KARAZIN UNIVERSITY

CLASSICS AHEAD OF TIME

Mariia Holub PhD.,

- *Karazin Kharkiv National University, Kharkiv, Ukraine*

- *Pavol Jozef Safarik University in Kosice, Slovakia*

- *SOLEIL synchrotron, France*

I am infinitely grateful to Faculty, especially to Vovk R.V., for my journey in physics!

Thank you for all knowledges, for lectures and for what you exist - the greatest people of science!

PAVOL JOZEF ŠAFÁRIK UNIVERSITY IN KOŠICE
FACULTY OF SCIENCE

RELAXATION PHENOMENA IN LOW-DIMENSIONAL AND MOLECULAR MAGNETS

Mariia Holub PhD.

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PhD in Kosice, Slovakia

UPJS in Kosice, Faculty of Science

Mariia Holub

UPJS in Kosice, Faculty of Science

QMAGNA is the university part of the Centre of Low Temperatures Physics – Centre of Excellence, formed by the Slovak Academy of Science and the P.J. Šafárik University in Košice.
Current scientific goal of the group is to study low-dimensional magnetic structures, especially single-molecule nanomagnets and other systems based on superconductors and glassy semiconductors by means of nanotechnologies for their prospective use in quantum computers CQ.

Dr. h. c., Prof. RNDr. Alexander Feher, DrSc.
Prof. Ing. Martin Orendáč, CSc.
Assoc. Prof. RNDr. Alžbeta Orendáčová,
DrSc. Assoc. Prof. RNDr. Erik Čižmár, Ph.D.
Mgr. Vladimír Komanický, Ph.D.
Mgr. Tomáš Samuely, Ph.D.
NDr. Róbert Tarasenko, Ph.D.

Mariia Holub

Facilities

MPMS3

For bulk and liquid samples

$T = 1.8 \div 400\ K$

$H = 0 \div 7$ T

DC/AC measurements, magnetization

PPMS

For bulk samples

$T = 350mK \div 350\ K$

$H = 0 \div 9$ T

Heat capacity, el. and thermal transport, magnetometer

EPR Brucker

For bulk samples

$T = 2\ K \div 300\ K$

$H = 0 \div 1$ T

$X_{paths} = 9.4\ GHz$

Electron Paramagnet Resonance

Quantum computing

GENERATION	1940s – 1950s	1950s – 1960s	1960s – 1970s	1970s – Present	Present & Beyond
ENABLER	Vacuum tubes	Transistors	Integrated circuits	Microprocessors	Quantum Computing

Quantum Insider

DiVincenzo's criteria:

1. A scalable physical implementation of the qubits without significantly increasing the complexity of the hardware.

2. Quantum mechanical systems with two well-defined stable states are used as qubits.

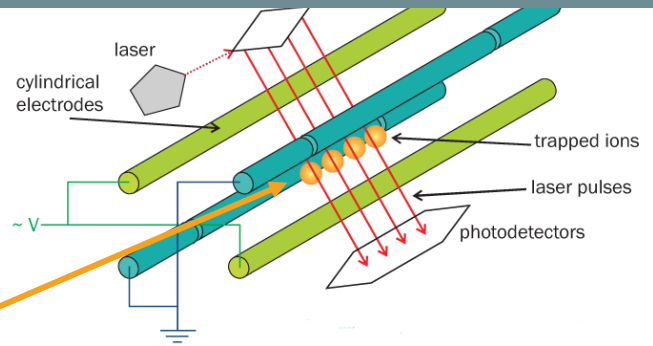
3. Long coherence times to maintain the quantum state of the system for a sufficient period to perform specific computations.

4. A universal set of quantum gates.

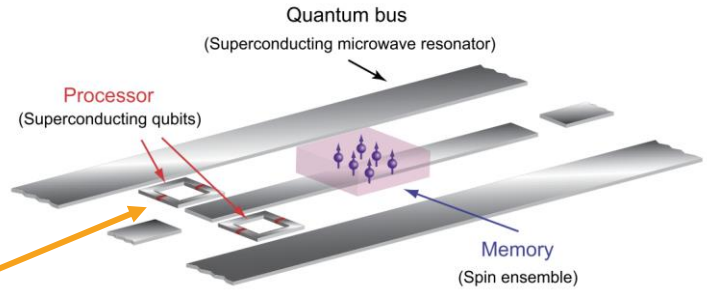
5. A qubit-specific measurement capability to obtain the state of the qubit with a low error correction.

