Magnetic properties of a Heisenberg coupled-trimer molecular magnet: General results and application to spin-$\frac{1}{2}$ vanadium clusters

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We report predictions for the energy eigenstates and inelastic neutron-scattering excitations of an isotropic Heisenberg hexamer consisting of general spin S and S' trimers. Specializing to spin-1/2 ions, we give analytic results for the energy excitations, magnetic susceptibility, and inelastic neutron-scattering intensities for this hexamer system. To examine this model further, we compare these calculations to the measured magnetic susceptibility of a vanadium material, which is considered to be well-defined magnetically as an isolated $S=1/2$ V^{4+} trimer model. Using our model, we determine the amount of intertrimer coupling that can be accommodated by the measured susceptibility and predict the inelastic neutron-scattering spectrum for comparison with future measurements.

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I. INTRODUCTION

Molecular magnetism and nanomagnetism has recently gained considerable attention in solid-state sciences due to interest in high-capacity data storage as well as unique quantum phenomena.[1–5] Advances in both the synthesis and physical characterization of magnetic cluster materials have been brought to the forefront of this research from both experimental and theoretical approaches.[6–8] While much attention has been given to large clusters, the limited number of magnetic centers in small spin clusters along with analytical theoretical techniques can be applied to elucidate the nature of the exchange interactions while employing conventional computational resources.

Magnetic properties of spin-1/2 clusters have been addressed in great detail in the literature. In 2004, Whangbo *et al.*[9] gave a comprehensive review of dimers with increasing spin. Haraldsen *et al.*[10] reviewed the magnetic properties and inelastic neutron-scattering (INS) intensities of spin-1/2 clusters with 2–4 ions. Recently, Waldmann[11] examined the inelastic neutron-scattering cross section of spin clusters with high molecular symmetry. Klemm and Efremov[12,13] have investigated single molecule anisotropies in small clusters of varying spin, using first-order perturbation theory. Most cases have restricted the Hilbert space from two to four magnetic ions within the clusters with small spin quantum numbers.

Assuming a Heisenberg isotropic exchange, we determine the closed-form expressions for the energy eigenstates of a general mixed spin hexamer. These eigenstates can then determine the heat capacity and magnetic susceptibility in the general system.[2] As illustrated in Fig. 1, two isolated isosceles trimers with difference spins are connected with a γJ superexchange as shown by the black and gray dotted lines. Using a basis set that consists of both dimers and trimers, we use methods similar to those presented in Haraldsen *et al.*[10,15] to investigate the hexamer model.

We examine this model further by restricting it to a spin-1/2 system and applying the calculations to the V^{4+} isolated trimer systems studied experimentally by Luban *et al.*[16] Because the V^{4+} trimer system consists of two trimers per units cell, this system is a good candidate for intertrimer interactions.[16] For this, we calculate the exact inelastic neutron-scattering intensities and other magnetic properties for a 1/2 hexamer and compare to the 1/2 trimer. Since the trimer and hexamer have two different ground states (1/2 for

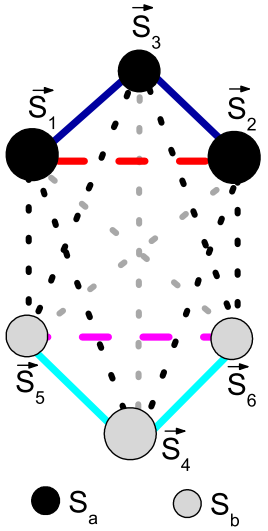

FIG. 1. (Color online) The hexamer model consists of six spin ions (black/gray circles) with intratrimer interactions of strength $\eta_a J$ (solid dark blue), $\eta_b J$ (solid light blue), $\alpha_a J$ (dashed dark red), $\alpha_b J$ (dashed light red), and intertrimer interaction γJ (dotted black/gray). The black and gray spin ions nominally denote trimers with different ion spins, S_a and S_b. In the discussion of V^{4+} clusters, we specialize to $S_a=S_b=\frac{1}{2}$, where the gray dotted lines represent different superexchange pathways that are present in the V^{4+} material (Ref. 14).

the trimer and 0 for the hexamer), an examination of the low-temperature magnetic susceptibility should yield a distinct difference even if the intertrimer interaction is small.[2]

