# Introduction to Molecular Magnets

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Molecular magnets are finite clusters of spin that interact in different ways to produce an overall magnetism in the cluster. In this paper, molecular magnets will be introduced, a clear description of them will be discussed, as well as, why they are important in science, what experimental techniques help determine them and their structure, and the theoretical background in how they are modeled.

# I. INTRODUCTION TO MOLECULAR MAGNETS

Every child learns about magnetism when they are young. This is usually the typical bar magnetism that kids see or the effects of magnetic field on particles as in the Aurora Borealis. However, magnetism has a much deeper meaning to scientists that study them. Magnetism was known and mentioned in literature as far back as the  $4^{th}$  century BC and has since grown into a major area of science.<sup>1</sup>

In the past couple of decades, molecular magnetism has caught the attention of condensed matter scientists because of the possible technological and industurial applications. The technology arena is always looking for new materials to expand the current demand on data



FIG. 1: The structure of Ni<sub>4</sub>: A molecular magnet that consists of four spin-1 Ni ions.<sup>5</sup>



FIG. 2: Schematic of the different types of magnetic coupling.<sup>3</sup>

storage and computing. With the possibility of using spin flips for binary systems, or an even more complex number system, quantum computing and molecular data storage gives molecular magnets a possibility to move technology forward.<sup>2</sup>

Most magnets the people are familiar with are the kinds that are metallic lattices that contain an overall magnetism or are in extended ordered systems.<sup>3,4</sup> While these types of magnets are important and merit mention, the topic of this paper is molecular magnets. Molecular magnets typically contain isolated clusters of spins that interact in various ways. Each of the identical molecular units can contain as few as two and up to several dozen spin ions.<sup>3</sup> Figure 1 shows the molecular magnet of Ni<sub>4</sub>, where there exist an isolated cluster of four spin-1 Ni ions.<sup>5</sup> It should be noted that molecular magnets do not have to be isolated magnetic structure. While the

TABLE I: Some Examples of Small S = 1/2 Clusters and Molecular Magnets.<sup>26</sup>

Material	Spin System	Ground State $\mathbf{S}_{tot}$	Refs.
	1.	0	9-11
$VO(HPO_4) \cdot 0.5H_2O$	dimer	0	10.10
$Cu_3(O_2C_{16}H_{23})_6 \cdot 1.2C_6H_{12}$	symmetric trimer	1/2	12,13
$Na_9[Cu_3] \cdot 26H_2O^1$	symmetric trimer	1/2	14
$[Cu_3(cpse)_3(H_2O)_3] \cdot 8.5H_2O$	symmetric trimer	1/2	15
$(CN_{3}H_{6})_{4}Na_{2}[V_{6}]\cdot 14H_{2}O^{2}$	isosceles trimer	1/2	16
$Na_6[V_6] \cdot 18H_2O^2$	general trimer	1/2	16
$K_{6}[V_{15}As_{6}O_{42}(H_{2}O)]\cdot 8H_{2}O$	symmetric trimer	1/2	17 - 21
NaCuAsO <sub>4</sub>	linear tetramer	Ő	$^{23,24}$
$(NHEt_3)[V_{12}As_8O_{40}(H_2O)] \cdot H_2O.$	rectangular tetramer	0	22
$K_7 Na[Cu_4] \cdot 5.5 H_2 O^3$	distorted tetramer	1	14

 ${}^{a}[Cu_{3}] = [Cu_{3}Na_{3}(H_{2}O)_{9}(\alpha - AsW_{9}O_{33})_{2}]$  ${}^{b}[V_{6}] = [H_{4}V_{6}O_{8}(PO_{4})_{4}((OCH_{2})_{3}CCH_{2}OH)_{2}]$  ${}^{c}[Cu_{4}] = [Cu_{4}K_{2}(H_{2}O)_{6}(\alpha - AsW_{9}O_{33})_{2}]$ 

more commonly known molecular magnets of  $Mn_{12}^{6}$  and Fe<sub>8</sub><sup>7</sup> usually take spotlight due to their size and complexity, it is important to show that the arena on molecular magnets is large consisting of many different types of materials. Table I shows some examples of spin 1/2 molecular magnets. The main point to molecular magnets is that, unlike traditional magnets, they do not contain extended long range magnetic ordering. This is important to note because of the fundemental difference between long range interactions and finite clusters that have local interactions.<sup>5</sup> The local interactions provide discrete energy level excitations instead of the continuum of states provided by long range order. While theory defines an isolated cluster as having no interaction between clusters, it is important to recognize that in real systems can have weak or moderate extended interactions between molecules. These different types of local and long range inteactions co-existing can be distinguished through the use of multiple experimental techniques.

