Advanced Physics Modeling of Metal Containing Materials: Magnetic Properties & Entanglement

N. Ananikian

CANDLE Synchrotron Research Institute
Yerevan, Armenia
ananik@asls.candle.am

Outline

- **Advanced Physics Modeling, Magnetization & Entanglement**
- **Natural Mineral Azurite & Thermal Concurrence**
- **Magnetization Plateaus in Spin-1 Ising - Heisenberg Model on a Diamond Chain & Thermal Negativity**
- **Plateaus in Spin 1 $[Ni(NN'\text{-}dmen)(\mu\text{-}N_3)_2]_n$ Polymer**
- **Ni Containing Clusters: $[Ni_8(\mu_3\text{-}OH)_4(OMe)_2(O_3PR)_2(O_2C^tBu)_6(HO_2C^tBu)_8]$, $[Ni_{12}(\mu_3\text{-}OH)_4(HCO_3)_6(O_3PR)_4(O_2C^tBu)_6(HO_2C^tBu)_6]$**
- **Schedule of actions**

Magnetization Plateaus

The **magnetization plateaus** have played a great role in understanding of a large family of nontrivial quantum phenomena of spin systems. For the first time **K. Hida** in a pioneering work has shown the appearance of magnetization plateau in Heisenberg model [**JPSJ 1994][Ferromagnetic-Ferromagnetic-Antiferromagnetic Trimerized Heisenberg]**. The **experimental observation** of **1/3 magnetization plateau** in the diamond-chain compound $\mathbf{Cu_3(CO_3)_2(OH)_2}$ known as **natural azurite** at temperatures below 4.2 K was detected [**Kikuchi's group, Phys. Rev. Lett.94, 227201 (2005)**].

My group with collaborators obtain magnetization plateaus and entanglement using the dynamical and transfer matrix methods [Arakelyan, Ohanyan, Ananikyan, N.A., Roger, **PRB 67,** 2003; Hovhannisyan,N.A., PLA 372, 2008; N.A., Ananikyan, Artuso, Lazaryan, PLA 374, 2010; Ohanyan, N.A., PLA 307, 2003; N.A.,Hovhannisyan, Physica **A 392**, 2013; N.A., Lazaryan, Nalbandyan, EPJB 85, 2012; Torrico, Rojas, de Souza, N.A, EPL **108** , 2014; Nalbandyan, Lazaryan, de Souza, N.A., JPSJ 83, 2014; Rojas, N.A. , de Souza, PRA 86, 2012; Abgaryan, N.A., Ananikyan, Hovhannisyan, Solid State Com. 203, 2015; Chakhmakhchyan, Leroy, N.A., PRA 90 (2014);Lazaryan, Nalbandyan, N.A. IJMP B 30, 2016; Hovhannisyan, Strecka, N.A. CM 28, 2016; Hovhannisyan, N.A., Kenna, Physica A 453, 2016; N. A., Burdík, Ananikyan, Poghosyan, J. of Physics: Conf. Series 804 (1), 012002 (2017); Hovhannisyan, N. A., Campa, Ruffo, Phys. Rev. E **96**, 062103 (2017); Zad, N.A., J. P.: C M. **29**, 455402 (2017) & **30**, 165403 (2018); SSC **276,** 24 (2018) ; N.A., Artuso, Poghosyan, Physica **A 503**, 892 (2018).

Entanglement

The term **“entanglement”** was introduced by **Erwin Schrödinger [Naturwissenschaften 23, 807]** in 1935 in order to describe an intrinsic feature of quantum mechanics.

There are many ways for measuring entanglement of mixed state and the quantum nature of the correlations, such as: **concurrence** (**Hill and Wootters, *PRL* 78 ,1997; Wootters, *ibid. 80* 1998); negativity** (**Vidal, Werner, PRA 65, 2002**); **quantum discord (Ollivier, Zurek, PRL 88, 2001; Dakic, Vedral, Brukner, PRL 105, 2010);entanglement fidelity (Schumacher, PRA 54, 1996; Barnum, Nielsen, Schumacher, PRA 57,1998)…**

The talk is devoted to analyze the **magnetization plateau, concurrence & negativity** behavior for experimental data of metal containing materials: **natural mineral azurite** $Cu_3(CO_3)_2(OH)_2$**;polymers** $[Ni(NN'\text{-dmen})(\mu\text{-}N_3)_2]_n$, $[CoL^2(N_3)_6(H_2O)_2]_n$, $[Mn(N_3)_2(4\text{-}Bzpy)_2]_n$ **; diamond chain** $[Ni_3(fum)_2(\mu_3OH)_2(H_2O_4)]_n \cdot (2H_2O)_n$ **; Ni contaning clusters:** $[Ni_8(\mu_3\text{-}OH)_4(OMe)_2(O_3PR)_2(O_2C^tBu)_6(HO_2C^tBu)_8]$ **(R = p-tert-Butylbenzyl),**

$[Ni_{12}(\mu_3\text{-}OH)_4(HCO_3)_6(O_3PR)_4(O_2C^tBu)_6(HO_2C^tBu)_6]$ **(R = p-tert-Butylphenyl);**

applying the **transfer matrix** method of **separated blocks, cluster with Heisenberg coupling**, the parallel **ALPS project** (Algorithms and Libraries for Physics Simulations) and **dynamical technique.**

Entanglement

State $|\psi>$ of a pair of quantum systems *A* and *B* is called entangled, if although the Hillbert space is of a structure $\mathcal{H} = \mathcal{H}_A \otimes \mathcal{H}_B$, but the state of the system cannot be factorized: $|\psi > \neq |\psi_A > \otimes |\psi_B >$

According to Schmidt decomposition theorem any state $|\psi>_{AB}$ of a pair of quantum systems *A* and *B* can be expanded as:

$$|\psi\rangle_{AB} = \sum_{i,\mu} a_{i\mu} |i\rangle_A |\mu\rangle_B$$

There are many ways for measuring entanglement of mixed state and the quantum nature of the correlations, such as: **concurrence (Hill and Wootters, *PRL* 78 ,1997; Wootters, *ibid. 80* ,1998); negativity (Vidal, Werner, PRA 65, 2002); quantum discord (Ollivier, Zurek, PRL 88, 2001; Dakic, Vedral, Brukner, PRL 105, 2010); entanglement fidelity (Schumacher, PRA 54, 1996; Barnum, Nielsen, Schumacher, PRA 57,1998)…**

Quantum Entanglement Measures - Concurrence & Negativity

Concurrence $C(\rho)$ quantifies PAIRWISE entanglement for a density matrix ρ of TWO QUBITS [5, 6] is defined for positive Hermitian matrix

$$R \equiv \sqrt{\rho}\tilde{\rho}\sqrt{\rho} = \sqrt{\rho}(\sigma^y \otimes \sigma^y)\rho^*(\sigma^y \otimes \sigma^y)\sqrt{\rho},$$

$$\rho = \frac{1}{Z}\sum_{k=1}^{16} \exp(-E_k/T)|\psi_k\rangle\langle\psi_k|,$$

with eigenvalues $\lambda_1^2 \geqslant \cdots \geqslant \lambda_4^2$ **in the following way:**

$$C = \max\{\lambda_1 - \lambda_2 - \lambda_3 - \lambda_4, 0\}$$

If we have many spins one can reduce density matrix $\rho_{12} = Tr_3\rho$

and calculate concurrence for ρ_{12}

[5] Hill and Wootters, *PRL* 78, 5022 (1997); Wootters, *ibid. 80, 2245* (1998).

[6] Arnesen et al., *PRL 87, 017901 (2001);* Wang et al., *PRA 64, 012313* (2001) ; *J. Phys. A 34, 11307 (2001).*

For spin-1 system the degree of pairwise entanglement, measured in terms of the negativity *Ne*, can be employed to evaluate the thermal state of concern [Vidal, Werner, PRA, 2002]. The negativity of a state is defined as

$$Ne = \sum_i | \mu_i |,$$

where μ_i -s are negative eigenvalues of ρ^{T_1} and T_1 denotes the partial pair wise transpose with respect to the first system, i.e., for bipartite system in state ρ it is defined as

$$\langle i_1, j_2 | \rho^{T_1} | k_1, l_2 \rangle \equiv \langle k_1, j_2 | \rho | i_1, l_2 \rangle,$$

for any orthonormal but fixed basis. This definition is equivalent to

$$Ne = \frac{|| \rho^{T_1} ||_1 - 1}{2},$$

For non-entangled states negativity vanishes, while *Ne*>0 gives a computable measure of thermal entanglement.

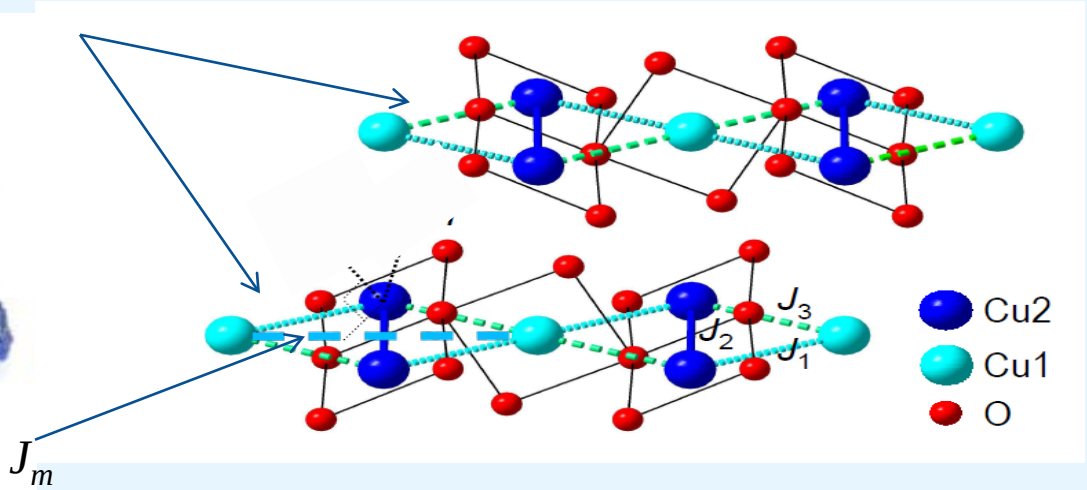
where $|| \rho^{T_1} ||_1$ is trace norm of ρ^{T_1} $\left(\|\rho\|_1 = Tr\sqrt{\rho^\dagger \rho} \right)$

For non-entangled states negativity vanishes, while *Ne*>0 gives a computable measure of **thermal entanglement.**

Natural mineral azurite $Cu_3(CO_3)_2(OH)_2$

Two equivalent but differently oriented chains

Azurite



Generalized distorted diamond chain geometry
(*C* and *H* atoms are not shown)

Cu1 ions (monomeric units) are coupled to each other by means of oxygen *(Cu-O-Cu)*
Cu2 are dimeric units

Experimental Observation of the 1/3 Magnetization Plateau in the Diamond-Chain Compound $Cu_3(CO_3)_2(OH)_2$

H. Kikuchi,[1] Y. Fujii,[1] M. Chiba,[1] S. Mitsudo,[2] T. Idehara,[2] T. Tonegawa,[3] K. Okamoto,[4] T. Sakai,[5,*] T. Kuwai,[6] and H. Ohta[7]

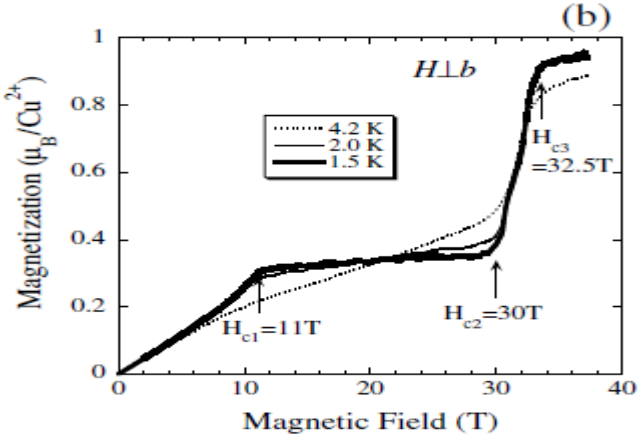


FIG. 2. The high field magnetization curves of $Cu_3(CO_3)_2 \times (OH)_2$ measured below 4.2 K. The magnetic field was applied along the b axis (a) and perpendicular to the b axis (b), respectively.

