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High-Nuclearity Magnetic Clusters: Generalized Spin Hamiltonian and Its Use for the Calculation of the Energy Levels, Bulk Magnetic Properties, and Inelastic Neutron Scattering Spectra

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A general solution of the exchange problem in the high-nuclearity spin clusters (HNSC) containing arbitrary number of exchange-coupled centers and topology is developed. All constituent magnetic centers are supposed to possess well-isolated orbitally non-degenerate ground states so that the isotropic Heisenberg−Dirac−Van Vleck (HDVV) term is the leading part of the exchange spin Hamiltonian. Along with the HDVV term, we consider higher-order isotropic exchange terms (biquadratic exchange), as well as the anisotropic terms (anisotropic and antisymmetric exchange interactions and local single-ion anisotropies). All these terms are expressed as irreducible tensor operators (ITO). This allows us to take full advantage of the spin symmetry of the system. At the same time, we have also benefitted by taking into account the point group symmetry of the cluster, which allows us to work with symmetrized spin functions. This results in an additional reduction of the matrices to diagonalize. The approach developed here is accompanied by an efficient computational procedure that allows us to calculate the bulk magnetic properties (magnetic susceptibility, magnetization, and magnetic specific heat) as well as the spectroscopic properties of HNSC. Special attention is paid to calculate the magnetic excitations observed by inelastic neutron scattering (INS), their intensities, and their **Q** and temperature dependencies. This spectroscopic technique provides direct access to the energies and wave functions of the different spin states of the cluster; thus, it can be applied to spin clusters in order to obtain deep and detailed information on the nature of the magnetic exchange phenomenon. The general expression for the INS cross-section of spin clusters interacting by all kinds of exchange interactions, including also the single-ion zero-field splitting term, is derived for the first time. A closed-form expression is also derived for the particular case in which only the isotropic exchange interactions are involved. Finally this approach has been used to model the magnetic properties as well as the INS spectra of the polyoxometalate anion $[Ni_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$, which contains a central magnetic cluster formed by nine exchange-coupled Ni(II) ions surrounded by diamagnetic phosphotungstate ligands $(PW_9O_{34})^{9-}$.

Introduction

Magnetic molecular clusters, i.e., molecular assemblies formed by a finite number of exchange-coupled magnetic moments, are currently receiving much attention in several active areas of research as molecular chemistry, magnetism, and biochemistry. A reason for this interest lies in the possibility to use simple molecular clusters as magnets of nanometer size exhibiting unusual magnetic properties as superparamagnetic-like behavior or quantum tunneling of magnetization.[2] Organic molecules of increasing sizes and large number of unpaired electrons are also being explored as a means of obtaining building blocks for molecule-based magnets.[3] Magnetic clusters of metal ions are also relevant in biochemistry. We mention, for instance, the mixed-valence Fe_4S_4 clusters contained in ferredoxins,[4] the manganese clusters present in photosystem II,[5] and the magnetic particles of iron found in the storage protein ferritin.[6]

This area between molecule and bulk will require new theoretical concepts and techniques for investigation of their peculiar properties. Still, the theoretical treatment required to understand the electronic and magnetic structures as well as the resulting magnetic and spectroscopic properties of this wide variety of compounds is a challenging problem in molecular magnetism.[7] For a long time, this problem has been mostly

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restricted to treat comparatively simple clusters comprising a reduced number of exchange-coupled centers and special spin topologies.[8] In these a quantitative description of the properties can be usually achieved using a spin Hamiltonian approach. Thus, in contrast to extended systems, exact solutions of the effective spin Hamiltonian are obtained either analytically or numerically. In this sense, simple spin clusters have been shown to be ideal model systems to test the validity of the theoretical models. In fact, they have significantly contributed in the past in our understanding of the exchange interaction phenomenon.[9] However, on increasing the spin nuclearity of the cluster, the problem rapidly becomes unapproachable because the lack of translational symmetry in the clusters precludes an efficient reduction of the size of the matrices to be diagonalized. An additional complication is the increase in the number of exchange parameters required to analyze the experimental data as the nuclearity of the cluster increases and the cluster symmetry decreases. In such a situation the usual magnetic techniques (magnetic susceptibility, EPR) are often insufficient to provide a clear picture of the coupling situation and other complementary techniques are necessary to obtain unambiguous and accurate values of these parameters. A powerful technique that has been used in this context is inelastic neutron scattering (INS). This spectroscopic technique has proved to be extremely well suited to provide direct access to both the energies and eigenfunctions of the different spin states of a cluster and therefore to the resulting exchange parameters.[10−12]

Note that a large spin nuclearity is not the only difficulty one can encounter. Other effects as the electron delocalization within the cluster (in the mixed-valence case),[13] or the presence of exchange interactions between orbitally degenerate ions,[14] bring also serious limitations since these effects cannot be expressed in terms of a simple spin Hamiltonian. Hence, the general form of the effective Hamiltonian for these two types of systems—mixed-valence clusters and clusters of orbitally degenerate ions—is unknown and requires a particular procedure for each considered system.

In the present paper we restrict our discussion to the study of high-nuclearity clusters of exchange-coupled spins (abbreviated as HNSC), which constitute the more broad class of magnetic clusters (and also the simplest one). An efficient computing procedure has been suggested for the calculation of the energy levels and the magnetic properties of these systems in the isotropic-exchange case (Heisenberg model).[15] The approach uses the method of the irreducible tensor operators (ITO) to take full advantage of the spin symmetry of the system, reducing the time required to calculate the energy matrices. Furthermore, it can use point group symmetry to reduce the dimension of the matrices.[16] Nevertheless, it considers neither the non-Heisenberg exchange contributions[17] to the spin Hamiltonian that are high-order perturbation terms (as the biquadratic, antisymmetric, and anisotropic exchange interactions) nor the single-ion anisotropy. Being usually relatively small compared to the isotropic exchange, these terms play a prominent role in many physical manifestations of the exchange interactions. For example, the magnetic anisotropy of the clusters has been shown to be a key factor for observing superparamagnetic-like behavior and quantum-tunneling of the magnetization.[2] The antisymmetric exchange has shown to produce nonlinear spin structures in trimeric clusters formed by half-integer spins,[17] an effect that is closely related to the spin-frustration concept.[18,19] On the other hand, in small magnetic clusters these terms have shown to produce important effects in the observed INS spectra. In fact, the position of the magnetic excitations, as well as their intensities and their dependencies with the scattering vector **Q**, depend on both the energy pattern and the wave functions of the different spin states of the cluster. In dimers the INS cross-section (proportional to the intensity) has been derived for the Heisenberg and the Ising Hamiltonians and used to analyze the **Q**-dependence in $Yb^{3+}-Yb^{3+}$ and $Yb^{3+}-Cr^{3+}$ pairs.[10i] The cross-section has also been calculated in isotropic systems with special symmetries like trimers and tetramers ($Fe^{3+}{}_2M^{2+}$, M = Mn(III) or Ni(II) and $Cr^{3+}{}_4$)[11] and for radial clusters like Ti^{2+}-$(Mn^{2+})_6$.[12] In clusters with higher spin multiplicities and nuclearities, or lower exchange network symmetries and/or exchange anisotropies, the evaluation of the cross-section is a very difficult task since the formulae become quite complicated and intractable using the existing conventional approaches.

