The compound [Ni(2aepy)$_2$Cl (H_2O)] Cl·H_2O as a candidate approaching a topological quantum critical point of a spin-1 one-dimensional antiferromagnet

Mariia Holub[1], Slavomíra Šterbinská[2], Juraj Kuchár[2], Juraj Cernák[2], Erik Čižmár[1]

[1]*Institute of Physics, Faculty of Science, P.J. Šafárik University, Park Angelinum 9, Košice, Slovakia*

[2]*Department of Inorganic Chemistry, Faculty of Sciences, P.J. Šafárik University in Košice, Moyzesova 11, 041 54 Košice, Slovakia*

mariia.holub@student.upjs.sk

What the systems we observe?

Strongly correlated systems based on Ni^{2+} compounds can give rise to many striking emergent phenomena, which provide a playground for theoretical condensed matter study.

What is the idea?

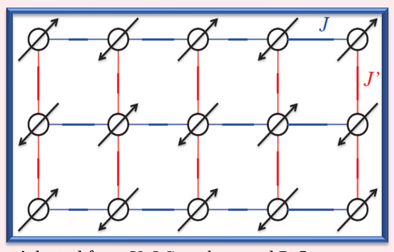
The idea of controlling the magnetic ground state of a spin-1 one-dimensional antiferromagnetic (1d AFM) quantum magnets has long been of interest to theorists and experimentalists. We are interested in the properties at low temperatures where quantum effects play an essential role. In the study of anisotropic 1d AFM systems based on Ni^{2+} compounds, a series of topologically protected quantum phases was observed. The magnetic ground state of such a system is sensitive to the relative magnitude of the single-ion anisotropy (D) and the intrachain exchange interaction (J) parameters. The D/J ratio dictates the system's placement in one of three competing phases: a Haldane gapped phase, a quantum paramagnet, and an XY-ordered state, with a quantum critical point at their junction at D/J = 1.

THEORY

Generally the quasi-1d system with anisotropic Hamiltonian of S = 1 spin operators with nearest-neighbor spin exchange interactions and on-site single-ion anisotropy:

$$\hat{H} = J\sum \hat{S}_i\hat{S}_j + J'\sum \hat{S}_i\hat{S}_j + D\sum (S_i^z)^2$$

J and J' are the two nearest neighbor antiferromagnetic exchange interactions.
D is the axial parameter of single-ion anisotropy.

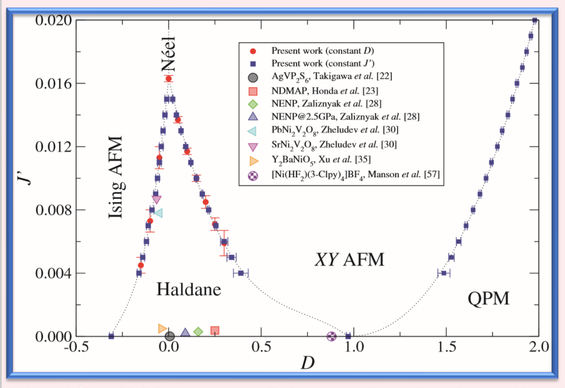


Adapted from K. Wierschem and P. Sengupta, Phys. Rev. Lett., 112, 247203 (2014).

The ground-state phase diagram of $\hat{H}$

Single-ion anisotropy D parameter (or D/J) defines phases:

- Ising AFM (D<0)
- Haldane (found out by FSS)
- XY AFM (D>0)
- QPM (D≥0)



Adapted from K. Wierschem and P. Sengupta, Phys. Rev. Lett., 112, 247203 (2014).

Real systems based on Ni^{2+} ions often require to include both axial (D) and rhombic (E) single-ion anisotropy parameters in the Hamiltonian of an isolated anisotropic S = 1 AFM spin chain:

$$\hat{H}_{aniso} = J\sum_i \hat{S}_i\hat{S}_{i+1} + \sum_i [D(S_i^z)^2 + E((S_i^x)^2 - (S_i^y)^2)]$$

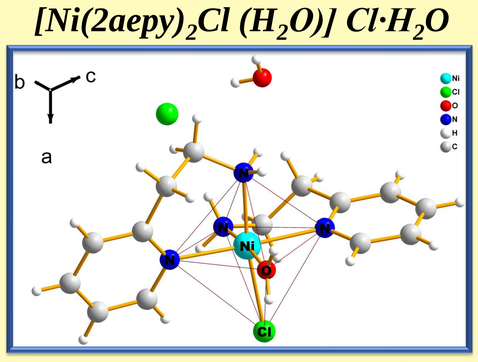
The presence of the rhombic anisotropy can change the ground-state nature of the system.

