anisotropy interactions} \quad J_b \quad \text{and} \quad J_d \quad \text{that affect the magnetization of} \quad s = 1/2 \quad \text{dimers, in Figs. 2 and 3, we}
\]
have respectively plotted the low-$T$ $M/\gamma$ versus $\gamma B/|J|$ with $J_b = 0.1 J$, $J_d = 0$ and $J_d = 0.1 J$, $J_b = 0$ for $B||\hat{z}$ (solid) and $B||\hat{x}$ (dashed), along with the isotropic case $J_b = J_d = 0$ (dotted). From Fig. 2, $J_b < 0$ and $J_d = 0$ causes a greater shift to higher $B$ values at the magnetization step with $B||\hat{z}$ than for $B||\hat{x}$, consistent with Eq. (52). In addition, $J_d$ finite with $J_b = 0$ has a very different effect upon the anisotropy of the magnetization step, as shown in Fig. 3. Although for $B||\hat{z}$, $B$ at the step is slightly reduced from its isotropic interaction value, for $B||\hat{x}$, the magnetization step occurs at a larger $B$. These results are consistent with Eq. (52). The midpoint slopes are universal, in accordance with Eq. (7?slope).

The specific heat of an $s_1 = 1/2$ dimer with $B||\hat{i}$ is

$$C_{V_i} = \frac{k_B \beta^2 N_i}{D_i^2},$$  \hspace{1cm} (53)

where the $D_i$ are given by Eq. (49), and the $N_i$ are given in Appendix A. Plots at low $T$ of $C_V/k_B$ versus $\gamma B/|J|$ for $s_1 = 1/2$ dimers with the corresponding global anisotropies $J_b = 0.1 J$ and $J_d = 0.1 J$ are shown in Figs. 4 and 5, respectively. We note the universal curve shapes, but non-universal level-crossing positions, in quantitative agreement with Eqs. (36)-(38). In Fig. 4, the positions of the maxima and the central minimum in $C_V$ track that of the magnetization step in Fig. 2 with the same parameters. With $J_d = 0.1 J$, the behaviors in $C_V$ and $M$ for $B||\hat{x}$ are also very similar. However, there is a slight difference in the behaviors for $B||\hat{z}$. Note that $M$ (Fig. 3) shows a slight reduction for $B||\hat{z}$ in the induction required for the step, whereas $C_V$ (Fig. 5) shows a slight increase in the positions of the peaks. This detail only appears when $J_d \neq 0$, for which the effective temperature

![Plot of $M/\gamma$ versus $\gamma B/|J|$ at $k_B T/|J| = 0.03$ for the AFM spin 1/2 dimer with $J_b = 0.1 J$, $J_d = 0$, with $B||\hat{z}$ (solid), $B||\hat{x}$ (dashed), along with the isotropic case $J_b = J_d = 0$ (dotted).](image1)

![Plot of $M/\gamma$ versus $\gamma B/|J|$ at $k_B T/|J| = 0.03$ for the AFM spin 1/2 dimer with $J_d = 0.1 J$, $J_b = 0$, with $B||\hat{z}$ (solid), $B||\hat{x}$ (dashed), along with the isotropic case $J_b = J_d = 0$ (dotted).](image2)

![Plot of $C_V/k_B$ versus $\gamma B/|J|$ for the AFM spin 1/2 dimer with $J_b = 0.1 J$, $J_d = 0$ at $k_B T/|J| = 0.03$ with the same curve notation as in Fig. 2.](image3)

![Plot of $C_V/k_B$ versus $\gamma B/|J|$ for the AFM spin 1/2 dimer with $J_b = 0.1 J$, $J_d = 0$ at $k_B T/|J| = 0.03$ with the same curve notation as in Fig. 2.](image4)

is slightly higher than for $J_d = 0$.

**ANALYTIC AND NUMERICAL RESULTS FOR SPIN 1**

For dimers with $s_1 = 1$, the allowed $s$ values are $s = 0, 1, 2$. The three $s = 1$ states are decoupled from the six remaining $s = 0, 2$ states. They satisfy a cubic equation given in Appendix A. For $B||i$ with $i = x, y, z$, this cubic equation simplifies to a linear and a quadratic equation, as for the $s = 1$ eigenstates of $s_1 = 1/2$ dimers.

The remaining six eigenstates corresponding nominally
to $s = 0, 2$ are in general all mixed. The matrix leading to the hexatic equation from which the six eigenvalues can be obtained is given in Appendix A. That is sufficient to evaluate the eigenvalues for $s_1 = 1$ using symbolic manipulation software. When combined with the three $s = 1$ eigenvalues, one can then use Eqs. (34) and (35) to obtain the resulting exact magnetization and specific heat at an arbitrary $B$. The combined nine eigenvalues depend upon all four anisotropy parameters $J_j$ for $j = a, b, d, e$.

To the extent that the eigenvalues can be obtained from the solutions to either linear or quadratic equations, the expressions for the $B_{s1}$ are simple, and are given in Appendix A. In the global anisotropy case $J_a = J_e = 0$, the first level crossing induction $B_{11}$ with $B$ is identical to $B_{11}^{c=1/2}$, the level crossing with $s_1 = 1/2$ given by Eq. (52). For comparison, we expand the first and second level crossing inductions to first order in each of the $J_j$ for $j = a, b, d, e$ for $B|i$ where $i = x, y, z$.

$$\gamma B_{11,1,x}^{c=1} = -J + \frac{J_a}{3} - J_b,$$  \hspace{1cm} (54)

$$\gamma B_{11,1,x,y}^{c=1} = -J - \frac{J_a}{6} - \frac{J_b}{2} + \frac{1}{2}(J_d - J_e),$$  \hspace{1cm} (55)

$$\gamma B_{11,1,z}^{c=1} = -2J - J_a - 3J_b,$$  \hspace{1cm} (56)

$$\gamma B_{11,1,z}^{c=1} = -2J + \frac{J_a}{2} - \frac{J_b}{2} + \frac{5J_d}{2} + 3J_e,$$  \hspace{1cm} (57)

where the upper (lower) sign is for $B|x$ ($B|y$), respectively.

From these simple first-order results, it is possible to understand the qualitatively different behavior obtained with local, single-ion, anisotropy from that obtained with global anisotropy. In the isotropic case $J_j = 0\forall j$, the first and second level crossings occur at $-J$ and $-2J$, respectively. For each induction direction, the signs of the $J_b$ and $J_d$ contributions to $B_{21}^{c=1} + 2J$ and $B_{11}^{c=1} + J$ are the same, whereas the signs of the $J_a$ and $J_e$ contributions to $B_{21}^{c=1} + 2J$ and $B_{11}^{c=1} + J$ are the opposite.

In Figs. 6-15, we plot $M/\gamma$ and $C_V/k_B$ versus $\gamma B/|J|$ for five low-$T$ cases of AFM $s_1 = 1$ dimers, taking $k_B T/|J| = 0.03$. The $M/\gamma$ curves all exhibit the universal features predicted by Eqs. (39) and (40). The corresponding $C_V/k_B$ curves also obey the universal features predicted in Eqs. (36)-(38). In these figures, only one of the five anisotropy interactions $J_j$ is non-vanishing, and we take $J_j/|J| = 0.1$, for $j = b, d, a, c$, and $e$, respectively. Unlike the case of $s_1 = 1/2$ dimers, for which $J_e$ merely renormalizes $J_d$, for $s_1 = 1$ all of these interactions lead to distinct anisotropy effects in the low-$T$ magnetization and specific heat. Of course, since the case $J_e = 0.1 J$ (and the remaining $J_j = 0$) can be evaluated by setting $J_d = 0.05J$ and $J_c = -0.05J$ for any $s_1$, it is not really distinct from the other anisotropy interactions, but only represents that particular combination of global and local azimuthal anisotropy interactions.

We first show the results for the global anisotropy interactions. In Figs. 6 and 7, we plot $M(B)$ and $C_V(B)$ for $J_b = 0.1 J$ (and all other $J_j = 0$) at $k_B T/|J| = 0.03$ for the AFM $s_1 = 1$ dimer. The level-crossing induction increases monotonically with level-crossing number, with the largest induction required occurring for $B|x$, as for $s_1 = 1/2$, quantitatively consistent with Eqs. (54)-(57). In Figs. 8 and 9, the corresponding results for $J_d = 0.1 J$ (and the other $J_j = 0$) are shown. Again, the level-crossing induction increases monotonically with level-crossing number, and the largest induction required
for each level crossing occurs for $B\parallel \hat{x}$, quantitatively consistent with Eqs. (54)-(57), as for $s_1 = 1/2$. We note that the solid curves for $B\parallel \hat{z}$ are nearly identical with the dotted curves for the isotropic case $J_d = 0$, as shown in Figs. 3 and 5, and is a detail of the shapes of the $M$ and $C_V$ curves arising from a slightly higher effective temperature with $J_d \neq 0$ than in the other cases studied.

Next, in Figs. 10-13, we show the corresponding curves for $M(B)$ and $C_V(B)$ at low $T$ for the local anisotropies $J_a = 0.1J$ and $J_c = 0.1J$, respectively, with the other $J_j = 0$. In contrast to the global anisotropies, the increase in $B$ required with the level crossing is not monotonic in the level-crossing number, quantitatively consistent with Eqs. (54)-(57). In particular, we note that in each of these figures, the deviations in the level crossings $B_{2,1}^k + 2J$ and $B_{1,1}^c + J$ are opposite in sign.

A careful examination of the exact formula for $C_V$ reveals that it vanishes at precisely the level crossing inductions as $T \to 0$. Similarly, the magnetization curve attains its midpoint values $\frac{1}{2}$ and $\frac{3}{2}$ between the two neighboring steps at the level crossing inductions as $T \to 0$.

Finally, in Figs. 14 and 15, we show the corresponding $M(B)$ and $C_V(B)$ curves for $J_c = 0.1J$, corresponding to the parameter choices $J_c = -0.05J$ and $J_d = 0.05J$. With this combination, the magnetization and specific heat curves shown in Figs. 14 and 15 resemble those for $J_d = 0.1J$ shown in Figs. 8 and 9, except that the second magnetization steps and the second set of specific heat peaks have nearly the same behavior as do the first magnetization steps and specific heat double peaks.