Here we develop a quite general approach for the calculation of the energy levels as well as the spin eigenfunctions and the INS cross-section of HNSC. The approach is based on the successive use of the ITO techniques, which allow us to take fully into account all kinds of magnetic exchange interactions between the metal ions comprised in clusters of arbitrary nuclearity and spin values. This includes the isotropic exchange terms (bilinear and biquadratic) as well as the anisotropic ones. The approach is accompanied by an efficient computing program that allows us to calculate the bulk thermodynamical properties (magnetic susceptibility, magnetization, magnetic specific heat),

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as well as spectroscopic properties (intensities of the INS magnetic excitations and their **Q** and temperature dependencies) in clusters for a given network of the exchange parameters implied by the symmetry conditions. The first part of this paper is devoted to present this theoretical approach. In the second part the potentialities of this approach are illustrated from an example comprising nine exchange-coupled Ni(II) ions encapsulated in a polyoxowolframate framework.

Theoretical Approach

Generalized Spin Hamiltonian. Let us consider a spin cluster formed by an arbitrary number of magnetic sites, N, with local spins S_1, S_2, ..., S_N which can have different values. A successive spin coupling scheme is adopted $S_1 + S_2 = \tilde{S}_2$, $\tilde{S}_2 + S_3 = \tilde{S}_3$, ..., $\tilde{S}_{N-1} + S_N = S$, where $\tilde{S}_2 = S_{12}$, $\tilde{S}_3 = S_{123}$, etc. are the intermediate spin values, and S is the full spin. The spin states can be labeled as

$$|S_1S_2(\tilde{S}_2)S_3(\tilde{S}_3)...S_{N-1}(\tilde{S}_{N-1})S_NM\rangle \equiv |(\tilde{S})SM\rangle \tag{1}$$

where $(\tilde{S})$ stands for the full set of $\tilde{S}_k$ ($N - 1$ intermediate spin states). In the general case of considering both isotropic and anisotropic exchange interactions, the spin state ν is the superposition of all $(\tilde{S})SM$ states:

$$|\nu\rangle = \sum_{(\tilde{S})SM} \langle(\tilde{S})SM|\nu\rangle|(\tilde{S})SM\rangle \tag{2}$$

where the summation is carried out over all sets $(\tilde{S})$. The coefficients $\langle(\tilde{S})SM|\nu\rangle$ are found by solving the eigenvector problem with the given spin-Hamiltonian of the system. The generalized spin-Hamiltonian operating in the spin space of the whole system is as follows:

$$\hat{H}_S = \sum_{k_1k_2...k_N} \sum_{\tilde{k}_1\tilde{k}_2...\tilde{k}_{N-1}} \sum_{kq} C_q^{(k)}(k_1k_2(\tilde{k}_2)...k_{\mathrm{N}-1}(\tilde{k}_{N-1})k_N) \times \hat{T}_q^{(k)}(k_1k_2(\tilde{k}_2)...k_{N-1}(\tilde{k}_{N-1})k_N) \tag{3}$$

where $\hat{T}_q^{(k)}(k_1k_2(\tilde{k}_2)...k_{N-1}(\tilde{k}_{N-1})k_N)$ is the qth component of the complex ITO of rank k composed from the ITO's $\hat{S}_{q_i}^{(k_i)}(i) \equiv S_{q_i}^{(k_i)}$ acting in the spin space of the individual spins ($k_i = 0$, 1, ..., $2S_i$):

$$T_q^{(k_i)}(...) = \{...\{S^{(k_1)} \otimes S^{(k_2)}\}^{(\tilde{k}_2)} \otimes S^{(k_3)}\}^{(\tilde{k}_3)}...\}^{(\tilde{k}_{N-1})} \otimes S^{(k_N)}\}_q^{(k)} \tag{4}$$

where $\otimes$ is the symbol of the tensor product, $\tilde{k}_2 = k_{12}$, $\tilde{k}_3 = k_{123}$, etc. and $\tilde{k}_2 = k_1 + k_2, k_1 + k_2 - 1, ..., |k_1 - k_2|$, etc.

This Hamiltonian involves all intercenters interactions. It can be applied to obtain the energy levels and the intensities of the INS magnetic excitations of the exchange system (see below). In both problems we must evaluate the matrix elements of $\hat{T}_q^{(k)}$ operators in the basis set of coupled spin states (eq 1). Using the Wigner–Eckart theorem we obtain

$$\langle(\tilde{S}')S'M'|\hat{T}_q^{(k)}(k_1k_2(\tilde{k}_2)...k_{N-1}(\tilde{k}_{N-1})k_N)|(\tilde{S})SM\rangle = \frac{(-1)^{2k}}{[S']^{1/2}} C_{SMkq}^{S'M'} \langle(\tilde{S}')S'||\hat{\boldsymbol{T}}^{(k)}(k_1k_2(\tilde{k}_2)...k_{N-1}(\tilde{k}_{N-1})k_N)||(\tilde{S})S\rangle \tag{5}$$

where $\langle(\tilde{S}')S'||\hat{\boldsymbol{T}}^{(k)}(k_1k_2(\tilde{k}_2)...k_{N-1}(\tilde{k}_{N-1})k_N)||(\tilde{S})S\rangle$ is the reduced matrix element of the ITO $\hat{\boldsymbol{T}}^{(k)}$ for the coupled spin state, $[S] = 2S + 1$, and $C_{SMkq}^{S'M'}$ is a Clebsch–Gordan coefficient.[20] Finally, using the successive decoupling procedure, these reduced matrix elements can be expressed in terms of single-spin reduced matrix elements and 9j-symbols:[17]

$$\langle(\tilde{S}')S'||\hat{T}_q^{(k)}(k_1k_2(\tilde{k}_2)...k_{N-1}(\tilde{k}_{N-1})k_N)||(\tilde{S})S\rangle = \langle S_N||\hat{S}^{(k_N)}||S_N\rangle \prod_{i=1}^{N-1} \{[\tilde{k}_{i+1}][\tilde{S}_{i+1}][\tilde{S}'_{i+1}]\}^{1/2} \times \langle S_i||\hat{\boldsymbol{S}}^{(k_i)}||S_i\rangle \begin{Bmatrix} \tilde{k}_i & k_{i+1} & \tilde{k}_{i+1} \\ \tilde{S}'_i & S_{i+1} & \tilde{S}'_{i+1} \\ S_i & S_{i+1} & \tilde{S}_{i+1} \end{Bmatrix} \tag{6}$$