Implementation

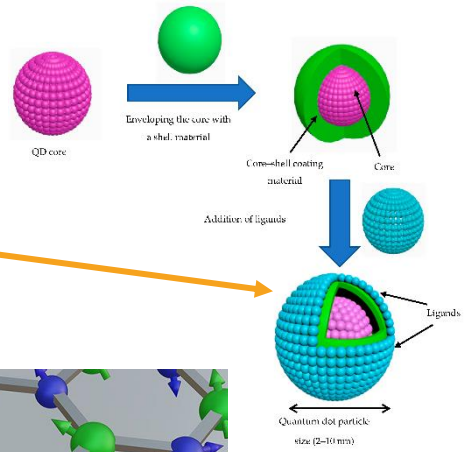
- trapped ions



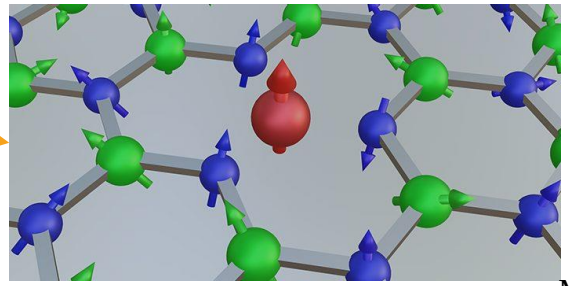
- superconducting qubits



- semiconductors (like silicon and germanium)



- electron spin



Molecular magnetic systems

Definition of MMs

Individual molecules/molecular units formed by transition metal ions or clusters surrounded by organic ligands. These complexes can exhibit intriguing magnetic phenomena: spin-crossover, single-molecule magnetism or magnetic bistability.

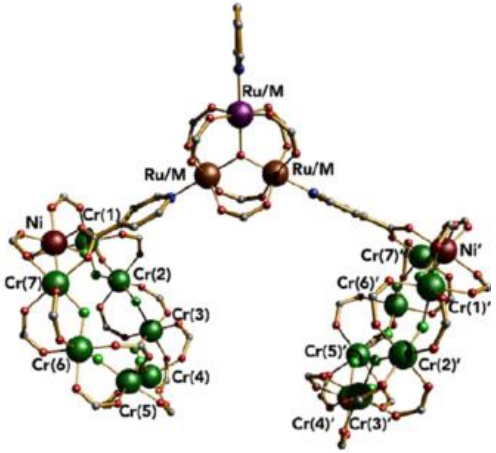
Interactions between the individual magnetic moments depend on molecular structure, bonding, and coordination environment.

Application as:

- information storage,
- in spintronics and
- quantum computing (QC).

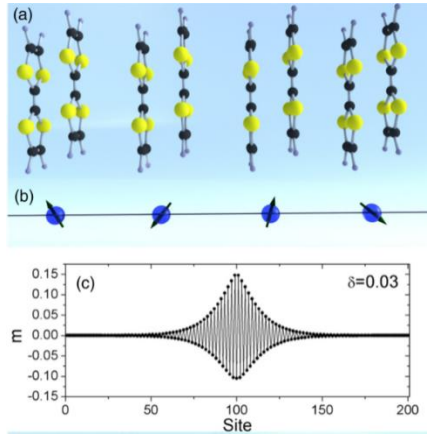
Clusters

- Quantum entanglement of two qubits
- The gate realization between clusters



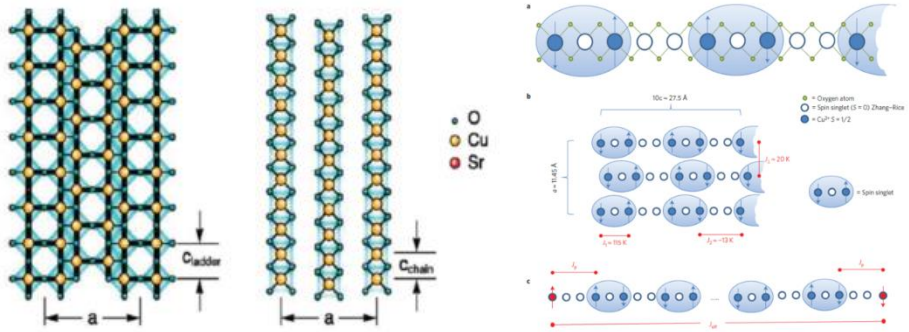
AFM dimerized spin chains

- The pinned-soliton qubit – the localized magnetic object with $S = 1/2$



Spin chain systems

- Incommensurability between ladder and chain layer creates $S = 1/2$ states in dimerized chain-> Long-Distance entanglement between induced $S = 1/2$ objects at low temperatures



Aims of dissertation thesis

Application potential in QC:

spatial arrangement of qubits (singe molecules or ensemble of them), manipulation and readout of the molecular qubit state (by pulsed EPR), implementation of molecular spins in QC circuits (resonator cavity for qubits, strong coupling condition for transfer of quantum information, electronics, etc.)