Figure 2 shows the types of magnetic coupling.<sup>3</sup> While figure 2 typically refers to long range systems, the types are the same for clusters. The magnetic coupling can be described as either disordered or ordered. Disordered coupling is called paramagnetism and consists of ion clusters that have random spin direction. Ordered means that there is a specific pattern to way the spins are oriented. Within the ordered category, there is ferromagnetism, antiferromagnetism, and ferrimagnetism. Ferromagnetism consists of all spins aligned in the same direction, while antiferromagnetism has the spins aligned in opposite directions. Antiferromagnets typically give a total spin ground state of 0. Ferrimagnetism is when you have antiferromagnetism with different strength spins which ends up giving a total net spin to the material. In molecular magnets, magnetic ordering tends to be described as either completely antiferromagnetic, ferromagnetic, or combinations of the two, where some ions are antiferromagnetically aligned to one ion and ferromagnetically aligned to another. This tends to cause frustration in the system.

In molecular magnets, the theory behind the interactions has been well developed. The main problem is that, with molecular magnets, there are different ways for the systems to couple. However, the interactions between ions can usually be described by local nearest neighbor coupling in the Heisenberg model.<sup>8</sup> This allows for most systems to be solved numerically. The analytical limit is held by the small spin clusters of a hand full of ions with low spin. Analytical results of small clusters can reveal trends and patterns that can help understand the larger spin clusters. Once the amount of spin and the number of ions increases, the Hilbert space becomes too large to solve analytically. The Heisenberg model is usually preferred over the Hubbard model since there are no significant long range interactions in molecular magnets.<sup>29,30</sup> The Heisenberg model and the different interactions will be discussed in detail later.

Once you have a theory behind the system of interest, it is necessary to use experimental techniques to test these interactions. Magnetism can be determined through a number of experimental techniques. These techniques range from bulk measurements (magnetization, magnetic susceptibility, and heat capacity) to microscopic measurements (inelastic neutron scattering and infrared and Raman spectroscopy). The use of both bulk and microscopic techniques can help clarify the types of interactions. To fully understand the magnetism in a molecular magnet, as well as, fully describe the interaction, it is necessary to use these methods to compliment each other.

# II. MOLECULAR MAGNETS - THEORY

# A. Heisenberg Hamiltonian

As mentioned earlier, molecular magnets can usually be described with a Heisenberg model. The isotropic Heisenberg Hamiltonian is given by

$$\mathcal{H} = \sum_{\langle ij \rangle} J_{ij} \vec{S}_i \cdot \vec{S}_j, \tag{1}$$

where  $J_{ij}$  is the magnetic interaction between the spins i and j. In this Hamiltonian, a positive J refers to an antiferromagnetic interaction and a negative J refers to a ferromagnetic interaction.<sup>8,26</sup> Eventhough this is the more common Hamiltonian used to model systems, it is important to expand the Heisenberg Hamiltonian to incorporate different interactions as well. The expansion

can be shown as

$$\mathcal{H} = \mathcal{H}_{iso} + (\mathcal{H}_{sym} + \mathcal{H}_{antisym})_{aniso} + \mathcal{H}_{Zee}$$

where each term is described in spin operator terms as

$$\mathcal{H} = \sum_{\langle ij \rangle} \left( J_{ij} \vec{S}_i \cdot \vec{S}_j + \vec{S}_i \cdot \mathbf{D}_{ij} \cdot \vec{S}_j + \mathbf{d}_{ij} \vec{S}_i \wedge \vec{S}_j \right) + g\mu_B B \cdot \sum_i \vec{S}_i$$
(2)

Here, the Heisenberg Hamiltonian is expanded into four main parts: isotropic, symmetric anisotropic, antisymmetric anisotropic, and Zeeman terms, respectively.<sup>8</sup> This allows for the detailed modelling of most spin configurations. The  $\langle ij \rangle$  means a sum over all nearest neighbors. This Hamiltonian can be expanded to next nearest neighbor and so on. The basis of the Heisenberg model is the treatment of spin as a vector that can be coupled in all directions. The isotropic term represents the interaction where all components are the same in a rotation of coordinate system.<sup>5</sup> With this, the anisotropic terms have interactions with different components. Anisotropy can be either symmetric or antisymmetric providing a zero-field splitting of the isotropic magnetic levels. The symmetric case arises from dipolar interactions, provided that the two ions are symmetry related, where  $\mathbf{D}_{ij}$  is both symmetric and traceless. The antisymmetric anisotropic term comes from local spin-orbit coupling and is described by Dzyaloshinski and Moriya as a cross product of the spin operators. The final term is the Zeeman magnetic term. This provides a perturbation of the Hamiltonian to relate the splitting of the energy levels with magnetic field.