where $\{\vdots\vdots\vdots\}$ are the 9j-symbols. For $k = 0$, 1, and 2, the single-spin reduced matrix elements $\langle S'_i||\hat{\boldsymbol{S}}^{(k_i)}||S_i\rangle$ are as follows:

$$\langle S'||\hat{\boldsymbol{S}}^{(0)}||S\rangle = [S]\delta_{S'S}$$

$$\langle S'||\hat{\boldsymbol{S}}^{(1)}||S\rangle = \sqrt{S(S+1)(2S+1)}\,\delta_{S'S} \tag{7}$$

$$\langle S'||\hat{\boldsymbol{S}}^{(2)}||S\rangle = \frac{1}{\sqrt{6}}\sqrt{(2S+3)(2S+1)(S+1)S(2S-1)}\,\delta_{S'S}$$

Exchange Hamiltonian. We present the exchange Hamiltonian in the following form:

$$\hat{H} = \hat{H}_{\mathrm{O}} + \hat{H}_{\mathrm{BQ}} + \hat{H}_{\mathrm{AS}} + \hat{H}_{\mathrm{AN}} \tag{8}$$

where H_{O} is the Heisenberg–Dirac–van Vleck (HDVV) Hamiltonian, H_{BQ} is the biquadratic exchange Hamiltonian, H_{AS} is the antisymmetric exchange, and H_{AN} is the anisotropic exchange Hamiltonian. In the conventional form these terms are expressed as

$$\hat{H}_{\mathrm{O}} = -2\sum_{i,f} J_{if}\hat{\mathbf{S}}_i\hat{\mathbf{S}}_f \tag{9}$$

$$\hat{H}_{\mathrm{BQ}} = -\sum_{i,f} j_{if}(\hat{\mathbf{S}}_i\hat{\mathbf{S}}_f)^2 \tag{10}$$

$$\hat{H}_{\mathrm{AS}} = \sum_{i,f} \mathbf{G}_{ij}[\hat{\mathbf{S}}_i \times \hat{\mathbf{S}}_f] \tag{11}$$

$$\hat{H}_{\mathrm{AN}} = -2\sum_{i,f}\sum_{\alpha} J_{if}^{\alpha}\,\hat{S}_i^{\alpha}\,\hat{S}_f^{\alpha}, \text{ with } \alpha = x, y, z \tag{12}$$

We do not consider here more complicated terms of biquadratic exchange, like $(S_iS_j)(S_kS_l)$ that are responsible for multicenter interactions in polynuclear compounds. For the sake of simplicity we consider highly symmetric systems omitting thus the low-symmetry contributions (like $S_i^{\alpha}\,S_i^{\beta}$) in H_{AN}. In eqs 9–12, J_{if} are the isotropic exchange parameters, j_{if} are the biquadratic exchange interactions, J_{if}^{α} are the parameters associated to the components of the anisotropic exchange interactions, and $\mathbf{G}_{if}$ ($= -\mathbf{G}_{if}$) are the antisymmetric exchange parameters, i.e., antisymmetric vectors, $[\hat{\mathbf{S}}_i \times \hat{\mathbf{S}}_f]$ is a vector product.

Single-Ion Anisotropy Hamiltonian. We can add to the exchange Hamiltonian the term due to the axial and rhombic single-ion anisotropy:

$$\hat{H}_{\mathrm{ZF}} = \sum_i D_i\,\hat{S}_z^2(i) + \sum_i E_i(\hat{S}_x^2(i) - \hat{S}_y^2(i)) \tag{13}$$

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Spin Hamiltonian in Terms of the ITO's. The three parts of the exchange Hamiltonian (eq 7) can be expressed in terms of the ITO's $\tilde{S}_q^{(k)}(i)$:

$$\hat{H}_{\mathrm{O}} = 2\sqrt{3}\sum_{i,j} J_{if}\hat{\boldsymbol{T}}^{(0)}(11|if) \tag{14}$$

$$\hat{H}_{\mathrm{BQ}} = \sum_{i,f} j_{if}\left[\sqrt{5}\hat{\boldsymbol{T}}^{(0)}(22|if) + \frac{\sqrt{3}}{2}\hat{\boldsymbol{T}}^{(0)}(11|if) + \frac{1}{3}S_0^2(S_0^2 + 1)^2\right] \tag{15}$$

$$\hat{H}_{\mathrm{AS}} = -\mathrm{i}\sqrt{2}\sum_{i,f}\sum_{q}(-1)^q G_{q,if}^{(1)}\, T_{-q}^{(1)}(11|if) \tag{16}$$

where

$$G_{q,ij}^{(1)} = \begin{cases} \mp(G_x \pm \mathrm{i}G_y)/\sqrt{2}, \; q = \pm 1 \\ G_z, \; q = 0 \end{cases}$$

and

$$\hat{H}_{\mathrm{AN}} = 2\sum_{i,f} J_{if}^{a}\hat{T}^{(0)}(11|if) + 2\sum_{i,f} J_{if}^{u}\frac{1}{\sqrt{2}}[\hat{T}_2^{(2)}(11|if) + \hat{T}_{-2}^{(2)}(11|if)] + 2\sum_{i,f} J_{if}^{v}\ \hat{T}_0^{(2)}(11|if) \tag{17}$$

where

$$J_{if}^{a} = \frac{1}{\sqrt{3}}(J_{if}^{x} + J_{if}^{y} + J_{if}^{z})$$

$$J_{if}^{u} = \frac{1}{\sqrt{2}}(J_{if}^{y} - J_{if}^{x})$$

$$J_{if}^{v} = \frac{1}{\sqrt{6}}(J_{if}^{x} + J_{if}^{y} - 2J_{if}^{z})$$

The operators $T_q^{(k)}(k_i k_f|if)$ so far introduced describe the pairwise interactions. They are obtained from the complex tensor $T_q^{(k)}(...)$ (eq 3) with the corresponding values of k_i and k_f and with all $k_l = 0$ if $l \neq k,f$.

