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Antisymmetric exchange interactions in Ni_4 clusters

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We show that in molecular Ni_4 clusters with S_4 symmetry, not only the local anisotropy but also the antisymmetric exchange interaction contributes to the observed fourth-order anisotropy terms in the single-spin Hamiltonian. From a group-theoretical classification of the exchange-coupled multiplets, the effective spin Hamiltonian terms are determined. We find that low-lying excited spin states possess an orbital angular momentum, which mixes into the spin ground state, leading to an effective antisymmetric exchange term. The simulation of the magnetic and spectroscopic experimental data allowed the extraction of parameter values for all interactions.

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I. INTRODUCTION

The magnetic properties of molecular nanomagnets are often well described by the strong-exchange (or giant-spin) approximation, in which the spin multiplets of the exchange-coupled cluster are well isolated in energy.[1] Hence, at low temperatures only the ground spin multiplet needs to be considered, which is very convenient because the much reduced Hilbert-space dimension drastically simplifies the analysis. The magnetic anisotropy of the cluster is then described by a spin Hamiltonian $\mathcal{H}_S$, which in the strong-exchange approximation consists of second-order anisotropy terms originating from the sum of the projections of the single-ion anisotropies onto the ground spin multiplet.[2] However, experiment often demonstrates the additional presence of quite significant fourth-order anisotropy terms in $\mathcal{H}_S$. These terms are fundamentally important for many phenomena because they create quantum superposition states which not only are important for quantum information processing (QIP) (Ref. 3) but also lead to quantum tunneling of the magnetization.[4,5] It has been suggested that they originate from a mixing of higher-lying spin multiplets into the ground spin multiplet (S mixing), which becomes increasingly important for larger single-ion anisotropy with respect to the isotropic exchange coupling in the cluster (in the strong-exchange approximation, the single-ion anisotropy is treated in first-order perturbation theory; fourth-order anisotropy terms in $\mathcal{H}_S$ or S mixing appear in second order).[4,6] Three recent papers provided strong evidence for this mechanism of generating higher-order anisotropy terms.[5,7,8]

However, S mixing can be induced also by other interactions, e.g., antisymmetric exchange (ASE) interactions (Dzyaloshinski-Moriya interactions), which are due to a combined effect of spin-orbit coupling and superexchange interactions.[9] It is well known that in magnetically ordered systems this interaction leads to spin canting or weak ferromagnetism.[10] The presence of ASE interactions in molecular nanomagnets has been suggested on theoretical grounds;[11] in trimeric clusters and a few others it has been shown experimentally.[9] Recent, very careful magnetization measurements also suggested the importance of ASE interactions in Mn_{12}.[12] Finally, the occurrence of ASE interactions in S_4 symmetry tetramers of $S=\frac{1}{2}$ and $S=1$ ions was predicted from the derivation of analytical formulas for the eigenstate energies of a Hamiltonian that contains isotropic and nonisotropic exchange contributions as well as single-ion anisotropy terms.[13]

In this work, we theoretically investigate ferromagnetically coupled Ni_4 cubane clusters with S_4 symmetry (Fig. 1), of which there are many.[14] These clusters have attracted a great deal of attention recently. They show quantum tunnel-