In short, the case $s_1 = 1$, for which the exact expressions from which the eigenvalues can be readily obtained are sufficiently short as to be writable on paper, are sufficient to exhibit the very different behaviors obtained from the single-ion, local spin anisotropy interactions from those obtained from the global spin anisotropy interactions. As $s_1$ increases beyond 1, the situation becomes not only more complicated, but also more interesting, as shown in the following.
EXACT NUMERICAL RESULTS FOR SPIN $5/2$

For $s_1 = 5/2$, one of the cases of greatest experimental interest, when $H_a$ and $H_e$ are present, none of the allowed $s, m$ values is a true quantum number. That is, $H_a$ and $H_e$ cause all of the states with nominally odd or even $s$ to mix with one another. For $B||\hat{i}$ for $i = x, y, z$, this simplifies in the crystal representation as for $s_1 = 1$, since only states with odd or even $m$ in the appropriately chosen representation can mix. By using symbolic manipulation software, it is possible to solve for the exact eigenvalues of the $s_1 = 5/2$ dimer. However, because the analytic expressions for the eigenvalues are much more complicated than those for $s_1 = 1$ presented in Appendix A, we shall not attempt to present them, but will instead focus upon their numerical evaluation for specific cases.

To first order in the $J_j$, the first three level crossings for $B||\hat{i}$ with $i = x, y, z$ are

$$
\gamma_{B_{1.5/2, z}^{le(1)}} = -J + \frac{32J_a}{15} - J_b, \quad (58)
$$

$$
\gamma_{B_{1.5/2, x,y}^{le(1)}} = -J - \frac{16J_a}{15} - \frac{J_b + J_d}{2} + \frac{16J_e}{15}. \quad (59)
$$
FIG. 14: Plot at $k_B T/|J| = 0.03$ and $J_c/|J| = 0.1$ of $M/\gamma$ versus $\gamma B/|J|$ for the AFM spin 1 dimer. Curves for $B||\hat{z}$ (solid), $B||\hat{x}$ (dashed), and the isotropic case ($J_c = 0$, dotted) are shown.

FIG. 15: Plot at $k_B T/|J| = 0.03$ and $J_c/|J| = 0.1$ of $C_V/k_B$ versus $\gamma B/|J|$ for the AFM spin 1 dimer. Curves for $B||\hat{z}$ (solid), $B||\hat{x}$ (dashed), and the isotropic case ($J_c = 0$, dotted) are shown.

$$
\gamma F_{2,5/2,z}^{(1)} = -2J - \frac{8J_a}{35} - 3J_b,
$$
(60)

$$
\gamma B_{2,5/2,x,y}^{(1)} = -2J + \frac{4J_a}{35} - \frac{J_d}{2} + \frac{5J_d}{2} + \frac{12J_c}{35},
$$
(61)

$$
\gamma D_{3,5/2,z}^{(1)} = -3J - \frac{106J_a}{63} - 5J_b,
$$
(62)

$$
\gamma B_{3,5/2,x,y}^{(1)} = -3J + \frac{53J_a}{63} - \frac{J_d}{2} + \frac{9J_d}{2} + \frac{53J_c}{21}.
$$
(63)

In Figs. 16-23, we plot $M/\gamma$ and $C_V/k_B$ versus $\gamma B/|J|$ for four low-$T$ cases of AFM $s_1 = 5/2$ dimers, $J_b = 0.1J$, $J_d = 0.1J$, $J_a = 0.1J$, and $J_c = 0.1J$, respectively, and the other $J = 0$, taking $k_B T/|J| = 0.03$. In Fig. 24, examples of $M(\theta)$ at fixed $B$ and $\phi = 0$ are shown. Figures 16-24 are sufficient to distinguish the more interesting local spin anisotropy effects in AFM dimers with higher $s_1$ values from the non-existent or less interesting ones present with $s_1 = 1/2, 1$, respectively. In Figs. 16, 18, 20, and 22, the solid and dashed curves represent the cases of $B||\hat{z}$ and $B||\hat{x}$, and the dotted curve is the isotropic case, $J = 0\forall j$, as in Figs. 2-15. Because of the number of peaks in the specific heat curves, in Figs. 17, 19, 21, and 23, we only showed $C_V/k_B$ versus $\gamma B/|J|$ for $B||\hat{z}$ (solid) and $B||\hat{x}$ (dashed). The isotropic curve with $J = 0\forall j$ was published previously.[14] That curve has
FIG. 18: Plot of $M/\gamma$ versus $\gamma B/|J|$ for the AFM spin 5/2 dimer at $k_B T/|J| = 0.03$ with $J_d/|J| = 0.1$. Curves for $B||z$ (solid), $B||x$ (dashed), and the isotropic case ($J_b = 0$, dotted) are shown.

FIG. 19: Plot of $k_B T/|J| = 0.03$ and $J_d/|J| = 0.1$ of $C_V/k_B$ versus $\gamma B/|J|$ at $k_B T/|J| = 0.03$ for the AFM spin 5/2 dimer. Curves for $B||z$ (solid), $B||x$ (dashed), and the isotropic case ($J_b = 0$, dotted) are shown.

minima at $\gamma B/|J| = s$ for $s = 1, \ldots, 5$, each of which is central to double peaks. $H_a$ and $H_b$ are invariant under $x \leftrightarrow y$, so curves for $B||x$ in Figs. 16, 17, 20, and 21 are identical to those for $B||y$. Since $H_d$ and $H_c$ are odd under $x \leftrightarrow y$, the $B||x$ curves in Figs. 18, 19, 22, and 23 correspond to $B||y$ with $J_d/|J| = -0.1 J$, $J_c/|J| = -0.1 J$, respectively.

We first examine the global spin anisotropy effects of $H_b$ and $H_d$ in Figs. 16-19. These figures exhibit the same behavior shown for $s_1 = 1/2, 1$ in the corresponding Figs. 2-9. Note that $B^{lc}_{s,5/2}(\theta, 0)$ is largest for $\theta = \pi/2$ with $J_b = 0.1 J$ and for $\theta = 0$ with $J_d = 0.1 J$, and increases monotonically with $s$, as for $s_1 = 1$ in both cases, nearly quantitatively consistent with Eqs. (58)-(63).

In contrast, the local field anisotropy interactions show very different and much more interesting behaviors. In Figs. 20-21, we present our results for the effects of the single-ion axial anisotropy interaction $H_a$, Eq. (5). As in Fig. 10 for $s_1 = 1$, $B^{lc}_{s,5/2}(\theta, 0) + s J$ changes sign with increasing $s$. $B^{lc}_{s,5/2}(\theta, 0) + J < 0$, whereas for $s \geq 2$, $B^{lc}_{s,5/2}(\theta, 0) + J > 0$ and increases monotonically with $s$. For $\theta = \pi/2$, nearly the opposite situation occurs. $B^{lc}_{s,5/2}(\pi/2, 0) + s J$ is positive for $s = 1$ and decreases monotonically with increasing $s$. In both cases, $B^{lc}_{s,5/2}(\pi/2, 0) + s J$ is a minimum for $s = 2$. These local axial anisotropy effects, consistent with Eqs. (58)-(63), are very different than the global anisotropy ones pictured in Figs. 16-19. They are also much richer and interesting than the corresponding case for $s_1 = 1$ pictured in Figs. 10 and 11.

In Figs. 22-23, we present $M/\gamma$ versus $\gamma B/|J|$ results for the case of the local azimuthally anisotropic exchange interaction, $H_e$, Eq. (8), evaluated for AFM dimers at $k_B T/|J| = 0.03$ with $J_e = 0.1 J$ and the remaining $J_f = 0$ and $J_d = J_b = 0$. $B^{lc}_{s,5/2}(\theta, 0)$ for this case is obtained from Eqs. (58)-(63) by setting $J_d, J_e, J_c = \pm J_c/2$, respectively, and $J_d = J_b = 0$. $B^{lc}_{s,5/2}(\theta, 0)$ is nearly indistinguishable from the isotropic case, as in Figs. 12 and 13 for $s_1 = 1$, except for some minor curve shape effects far from the step midpoints. $B^{lc}_{s,5/2}(\pi/2, 0) + s J$ is always positive, as for $s_1 = 1$ shown in Figs. 12 and 13, but has a minimum at $s = 3$. This is also in stark contrast to the monotonic global anisotropy behavior for $s_1 = 5/2$ seen in Figs. 16-19. Both of these behaviors are nearly quantitatively consistent with Eqs. (58)-(63) as modified to include $J_e$.

In contrast, the local field anisotropy interactions show very different behaviors. In Figs. 20 and 21, our results for the effects of the single-ion axial anisotropy interaction $H_a$, Eq. (5), are shown. As in Figs. 10 and 11, the induction anisotropy effects of $H_a$ change sign with increasing $B$. In Fig. 20, for $B||z$ the first magnetization step appears at a lower value of $|B|$ than in the isotropic case, and for steps 3-5, there is a monotonic increase in the extra field required for each step. The opposite is true for $B||x$, for which the first step appears at a larger $|B|$ value than for the isotropic case, and subsequent magnetization steps appear at monotonically decreasing values of $|B|$. A cross-over occurs at about the second step, for which the effects of this type of anisotropy are small. The corresponding shifts in the positions of the double peaks in the specific heat are shown in Fig. 21. These local axial anisotropy effects are very different than the global anisotropy ones pictured in Figs. 16-19.
In Figs. 22 and 23, we present our $M$ and $C_V$ results for the case of the local azimuthally anisotropic exchange interaction, $H_c$, Eq. (8), evaluated for AFM dimers at $k_B T/|J| = 0.03$ with $J_c = 0.1 J$, or equivalently with $J_d = 0.05 J$ and $J_e = -0.05 J$ (and the remaining $J_j = 0$). For $B||\hat{z}$, there is almost no change from the isotropic case, as occurred with the global azimuthal anisotropy pictured in Figs. 128 and 19. For $B||\hat{x}$, the field required for each step is larger than in the isotropic interaction case, as in Figs. 14 and 15 for $s_1 = 1$, and for global azimuthal anisotropy shown in Figs. 18 and 19. However, in this case, the extra induction required for each level crossing is non-monotonic in the crossing number, with the largest extra induction required for the first crossing, and the minimum extra induction required for the intermediate, third crossing. This is in stark contrast to the monotonic global anisotropy behavior for $s_1 = 5/2$ seen in Figs. 16-19. Although not pictured explicitly, the behavior for $J_e =$
0.1\(J\) with the other \(J_j = 0\) is rather like that of the 
\(J_a = 0.1J\) curves pictured in Figs. 20 and 21 with \(\hat{z} \leftrightarrow \hat{x}\), differing in ways similar to those differences between 
the \(J_a = 0.1J\) and \(J_c = 0.1J\) curves pictured for \(s_1 = 1\) in Figs. 10-13. As indicated in Eqs. (58)-(63), the 
\(B_{sc,5/2}(0,0)\) are nearly independent of \(J_c\). However, the 
\(B_{sc,5/2}(\pi/2,0) + sJ\) with \(J_c = 0.1J\) are nearly three times as large as for \(J_a = 0.1J\) case, so that the minimum 
\(|B_{sc,5/2}(\pi/2,0) + sJ|\) is also a minimum for \(s = 2\). More 
details are given in Section VII and Appendix D.