#### B. Ising and XY

The Heisenberg Hamiltonian can be simplified in many ways to describe the systems needed. In the previous case, there was an assumption that the local ground state of the magnetic centers was an orbital singlet without considering the first-order angular momentum.<sup>8</sup> When first-order angular momentum needs to be considered the Hamiltonian needs to be simplified to the following

$$\mathcal{H} = \sum_{ij} J_{ij} \left( \alpha \vec{S}_{ix} \cdot \vec{S}_{jx} + \beta \vec{S}_{iy} \cdot \vec{S}_{jy} + \gamma \vec{S}_{iz} \cdot \vec{S}_{jz} \right) \quad (3)$$

This general expression introduces the provides limiting situations, where

$$\alpha = \beta = \gamma = 1 \text{ (Heisenberg)}$$
  

$$\alpha = \beta = 0 \text{ and } \gamma = 1 \text{ (Ising)}$$
  

$$\alpha = \beta = 1 \text{ and } \gamma = 0 \text{ (XY)}$$

The Ising and XY models are typically useful to describe effective local spins at low temperatures. Most Ising and XY models have been used to describe chains of ions.<sup>8</sup>

# C. Dimensionality

This a quick note on the dimensionality of molecular magnets. The Hilbert space of the Hamiltonians is clearly dependent on the number of spins and will as the spin quantum number of the ions. The dimensions of the Hilbert space can be determined by

$$\dim(\mathcal{H}) = \prod_{1}^{N} 2S_i + 1 \tag{4}$$

where there is no spin symmetry present in the system.<sup>31</sup> If the system is spin symmetric then the dimensionality can be described as

$$\dim(\mathcal{H}) = (2S_i + 1)^N \tag{5}$$

where N is the number of ions.<sup>31</sup> This means that if you have two spin-1/2 ions interacting, then the dimensions of the Hilbert space are

$$dim(\mathcal{H}) = (2(1/2) + 1)^2 = 4 \tag{6}$$

which is pretty nice. However, if you consider 5 spin-1/2 or spin-3/2 ions, then the Hilbert space increases

$$dim(\mathcal{H}) = (2(1/2) + 1)^5 = 32 \tag{7}$$

for spin-1/2 ions and

$$dim(\mathcal{H}) = (2(3/2) + 1)^5 = 1024 \tag{8}$$

for spin-3/2 ions. Now if we examine one of the more popular molecular magnets,  $Mn_{12}$  (4 spin-3/2 ions and 8 spin-2 ions), you find it has a dimensionality of

$$dim(\mathcal{H}) = (2(3/2) + 1)^4 * (2(2) + 1)^8 = 1 \ge 10^8.$$
(9)

It is clear that the Hilbert space of  $Mn_{12}$  is outside the analytical range. This dimensionality helps determine whether the system can be determined analytically or numerically. The analytical limit is not a finely defined line. It depends on the diagonalization of the Hilbert space. If you have a nice isotropic Hamiltonian with equal interactions everywhere, then the limit in dimensionality is quite high. However, adding different interactions as well as increasing spin quantum numbers greatly complicates the exact analytical determination of the Hamiltonian.

When the Hilbert space is too large to be solved analytically or diagonalized exactly, numerical methods must be applied. Some of the numerical methods are projection, the Lanczos method and DMRG. Projection is a simple method that is based on multiple applications of



FIG. 3: Magnetization of  $Ni_4$  from 0 to 60 T. The black line is the experimental data and the red and green lines correspond to theoretical predictions to the spin-1 tetramer model. Red consists of a constant interaction and green introduces a field dependent interaction.<sup>5</sup>

the Hamiltonian on random trail states. The Lanczos method generates an orthonormal system that creates an operator that is tridiagonal. DMRG is a technique that divides that system into multiple blocks and then reduces the matrix accordingly.