Objectives is investigation of:

- AFM *S* = 1/2 bond-alternating (dimerized) chain based on TCNQ ARS – prototype of a complex qubit system

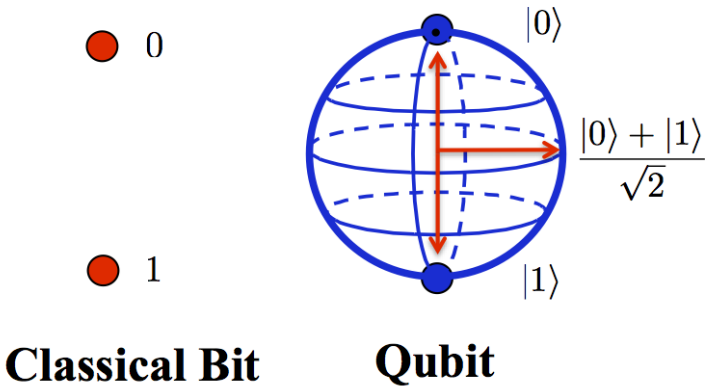
  (Et-2,6-diMe-Pz)(TCNQ)$_2$
- Hybrid transition metal - ARS complexes - alternating spin and exchange interaction chain - understanding of magneto-structural correlations for design of gapped spin systems

  M(2ampy)$_2$(TCNQ)$_2$, M=Ni, Zn; [Ni(bpy)$_3$]$_2$(TCNQ-TCNQ)(TCNQ)$_2$·6H$_2$O; [Ni(bpy)(Bz)$_2$]
- AFM diamond spin cluster systems based on *S* = 1 Ni(II) ions as model system for the understanding and tuning of quantum entanglement

  [Ni$_4$(ClQ)$_6$Cl$_2$(H$_2$O)$_2$]·2DMF

Aims of dissertation thesis

Realization of qubit by electron spin:

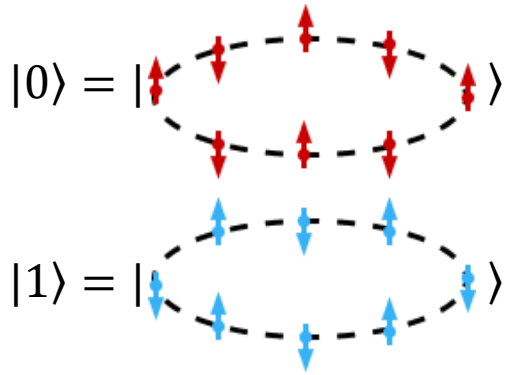


Definition of qubit – electron spin!

$$|\Psi\rangle = \alpha|0\rangle + \beta|1\rangle$$

$$|\alpha|^2 + |\beta|^2 = 1$$

$$|0\rangle = |S = 1/2, m_s = -1/2\rangle$$



$$|1\rangle = |S = 1/2, m_s = 1/2\rangle$$

To understand the magnetic properties of these systems:

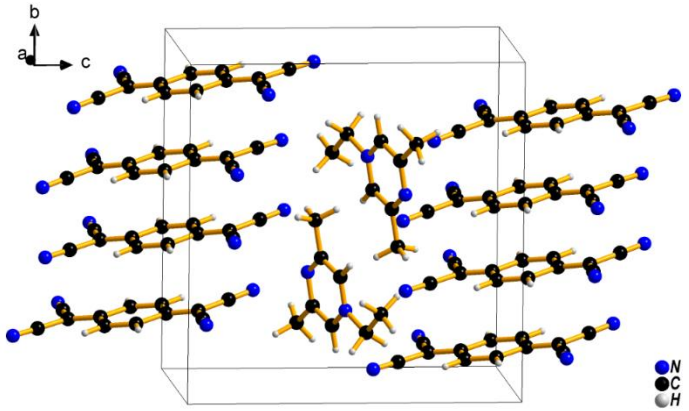
- superconducting quantum interference device (SQUID) magnetometry,
- electron paramagnetic resonance (EPR),
- *ab initio/DFT* calculations.

To manipulate and read the quantum state:

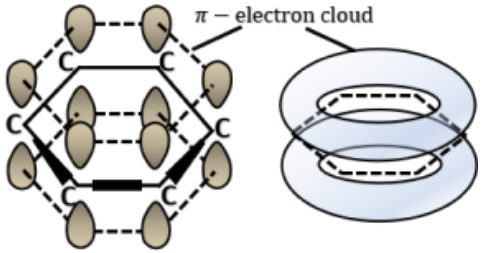
- pulsed (time-resolved) EPR method,
- optical readout of quantum state possible in some cases (NV defects in diamond).