In 2002, Luban *et al.*[16] presented data for two vanadium molecular magnets that were found to consist of magnetically isolated V_3 trimers. A trimer model was introduced for these materials,

$$Na_6\{H_4V_6O_8(PO_4)_4[(OCH_2)_3CCH_2OH]_2\}\cdot 18H_2O$$

(denoted as V_{blue}) and

$$(CN_3H_6)_4Na_2\{H_4V_6O_8(PO_4)_4[(OCH_2)_3CCH_2OH]_2\}\cdot 14H_2O$$

(denoted as V_{green}). (The shorthand name denotes the color of the material.[17]) These molecular magnets consist of six $S=1/2$ V^{4+} ions per formula unit and isosceles trimer V^{4+} units are evident in the structure. Luban *et al.* found that the magnetic properties of both materials were well described by a Heisenberg model. A fit of this two-parameter model to the susceptibility gave exchange constants of $J=63.8$ K and $J'=5.9$ K for V_{blue} and $J=64.6$ K and $J'=6.9$ K for V_{green}. Unpublished inelastic neutron-scattering data purportedly confirmed the two excited energy levels predicted by this model.[18] Because the two V_3 trimers are relatively close to one another, it is possible that weak intertrimer interactions may exist and could be predicted by the hexamer model. By applying our calculations for the spin-1/2 hexamer model with a fit to magnetic-susceptibility measurements, we will give predictions of the INS excitations and structure factors for the two V^4 materials, which are useful for future INS experiments.

II. TRIMER PAIR MODEL FOR GENERAL SPIN

We introduce a spin hexamer to model intertrimer interactions. The energy eigenstates of this system in our model can be determined exactly, which allows us to evaluate the partition function and magnetic susceptibility. A numerical integration of the heat capacity allows a check of our results using the zero-temperature entropy. With exchange parameters determined by magnetic susceptibility, the ground state of the magnetic structure, excitation energies, and inelastic neutron-scattering structure factors can be predicted.

A. Hamiltonian and energy eigenstates

Our hexamer model (Fig. 1) consists of two isosceles trimers that interact through multiple superexchange pathways. Since the system can be considered as two interacting trimers, the hexamer can be discussed within the basis of the individual components. Assuming nearest-neighbor Heisenberg interactions,[19] the Hamiltonian of this system can be written as

$$\begin{aligned}\mathcal{H} = J[&\eta_a(\vec{S}_1\cdot\vec{S}_3+\vec{S}_2\cdot\vec{S}_3)+\eta_b(\vec{S}_4\cdot\vec{S}_5+\vec{S}_4\cdot\vec{S}_6)+\alpha_a\vec{S}_1\cdot\vec{S}_2\\&+\alpha_b\vec{S}_5\cdot\vec{S}_6+\gamma(\vec{S}_1\cdot\vec{S}_4+\vec{S}_1\cdot\vec{S}_5+\vec{S}_1\cdot\vec{S}_6+\vec{S}_2\cdot\vec{S}_4\\&+\vec{S}_2\cdot\vec{S}_5+\vec{S}_2\cdot\vec{S}_6+\vec{S}_3\cdot\vec{S}_4+\vec{S}_3\cdot\vec{S}_5+\vec{S}_3\cdot\vec{S}_6)]\\&-g\mu_B B\sum_i^6 S_{z_i},\end{aligned} \tag{1}$$

where J is an overall interaction scale, $\eta_{a,b}=J_{a,b}/J$, $\alpha_{a,b}=J'_{a,b}/J$, $\gamma=J''/J$, and $J_{a,b}$, $J'_{a,b}$, and J'' are the trimer, dimer, and hexamer superexchange interactions, respectively. These magnetic interactions are positive for antiferromagnetic interactions and negative for ferromagnetic interactions. $\vec{S}_i$ is the quantum spin operator a specific ion at sites $i=1\cdots6$. The Zeeman term interacts with the z component of the spin operator. This makes the degenerate energy eigenstates split in field.

Using the Kambe[3,15] approach and arranging the Hamiltonian to take advantage of total spin, the energy eigenstates and eigenvalues may be found. This allows the Hamiltonian to be diagonalized on a convenient dimer and trimer basis. (In practice we will employ the usual set of $\hat{z}$-polarized magnetic basis states.) By taking advantage of spin structure of the individual components, the energy eigenvalues of the general S hexamer are given by