## III. EXPERIMENTAL TECHNIQUES

Now that a basic introduction to the theoretical models for molecular magnets, it is important to give some introduction to the experimental techniques that help determine the magnetism in molecular magnets.

# A. Bulk Quantities

The bulk quantities are properties of the material or system as a whole. The measurements can not discriminate between different interactions, because it reports the measurements of the magnetic moment of the system. This are typically thermodynamic properties.

# 1. Magnetization

Magnetization is a bulk experimental technique that examines the overall magnetic moment of a material as a function of magnetic field.<sup>29,30</sup> In figure 3, the magnetization of a spin-1 Ni tetramer as compared to the magnetization data. By studying the magnetization of a molecular magnet, it is possible to determine the interaction strength in the material. The steps that appear in the magnetization are spin flip transition within the material as magnetic field is increased. For example, in the tetramer in figure 3, there are four steps corresponding to different to the four spin states in Ni<sub>4</sub>. Since Ni<sub>4</sub> is a spin-1 tetramer, it has spin states that have total spin 0, 1, 2, 3, and 4.5 Therefore, the magnetization examines these transitions directly. It is also needed to be mentioned that the red line is a prediction for the a constant interaction, which does not seem to correlate with the black line of the data. This is due to the fact that the interaction is dependent on field. The green line shows the corrected magnetization with a field dependent interaction.

Molar magnetization can be defined as

$$M = \frac{N_A}{\beta} \frac{\partial \ln Z}{\partial H} \tag{10}$$

where  $N_A$  is Avogadro's number,  $\beta$  is  $\frac{1}{k_B T}$ ,  $k_B$  is Boltzman's constant, T is temperature, and H is the applied field. Z is defined as the partition function and will make its way into the discussion of the other bulk quantities. The partition function is given by

$$Z = \sum_{i=1}^{N} e^{-\beta E_{i}} = \sum_{E_{i}} (2S_{tot} + 1) e^{-\beta E_{i}} , \qquad (11)$$

where  $E_i$  corresponds to the energy levels of the system.

TABLE II: Specific Heats for Small Spin $1/2$ Cluster <sup>26a</sup>		
Spin System	$C/k_B$	
Dimer	$3(\beta\mathrm{J})^2e^{\beta\mathrm{J}}/(3+e^{\beta\mathrm{J}})^2$	
Symmetric Trimer	$\frac{9}{4}(\beta \mathbf{J})^2 e^{\frac{3}{2}\beta \mathbf{J}} / \left(1 + e^{\frac{3}{2}\beta \mathbf{J}}\right)^2$	
Isosceles Trimer	$\frac{1}{2}(\beta \mathbf{J})^2 \Big( 2(1-\alpha)^2 e^{(1+2\alpha)\beta \mathbf{J}} + (2+\alpha)^2 e^{(1+\frac{1}{2}\alpha)\beta \mathbf{J}} + 9\alpha^2 e^{\frac{3}{2}\alpha\beta \mathbf{J}} \Big) / \Big( 2 + e^{\frac{3}{2}\alpha\beta \mathbf{J}} + e^{(1+\frac{1}{2}\alpha)\beta \mathbf{J}} \Big)^2$	
General Trimer	$\frac{1}{16}(\beta \mathbf{J})^2 e^{\frac{1}{2}(1+\alpha_s)\beta \mathbf{J}} \left( f_0^2 e^{\frac{1}{2}(1+\alpha_s)\beta \mathbf{J}} + \left(4(1+\alpha_s)^2 + f_0^2\right) \cosh(f_0\beta \mathbf{J}/4) + 4f_0(1+\alpha_s)\sinh(f_0\beta \mathbf{J}/4) \right) / \left(1 + e^{\frac{1}{2}(1+\alpha_s)\beta \mathbf{J}}\cosh(f_0\beta \mathbf{J}/4)\right)^2$	
Tetrahedron	$\frac{18(\beta J)^2 \left(10e^{2\beta J} + 5e^{3\beta J} + e^{5\beta J}\right) / \left(5 + 9e^{2\beta J} + 2e^{3\beta J}\right)^2}{18(\beta J)^2 \left(10e^{2\beta J} + 5e^{3\beta J} + e^{5\beta J}\right) / \left(5 + 9e^{2\beta J} + 2e^{3\beta J}\right)^2}$	
	<sup>a</sup> This table uses the abbreviation $f_0 = \sqrt{(2-\alpha_s)^2 + 3\alpha_d^2}$ .	

