Intermolecular interactions effects on magnetization tunnelling in molecular magnets

M. A. Falloul and M. El Hafidi[1]

Laboratoire "Modélisation & Instrumentation" Faculté des Sciences Ben M'sik - Département de Physique
Université Hassan II Mohammedia-Casablanca B.P: 7955 Sidi Othmane – 20430 Casablanca Morocco

Abstract: Using a pure quantum calculations and magnons approach, we investigated the magnetic properties of SMMs with crystal-field anisotropy. Our analysis introduces a clear physical mechanism for the appearance of the magnetic plateaus in the system which is related to tunnel and relaxation magnetization effects. We consider two cases of interest: when the SMM are completely independent and when there are inter-cluster magnetic couplings, especially super exchange and dipolar interactions. In such case, we give a special attention to single-ion anisotropies and dipole-dipole interactions. The dispersion relations and magnetization behaviours are explored and analyzed in the quantum magnons formalism taking into account the experimental reality and using commonly parameters values.

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[1] Corresponding author : *E-mail adress* : elhafidimohamed@menara.ma
Tel : +212 6 60 48 30 40

I. Introduction

Over the last two decencies, the skill to consistently elaborate molecular structures with predefined magnetic properties has given rise to a field known, appropriately, as molecular magnetism. Currently, there are several such molecules studied. Two of the more common are $Mn_{12}O_{12}(CH_3OO)16(H_2O)_4$, or just Mn_{12} for brevity [1,2,3], and $[Fe_8O_2(OH)_{12}(tacn)_6]_8^+$, known as Fe_8 [4]. Structurally, these are complicated clusters, but the important elements concerning us in the first plan are the magnetic species. Actually, these metallic ions are arranged in such away giving place to a ground state with a total spin of S = 10, which is essentially fixed at this value (the first excited state of S = 9 has an energy of 30 K for Mn_{12} [5,6]. Moreover, single ionic anisotropy is important and plays a crucial role in the quantum magnetization tunneling phenomen (QMT) [7]. The energy barrier between spin projection $S_z=\pm10$ and $S_z=0$ in zero field is 67 K and 27 K for Mn_{12} and Fe_8, respectively (2). These molecules show QTM at regularly spaced steps in the hysteresis loops and exhibit remarkable staircase in the magnetization curves [8, 9].

Typically when these molecules are synthesized, they form a crystalline structure. The intermolecular interactions in the crystal (super exchange and/or dipolar interactions) are weak (0.1-1K) compared to the intramolecular ones (20-200K) [10, 11]. In such away, the magnetic lattice can be viewed as an assembly of individual S=10 while preserving its quantum nature.

The spin of these single molecule magnets (SMM) can tunnel between classically degenerate orientations, but for certain values of the applied magnetic field, it is found that the tunneling is eliminated, or quenched. Between quenching points, the tunnel splitting oscillates as a function of applied field. Some of the future potential applications of SMM are in quantum computation [12, 13], as multi-bit magnetic memory [14], as an essential part in spintronics and as in MRI contrast [15].

In this paper, we intend to treat a biaxial anisotropic with integer spin system and study the tunnel splitting of the level crossing in such a system by direct digitalization of the magnetic Hamiltonian. The first aim is to elucidate the transverse anisotropy effect for S = 10. Then, we incorporate the mutual interactions between molecules super exchange and dipolar interactions. We apply the Schrödinger's equation of quantum mechanics to determine the energy spectrum as well as the related physical properties of the spin systems. Obviously, we assume that each isolated SMM is placed at sufficiently low temperature in such manner that the thermal agitation

is negligible; the total spin is effectively in its highest value and to be sure that the system is in the pure quantum tunnelling regime.

This article will be divided in two parts: the first part will be devoted to the single molecular magnets (SMMs), while the second treats the intermolecular couplings and the effects on the magnetic behaviour of the system.

In the first part, we analyze the spin Hamiltonian for S =10 and establish the eigenvalues equations in the framework of Schrödinger's schema. In order to discuss possibility of MQT based on this Hamiltonian, the effects of the longitudinal and transverse biaxial anisotropy combined with the applied field effect anisotropy are carefully examined. The quenching points and the splitting oscillations are investigated.

In the same first part, we describe the magnetization and its staircase appearance transitions under a magnetic field in the pure quantum regime, where MQT is not assisted without thermal activation.

In the second part, we have introduced several interactions between SMMs. In addition to uni- and bi axial anisotropies effects, we approach the interclusters exchange and dipole-dipole interactions. Energy dispersion and magnetization behaviours will be treated within the framework of magnons formalism.

We underline that we have limited our study to independent excitations, valid especially at low temperature where magnons diffusion process is negligible.

A. Single Molecule Magnets

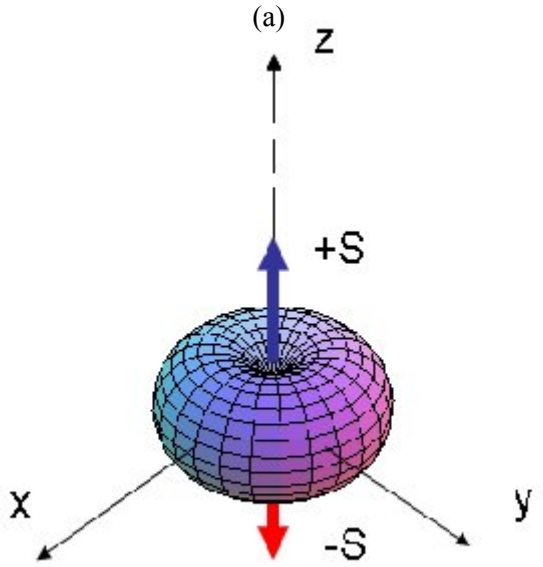
A-1. The model: spin Hamiltonian

The model used here is particularly useful for single molecule magnetic compounds described by the effective spin Hamiltonian [16]

$$H = -D S_z^{\,2} + E (S_x^{\,2} - S_y^{\,2}) - g\mu_B\mu_0 \; S.H$$
$$= -D S_z^{\,2} + (E/2) (S^{+\,2} + S^{-\,2}) - g\mu_B\mu_0 \; S.H \qquad (1)$$