Spin-1/2 Ising-Heisenberg diamond chain

- $J_1 : J_2 : J_3 = 1 : 2 : (-0.5)$, $J_m = 0$ [18]
- $J_1 : J_2 : J_3 : J_m = 0.018 : 1 : (-0.36) : 0.18$ [19]
- $J_1 : J_2 : J_3 : J_m = 1 : 3 : 0.7 : 0.068$ [20]

[18] Gu and Su, *PRB* **75**, 174437(2007).
[19] Rule et al.,*PRL* **100**, 117202 (2008).
[20] Jeschke et al., *PRL* **106**, 217201 (2011).

In our discussion we will stop on symmetrical case and investigate different regimes depending on J_2, $J_1 = J_3 = J$, J_m and distorted diamond chain model $J_1 \neq J_3$.

We studied **magnetic plateaus** of **natural azurite** by means of variational mean-field like treatment based on Gibbs-Bogoliubov inequality **[N.A., Lazaryan, Nalbandyan, Eur. Phys. J. B 85, 2012]** and quantum entanglement properties of the distorted diamond chain model.

Eur. Phys. J. B (2012) 85: 223

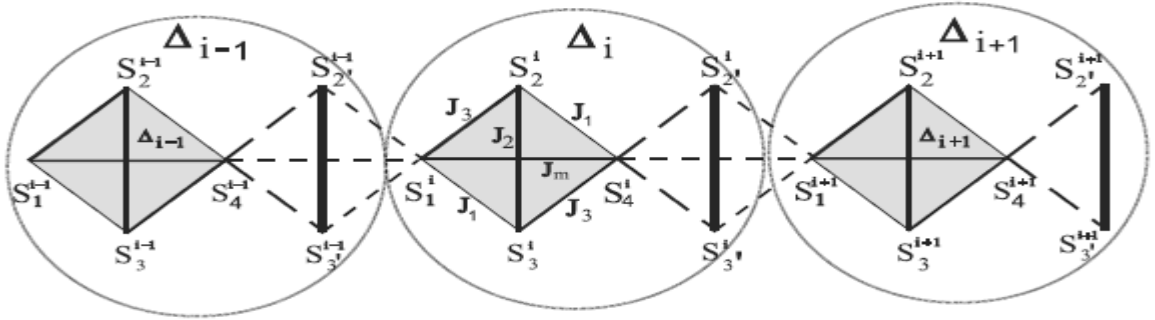


Fig. 2. Each Δ_i cluster consists of one rectangle of $\vec{S}_1^i$, $\vec{S}_2^i$, $\vec{S}_3^i$, $\vec{S}_4^i$ sites (grey rectangle) and dimer of $\vec{S}_{2'}^i$, $\vec{S}_{3'}^i$ sites (bold line).

The Hamiltonian for the distorted diamond chain

$$H = \sum_i \left[J_1 \boldsymbol{\alpha}_i - \frac{h}{2} \left(S_1^{iz} + S_4^{iz} \right) - h \left(S_2^{iz} + S_3^{iz} \right) \right]$$

where

$$\boldsymbol{\alpha}_i = \vec{S}_2^i \vec{S}_3^i + \delta_m \vec{S}_1^i \vec{S}_4^i + \delta_2 (\vec{S}_1^i \vec{S}_3^i + \vec{S}_2^i \vec{S}_4^i) + \delta_3 (\vec{S}_1^i \vec{S}_2^i + \vec{S}_3^i \vec{S}_4^i)$$

$$\delta_2 = J_1/J_2, \quad \delta_3 = J_3/J_2 \text{ and } \delta_m = J_m/J_2$$

Spin-1/2 Ising-Heisenberg diamond chain

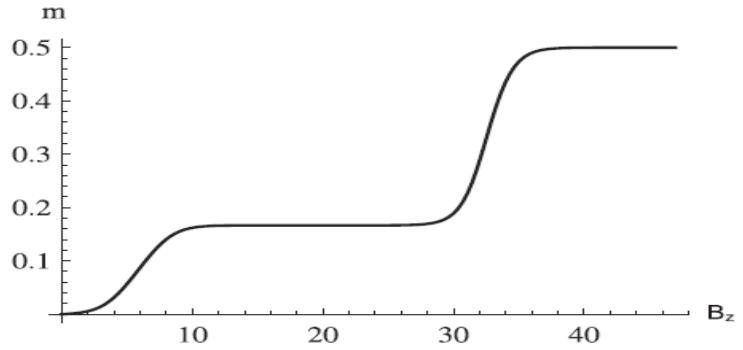


Fig. 3. Magnetization m (in units of $g\mu_B$) of the cluster versus external magnetic field B_z (Tesla) for $J_2 = 33$ K, $J_1 = 15.51$ K, $J_3 = 6.93$ K, $J_m = 4.62$ K at and $T = 1.3$ K.

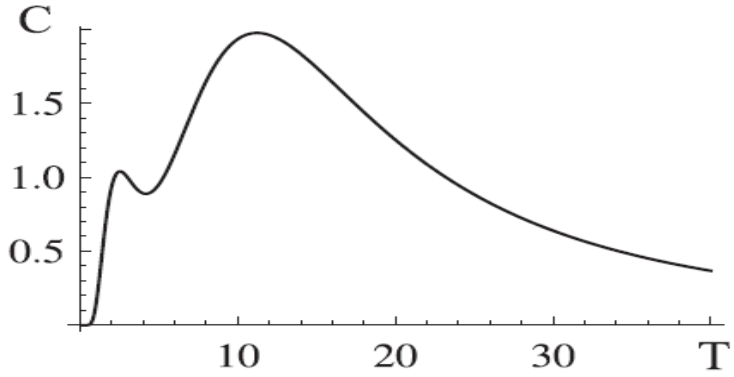


Fig. 6. Zero field specific heat versus temperature.

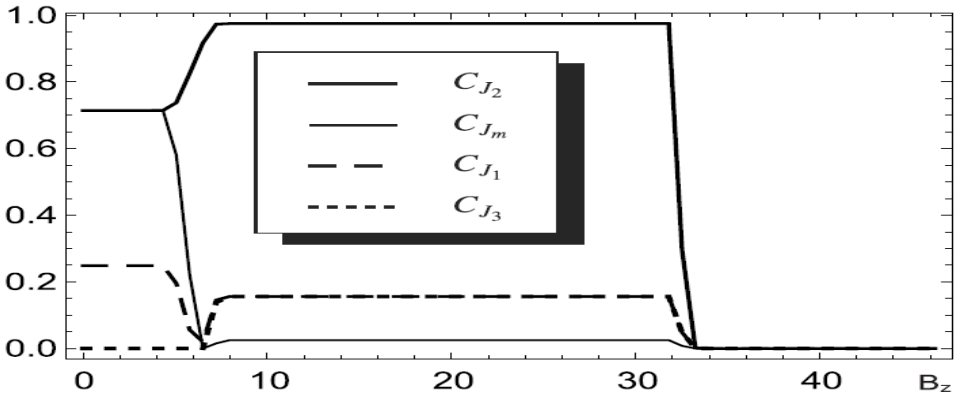
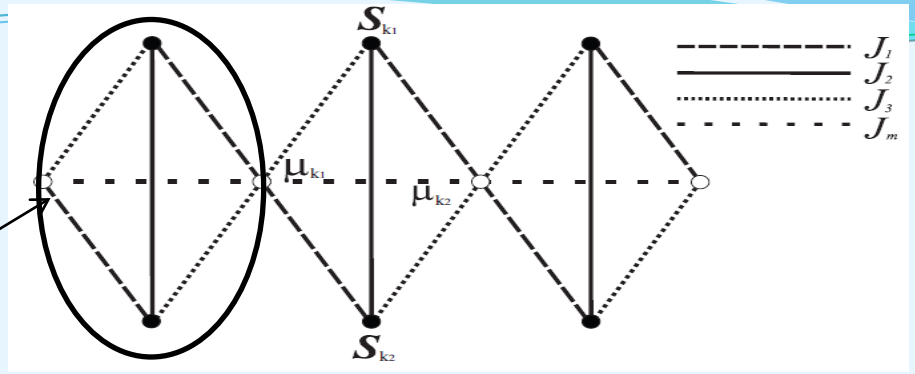


Fig. 7. The concurrences $C_{J_2}, C_{J_1}, C_{J_3}$ and C_{J_m} versus external magnetic field B_z (Tesla) at $T = 0.1$ K for $J_2 = 33$ K, $J_1 = 15.51$ K, $J_3 = 6.93$ K, $J_m = 4.62$ K.

Spin-1/2 Ising-Heisenberg diamond chain



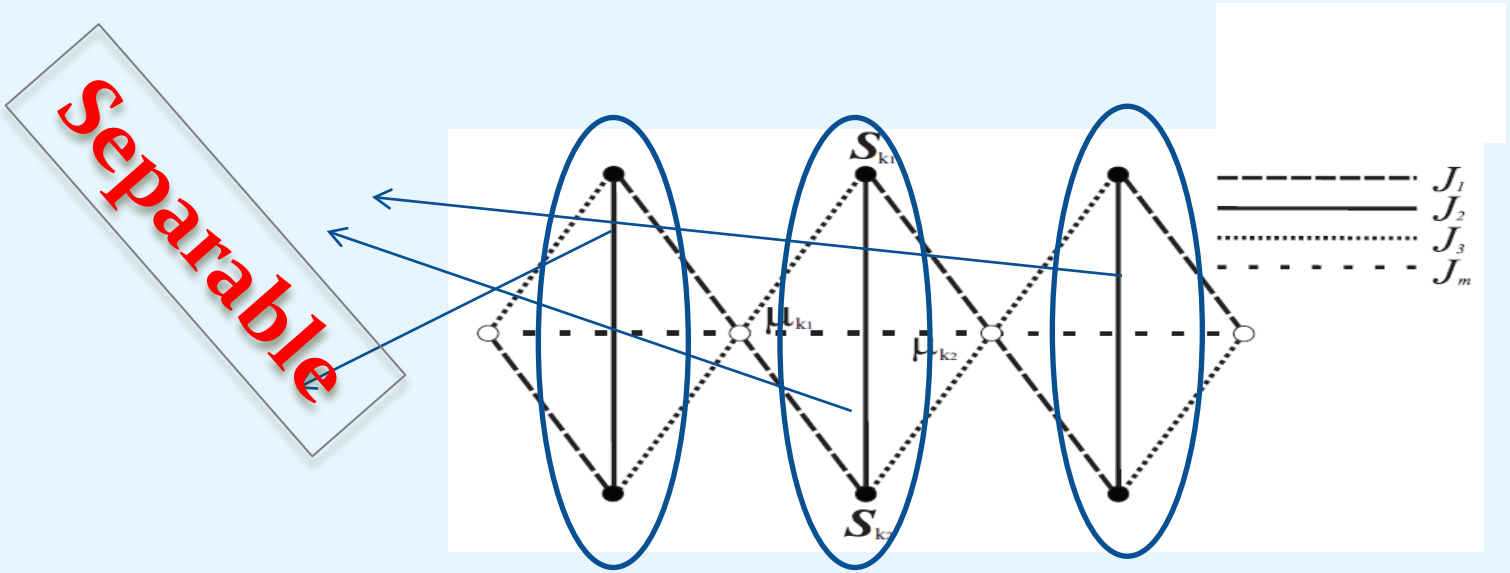
(k-1)-th cluster

A cross-section of a generalized distorted diamond chain (*k* labels the number of the cluster). The empty and full circles denote lattice positions of the Heisenberg and Ising spins (within the proposed Ising-Heisenberg model), respectively. Solid lines schematically reproduce the Heisenberg (J_2) interactions between dimeric units, while the broken ones label the interactions.