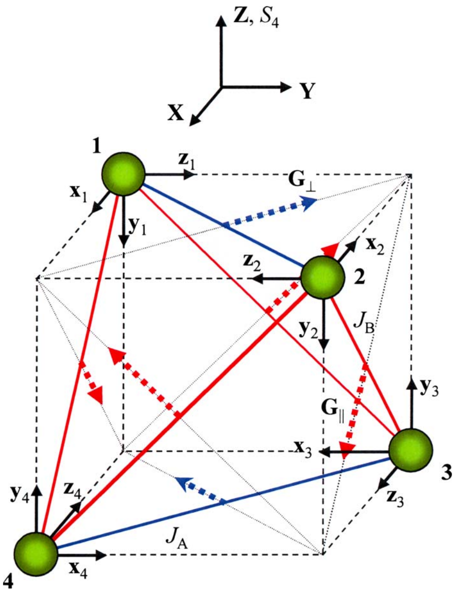

FIG. 1. (Color online) Ni_4 cluster geometry and orientations of the various tensors. The thick solid lines are the isotropic exchange interactions with constants J_A (blue, between ions 1 and 2, and between ions 3 and 4) and J_B (red, all other interactions). The solid arrows indicate the local anisotropy coordinate systems. The dashed arrows show the antisymmetric exchange interaction vectors $\mathbf{G}_\parallel$ and $\mathbf{G}_\perp$. **X**, **Y**, and **Z** denote the cluster coordinate system. S_4 is the molecular axis of improper rotation.

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ing of the magnetization at low temperatures,[15,16] and in fact allowed the experimental realization of quantum superposition of high-spin states, which are fundamental for QIP purposes.[17] Furthermore, their comparatively small number of metal ions and favorable symmetry makes them ideal models for studying S-mixing effects.[6] We will show that the ASE interaction can be an important source of higher-order anisotropy terms, via the S-mixing mechanism. In contrast to other systems for which ASE interactions have been considered, in Ni_4 the orbital moment that is required in these interactions is derived from the lowest spin-excited state, which is ca. 20 cm^{-1} above the ground state, rather than from an electronically excited state of one of the ions, which are typically 10^4 cm^{-1} above the ground state. Accordingly, the effect of ASE interactions is much stronger than in other systems in which ASE interactions have been considered. Therefore, we show that the ASE interactions in *all* high-symmetry molecular nanomagnets could be very strong because they all possess excited cluster spin states which carry orbital angular momenta. Using our theoretical results, we also analyze the magnetization and inelastic-neutron-scattering (INS) data we obtained recently on a Ni_4 cluster, $[\mathrm{Ni}_4(\mathrm{MeOH})_4\mathrm{sae}_4]$ (sae is the anion of salicylidene-2-ethanolamine).[15] These data were fitted using the giant-spin approximation in the original work. However, no set of parameters was found that allowed the simulation of all experimentally found INS peaks. In particular, a peak at ca. 3.5 cm^{-1} was not reproduced in the simulation. In addition, sizable fourth-order anisotropy parameters were found, but the giant-spin model does not shed light on the physical origin of these parameters. These two factors led us to consider the origin of the magnetic anisotropy in this Ni_4 cluster in more detail.

II. RESULTS AND DISCUSSION

A. Group-theoretical analysis

Because the ground crystal-field term of Ni^{2+} ions is orbitally nondegenerate, the leading exchange contribution is given by the isotropic Heisenberg–Dirac–Van Vleck Hamiltonian. For a S_4 symmetry Ni_4 cluster this is[2]

$$\mathcal{H}^{\mathrm{iso}} = -2J_A(\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_3\cdot\hat{\mathbf{S}}_4) - 2J_B(\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_3 + \hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_4 + \hat{\mathbf{S}}_2\cdot\hat{\mathbf{S}}_3 + \hat{\mathbf{S}}_2\cdot\hat{\mathbf{S}}_4), \tag{1}$$

where J_A and J_B are the two independent isotropic coupling constants (Fig. 1), and $\hat{\mathbf{S}}_i=1$ are the spin operators for the Ni^{2+} spins. The eigenvalues of $\mathcal{H}^{\mathrm{iso}}$ depend on the total spin S and the intermediate spins S_{12} and S_{34}; the eigenstates can be expressed as $|S_{12}S_{34}SM_S\rangle$. Following the angular momentum coupling rules, the coupling of 4 $S_i=1$ spins leads to 19 spin multiplets:

$$D^{(S_1=1)}\otimes D^{(S_2=1)}\otimes D^{(S_3=1)}\otimes D^{(S_4=1)} = 3D^{(S=0)} + 6D^{(S=1)} + 6D^{(S=2)} + 3D^{(S=3)} + 1D^{(S=4)}. \tag{2}$$