AFM dimerized chain with soliton qubits - $(Et\text{-}2,6\text{-}diMe\text{-}Pz)(TCNQ)_2$

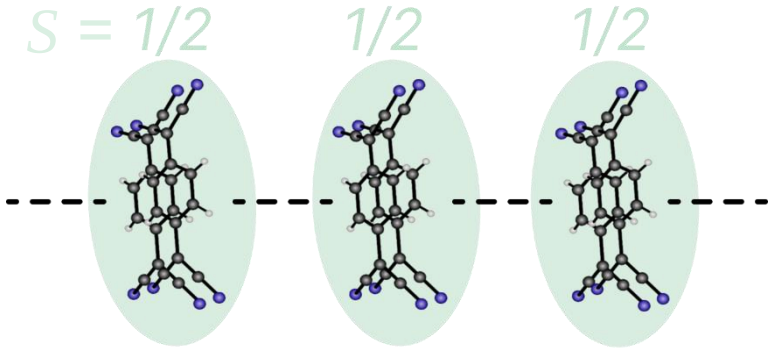
Crystal structure



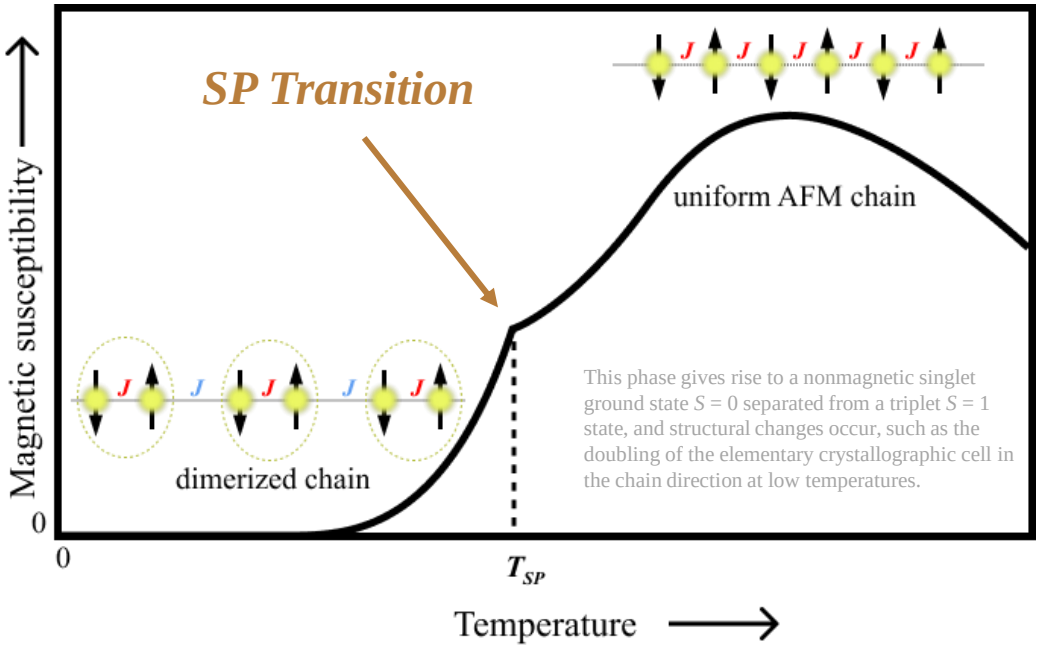
Orbital overlapping



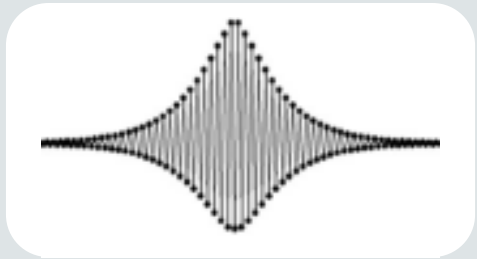
Dimerization of TCNQ stacks