where S = (S_x, S_y, S_z) is the spin operator (S = 10), H is the applied magnetic field in the x-z plane, g is the Landé factor, μ_B is the Bohr magnetron, and D>0, E>0 are respectively the longitudinal and transverse anisotropy parameters. The D term tends to align the spin vector along z-axis while the E term tempts to confine it in the x-y plane. Moreover, when the spin vector is in the x-y plane, it prefers to point in the y-direction. That means that x, y and z correspond respectively to the hard, medium and easy axis. In order to clarify the consequence of each anisotropy term, we represent in fig. 1 the profile of the classical anisotropy barrier separating antiparallel orientations of the spin z-projections (upward and downward arrows). In the absence of transverse term (E = 0; see fig. 1(a), the anisotropy barrier is determined by the uniaxial anisotropy of the molecules (term in D of Eq.1). This uniaxial anisotropy term determines a hard anisotropy plane between opposite orientations of the spin states along the easy magnetic z-axis. It is important to note that this barrier is isotropic in the x-y plane. Consequently, in this case, the tunnel splitting does not depend on the orientation of the applied transverse field in the hard plane. Since D>0 favours high |m| states, the levels m = ±S among the 2S+1 ones have the lowest energy in absence of field. When a field H_z is applied, the energy levels with m<0 increase, while those with m>0 decrease. Therefore, energy levels of positive and negative quantum numbers cross at particular values of H_z, given by $\mu_0 H_z = n D k_B/\gamma$, with n = 0,1,2,3,...(see fig.2).

When the transverse anisotropy is introduced, the situation is modified. Fig. 1(b) illustrates how the anisotropy barrier is modified by the second order anisotropy term E ($S_x^{\,2} - S_y^{\,2}$). This term creates a hard and a medium axis in the hard plane (the x-y plane) that are orthogonal. That means that for E>0 (respect. E<0), the x (respect. y) is hard and y (respect. x) axis is medium. In this case, the tunnel splitting depends on the azimuth angle, φ, of the applied transverse field. A transverse magnetic field HT, applied along the medium axis produces a larger tunnel splitting than the same field applied along the hard axis.



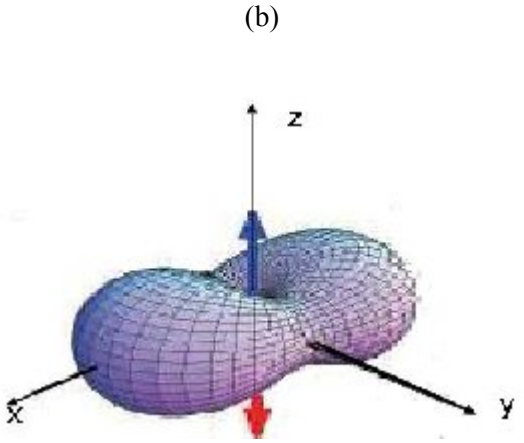


Fig. 1: 3D representations of the anisotropy barrier: (a) with only uniaxial anisotropy term. The thick arrows represent the preferred orientations (up/down) of the spin along the z-axis. (b) in presence of both axial and transverse (term in E) anisotropies. Here E>0, x and y correspond respectively to hard and medium axes.

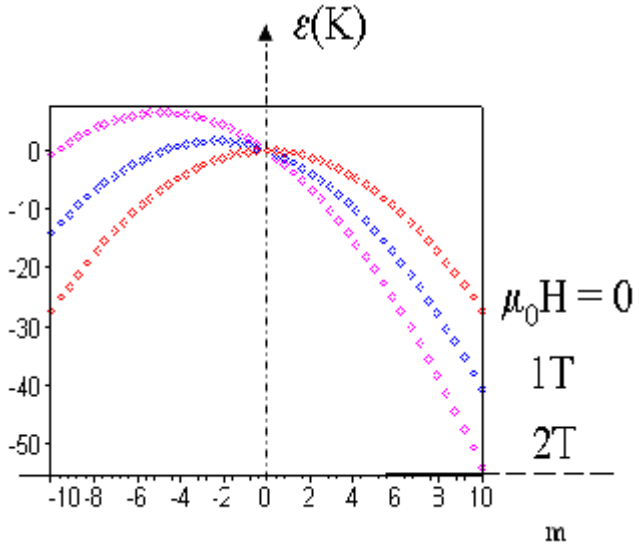


Fig.2: Energy levels as a function of the quantum number m in the uniaxial case with D = 0.275K and S=10, for various longitudinal fields. At certain values of the z-axis field (resonance fields) the levels m and m′ with antiparallel projections onto the z-axis have nearly the same energy.

From the quantum standpoint, when a significant transverse term E is present, the level crossings can be avoided. The spin is in resonance between two states when the applied longitudinal field is close to an avoided level crossing. The energy gap, well known as tunnel splitting Δ, can be tuned by a transverse field via the S_x H_x and/or S_y H_y Zeeman terms. In the presence of the transverse term, it was shown that Δ oscillates periodically with applied magnetic field [4].

The oscillatory magnetic field dependence of the tunnel splitting has been confirmed in the case of Fe_8, by Wernsdorfer and Sessoli [4]. Theoretically, these oscillations have been explained by constructive or destructive interference of quantum spin phases (Berry phases) of two tunnel paths. However, such oscillations represent a very important difference between spin and massive particles. This difference can be attributed essentially to the difference in the commutation relations [17, 18].

More generally, one can have tunnelling between excited states in the two wells. Here, however, we will restrict our study to tunnelling in the ground states.

A-II. Energy levels and quenching points

In order to determine the energy spectrum of the Hamiltonian (II.1), we start with Schrödinger's equation $H|\psi>=\varepsilon|\psi>$ (where ε and $|\psi>$ are respectively the Eigen energies and Eigen states of the operator H) in the S_z standard representation $\{|S, m>\}=\{|m>\}$ which has the properties $S_z|m> = m|m>$, $S^2|s,m >= S(S+1)|m >$ and $S^{\pm}|m >= (S_x \pm iS_y)|m >= 1/2\ [S(S + 1) - m(m\pm 1)]\ |m \pm 1 >$, where S is the spin quantum number which can be an integer or a half odd integer, m = -S,-S+1, · · · , S (here we have used ħ = 1. Thus, $|\psi>$ can be expanded as $|\psi>= \Sigma\ c_m|m>$ where $c_m=<m|\psi>$ are the corresponding components. Assuming H = (H_T, H_z), the Schrödinger's equation takes the form

$$\sum_m c_m\{-Dm^2 - \gamma mH_z\}|m> + \sum_m c_m \frac{E}{2}\{[S(S+1)-(m+1)^2]^2-(m+1)^2\}^{1/2}|m+2> + \sum_m c_m \frac{E}{2}\{[S(S+1)-(m-1)^2]^2-(m-1)^2\}^{1/2}|m-2> - \gamma \frac{H_T e^{-i\varphi}}{2}\sum_m c_m \{[S(S+1) - m(m+1)]^{1/2}|m+1> + [S(S+1) - m(m-1)]^{1/2}|m-1>\} = \sum_m c_m \varepsilon|m>$$

