Magnetic cluster excitations

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Abstract. Magnetic cluster systems can be considered as nanomagnets consisting of a small number of interacting spins that are magnetically isolated from the neighboring clusters of the compound by nonmagnetic ligands. Inelastic neutron scattering is a powerful experimental tool for the study of magnetic clusters, since it provides direct access to energy splittings. The present work presents the underlying concepts, which are illustrated for some representative examples such as single-molecule magnets, diluted magnets and magnetic polarons. It is shown that - besides the dominant Heisenberg interaction - higher-order exchange terms are often needed to rationalize the experimental data.

1. Introduction

Isolated clusters of magnetic ions may be divided into two classes, those which occur naturally in pure compounds and those which are formed artificially by forming solid solutions of magnetic and nonmagnetic compounds. Ideal examples of pure compounds are molecular transition-metal complexes in which a polynuclear metal core is embedded in a diamagnetic ligand matrix, so that exchange interactions take place among a limited number of magnetic ions. Information more directly associated with cooperative systems results from studying diluted magnetic compounds, in which the magnetic ions are randomly distributed, so that different types of magnetic clusters (n-mers, n=1,2,3,...) are simultaneously present.

In the past decade, there has been an increasing interest in single-molecule magnets, because they have a promising application potential as the smallest nanomagnetic units capable of storing information on the molecular level [1]. In particular, spin clusters with large spin ground states and negative axial anisotropy were found to exhibit some outstanding properties, namely stepped hysteresis curves and slow relaxation of the magnetization at low temperatures [2]. Another emerging field concerns transition-metal perovskites in which magnetic polarons evolve upon hole doping and behave like magnetic nanoparticles embedded in a nonmagnetic matrix [3].

In contrast to measurements of bulk properties, spectroscopic techniques probe directly the low-energy electronic states of magnetic clusters, so that the applicability of empirical spin Hamiltonians can be tested rigorously, and the origin, the nature and the size of the magnetic coupling mechanisms can be unambiguously explored. Among the spectroscopic methods, inelastic neutron scattering (INS) plays a key role, since the wave-vector dependence of the intensities yields direct information about the wavefunctions of the states and – most importantly – about the geometrical configuration of the magnetic ions in the cluster. The present work presents the underlying concepts, illustrated by representative examples out of the compound classes mentioned above.
2. Spin dimer excitations

2.1. Eigenvalues and neutron cross-section
The simplest magnetic cluster system is the dimer (two spins $s_1$ and $s_2$ coupled by an exchange parameter $J$). In the Heisenberg model, the spin Hamiltonian reads

$$H = -2J s_1 \cdot s_2$$

(1)

$H$ commutes with the total spin $S=s_1+s_2$, thus $S$ is a good quantum number to describe the spin states as $|S,M\rangle$ with $-S \leq M \leq S$. In the absence of a magnetic field, the states $|S,M\rangle$ are degenerate with respect to $M$. Assuming identical magnetic ions ($s_1=s_2$) the eigenvalues of Eq. (1) are

$$E(S) = -J[S(S+1)-2s_i(s_i+1)] , \quad 0 \leq s_i \leq S$$

(2)

and the energy splittings satisfy the Landé interval rule

$$E(S) - E(S-1) = -2JS$$

(3)

The differential neutron cross-section for dimer transitions $|S\rangle \rightarrow |S'\rangle$ is given by [4]

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{N}{Z} \gamma r_0^2 k'$$

$$\times \left\{ \begin{array}{c}
\left[ F(Q) \exp \left\{ -2W(Q) \right\} \right]
\times \exp \left\{ -\frac{E(S)}{k_B T} \right\}
\times \sum_{\alpha} \left[ 1 - \left( \frac{Q_{\alpha}}{Q} \right)^2 \right]
\times \left[ \delta\{\hbar \omega + E(S) - E(S')\} \right]
\end{array} \right\}$$