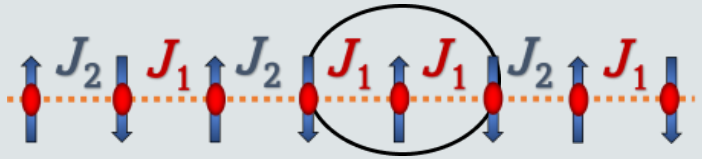


Dimerization of spin chain at spin-Peierls (SP) transition



Pinned solitons

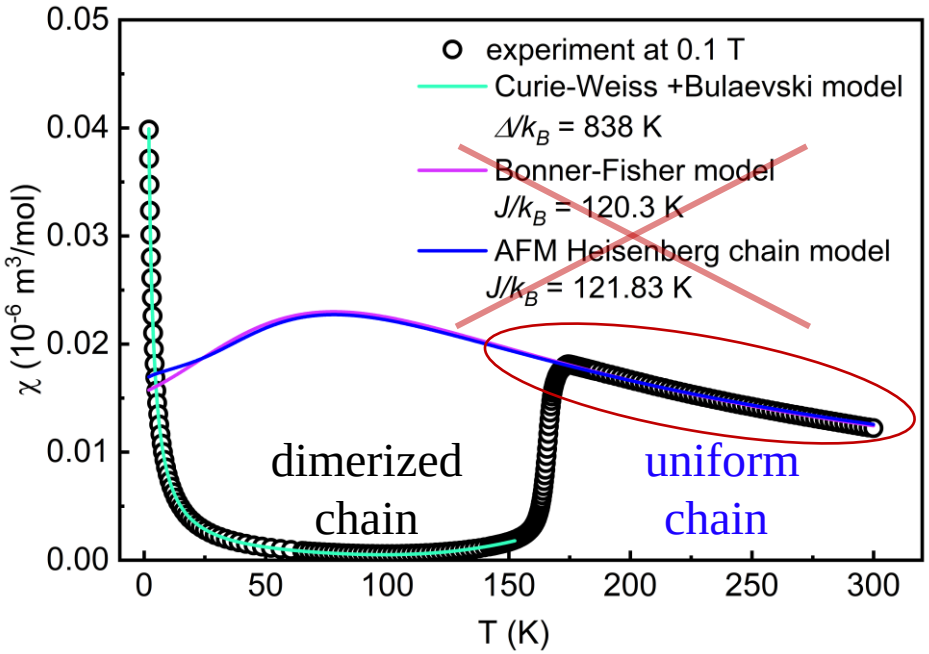


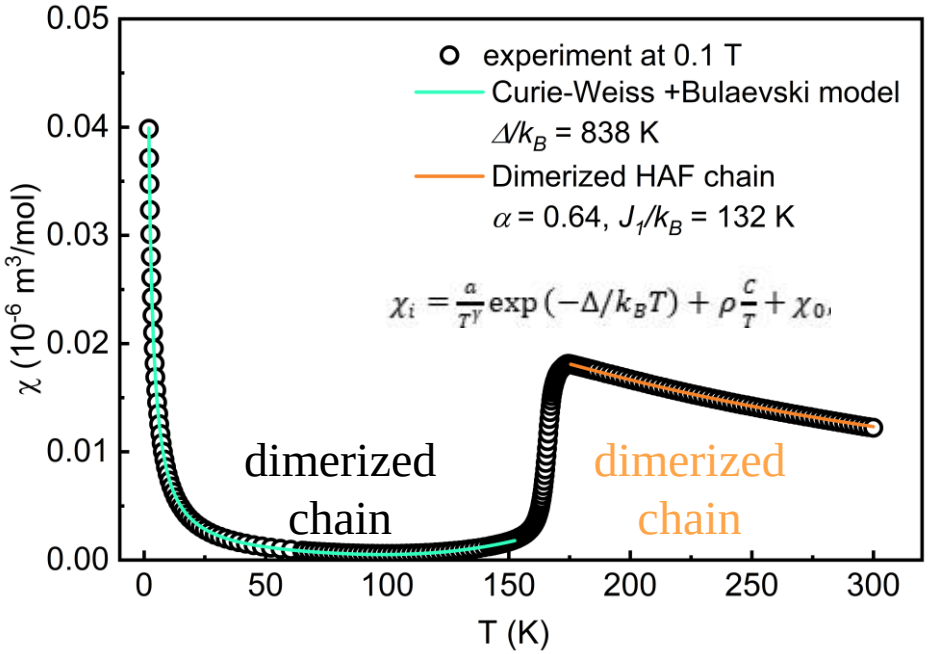


Pinned solitons - consequence of crystallographic deformation, disorder, bond alternation, chain ends, etc.