General Hamiltonian of this system is defined as (the interchain interaction of the monomers of one chain with the dimers of its adjacent chains through a CO_3 bridge is neglected)

$$\mathcal{H} = \sum_{k=1}^{N} \mathcal{H}_k = \sum_{k=1}^{N} \Big[J_2 \mathbf{S}_{k_1} \mathbf{S}_{k_2} + \mu_{k_1}^z (J_3 S_{k_1}^z + J_1 S_{k_2}^z) + \mu_{k_2}^z (J_1 S_{k_1}^z + J_3 S_{k_2}^z) + J_m \mu_{k_1}^z \mu_{k_2}^z - H \Big(S_{k_1}^z + S_{k_2}^z + \frac{\mu_{k_1}^z + \mu_{k_2}^z}{2} \Big) \Big],$$

Spin-1/2 Ising-Heisenberg diamond chain



Due to the **classical** character of Ising-type interactions the states of two neighboring Heisenberg dimers are **separable**, *i.e.* **not entangled**. Using this fact, we can study the entanglement of each such “subdivision" of the cluster individually by tracing out Ising-type spins. Thus, when investigating entanglement properties of the system, we will be interested in only one cluster.

Spin-1/2 Ising-Heisenberg diamond chain

$$\mathcal{H} = \sum_{i=1}^{N} J(\boldsymbol{S}_{a,i}, \boldsymbol{S}_{b,i})_{\Delta} + J_1\left(S^z_{a,i} + S^z_{b,i}\right)(\mu_i + \mu_{i+1})$$
$$- h_0\left(S^z_{a,i} + S^z_{b,i}\right) - \frac{h}{2}(\mu_i + \mu_{i+1}),$$

where $(\boldsymbol{S}_{a,i}, \boldsymbol{S}_{b,i})_{\Delta} = S^x_{a,i} S^x_{b,i} + S^y_{a,i} S^y_{b,i} + \Delta S^z_{a,i} S^z_{b,i}$ corresponds to the interstitial anisotropic Heisenberg spins coupling (J and Δ), while the nodal-interstitial (dimer-monomer) spins are representing the Ising-type exchanges (J_1). The Hamiltonian also includes a longitudinal external magnetic field h_0 acting on Heisenberg spins and a magnetic h acting on Ising spins. For convenience, we will consider the case $h_0 = h$.

The quantum Heisenberg spin coupling can be expressed using matrix notation. We have

$$(\boldsymbol{S}_{a,i}, \boldsymbol{S}_{b,i})_{\Delta} = \begin{bmatrix} \frac{\Delta}{4} & 0 & 0 & 0 \\ 0 & -\frac{\Delta}{4} & \frac{1}{2} & 0 \\ 0 & \frac{1}{2} & -\frac{\Delta}{4} & 0 \\ 0 & 0 & 0 & \frac{\Delta}{4} \end{bmatrix}$$

Taking into account the symmetries, when $J_1 = J_3 = J$ and Hillbert space structure we construct the eigenstates of H_k (2-nd and 4-th are Heisenberg spins $\boldsymbol{S}_{k1}$ and $\boldsymbol{S}_{k2}$, 1-st and 3-rd - μ_{k1} and μ_{k2} respectively) and find corresponding eigenvalues $(J_m = 0)$ **[Rojas, Ananikian, de Souza, PRA 86, 2012; Ananikian,Ananikyan, Chakhmakhchyan, Rojas, J. Phys.: CM 24, 2012; Torrico, Rojas, Souza, Ananikian, EPL 108 (201]**

$$\mathcal{E}_1(\mu_i,\mu_{i+1}) = \frac{J\Delta}{4} + \left(J_1 - \frac{h}{2}\right)(\mu_i + \mu_{i+1}) - h,$$
$$\mathcal{E}_2(\mu_i,\mu_{i+1}) = \frac{J}{2} - \frac{J\Delta}{4} - \frac{h}{2}(\mu_i + \mu_{i+1}),$$
$$\mathcal{E}_3(\mu_i,\mu_{i+1}) = -\frac{J}{2} - \frac{J\Delta}{4} - \frac{h}{2}(\mu_i + \mu_{i+1}),$$
$$\mathcal{E}_4(\mu_i,\mu_{i+1}) = \frac{J\Delta}{4} - \left(J_1 + \frac{h}{2}\right)(\mu_i + \mu_{i+1}) + h,$$

$$|\varphi_1\rangle = |\uparrow\uparrow\rangle,$$
$$|\varphi_2\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle),$$
$$|\varphi_3\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle),$$
$$|\varphi_4\rangle = |\downarrow\downarrow\rangle.$$

$$\varrho(\mu,\mu') = \sum_{i=1}^{4} \mathrm{e}^{-\beta\varepsilon_i(\mu,\mu')} |\varphi_i\rangle\langle\varphi_i|$$

$$Z_N = \sum_{\{\mu\}} w(\mu_1,\mu_2)\cdots w(\mu_N,\mu_1)$$

$$w(\mu,\mu') = \mathrm{tr}_{ab}[\varrho(\mu,\mu')] = \sum_{i=1}^{4} \mathrm{e}^{-\beta\varepsilon_i(\mu,\mu')}$$

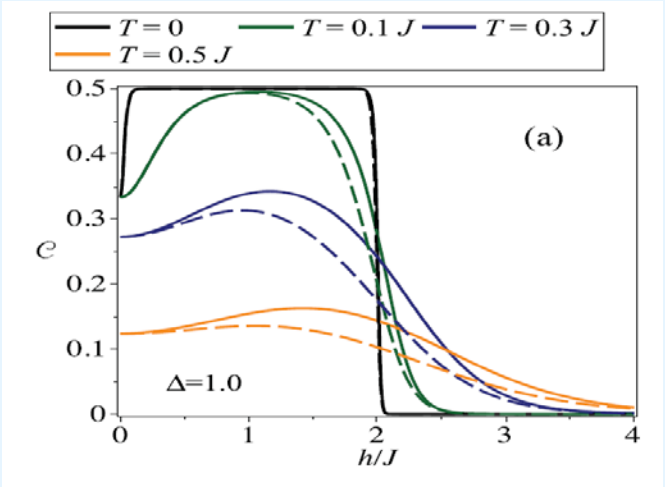
Spin-1/2 Ising-Heisenberg diamond chain

The concurrence could be expressed in terms of a matrix R:

$$R = \rho \cdot (\sigma^y \otimes \sigma^y) \cdot \rho^* \cdot (\sigma^y \otimes \sigma^y)$$

Hill and Wootters, *PRL* 78, 5022 (1997); Wootters, *ibid.* 80, 2245 (1998).
Arnesen et al., *PRL 87, 017901 (2001);*
Wang et al., *PRA 64, 012313* (2001) ; *J. Phys. A 34, 11307 (2001).*

$$(\boldsymbol{S}_{a,i}, \boldsymbol{S}_{b,i})_\Delta = S^x_{a,i} S^x_{b,i} + S^y_{a,i} S^y_{b,i} + \Delta S^z_{a,i} S^z_{b,i}$$



Concurrence against external magnetic

Spin-1/2 Ising-Heisenberg diamond chain

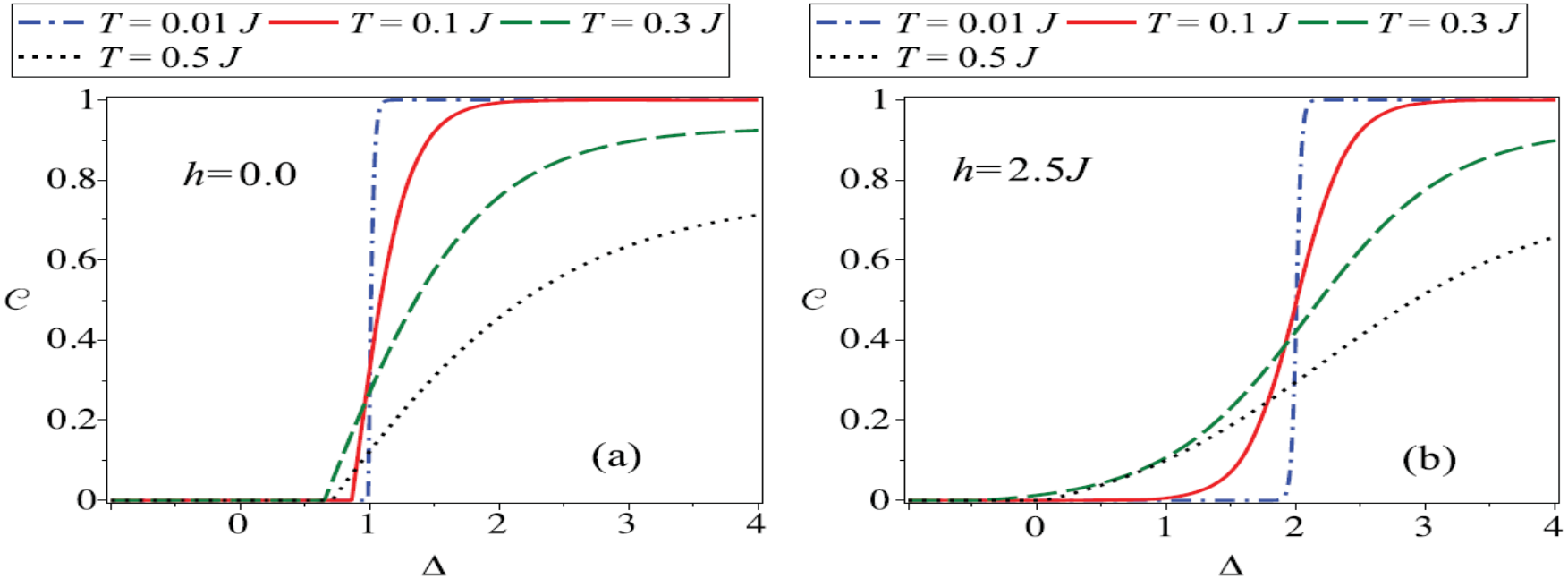
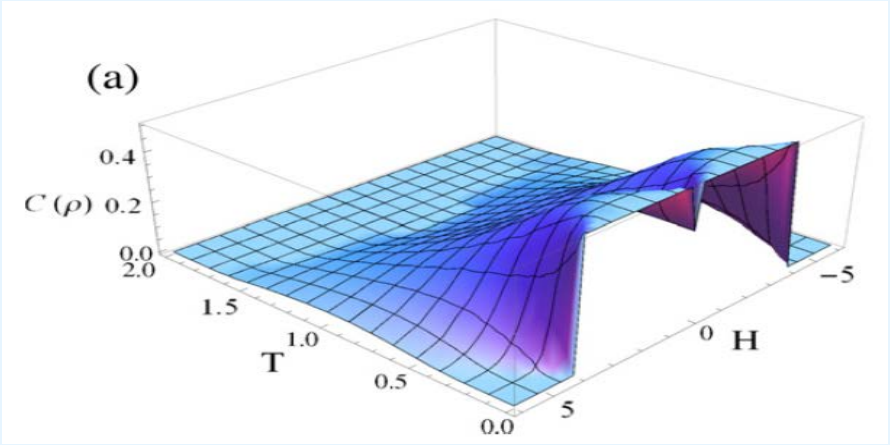
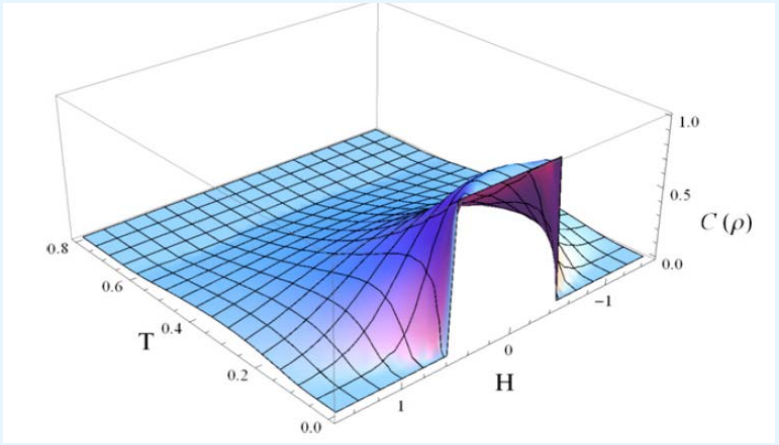


FIG. 7. (Color online) Concurrence as a function of anisotropic parameter Δ: (a) $h/J = 0$ and (b) $h/J = 2.5$ with different fixed values of temperature.