$$\begin{aligned}E=\frac{J}{2}[&\eta_a(\mathcal{S}_{\mathbf{\Delta,a}}-\mathcal{S}_{\mathbf{d,a}}-\mathcal{S}_{\mathbf{a}})+\eta_b(\mathcal{S}_{\mathbf{\Delta,b}}-\mathcal{S}_{\mathbf{d,b}}-\mathcal{S}_{\mathbf{b}})\\&+\alpha_a(\mathcal{S}_{\mathbf{d,a}}-2\mathcal{S}_{\mathbf{a}})+\alpha_b(\mathcal{S}_{\mathbf{d,b}}-2\mathcal{S}_{\mathbf{b}})\\&+\gamma(\mathcal{S}_{\mathbf{tot}}-\mathcal{S}_{\mathbf{\Delta,a}}-\mathcal{S}_{\mathbf{\Delta,b}})]-g\mu_B BS^z_{tot},\end{aligned} \tag{2}$$

where $\mathcal{S}_{\mathbf{tot}}=S_{tot}(S_{tot}+1)$ specifies the total hexamer spin, $\mathcal{S}_{\mathbf{\Delta,(a,b)}}=S_{\Delta,(a,b)}(S_{\Delta,(a,b)}+1)$ gives the spin state of the individual trimers, $\mathcal{S}_{\mathbf{d,(a,b)}}=S_{d,(a,b)}(S_{d,(a,b)}+1)$ is the spin state of the individual dimers, and $\mathcal{S}_{\mathbf{(a,b)}}=S_{(a,b)}(S_{(a,b)}+1)$ gives the spin state of each ion in each trimer (1/2, 1, 3/2, etc.). S^z_{tot} is the total hexamer spin z component. When we refer to individual trimers and dimers, we are referencing the individual components that make up the hexamer as shown in Fig. 1.

The total spin states of the hexamer, trimers, and dimers can be determined by examining the spin decomposition of

$$S_a\otimes S_a\otimes S_a\otimes S_b\otimes S_b\otimes S_b. \tag{3}$$

The Hilbert space is $(2S_a+1)^3(2S_b+1)^3$ dimensional. Since this is a rotationally invariant Hamiltonian in spin space, the total spin S_{tot} and S^z_{tot} are trivially good quantum numbers. Given the energy eigenvalues and eigenstates, we may determine the partition function, magnetic susceptibility, and heat capacity for a given system.[10]

B. Magnetic observables for spin-1/2 hexamer

By solving this model for a spin-1/2 hexamer, the results can be used for comparison to the V^{4+} clusters presented by Luban *et al.*[16] Here, the model is examined for a system of two spin-1/2 trimers with the trimers having equal interactions between the moieties. Specializing to this case provides a $[2(\frac{1}{2})+1]^6=64$ dimensional Hilbert space, where the decomposition into spin states is as follows:

$$\left(\frac{1}{2}\otimes\frac{1}{2}\otimes\frac{1}{2}\right)\otimes\left(\frac{1}{2}\otimes\frac{1}{2}\otimes\frac{1}{2}\right)=3\oplus2^5\oplus1^9\oplus0^5. \tag{4}$$

The superscript specifies the number of independent multiplets of each S_{tot}. Each of these states contain $2S_{tot}+1$ magnetic substates, which are degenerate given an isotropic magnetic Hamiltonian such as the Heisenberg form (1).

TABLE I. Energy levels and INS properties of the $S=1/2$ Heisenberg hexamers.