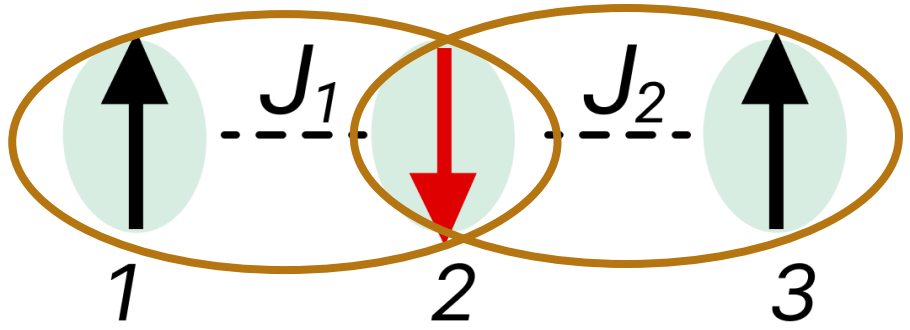
Nishino *et al*. Phys. Rev. B - Condens. Matter Mater. Phys. 61, 4033 (2000).
S. Bertaina *et al.*, Phys. Rev. B - Condens. Matter Mater. Phys. 90, 060404 (2014).

AFM dimerized chain with soliton qubits - $(Et\text{-}2,6\text{-}diMe\text{-}Pz)(TCNQ)_2$





Broken symmetry calculations for radicals

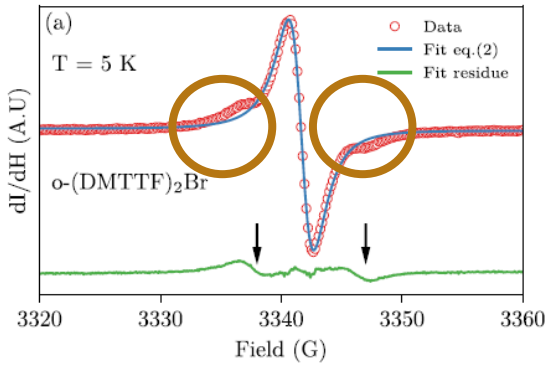


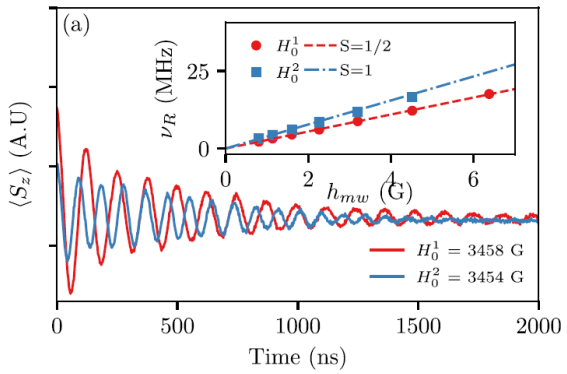
dimerization parameters

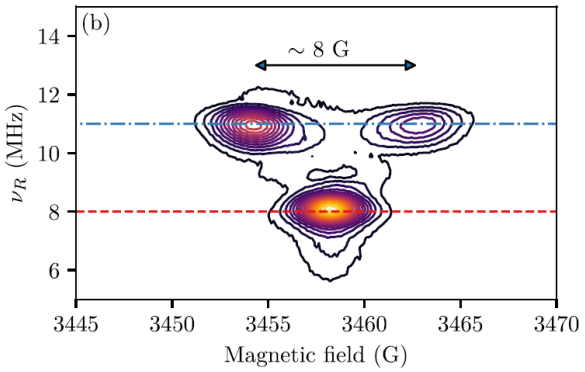
$$\alpha = J_2/J_2 \qquad \delta = \frac{1-\alpha}{1+\alpha}$$

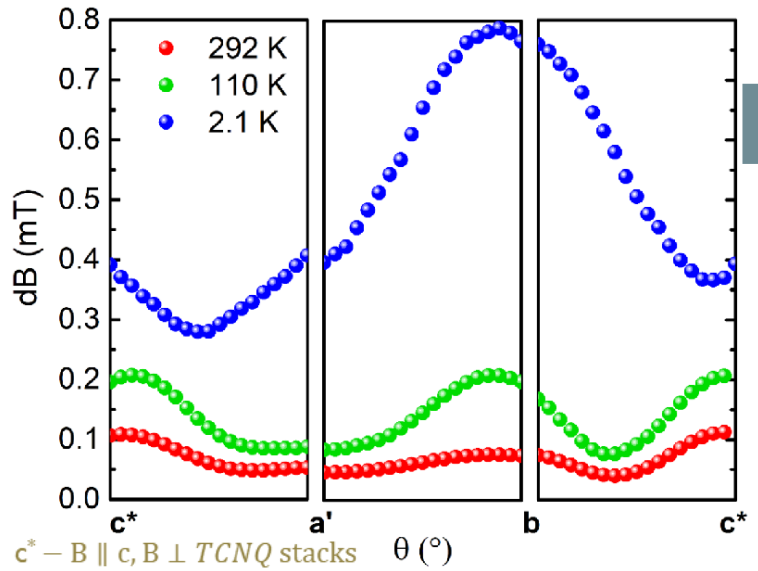
3×(TCNQ$_2$)	J_1/k_B, K	J_2/k_B, K	α	δ	Δ/k_B, K
250 K	92.2	58.5	0.634	0.224	49
95 K	484.7	81.2	0.167	0.713	439