Spin-1/2 Ising-Heisenberg diamond chain





$J_2 = 2$ and $J = 2$

$J_2 = 1$ and $J = 1.5$ and $J_m = 1.5$

Concurrence $C(\rho)$ versus magnetic field H and temperature T

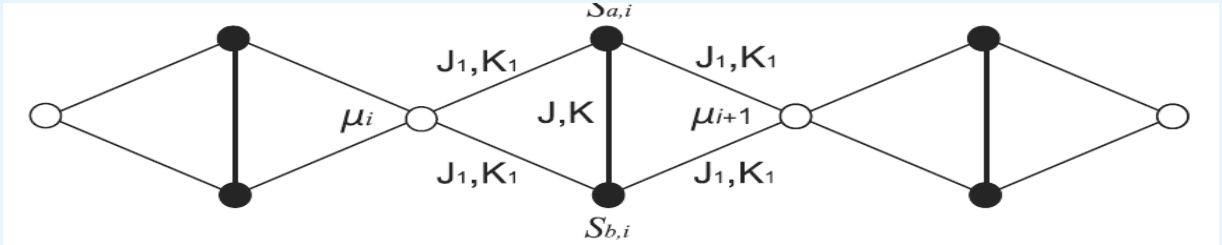
Spin-1 Ising-Heisenberg on a diamond chain: Ni- containing complex $[Ni_3(fum)_2\ (\mu_3OH)_2(H_2O_4)]_n \bullet (2H_2O)_n$

The second part of my talk will focus on **Ni-containing complexes** on a diamond chain $[Ni_3(fum)_2\ (\mu_3OH)_2(H_2O_4)]_n \bullet (2H_2O)_n$.

An infinite diamond chain is organized by interstitial-interstitial and nodal-interstitial (dimer-monomer) site couplings. Two interstitial particles are coupled through spin 1 Heisenberg interaction or simply two-qubit Heisenberg, which could be responsible for the emergence of thermal entanglement. These two-qubit Heisenberg operators are interacted with two spin1 nodal Ising spins. I'd like to mention the articles **[Hovhannisyan ,N.A., Kenna, Physica A (2016); Strecka, Hovhannisyan, N. A., CM 28 (2016); Abgaryan, N.A., Ananikyan, Hovhannisyan, Solid State Com.224 (2015)]** where it was done. The first two articles there were considered the general properties of magnetization plateaus. And third we studied the thermal negativity (entanglement) of the dipolar exchange interaction with crystal or single-ion anisotropy field and compare it with experimental data **[Konar, Mukherjee, Zangrando, etc., Angew. Chem. Ind. Ed. 41 (2002)]**

Spin-1 Ising-Heisenberg on a diamond chain: Ni- containing complex

$[Ni_3(fum)_2\ (\mu_3OH)_2(H_2O_4)]_n \bullet (2H_2O)_n$



$$\mathcal{H}_i = J(S^x_{a,i}S^x_{b,i} + S^y_{a,i}S^y_{b,i} + \Delta S^z_{a,i}S^z_{b,i}) + K(S^x_{a,i}S^x_{b,i} + S^y_{a,i}S^y_{b,i} + \Delta_1 S^z_{a,i}S^z_{b,i})^2$$
$$+ J_1\left(S^z_{a,i} + S^z_{b,i}\right)\left(\mu^z_i + \mu^z_{i+1}\right) + D\left[(S^z_{a,i})^2 + (S^z_{b,i})^2\right] + D_1\frac{(\mu^z_i)^2 + (\mu^z_{i+1})^2}{2}$$
$$+ K_1\left[(S^z_{a,i}\mu^z_i)^2 + (S^z_{b,i}\mu^z_i)^2 + (S^z_{a,i}\mu^z_{i+1})^2 + (S^z_{b,i}\mu^z_{i+1})^2\right] - H_{\mathrm{H}}\left(S^z_{a,i} + S^z_{b,i}\right) - H_{\mathrm{I}}\frac{\mu^z_i + \mu^z_{i+1}}{2}.$$

In this equation, $S^\alpha_{a,i}$, $S^\alpha_{b,i}$ $(\alpha = x, y, z)$ and μ^z_i are the components of Heisenberg and Ising spin-1 operators, J is the bilinear XXZ Heisenberg interaction term, K is the biquadratic XXZ-interaction term parameter, Δ and Δ_1 are anisotropy parameters, J_1 is the interaction parameter between the nearest-neighboring Ising and Heisenberg spins, D (D_1) is the single-ion anisotropy parameter of Heisenberg (Ising) spins and the parameter K_1 is the analogue of a biquadratic Ising interaction

Spin-1 Ising-Heisenberg on a diamond chain: Ni- containing complex

$[Ni_3(fum)_2\ (\mu_3OH)_2(H_2O_4)]_n \bullet (2H_2O)_n$

$$m_{\mathrm{I}} = -\frac{\partial f}{\partial H_{\mathrm{I}}}, \qquad m_{\mathrm{H}} = -\frac{\partial f}{\partial H_{\mathrm{H}}},$$

$$q_{\mathrm{I}} = \frac{\partial f}{\partial D_1}, \qquad q_{\mathrm{H}} = \frac{\partial f}{\partial D}.$$

$$S_x = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad S_y = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix},$$

$$S_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}.$$

$$[\mathcal{H}_i,\ \mu_j^z] = [\mathcal{H}_i,\ S_{a,j}^z + S_{b,j}^z] = 0$$

$$[\mathcal{H}_i,\ (S_{a,i}^z)^2 + (S_{b,i}^z)^2] = 0, \text{ only when } J = K\Delta_1$$

Finally, for the total magnetization and quadrupole moment of per site, we get

$$m = \frac{1}{3}m_{\mathrm{I}} + \frac{2}{3}m_{\mathrm{H}}, \qquad q = \frac{1}{3}q_{\mathrm{I}} + \frac{2}{3}q_{\mathrm{H}}.$$

$$j = \frac{J}{J_1}, \qquad k_1 = \frac{K_1}{J_1}, \qquad d = \frac{D}{J_1}, \qquad h = \frac{H}{J_1}, \qquad t = \frac{T}{J_1}.$$

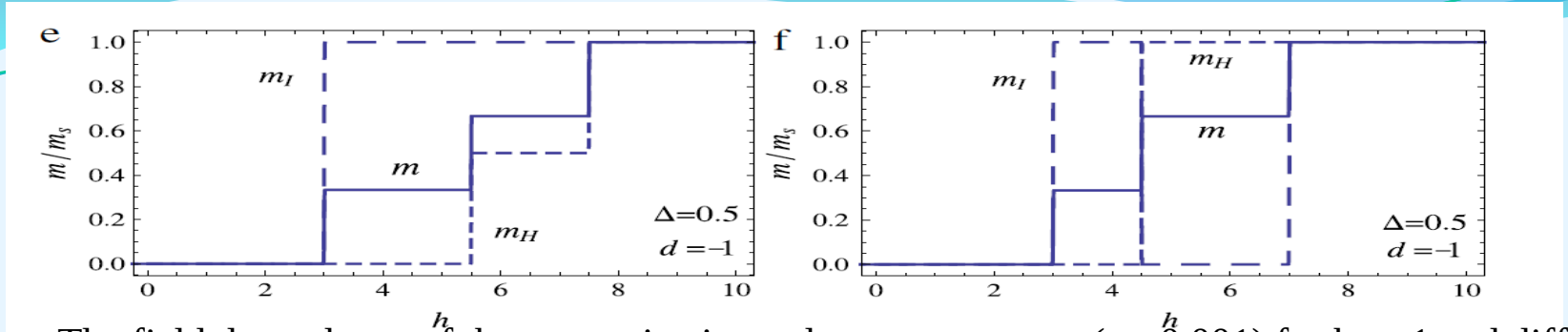


Figure: The field dependence of the magnetization at low temperature (t = 0.001) for k_1 = 1 and different values of the interaction parameter j, anisotropy parameter Δ and the single-ion anisotropy parameter d (e) j = −9, (f) j = −7.5.

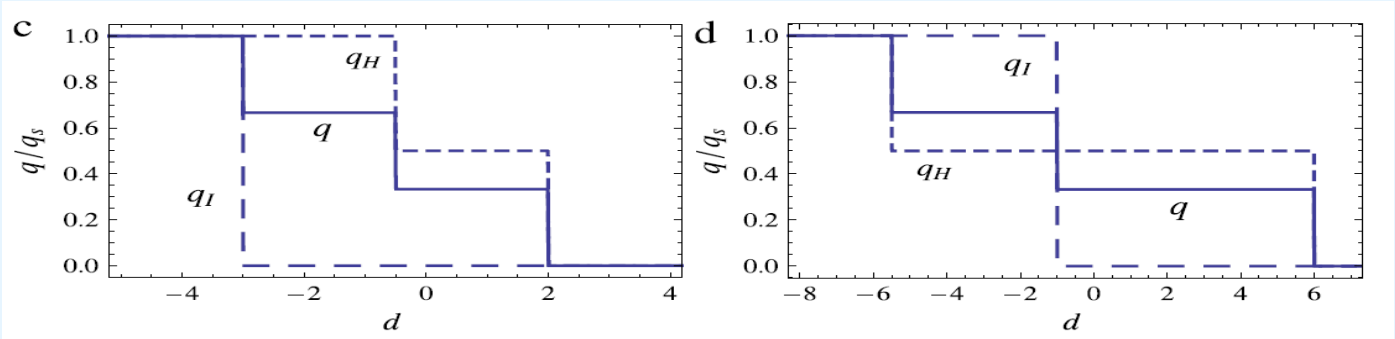
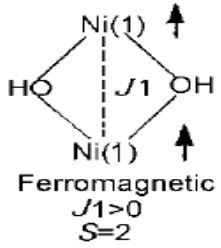
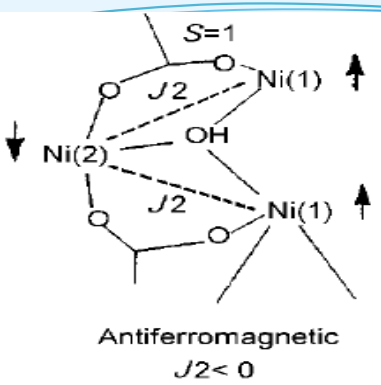
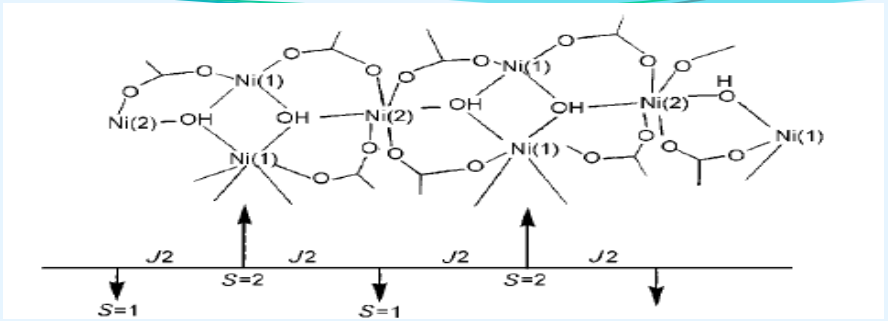


Figure: Single-ion anisotropy parameter dependence of the quadrupole moment for fixed values of Δ = 0.5, k_1 = 1.5, t = 0.001 and the absence of magnetic field (c) j = 1, (d) j = 3.