Ab initio calculations of anisotropy parameters in **ORCA** package yields:

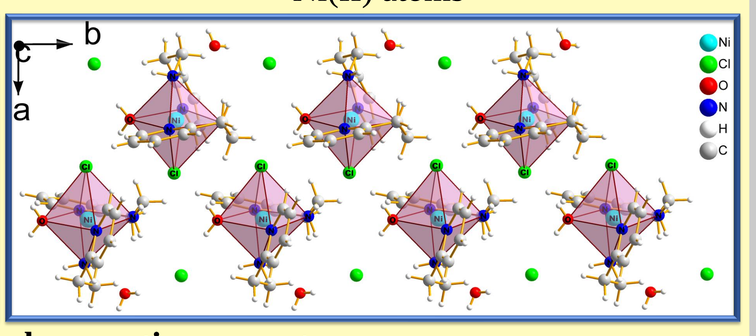
	D/k_B	**E/D**	**g_1**	**g_2**	**g_3**	**g_{avg}**
	[Ni(2aepy)$_2$Cl(H_2O)]$^+$					
CAS(8,5)	3.05	0.093	2.200	2.214	2.217	2.211
CAS(8,10)	3.44	0.036	2.230	2.250	2.250	2.243
	[Ni(2aepy)$_2$Cl(H_2O)]Cl					
CAS(8,5)	3.41	0.154	2.200	2.215	2.221	2.190
CAS(8,10)	3.75	0.095	2.230	2.240	2.250	2.240
	Experimentally determined parameters					
	4.05					2.35

EXPERIMENT

Molecule of ***[Ni(2aepy)$_2$Cl (H_2O)] Cl·H_2O***

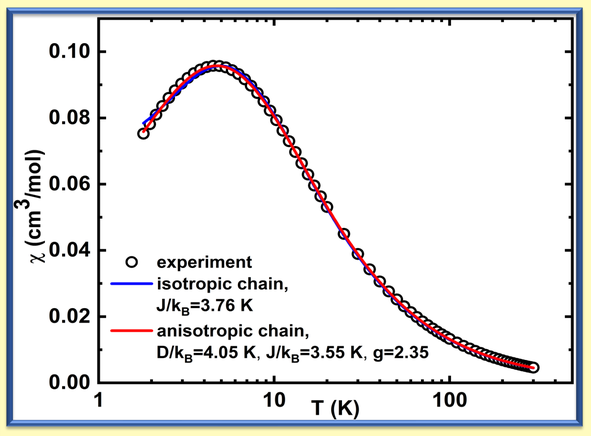


Supramolecular zig-zag chain-like arrangement of Ni(II) atoms

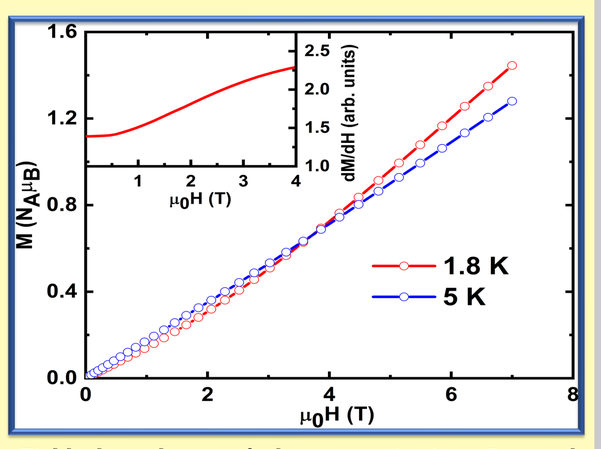


General magnetic parameters:

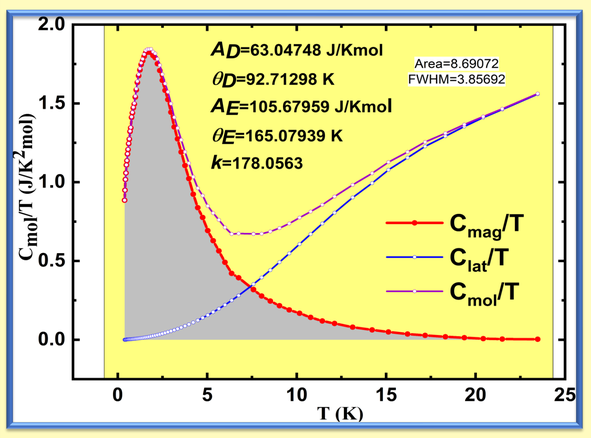
- The effective magnetic moment at 300 K is μ_{eff} = **3.32** μ_B
- An average g-factor is equal to **2.35**



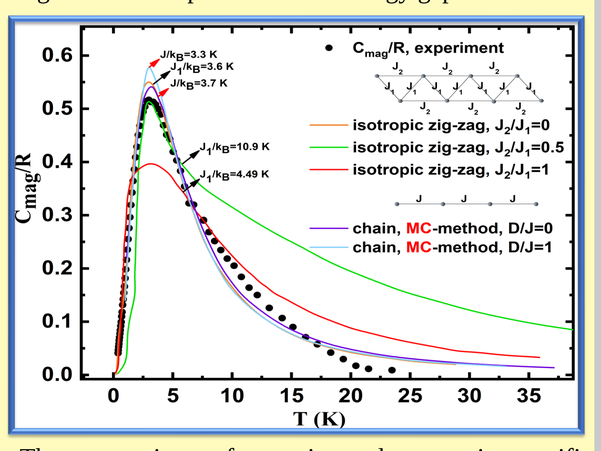
Temperature dependence of the susceptibility including the models of isotropic (blue line) and anisotropic (red line) S = 1 AFM spin chain.



Field dependence of the magnetization. Inset: the derivative of the magnetization at 1.8 K shows a signature of the possible small energy gap.



Temperature dependence of powder heat capacity showing the estimation of the lattice contribution using Debye-Einstein model. (Magnetic entropy defined by the grey area ***S_{mag} = 8.738 J/Kmol*** is close to the theoretical value.)



The comparison of experimental magnetic specific heat and models: isotropic zig-zag AFM model [6] and AFM chain model calculated by MC (Monte-Carlo) method with length L=100 spins using ALPS package.

CONCLUSION

The analysis of the experimental susceptibility using a model of spin-1 anisotropic AFM chain yielded parameter values D/k_B = 4.05 K and J/k_B = 3.55 K. A theoretical prediction of D/k_B = 3.7 K using ab initio approach is very close to the experimental value. In a first approximation, the resulting D/J = 1.14 ratio suggests that the system is close to the topological quantum critical point. Specific heat analysis shows no long-range order down to 400 mK and that a presence of weak next-nearest neighbor exchange interaction is possible to form a zig-zag frustration. So far only one 1d material has been proposed to lie as close to D/J = 1, but it is still not clear, from which side of the quantum critical point [3,4], so our system is a good candidate for further research (multi-frequency electron paramagnetic resonance, magnetization and specific heat at milikelvin temperatures).

1. F.D.M. Haldane, Phys. Lett. A 93, 464-468 (1983).
2. F.D.M. Haldane, Phys. Rev. Lett. 50, 1153 (1983).
3. J.L. Manson, et al., Inorg. Chem. 51, 7520-7528 (2012).
4. D.M. Pajerowski, et al., Phys. Rev. B 101, 094431 (2020).
5. F. D. M. Haldane, Rev. Mod. Phys., 89, 040502 (2017).
6. A. Niazi, et.al., Phys. Rev., 79, 104432 (2008).
7. S. Šterbinská, M. Holub, J. Kuchár, E. Čižmár, J. Černák, Polyhedron, 187, 114654 (2020).

This work was supported by VEGA 1/0426/19, APVV-18-0197, and APVV-18-0016 projects.