S_{tot}	Spin state $\lvert S_{tot}S^z_{tot}\rangle_{\Delta 1,\Delta 2,d1,d2}$	Energy	INS excitation gap	INS structure factor[a]
3	$\lvert 3S^z_{tot}\rangle_{3/2,3/2,1,1}$	$\frac{J}{2}(\frac{9\gamma}{2}+2+\alpha)$		
2	$\lvert 2S^z_{tot}\rangle_{3/2,3/2,1,1}$	$\frac{J}{2}(\frac{-3\gamma}{2}+2+\alpha)$		
	$\lvert 2S^z_{tot}\rangle_{1/2,3/2,1,1}$	$\frac{J}{2}(\frac{3\gamma}{2}-1+\alpha)$		
	$\lvert 2S^z_{tot}\rangle_{1/2,3/2,0,1}$	$\frac{J}{2}(\frac{3\gamma}{2}+1-\alpha)$		
	$\lvert 2S^z_{tot}\rangle_{3/2,1/2,1,1}$	$\frac{J}{2}(\frac{3\gamma}{2}-1+\alpha)$		
	$\lvert 2S^z_{tot}\rangle_{3/2,1/2,1,0}$	$\frac{J}{2}(\frac{3\gamma}{2}+1-\alpha)$		
1	$\lvert 1S^z_{tot}\rangle_{3/2,3/2,1,1}$	$\frac{J}{2}(\frac{-11\gamma}{2}+2+\alpha)$		
	$\lvert 1S^z_{tot}\rangle_{1/2,3/2,1,1}$	$\frac{J}{2}(\frac{-5\gamma}{2}-1+\alpha)$	$\frac{J}{2}(3-\gamma)$	$\frac{2}{7}[3+\cos(qd_{\alpha_b})-4\cos(qd_{\eta_b})]$
	$\lvert 1S^z_{tot}\rangle_{1/2,3/2,0,1}$	$\frac{J}{2}(\frac{-5\gamma}{2}+1-\alpha)$		
	$\lvert 1S^z_{tot}\rangle_{3/2,1/2,1,1}$	$\frac{J}{2}(\frac{-5\gamma}{2}-1+\alpha)$	$\frac{J}{2}(3-\gamma)$	$\frac{2}{7}[3+\cos(qd_{\alpha_a})-4\cos(qd_{\eta_a})]$
	$\lvert 1S^z_{tot}\rangle_{3/2,1/2,1,0}$	$\frac{J}{2}(\frac{-5\gamma}{2}+1-\alpha)$		
				$\frac{3}{7}[9+8\cos(qd_{\alpha_a})+8\cos(qd_{\alpha_b})-8\cos(qd_{\eta_a})$
	$\lvert 1S^z_{tot}\rangle_{1/2,1/2,1,1}$	$\frac{J}{2}(\frac{\gamma}{2}-4+\alpha)$	γJ	$-8\cos(qd_{\eta_b})-\Sigma_{i=1}^{9}\cos(qd_{\gamma_i})]$
	$\lvert 1S^z_{tot}\rangle_{1/2,1/2,1,0}$	$\frac{J}{2}(\frac{\gamma}{2}-2-\alpha)$	$J(\gamma+1-\alpha)$	$1-\cos(qd_{\alpha_b})$
	$\lvert 1S^z_{tot}\rangle_{1/2,1/2,0,1}$	$\frac{J}{2}(\frac{\gamma}{2}-2-\alpha)$	$J(\gamma+1-\alpha)$	$1-\cos(qd_{\alpha_a})$
	$\lvert 1S^z_{tot}\rangle_{1/2,1/2,0,0}$	$\frac{J}{2}(\frac{\gamma}{2}-3\alpha)$		
0	$\lvert 00\rangle_{3/2,3/2,1,1}$	$\frac{J}{2}(\frac{-15\gamma}{2}+2+\alpha)$		
	$\lvert 00\rangle_{1/2,1/2,1,1}$	$\frac{J}{2}(\frac{-3\gamma}{2}-4+\alpha)$	Ground state	
	$\lvert 00\rangle_{1/2,1/2,0,1}$	$\frac{J}{2}(\frac{-3\gamma}{2}-2-\alpha)$		
	$\lvert 00\rangle_{1/2,1/2,1,0}$	$\frac{J}{2}(\frac{-3\gamma}{2}-2-\alpha)$		
	$\lvert 00\rangle_{1/2,1/2,0,0}$	$\frac{J}{2}(\frac{-3\gamma}{2}-3\alpha)$		

[a]The functional form of the structure factors can be used for any spin hexamer.

The energy eigenvalues and INS properties are given for this $S-1/2$ hexamer model in Table I. In the case of the vanadium materials, the Hamiltonian is simplified by constraining $J_a=J_b=J$ and $J'_a=J'_b=J'$, which makes $\eta_{(a,b)}=1$ and $\alpha_1=\alpha_2=\alpha$. The intertrimer interaction couples the individual trimer energy eigenstates. The origin of the hexamer energy eigenstates, as formed by the coupled-trimer states and indicated by the spin decomposition [Eq. (4)] is characterized in Fig. 2, which qualitatively represents the effect of the hexamer coupling on the energy levels of the two spin-1/2 trimers. The relative simplicity of these hexamer states is largely due to the symmetry of this identical-trimer problem; were the intertrimer interactions different, then there would be additional mixing between the basis states, which would greatly complicate the energy eigenvalues and eigenvectors.