Spin-1 Ising-Heisenberg on diamond chain:Ni containing complex $[Ni_3(fum)_2\ (\mu_3OH)_2(H_2O_4)]_n \cdot (2H_2O)_n$







$$[Ni_3(fum)_2(\mu_3-OH)_2(H_2O_4)]\cdot(2H_2O)$$

Abgaryan, N.A. , Ananikyan, Hovhannisyan, Solid State Com. 224, 15.

S. Konar, Angew. Chem. Ind. Ed. 41, 1561 (2002)

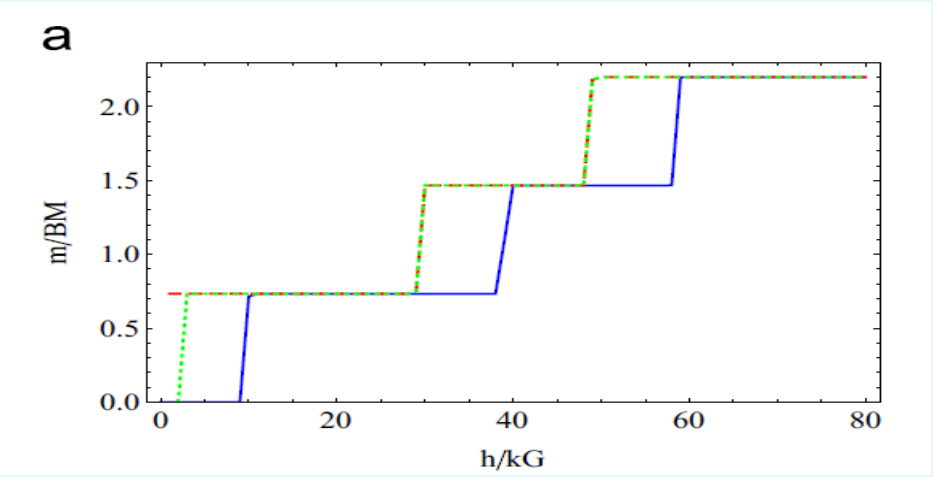
Experiment data: Ni (1) –Ni (1) ferromagnrtic and Ni (1) –Ni (2) antiferromagnrtic couplings.

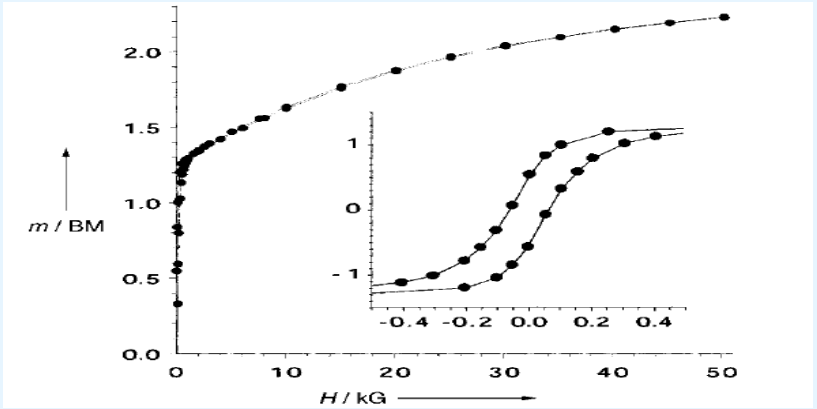
Spin-1 Ising-Heisenberg on a diamond chain:Ni- containing complex $[Ni_3(fum)_2\ (\mu_3OH)_2(H_2O_4)]_n \cdot (2H_2O)_n$

$$\mathcal{H}_i = J\vec{S}_{a,i}\vec{S}_{b,i} + J_1(S^z_{a,i}+S^z_{b,i})(\sigma^z_i+\sigma^z_{i+1}) + D_H((S^z_{a,i})^2+(S^z_{b,i})^2) + \frac{D_I}{2}\left((\sigma^z_i)^2+(\sigma^z_{i+1})^2\right) - h_H g\mu_B(S^z_{a,i}+S^z_{b,i}) - \frac{h_I g\mu_B}{2}(\sigma^z_i+\sigma^z_{i+1})$$

$$Z_N = \lambda_1^N + \lambda_2^N + \lambda_3^N$$

$$f = -\frac{1}{\beta}\lim_{N\to\infty}\frac{1}{N}\ln Z_N = -\frac{1}{\beta}\ln\lambda.$$





Low temperature (T= 0.01 K) magnetization curves in Bohr magneton units for $J_1 = D_I = 1\ cm^{-1}$, $J = 6\ cm^{-1}$, $D_H = 1\ cm^{-1}$ (dashed), $D_H = 2.25\ cm^{-1}$ (dotted), $D_H = 4\ cm^{-1}$ (solid)

Spin-1 Ising-Heisenberg on a diamond chain: Ni- containing complex $[Ni_3(fum)_2\ (\mu_3OH)_2(H_2O_4)]_n \cdot (2H_2O)_n$

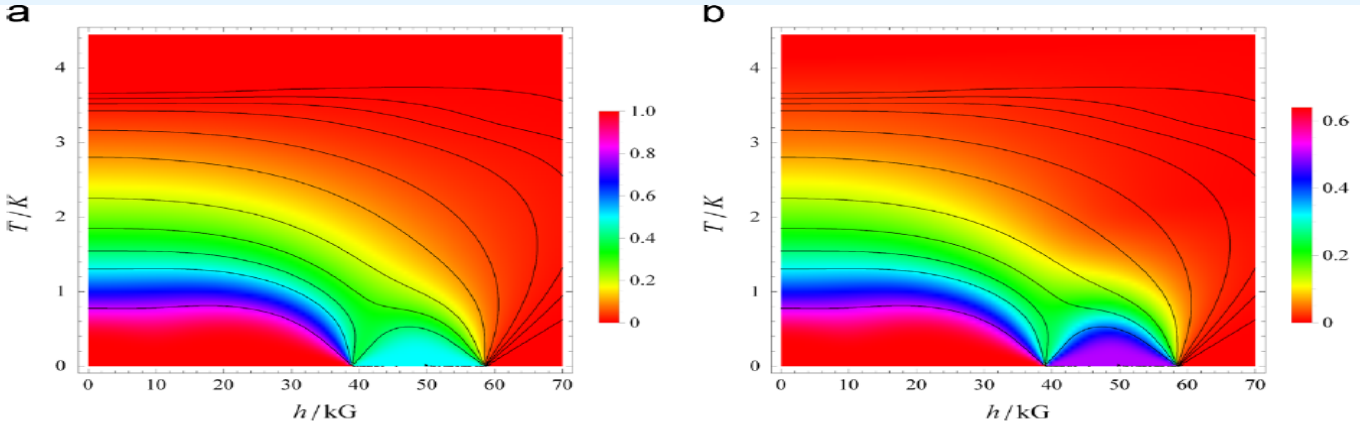
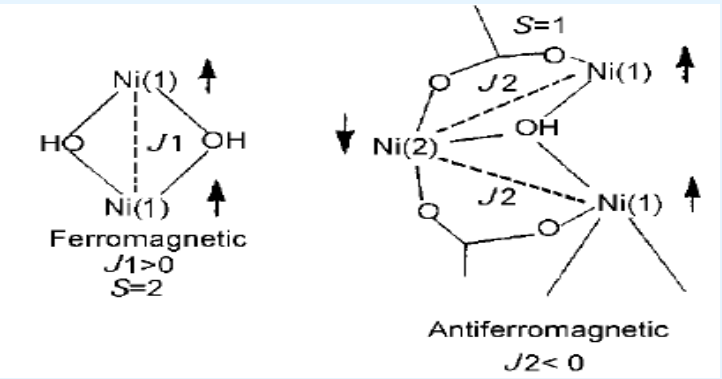


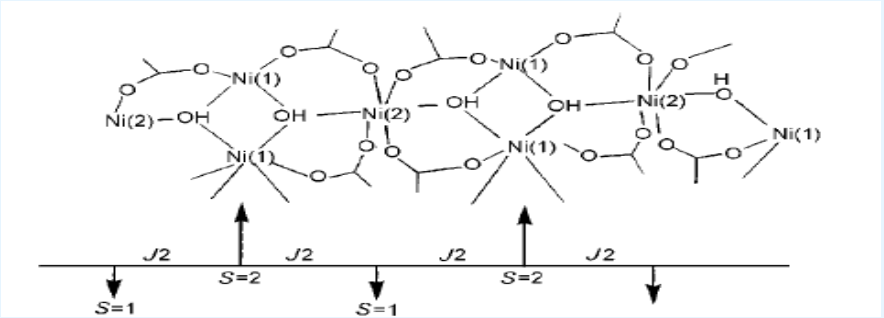
Fig. 6. Density plot of negativity when (a) $J = 2\ \mathrm{cm}^{-1}$, $D_H = 0$ and $J_1 = D_I = 1\ \mathrm{cm}^{-1}$ with the lines of constant entanglement at $Ne = 0, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.8$ and (b) $J = -6\ \mathrm{cm}^{-1}$, $D_H = 4\ \mathrm{cm}^{-1}$ and $J_1 = D_I = 1\ \mathrm{cm}^{-1}$ with the lines of constant entanglement at $Ne = 0, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6$.

We also find that the model is principally applicable for explanation of magnetization process of the homometallic molecular ferrimagnet $[Ni_3(fum)_2 - (\mu_3 - OH)_2(H_2O)_4]_n \cdot (2H_2O)_n$. The qualitative description is made possible by the introduction of the single-ion anisotropy of Heisenberg spins. More detailed experimental results regarding the plateau region ($h \approx 0.4$ kG at $T = 2$ K) would clarify the role of the single-ion anisotropy in the magnetization process.

Magnetization plateaus in spin-1 Ising - Heisenberg model on a diamond chain

$[Ni_3(fum)_2(\mu_3-OH)_2(H_2O_4)]\bullet(2H_2O)$





Abgaryan, Ananikian, Ananikyan, Hovhannisyan, Quantum transitions, magnetization, entanglement (spin-1 Ising-Heisenberg diamond chain), Solid State Com. 224, 15; 203, 5 (2015)

Hovhannisyan, Ananikian, Kenna, Partition function zeros, magnetization plateaus (spin-1 Ising-Heisenberg diamond chain), Physica A (2016).

Hovhannisyan, Strecka, Ananikian, Exactly solvable spin-1 Ising-Heisenberg diamond chain (second-neighbor interaction between nodal spins), J. Phys.: Condens. Matter 28 (2016) 085401

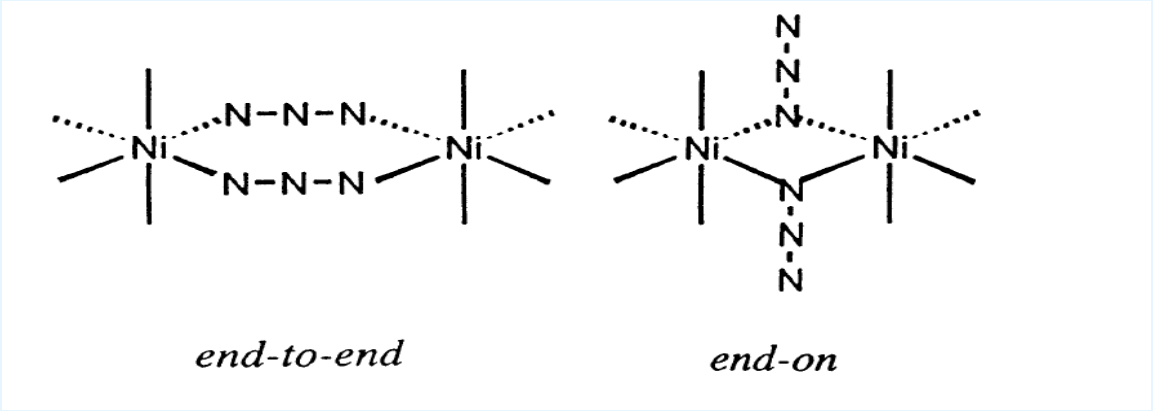
Plateaus in Spin 1 $[Ni(NN'\text{-dmen})(\mu\text{-}N_3)_2]_n$ Polymer

Analyze the magnetization process and thermal negativity behavior of $[Ni(NN'\text{-dmen})(\mu\text{-}N_3)_2]_n$ polymer (low temperature) :

J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Corte´s, Luis Lezama, T. Rojo, Coordination Chem. Rev. 193–195, 1027 (1999);
J. Ribas, M. Monfort, I. Resino, X. Solans, P. Rabu, F. Maingot, M. Drillon, Angew. Chem. Int. Ed. Engl. 35, 2520 (1996);
F. A. Mautner, M. Scherzer, C. Berger, R. C. Fischer, R. Vicente, S. S. Massoud, Polyhedron 85, 329 (2015).