Here, $D^{(S)}$ indicates the irreducible representation corresponding to the spin S. Hence, in addition to the M_S degeneracy, all spin multiplets of the same total spin are degenerate except for the maximum-spin state $S=4$. The analysis of these "accidental" degeneracies is the key point in understanding which non-Heisenberg interactions may be present to give fine structure of the spin multiplets.[18] To that end, the effect of the point-group symmetry operations on the many-electron wave functions must be determined. These wave functions can be constructed from the Slater determinants $|m_1m_2m_3m_4|$ composed of the orbitally nondegenerate single-site states of Ni^{2+} ions with spin projections m_i, using conventional coupling procedures:[18–20]

$$|S_{12}S_{34}SM_S\rangle = \sum_{\{m_i\}}\sum_{m_{12},m_{34}} C^{S_{12}m_{12}}_{S_1m_1S_2m_2} C^{S_{34}m_{34}}_{S_3m_3S_4m_4} C^{Sm_S}_{S_{12}m_{12}S_{34}m_{34}} \times |m_1m_2m_3m_4|. \tag{3}$$

By reducing the matrices which describe the action of each point-group symmetry operator on these wave functions, we were able to extract the irreducible representations A, B, and E of the S_4 point group spanned by the multiplets of a certain spin value S. In other words, we extract the symmetries of the different spin multiplets, which determine how and which multiplet splitting and mixing may occur:[18,19]

$$\begin{aligned} D^{(4)} &\Rightarrow {}^9B,\\ 3D^{(3)} &\Rightarrow {}^7A + {}^7E,\\ 6D^{(2)} &\Rightarrow {}^5A + {}^5B + 2\ {}^5E,\\ 6D^{(1)} &\Rightarrow {}^3A + {}^3B + 2\ {}^3E,\\ 3D^{(0)} &\Rightarrow {}^1A + 2\ {}^1B. \end{aligned} \tag{4}$$

This analysis shows that the $S=4$ ground state belongs to the nondegenerate irreducible representation B, while the $S=3$ states span a nondegenerate A and degenerate E irreducible representations (labeled ${}^7A$ and ${}^7E$). We used the projector operator method[18,19] to assign the symmetry labels to specific $|S_{12}S_{34}S\rangle$ states which showed the ${}^7A$ and ${}^7E$ states to be the $|S_{12}S_{34}S\rangle=|223\rangle$ and $(|213\rangle,|123\rangle)$ states, respectively. They can be viewed as the $M_L=0$ and $M_L=\pm1$ components, respectively, of a state with pseudoangular momentum $L=1$. Importantly, the orbitally degenerate ${}^7E$ state will prove to be the first excited state of the Ni_4 cluster we have studied experimentally.[15]

We will now use the symmetries we have derived for the different spin multiplets to identify which multiplets will split under the influence of spin-orbit coupling (SOC) and which multiplets will be mixed by SOC. We will focus on the lowest two multiplets, ${}^9B$ and ${}^7E$. The *splitting* of multiplets is assessed by considering the direct product $\Gamma\times\Gamma$ of the irreducible representation Γ that characterizes a particular multiplet ${}^{2S+1}\Gamma$.[18] For *integer* spin systems, a spin multiplet will be split if the *antisymmetric* part of this product contains one of the angular momentum irreducible representations ($\hat{S}_z,\hat{L}_z$: A; $\hat{S}_{x,y},\hat{L}_{x,y}$: E in S_4). Because the ground spin multiplet is orbitally nondegenerate, it will show no first-order splitting due to SOC but will be split only in second