(4)

where $N$ is the total number of dimers, $Z$ the partition function, $\gamma=-1.91$, $r_0$ the classical electron radius, $k$ and $k'$ the wavenumbers of the incoming and scattered neutrons, respectively, $Q$ the scattering vector, $F(Q)$ the magnetic form factor, $\exp \left\{ -2W(Q) \right\}$ the Debye-Waller factor, $R$ the vector defining the intradimer separation, $T_1$ an irreducible tensor operator of rank 1 (related to the spin operators $s_i$), and $\hbar \omega = E(S')-E(S)$ the energy transfer. The selection rules are $\Delta S=S-S'=0, \pm 1$; $\Delta M=M-M'=0, \pm 1$. For polycrystalline material Eq. (4) has to be averaged in $Q$ space:

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{N}{Z} \gamma r_0^2 k'$$

$$\times \left\{ \begin{array}{c}
\left[ F(Q) \exp \left\{ -2W(Q) \right\} \right]
\times \exp \left\{ -\frac{E(S)}{k_B T} \right\}
\times \sum_{\alpha} \left[ 1 - \left( \frac{Q_{\alpha}}{Q} \right)^2 \right]
\times \left[ \delta\{\hbar \omega + E(S) - E(S')\} \right]
\end{array} \right\}$$

(5)

2.2. The molecular magnet copper acetate
Copper acetate, Cu$_2$(CH$_3$COO)$_4$·2H$_2$O, is one of the simplest and best known dimeric clusters of paramagnetic ions. The distance $R=2.61$ Å between the two Cu$^{2+}$ ions with $s_i=1/2$ is remarkably short, leading to a strong intramolecular antiferromagnetic interaction through four O-C-O superexchange bridges. An energy spectrum obtained by INS experiments for a fully deuterated polycrystalline sample is shown in Fig. 1a, which is characterized by a large number of peaks. A priori it is not possible to decide which of these peaks corresponds to the singlet-triplet splitting $|0\rangle \rightarrow |1\rangle$ predicted by Eq. (2). Compared with other spectroscopic techniques, the great advantage of INS lies in the possibility to unambiguously discriminate between magnetic transitions and molecular excitations (translations, external and internal vibrations of molecules). Among the peaks present in Fig. 1a, only
the line at the energy transfer $\Delta E=37$ meV is in agreement with the $Q$ dependence of the cross section (5), see Fig. 1b, whereas the most intense lines at low energy transfers can be assigned to molecular excitations. The exchange parameter can be readily determined from Eq. (2): $J=-\Delta E/2=-18.5(5)$ meV.

Figure 1: (a) Energy spectrum of neutrons scattered from a polycrystalline sample of fully deuterated copper acetate [5]. (b) $Q$ dependence of the intensity of the singlet-triplet transition in copper acetate measured at 4.2 K [5].

3. Higher-order exchange interactions in spin dimers and trimers

3.1. Evidence for biquadratic exchange interactions in $\text{CsMn}_x\text{Mg}_{1-x}\text{Br}_3$

Fig. 2a shows the magnetic excitations observed for $\text{Mn}^{2+}$ pairs introduced into a single crystal of $\text{CsMgBr}_3$ [6]. The observed intensities are in agreement with the predictions by the cross section (4); with $R=(0,0,1/2)$ the intensity has a maximum for $Q=(0,0,1)$ and vanishes for $Q=(0,0,2)$. The dimer splittings exhibit slight deviations from the Landé interval rule (3):

$$E(1)-E(0)=E_1=1.80(1) \text{ meV}, \ E_2=3.60(1) \text{ meV}, \ E_{3}=5.27(2) \text{ meV}, \ E_{4}=6.74(3) \text{ meV}$$

This behavior can be explained by adding a biquadratic exchange term (parameter K) to Eq. (1):

$$H=-2J_{ij}s_i\cdot s_j-K(s_i\cdot s_j)^2$$

with eigenvalues

$$E(S)=-J\eta-0.25K\eta^2, \ \eta=S(S+1)-2s_1(s_1+1)$$

as listed for $\text{Mn}^{2+}$ ions with $s_1=5/2$ in Fig. 2b. A least-squares fit to the observed dimer splitting energies $E_j$ yields $J=-838(5)$ $\mu$eV and $K=8.8(8)$ $\mu$eV [6].