In addition, the angular dependencies of \(M\) are different 
for each of the four \(J_j\) we presented for \(s_1 = 5/2\). In 
Fig. 24, we present the results for \(|M(B,\theta,\phi = 0)|/\gamma\) 
varying \(J_1\) near the second level crossing at \(\gamma|B|/J| = 
0.2.1\) and \(k_B T/|J| = 0.03\) for each of the four \(s_1 = 5/2\) 
AFM magnetization cases pictured in Figs. 16, 18, 20, 
and 22. Note that \(|M(B,\pi - \theta, 0)| = |M(B,\theta, 0)|\). The 
\(J_a\) and \(J_b\) curves, while rather similar at \(\gamma|B|/J| = 
2.0\), are very different at \(\gamma|B|/J| = 2.1\). Hence, 
\(M(B)\) depends strongly upon the particular type of spin 
anisotropy.

**Analytic Results for Weakly Anisotropic Dimers of Arbitrary Spin**

Induction representation eigenstates first order in the anisotropies

Since the diagonalization of the Hamiltonian matrix 
is difficult for an arbitrary magnetic field \(B\) direction 
and for an arbitrary combination of spin anisotropy 
interactions, and must be done for each value of \(s_1\) separately, it is useful to consider a perturbative solution in 
the relative strengths \(J_j/J\) of the anisotropy interactions. 
We nominally assume \(|J_j/J| \ll 1\) for \(j = a, b, d, e\). 
However, to compare with low-\(T\) \(M(B)\) and \(C_V(B)\) ex-
periments at various \(H\) directions and magnitudes, one 
cannot take \(B\) to be small. In order to incorporate an 
arbitrary \(B\) accurately, we rotate the crystal axes \((\hat{x}, \hat{y}, \hat{z})\) 
to \((\hat{x}', \hat{y}', \hat{z}')\), so that \(B = B\hat{z}'\). The rotation matrix 
and a brief discussion of its ramifications are given in 
Appendix B.

In these rotated coordinates, the Zeeman interaction 
\(-\gamma B S z\) is diagonal. We therefore denote this representation 
as the induction representation. The Hamiltonian \(\mathcal{H}'\) in this representation is given in Appendix B. In the 
induction representation, we choose the quantum states to be \(|\varphi^m_s\rangle\). In the absence of the four anisotropy inter-
actions \(J_j\), \(\mathcal{H}' = \mathcal{H}'_0\) is diagonal,

\[
\mathcal{H}'_0|\varphi^m_s\rangle = E_{s}^{(0)}|\varphi^m_s\rangle,
\]

where

\[
E_{s}^{(0)} = -J_s(s+1)/2 - \gamma B m.
\]

The operations of the remaining terms in \(\mathcal{H}'\) on the 
eigenstates \(|\varphi^m_s\rangle\) are given in Appendix C. The first order correction to the energy in this representation is \(E_{s}^{(1)} = 
\langle \varphi^m_s | \mathcal{H}' | \varphi^m_s \rangle\), which is found to be

\[
E_{s,s_1}^{(1)} = -\frac{J_b}{2}[2s(s+1)-1] - \frac{J_a}{2}[s(s+1)-1]
\]

\[
+ \frac{J_{d,e}}{2}[m^2 + s(s+1)-1]
\]

\[
+ \frac{1}{2}[s(s+1) - 3m^2]
\]

\[
\times \left( \frac{J_{b,a}^s}{2} \cos^2 \theta + \frac{J_{d,e}^s}{2} \sin^2 \theta \cos(2\phi) \right),
\]

where

\[
\frac{J_{b,a}^s}{2} = J_b + \alpha_{s,s_1} J_a,
\]

\[
\frac{J_{d,e}^s}{2} = J_d + \alpha_{s,s_1} J_e,
\]

and \(\alpha_{s,s_1}\) is given by Eq. (29).

Since the \(\theta, \phi\) dependence of \(E_{s}^{(1)}\) arises from the term proportional to \(J_{b,a}^s \cos^2 \theta + J_{d,e}^s \sin^2 \theta \cos(2\phi)\), it is tempting to think that the thermodynamics with 
\(J_{b,a}^s = 0\) and \(B||z\) are equivalent to those with \(J_{b,a}^s = 0\) 
and \(B||\hat{z}\). However, as shown explicitly in the following, 
the \(\theta, \phi\)-dependent parts of Eq. (66) strongly break this 
anapparent equivalence, causing the \(B_{s,s_1}(\theta, \phi)\) for these 
two cases to differ. This implies that \(J_b\) and \(J_d\) are 
equivalent, as are \(J_a\) and \(J_e\), even to first order in the anisotropy strengths.

**First order thermodynamics**

To first order in the anisotropy interactions, \(s\) and \(m\) 
are still good quantum numbers, so the partition function

\[
Z \approx \sum_{s=0}^{2s_1} \sum_{m=-s}^{s} e^{-\beta E_{s,s_1}^{(1)}},
\]
where \( E_{m,s,s_1} = E_{m,(0)} + E_{m,(1)} \). Although it is difficult to perform the summation over the \( m \) values analytically, it is nevertheless elementary to evaluate \( Z \) numerically for an arbitrary \( B, \theta, \phi, \) and \( T \) from the eigenstate energies. The magnetization is obtained from

\[
M(B, \theta, \phi) \approx \frac{\beta}{2} \sum_{s=0}^{2s_1} \sum_{m=-s}^{s} m e^{-\beta E_{m,s,s_1}}. \tag{70}
\]

Similarly, the specific heat to first order in the anisotropy interactions is found from

\[
C_V(B, \theta, \phi) \approx \frac{k_B \beta^2}{Z^2} \left[ Z \sum_{s=0}^{2s_1} \sum_{m=-s}^{s} \left( E_{m,s,s_1}^{(0)} \right)^2 e^{-\beta E_{m,s,s_1}^{(0)}} \right. \\
\left. - \left( \sum_{s=0}^{2s_1} \sum_{m=-s}^{s} E_{m,s,s_1}^{(0)} e^{-\beta E_{m,s,s_1}^{(0)}} \right)^2 \right]. \tag{71}
\]

As a test of the accuracy of this first-order calculation, we have compared the first-order and exact \( M(B) \) obtained for the \( s_1 = 5/2 \) dimer with \( J_a = 0.1J \) and \( B \parallel \hat{z} \) in Fig. 25. The corresponding comparison between the first-order and exact \( C_V(B) \) is shown in Fig. 26. We see that the curves evaluated using the first-order and the exact expressions for \( M \) and \( C_V \) with \( s_1 = 5/2 \) are indistinguishable at \( k_B T/|J| = 0.03 \). The \( C_V \) curves are noticeably different at \( k_B T/|J| = 0.1 \) for \( \gamma B/|J| < 0.4 \), and at \( k_B T/|J| = 0.3 \), they are noticeably different for \( \gamma B/|J| < 2.6 \). Corresponding noticeable differences in the \( M \) curves at the same \( B \) values appear at \( T \) values roughly three times as high as in the \( C_V \) curves.

At very low \( T \), \( k_B T/|J| \ll 1 \), the most important states in this perturbative scheme are the minima for each \( s \) value, \( E_{s,s_1}^{(0)} \), which determine the first-order level crossings. As \( T \to 0 \), we can ignore all of the \( m \neq s \) states in Eqs. (69)-(71).

**Level crossings first order in the anisotropies**

We can find an expression for the \( s^{th} \) AFM level crossing at the induction \( B_{s_{s_1}}^{(1)} \) to first order in the anisotropy interactions for a general \( s_1 \) spin dimer by equating \( E_{s_{s_1}}^{(0)} + E_{s_{s_1}}^{(1)} \) to \( E_{s_{s_1}}^{(0)} - E_{s_{s_1}}^{(1)} \),

\[
\gamma B_{s_{s_1}}^{(1)} = -J_s - J_b/2 - c_{s_{s_1}} J_a \\
\left\{ \frac{(4s - 3)}{2} [J_b \cos^2 \theta + J_c \sin^2 \theta \cos(2\psi)] \right\} \\
+ 3c_{s_{s_1}} [J_a \cos^2 \theta + J_c \sin^2 \theta \cos(2\psi)], \tag{72}
\]

\[
c_{s,s_1} = \frac{[3 + 3s^2 - 4 \sin^2 (s_1 + 1)]}{2(s_1 + 1)(2s_1 + 3)}. \tag{73}
\]

This expression is consistent with those obtained for \( s_1 = 1/2 \) given by Eqs. (52) and (54)-(57). In addition, this expression is nearly quantitatively in agreement with the \( M(B) \) and \( C_V(B) \) behaviors pictured for \( s_1 = 5/2 \) in Figs. 16-23. We note that \( \gamma B_{s_{s_1}}^{(1)} \) contains the \( \theta, \phi \)-independent terms, \( -J_s - J_b/2 - c_{s_{s_1}} J_a \), which distinguish \( J_b \) from \( J_a \) and \( J_a \) from \( J_c \).