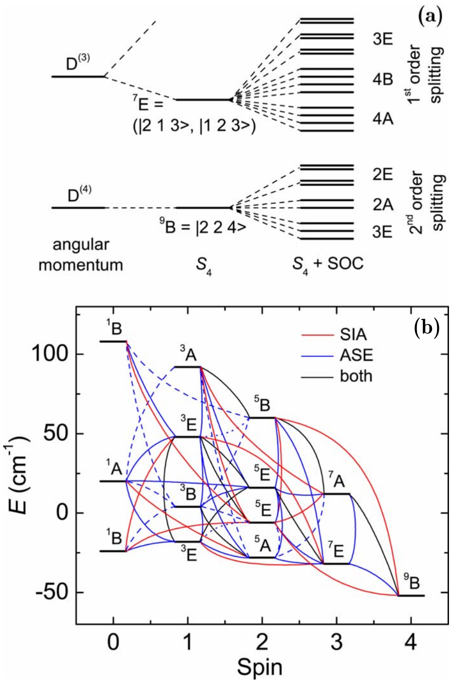

FIG. 2. (Color online) (a) Splitting of the $S=4$ and $S=3$ coupled spin states under the influence of symmetry lowering to S_4 symmetry and the action of SOC, respectively. (b) The energies of all spin multiplets as a function of spin on the basis of isotropic exchange interactions only. Curved lines indicate mixing of these multiplets by the collective action of the single-ion anisotropy (SIA, red), both components of the antisymmetric exchange (ASE, blue, solid), the axial ASE component (blue, dashed), the transverse ASE component (blue, dotted), and the simultaneous action of SIA and ASE terms (black).

order, by terms of order λ^2. However, the orbitally degenerate ^7E multiplet will be split in first order (Fig. 2). The direct product $\Gamma \times \Gamma$ is $E \times E = 2A + 2B$, where the symmetric part is $[E^2] = A + 2B$ and the antisymmetric part is $\{E^2\} = A$. Because only the z component of the angular momentum operator transforms as A, the ^7E state will be split only by the z component of SOC, i.e., $\lambda \hat{S}_z \hat{L}_z$.

The possibility of mixing of different multiplets with $\Delta S = 1$ by SOC can be evaluated by constructing the direct product of the irreducible representations of these multiplets, $\Gamma_1 \times \Gamma_2$.[18] Mixing will occur if this direct product contains an angular momentum irreducible representation. Considering the ^9B and ^7E multiplets, the direct product is $B \times E = E$. The x and y components of SOC form a basis for the E irreducible representation. Therefore the ^9B and ^7E multiplets are admixed by the transverse component $\lambda \hat{S}_x \hat{L}_x + \hat{S}_y \hat{L}_y$ of the SOC operator. Very importantly, this analysis shows that the SOC can indeed mix the ^9B ground and ^7E excited spin multiplets, resulting in a splitting or magnetic anisotropy of the ground spin multiplet.

We were also able to determine into which components SOC will split the $^{2S+1}\Gamma$ multiplets (in any order of perturbation theory). To this end we constructed the direct product $\Gamma \times D^{(S)}$ of the irreducible representations that characterize the orbital and spin angular momenta (Γ and $D^{(S)}$, respectively).[18] To do this, the full rotation group irreducible representations $D^{(S)}$ have to be reduced to S_4 symmetry. This gives $D^{(3)} \Rightarrow A + 2B + 2E$ and $D^{(4)} \Rightarrow 3A + 2B + 2E$ for $S=3$ and $S=4$, respectively. In this manner the SOC-induced splitting was found to be $B \times (3A + 2B + 2E) = 3B + 2A + 2E$ for the ^9B ground state and $E \times (A + 2B + 2E) = 4A + 4B + 3E$ for the ^7E excited state (Fig. 2).

B. Construction of the spin Hamiltonian

Because group theory does not predict the size of the splittings, we must construct the spin Hamiltonian corresponding to the active interactions. The first term is the isotropic exchange interaction [Eq. (1)]. Furthermore, we have seen above that SOC induces splitting and mixing of spin multiplets. This leads to an effective ASE interaction,[18] which in the local coordinate frame of a spin pair has the form

$$\mathcal{H}^{\mathrm{ASE}} = \sum_{i=1}^{4} \sum_{j<i}^{4} \mathbf{G}_{ij} \cdot [\hat{\mathbf{S}}_i \times \hat{\mathbf{S}}_j]. \tag{5}$$