By projection of this equation on each basis vector |m'> (m'= -S,…,+S), we obtain a set of 2S+1 secular relations, each one containing five terms connecting $c_{m\pm2}$, $c_{m\pm1}$ and c_m :

$$\lambda_{m-1}c_{m-2} + \lambda_{m+1}c_{m+2} - \tau_{m-1}\ c_{m-1} - \tau_{m+1}\ c_{m+1} - (\alpha_m+\gamma H_z m+\varepsilon)\ c_m = 0 \quad (II.2)$$

Where $\gamma = \mu_0 g\mu_B, \varphi = (H_T, x)$, $\lambda_{m\pm1} = \frac{E}{2}\{[S(S+1)-(m\pm1)^2]^2-(m\pm1)^2\}^{1/2}$, $\tau_{m\pm1} = \gamma \frac{H_T e^{\mp i\varphi}}{2}$ $[S(S+1)-m(m\pm1)]^{1/2}$, $\alpha_m = Dm^2$

Actually, it is very difficult to solve rigorously the equation (II.2) for quite large spin (S>1). To overcome this issue, we have developed an efficient program providing a numerical diagonalization of this algebraic equation for an arbitrary set of the parameters S, D, E, H_T and H_z. This numerical method is available for any value of the spin S. The other known methods consisting on mapping the spin problem onto a particle problem are restrained to very large S values (S>>1).

Diagonalization of Eq. II. 2 has allowed us to compute the energy spectrum for the spin system in presence of magnetic field, H_T applied in the x-direction (φ =0). Using the set of parameters S = 10, D= 0.275K, E =0.055K and g = 2 which are in agreement with experimental data of Fe_8 [19], we determine all permitted energies as well as their corresponding states. Table1 lists the identified levels for H=0 and $\mu_0 H_x$= 4.2T. As shown in Table 1, when H=0T, the ground state's level which corresponds to the lowest energy E_g = -27.559K corresponding to the pair of states that have the most of their weight respectively in the |m =±10> states. For the excited states, the degeneracy is progressively lifted and the probability to be in other states as |m =±9>, |m =±8>, becomes significant. When a magnetic field is applied along the hard axis, the ground state's level is lowered i.e. the system is better stabilized. In a weak field such H_x=4.2T along the x direction (see Table 1), the situation begins to change appreciably: in the ground state, the system has now a non negligible probability to be in the state |±9>. In fact, the term in H_x gives rise to Δm =±1 transitions, and mixes the state m=-10 with m=+10 via intermediate levels from -9 to +9, while the presence of the transverse anisotropy favours admixing states where Δm =±2.

Table 1. Energy eigenvalues and Eigenvectors components c_m of the spin Hamiltonian with S = 10, g= 2, D = 0.275K and E = 0.055K at H_x = 0 T and at $\mu_0 H_x$=*4.2*T.

See Appendix

Figure 3.a shows the obtained eigenvalues energy spectrum for the considered system. In this figure, the field was expressed in term of the $\mu\Delta H_x$ = 0.2836T step units. For each given field, it is easy to see that the ground state of the present Hamiltonian corresponds to the allowed lowest eigenvalues levels. The transverse term has for effect to partially lift the degeneracy. At the avoided crossing level, the spin may pass from a state to the other through the tunnel barrier Δ. The quenching points are deduced and reported in fig.2.b. The existence of such points confirms that the tunnel splittings Δ are oscillatory as a function of the transverse field H_x with an oscillation's period $\Delta H_x = 2k_B/\mu_0\gamma \sqrt{2}E(E+D)$ in the interval [0, n ΔH_x] [20]. By increasing the applied magnetic field, the quenching points decrease gradually and finally disappear when n≥2S-1 in harmony with results of Garg [20, 21] as well as those of Zhang et al. [22].

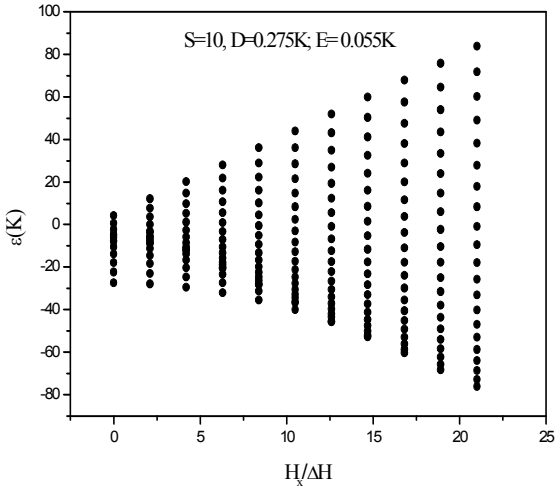


Fig.3.a: Energy levels obtained from numerical Diagonalization of the [21x21] Hamiltonian (S = 10) including longitudinal (D=0.275K) and transverse (E = 0.055K) anisotropies in presence of applied field in the hard **x**-direction (here the step field is $\mu_0\Delta H_x$=0.2836T).

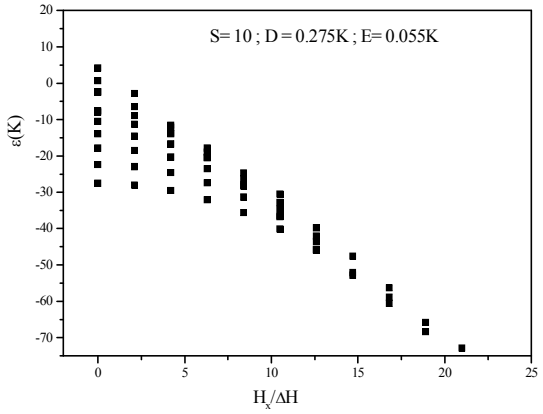


Fig.3.b: Quenching points deduced from the energy levels graphs for the biaxial spin system with S=10; D=0.275K; E= 0.055K.

Most of the many energy eigenvalues are doubly degenerate although in presence of magnetic field. These crossing points reflect the oscillation of tunnel splitting with external field.

We have been interested also in the detail of tunnel splitting oscillations. For this aim, we have used a semi-classical model due to Garg [23]. Based on it, the tunnel splitting Δ can be expressed as $\Delta \sim \exp(-S_R)\cos\Omega$, where S_R is the real part of interfering instantons action and $\Omega = \pi[S - H_x/\Delta H_x]$. Thus, it is easy to verify that D vanishes effectively whenever $H_x/\Delta H_x = S - \frac{1}{2} - n$ where n = 0, 1,…., 2S-1 as we have seen previously. Numerical results are shown in Fig. 4 for the system S= 10, D= 0.275K and E=0.055K. It is clear through this figure that the tunnel splitting between various pair of Zeeman levels oscillates as a function of the applied magnetic field, vanishing completely at quenching points. Present results agree qualitatively with experimental data for the Fe_8 molecular magnet [4, 24].