In particular, we note that the single-ion anisotropy interactions behave very differently with increasing step number than do the global anisotropy interactions, especially for large \( s_1 \). For the three cases we studied in detail, for \( s_1 = 1/2 \), \( c_{1,1/2} = 0 \), so that the local anisotropy terms are irrelevant, for \( s_1 = 1 \), \( c_{1,1} = \frac{1}{2} \) and \( c_{2,1} = -\frac{1}{2} \) have different signs, and for \( s_1 = 5/2 \) as in Fe\(_2\) dimers, the
first three $c_{s,5/2}$ coefficients are $\frac{15}{4}$, $\frac{3}{4}$, and $\frac{-5}{4}$, respectively, the second being an order of magnitude smaller than the other two, and opposite in sign from the first. For $s_1 = 9/2$ dimers such as $[\text{Mn}_4]_2$, the first four $c_{s,9/2}$ are $\frac{15}{4}$, $\frac{3}{4}$, $\frac{-5}{4}$, and $\frac{-25}{3}$, which changes sign between $s = 2$ and $s = 3$, where its magnitude is a minimum.

This is in sharp contrast to the global anisotropy interactions, for which the analogous coefficient $(4s - 3)/2$ increases monotonically from $\frac{4}{5}$ to $\frac{3}{2}$ as $s$ increases from 1 to 2, independent of $s_1$. These differences should be possible to verify experimentally in careful low-temperature experiments at high magnetic fields applied at various directions on single crystals of those $s_1 = 5/2$ Fe$_2$ and $s_1 = 9/2$ [Mn$_4$]$_2$ dimers for which $|J|$ is sufficiently small.

**Level crossings to second order in the anisotropy energies**

To aid in the analysis of experimental data, we have extended this perturbative calculation to second order. Since we expect the $|J_x/J| \leq 0.1$ in most circumstances, this extension should be sufficient to accurately analyze most experimentally important samples. To second order in the anisotropy interactions, the eigenstate energies $E^{(2)}_{s,s_1}$ are given in Appendix C. We note that the $E^{(2)}_{s,s_1}$ contains divergences at $\gamma B/|J| = 0, 2s - 1, 2s + 3, s - 1/2$, and $s + 3/2$, so that near to those values, one would need to modify the perturbation expansion to take proper account of the degeneracies. Hence, the expressions for $E^{(2)}_{s,s_1}$ cannot be used in the asymptotic expressions for the thermodynamics, Eqs. (69)-(71). However, as the 8th AFM level crossing occurs approximately at $\gamma B/|J| = s$, which is far from any divergences, we can safely use this second order expansion to obtain an expression for the level crossings second order in the anisotropy interaction energies. We find

$$\gamma B^{lc(2)}_{s,s_1} = \gamma B^{lc(1)}_{s,s_1} + \left( E^{(2)}_{s,s_1} - E^{(2)}_{s-1,s_1} \right) \bigg|_{B = -J_s/\gamma}$$

(74)

where $\gamma B^{lc(1)}_{s,s_1}$ is given by Eq. (73).

The full expression for $B^{lc(2)}_{s,s_1}$ is given in Appendix D. From this expression, it is easy to see that for $s_1 = 1/2$, $E^{lc(2)}_{1,1/2} = f_1(\theta, \phi) + \frac{1}{2} f_2(\theta, \phi)$, where $f_1$ and $f_2$ are given in Appendix D. For $B||\hat{x}$, $E^{lc(2)}_{1,1/2} = -\frac{1}{2} T_x^2/|J|$, and with $B||\hat{x}, \hat{y}$, $E^{lc(2)}_{1,1/2} = -\frac{1}{8} (J_x + J_d)/|J|$, in agreement with the expansion to second order in the $J_y$ of our exact formulas in Eq. (52). However, the second order functions have more complicated $\theta, \phi$ dependencies than do the first order $B^{lc(1)}_{s,s_1}$ in Eq. (73). We have also explicitly checked each formula in Appendix D for $s_1 = 1$ and $s = 1, 2$. Thus, Eq. (74) is a highly accurate expression for the full $\theta, \phi$ dependencies of all $s = 1, \ldots, 2 s_1 + 1$ level crossings of a single crystal dimer of single ion spin $s_1$.

By superposing this non-universal level-crossing formula, Eq. (74), combined with the universal behavior presented in Eqs. (77)-(80), it is easy to use our results in accurate fits to experimental data at low temperatures and high magnetic fields on dimers with arbitrary $s_1$ values.

**SUMMARY AND CONCLUSIONS**

In summary, we solved for the low-temperature magnetization and specific heat of equal spin $s_1$ antiferromagnetic dimer single molecule magnets, including the most general forms of anisotropic spin exchange interactions quadratic in the spin operators. The magnetization and specific heat exhibit steps and zeroes, respectively, at the non-universal level-crossing induction values $B^{lc}_{s,s_1}(\theta, \phi)$, but the magnetization steps and their mid-point slopes, plus the two peaks surrounding the specific heat zeroes all exhibit universal behavior at sufficiently low temperatures. Local (or single-ion) anisotropy interactions lead to low-temperature magnetization step plateaus that have a much richer variation with the magnetic induction $B$ than do those obtained from global anisotropy interactions, provided that $s_1 > 1/2$. We derived simple, accurate asymptotic analytic expressions for the low-temperature magnetization and specific heat for the most general quadratic anisotropic spin interactions at an arbitrary $B$, and an accurate expression for $B^{lc}_{s,s_1}(\theta, \phi)$, enabling fast and accurate fits to experimental data.

There were two low-$T$ $M(B)$ studies of Fe$_2$ dimers. [16, 17] For $\mu$-oxalotetetakis(acetylacetonato)Fe, all five peaks in $dM/dB$ were measured in pulsed magnetic fields $H$. These evenly spaced peaks indicated little, if any, spin anisotropy effects.[16] On the other hand, studies of the first 2-3 $dM/dH$ peaks in powdered samples of $[\text{Fe(salen)}\text{Cl}]_2$, where salen is $N, N'$-ethylenebis(saliclylidenemimino), were much more interesting.[17] These data showed a broad first peak at $B = 17 - 20T$ that was only partially resolvable into two separate peaks, followed by a sharp second peak at $B = 36 T$, consistent with local axial anisotropy of strength $|J_a/|J| \approx 0.1$, as obtained from the derivatives of the curves shown in Fig. 20 From Eqs. (58)-(63), one could also have $(|J_a| + 3|J_d|)/|J| \approx 0.1$. These values might perhaps be combined with a smaller $|J_e/|J|$, obtained from the derivatives of the curves pictured in Fig. 22.

Without a detailed single crystal study with the magnetic field directed along a number of different crystal directions, it is impossible to determine the relative amounts of $J_a$ and $J_e$ that would best fit the data. However, the existing data on $[\text{Fe(salen)}\text{Cl}]_2$ appear to be
inconsistent with a predominant global anisotropy inter-
action of either type, as obtained from the derivatives of
the curves shown in Figs. 16 and 18. Only single crystal
studies could determine if a small amount of such global
anisotropy interactions were present in addition to one
or more presumably larger local spin anisotropy interac-
tions. In comparing the two materials cited above, it ap-
pears that the interaction of a Cl− ion neighboring each
Fe3+ ion leads to strong local (or single-ion) anisotropy
effects. In order to verify this hypothesis and to eluci-
date the details of the interactions, further experiments
using single crystals in different field orientations on this
and related Fe2 dimers with 1-3 similarly bonded Cl−
ions are urged.[19, 20] We also urge single crystal data
on some of the s1 = 9/2 [Mn4]2 dimers,[21, 22] as well
as on s1 = 1/2 dimers lacking in predicted local spin
anisotropy effects. [11–14] To aid in the fits, we derived
simple, useful formulas for the magnetization and specific
heat with

\[ N_z = F_z^2 \cosh(2\beta F_z) + \frac{J^2}{4} e^{-\beta(J+2J_0)} \]

\[ + \frac{1}{2} e^{-\beta F_z} \cosh(\beta F_z) \]

\[ \times \left( \left( [J + J_{x,y}]^2 + F_{x,y}^2 \right) e^{-\beta J} + \left( [2J_{y,x} - J_{x,y}]^2 + F_{x,y}^2 \right) e^{2\beta J_{x,y}} \right), \]  

(75)

**APPENDIX A**

**Specific heat details for s1 = 1/2**

We first present the numerators of the exact expres-
sions for the specific heat with s1 = 1/2 and \( B_i \) for

\[ N_{x,y} = F_{x,y}^2 + \frac{1}{4} (J + 2J_{x,y})^2 e^{\beta[2(J_{y,x} - J_{x,y}) - J]} + F_{x,y} \sinh(\beta F_{x,y}) e^{-\beta J_{x,y}} \]

\[ \times \left( (J + J_{x,y}) e^{-\beta J} + (J_{x,y} - 2J_{y,x}) e^{2\beta J_{x,y}} \right] \]

\[ \times \left( (J + J_{x,y}) e^{-\beta J} + (J_{x,y} - 2J_{y,x}) e^{2\beta J_{x,y}} \right], \]

(76)

\[ \epsilon_n = -J - J_b - J_a + \lambda_n, \quad \text{for } n = 2, 3, 4, \]

(77)

\[ 0 = -\lambda_n^3 - (J_a - J_b) \lambda_n^2 + \lambda_n [b^2 + (J_d - J_e)^2] \]

\[ + (J_a - J_b) [b_x^2 + (J_d - J_e)^2] \]

\[ - (J_d - J_e) [b_y^2 - b_y^2], \]

(78)

where the \( b_i = \gamma B_i \) as in Eq. (77). For \( B_i \mid \hat{z} \), the cubic equation is easily solved to yield

\[ \lambda_n = J_b - J_a \pm \sqrt{b^2 + (J_d - J_e)^2}. \]

(79)

\[ \epsilon_n = -3J - \frac{4}{3} J_a - 2J_b + \lambda_n \]

(82)

We then define

\[ \tilde{J}_a = \frac{\sqrt{8}}{3} J_a, \]

(83)

\[ \tilde{J}_b = J_b + J_a/3, \]

(84)

\[ \tilde{J}_d = J_d + J_e/3, \]

(85)

\[ \tilde{J}_e = \frac{2}{\sqrt{3}} J_e, \]

(86)

\[ \tilde{J} = J - \frac{2}{9} J_a, \]

(87)

**ACKNOWLEDGMENTS**

We thank the Max-Planck-Institut für Physik kom-
plexer Systeme, Dresden, Germany, the University of
North Dakota, Grand Forks, ND, USA, and Talat S. Rah-
man for their kind hospitality and support. This work
was supported by the Netherlands Foundation for the
Fundamental Research of Matter and by the NSF under
contract NER-0304665.