The partition function and susceptibility can be determined directly from the energy eigenvalues. The zero-field magnetic susceptibility for the $S=1/2$ hexamer is given by

$$\chi=\frac{N_A(g\mu_B)^2\beta}{Z}[2e^{-J\beta(\gamma-6\alpha)/4}+4e^{-J\beta(\gamma-4-2\alpha)/4}+2e^{-J\beta(\gamma-8+2\alpha)/4}+4e^{J\beta(5\gamma-2+2\alpha)/4}+4e^{J\beta(5\gamma+2-2\alpha)/4}+2e^{J\beta(11\gamma-4-2\alpha)/4}+20e^{-J\beta(3\gamma+2-2\alpha)/4}+20e^{-J\beta(3\gamma-2+2\alpha)/4}+10e^{J\beta(3\gamma-4-2\alpha)/4}+28e^{-J\beta(9\gamma+4+2\alpha)/4}], \quad (5)$$

where Z is the partition function, $\beta=1/k_BT$, k_B is Boltzmann's constant, N_A is Avogadro's number, μ_B is the Bohr magneton, and g is the electron g factor. Only the zero-field susceptibility is shown due to the length of the in-field expression. We have confirmed numerically that the zero-temperature entropy of the hexamer satisfies

$$\frac{S}{k_B}=\int_0^\infty \beta\frac{d^2\ln(Z)}{d\beta^2}d\beta=\ln(\mathcal{N}/\mathcal{N}_0)=\begin{cases}\ln\left(\frac{2^6}{5}\right) & \alpha=\gamma=1\\ 4\ln(2) & \alpha=1,0<\gamma<1\\ 2\ln(2) & \alpha=1,\gamma=0\\ 6\ln(2) & \alpha\neq 1,\gamma>0,\end{cases} \quad (6)$$

where $\mathcal{N}$ is the dimensionality of the full Hilbert space and $\mathcal{N}_0$ is the degeneracy of the ground state; for the $S=1/2$ hexamer, $\mathcal{N}=2^6$ and $\mathcal{N}_0=5$ for $\alpha=\gamma=1$.[10,20] The zero-temperature entropy will clearly change with the multiplicity of the ground state. Here, in the $\gamma\to 0$ limit, the entropy of individual trimers is recovered.

Table I shows the INS energy gaps and structure factors for a spin-1/2 hexamer, which were determined from the energy eigenvalues and eigenvectors. For transitions between discrete energy levels, the excitation energy is equal to the

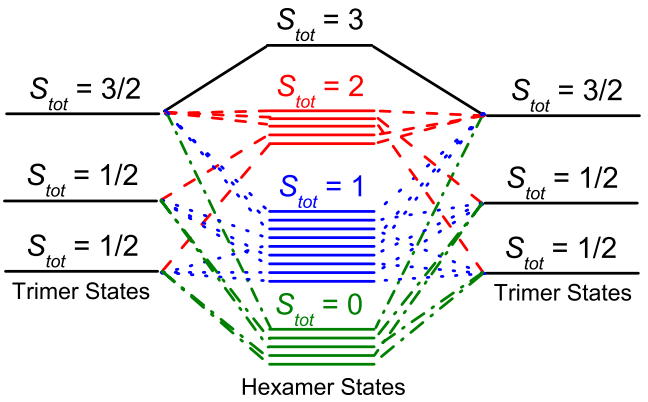

FIG. 2. (Color online) Characterization for the formation of hexamer states from the isolated trimer-pair basis, for the $S_a = S_b = 1/2$ case. The trimer product basis states combine to give a spin-3 septet (black solid), five spin-2 quintets (red dashed), nine spin-1 triplets (blue dotted), and five spin-0 singlets (green dot dashed). With the isotropic Heisenberg model assumed here, all energy eigenstates with the same S_{tot} are degenerate.

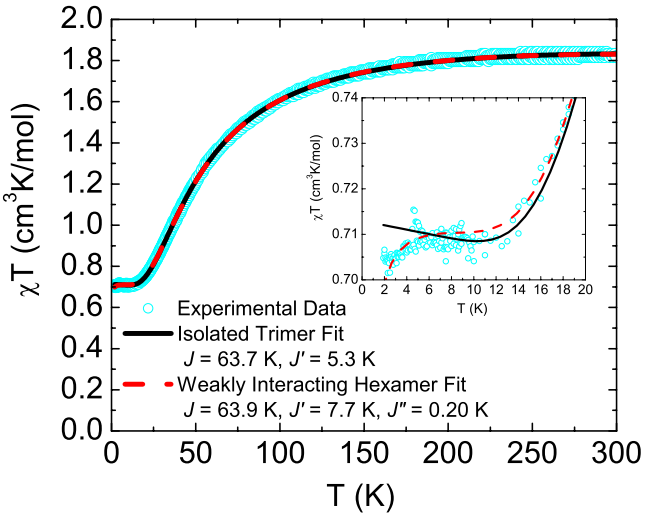

FIG. 3. (Color online) Magnetic susceptibility of V_{blue} (blue circles), showing fits to the isolated trimer (solid black line) and weakly interacting hexamer (dashed red line) models. Error bars on the values are discussed in text. The inset shows a closeup view of the low-temperature data and the fits with $T < 20$ K.