From eqs 14 and 17 one can see that both biquadratic and anisotropic exchange hamiltonians contain scalar terms ($\approx \hat{T}^{(0)}(11|if)$) that can be included in the isotropic HDVV Hamiltonian. The redefined components of the exchange Hamiltonian are as follows:

$$\hat{H}_{\mathrm{O}} = 2\sqrt{3}\sum_{i,f}\tilde{J}_{if}\hat{T}^{(0)}(11|if) \tag{18}$$

where $\tilde{J}_{if}$ is the effective isotropic exchange parameter ($\tilde{J}_{if} = J_{if} + {}^1/_3(J_{if}^x + J_{if}^y + J_{if}^z) - {}^1/_4 j_{if}$).

$$\hat{H}_{\mathrm{BO}} = -\sqrt{5}\sum_{i,f} j_{if}\hat{T}^{(0)}(22|if) \tag{19}$$

$$\hat{H}_{\mathrm{AN}} = \frac{2}{\sqrt{2}}\sum_{i,f}[J_{if}^{u}(\hat{T}_2^{(2)}(11|if) + \hat{T}_{-2}^{(2)}(11|if))] + 2\sum_{i,f} J_{if}^{v}\ \hat{T}_0^{(2)}(11|if) \tag{20}$$

Using the same procedure, the local anisotropy Hamiltonian expressed in terms of ITO's becomes

$$\hat{H}_{\mathrm{ZF}} = \sum_i D_i\left[-\frac{1}{\sqrt{3}}\hat{S}_0^{(0)}(i) + \frac{\sqrt{2}}{\sqrt{3}}\hat{S}_0^{(2)}(i)\right] + \sum_i E_i[\hat{S}_2^{(2)}(i) + \hat{S}_{-2}^{(2)}(i)] \tag{21}$$

The three considered terms of the above exchange Hamiltonian can be viewed as particular contributions to the generalized Hamiltonian (eq 3). Thus, Heisenberg and biquadratic exchanges can be obtained providing $k = 0$. In fact, operator $\hat{T}^{(0)}(11|if)$ in eqs 18−20 corresponds to $\hat{T}^{(0)}(k_1k_2(\tilde{k}_2)...k_{N-1}(\tilde{k}_{N-1})k_N)$ in eq 3, providing $k_i = k_f = 1$ and all $k_l = 0$ if $l \neq i,f$. Similarly, to express the biquadratic interaction in eq 18 in terms of eq 3 we put $k_i = k_f = 2$, and $k_l = 0$ if $l \neq i,f$. Since these two exchange interactions are isotropic, the corresponding $\hat{H}_{\mathrm{O}}$ and $\hat{H}_{\mathrm{BO}}$ matrices are blocked according to the value of the total spin, S, in such a way that the nonzero matrix elements can be found only between states with the same values of S and M. On the other hand, for all terms of $\hat{H}_{\mathrm{AN}}$ $k = 2$. Operators $\hat{T}_q^{(2)}(11|if)$ in eq 20 correspond to $k_i = k_f = 1$ and all $k_l = 0$ ($l \neq i, f$). In general the matrices for $\hat{H}_{\mathrm{AN}}$ are not blocked according to the full-spin S due to the mixing of the different SM values (for the $\boldsymbol{T}^{(2)}$ tensor the selection rule is $\Delta S = 0, 1, 2$). Finally, in eq 20 one can see that the local anisotropic term implies an ITO with $k = 2$, so in general $\hat{H}_{\mathrm{ZF}}$ mixes SM states but when rhombic local anisotropy is zero the matrix is blocked according to the total spin projection, M. AS exchange ($\boldsymbol{T}^{(1)}$) mixes the spin states with $\Delta S = 0, 1$.

Symmetry Considerations. The dimension of the matrices to be diagonalized for these systems increases dramatically with the increase in the number of centers. In the case of isotropic systems the matrices are reduced by classifying the states according to the total spin values. For a cluster exhibiting high symmetry, this problem can be attacked more efficiently by taking advantage of the point group symmetry of the cluster, which results in an additional reduction of the matrices.[13,14]

For the isotropic systems, the eigenmatrix is blocked according to the value of total spin S, its projection M, and the irreducible representation Γ of the point symmetry group of the cluster. The point group operator produces interchanges of the sites (permutation of the orbitals in the Slater determinants), thus mixing the $|(\tilde{S})SM\rangle$ states with different $(\tilde{S})$ that belong however to the same SM space

$$\hat{R}|(\tilde{S})SM\rangle = \sum_{\tilde{S}'} \mathbf{G}_{\tilde{S}'\tilde{S}}(\hat{R})|(\tilde{S}')SM\rangle \tag{22}$$

where $\mathbf{G}$ is the matrix of $\hat{R}$ in the $\{(\tilde{S})SM\}$ representation

$$\mathbf{G}_{\tilde{S}'\tilde{S}}(\hat{R}) = \langle(\tilde{S}')SM|\hat{R}|(\tilde{S})SM\rangle \tag{23}$$

The wave function $|(\tilde{S})SM\rangle$ can be expressed in terms of a linear combination of Slater determinants

$$|(\tilde{S})SM\rangle = \sum_{m_1m_2\cdots m_N} C_{S_1m_1S_2m_2}^{\tilde{S}_2\tilde{m}_2}\, C_{\tilde{S}_2\tilde{m}_2S_3m_3}^{\tilde{S}_3\tilde{m}_3} \cdots C_{S_{N-1}\tilde{m}_{N-1}S_Nm_N}^{SM}|m_1m_2\cdots m_N| \tag{24}$$

Applying the symmetry operators to each determinant of these linear combinations one can calculate all the elements $\mathbf{G}_{\tilde{S}'\tilde{S}}(\hat{R})$ and then find the character of the representation $\Gamma_{\hat{R}}$. Decompos-

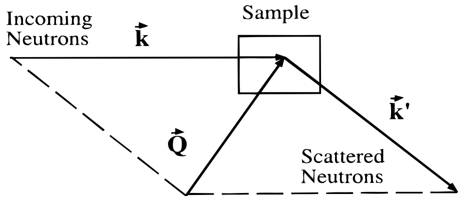

Figure 1. INS spectroscopy: schematic representation of the neutron scattering process.

ing $\Gamma_{\hat{R}}$ into irreducible parts one can find all $S\Gamma$ terms. The group-theoretical procedure of classification of spin multiplets is developed in ref 17.

To obtain the $|S\Gamma M\gamma\rangle$ basis belonging to the total spin S and irreducible representation Γ, the point group projection operator is applied:

$$\hat{P}^{(\Gamma)}{}_{\gamma\gamma'} = \frac{f_\Gamma}{g}\sum_R G^{(\Gamma)}_{\gamma\gamma'}(\hat{R})^*\hat{R} \tag{25}$$

where f_Γ is the dimension of the irreducible representation Γ. $G^{(\Gamma)}_{\gamma\gamma'}(\hat{R})$ is the matrix element of the matrix of the irreducible representation Γ corresponding to the operator $\hat{R}$.