In the remainder of this appendix, we provide the de-
tails of our exact results for s1 = 1. The cubic equation
for the three s = 1 eigenvalues is given by
and obtain the Hermitian matrix $\hat{M}$ for the six $s = 0, 2$ states, the eigenvalues of which are the $\lambda_n$. For brevity, we let

\begin{align*}
Q_n^p &= n \bar{J}_b + pb \cos \theta, \\
b_\perp &= b \sin \theta e^{-i\phi}, \\
b_3 &= \sqrt{\frac{3}{2}} b_\perp, \\
a &= \bar{J}_a, \\
d_3 &= 3 \bar{J}_b, \\
d_6 &= \sqrt{6} \bar{J}_d, \\
e &= \bar{J}_e. 
\end{align*}

Then, the matrix $\hat{M}$ is given by

\begin{equation}
\hat{M} = \begin{pmatrix}
Q_{-2}^2 & -b_\perp & -d_6 & 0 & 0 & -e \\
-b_\perp^* & Q_{-1}^2 & -b_3 & -d_3 & 0 & 0 \\
-b_6^* & b_3 & Q_2^0 & -b_3 & -d_6 & -a \\
0 & -d_3 & -b_3^* & Q_{1}^1 & -b_\perp & 0 \\
0 & 0 & -d_6 & -b_3^* & Q_{2}^2 & -e \\
-e & 0 & -a & 0 & -e & Q_3^0 + 3 \bar{J}
\end{pmatrix}.
\end{equation}

After some rearrangement, the $\lambda_n$ are found to satisfy

\begin{align*}
0 &= \sum_{p=0}^{6} c_p (\lambda_n)^p, \\
c_0 &= 1, \\
c_5 &= -2 \bar{J}_b - 3 \bar{J}_d, \\
c_4 &= -2 \bar{J}_b^2 - 7 \bar{J}_d^2 - 21 \bar{J}_b^2 - 2 \bar{J}_d^2 - 5b^2, \\
c_3 &= 3 \bar{J}_b \left( 7 \bar{J}_d^2 + 21 \bar{J}_b^2 + 5b^2 \right) \\
&\quad + 2 \bar{J}_b \left( -\bar{J}_d^2 + 8 \bar{J}_d^2 + 12 \bar{J}_b^2 + 2 \bar{J}_e^2 \right) \\
&\quad + 4 \sqrt{6} \bar{J}_a \bar{J}_d \bar{J}_e + 21 \bar{J}_d (b_7^2 - b_9^2) \\
&\quad + 3 \bar{J}_b (b_7^2 + 7b_7^2), \\
c_2 &= 3 \bar{J}_b \left( -2 \bar{J}_b^2 + 18 \bar{J}_d^2 + 7 (b_7^2 - 3b_7^2) \right) \\
&\quad - 21 \bar{J}_d (b_7^2 - b_9^2) \\
&\quad + 2 \bar{J}_b \left[ 6 \bar{J}_b^2 + 9 \bar{J}_d^2 + 2b^2 + 3b_7^2 \right] \\
&\quad + 2 \bar{J}_b \left[ 4 \bar{J}_b^2 + 3 \bar{J}_e^2 + 11 (b_7^2 - 3b_7^2) \right] \\
&\quad + 2 \bar{J}_b \left[ 5 \bar{J}_b^2 + \bar{J}_d^2 + 9 \bar{J}_d^2 - 12 (b_7^2 - 3b_7^2) \right] \\
&\quad + 2 \bar{J}_d (4b^2 - 3b_7^2) + 4b^4 \\
&\quad + 2 (3 \bar{J}_b \bar{J}_d - \sqrt{6} \bar{J}_a \bar{J}_d) (b_7^2 - b_9^2), \\
c_1 &= -12 \bar{J}_b \left( b^4 + 3 \bar{J}_b^2 + 18 \bar{J}_d^2 \bar{J}_b^2 + 27 \bar{J}_d^4 \right) \\
&\quad + 2 \bar{J}_b \left( -3 \bar{J}_d^2 \right) (b_7^2 - 3b_7^2) \\
&\quad + 12 \bar{J}_b \bar{J}_d (b_7^2 - b_9^2) \\
&\quad - 2 \bar{J}_b \left( 2 \bar{J}_b \bar{J}_d^2 + b_7^2 \right) (b_7^2 + 3b_7^2) \\
&\quad - \bar{J}_b (b_7^2 - 3b_7^2) + 6 \bar{J}_b \bar{J}_d (b_7^2 - 5b_7^2) \\
&\quad + 42 \bar{J}_b \bar{J}_d + \sqrt{6} \bar{J}_a \bar{J}_d) (b_7^2 - b_9^2), \\
&\quad + 6 \sqrt{6} \bar{J}_a \bar{J}_d \bar{J}_e(\bar{J}_e^2 - \bar{J}_b^2).
\end{align*}

Thus, for the $s = 2$ states, we have

\begin{align*}
\lambda_n &= \sum_{p=0}^{6} c_p (\lambda_n)^p, \\
c_0 &= -2 \bar{J}_d (\bar{J}_b^2 + 9 \bar{J}_d^2) + 8 \bar{J}_d^2 (2 \bar{J}_b^2 + 6 \bar{J}_d^2 + \bar{J}_e^2) \\
&\quad + 6 \sqrt{6} \bar{J}_a \bar{J}_b \bar{J}_d \bar{J}_e, \\
c_1 &= -2 \bar{J}_d \left( b_7^2 - 3 \bar{J}_b^2 + \bar{J}_d^2 \right) (b_7^2 - b_9^2) \\
&\quad - \sqrt{6} \bar{J}_a \bar{J}_d (b_7^2 - 3b_7^2 - 18 \bar{J}_d^2), \\
c_2 &= -2 \bar{J}_d \left( 6b^2 - 3 \bar{J}_b^2 + \bar{J}_d^2 \right) (b_7^2 - b_9^2) \\
&\quad - \sqrt{6} \bar{J}_a \bar{J}_d (b_7^2 - 3b_7^2 - 18 \bar{J}_d^2), \\
c_3 &= -2 \bar{J}_d \left( b_7^2 - 3 \bar{J}_b^2 - \bar{J}_d^2 \right) (b_7^2 - b_9^2) \\
&\quad + \sqrt{6} \bar{J}_a \bar{J}_d (b_7^2 - 3b_7^2 - 18 \bar{J}_d^2), \\
c_4 &= -2 \bar{J}_d \left( b_7^2 - 3 \bar{J}_b^2 - \bar{J}_d^2 \right) (b_7^2 - b_9^2) \\
&\quad + \sqrt{6} \bar{J}_a \bar{J}_d (b_7^2 - 3b_7^2 - 18 \bar{J}_d^2), \\
c_5 &= -2 \bar{J}_d \left( b_7^2 - 3 \bar{J}_b^2 - \bar{J}_d^2 \right) (b_7^2 - b_9^2) \\
&\quad + \sqrt{6} \bar{J}_a \bar{J}_d (b_7^2 - 3b_7^2 - 18 \bar{J}_d^2), \\
c_6 &= -2 \bar{J}_d \left( b_7^2 - 3 \bar{J}_b^2 - \bar{J}_d^2 \right) (b_7^2 - b_9^2) \\
&\quad + \sqrt{6} \bar{J}_a \bar{J}_d (b_7^2 - 3b_7^2 - 18 \bar{J}_d^2).
\end{align*}

\section*{B along a crystal axis}

We recall that the six Hamiltonian matrix eigenvalues $\epsilon_n$ are generally given by Eq. (82). For the special case $B||\hat{z}$, $\hat{M}$ is block diagonal. The resulting eigenvalues of the nominal $s = 2, m = \pm 1$ notation are

\begin{align*}
\lambda_{n,8}^0 &= \bar{J}_b \mp \sqrt{b_7^2 + 9 \bar{J}_b^2}. 
\end{align*}

The remaining four states are obtained from

\begin{align*}
0 &= \sum_{p=0}^{4} k_p^0 (\lambda_n^0)^p, \\
k_1^0 &= 1, \\
k_3^0 &= -3 \bar{J}_b, \\
k_2^0 &= -6 \bar{J}_b \bar{J}_d - \bar{J}_b^2 - 8 \bar{J}_d^2 - 12 \bar{J}_d^2 - 2 \bar{J}_d^2 - 4b_7^2, \\
k_1^0 &= 12 \bar{J}_b (b_7^2 + \bar{J}_d^2 + 3 \bar{J}_d^2), \\
&\quad + 4 \sqrt{6} \bar{J}_a \bar{J}_d \bar{J}_e, \\
k_0^0 &= 24 \bar{J}_b \bar{J}_d (-b_7^2 + \bar{J}_b^2 + 3 \bar{J}_d^2) + 4 \bar{J}_d^2 (b_7^2 - \bar{J}_d^2) \\
&\quad + 8 \sqrt{6} \bar{J}_a \bar{J}_d \bar{J}_e. 
\end{align*}

Similarly, for $B||\hat{x}, \hat{y}$, $\hat{M}$ is also block diagonal. The resulting eigenvalues of the nominal $s = 2, m = \pm 1$ notation are

\begin{align*}
\lambda_{n,8}^{x,y} &= \frac{3}{2} \bar{J}_x \bar{y} - 2 \bar{J}_b \mp \sqrt{b_7^2 + \bar{J}_b^2}. 
\end{align*}
\[ \dot{J}_{x,y} = \frac{3}{2}(\dot{J}_b + \dot{J}_d). \]  

(112)

The remaining four states are obtained from

\[ 0 = \sum_{p=0}^{4} n_{p}^x y (\lambda_{n}^{x,y})^{p}, \]

(113)

\[ n_{4}^{x,y} = 1, \]

(114)

\[ n_{3}^{x,y} = -3(\dot{J} + \dot{J}_b + \dot{J}_d), \]