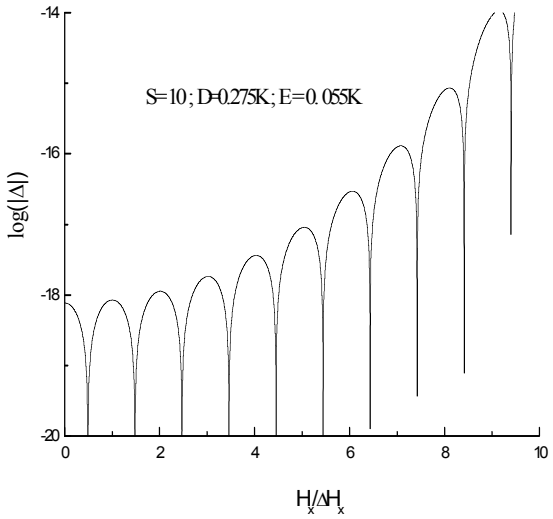


Fig. 4: Tunnel splitting oscillations for a model system with S=10, D=0.275K and E=0.055K where the applied field is H_T//**x**.

A-III. Thermal activated regime and staircase Magnetization behaviour

Up to now, we have not taken into account the temperature effects. We present here a model to describe the thermal behaviour at the equilibrium. Actually, magnetization describes the energy variation of a system under a perturbation produced by an external magnetic field $m_\nu = -\partial\varepsilon/\partial H_\nu$ (ν = x, y, z). In the quantum language, for each energy level ε_n (n = 1, 2,…) of a spin system under a magnetic field, one can define a microscopic magnetization in the ν direction $\mu_{n\nu} = -\partial\varepsilon_n/\partial H_\nu$. Therefore, the macroscopic magnetization is obtained by summation over all microscopic magnetizations pondered by the Boltzmann distribution $M_\nu = N/Z \sum_n \mu_{n\nu} \exp(-\beta\varepsilon_n)$ where $Z = \sum\exp(-\beta\varepsilon_n)$ is the partition function, and $\beta = 1/k_BT$ (k_B is the Boltzmann constant and T is the absolute temperature).

In terms of the spin Hamiltonian, the magnetization per spin can be also written $M_\nu = -\mathrm{Trace}[\gamma S_\nu \exp(-\beta H)]/\mathrm{Trace}[Z]$ where S_ν is the component of the spin operator in the ν-direction.

Generally, one can calculate numerically curves of magnetization for different temperature and field values. However, the difficulty comes essentially from the term in $\exp(-\beta H)$ corresponding to the exponential of the large range $(2S+1)(2S+1)$ but non diagonal matrix [H] (S =10, …).

To surmount this difficulty, we have developed a systematic method for calculating $\exp(-\beta H)$. It consists to transforming βH by a change of basis which provides us a simpler form of $\exp(-\beta H)$: $\exp(-\beta H) = P^{-1} \exp(-\beta H_D) P$ where H_D is the diagonal form of H and P is the matrix constructed with corresponding eigenvectors of H (since H is real and symmetric, i.e. Hermitian matrix) [25]. Thus, we have developed a numerical program which computes all eigenvalues and, optionally, eigenvectors of a Hermitian tridiagonal matrix of any order (S=10, …).

Fig.5. shows typical magnetization curves for the selected systems S = 10, D = 0.275K and E=0.055K when the field is applied in x-direction. The effect of avoided level crossings can be observed especially in the x-direction. When the applied field is in proximity of an avoided level crossing, the magnetization relaxes faster, yielding jumps separated by plateaus. As the temperature is lowered, there is a decrease in the transition rate as a result of reduced thermally activated tunnelling. At sufficiently low temperature (T<Tc), the magnetization steps become stable and temperature independent. The field between two successive resonances is equally given by the same rule ΔH_x as seen previously.

Experimentally, these successive staircases are related to large hysteresis loops as observed in many molecular magnets such Mn12 [26, 27] and Fe8 [28]. Actually, when the applied field is near an avoided level crossing, the magnetization relaxes faster, yielding steps separated by plateaus.

However, it is worth to note that for an even correct numerical simulation above 10 K, it would be necessary at least to take into account excited levels of the total spin.

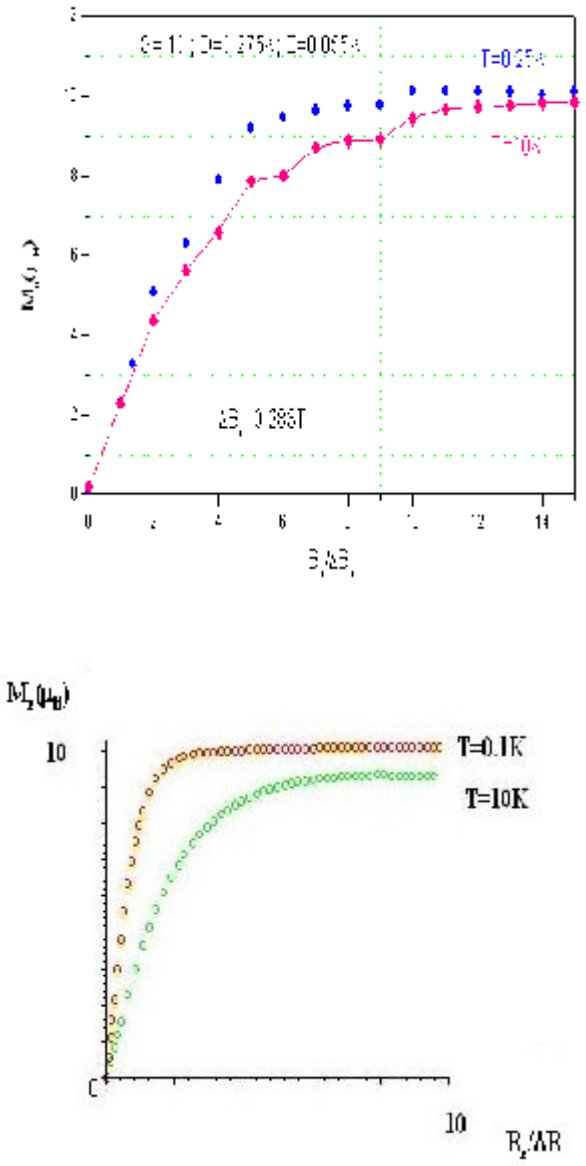


Fig.5: (a) Magnetization curves at two selected temperatures (T=0.25K and 10K) for the system with S=10, D= 0.275K and E=0.055K. The magnetization expressed in Bohr magnetron per spin and the field is normalized to the step ΔH_x. (b) Magnetization curves in a longitudinal field.