The symmetry-adapted wave functions built in this way are linear combinations of the wave functions $|(\tilde{S})SM\rangle$ of the initial set:

$$|(\tilde{S})SM\rangle = \frac{f_\Gamma}{g}\sum_R G^{(\Gamma)}_{\gamma\gamma'}(\hat{R})\sum_{\tilde{S}'}\mathbf{G}_{\tilde{S}'\tilde{S}}(\hat{R})\left|(\tilde{S}')SM\right\rangle \tag{26}$$

It should be noted, however, that the advantage of significantly reducing the size of the matrices, due to the use of a symmetry-adapted basis, increases drastically the time consumption (for high symmetries, sometimes this factor increases by 1 or 2 orders of magnitude). In these cases a compromise between the size of the matrices (degree of symmetry) and time consumption is necessary. When the size of the problem is close to the computing possibilities, the consideration of a single symmetry element (an inversion center or a plane, for example) may be enough to make possible the evaluation of the problem with a reasonable time consumption.

INS Cross-Section of Spin Clusters. When neutrons having an incident wave vector $\vec{\mathbf{k}}$ interact with a magnetic sample, they are scattered in such a way that their final wave vector is $\vec{\mathbf{k}}'$ (Figure 1). The difference between these two vectors defines the scattering vector $\vec{\mathbf{Q}}$. The differential cross-section is defined by the number of neutrons that are scattered per second into a solid angle dΩ in the direction θ, ϕ, having an energy comprised between E' and $E' + dE'$, divided by the number of incident neutrons. This is a useful measure of the intensity of the magnetic excitations. For a cluster of interacting spins this cross-section can be expressed as[21]

$$\frac{\partial^2\sigma}{\partial\Omega\partial\omega} = A\sum_{\nu,\nu'}\exp\left\{-\frac{E(\nu)}{kT}\right\}\sum_{\alpha,\beta}\left(\delta_{\alpha\beta} - \frac{Q_\alpha Q_\beta}{Q^2}\right)\sum_{i,f}\times$$
$$F_i^*(\vec{\mathbf{Q}})F_f(\vec{\mathbf{Q}})\exp\{\mathrm{i}\vec{\mathbf{Q}}(\vec{\mathbf{R}}_i - \vec{\mathbf{R}}_f)\}\langle\nu|\hat{S}_i^\alpha|\nu'\rangle\langle\nu'|\hat{S}_f^\beta|\nu\rangle\delta(\hbar\omega + E_\nu - E_{\nu'}) \tag{27}$$

where α, $\beta = x, y, z$; i and f number the magnetic ions; $F_i(\vec{\mathbf{Q}})$ is the magnetic form factor; $\hbar\vec{\mathbf{Q}} = \hbar(\vec{\mathbf{k}} - \vec{\mathbf{k}}')$ is the transferred momentum; $\hbar\omega = \epsilon(\nu) - \epsilon(\nu')$ is the energy gap between the two spin levels of the cluster ν and ν' that are involved in the transition. The spin functions associated with these levels are defined in eq 2. $\vec{\mathbf{R}}_i$ are the spin position vectors; and $A = (\gamma e^2/m_e c^2)(k'/k)\exp(-2W)$.

In eq 27 the spin operators can be expressed in terms of ITOs components with $k = 1$ and $q = 0, \pm1$:

$$\begin{aligned}\hat{S}^x(i) &= (\hat{\mathbf{S}}^{(1)}_{-1}(i) - \hat{\mathbf{S}}^{(1)}_{1}(i))/\sqrt{2}\\ \hat{S}^y(i) &= i(\hat{\mathbf{S}}^{(1)}_{-1}(i) - \hat{\mathbf{S}}^{(1)}_{1}(i))/\sqrt{2}\\ \hat{S}^z(i) &= \hat{S}^{(1)}_0(i)\end{aligned} \tag{28}$$

By applying the Wigner−Eckart theorem the matrix elements of these operators can be expressed as

$$\langle SM|\hat{\mathbf{S}}^{(k)}_q(i)|S'M'\rangle = \frac{(-1)^{2k}}{\sqrt{2S'+1}}C^{SM}_{S'M'kq}\langle S||\hat{\mathbf{S}}^{(k)}||S'\rangle \tag{29}$$

In order to calculate the magnetic cross-section for a powder sample, an average over all directions of $\vec{\mathbf{Q}}$ should be performed. By transforming $\vec{\mathbf{Q}}$ from the Cartesian coordinates to the spherical ones, the following expression for the magnetic cross-section is obtained:

$$\frac{\partial^2\sigma}{\partial\Omega\partial\omega} = A\exp\left\{-\frac{E(\nu)}{kT}\right\}\sum_{i\le f}F_i(\vec{\mathbf{Q}})F_j^*(\vec{\mathbf{Q}})\times$$
$$\sum_{(\tilde{S})SM}\sum_{(\tilde{S}')S'M'}\sum_{(\tilde{S}'')S''M''}\sum_{(\tilde{S}''')S'''M'''}\langle\nu|(\tilde{S})SM\rangle\langle(\tilde{S}')S'M'|\nu'\rangle\times$$
$$\langle\nu'|(\tilde{S}'')S''M''\rangle\langle(\tilde{S}''')S'''M'''|\nu\rangle\langle(\tilde{S})S||\hat{\mathbf{S}}^{(1)}(i)||(\tilde{S}')S'\rangle\times$$
$$\langle(\tilde{S}'')S''||\hat{\mathbf{S}}^{(1)}(f)||(\tilde{S}''')S'''\rangle/\sqrt{(2S'+1)(2S'''+1)}\times$$
$$\left\{\left[\frac{2}{3}\delta_{if} + 4\left(-\frac{\cos(\vec{\mathbf{Q}}\vec{\mathbf{R}}_{if})}{(\vec{\mathbf{Q}}\vec{\mathbf{R}}_{if})^2} + \frac{\sin(\vec{\mathbf{Q}}\vec{\mathbf{R}}_{if})}{(\vec{\mathbf{Q}}\vec{\mathbf{R}}_{if})^3}\right)(1-\delta_{if})\right]\times\right.$$
$$C^{SM}_{S'M'10}\,C^{S''M''}_{S'''M'''10} - \left[\frac{2}{3}\delta_{if} + 2\left(\frac{\sin(\vec{\mathbf{Q}}\vec{\mathbf{R}}_{if})}{(\vec{\mathbf{Q}}\vec{\mathbf{R}}_{if})} + \frac{\cos(\vec{\mathbf{Q}}\vec{\mathbf{R}}_{if})}{(\vec{\mathbf{Q}}\vec{\mathbf{R}}_{if})^2} - \right.\right.$$
$$\left.\left.\left.\frac{\sin(\vec{\mathbf{Q}}\vec{\mathbf{R}}_{if})}{(\vec{\mathbf{Q}}\vec{\mathbf{R}}_{if})^3}\right)(1-\delta_{if})\right](C^{SM}_{S'M'11}\,C^{S''M''}_{S'''M'''1-1} + C^{SM}_{S'M'1-1}\,C^{S''M''}_{S'''M'''11})\right\} \tag{30}$$

This formula is valid for spin systems interacting by all kinds of exchange interactions, including also the single-ion zero-field splitting term.