(115)

\[ n_{2}^{x,y} = -j_3^2 - 2j_5^2 - 12j_d^2 - 2j_3^2 + 3\dot{J} \dot{J}_b - 4b^2 + 3j_d(2j_3 + 3\dot{J}), \]

(116)

\[ n_{1}^{x,y} = 6j_3^2(\dot{J}_b + 3\dot{J}_d) + 4b^2(3\dot{J} + \dot{J}_b + 3\dot{J}_d) + 12(j_3^2 + 3j_d^2)(\dot{J} + \dot{J}_b + \dot{J}_d) - j_3^2(\dot{J}_b + 3\dot{J}_d) + 4\sqrt{6}j_3j_d, \]

(117)

\[ n_{0}^{x,y} = b^2[j_3^2 + 12j(\dot{J}_b + 3\dot{J}_d) + 8j_5^2 + 6j_3^2 + 24\dot{J}_b\dot{J}_d + 2\sqrt{6}j_d \dot{J}_d] + 2j_3^2(j_3^2 - 4j_5^2 - 6j_3j_d - 12j_d^2 - 2j_3^2) \pm 12j_d(2j_3 + j_d)(j_3^2 + 3j_d^2) \mp 6j_3j_d(j_3^2 + 6j_3^2 - 2j_3^2) - 4\sqrt{6}j_3j_d, \]

(118)

**Simple special cases**

When only one of the \( J_3 \neq 0 \), the eigenvalues for \( B||\dot{J} \) simplify considerably. For \( J_b \neq 0 \), we have

\[ \lambda_n^x = 3J + 2J_b, 2J_b, J_b \pm b, -2J_b \pm 2b. \]

(119)

For \( J_d \neq 0 \), we find

\[ \lambda_n^x = 0, 3j_b \pm \sqrt{b^2 + 9j_d^2}, \pm 2\sqrt{b^2 + 3j_d^2}. \]

(120)

For \( J_a \neq 0 \), the eigenvalues can also be found analytically,

\[ \lambda_n^x = \frac{-2j_3}{3} \pm 2b, \frac{j_3}{3} \pm b, \frac{j_3}{3} \pm \frac{3j_2}{2} \pm \frac{9}{4}j_d^2 + j_3^2 - J_a. \]

(121)

We note that the ground state energy in this case is

\[ E_1 = \frac{3}{2}J - J_a - \sqrt{\frac{9}{4}j_d^2 + j_3^2 - J_d}, \]

(122)

which explicitly involves mixing of the \( s = m = 0 \) and the \( s = 2, m = 0 \) states. For \( J_3 \neq 0 \), three of the eigenvalues are

\[ \lambda_n^x = 0, \pm \sqrt{b^2 + j_3^2}, \]

(123)

(124)

and the remaining three satisfy the cubic equation,

\[ 0 = x^3 - 3Jx^2 - 4x(b^2 + j_3^2) + 4(J_3^2 + 3b^2). \]

(125)

We note that the cubic equation must be solved to obtain the ground state energy, since the \( s = m = 0 \) state mixes with the \( s = 2, \pm 2 \) states. For \( B||\dot{J}, \dot{y} \), with \( J_b \neq 0, J_d \neq 0 \), the eigenvalues are

\[ \lambda_n^{x,y} = 3J + 2J_b, -2J_b + J_{x,y} \pm \sqrt{b^2 + j_2^2}, \]

(126)

where \( J_{x,y} \) is given by Eq. (112), and the other three eigenvalues satisfy the cubic equation,

\[ 0 = -x^3 + (J_b + J_d)x^2 + 2(J_3^2 + 3j_d^2)x + 4(J_3^2 + 3j_d^2)(J_b + 3J_d). \]

(127)

For \( J_a \neq 0 \), two of the eigenvalues satisfy

\[ \lambda_n^{x,y} = \frac{-j_3}{6} \pm \sqrt{b^2 + j_2^2}/4, \]

(128)

and the other four eigenvalues satisfy the quartic equation,

\[ 0 = 81x^4 - 27(J_a + 9J_3)x^3 - 9(36b^2 - 9JJ_3 + 12J_a^2)x^2 + 12(-J_3^2 + 9JJ_3^2 - 9b^2J_a + 81b^2J)x + 4(9J_3^4 - 9JJ_3^3 + 18b^2J_a^2 + 81b^2J_aJ_a). \]

(129)

Finally, for \( J_e \neq 0 \), two eigenvalues are

\[ \lambda_n^x = \pm \frac{j_2}{2} + \sqrt{b^2 + j_2^2}/4, \pm \frac{j_2}{2} - \sqrt{b^2 + j_2^2}/4, \]

(130)

and the other four eigenvalues satisfy the quartic equation,

\[ 0 = x^4 - (3J \mp J_3)x^3 - (4b^2 + 4J_2^2 \mp 3JJ_3)x^2 + 4[9b^2J + J_2^2 \pm J_3((b^2 - j_2^2))]x \pm 4J_a(-9b^2J + 2b^2J_a + J_2^2). \]

(131)

At the first level crossing with \( B||\dot{Z} \), we have for \( J_a \neq 0 \),

\[ \gamma B_{1,1}^{k,z} = \frac{1}{2} \left( J + [9J_3^2 + 4J_2^2 - 4JJ_3]^{1/2} \right). \]

(132)

At the second level crossing, simple formulas are only obtained for \( B||\dot{Z} \) with one \( J_3 \neq 0 \). For \( B||\dot{Z} \) and \( J_a \neq 0 \), \( J_b \neq 0 \) and \( J_d \neq 0 \), respectively, we have

\[ \gamma B_{2,1}^{k,z} = \begin{cases} \frac{-2J - J_a}{4}, \\ \frac{-2J - 3J_b}{4}, \end{cases} \]

(133)

\[ \frac{1}{2} \left( 20J_2^2 - 30J_d^2 + 8[4J_3^4 - 6J_2^2J_d^2]^{1/2} \right)^{1/2}. \]
APPENDIX B

Rotation to the Induction Representation

The rotation from the crystal representation to the induction representation is obtained from

\[
\begin{pmatrix}
\hat{x} \\
\hat{y} \\
\hat{z}
\end{pmatrix} = 
\begin{pmatrix}
\cos \theta \cos \phi - \sin \phi \sin \theta & \cos \theta \sin \phi + \sin \theta \cos \phi & 0 \\
-\sin \theta & \cos \theta & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
\hat{x}' \\
\hat{y}' \\
\hat{z}'
\end{pmatrix},
\]

(134)

leading to \( \mathbf{B} = \mathbf{B}' \).

The operations of the rotated local anisotropy interactions upon these states may be written as

\[
\mathcal{H}'_d|\varphi''^m\rangle = -\frac{J_d}{4} \left[ (4m^2 + m^2 - s(s + 1))|\varphi''^m\rangle + \sin(2\theta) \sum_{\sigma = \pm 1} (2m + \sigma)A_s^m|\varphi''^{m+\sigma}\rangle + \sin^2 \theta \sum_{\sigma = \pm 1} F_s^m|\varphi''^{m+2\sigma}\rangle \right],
\]

(137)

and

\[
\mathcal{H}'_b|\varphi''^m\rangle = -\frac{J_b}{4} \left[ (4m^2 + 2[s(s + 1) - 3m^2] \sin^2 \theta)|\varphi''^m\rangle - \sin(2\theta) \sum_{\sigma = \pm 1} (2m + \sigma)A_s^m|\varphi''^{m+\sigma}\rangle + \sin^2 \theta \sum_{\sigma = \pm 1} F_s^m|\varphi''^{m+2\sigma}\rangle \right],
\]

(138)

where \( F_s^m \) is defined by Eq. (17).

Global Hamiltonian

The operations of the rotated global anisotropy interactions upon these states may be written as

\[
\mathcal{H}'_b|\varphi_s^m\rangle = -\frac{J_b}{4} \left[ (4m^2 + 2[s(s + 1) - 3m^2] \sin^2 \theta)|\varphi_s^m\rangle - \sin(2\theta) \sum_{\sigma = \pm 1} (2m + \sigma)A_s^m|\varphi_s^{m+\sigma}\rangle + \sin^2 \theta \sum_{\sigma = \pm 1} F_s^m|\varphi_s^{m+2\sigma}\rangle \right],
\]

and

\[
\mathcal{H}'_d|\varphi_s^m\rangle = -\frac{J_d}{4} \left[ (2 \sin^2 \theta \cos(2\theta)(3m^2 - s(s + 1))|\varphi_s^m\rangle + 2 \sin \theta \sum_{\sigma = \pm 1} (2m + \sigma)A_s^m|\varphi_s^{m+\sigma}\rangle + \sum_{\sigma = \pm 1} F_s^m((1 + \cos^2 \theta) \cos(2\theta) + 2i \sin \theta \cos(2\theta)|\varphi_s^{m+2\sigma}\rangle \right].
\]

(139)

(140)

Local Hamiltonian

With regard to the local spin anisotropy terms in the rotated coordinate system, we write

\[
\mathcal{H}'_a = -J_a \left( \mathcal{O}_1 \cos^2 \theta + \mathcal{O}_2 \sin^2 \theta - \frac{\sin(2\theta)}{2} \mathcal{O}_3 \right),
\]

and

\[
\mathcal{H}'_c = -J_c \left[ \cos(2\phi) \left( \mathcal{O}_1 \sin^2 \theta + \mathcal{O}_2 \cos^2 \theta + \frac{1}{2} \sin(2\theta) \mathcal{O}_3 - \mathcal{O}_4 \right) - \sin(2\phi) \left( \mathcal{O}_5 \cos \theta + \mathcal{O}_6 \sin \theta \right) \right],
\]

(141)

(142)

where

\[
\mathcal{O}_1 = \sum_{i=1}^{2} S^2_{ix'}, \quad \mathcal{O}_2 = \sum_{i=1}^{2} S^2_{iz'}, \quad \mathcal{O}_3 = \sum_{i=1}^{2} (S_{ix'} S_{ix'} - S_{iz'} S_{iz'}),
\]