# 2. Specific Heat Capacity

Heat capacity is the quantity of a material to store heat as temperature is changed. In figure 4, the magnetic contribution to the specific heat of a general spin



1/2 dimer is shown. Here, it is clear that the specific heat has a transition peak. This peak corresponds to either a cooperative phase transition in the material or non-cooperative anomaly depending on the magnetic interaction acting on the spins. The heat capacity is given by

$$C = k_B \beta^2 \, \frac{\partial^2 \ln(Z)}{\partial \beta^2} \, . \tag{12}$$

where the units are typically given in K/(erg mol).<sup>8,26</sup> Table II shows the analytical results for small spin 1/2 clusters. As the size of the cluster increases, it is clear to see that the calculations become more complex.

## 3. Magnetic Susceptibility

Magnetic susceptibility is defined as the change in magnetization over the change in magnetic field. If a weak field is applied, then the magnetic susceptibility is in-

FIG. 4: The magnetic contribution to the specific heat of a spin dimer (dimensionless units).  $^{26}$ 

Spin System	$\chi/(g\mu_B)^2$
Dimer	$2eta/(3+e^{eta { m J}})$
Symmetric Trimer	$\frac{1}{4}\beta\left(5+e^{\frac{3}{2}\beta\mathbf{J}}\right)/\left(1+e^{\frac{3}{2}\beta\mathbf{J}}\right)$
Isosceles Trimer	$\frac{1}{4}\beta \left(10 + e^{\frac{3}{2}\alpha\beta\mathbf{J}} + e^{(1+\frac{1}{2}\alpha)\beta\mathbf{J}}\right) / \left(2 + e^{\frac{3}{2}\alpha\beta\mathbf{J}} + e^{(1+\frac{1}{2}\alpha)\beta\mathbf{J}}\right)$
General Trimer	$\frac{1}{4}\beta \left(5 + e^{\frac{1}{2}(1+\alpha_s)\beta \mathbf{J}}\cosh(f_0\beta \mathbf{J}/4)\right) / \left(1 + e^{\frac{1}{2}(1+\alpha_s)\beta \mathbf{J}}\cosh(f_0\beta \mathbf{J}/4)\right)$
Tetrahedron	$2\beta \Big(5+3e^{2\beta \mathbf{J}}\Big)/\Big(5+9e^{2\beta \mathbf{J}}+2e^{3\beta \mathbf{J}}\Big)$
Rectangular Tetramer	$2\beta \Big(5 + e^{\beta \mathbf{J}} + e^{\alpha\beta \mathbf{J}} + e^{(1+\alpha)\beta \mathbf{J}}\Big) / \Big(5 + 3e^{\beta \mathbf{J}} + 3e^{\alpha\beta \mathbf{J}} + 3e^{(1+\alpha)\beta \mathbf{J}} + 2e^{(1+\alpha)\beta \mathbf{J}} \cosh(f_1\beta \mathbf{J}/2)\Big)$
Linear Tetramer	$\frac{2\beta \left(5+e^{\beta \mathbf{J}}+2e^{\frac{1}{2}(1+\alpha)\beta \mathbf{J}}\cosh(f_{3}\beta \mathbf{J}/2)\right)}{\left(5+3e^{\beta \mathbf{J}}+2e^{(1+\frac{1}{2}\alpha)\beta \mathbf{J}}\cosh(f_{2}\beta \mathbf{J})+6e^{\frac{1}{2}(1+\alpha)\beta \mathbf{J}}\cosh(f_{3}\beta \mathbf{J}/2)\right)}$

<sup>a</sup> This table uses the abbreviations 
$$f_0 = \sqrt{(2-\alpha_s)^2 + 3\alpha_d^2}$$
,  $f_1 = \sqrt{1-\alpha+\alpha^2}$ ,  $f_2 = \sqrt{1-\alpha/2+\alpha^2/4}$ ,  $f_3 = \sqrt{1+\alpha^2}$ .