In the framework of the isotropic exchange model the above general expression can be significantly simplified. Using the basis (eq 2), the Wigner−Eckart theorem, and the following property of Clebsch−Gordan coefficients,

$$\sum_{\alpha,\gamma}C^{c\gamma}_{a\alpha b\beta}\,C^{c\gamma}_{a\alpha b'\beta'} = \frac{\sqrt{2c+1}}{\sqrt{2b+1}}\delta_{bb'}\delta_{\beta\beta'} \tag{31}$$

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[21] (a) Halpern, O.; Johnson, M. H. *Phys. Rev.* **1939**, *55*, 898. (b) Lovesey, S. W. *Theory of Neutron Scattering from Condensed Matter, Vol. 2, International Series of Monographs on Physics*; Oxford Science Publications: Oxford, 1987; p 1.

one can find the following expression (eq 32) for the cross-section of the INS:

$$\frac{\partial^2\sigma}{\partial\Omega\partial\omega} = A\frac{2}{3}\exp\left\{-\frac{E(\nu)}{kT}\right\}\sum_{i\leq f} F_i(\vec{\mathbf{Q}})\mathbf{F}_j^*(\vec{\mathbf{Q}})(-1)^{S-S'} \times$$
$$[\delta_{if} + 2(1-\delta_{if})\cos(\vec{\mathbf{Q}}\vec{\mathbf{R}}_{if})]\sum_{\tilde{S}\tilde{S}'\tilde{S}''\tilde{S}'''}\langle\nu S|(\tilde{S})S\rangle\langle(\tilde{S}')S'|\nu' S'\rangle \times$$
$$\langle\nu' S'|(\tilde{S}'')S'\rangle\langle(\tilde{S}''')S|\nu S\rangle\langle(\tilde{S})S\|\hat{\mathbf{S}}^{(1)}(i)\|(\tilde{S}')S'\rangle \times$$
$$\langle(\tilde{S}'')S'\|\hat{\mathbf{S}}^{(1)}(f)\|(\tilde{S}''')S\rangle\delta(\hbar\omega + E(\nu) - E(\nu')) \quad (32)$$

where $\langle(\tilde{S})S\|\hat{\mathbf{S}}^{(1)}(i)\|(\tilde{S}')S'\rangle$ is the reduced matrix element of the first-order tensor $\hat{\mathbf{S}}^{(l)}(i)$ operating in the full-spin space. As far as the isotropic model is used, it is expressed exclusively in terms of reduced matrix elements and does not involve Clebsch−Gordan coefficients. Since the basic functions belong to the coupled states, we shall employ the generalized spin Hamiltonian approach in order to evaluate these matrix elements. All matrix elements of $\hat{\mathbf{S}}^{(1)}(i)$ in eqs 30 and 32 can be obtained from the general expression of eq 6. In order to evaluate $\langle(\tilde{S}')S'\|\hat{\mathbf{S}}^{(1)}(i)\|(\tilde{S})S\rangle$ we must substitute in eq 6 $k_i = 1$, all $k_f = 0$ if $f = i$ ($\hat{\mathbf{S}}^{(0)}(f)$ are simply the identity operators), in this case all $\tilde{k}_{\mathrm{f}} = 0$ if $f < i$, all $\tilde{k}_f = 1$ if $f \geq i$, finally $k = 1$. Equation 6 proves to be considerably simplified due to the fact that 9j-symbols with one of the arguments equal to zero are proportional to 6j-symbols; thus, the probabilities of the INS do not contain 9j-symbols and can be expressed in terms of 6j-symbols only.

Application of the Approach to Magnetic Clusters. The above developed approach is accompanied by a fast and efficient computational procedure for the calculation of the spin levels and derived properties of HNSC.[22] Using this procedure we can model the magnetic properties and the inelastic neutron scattering spectra of a variety of magnetic clusters including the anisotropic ones. Thus, the tetranuclear Co(II) cluster encapsulated in between two diamagnetic ligands $(PW_9O_{34})^{9-}$ have been modeled assuming an anisotropic-exchange Hamiltonian.[23] In this case the power of the INS to provide information on the energy levels and wave functions has been combined with the power of the computational approach to quantify such information in terms of the relevant magnetic parameters. Just to illustrate the potentialities of the theoretical approach in the isotropic case we will focus in a higher nuclearity magnetic cluster formed by nine exchange-coupled Ni(II) ions recently reported by our group.[24] The compound is a giant polyoxometalate formulated as $(Ni_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3)^{16-}$. The Ni(II) cluster is formed by a triangle of triangular Ni_3O_{12} clusters surrounded by three diamagnetic ligands $(PW_9O_{34})^{9-}$ which guarantee the magnetic insulation (Figure 2a). The three Ni_3O_{12} triangles are joined together through three OH^- bridging groups and two central HPO_4^{2-} groups. The presence of two types of connections between the NiO_6 octahedra, one within the Ni_3 triangles (with Ni−O−Ni angles in the range 90−100°) and the other between the triangles (with Ni−O−Ni angles close to 120°), leads to two types of pairwise isotropic exchange interactions between the $S = 1$ Ni(II) spins (J and J' in Figure 2b).

The magnetic properties of the Ni_9 cluster have been modeled assuming a fully isotropic exchange model (Figure 3). The best fit of the magnetic susceptibility data indicates a ferromagnetic intra-triangle interaction ($J = 3.9$ cm^{-1} $\equiv 0.49$ meV) and a smaller antiferromagnetic (AF) inter-triangle interaction ($J' = -1.4$ cm^{-1} $\equiv -0.17$ meV) (Figure 3a).[22] In this treatment the spin anisotropy of nickel(II) has been neglected to take full advantage of the spin symmetry, as otherwise the problem becomes intractable using our computational capabilities. Then, using the ITOs we have exploited the symmetry associated to the total spin functions in such a way that the exchange matrix, initially of size 19683 × 19683, is formed by S-block matrices of maximum size 750 × 750. We can also exploit the point group symmetry of the cluster in order to obtain a further reduction of these S-block matrices. For example, the size of the matrices can be divided by 2 by taking into consideration the symmetry plane of the cluster. In this case each S-matrix is blocked into two submatrices associated to the symmetrical and antisymmetrical functions with respect to the plane. The results are shown in Table 1.