energy difference, $\hbar\omega = E_f - E_i$. Using techniques and methods described in Ref. 10, the INS differential cross section is proportional to the neutron-scattering structure factor, $S(\vec{q})$. The results given in Table I apply to neutron scattering from single crystals. To interpret neutron experiments on powder samples, we require an orientation average over the solid angle, Ω, of the unpolarized single-crystal neutron-scattering structure factor. We define this powder average by

$$\bar{S}(q) = \int \frac{d\Omega_{\hat{q}}}{4\pi} S(\vec{q}). \tag{7}$$

Therefore, the powder average intensity including the magnetic form factor for each transition is given by

$$\bar{S}(q) = F^2(q)[1 - j_0(qd_{\alpha_{a/b}})] \tag{8}$$

(dimer excitation),

$$\bar{S}(q) = \frac{2F^2(q)}{7}[3 + j_0(qd_{\alpha_{a/b}}) - 4j_0(qd_{\eta_{a/b}})] \tag{9}$$

(trimer excitation), and

$$\bar{S}(q) = \frac{3F^2(q)}{7}\Bigg[9 + 8j_0(qd_{\alpha_a}) + 8j_0(qd_{\alpha_b}) - 8j_0(qd_{\eta_a}) - 8j_0(qd_{\eta_b}) - \sum_{i=1}^{9} j_0(qd_{\gamma_i})\Bigg] \tag{10}$$

(hexamer excitation), where $F(q)$ is the V^{4+} magnetic form factor,[21] d is the interatomic separation corresponding to the interaction, and $j_0(x) = \sin(x)/x$. For the spin-1/2 hexamer at zero temperature, there are five observable INS excitations. Two of these transitions involve dimer excitations only, two are trimer excitations only, and the fifth is an excitation of the full hexamer system. While the relative intensities are for the spin-1/2 case, the functional form for the excitations is same for any spin case. Note that not all spin-1 levels have corresponding INS intensities. This is due to the inability of the neutron (which can only produce a $S = \pm 1$ or 0 transitions) to excite more than one component of the hexamer. Since the ground-state configuration has the trimers in spin-1/2 states and the dimers in spin-1 states, the only configurations that can be produced by a neutron is to excite the whole hexamer into the same configuration or excite a trimer or dimer by one. Therefore, this demonstrates a new constraint to the neutron-scattering selection rules, which is that neutron can only effect individual components. Furthermore, this can be extended to the INS intensity since the intensities for each excitation have the functional form of the component that is excited.

III. APPLICATION TO THE V^{4+} MATERIALS

A. Experimental techniques

The two different vanadium compounds (V_{blue} and V_{green}) were synthesized under a nitrogen atmosphere using the methods described by Bogge *et al.*[17] The materials were subsequently stored under a nitrogen atmosphere. For study of their static magnetic response, samples of several milligram quantities were prepared for measurement in a Quantum Design MPMS-XL magnetometer with a 7 T magnet. For sample preparation, portions of the powdered material were quickly wrapped in weighing paper lined with a very small amount of Apiezon N grease to immobilize and protect them. The samples were weighed and then placed in the superconducting quantum interference device (SQUID) magnetometer. The sample space in the SQUID magnetometer contains static He gas, so the samples were again in an inert atmosphere. Measurements of the magnetic moment of the samples were made from 2 to 300 K in an applied field of 0.2 T. The small background signal from the paper and grease was accounted for after the measurements.

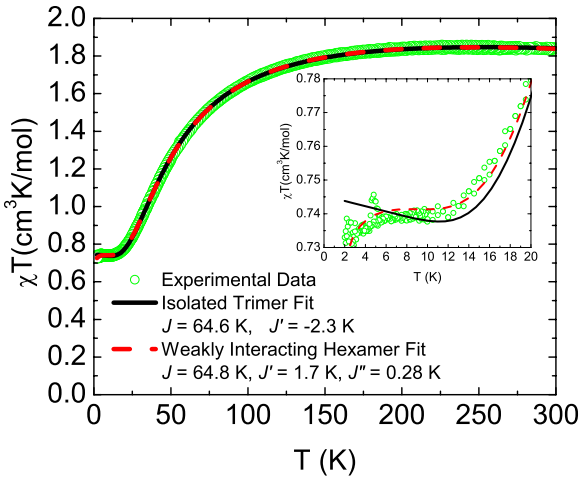

FIG. 4. (Color online) Magnetic-susceptibility data of V_{green} (green circles), showing fits to the isolated trimer (solid black line) and weakly interacting hexamer (dashed red line) models. Error bars on the values are discussed in text. The inset shows a closeup view of the low-temperature data and the fits with $T<20$ K.