A-IV. Preliminary Conclusions

Before passing to the next part, let us remind here the main results. In this part, we have investigated a quantum model of biaxial high spin system magnets with both axial and transverse anisotropies. Since the problem starts from the Diagonalization of the (2S+1) (2S+1) matrix Hamiltonian, we have elaborated a computational program.

Our numerical results concerning quenching points, tunnelling split oscillations and magnetization jumps are consistent with experimental data. The advantage of the present numerical program which we have performed resides in its applicability to any biaxial spin system at any temperature and field. That should provide a way for designing nanostructures with predefined magnetic interactions and properties, a highly useful for developing new molecular magnets.

In the next part, we plan to examine the intermolecular interactions such exchange and dipolar couplings which are present in the most real molecular magnets.

B. Inter clusters interactions influence

The aim of this part is to apply the quantum magnons formalism in molecular magnets coupled through exchange or dipolar interactions that are the two main spin-spin interactions.

For very weak distances between magnetic species (typically d <0.5 nm), exchange constitutes the most important mechanism of interactions. This type of interaction is remarkably important inside molecules constituted of several magnetic centres. The giant spin results essentially from the strong intramolecular exchange.

Furthermore, in the limit of large distances between spins, exchange interaction becomes weak and dipolar interactions should play important role in the mechanism of spin-spin coupling. It is for example the case of the interaction between giant spins in a molecular magnet system. The distance between two adjacent spins in such arrangement being in the order of 1 to 2 nm. Thus, influence of the long range dipole-dipole in such a system must be taken into account. In the molecular magnet Fe8, dipolar energy reaches 120mK corresponding to a magnetic dipolar field of 50mT acting from a S = 10 spin on the adjacent one [29]. We particularly study the role of the dipole-dipole interaction within the framework of a Heisenberg model with nearest-neighbours exchange, single-ion anisotropy and

additional dipolar interaction.

After a bosonization of the spin operators via a Holstein-Primakoff transformation and a truncation in the harmonic order of the bosons, we obtain the spin-wave spectra for experimentally relevant parameters without further approximation by numerical diagonalization

B-I. Magnons Approach

Spin waves were proposed initially by Bloch, but the microscopic theory of magnons was accomplished by Holstein and Primakoff taking into account

exchange, Zeeman and dipole-dipole interactions. Since then, this formalism was an object of numerous theoretical and computational investigations at sufficiently low temperature when the spin deviations are weak giving rise to elementary magnetic excitations [30]. However, the approach was usually restricted to isotropic magnets with small spin. Here, we apply this technique to magnets with a really high spin, such giant spin molecular magnets, in presence of single -ion anisotropies and dipolar couplings. This confers to the present contribution a special originality.

$$H_M = -\sum_{(i,j)} J_{ij}\mathbf{S}_i.\mathbf{S}_j - \sum_i D_i S_{iz}^2 + \sum_i E_i (S_{ix}^2 - S_{iy}^2) - \gamma \sum_i \mathbf{S}_i.\mathbf{H}$$

where Jij is the exchange constant between neighbours, $\gamma = \mu_0 g\mu_B$. D_i and E_i correspond respectively to uni and bi-axial anisotropy acting on a spin located at the site i. The operators $S_{\upsilon\alpha}$ (α = x, y, z, υ = i, j) obey the habitual commutation relation $[S_{\upsilon\alpha}, S_{\upsilon'\beta}] = i\delta_{\upsilon\upsilon'}\varepsilon_{\alpha\beta\gamma}S_{\upsilon\gamma}$. The last term corresponds to the dipolar interaction which will be well detailed later. Here we focus on the ferromagnetic coupling between nearest neighbours ($J_{ij} = J > 0$). We also suppose D > E > 0, i.e. that x, y and z correspond respectively to hard, medium and easy axis for each giant spin molecule. This situation is mainly frequent in a numerous molecular magnets with high spin [31-34]. In these materials, the magnetic molecules are sufficiently distant from each other that the intermolecular exchange is less favoured. One may imagine indirect super-exchange through electrons of ions which spear these molecules. This last mechanism was largely described by Van Vleck [35] and Anderson [36].

When a magnetic system is ordered, spins choose a particular direction in the space that minimizes energy, but thermal fluctuations tempt to deviate them from their fundamental configuration.

In the case of small fluctuations, elementary excitations take place and the problem may be mapped in a bosons description.

B-II. Holstein-Primakoff transformation

Transformation of the spin Hamiltonian into harmonic oscillators may be accomplished by using the formalism of second quantization. Thus, following the well-known procedure, the spin operators are mapped onto a boson harmonic terms as $S_i^+ = \sqrt{2S}\, a_i^+ f_i(S)$ and $S_i^- = \sqrt{2S}\, a_i f_i(S)$ where

$$f_i(S) = \sqrt{1 - \frac{a_i^+ a_i}{2S}}$$

a+ and a are the creation and annihilation operators of the conventional theory of harmonic oscillator. This transformation preserves the commutation relations both for spin and bosonic operators, i.e $[S_i^z, S_j^\pm] = \pm S_i^\pm \delta_{ij}$ and $[a_i, a_j^+] = \delta_{ij}$ [37]. The number ni of excited bosons is exactly the eigenvalues of the $\hat{n}_i = a_i^+ a_i$ operator.

After transformation in the Fourier space, one can rewrites Hamiltonian in terms of independent harmonic oscillators which translate elementary excitations into the system. Nevertheless, this transformation requires a large spin value and/or a sufficiently low temperature: ($n_i/2S$ << 1).This condition is satisfied in the new giant spin magnets where the effective spin is quite large (S≥10), so the present approach is well justified.