3.2. Evidence for three-spin interactions in $\text{CsMn}_x\text{Mg}_{1-x}\text{Br}_3$

The smallest magnetic systems to identify three-spin interactions are spin trimers. The dimer Hamiltonian (6) extended to a linear trimer reads:

$$H=-2[J(s_1\cdot s_2+s_2\cdot s_3)+J's_1\cdot s_3]-K[(s_1\cdot s_2)^2+(s_2\cdot s_3)^2]-L[(s_1\cdot s_2)(s_2\cdot s_3)+(s_3\cdot s_2)(s_2\cdot s_1)]$$

This behavior can be explained by adding a biquadratic exchange term (parameter K) to Eq. (1):
L denotes the three-spin exchange parameter, which gives rise to off-diagonal matrix elements, so that Eq. (8) has to be diagonalized in first-order perturbation theory. The biquadratic term $K'(s_1 \cdot s_3)^2$ is neglected, since $|K'| \ll |K|$. In order to unambiguously define the trimer spin states, an additional spin quantum number $S_{13}$ has to be introduced which results from the vector sum $S_{13} = s_1 + s_3$ with $0 \leq S_{13} \leq 2s_i$. The total spin is $S = S_{13} + s_2$ with $|S_{13} - s_i| \leq S \leq (S_{13} + s_i)$, assuming $s_1 = s_2 = s_3$. The trimer states are therefore defined as $|S_{13}, S>$, and their degeneracy is $(2S+1)$.

Figure 2: Energy splittings of Mn$^{2+}$ dimers and trimers in CsMn$_{0.28}$Mg$_{0.72}$Br$_3$. (a) Energy spectra of neutrons scattered from Mn dimers at $T=30$ K [6]. (b) Energy level splittings of Mn dimers. (c) Energy level splittings of Mn trimers [7]. The arrows in (b) and (c) denote the observed transitions.

The low-energy part of the eigenvalues $E(S_{13}; S)$ is illustrated in Fig. 2c for the case of Mn trimer excitations in a single crystal of CsMn$_{0.28}$Mg$_{0.72}$Br$_3$, which were identified in INS experiments according to the characteristic dependence of the cross section upon $Q$ and $T$ [7]. The observed transitions are marked by arrows in Fig. 2c. Least-squares fits based on Eq. (8) with different parameter selection gave the results listed in Table 1. The model including only bilinear exchange interactions failed as expected. The model including the bilinear and biquadratic terms resulted in an improved standard deviation $\chi^2$, but only the least-squares fit including the three-spin interaction was able to reproduce the observed transitions satisfactorily.

Table 1: Resulting parameters from least-squares fits to the observed Mn trimer transitions in CsMn$_{0.28}$Mg$_{0.72}$Br$_3$.

| Model | $J$ $[\mu$eV$]$ | $J'$ $[\mu$eV$]$ | $K$ $[\mu$eV$]$ | $L$ $[\mu$eV$]$ | $\chi^2$ |
|-------|-----------------|-----------------|-----------------|-----------------|---------|
| a (K=L=0) | -870(12) | -8(14) | 0 | 0 | 5.22 |
| b (K≠0, L=0) | -786(7) | -12(10) | 14(2) | 0 | 3.13 |
| c (K≠0, L≠0) | -777(6) | -11(9) | 8(1) | 6(1) | 1.67 |
4. Evolution of spin-state polarons in hole-doped cobaltates

Hole-doped lanthanum cobaltates of type La$_{1-x}$Sr$_x$CoO$_3$ have been subject of growing interest due to their rich temperature-concentration phase diagram [3]. The ground state of the parent compound LaCoO$_3$ is nonmagnetic, corresponding to a low-spin state of Co$^{3+}$ ions with S=0. It was widely believed that the addition of each hole into pristine LaCoO$_3$ through the substitution of a Sr$^{2+}$ ion for the La$^{3+}$ ion creates a Co$^{4+}$ ion in the lattice which has a nonzero S in any spin-state configuration, thereby inducing a magnetic moment in the system. However, already lightly doped cobaltates with $x \approx 0.002$ give rise to an order of magnitude larger magnetic susceptibility than expected [8]. It was proposed that the holes introduced by Sr doping do not remain localized at the nearby Co site, but each hole is distributed among several neighboring Co sites, leaving the latter in the intermediate Co$^{3+}$ state (with S=1) and thereby forming a multi-site magnetic polaron. Such spin-state polarons behave like ferromagnetic nanoparticles with a very large total spin in an insulating nonmagnetic matrix.