Plateaus in Spin 1 $[Ni(NN'\text{-}dmen)(\mu\text{-}N_3)_2]_n$ Polymer

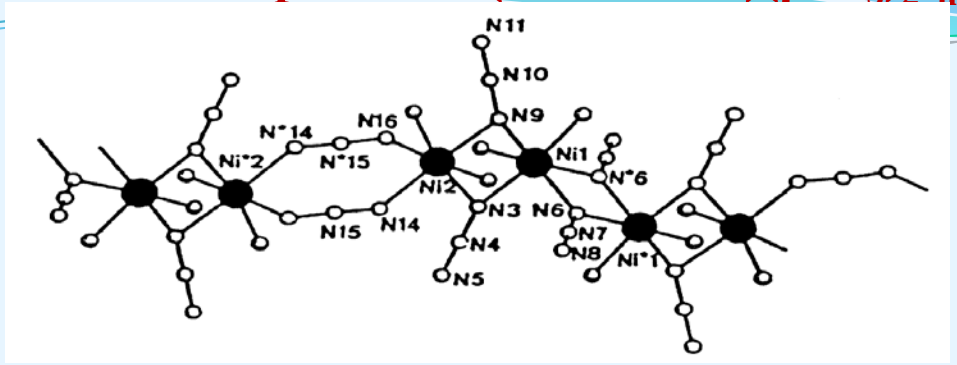
The azide anion is a good bridging ligand for divalent metal ions. It may give end-to-end (1,3) or end-on (1,1) coordination modes



The end-to-end (EE) coordination mode gives antiferromagnetic coupling while the end-on (EO) gives ferromagnetic coupling.

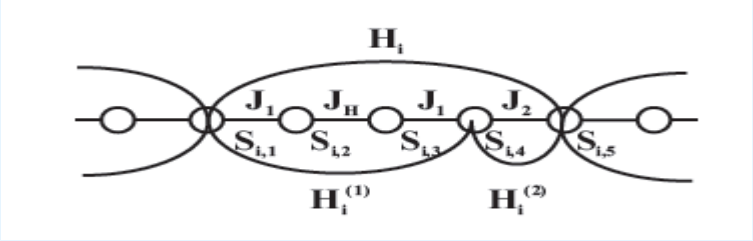
In order to compare experimental magnetic results reported in the literature, it is necessary to establish the general spin-1 Heisenberg-Ising Hamiltonian with bilinear (dipolar J), biquadratic (quadrupolar K) exchange couplings, single-ion anisotropy (D) and magnetic (h) fields.

Plateaus in Spin 1 $[Ni\ (NN'\text{-}dmen)(\mu\text{-}N_3)_2]_n$ Polymer



Structure of 1D system with the F–F–F–AF azido bridging ligands set of polymer $[Ni(NN'\text{-}\ dmen)(\ \mu\text{-}N_3)_2]_n$

The antiferromagnetic coupling corresponds to the end-to-end (EE) coordination mode: J_{AF} = -120cm^{-1} (Heisenberg-type interaction), while ferromagnetic couplings ($J_{F\,1}$ = 20cm^{-1} and J_{F2} = 37cm^{-1} Ising-type interaction) corresponds to the end-on (EO) coordination mode. Due to the classical character of Ising-type interactions, the states of two neighboring blocks on the spin-1 Ising-Heisenberg model of the polymer are separable.



Plateaus in Spin 1 [Ni (NN'-dmen)(μ-N_3)$_2$]$_n$ Polymer

We calculated the susceptibility at zero external magnetic field for the same two block quantum (Heisenberg) system which includes the peak at lower temperatures. The best fit to the experimental data presented by Ribas et. al. was obtained by introducing a anisotropy parameter δ in the following way:

$$\vec{S}_i \vec{S}_j = \delta(S_i^x S_j^x + S_i^y S_j^y) + S_i^z S_j^z$$

where i and j are adjacent spins corresponding to coupling constants J_i or J_j.
The susceptibility and susceptibility times temperature for **δ =1.44** is shown in Figure

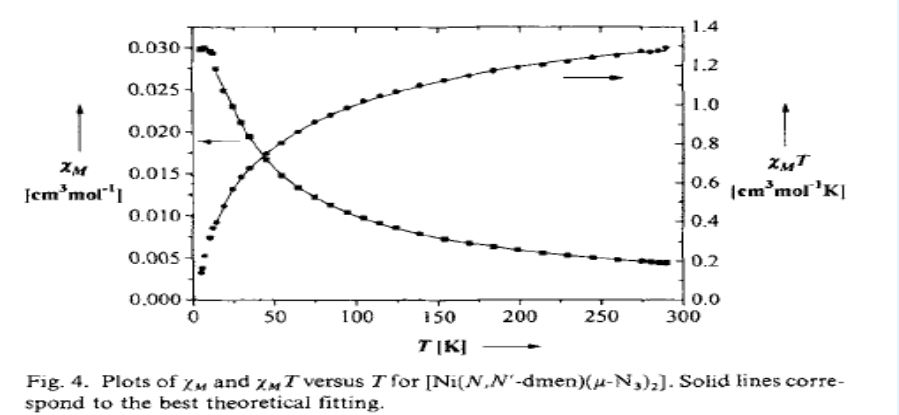
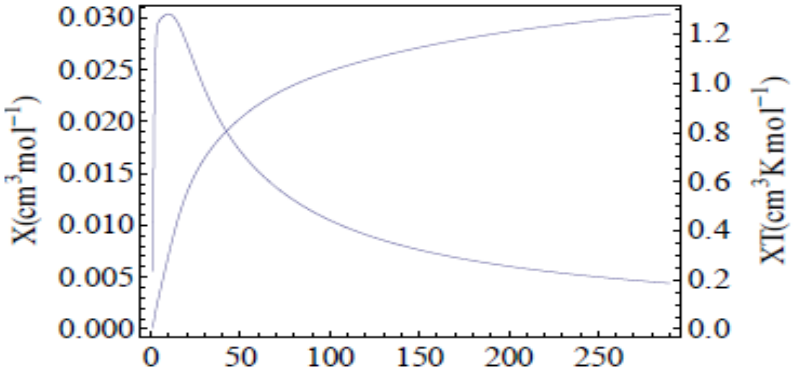


Fig. 4. Plots of χ_M and $\chi_M T$ versus T for [Ni(N,N'-dmen)(μ-N_3)$_2$]. Solid lines correspond to the best theoretical fitting.



Plateaus in Spin 1 $[Ni(NN'\text{-}dmen)(\mu\text{-}N_3)_2]_n$ Polymer

The theoretical model can be described: ***(F_1–AF—F_1—F_2)* (F_1–AF—F_1—F_2)*** or

• —F_1—•—AF—•—F_1—• —F_2—•—F_1—•—AF—•—F_1—• —F_2—•—F_1—•—AF—•

Using transfer-matrix methods on the spin-1 Ising-Heisenberg model of the polymer $[Ni(NN'\text{-}dmen)(\mu\text{-}N_3)_2]_n$ one can:

- ***Show that the free energy is represented as the sum of blocks $[Ni(NN'\text{-}dmen)(\mu\text{-}N_3)_2]_I$***
- ***Theoretically get different magnetization plateaus on the polymer***
- ***Obtain plateau of the second parameter via crystal field (D)***
  - ***Find the strong correlations between magnetic properties and quantum entanglement (negativity)***
- ***Find the thermal entanglement plateaus via exchange couplings of the quantum interactions***

Plateaus in Spin 1 $[Ni\ (NN'\text{-}dmen)(\mu\text{-}N_3)_2]_n$ Polymer

We obtain on the magnetic properties of the same polymer through introducing an exactly solvable model that truly describes the interaction characteristics of the spin-1 Ni-containing polymer at low temperatures. The susceptibility of our long Ising-Heisenberg model and Heisenberg eight spin quantum models are somewhat different. Moreover our best fit to the short systems experimental data was obtained by introducing an anisotropy parameter. Nevertheless the magnetization curves for the same parameters of the long Ising-Heisenberg and short quantum Heisenberg model are very similar see Figure

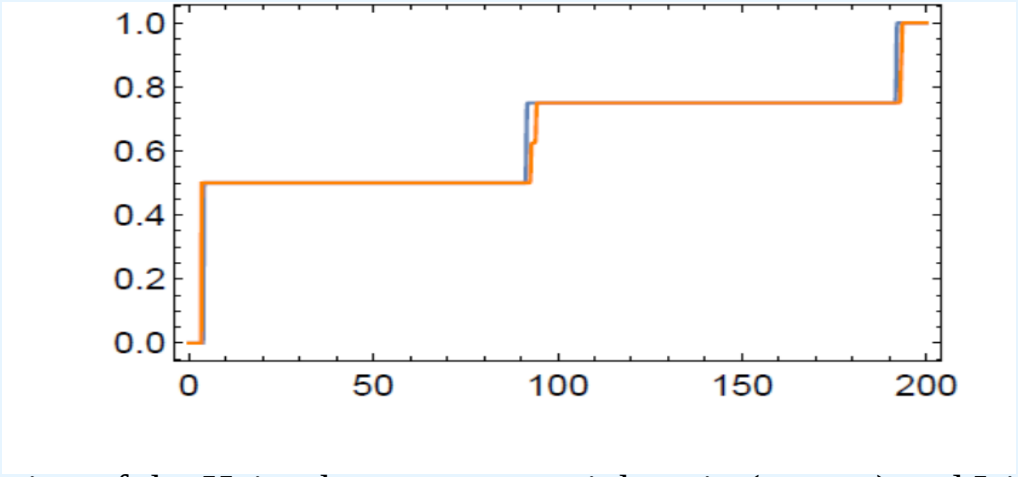


Fig. 2 Magnetization of the Heisenberg quantum eight spin (orange) and Ising-Heisenberg (blue) one.