Spin operators are in this way mapped onto the new magnon form ak as [38]

$$a_k = \frac{1}{N}\sum_i exp(-i\mathrm{k}.\mathrm{R}_i) a_i$$ where

$$[a_k, a_{k'}^+] = \delta(k - k')$$ and

$$\delta(\mathrm{R}_i - \mathrm{R}'_i) = \frac{1}{N}\sum_i exp(i\mathrm{k}.(\mathrm{R}_i - \mathrm{R}'_i))$$

B-II.1. Exchange term

For ferromagnetic exchange interaction between nearest neighbours, it is sufficient to sum only on the relative positions δ of immediately neighbours of a given spin Si. Thus, the exchange, term may be written

$$H_e = -J\sum_{i,\delta} \mathrm{S}_i.\mathrm{S}_{i+\delta} = -J\sum_{i,\delta}[\frac{1}{2}(\mathrm{S}_i^+ \mathrm{S}_{i+\delta}^- + \mathrm{S}_i^- \mathrm{S}_{i+\delta}^+) + \mathrm{S}_i^z \mathrm{S}_{i+\delta}^z]$$

.

Consequently, in magnons framework, this hamilltanian writes, in the quadratic approximation

$$H_e = -JzNS^2 + 2zJS\sum_k [1 - \eta_k] a_k^+ a_k$$

Where N is the total number of spin sites, z is the nearest neighbours' number of a given spin within the lattice and η_k is the over lattice summation $\eta_k = \frac{1}{z}\sum_\delta e^{ik.\delta}$. Let remember that the allowed k values are limited by the first Brillouin zone under periodical Born-von Karman boundary conditions [39]. The operators a_k^+ and a_k obey the similar commutation relations as a^+ and a. They can be

regarded as creation and annihilation operators of some quasi-particles (magnons). These magnons are note localized on the lattice sites but belong to the entire lattice.

B-II.2 Zeeman term

The previous relations permit a simple transformation of the Zeeman term. Then, under a magnetic uniform applied along the z axis, this Hamiltonian's part can be written in the harmonic approximation

$$H_Z = -\gamma H \sum_i S_i^z = -\gamma HNS + \gamma H \sum_k a_k^+ a_k$$

B-II.3 Anisotropic terms

Firstly, let us notice that in SMMs, the distances separating molecules are typically in the range of 0.10 to 0.20 nm and each molecule with giant spin may be regarded as a dipole. This suggests that dipole-dipole interaction is quite important source of energy in these compounds.

The single-ion anisotropic Hamiltonian can be decomposed into two contributions

$H_a = H_{ax} + H_{tr}$

where

$$H_{ax} = \sum_i D_i S_{iz}^{\ 2} = -DNS^2 + (2S+1)D\sum_k a_k^+ a_k$$

And

$$H_{tr} = \sum_i E_i (S_{ix}^{\ 2} - S_{iy}^{\ 2}) = ES\sum_k [a_k^+ a_{-k}^+ + a_k a_{-k}]$$

Because of the last term which breaks the invariance around z-axis, we note that the global Hamiltonian has no diagonal form.

B-II.4 Dipolar interactions

In the quantum point of view, dipole-dipole interaction may be introduced in terms of spin operators

$$H_D = \frac{\gamma^2}{2} \sum_{i \neq j} \frac{S_i . S_j - 3(S_i . \hat{R}_{ij})(S_j . \hat{R}_{ij})}{R^3_{ij}}$$

where $R_{ij} = R_i - R_j$ is the relative vector position between spin S_i and S_j,

$$\hat{R}_{ij} = \frac{R_{ij}}{|R_{ij}|}$$

Here, we take the simple form including only nearest neighbours of a given spin S_i. Setting $R_{ij} = \delta$, and assuming the wave-vector k//z , we may expand HD in the simplest form

$$H_D = \frac{\gamma^2}{2} \sum_{(i,\delta)} \frac{1 - 3\cos^2 \theta_{i,i+\delta}}{\delta^3} [\frac{1}{2}(S^+_i S^-_{i+\delta} + S^-_i S^+_{i+\delta} + S^z_i S^z_{i+\delta}]$$

Where $\theta_{i,\delta}$ is the angle between the spin-wave k vector and δ. Under these special conditions, a simple calculation in the Fourier space gives

$$H_D = \frac{8\gamma^2}{a^3} S \sum_k \sin^2(\frac{ka}{2}) a^+_k a_k$$

Here, we have restricted ourselves to the description of a system consisting in SMM clusters that are organized in a cubic simple lattice with spacing a and the field is applied in the z-direction.

B-III. Bogoliubov Transformation

The global Hamiltonian has no diagonal form in the magnons Holstein-Primakoff basis. It writes formally as

$$H_M = \varepsilon_0 + \sum_k [\xi_k a_k^+ a_k + \frac{\Delta_k}{2} a_k a_{-k} + \frac{\Delta^*_k}{2} a_k^+ a_{-k}^+]$$

where

$$\varepsilon_0 = -\gamma NSH - DNS^2 - NzJS^2 \ ,$$

$$\xi_k = \gamma H + D(2S+1) + 4JSz\sin^2(\frac{ka}{2}) + 8\frac{\gamma^2}{a^3} S^2 \sin^2(\frac{ka}{2})$$

And $\Delta_k = 2ES$

Furthermore, this Hamiltonian can be diagonalized by a rotation in the magnons space (k,-k) by expressing it in the following matricial form [40]

$$H_M = \varepsilon_0 + \frac{1}{2} \sum_k (X_k^+ H_k X_k - \xi_k)$$

where

$$H_k = \begin{pmatrix} \xi_k & \Delta^*_k \\ \Delta_k & \xi_k \end{pmatrix} \text{ and } X_k = \begin{pmatrix} a_k \\ a^+_{-k} \end{pmatrix}$$

By Bogoliubov trantsformation, we can determine the dispersion spectrum of magnons by

$$\varepsilon_k = \sqrt{\xi_k^2 - |\Delta_k|^2}$$

This usually may be investigated experimentally using inelastic neutron diffusion (see e.g [41])

B-IV. Numerical Results

Previous calculations have permitted us to investigate dispersion curves and elucidate the magnetization shape with temperature or filed without and in the presence of dipolar interactions. In the present study, the field is assumed to be applied along z axis, magnetization Mz is simply noted M (H, T). Moreover, the spin waves propagation are restricted to the longitudinal case k//z.

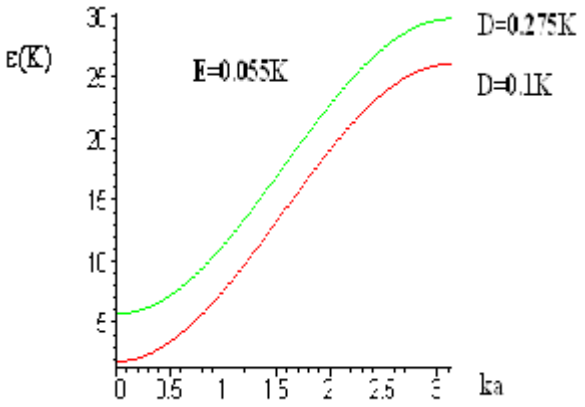


Fig.6: Spin-wave dispersion for the system with S=10, E=0.055K and two selected values of the uniaxial anisotropy constant D=0.275 and 0.100K.