(143)
Local Hamiltonian matrix element components

The operations of these interactions are given by

\begin{align}
    \mathcal{O}_1 |\psi_s^{m}\rangle & = \frac{1}{2} \left( G_{s,s_1}^{m} |\psi_s^{m}\rangle + \sum_{\sigma' = \pm 1} H_{s,s_1}^{m,\sigma'} |\psi_s^{m\sigma'}\rangle \right), \\
    \mathcal{O}_2 |\psi_s^{m}\rangle & = \frac{1}{8} \left( M_{s,s_1}^{m} |\psi_s^{m}\rangle - \sum_{\sigma' = \pm 1} N_{s,s_1}^{m,\sigma'} |\psi_s^{m\sigma'}\rangle + \sum_{\sigma = \pm 1} L_{s,s_1}^{m,\sigma} |\psi_s^{m\sigma}\rangle \right) \\
    & \quad - \sum_{\sigma,\sigma' = \pm 1} \sigma R_{s,s_1}^{m,\sigma,\sigma'} |\psi_s^{m\sigma'}\rangle, \\
    \mathcal{O}_3 |\psi_s^{m}\rangle & = \frac{1}{4} \left( \sum_{\sigma = \pm 1} \left( P_{s,s_1}^{m,\sigma} |\psi_s^{m\sigma}\rangle - \sum_{\sigma' = \pm 1} \sigma R_{s,s_1}^{m,\sigma,\sigma'} |\psi_s^{m\sigma'}\rangle \right) \right), \\
    \mathcal{O}_4 |\psi_s^{m}\rangle & = \frac{1}{8} \left( M_{s,s_1}^{m} |\psi_s^{m}\rangle - \sum_{\sigma' = \pm 1} N_{s,s_1}^{m,\sigma'} |\psi_s^{m\sigma'}\rangle \\
    & \quad - \sum_{\sigma = \pm 1} L_{s,s_1}^{m,\sigma} |\psi_s^{m\sigma}\rangle \right), \\
    \mathcal{O}_5 |\psi_s^{m}\rangle & = \frac{1}{4i} \sum_{\sigma = \pm 1} \left( \sum_{\sigma' = \pm 1} \sigma R_{s,s_1}^{m,\sigma,\sigma'} |\psi_s^{m\sigma'}\rangle \right), \\
    \mathcal{O}_6 |\psi_s^{m}\rangle & = \frac{1}{4i} \sum_{\sigma = \pm 1} \left( \sum_{\sigma' = \pm 1} \sigma R_{s,s_1}^{m,\sigma,\sigma'} |\psi_s^{m\sigma'}\rangle \right),
\end{align}

where

\begin{align}
    M_{s,s_1}^{m} & = -4m^2 \alpha_{s,s_1} + 4[s(s + 1) - 1](1 - \alpha_{s,s_1}), \\
    N_{s,s_1}^{m,\sigma'} & = \sum_{\sigma = \pm 1} C_{s(s + 1)/2}^{m\sigma\sigma's} C_{s(s + 3\sigma' + 1)/2}^{m\sigma's}, \\
    & \quad \text{and} \quad R_{s,s_1}^{m,\sigma,\sigma'} = C_{s(s + \sigma' + 1)/2}^{m\sigma's} \rho_{s(s + 3\sigma' + 1)/2}^{m\sigma's}.
\end{align}

Second order induction representation Hamiltonian

In this appendix, we evaluate the corrections to the eigenstate energies second order in the four anisotropy interaction energies \( J \) for \( j = a, b, d, e \). The operations of the rotated Hamiltonian \( H' \) upon the eigenstates \( |\psi_s^{m}\rangle \) may be written as

\begin{equation}
    H' |\psi_s^{m}\rangle = \left( E_s^{(0)} + E_s^{(1)} \right) |\psi_s^{m}\rangle + \sum_{\sigma = \pm 1} W_{s,s_1}^{m,\sigma'} |\psi_s^{m\sigma'}\rangle
\end{equation}

where

\begin{align}
    U_{s,s_1}^{m,\sigma}(\theta, \phi) & = \frac{1}{4} \left( 2m + \sigma \right) A_{s,s_1}^{\sigma m} \left[ \sin(2\theta) \left( \tilde{J}_{s,s_1}^{m,\sigma} \right) \right. \\
    & \quad - J_{d,e}^{s,s_1} \cos(2\theta) \left. \right], \quad \text{and} \quad \psi_{s,s_1}^{m,\sigma'} \\
    V_{s,s_1}^{m,\sigma}(\theta, \phi) & = \frac{1}{4} \left( 2m - \sigma \right) A_{s,s_1}^{\sigma m} \left[ \cos(2\theta) \left( \tilde{J}_{s,s_1}^{m,\sigma} \right) \right. \\
    & \quad + J_{d,e}^{s,s_1} \cos(2\theta) \left. \right], \quad \text{and} \quad \psi_{s,s_1}^{m,\sigma'} \\
    W_{s,s_1}^{m,\sigma}(\theta, \phi) & = \frac{1}{4} \left( 2m + \sigma \right) A_{s,s_1}^{\sigma m} \left[ \sin(2\theta) \left( \tilde{J}_{s,s_1}^{m,\sigma} \right) \right. \\
    & \quad + J_{d,e}^{s,s_1} \cos(2\theta) \left. \right], \quad \text{and} \quad \psi_{s,s_1}^{m,\sigma'} \\
    X_{s,s_1}^{m,\sigma}(\theta, \phi) & = \frac{1}{4} \left( 2m - \sigma \right) A_{s,s_1}^{\sigma m} \left[ \cos(2\theta) \left( \tilde{J}_{s,s_1}^{m,\sigma} \right) \right. \\
    & \quad - J_{d,e}^{s,s_1} \cos(2\theta) \left. \right], \quad \text{and} \quad \psi_{s,s_1}^{m,\sigma'}
\end{align}
are given by Eqs. (67) and (68), respectively. From Eq. (157), the second order eigenstate energies may be written as

\[ E_{s,s_1}^{(2)} = \frac{1}{\gamma B} \sum_{\sigma = \pm 1} \left( |W_{s,s_1}^{m,\sigma}|^2 + \frac{1}{2} |V_{s,s_1}^{m,\sigma}|^2 \right) \]

\[ + \sum_{\sigma' = \pm 1} \left( |\Lambda_{s,s_1}^{m,\sigma,\sigma'}|^2 / J^2 [2 + (2 + 1)\sigma'] + \gamma B \right) \]

\[ + \frac{1}{J^2 [2 + (2 + 1)\sigma'] + 2\gamma B} \].

(163)

For simplicity, we rewrite this as

\[ E_{s,s_1}^{(2)\mu} = E_{s,s_1}^{(2)\mu}\theta + E_{s,s_1}^{(2)\nu} + E_{s,s_1}^{(2)\omega} \]

(164)

\[ E_{s,s_1}^{(2)\mu} = \frac{m \sin^2 \theta}{2\gamma B} \left( 4s(s + 1) - 8m^2 - 1 \right) \]

\[ \times \left( \cos^2 \theta \left| \tilde{j}_{b,a}^{s,s_1} - \cos(2\phi) \tilde{j}_{d,c}^{s,s_1} \right|^2 \right. \]

\[ + \sin^2(2\phi) \left( \tilde{j}_{d,c}^{s,s_1} \right)^2 \right) \].

(165)

\[ E_{s,s_1}^{(2)\nu} = -\frac{m}{8\gamma B} \left[ 2s(s + 1) - 2m^2 - 1 \right] \]

\[ \times \left( \sin^2 \theta \tilde{j}_{b,a}^{s,s_1} + (1 + \cos^2 \theta) \cos(2\phi) \tilde{j}_{d,c}^{s,s_1} \right)^2 \]

\[ + 4 \cos^2 \theta \sin^2(2\phi) \left( \tilde{j}_{d,c}^{s,s_1} \right)^2 \].

(166)

\[ E_{s,s_1}^{(2)\omega} = \frac{d_{s,s_1}^m}{16J} \left( J_a - 3 [ J_a \cos^2 \theta + J_c \sin^2 \theta \cos(2\phi) ] \right)^2 \].

(167)

\[ E_{s,s_1}^{(2)X} = \frac{f_{s,s_1}^m (\gamma B / J) \sin^2 \theta}{2J} \]

\[ \times \left( [ J_a - J_c \cos(2\phi) ]^2 \cos^2 \theta \right. \]

\[ + \sin^2(2\phi) J_c^2 \right) \].

(168)

\[ E_{s,s_1}^{(2)Y} = \frac{g_{s,s_1}^m (\gamma B / J)}{64J} \left( J_a \sin^2 \theta \right. \]

\[ + J_c (1 + \cos^2 \theta) \cos(2\phi) \left. \right)^2 \].

(169)

where

\[ \frac{d_{s,s_1}^m}{\gamma B} = -\frac{(s^2 - m^2) [(s - 1)^2 - m^2] \eta_{s,s_1}^2 \eta_{s-1,s_1}^2}{2(s - 1)} \]

\[ + \eta_{s+2,s_1}^2 \eta_{s+1,s_1}^2 \times \frac{[(s + 1)^2 - m^2][(s + 2)^2 - m^2]}{(s + 3)^2 - x^2} \]

\[ \times [(s - 1)[(s - 1)(s - 2) + m^2] \]

\[ - m(2s - 3)x \]

\[ + \eta_{s+2,s_1}^2 \eta_{s+1,s_1}^2 [(s + 1)^2 - m^2] \]

\[ \times [(s + 3)((s + 2)(s + 3) + m^2) \]

\[ - m(2s + 5)x] \].

(170)

There is a remarkable amount of symmetry in the angular dependence of the eigenstate energies. We note that \( E_{s,s_1}^{(2)\mu}(\theta, \phi) \) and \( E_{s,s_1}^{(2)\nu}(\theta, \phi) \) have the same forms, differing in the replacements of the interactions \( J_{b,a}^{s,s_1} \) and \( J_{d,c}^{s,s_1} \) with \( J_a \) and \( J_c \), respectively, and with different overall constant functions. The same comparison can also be made with \( E_{s,s_1}^{(2)\omega}(\theta, \phi) \) and \( E_{s,s_1}^{(2)\nu}(\theta, \phi) \). In addition, we note that there is a remarkable similarity in the \( \theta, \phi \) dependence of \( E_{s,s_1}^{(2)\omega} \) with that of the local spin anisotropy part of \( B_{s,s_1}^{(1)}(\theta, \phi) \) in Eq. (73).