The direction of the antisymmetric exchange interaction vectors $\mathbf{G}_{ij}$ between the spins i and j is given by the molecular symmetry (see below).[10]

The collective action of the single-ion anisotropies (SIAs) leads to (additional) multiplet splitting and mixing in second order. In the local coordinate frame, the SIA term is written as

$$\mathcal{H}^{\mathrm{SIA}} = \sum_{i=1}^{4} \hat{\mathbf{S}}_i \cdot \mathbf{D}_i \cdot \hat{\mathbf{S}}_i = \sum_{i=1}^{4} D_i \left[\hat{S}_{iz}^2 - \frac{1}{3} S_i (S_i + 1) \right] + E_i (\hat{S}_{ix}^2 - \hat{S}_{iy}^2). \tag{6}$$

The microscopic spin Hamiltonian of the cluster is then the sum of the three terms given by Eqs. (1), (5), and (6). Contributions from anisotropic (dipolar and exchange) interactions were considered to be negligibly small.

The Hamiltonian matrix elements can be evaluated using either the basis of the uncoupled m_s states of the single ions or the basis of the coupled spin states. The latter has the advantage that a great deal of insight is obtained into which spin multiplets mix and by what types of interactions. To this end, we constructed the Hamiltonian matrix, where we expressed the spin Hamiltonian terms in terms of irreducible tensor operators (ITOs) and evaluated the matrix elements using the Wigner-Eckart theorem.[19] The general form of the effective spin Hamiltonian terms is[2,18,19,21]

$$\mathcal{H} = \sum_{k_1 k_2 k_3 k_4} \sum_{k_{12} k_{34}} \sum_{kq} C_q^{(k)}(k_1 k_2 k_3 k_4 k_{12} k_{34}) \hat{T}_q^{(k)}(k_1 k_2 k_3 k_4 k_{12} k_{34}), \tag{7}$$

where $C_q^{(k)}(k_1 k_2 k_3 k_4 k_{12} k_{34})$ are the adjustable parameters of the spin Hamiltonian, which in this case are the isotropic exchange constants J_{ij}, the single-ion anisotropy parameters (D_i, E_i), and the antisymmetric exchange interaction vector $\mathbf{G}_{ij}$, where D_i, E_i, and $\mathbf{G}_{ij}$ are expressed on the corresponding *local* coordinate systems. $\hat{T}^{(k)}_q(k_1k_2k_3k_4k_{12}k_{34})$ are the compound ITOs composed from the ITOs acting in the spin space of the individual spins. Below we discuss the particular form that the spin Hamiltonian terms assume for an S_4 symmetry cluster of $S=1$ ions.

The isotropic exchange term is the sum of the compound ITOs describing the pairwise isotropic exchange interactions,[18]

$$\mathcal{H}^{\text{iso}} = \sum_{j<i} 2\sqrt{3}J_{ij}\hat{T}^{(0)}_0(\hat{\mathbf{S}}_i \otimes \hat{\mathbf{S}}_j), \tag{8}$$

where $J_{12}=J_{34}=J_A$ and $J_{13}=J_{14}=J_{23}=J_{24}=J_B$.

The molecular symmetry dictates the direction and number of independent antisymmetric exchange interactions (see above). Thus, there will be only two independent corresponding parameter values (Fig. 1), namely, $G_{12}=G_{34}=G_\perp$ and $G_{13}=G_{14}=G_{23}=G_{24}=G_\parallel$, which are related to the transverse ($L_{x,y}$) and longitudinal (L_z) components of the orbital angular momentum. $G_\perp$ corresponds directly to $L_{x,y}$, while $G_\parallel$ is related to both components of the orbital angular momentum. The Cartesian components of the spin operators were expressed as ITOs and transformed from the local to the cluster coordinate system. Rewriting the compound ITOs in terms of the single-spin ITOs, we obtained the following for each pairwise antisymmetric exchange interaction:

$$\mathcal{H}^{\text{ASE}}_{ij} = G_{ij} \sum_{q=-1,0,+1} a^q_{ij}[\hat{T}^1(j) \otimes \hat{T}^1(i)]^{(1)}_q, \tag{9}$$