B-IV.1. Energy spectrum

It is easy to observe that in presence of uniaxial anisotropy, a gap $\Delta_0 = D(2S + 1)$ is opened in the Brillouin zone center i.e k = 0, even in absence of applied field.

In Fig. 6, we have reported, in a (k_a, J, ε_k) diagram, the dispersion spectrum of magnons

in the considered system, in the first Brillouin zone, within the arbitrary choice of Hamiltonian parameters: S = 10; D = 0.275K; E = 0.055K in absence of external field. The exchange constant takes values from0 up to 0.5K, without dipolar interactions. We remark that the exchange enhances the dispersion in the Brillouin zone border's ($k \rightarrow \pi$).

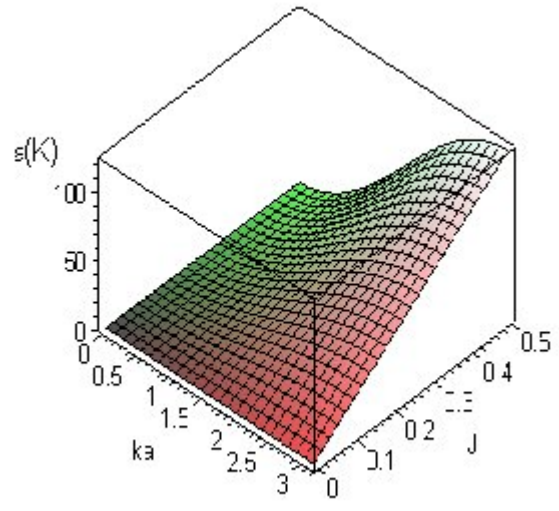


Fig.6 : Spin-wave dispersion of a SMM with S = 10; D = 0.275K; E = 0.055K without external field. The inter-clusters super exchange J s assumed to be ferromagnetic.

Moreover in presence of uniaxial anisotropy, one can remark a gap $\Delta_0 = D(2S + 1)$ which is opened in the Brillouin zone center i.e k = 0, even in absence of applied field.

Transverse bi-axial anisotropy (term in E) favours the spin confinement into the yOz plan (x being a difficult axis). This anisotropy breaks the invariance by rotation around the z axis and makes the Hamiltonian in non diagonal form by coupling of magnons with k and −k wave vectors. Figure 7 summarizes effects of the bi-axial anisotropy on dispersion relations of magnons corresponding to the choice S = 10, D = 0.1K and J = 0.1K. Here we note that dispersion without the external field can take place only if $E < 2D (+1/2S) + 2zJ (1 - \eta k)$. But since one has often E << D in the practice, this condition is well satisfied and the magnons dispersion has to take place for reasonable values of E. In these conditions, the bi - axial anisotropy tents to decrease slightly the excitation energy of magnons especially for the small values of k.

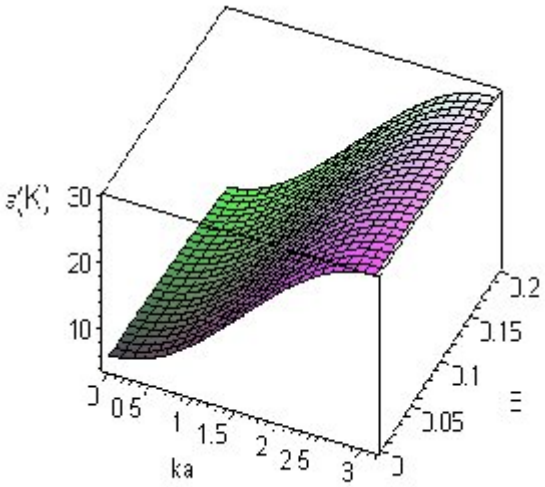


Fig.7: 3D representation of the dispersion magnons curves for S = 10,D =0.275K, J = 0.1K and E taking values between 0 and 0.2K.

Dispersion under an applied magnetic field has also been investigated. The well known resonance frequency $\omega 0 = \gamma[(H + D(2S+1)\gamma - ES\gamma)(H + D(2S+1)\gamma + S\gamma)]1/2$ (when $k \rightarrow 0$) is located in the micro-waves domain (GHz). Il may be also expressed in terms of axial (H_{ax}) and transverse (H_t) fields by $\omega = \gamma [(H + H_{ax} + H_t)(H + H_{ax} - H_t)]1/2$ where $\gamma/h \sim 2.803$ GHz/kOe for $\gamma = 2\mu_B$. Looking at the H_{ax} and H_t values, the curve of resonance is nearly linear with a light curvature in weak fields (cf figure 8). Energy spectrum is also enhanced by dipolar couplings, as seen in fig.9.

Since magnons have energy of few GHz, one may estimate th relaxation time TR through the Heisebnerg relation $\omega k.TR \approx 1$. TR is typically in the order of 10^{-12}s.

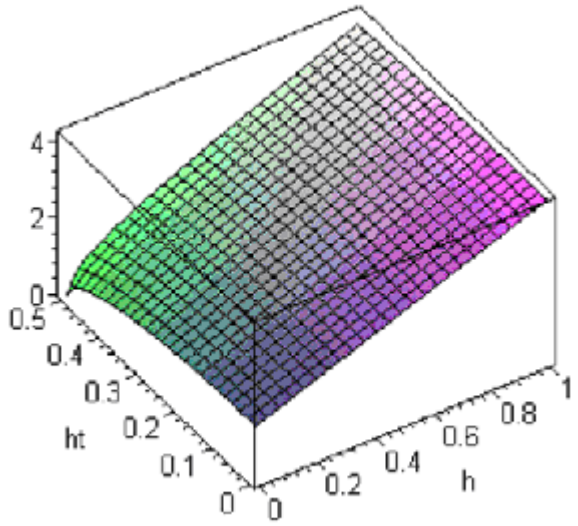


Fig.8: Resonance frequency (in GHz for k → 0) vs the applied field H (in kOe), simulated with H_{ax} = 0.5 and H_t taking values from 0 up to 0.5.

It is easy to observe that in presence of uniaxial anisotropy, a gap $\Delta_0 = D(2S + 1)$ is opened in the Brillouin zone center i.e k = 0, even in absence of applied field.

The return to the basis state is generally accompanied by phonons emission [42]. It's the most efficient mechanism to transfer energy from magnons to phonons [42].