SOLVABLE MODEL SPIN -1 HAMILTONIAN

$$H = -\sum_{i=1}^{N} J_H \vec{S}_{4i-2}.\vec{S}_{4i-1} + J_{I_1}(S^z_{4i-3}S^z_{4i-2} + S^z_{4i-1}S^z_{4i}) + J_{I_2}S^z_{4i}S^z_{4i+1} + g\mu_B h(\frac{1}{2}S^z_{4i-3} + S^z_{4i-2} + S^z_{4i-1} + S^z_{4i} + \frac{1}{2}S^z_{4i+1}) - D(\frac{1}{2}(S^z_{4i-3})^2 + (S^z_{4i-2})^2 + (S^z_{4i-1})^2 + (S^z_{4i})^2 + \frac{1}{2}(S^z_{4i+1})^2) \quad (1)$$

$J_{I_1} = 20cm^{-1}$, $J_{I_2} = 37cm^{-1}$, $J_H = -120cm^{-1}$, $D = -6cm^{-1}$

$g = 2.39$ Landé factor and $\mu_B = 4.667 \times 10^{-1} Tesla^{-1}cm^{-1}$

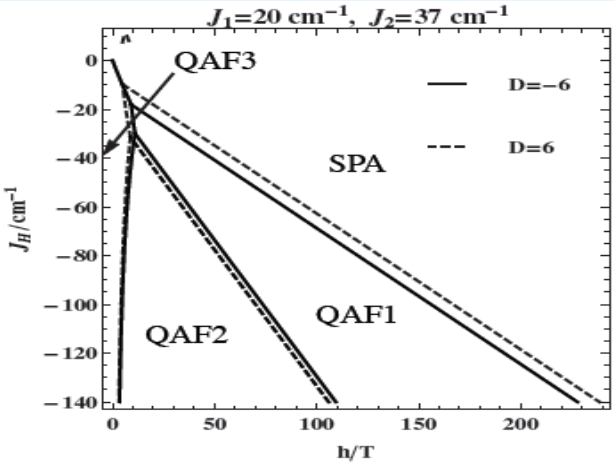
$K_B \approx 0.695\ cm^{-1}K^{-1}$; $H = \sum_{i=1}^{N} H_i$

$$H_i = -[J_H \acute{S}_{4i-2}.\acute{S}_{4i-1} + J_{I_1}(S^z_{4i-3}S^z_{4i-2} + S^z_{4i-1}S^z_{4i}) + J_{I_2}S^z_{4i}S^z_{4i+1} + g\mu_B h(\frac{1}{2}S^z_{4i-3} + S^z_{4i-2} + S^z_{4i-1} + S^z_{4i} + \frac{1}{2}S^z_{4i+1}) - D(\frac{1}{2}(S^z_{4i-3})^2 + (S^z_{4i-2})^2 + (S^z_{4i-1})^2 + (S^z_{4i})^2 + \frac{1}{2}(S^z_{4i+1})^2)]$$

Plateaus in Spin 1 $[Ni(NN'\text{-dmen})(\mu\text{-}N_3)_2]_n$ Polymer

- Saturated Paramagnetic Phase (SPA)
  $|SPA\rangle = \bigotimes_{i=1}^{N} |1,1,1,1\rangle_i$
  $m = 1$

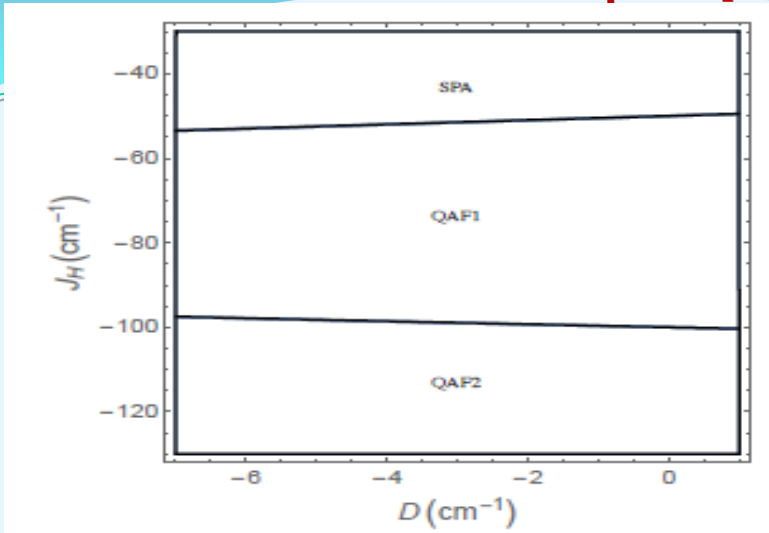
- Quantum Antiferromagnetic Phase (QAF1)
  $|QAF1\rangle = \bigotimes_{i=1}^{N} \frac{1}{\sqrt{2}}(|1,0,1,1\rangle - |1,1,0,1\rangle)_i$
  $m = \frac{3}{4}$



- Quantum Antiferromagnetic Phase (QAF2)
  $|QAF2\rangle = \bigotimes_{i=1}^{N} |1\rangle_i \otimes$
  $\left[\frac{2|J_H|}{\sqrt{8J_H + (2D + J_H + \lambda_3)^2}} \left(|1,-1\rangle + \frac{(2D + J_H + \lambda_3)}{J_H}|0,0\rangle + |-1,1\rangle\right)\right]_i \otimes |1\rangle_i$
  $m = \frac{1}{2}$

- Quantum Antiferromagnetic Phase (QAF3)
  $|QAF3\rangle = \bigotimes_{i=1}^{N} |\pm(-1)^i\rangle_i \otimes$
  $\left[\frac{1}{\sqrt{1+\alpha_i(\pm(-1)^i,0,0,\pm(-1)^{i+1})^2 + (1-\alpha_i(\pm(-1)^i,0,0,\pm(-1)^{i+1})\,\alpha_i(\pm(-1)^i,-1,1,\pm(-1)^{i+1}))^2}}\right.$
  $(|-1,1\rangle - (1 - \alpha_i(\pm(-1)^i,0,0,\pm(-1)^{i+1})\,\alpha_i(\pm(-1)^i,-1,1,\pm(-1)^{i+1}))$
  $\left.\times|0,0\rangle + \alpha_i(\pm(-1)^i,0,0,\pm(-1)^{i+1})\,|1,-1\rangle)\right]_i \otimes |\pm(-1)^{i+1}\rangle_i$
  $m = 0$

Plateaus in Spin 1 $[Ni\,(NN'\text{-}dmen)(\mu\text{-}N_3)_2]_n$ Polymer



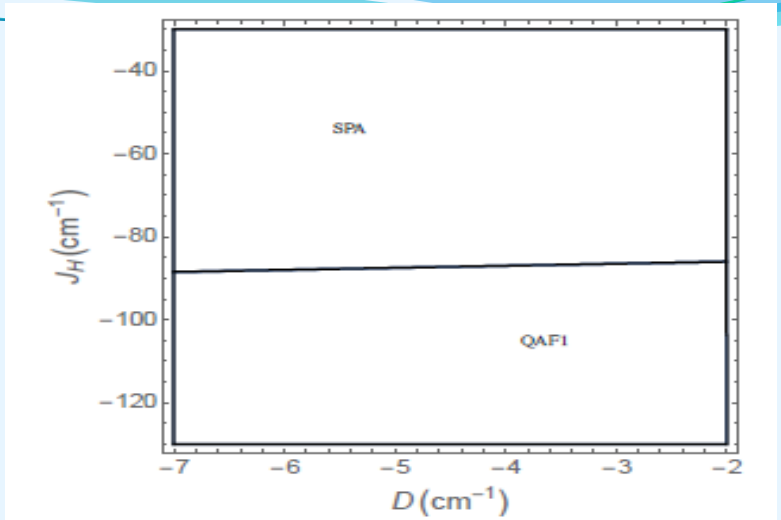


Figure 3: Ground State Phase Diagram of the spin-1 $[Ni(NN'-dmen)(\mu-N_3)_2]$ polymer for different values of J_H and single ion anisotropy D and for $J_1 = 20cm^{-1}$, $J_2 = 37cm^{-1}$, and $g\mu_B h = 80cm^{-1}$ (above) and $g\mu_B h = 150cm^{-1}$ (below)

Plateaus in Spin 1 [Ni (NN'-dmen)(μ-N_3)$_2$]$_n$ Polymer

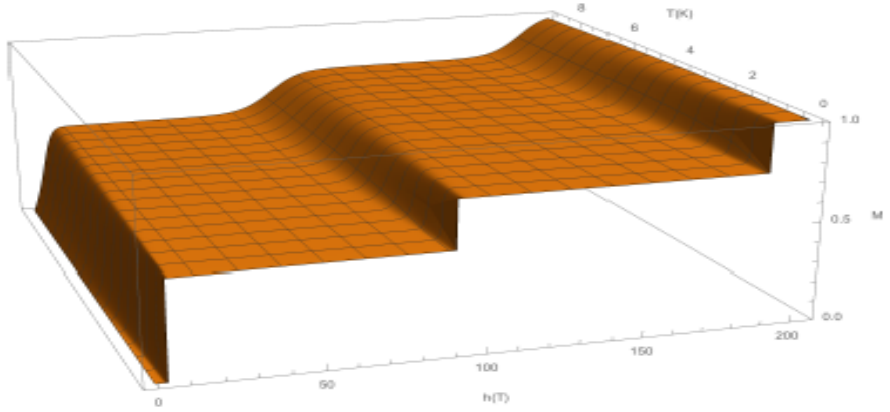
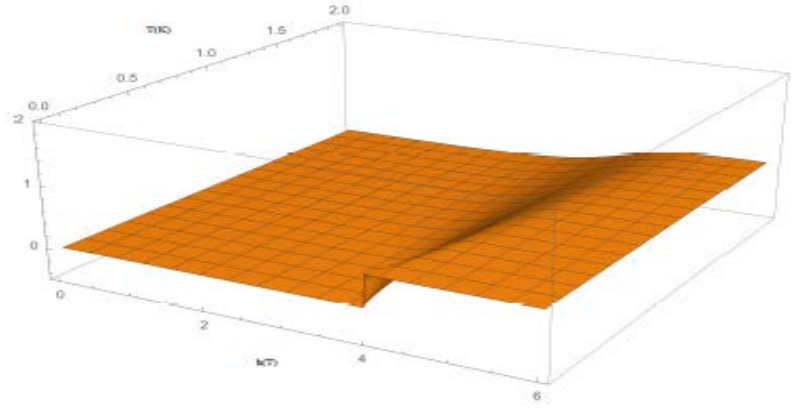


FIG. 2: the magnetization behavior of the spin-1 $[Ni(NN' - dmen)(\mu - N_3)_2]$ polymer as a function of the absolute temperature T and the magnetic field h



Plateaus in Spin 1 $[Ni\ (NN'\text{-}dmen)(\mu\text{-}N_3)_2]_n$ Polymer

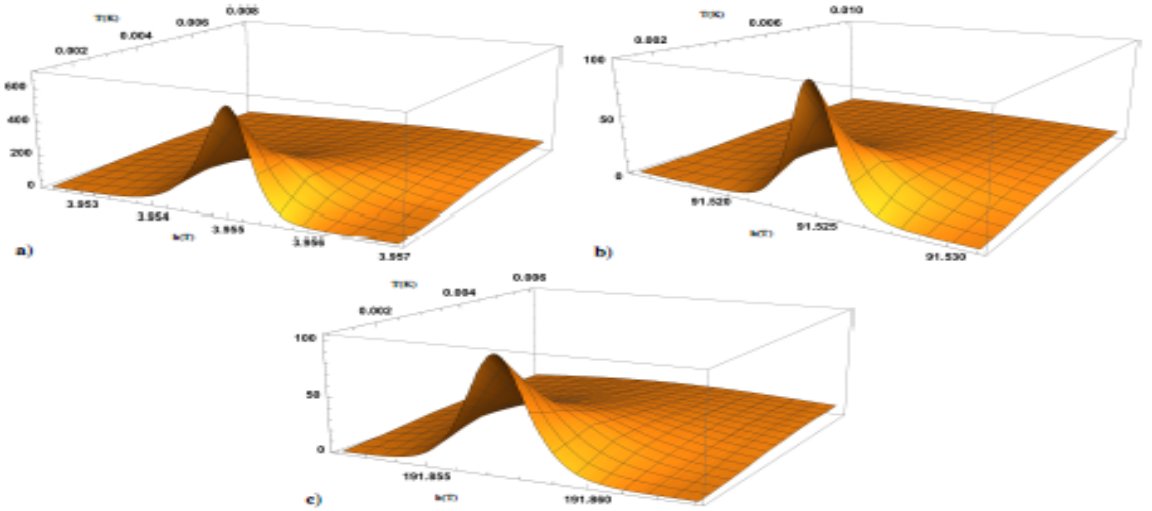


FIG. 4: The three peaks of the magnetic susceptibility of the spin-1 $[Ni(NN' - dmen)(\mu - N_3)_2]$ polymer as a function of the absolute temperature T and the magnetic field h at low temperatures.