with the coefficients

$$-ia^{-1}_{12} = a^{+1}_{12} = -a^{-1}_{34} = ia^{-1}_{34} = \frac{i\sqrt{2}}{2}(i+1),$$

$$a^0_{12} = a^0_{34} = 0,$$

$$-a^{+1}_{23} = a^{-1}_{23} = -a^{+1}_{14} = a^{-1}_{14} = -ia^{+1}_{24} = -ia^{-1}_{24} = ia^{+1}_{13} = ia^{-1}_{13} = \frac{i\sqrt{2}}{2},$$

$$a^0_{23} = -a^0_{14} = a^0_{13} = a^0_{24} = -i.$$

The orientations of the single-ion anisotropy tensors are also linked by the point-group symmetry elements. The elongation of the local geometry around the Ni^{2+} ions in our cluster suggests that the single-ion anisotropy unique axis (z axis) is along the elongation and hence perpendicular to the cluster Z axis (Fig. 1). Following the above procedure and transforming from the local to the cluster coordinate frame, we obtained the following for the single-ion anisotropy term for each ion:

$$\mathcal{H}^{\text{SIA}}_i = \frac{b_i}{2}(D_{\text{Ni}} - E_{\text{Ni}}) \sum_{q=-2,+2} [\hat{T}^{(1)}(i) \otimes \hat{T}^{(1)}(i)]^{(2)}_q$$

$$- \frac{1}{\sqrt{6}}(D_{\text{Ni}} - 3E_{\text{Ni}})[\hat{T}^{(1)}(i) \otimes \hat{T}^{(1)}(i)]^{(2)}_0, \tag{10}$$

with $-b_1=-b_2=b_3=b_4=1$. In all, the model contains the adjustable parameters J_A, J_B, $G_\perp$, $G_\parallel$, D_{Ni}, and E_{Ni}.

From the constructed Hamiltonian matrix we were able to extract how the spin multiplets mix, in other words, which Hamiltonian terms have nonzero matrix elements between the diagonal blocks corresponding to the different spin multiplets. The results of this analysis are shown in Fig. 2(b), which shows that the spin multiplets are mixed to a large extent. In this figure the energies of the different spin multiplets were calculated on the basis of isotropic exchange interactions alone. Importantly, it shows that the $S=4$ (^9B) ground state is indeed mixed with the first $S=3$ (^7E) excited state by antisymmetric exchange interactions.

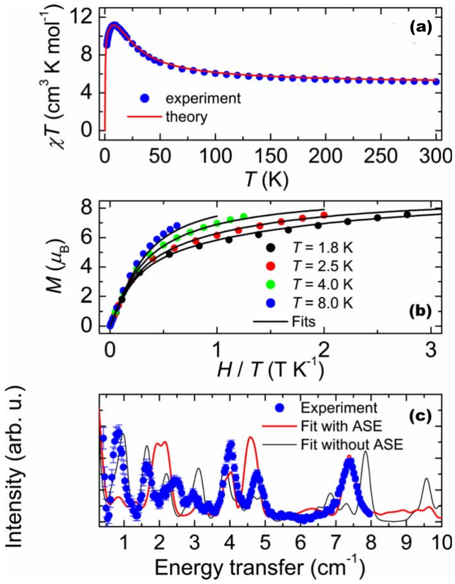

FIG. 3. (Color online) (a) Experimental magnetic-susceptibility temperature product (symbols) and fit (line) for (in cm^{-1}) $D=6.5$, $E=2.27$, $G_\perp=5$, and $G_\parallel=-6$. (b) Experimental magnetization as a function of magnetic field divided by temperature at various temperatures (symbols) and fits (lines) for (in cm^{-1}) $J_A=-1.2$, $J_B=7$, $D=6$, $E=2.89$, $G_\perp=4.8$, and $G_\parallel=-10$. (c) Experimental (symbols) and fitted (lines) INS spectra for the Ni_4 cluster at $T=22$ K. The thick red line corresponds to the best fit including antisymmetric exchange, while the thin black line is the best fit without antisymmetric exchange. Fit parameters are given in the text.