![Figure 3](image-url)

**Figure 3:** (a) Energy spectra of neutrons scattered from La$_{1-x}$Sr$_x$CoO$_3$ [9]. For clarity, the intensities of the T=10 K data are enhanced by 400 neutron counts. (b) Q dependence of the intensity of the transition observed at 0.75 meV in La$_{0.998}$Sr$_{0.002}$CoO$_3$ [9]. The insert sketches different types of Co multimers. The lines are the result of structure factor calculations based on Eq. (9).

The existence of spin-state polarons was confirmed by inelastic neutron scattering experiments as shown in Fig. 3a. A magnetic excitation is observed for La$_{0.998}$Sr$_{0.002}$CoO$_3$ at an energy transfer of 0.75 meV, which is absent for the undoped parent compound LaCoO$_3$ [9]. The ground state of Co$^{4+}$ in the intermediate spin state is an orbitally degenerate triplet which is split by a small trigonal ligand field into a singlet and a doublet. The transition between these two levels is the source of the peak observed at 0.75 meV. The peak intensity diminishes with increasing temperature, in agreement with the Boltzmann population factor for a singlet-doublet transition. The Q dependence of the intensity of the observed excitation exhibits a clear oscillatory behavior as shown in Fig. 3b, which reflects the size as well as the shape of the polaron through the structure factor. The neutron cross-section of a cluster comprising n magnetic ions can be approximated for polycrystalline material by [9]

\[
\frac{d^2\sigma}{d\Omega d\omega} \propto F^2(Q) \sum_{i<j}^{n} \left[ \langle S_i \mid T_i \mid S_j \rangle \right]^2 + 2 \frac{\sin Q|R_i - R_j|}{Q|R_i - R_j|} \langle S_i \mid T_i \mid S_i \rangle \langle S_i \mid T_i \mid S_i \rangle \right]
\]  

(9)
where $\mathbf{R}_i$ denotes the position vector of the $i$th ion in the cluster. For the special case of a $\Delta S=0$ transition (which is relevant in the present context), the reduced matrix elements can be factorized and set to 1. We clearly see from Fig. 3b that the Q dependence of the cross section is an unambiguous fingerprint of the geometry of the multimers; in particular, the data observed for the 0.75 meV transition in $\text{La}_{0.998}\text{Sr}_{0.002}\text{CoO}_3$ are perfectly explained by the scattering from an octahedrally shaped Co heptamer. The total moment of this heptamer (consisting formally of one central Co$^{4+}$ ion with $s_i=1/2$ and six surrounding Co$^{3+}$ ions with $s_i=1$) is $13 \mu_B$, in good agreement with the magnetic susceptibility data [8].

The result of the above experiment gives a clear microscopic explanation why hole doping of as little as 0.2% dramatically affects the overall magnetic properties of the entire system, i.e., the magnetic susceptibility is an order of magnitude larger than expected. Additional charge carriers increase the number of such spin-state polarons, which form a percolative network resulting in a metallic state with long-range ferromagnetic order at the critical Sr concentration $x_c=0.18$ [3]. The formation of spin-state polarons may be a common mechanism present in other Co-based oxide compounds as well.

5. Conclusions

INS investigations of magnetic cluster excitations are relevant from a fundamental point of view. Unravelling the origin, the nature, and the size of the exchange interactions, particularly the existence of higher-order terms, is important to understand magnetic phase diagrams [10]. Applications in both technology and science are manifold. Single-molecule magnets are currently considered among the most promising candidates for miniaturization of the storing and processing of quantum information [11]. Magnetic polarons largely control the complex phase diagrams of hole-doped oxide perovskites [9]. Compounds with built-in copper dimers stand at the forefront of the investigation of quantum phase transitions accompanied by Bose-Einstein condensation [12]. Even in biology, proteins like adrenodoxin and ferredoxin contain magnetic iron clusters as important subunits which are essential for the photosynthesis [13]. In all these fields, INS investigations of magnetic cluster excitations will contribute to a detailed understanding of the underlying mechanisms.

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