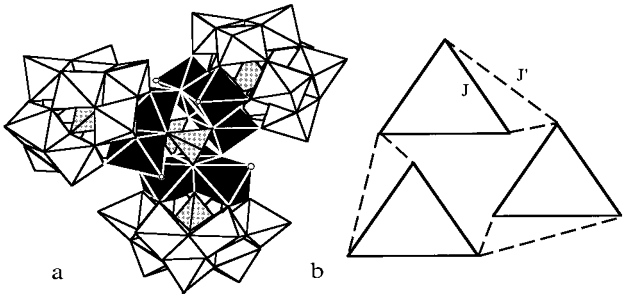

Figure 2. (a) Polyhedral representation of the $[Ni_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$ anion. (b) Exchange network of the M_9O_{33} cluster showing the two different exchange parameters J and J'.

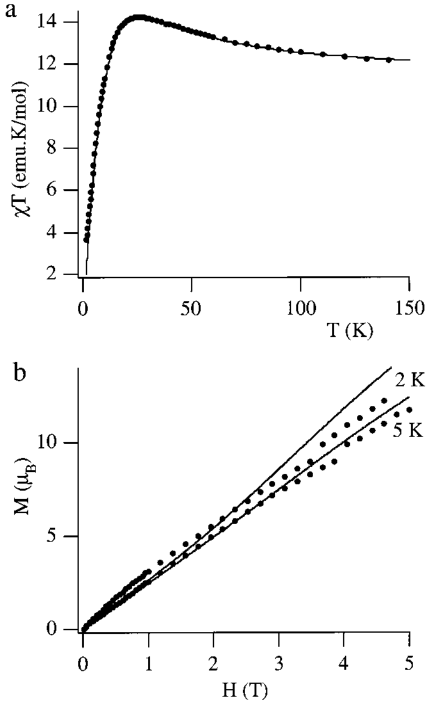

Figure 3. Magnetic properties of the $[Ni_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$ anion. (a) Thermal dependence of the product of the magnetic susceptibility times the temperature; (b) experimental and calculated magnetization curve vs H at 2 and 5 K.

The energy spectrum of Ni_9 is reported in Figure 4 and compared to that calculated for the ferromagnetic Ni_3 cluster. We observe that while the energy spectrum of Ni_3 is formed by four discrete levels at energies $E(S) = -JS(S + 1)$, the

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(22) Clemente-Juan, J. M. Ph.D. Thesis, University of Valencia, Spain, 1998.

(23) Andres, H.; Clemente-Juan, M.; Aebersold, M.; Güdel, H. U.; Coronado, E.; Büttner, H.; Kearly, G.; Melero, J.; Burriel, R. *J. Am. Chem. Soc.* **1999**, *121*, 10028.

(24) Clemente-Juan, M.; Coronado, E.; Galán-Mascarós, J. R.; Gómez-García, C. J. *Inorg. Chem.* **1999**, *38*, 55.

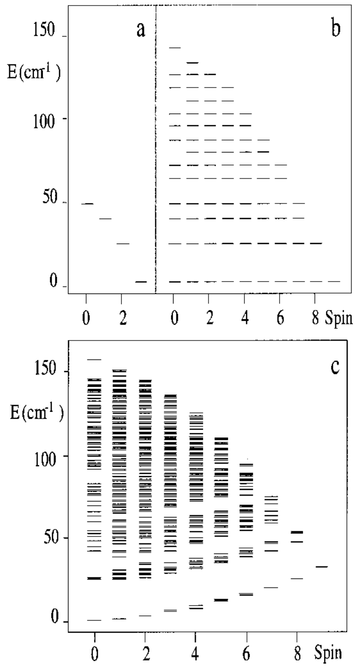

Figure 4. Energy-level diagram for Ni_9 cluster derived from the fitting of the magnetic susceptibility data (c). Comparison with the energy levels of a ferromagnetic Ni_3 trimer (a) and with three independent ferromagnetic Ni_3 trimers (b).

Table 1. Symmetry Classification of the Total Spin States of Ni_9 in the Point Group C_s

S	A'	A''	total
0	117	115	232
1	294	309	603
2	370	380	750
3	326	346	672
4	228	240	468
5	122	136	258
6	52	59	111
7	15	21	36
8	3	5	8
9	–	1	1

increase in the magnetic nuclearity leads in Ni_9 to a complex spectrum in which the energy levels tend to merge into a continuum as in an extended solid, although the lowest lying energy levels are still well separated one from the other. This structure of levels can be rationalized taking as starting point the spin structure of the ferromagnetic trimer (Figure 3a). If we consider the presence of three non-interacting ferromagnetic trimers, the resulting energy diagram of the nonanuclear cluster will be the sum of all the possible combinations of these four levels (Figure 3b). This gives rise to a diagram with many degenerate spin levels. Such a degeneracy is broken as soon as the antiferromagnetic exchange interactions between the trimers are taken into account. As a result the fully degenerate ground level is split, leading to the stabilization of the lower spin states in such a way that the $S = 0$ spin state becomes the ground state of the Ni_9 cluster.

Besides the calculation of the magnetic susceptibility, the computational approach can calculate the magnetization of the cluster as a function of the applied magnetic field and the temperature. Figure 3b compares the experimental magnetization (at 2 and 5 K) with the theoretical prediction. This last has been calculated from the parameters deduced from the fitting of the magnetic susceptibility data. As we can see, the model quantitatively reproduces the linear dependence of the magnetization with the field. This result constitutes an additional support of the validity of the proposed magnetic model and of the structure of the lowest-lying spin levels. The small discrepancies between theory and experiment observed at 2 K may be due to the fact of neglecting the spin anisotropy of the cluster coming from the zero-field splitting of the Ni(II) ion. In fact, the model reproduces better the curve at 5 K, as at this temperature the splitting of the lower spin levels caused by the anisotropy is smaller than the thermal energy and therefore, all these split levels are populated. Notice that spin anisotropy is expected to have significant effects in the magnetization curves, especially in clusters having magnetic ground spin state. In these cases the magnetization becomes anisotropic and difficult to evaluate in a simple way, due to the spin anisotropy. An averaging of the magnetization, calculated with the magnetic field applied in the different directions of the space, is then required in order to reproduce the measurements performed on powder samples. The computational approach reported here allows to perform such a calculation. However, the size of the nonanuclear cluster is too large to be treated in the anisotropic case. In smaller clusters such a possibility has been exploited. For example, in the related Ni_4 cluster encapsulated by two diamagnetic ligands $(PW_9O_{34})^{9-}$, the low-temperature experimental magnetization curves have been closely reproduced[25] by a model that considers both ferromagnetic exchange interactions and single-ion anisotropies in the range 4–6 cm^{-1}.