AFM dimerized chain with soliton qubits - $(Et\text{-}2,6\text{-}diMe\text{-}Pz)(TCNQ)_2$



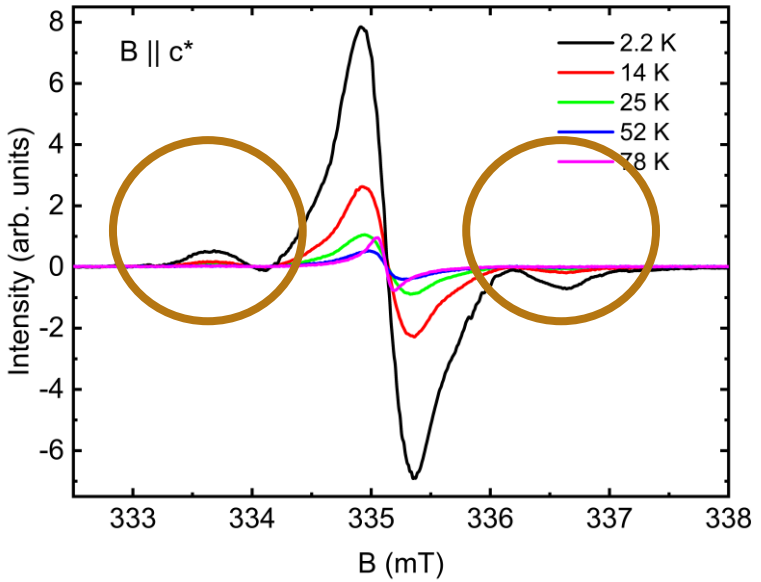






Existence of solitons

Triplet in dimer of two solitons



Two types of solitons:

- not interacting (S = 1/2, red line)
- interacting (S = 1, blue line)

Maxima on both sides of central EPR spectral line correspond to interacting solitons.