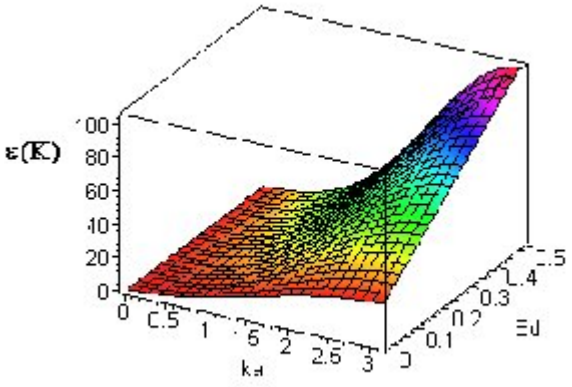


Fig.9: Dipolar interaction effects. Here D=0.275K, J=0.1K and E=0.055K. The dipole-dipole energy has been computed for a simple cubic array of spins S=10.

B-IV.2 Magnetization thermodynamic's

At sufficiently low temperature, few magnons are excited and their mutual interactions are negligible. In this way, they are viewed as pure harmonic oscillator's modes and obey to Bose-Einstein statistics where the chemical potential doesn't appear. At a given temperature T, there are n_k excited magnons with wave vectors k and frequency ω_k where

$$< n_k >=< a_k^+ a_k >= [\exp(\beta\varepsilon_k) - 1]^{-1} \quad (4.1)$$

Where $\beta = 1/k_B T$. These excitations give rise to a decrease of magnetization from its saturation value M(0) which is described by the following expression [40]

$$\Delta M(T) = M(0) - M(T) = \gamma / V \sum_k < n_k > \quad (4.2)$$

Since, the current values of |k| are in the range of 106cm−1 and a ~10 nm, we can consider that ka<<1[39]. Consequently, the dispersion relation is simplified in such a way as

$$\varepsilon_k = \sqrt{(\gamma H + (2S+1)D - SE + \Gamma k^2)(\gamma H + (2S+1)D + SE + \Gamma k^2)}$$

where

$$\Gamma = \frac{\hbar^2 z S a^3}{3}$$

is the stiffness spin constant for a simple cubic lattice, and z is the spin coordination [40].

Furthermore, the summation 4.2 is carried out over the first Brillouin zone and can be converted into an integral. Generally, evaluation of the latter integral is not simple. However, at sufficiently low temperature, there few excited magnons with large k values. Consequently, the integral can be extended in the whole of the Fourier space. Under these conditions, we can then write

$$\Delta M(T) = \sqrt{\frac{2}{\pi}} \gamma \int_0^\infty \frac{k^2 dk}{e^{\beta\varepsilon_k} - 1}$$

Figure 10 shows ΔM vs T for several applied fields H, in the spin S = 10.

We notice that magnetization decreases while increasing temperature with respect to a Bloch's low. Moreover, the magnetization decreases more slowly when one adds a field which attempts to maintain the spins in an alone ordered direction.

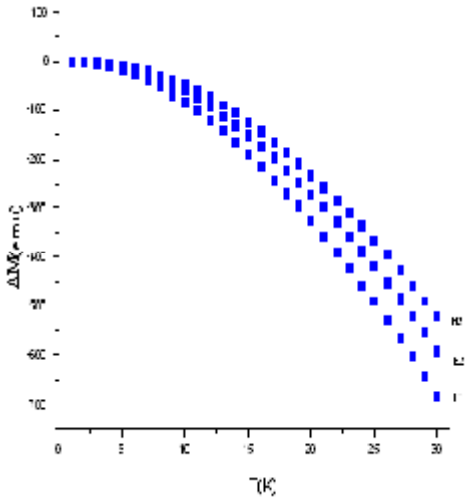


Fig.10: Thermal variations of magnetization for selected fields (H_3>H_2>H_1).

It is clear from these curves that magnons have effects on magnetization behaviour along z axis.

Finite size effects should be equally important especially at nanometric scale [43].

In addition, magnetization isotherms have been investigated. Figure 11 describes the magnetization behaviour with applied field for different temperatures for S = 10

Magnetization increases with the applied field until the saturation. When temperature is increased, it becomes more difficult to reach saturation because of thermal agitation driving to disorder.

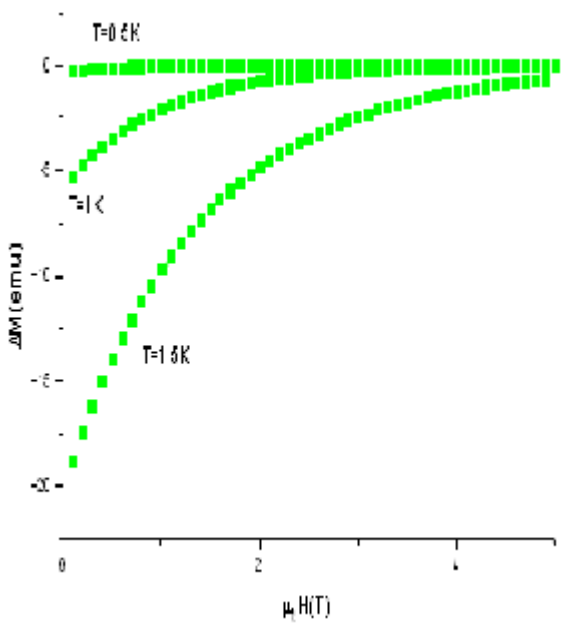


Fig. 11: Isotherm curves of magnetization for S= 10.

In the present case, we remark that dipolar interaction enhances the magnetization, i.e. ferromagnetic couplings.

This tendency is confirmed through thermal magnetization shape which shows that dipolar interactions favours a rapid saturation in despite of thermal agitation.

B-V. Conclusions

In conclusion, we studied quantum tunneling of large spin in the biaxial spin systems by using quantum mechanics. The energy spectrum of the spin model is obtained by numerical solving Schrodinger's equation, which is derived directly from the eigenvalues equation of the spin problem. The quenching points are determined permitting a natural way to explain the oscillations of tunnel splitting in the biaxial spin system.

In the second part, we have focused on different interactions acting within giant spin magnets.

Besides spin and uni- and bi axial anisotropies effects, we have explored the dipole-dipole interactions influences between high spin molecules in energy dispersion and magnetization behaviours within the framework of magnons formalism.

Notice that we have restricted our study to independent excitations, justified at sufficiently low temperature where magnons diffusion process is negligible. Actually, a rigorous treatment requires that the extended character of molecules in space must be taken into account instead of the punctual picture of dipoles which is often assumed. It's worth to study the other orientation of magnons propagation and take into account finite size effects which are frequently present in new nano-magnets.

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