dependent of field. Therefore, it is possible to examine magnetic susceptibility as a function of temperature which can be determined by

$$\chi = \frac{\beta}{Z} \sum_{i=1}^{N} (M_z^2)_i e^{-\beta \mathbf{E}_i}$$

$$= \frac{1}{3} (g\mu_B)^2 \frac{\beta}{Z} \sum_{\mathbf{E}_i} (2\mathbf{S}_{tot} + 1) (\mathbf{S}_{tot} + 1) \mathbf{S}_{tot} e^{-\beta \mathbf{E}_i} , \quad (13)$$

where the sum i = 1...N is over all N independent energy eigenstates (including magnetic substates), the sum  $\sum_{E_i}$  is over energy levels only,  $M_z = mg\mu_B$  where  $m = S_{tot}^z/\hbar$  is the integral or half-integral magnetic quantum number, and g is the electron  $g\mbox{-}factor.^8$  This is typically referred to as the Van Vleck equation.^8

Figure 5 shows the magnetic susceptibility of a general spin-1/2 dimer. Through a fit of the magnetic susceptibility, it is possible to extract the magnetic interactions for a particular models. In figure 5, the magnetic susceptibility is shown in dimensionless units, where as susceptibility is usually found in cm<sup>3</sup> per mole. The units of susceptibility have been a point of confusion in the literature. However, since the units are erg/G<sup>2</sup> and  $E = \int (B \cdot H \, dV)$ , the units can be converted to cm<sup>3</sup>. Some people have used the unit of emu, but this unit is for magnetic moment. Table III shows the analytical results for small 1/2 clusters.<sup>26</sup> Similiar to the heat capacity, the table of susceptibilities demonstrates how the complexity of the calculations become as the cluster size grows.

## B. Microscopic Techniques

Microscopic techniques are quantities that can measure spin transitions and interactions directly. These techniques are able to distingush between different interactions and can distinctly show the difference between long range magnetic order and local excitations.

# 1. Inelastic Neutron Scattering

Inelastic neutron scattering is a very useful tool for examining magnetic interactions. Since the neutron has spin with no charge (unlike an electron), the neutron is able to penetrate the electron cloud and scatter directly off magnetic interactions. Inelastic neutron scattering is slightly more complex than the bulk quantities.<sup>28</sup>

In "spin-only" magnetic neutron scattering at zero temperature, the differential cross section for the inelastic scattering of an incident neutron from a magnetic system in an initial state  $|\Psi_i\rangle$ , with momentum transfer  $\hbar \vec{q}$  and energy transfer  $\hbar \omega$ , is proportional to the neutron scat-



FIG. 5: The magnetic susceptibility of a spin dimer (dimensionless units).  $^{26}$ 



FIG. 6: Experimental data and theoretical predictions for  $Na_3RuO_4$ .<sup>27</sup>

tering structure factor tensor

$$S_{ba}(\vec{q},\omega) =$$

$$\int_{-\infty}^{\infty} \frac{dt}{2\pi} \sum_{\vec{x}_i, \vec{x}_j} e^{i\vec{q} \cdot (\vec{x}_i - \vec{x}_j) + i\omega t} \langle \Psi_i | \mathbf{S}_{\mathbf{b}}^{\dagger}(\tilde{\mathbf{x}}_j, \mathbf{t}) \mathbf{S}_{\mathbf{a}}(\tilde{\mathbf{x}}_i, 0) | \Psi_i \rangle .$$
(14)

The site sums in Eq.(14) run over all magnetic ions in one unit cell, and a, b are the spatial indices of the spin operators.

For transitions between discrete energy levels, the time integral gives a trivial delta function  $\delta(\mathbf{E}_{\rm f} - \mathbf{E}_{\rm i} - \hbar\omega)$  in the energy transfer, so it is useful to specialize to an "exclusive structure factor" for the excitation of states within a specific magnetic multiplet (generically  $|\Psi_f(\lambda_f)\rangle$ ) from the given initial state  $|\Psi_i\rangle$ ,

$$S_{ba}^{(fi)}(\vec{q}) = \sum_{\lambda_f} \langle \Psi_i | V_b^{\dagger} | \Psi_f(\lambda_f) \rangle \langle \Psi_f(\lambda_f) | V_a | \Psi_i \rangle , \quad (15)$$

where the vector  $V_a(\vec{q})$  is a sum of spin operators over all magnetic ions in a unit cell,

$$V_a = \sum_{\vec{x}_i} \mathcal{S}_a(\vec{x}_i) \ e^{i\vec{q}\cdot\vec{x}_i} \ . \tag{16}$$