Plateaus in Spin 1 $[Ni\ (NN'\text{-}dmen)(\mu\text{-}N_3)_2]_n$ Polymer

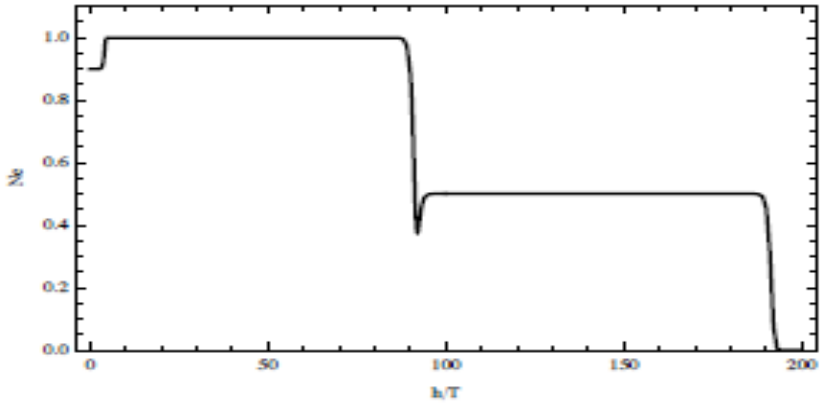
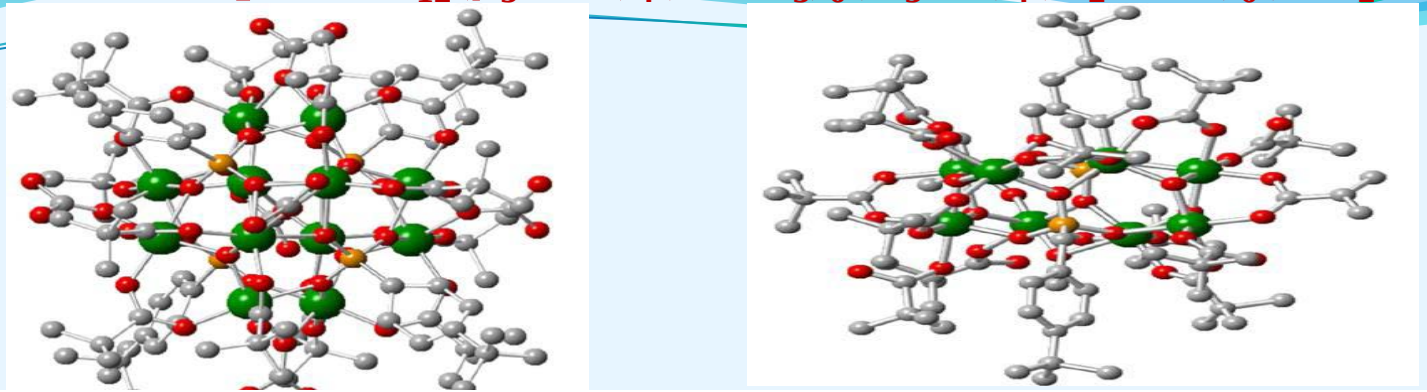


FIG. 5: the plateaus of the negativity in correspondence with the magnetization plateaus

We can see the one to one **correspondence between the negativity plateaus** Fig. 5 and those of the **magnetization plateaus** in Figure 2

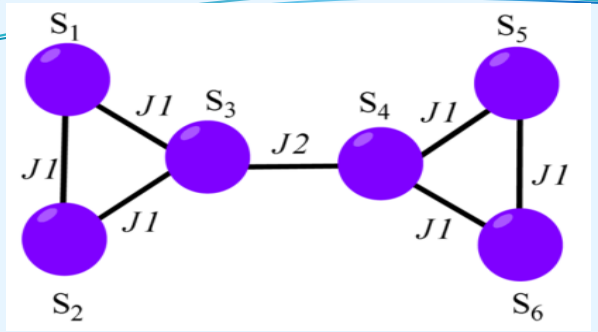
Plateaus in spin 1 $Ni_{12}(\mu_3\text{-}OH)_4(HCO_3)_6(O_3PR)_4(O_2C^tBu)_6(HO_2C^tBu)_6$



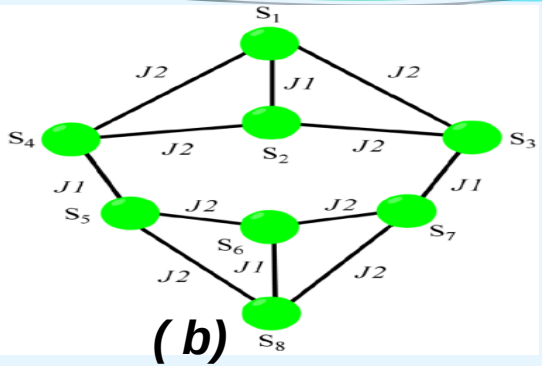
Molecular structures of $Ni_{12}(\mu_3-OH)_4(HCO_3)_6(O_3PR)_4(O_2C^tBu)_6(HO_2C^tBu)_6]$ *in the crystal (color code: green, nickel; orange, phosphorus; red, oxygen; gray, carbon) (left) and molecular structures of* $Ni_8(\mu_3-OH)_4(OMe)_2(O_3PR)_2(O_2C^tBu)_6(HO_2C^tBu)_8]$ ***(right).***

One can study the entanglement (negativity) at finite temperatures for single Ni-containing clusters, using the spin-1 Heisenberg-Ising Hamiltonian with bilinear (J), biquadratic (K) exchange couplings, single-ion anisotropy (D) and magnetic (h) fields. Structures of the finite lattices are demonstrated below:

Plateaus in spin 1 $Ni_{12}(\mu_3\text{-}OH)_4(HCO_3)_6(O_3PR)_4(O_2C^tBu)_6(HO_2C^tBu)_6$



(a)



(b)

We make the following approximation considering the quantum spins for J_2, K_2 and classical spins for J_1, K_1 of the theoretical model (a) and the quantum spins for J_1, K_1 and classical spins for J_2, K_2 of the theoretical model (b). Due to the biquadratic exchange coupling and single-ion anisotropy field of the clusters

$Ni_8(\mu_3-OH)_4(OMe)_2(O_3PR)_2(O_2C^tBu)_6(HO_2C^tBu)_8]$ **(R=p-tert-Butylbenzyl) and**

$Ni_{12}(\mu_3-OH)_4(HCO_3)_6(O_3PR)_4(O_2C^tBu)_6(HO_2C^tBu)_6]$ **(R=p-tert-Butylphenyl)**

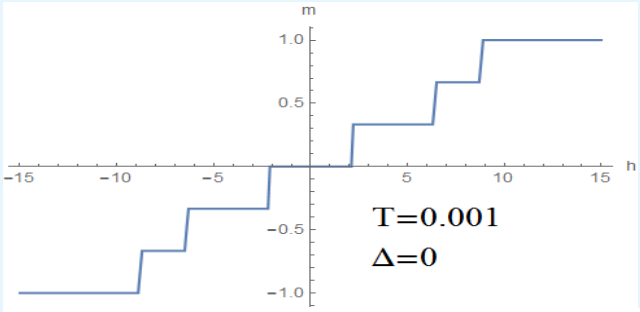
containing ferromagnetic and antiferromagnetic exchange couplings.

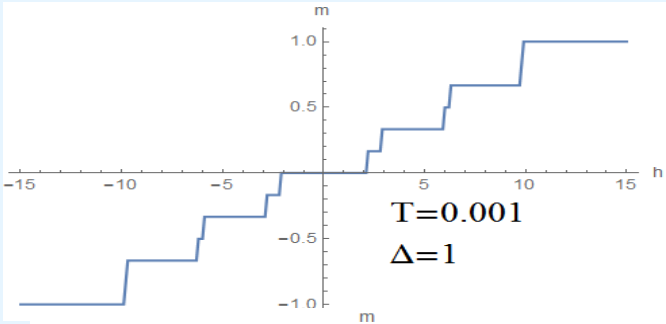
Plateaus in spin 1 $Ni_{12}(\mu_3\text{-}OH)_4(HCO_3)_6(O_3PR)_4(O_2C^tBu)_6(HO_2C^tBu)_6$

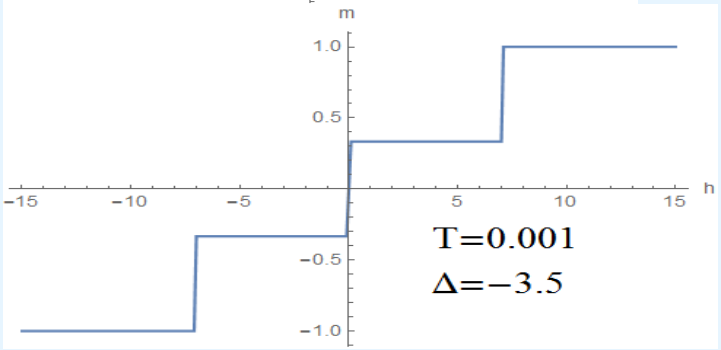
$$H = -J1(S_1S_2 + S_2S_3 + S_3S_1 + S_4S_5 + S_4S_6 + S_5S_6) - J2(S_3S_4) - g\mu_B h\sum_{i=1}^{6} S_i^z + \Delta\sum_{i=1}^{6}(S_i^z)^2$$

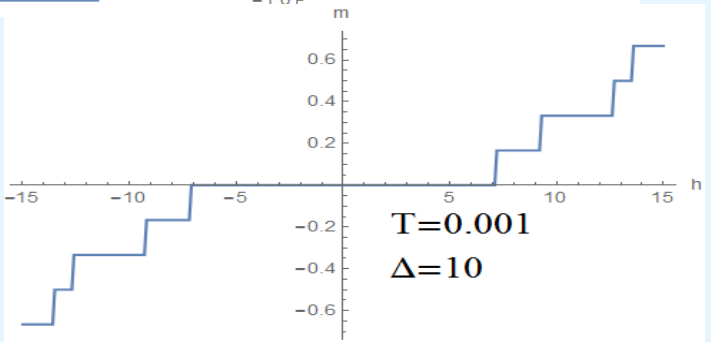
$$S_iS_j = S_i^xS_j^x + S_i^yS_j^y + S_i^zS_j^z$$

$where \quad g = 2.14, J1 = -3.1cm^{-1}, J2 = 2.5cm^{-1}$ for different values of Δ









Schedule of actions

- ***Research magnetization plateaus,*** **specific heat & magnetic susceptibility** ***at low temperatures for polymers*** **[Ni (NN'-dmen)(μ-N_3)$_2$]$_n$ using dynamical technique (super- stable cycles) and ALPS**
- ***Obtain magnetization plateaus,*** **specific heat & magnetic susceptibility** ***at low temperatures for polymers*** **[$CoL^2(N_3)_6(H_2O)_2]_n$ and [$Mn(N_3)_2$(4-Bzpy)$_2$]$_n$ using transfer matrix, dynamical technique (super-stable cycles) and ALPS** ***project .***
- ***Entanglement for polymers*** **[$CoL^2(N_3)_6(H_2O)_2]_n$ and [$Mn(N_3)_2$(4-Bzpy)$_2$ using transfer matrix**
- ***Obtain the thermal negativity by parallel computing (Wolfram Mathematica Language) of*** **$Ni_{12}(\mu_3\text{-}OH)_4(HCO_3)_6(O_3PR)_4(O_2C^tBu)_6(HO_2C^tBu)_6$** ***molecular structures***
- ***Researching of the entanglement for*** **<u>biopolymer-metal complexes</u>**
- **Entanglement** of electron clouds of nucleic acids in **DNA** & **dipolar-dipolar entanglement** for **DNA** containing ***Cu***

THANKS!!!