APPENDIX D

The contributions to the \( s \)th level crossing second order in the anisotropy interactions are calculated as indicated in Eq. (74), and are found to be

\[ (E_{s,s_1}^{(2)} - E_{s-1,s_1}^{(2)}) \bigg|_{B = -J_s / \gamma} = \sum_{n=1}^{7} a_n(s, s_1) f_n(\theta, \phi). \]
Second order level crossing angular functions

\[
f_1(\theta, \phi) = \frac{\sin^2 \theta}{J} \left( |J_b - \cos(2\phi)J_d|^2 \cos^2 \theta + J_d^2 \sin^2(2\phi) \right),
\]

\[
f_2(\theta, \phi) = \frac{\sin^2 \theta}{J} \left( |J_b - J_d \cos(2\phi)| |J_a - J_c \cos(2\phi)| \times \cos^2 \theta + J_d J_c \sin^2(2\phi) \right),
\]

\[
f_3(\theta, \phi) = \frac{\sin^2 \theta}{J} \left( |J_a - \cos(2\phi)J_c|^2 \cos^2 \theta + J_c^2 \sin^2(2\phi) \right),
\]

\[
f_4(\theta, \phi) = \frac{1}{J} \left( J_b \sin^2 \theta + J_d (1 + \cos^2 \theta) \cos(2\phi) \right)^2 + 4J_d^2 \cos^2 \theta \sin^2(2\phi),
\]

\[
f_5(\theta, \phi) = \frac{1}{J} \left[ J_b \sin^2 \theta + J_d (1 + \cos^2 \theta) \cos(2\phi) \right] \times \left[ J_a \sin^2 \theta + J_c (1 + \cos^2 \theta) \cos(2\phi) \right] + 4J_d J_c \cos^2 \theta \sin^2(2\phi),
\]

\[
f_6(\theta, \phi) = \frac{1}{J} \left( J_a \sin^2 \theta + J_c (1 + \cos^2 \theta) \cos(2\phi) \right)^2 + 4J_c^2 \cos^2 \theta \sin^2(2\phi),
\]

\[
f_7(\theta, \phi) = \frac{1}{J} \left( J_a - 3|J_a \cos^2 \theta + J_c \sin^2 \theta \cos(2\phi)| \right)^2.
\]

Second order level crossing coefficients

The coefficients are given by

\[
a_1(s, s_1) = \frac{(8s - 9)}{2s},
\]

\[
a_2(s, s_1) = -\frac{a_{2,0}(s) + 4s_1(s_1 + 1)}{s(2s + 1)(2s + 3)},
\]

\[
a_{2,0}(s) = -3(9s - 23s^2 + 4s^3 + 12s^4),
\]

\[
a_{2,1}(s) = -9 + 8s + 4s^2,
\]

\[
a_{3}(s, s_1) = a_3^H(s, s_1) + a_3^X(s, s_1),
\]

\[
a_{3}^H(s, s_1) = \frac{[3 - 3s - 3s^2 + 4s_1(s_1 + 1)]^2}{2(2s + 3)^2}
\]

\[
- \frac{(s - 1)[3 + 3s - 3s^2 + 4s_1(s_1 + 1)]^2}{2s(2s + 1)^2},
\]

\[
a_{3}^X(s, s_1) = \frac{[s(s + 2) - 4s_1(s_1 + 1)]}{2(s + 1)(s + 3)(2s + 1)^2(2s + 3)^2}
\]

\[
a_{3,0}^X(s) = \frac{(s + 1)(s + 3)(51 + 114s + 209s^2 + 302s^3 + 164s^4 + 24s^5)}{(2s + 5)(3s + 1)},
\]

\[
a_{3,1}^X(s) = \frac{129 + 318s + 395s^2 + 442s^3 + 300s^4 + 72s^5}{(4s - 3)},
\]

\[
a_4(s, s_1) = \frac{8s}{3},
\]

\[
a_5(s, s_1) = \frac{3[a_{5,0}(s) + 4s_1(s_1 + 1)]}{4s(2s + 1)(2s + 3)},
\]

\[
a_{5,0}(s) = 3 + 3s - 5s^2 - 4s^3,
\]

\[
a_6(s, s_1) = a_6^H(s, s_1) + a_6^X(s, s_1),
\]

\[
a_{6}^H(s, s_1) = \frac{[3 - 3s - 3s^2 + 4s_1(s_1 + 1)]^2}{8(2s - 1)(2s + 3)^2}
\]

\[
- \frac{(s - 1)[3 + 3s - 3s^2 + 4s_1(s_1 + 1)]^2}{8(2s - 3)(2s + 1)^2},
\]

\[
a_{6,0}^X(s, s_1) = \frac{-1}{96(2s - 3)(2s - 1)(2s + 1)^2(2s + 3)^2}
\]

\[
\times \sum_{n=0}^2 a_{6,n}^X(s)[4s_1(s_1 + 1)]^n
\]

\[
(2s + 5)(4s + 1)(4s + 3).
\]

\[
a_{6,0}^X(s) = \frac{1}{96(2s - 3)(2s - 1)(2s + 1)^2(2s + 3)^2}
\]

\[
\times \sum_{n=0}^2 a_{6,n}^X(s)[4s_1(s_1 + 1)]^n
\]

\[
(2s + 5)(4s + 1)(4s + 3).
\]

\[
a_{6,0}^X(s) = \frac{1}{96(2s - 3)(2s - 1)(2s + 1)^2(2s + 3)^2}
\]

\[
\times \sum_{n=0}^2 a_{6,n}^X(s)[4s_1(s_1 + 1)]^n
\]

\[
(2s + 5)(4s + 1)(4s + 3).
\]

\[
a_{6,0}^X(s) = \frac{1}{96(2s - 3)(2s - 1)(2s + 1)^2(2s + 3)^2}
\]

\[
\times \sum_{n=0}^2 a_{6,n}^X(s)[4s_1(s_1 + 1)]^n
\]

\[
(2s + 5)(4s + 1)(4s + 3).
\]

By expanding the solutions in the crystal representation to second order in the \(J_j\), we have explicitly checked these expressions for \(s_1 = 1/2, s = 1\), and for \(s_1 = 1, s = 1, 2\). We note that for \(s_1 = 1/2\), only \(a_1\) and \(a_4\) are non-vanishing.
[1] R. Sessoli, D. Gatteschi, A. Caneschi, and M. A. Novak, Nature (London) 365, 141 (1993).
[2] J. R. Friedman, M. P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. 76, 3830 (1996).
[3] M. N. Leuenberger and D. Loss, Nature (London) 410, 789 (2001).
[4] W. Wernsdorfer, T. Ohm, C. Sangregorio, R. Sessoli, D. Mailly, and C. Paulsen, Phys. Rev. Lett. 82, 3903 (1999).
[5] W. Wernsdorfer and R. Sessoli, Science 284, 133 (1999).
[6] D. Zipse, J. M. North, N. S. Dalal, S. Hill, and R. S. Edwards, Phys. Rev. B 68, 184408 (2003).
[7] M. Affronte, A. Cornia, A. Lascialfari, F. Borsa, D. Gatteschi, J. Hinderer, M. Horvatić, A. G. M. Jansen, and M.-H. Julien, Phys. Rev. Lett. 88, 167201 (2002).
[8] O. Waldmann, J. Schülein, R. Koch, P. Müller, I. Bernt, R. W. Saalfrank, H. P. Andres, H. U. Güdel, and P. Alenspach, Inorg. Chem. 38, 5879 (1999).
[9] O. Waldmann, R. Koch, S. Schromm, J. Schülein, P. Müller, I. Bernt, R. W. Saalfrank, F. Hempel, and E. Balthes, Inorg. Chem. 40, 2086 (2001).
[10] H. Nakano and S. Miyashita, J. Phys. Chem. Solids 63, 1519 (2002).
[11] D. A. Tennant, S. E. Nagler, A. W. Garrett, T. Barnes, and C. C. Torardi, Phys. Rev. Lett. 78, 4998 (1997).
[12] H. U. Güdel, Neutron News 7, 24 (1996).
[13] A. W. Garrett, S. E. Nagler, D. A. Tennant, B. C. Sales, and T. Barnes, Phys. Rev. Lett. 79, 745 (1997).
[14] D. V. Efremov and R. A. Klemm, Phys. Rev. B 66, 174427 (2002).
[15] P. Le Gall, F. Fabrizi de Biani, A. Caneschi, P. Cinelli, A. Cornia, A. C. Fabretti, and D. Gatteschi, Inorg. Chim. Acta 262, 123 (1997).
[16] Y. Shapira, M. T. Liu, S. Foner, R. J. Howard, and W. H. Armstrong, Phys. Rev. B 63, 094422 (2001).
[17] Y. Shapira, M. T. Liu, S. Foner, C. E. Dubé, and P. J. Bonitatebus, Jr., Phys. Rev. B 59, 1046 (1999).
[18] K. L. Taft, C. D. Delfs, G. C. Papaefthymiou, S. Foner, D. Gatteschi, and S. J. Lippard, J. Am. Chem. Soc. 116, 823 (1994).
[19] J. D. Walker and R. Poli, Inorg. Chem. 29, 756 (1990).
[20] J. A. Bertrand, J. L. Breece, and P. G. Eller, Inorg. Chem. 13, 125 (1974).
[21] R. Tiron, W. Wernsdorfer, D. Foquet-Albiol, N. Aliaga-Alcalde, and G. Christou, Phys. Rev. Lett. 91, 227203 (2003).
[22] J. M. North, N. S. Dalal, D. Foquet-Albiol, A. Vinslava, and G. Christou, Phys. Rev. B 69, 174419 (2004).
[23] O. Waldmann, J. Hassmann, P. Müller, D. Volkmer, U. S. Schubert, and J.-M. Lehn, Phys. Rev. B 58, 3277 (1998).
[24] J. J. Borrás-Almenar, J. M. Clemente-Juan, E. coronado, and B. S. Tsukerblat, Inorg. Chem. 38, 6081 (1999).
[25] R. A. Klemm and J. R. Clem, Phys. Rev. B 21, 1868 (1980); R. A. Klemm, SIAM J. Appl. Math. 55, 986 (1995).
[26] H. Goldstein, Classical Mechanics, (Addison-Wesley, Reading, MA 1965), p. 109.