B. Results and discussion

In Fig. 3, we show magnetic-susceptibility data for V_{blue}, where the black and red lines show the fit to the isolated trimer and weakly interacting hexamer models for zero field. For the isolated trimer model, a fit of the data to Eq. (5) shows that $J=63.7\pm0.1$ K and $J'=5.3\pm0.6$ K, which is in good agreement with the result of Luban *et al.*[16] On incorporating an intertrimer interaction the fitted values change to $J=63.9\pm0.1$ K, $J'=7.7\pm0.6$ K, and $J''=0.20\pm0.02$ K. The data evidently suggest a weak intertrimer interaction of strength $J''\approx0.2$ K. The inset of Fig. 3 shows the differences between the trimer and hexamer fits at $T<20$ K. This is the range where the intertrimer interactions will be most prevalent. Here, the hexamer fit seems to clearly follow the nature of low-temperature susceptibility.

In Fig. 4, we show magnetic-susceptibility data for V_{green}. The black and red line show the fits to the isolated trimer and weakly interacting hexamer models for zero field, respectively. A fit to our data gives $J=64.6\pm0.1$ K and $J'=-2.3\pm0.4$ K; this ferromagnetic J' is not in agreement with Luban *et al.*[16] When we incorporate an intertrimer (hexamer) interaction, the value for J' is closer to Luban *et al.*; we find $J=64.8\pm0.1$ K, $J'=1.7\pm0.4$ K, and $J''=0.28\pm0.01$ K. Evidently the fitted J' has shifted from ferromagnetic to antiferromagnetic by 3–4 K. This fit suggests a possible scale for a very weak intertrimer interaction (≈0.3 K). Note that the interaction J is dominant, and J' and J'' are much smaller and are much less well defined. Since they are very sensitive, we show the best fit parameters after 100 iterations. However, the functions, while having different parameters than those obtained by Luban *et al.*,[16] show very little graphical difference. Therefore, we are looking mainly at the differences between the trimer and hexamer models, which is clearly shown in the inset of Fig. 4.

It is clear that a weak intertrimer interaction is consistent with the susceptibility data. As shown in Table II, the fitted values of the dominant coupling J are all in close agreement. A slight discrepancy between theory and experiment is evident in fitting the isolated trimer model for V_{green}. Allowing a hexamer interaction, J'' results in a shift in J' of a few K in these materials. While this is only a small change, it may be observable in the INS excitation spectrum for these materials.

TABLE II. Comparison of exchange constants determined by magnetic susceptibility.

$Na_6\{H_4V_6O_8(PO_4)_4[(OCH_2)_3CCH_2OH]_2\}\cdot18H_2O$ (V_{blue})			
Model	J (K)	J' (K)	J'' (K)
Isolated trimer	63.7 ± 0.1	5.3 ± 0.6	$\equiv0$
Hexamer	63.9 ± 0.1	7.7 ± 0.6	0.20 ± 0.02
Luban *et al.* (Ref. 16)	63.8 ± 0.6	5.9 ± 1.1	$\equiv0$
$(CN_3H_6)_4Na_2\{H_4V_6O_8(PO_4)_4[(OCH_2)_3CCH_2OH]_2\}\cdot14H_2O$ (V_{green})			
Model	J (K)	J' (K)	J'' (K)
Isolated trimer	64.6 ± 0.1	-2.3 ± 0.4	$\equiv0$
Hexamer	64.8 ± 0.1	1.7 ± 0.4	0.28 ± 0.01
Luban *et al.* (Ref. 16)	64.6 ± 0.5	6.9 ± 1	$\equiv0$