A powerful possibility of the developed approach is that of simulating the INS spectra of large-spin clusters, i.e., the energies and intensities of the magnetic excitations, and their **Q** and temperature dependencies. This is well-illustrated by solving the problem of the INS cross-section in the Ni_9 cluster. Until now, this problem was solved only in relatively simple and small clusters having fully isotropic (Heisenberg) or fully anisotropic (Ising) exchange interactions.[9,16] The present computing approach represents a significant advance in this area as it allows to treat the problem in a quite general and efficient way, including the non-Heisenberg terms as well as the spin anisotropy (see refs 23 and 24). In the case under consideration, the INS spectra calculated for Ni_9 can be better understood if they are compared with the predictions made for the Ni_3 cluster, as the energy level patterns of these two systems are closely related. In fact, the energy spectrum of Ni_9 can be derived from the spectrum of three independent Ni_3 clusters by considering a small perturbation due to the antiferromagnetic interaction between them (see Figure 4). From these spectra and using the formulae derived for the cross-section of the INS we can evaluate the magnetic excitations in these two clusters. In Figure 5 is reported the calculated INS spectra at two different temperatures. We observe that while the low T spectrum of Ni_3 has only an inelastic peak at energy $6J = 2.9$ eV corresponding to the excitation from the ground spin state $S = 3$ to the state $S = 2$, the presence of inter-triangle AF exchanges leads to a splitting of this single line into many excitations in the range 2.9–3.5 meV. Thus, a broad and complex band is observed in this region of the spectrum. For the same reason, intense excitations appear near to the elastic peak (in the range 0–0.2 meV) forming a second band. At higher T the complexity of the INS spectrum calculated for Ni_9 is even larger. Thus, from the simple spectrum calculated for Ni_3 consisting in three peaks (associated to the three allowed transitions of $S \rightarrow S'$: $3 \rightarrow 2$, $2 \rightarrow 1$, $1 \rightarrow 0$), we pass in Ni_9 to an INS spectrum formed by a large number of broad bands arising from the many allowed

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(25) Clemente-Juan, M.; Andres, H.; Borrás-Almenar, J. J.; Coronado, E.; Güdel, H. U.; Aebersold, M.; Kearly, G.; Büttner, H.; Zolliker, M. *J. Am. Chem. Soc.* **1999**, *121*, 10021.

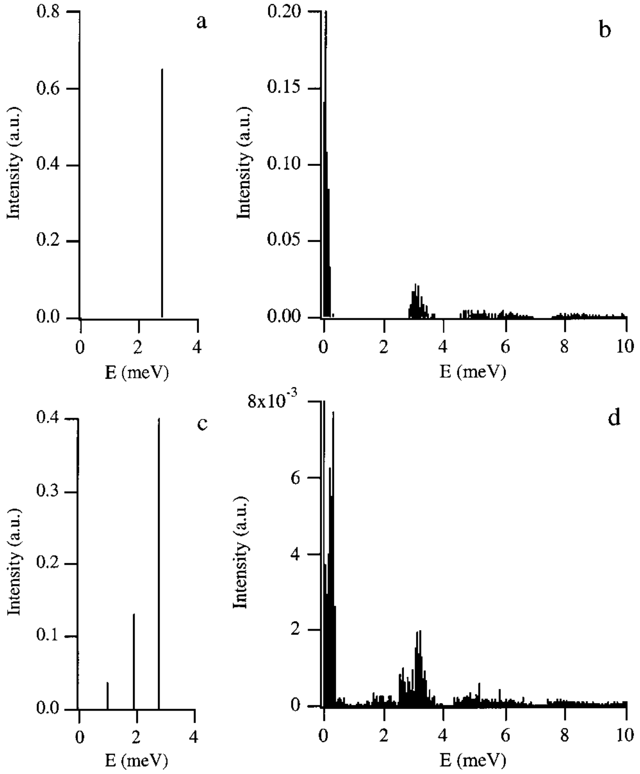

Figure 5. Calculated INS spectra (in the neutron-energy loss part) for a polycrystalline sample of $K_5Na_{11}[Ni_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]\cdot nH_2O$ with a neutron incident wavelength of 6.5 Å, at temperatures of 2 (upper panels, a and b) and 30 K (lower panels, c and d). (a, c) Comparison with the calculated INS spectra of the ferromagnetic Ni_3 trimer.

magnetic excitations between the very close energy levels of this cluster. In the near future an experimental INS study on this nonanuclear cluster will be performed in order to check these predictions.

Conclusion

Molecular chemists working in magnetism are producing more and more complex clusters from elementary building blocks. A variety of reasons, already mentioned in the introduction, justify the multidisciplinary interest for these complex systems. A common central point in this area is that of obtaining as much information as possible on the magnetic structure of the cluster (energies and wave functions of the different spin states), since it determines the peculiar properties of this class of magnetic molecular materials. However, as the complexity of the magnetic cluster increases, this information is more difficult to extract and then a combination of bulk magnetic techniques with spectroscopic techniques is needed. Such a progress must be accompanied by a development of new theoretical models adapted to quantitatively analyze these experimental data. In this paper we have developed a quite general approach from which exact solutions of an effective spin Hamiltonian that considers all kinds of exchange couplings (isotropic as well as anisotropic terms) between constituent spins, along with the single-ion anisotropy, can be obtained. This approach has allowed us to build an efficient computational procedure to evaluate the eigenvalues and eigenfunctions of high nuclearity spin clusters with the unique restriction of the computer capacity. Both spin and point group symmetries of the cluster have been considered in order to reduce the computational work. The additional advantage of this approach in comparison with other related programs is that the anisotropic terms are also taken into account. This enables us to perform a quantitative evaluation of these effects in clusters. On the other hand, the present approach is not restricted to model the bulk magnetic properties of a spin cluster (magnetic susceptibility, magnetization, and specific heat). Spectroscopic properties, as for example the inelastic neutron scattering, can also be treated. In this respect, we have derived in this work a general expression for the INS cross-section of spin clusters interacting by all kinds of exchange interactions. This allows us to simulate the INS spectra of large spin clusters, including an evaluation of the intensities of the magnetic transitions as well as their **Q** and *T* dependencies. The study of the nonanuclear nickel(II) cluster reported in this work illustrates the power of the developed approach in the isotropic case. The study of the tetranuclear nickel(II) and cobalt(II) clusters reported in refs 23 and 25 illustrates the application of the approach to treat anisotropic clusters.

To finish we would like to emphasize that the present approach is not restricted to the magnetic clusters. It can also be applied to model the properties of other complex systems of current interest in magnetism, as for example the one-dimensional magnetic materials. In these cases the behavior of the infinite chain is obtained by extrapolation of the exact results performed on clusters of increasing size.

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