For a rotationally invariant magnetic interaction and an  $S_{tot} = 0$  initial state (as is often encountered in T=0 inelastic scattering from an antiferromagnet), only  $S_{tot} = 1$  final states are excited, and  $S_{ba}^{(fi)}(\vec{q}) \propto \delta_{ab}$ . In this case we may define a scalar neutron scattering structure factor  $S(\vec{q})$  by

$$S_{ba}^{(fi)}(\vec{q}) = \delta_{ab} S(\vec{q}) .$$
 (17)

The results given above apply to neutron scattering from single crystals. To interpret neutron experiments on powder samples, we require an orientation average of the unpolarized single-crystal neutron scattering structure factor. We define this powder average by

$$\bar{S}(q) = \int \frac{d\Omega_{\hat{q}}}{4\pi} S(\vec{q}) \ . \tag{18}$$

A good example of how inelastic neutron scattering helps distingush between local and long range order is the material of Na<sub>3</sub>RuO<sub>4</sub>.<sup>27</sup> In Na<sub>3</sub>RuO<sub>4</sub>, there is a dominant finite cluster of four spin-3/2 ions with moderate long range order. Since there is moderate long range order, bulk measurements show all interactions. However, using inelastic neutron scattering, it is possible to examine the discrete energy levels. Figure 6 shows the prediction of magnetic excitations of a spin-3/2 tetramer compared to the experimental data. It is clear that the discrete levels of the finite clusters are present.<sup>27</sup> However, the data also shows how the finite clusters have long range order associated with them. This system is currently under investigation, but the data is quite clear.

## 2. Infrared and Raman Spectroscopy

Infrared and Raman spectroscopy are not usual techniques when discussing magnetic excitations and interactions. However, through the presents of anisotropic interactions in a system, magnetic excitations can be visible. This is possible through a coupling of lattice



FIG. 7: Magnetic field dependence of the single to triple excitation in  $\alpha$ -NaVO using infrared spectroscopy.<sup>32</sup>

symmetry to the typical selection rules. The typical selection rules for Raman and Infrared spectroscopies are usually changes in polarizability and dipole moment, respectively.<sup>32</sup> Through a breaking a certain crystal symmetries with vibrations and phonons, magnetic excitations can couple to the vibrational excitations making them visible in light scattering.

Figure 7 shows the magnetic excitations of  $\alpha$ -NaVO visible in infrared spectroscopy. Through the use of applied field, these magnetic excitations are clearly split with field.<sup>32</sup>

## IV. CONCLUSION

Molecular magnets are an interesting and complex area of condensed matter physics. Whether the systems being examined are small or large, there are areas to be investigated that can contribute to the overall realm of

- magnetism. Through the use of multiple experimental techniques and analytical and numerical model, a picture of the magnetic structure of molecular magnets can be determined clearly.
- <sup>1</sup> D. Gatteschi, R. Sessoli, J. Villain (Eds.), *Molecular Nano*magnets (Oxford, 2006).
- <sup>2</sup> M.A.Nielsen and I.L.Chuang, Quantum Computation and Quantum Information (Cambridge, 2000).
- <sup>3</sup> M.M. Turnbull, T. Sugimoto, and L.K. Thompson, Molecule-Based Magnetic Materials: Theory, Techniques, and Applications (American Chemical Society, 1996).
- $^4\,$  E.Dagotto and T.M.Rice, Science 271, 618 (1996).
- <sup>5</sup> J. Schnack, M. Bruger, M. Luban, P. Kogerler, E. Morosan, R. Fuchs, R. Modler, H. Nojiri, R.C. Rai, J. Cao, J.L. Musfeldt, and X. Wei, Phys. Rev. B 73, 094401 (2006)
- <sup>6</sup> T. Lis, Acta Crystallogr. Sect. B:Struct. Crystallogr. Cryst. Chem. 36, 2042 (1980)
- <sup>7</sup> T. Baruah, J. Kortus, M.R. Pederson, R. Wesolowski, J.T. Haraldsen, J.L. Musfeldt, M. North, D. Zipse, and N.S. Dalal, Phys. Rev. B 70, 214410 (2004)
- <sup>8</sup> O. Kahn, *Molecular Magnetism* (VCH Publishers, 1993).
- <sup>9</sup> J.W.Johnson, D.C.Johnston, A.J.Jacobson and J.F.Brody, J. Am. Chem. Soc. 106, 8123 (1984).
- <sup>10</sup> D.A.Tennant, S.E.Nagler, A.W.Garrett, T.Barnes and C.C.Torardi, Phys. Rev. Lett. 78, 4998 (1997).
- <sup>11</sup> H.-J.Koo, M.-H.Whangbo, P.D.verNooy, C.C.Torardi and W.J.Marshall, Inorg. Chem. 41, 4664 (2002).
- <sup>12</sup> B.Cage, F.A.Cotton, N.S.Dalal, E.A.Hillard, B.Ravkin and C.M.Ramsey, J. Am. Chem. Soc. 125, 5270 (2003).
- <sup>13</sup> B.Cage, F.A.Cotton, N.S.Dalal, E.A.Hillard, B.Ravkin and C.M.Ramsey, C. R. Chemie 6, 39 (2003).
- <sup>14</sup> U.Kortz, S.Nellutla, A.C.Stowe, N.S.Dalal, J.van Tol and B.S.Bassil, Inorg. Chem. 43, 144 (2004).
- <sup>15</sup> H.López-Sandoval, R.Contreras, A.Escuer, R.Vicente, S.Bernès, H.Nöth, G.J.Leigh and N.Barba-Behrens, J. Chem. Soc., Dalton Trans. 2648 (2002).
- <sup>16</sup> M.Luban, F.Borsa, S.Bud'ko, P.Canfield, S.Jun, J.K.Jung, P.Kögerler, D.Mentrup, A.Müller, R.Modler, D.Procissi,