Based on our magnetic-susceptibility fitted parameters, the $|0S^z_{tot}\rangle_{1/2,1/2,1,1}$ hexamer state is the ground state in these materials. This implies that only three excitations will be visible in INS (see Table I), where two of these states are doubly degenerate, which will split if the trimers are inequivalent. As explained in the theory section, the reason the system has only five spin-1 states excited is determined by the spin states of the hexamer components (dimer and trimer states). Given our fitted values of the exchange interactions in the spin hexamer model, the INS excitations would be visible at 0.02, 5.46, and 8.36 meV in V_{green}, and 0.02, 4.84, and 8.23 meV in V_{blue}. Although the low-lying excitation may be difficult to resolve, the two higher excitations should be clearly evident in INS. In an isolated trimer model these excitations would lie at 5.03 and 8.24 meV for V_{blue}, which means that by allowing a hexamer interaction, the fit parameters changed enough to lower the energies of the dimer and trimer excitations. This difference should be evident in high-resolution INS measurements. According to Luban *et al.*, preliminary INS measurements on V_{blue} show excitations at ~5.0 and ~8.25 meV, although this data are unpublished.[18] It should be noted that the difference 0.2 meV in the excitations of the isolated and nonisolated cases arise from the introduction of J'' in the magnetic-susceptibility fits. By introducing this intertrimer interaction, all the interaction parameters change. It is the overall contribution of these changes that shift the energy levels from isolated case. This should not be confused with the small change the γJ provides in the excitation gap.

Figure 5 shows the predicted INS intensity for V_{blue} as a function of energy and momentum transfer (V_{green} would have a similar Q dependence but slightly different energy profile.) In this system, the two high energy excitations are

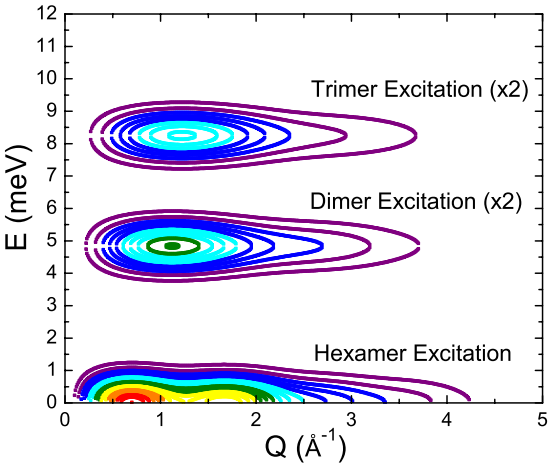

FIG. 5. (Color online) Predicted INS intensity for V_{blue}. Excitations for V_{blue} result at 0.02 meV (hexamer excitation), 4.84 meV (dimer excitations), and 8.23 meV (trimer excitations). V_{green} would have the same Q dependence but the energy levels will be at 0.02 meV (hexamer excitation), 5.46 meV (dimer excitations), and 8.36 meV (trimer excitations).

transitions involving the individual dimers and trimers. Since the individual trimers are identical and the coupling is weak, the two trimer excitations are at identical energies (similar for the dimer excitations). It is evident that introduction of a weak hexamer interaction gives the presence of a new low-lying excitation of 20 μeV. The INS structure factors of the two higher energy excitations are not affected by the intertrimer coupling. Only the first low-lying excitation shows a dependence on the intertrimer distances. The two higher energy excitations will be observable since these higher energy excitations arise from neutron interactions with the individual trimers and dimers. In Fig. 5, the 4.8 meV excitations are from the dimer transitions and the 8.3 meV excitation is a transition of the individual trimers. It will be very interesting in the future to see whether INS can indeed observe the effect of the weak intertrimer interaction on these energy levels and, in particular, observe the expected low-lying excitation.

While inelastic neutron scattering may be able to distinguish the energy shift from isolated trimers to weakly interacting hexamer, it should be noted that there could be issues with thermal statistics due to the low-lying excitation being only 0.2 K. Therefore, the observed excitations may have a thermal averaging of excitations, which could complicate measured energies. This may be remedied by a detailed examination of the excitations or by ultracooling the samples below the 0.2 K excitation. Hopefully, future INS studies of deuterated samples can meet these challenges to determine a limit on the intertrimer coupling, which would be very useful in solidifying the trimer and intertrimer interactions in these materials.

IV. CONCLUSION

In conclusion, we present the closed-form solutions for the energy eigenstates for a general spin hexamer, with Heisenberg interactions only, as well as the general functional form for the basic hexamer structure factors. It is also observed that the INS structure factors for symmetric clusters are characterized by the excitations of the individual components of a cluster. For a comparison with materials, we specialize this model to the spin-1/2 case and determine the energy excitations and zero-field magnetic susceptibility. We have applied these calculations to two vanadium molecular magnets that have been previously discussed by Luban *et al.*[16]. Through the use of magnetic-susceptibility measurements, we were able to determine that a small intertrimer interactions may be present. Examination of the low temperature magnetic susceptibility illustrates the differences between the trimer and hexamer models. It can be concluded that the presence of intertrimer interactions only introduces extra excitations which shift the energy levels and do not affect the INS intensities of the individual components. Due to the overall size of the intertrimer interaction, this effect may be too small for current experimental resolutions.

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