C. Data simulation

We now turn to the analysis of the magnetic and INS data of our Ni_4 cluster.[15] The crystallographic symmetry of this cluster is not exactly S_4, as evidenced by a second-order transverse anisotropy of the ground state (E term). Thus, only the high-frequency transitions, which are little influenced by the E term, will be simulated reliably. Unfortunately, for Ni_4 clusters with crystallographic S_4 symmetry, detailed zero-field spectroscopic data are not available. [High-field electron-paramagnetic-resonance (EPR) data are available, but the Zeeman term complicates the analysis enormously because it might itself influence the level mixing.] From the energies and eigenfunctions obtained from the numerical diagonalization of the microscopic Hamiltonian, the magnetization was calculated using standard equations. For the INS spectrum we used the equations in Ref. 22. We performed a grid search in parameter space, where *all* available experimental data were included. The only *a priori* criteria we used were that the simulation should reproduce the three highest-energy transitions and that no further strong INS transitions should be predicted up to 20 cm^{-1}, as required by experiment. The best fit is obtained for the parameter set $J_A=-1.2\ \mathrm{cm}^{-1}$, $J_B=7\ \mathrm{cm}^{-1}$, $D=7.8\ \mathrm{cm}^{-1}$, $E=3.0\ \mathrm{cm}^{-1}$, $G_\perp=4.9\ \mathrm{cm}^{-1}$, and $G_\parallel=-7\ \mathrm{cm}^{-1}$ (Fig. 3). No good fit could be obtained if $G_\perp$ and $G_\parallel$ were forced to be zero (Fig. 3). Best fits with similar parameters were obtained for the magnetization and magnetic susceptibility (Fig. 3). The simulated INS spectra were found to be extremely sensitive on the parameter values; a single set of parameters could not fit all data simultaneously. The difference in the parameter values should be taken as a measure of their error bars.

The single-ion anisotropy is almost perfectly rhombic, $E/D=\frac{1}{3}$. Since actually $E/D>\frac{1}{3}$ the single-ion anisotropy tensor is probably not exactly collinear with the cluster symmetry axis, i.e., somewhat tilted. Single-crystal EPR data on a doped diamagnetic analog could give the single-ion anisotropy orientation;[23] such data are not yet available for this cluster. Introduction of the single-ion anisotropy orientation as a free fit parameter leads to an overparametrized model. The magnitude of the antisymmetric interaction is of the same order as the isotropic interaction, in contrast to the Moriya estimate that $G \propto (\Delta g/g)|J|$ (for Ni^{2+} the deviation Δg of the g value from the free-electron value is about $0.1g$).[10] However, the J value in the Moriya estimate is the isotropic exchange interaction between two spins in their electronic ground states, whereas here the relevant isotropic exchange interaction is that between one ion in its ground state and one in its excited state.[9] In addition, the strength of the antisymmetric exchange interaction depends on the actual overlap of the ground- and excited-state d orbitals on the different ions, which can vary strongly from complex to complex.[9] This could explain why for other Ni_4 clusters no evidence for antisymmetric exchange interactions was found.[5] In our simulation we find that if we describe the ground spin multiplet by a single-spin Hamiltonian $\mathcal{H}_S$, then fourth-order transverse anisotropy terms appear due to the antisymmetric exchange interaction, and fourth-order axial terms appear due to the concerted effect of the antisymmetric exchange interaction and the single-ion anisotropy.

III. CONCLUSIONS

For any high-symmetry molecular nanomagnet, it can be expected that there are excited spin multiplets, which belong to a degenerate representation of the cluster symmetry point group. The associated pseudoangular momentum can mix into the ground spin multiplet by the spin-orbit coupling, which leads to splitting of the ground state. Therefore, one would expect that antisymmetric exchange interactions occur frequently in these systems. Careful combined experimental and theoretical studies will be needed to confirm this expectation.

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