B.J.Suh and M.Torikachvili, Phys. Rev. B66, 054407 (2002).

- <sup>17</sup> A.Müller and J.Döring, J. Angew. Chem., Int. Ed. Engl. 27, 1721 (1988).
- <sup>18</sup> A.L.Barra, D.Gatteschi, L.Pardi, A.Müller and J.Döring, J. Am. Chem. Soc. 114, 8509 (1992).
- <sup>19</sup> D.Gatteschi, L.Pardi, A.L.Barra, A.Müller and J.Döring, Nature, 354, 463 (1991).
- <sup>20</sup> G.Chaboussant, R.Basler, A.Sieber, S.T.Ochsenbein, A.Desmedt, R.E.Lechner, M.T.F.Telling, P.Kögerler, A.Müller and H.-U.Güdel, Europhys. Lett. 59, 291 (2002).
- <sup>21</sup> G.Chaboussant, S.T.Ochsenbein, A.Sieber, H.-U.Güdel, H.Mutka, A.Müller and B.Barbara, arXiv:condmat/0401614.
- <sup>22</sup> R.Basler, G.Chaboussant, A.Sieber, H.Andres, M.Murrie, P.Kögerler, H.Bögge, D.C.Crans, E.Krickemeyer, S.Janssen, H.Mutka, A.Müller and H.-U.Güdel, Inorg. Chem. 41, 5675 (2002).
- <sup>23</sup> M. Ulutagay-Kartin, S.-J Hwu and J.A.Clayhold, Inorgan. Chem. 42, 2405 (2003).
- <sup>24</sup> S.E.Nagler, G.E.Granroth, J.A.Clayhold, S.-J.Hwu, M.Ulutagay-Kartin, D.A.Tennant and D.T.Adroja (unpublished).
- <sup>25</sup> G.L.Squires, Introduction to the Theory of Thermal Neutron Scattering (Dover, 1996).
- <sup>26</sup> J.T. Haraldsen, T. Barnes, and J.L. Musfeldt Phys. Rev. B 71, 064403 (2005)
- <sup>27</sup> M. B. Stone, M. D. Lumsden, S. Nagler, J.T. Haraldsen, and T. Barnes, Unpublished Data.
- <sup>28</sup> T. Chatterji, Neutron Scattering from Magnetic Materials (World Scientific, 2005).
- <sup>29</sup> J.S. Miller and M. Drillon (Eds.), *Magnetism: Molecules to Materials* (VCH Publishers, 2001).
- <sup>30</sup> J.S. Miller and M. Drillon (Eds.), *Magnetism: Molecules*

to Materials II (VCH Publishers, 2001).

- <sup>31</sup> U. Schollwock, J. Richter, D.J.J. Farnell, and R.F. Bishop (Eds.), *Quantum Magnetism* (Springer, 2004).
- <sup>32</sup> T. Room, D. Huvonen, R, Nagel, Y.-J. Wang, and R.K. Kremer, Phys. Rev. B 69, 144410 (2004)