Soriano L, Pilone O, Bertaina S, *Physical Review B (2022) 105(6) 064434*

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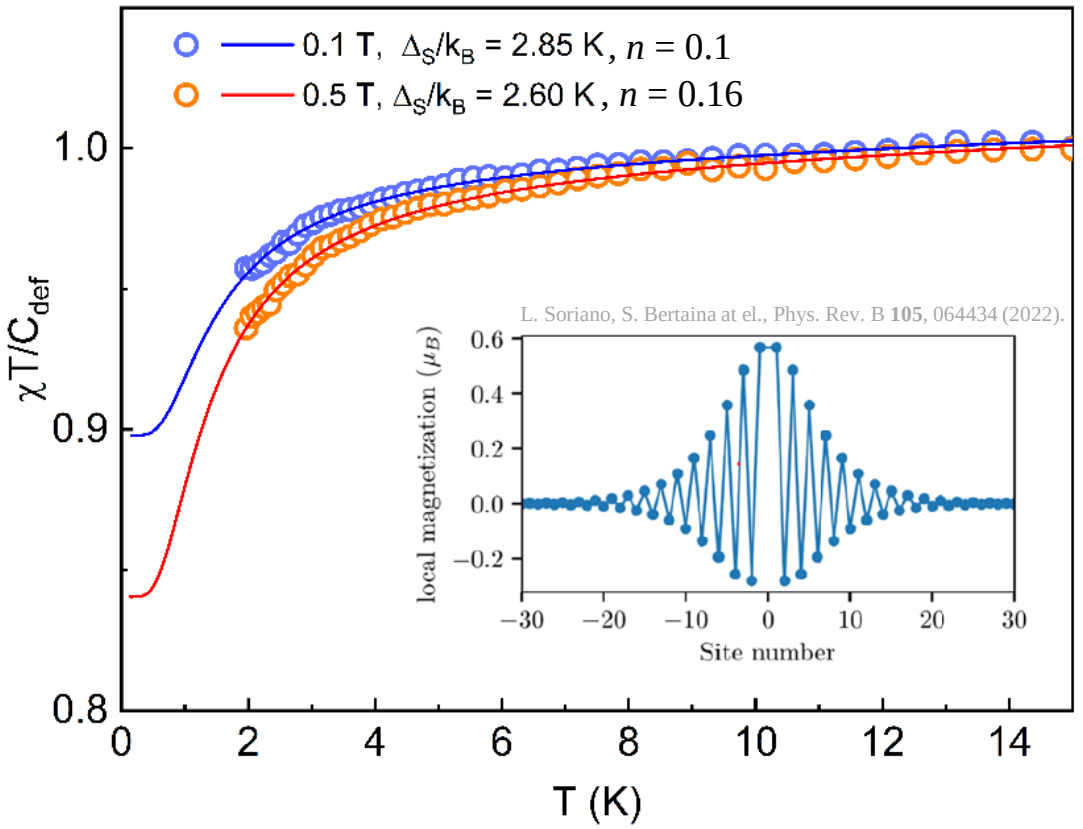
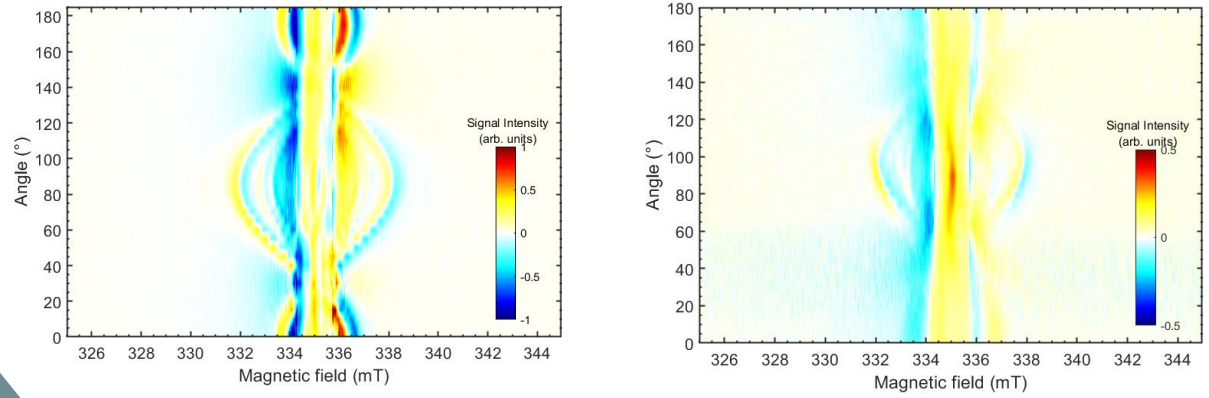
AFM dimerized chain with soliton qubits - $(Et\text{-}2,6\text{-}diMe\text{-}Pz)(TCNQ)_2$

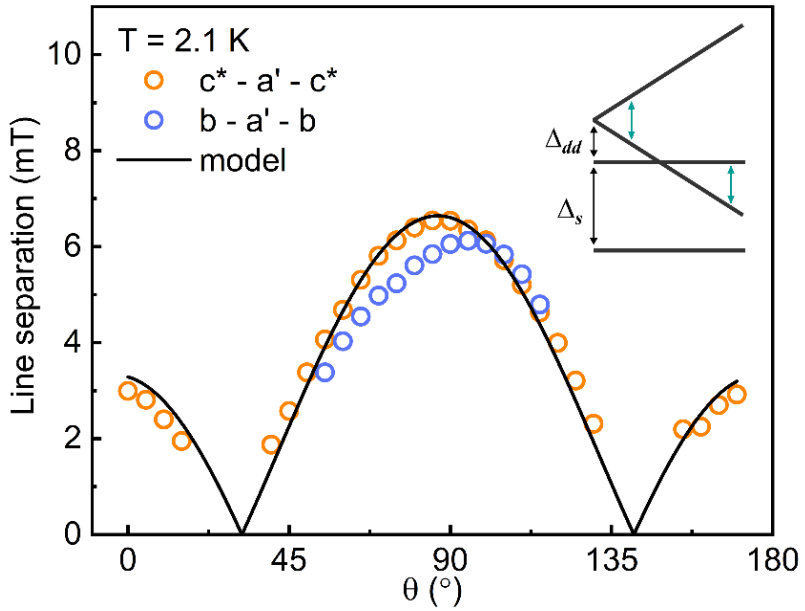
Interacting defects - soliton pairs in magnetic data



L. Soriano, S. Bertaina at el., Phys. Rev. B **105**, 064434 (2022).



The angular dependence of the line separation of two satellite resonances



Bleaney-Bowers model for S = 1/2 AFM dimer

$$\frac{\chi T}{C_{def}} = n\frac{3n}{2\left(3+exp^{\frac{\Delta_S}{k_B T}}\right)} + \frac{3(1-n)}{8}$$

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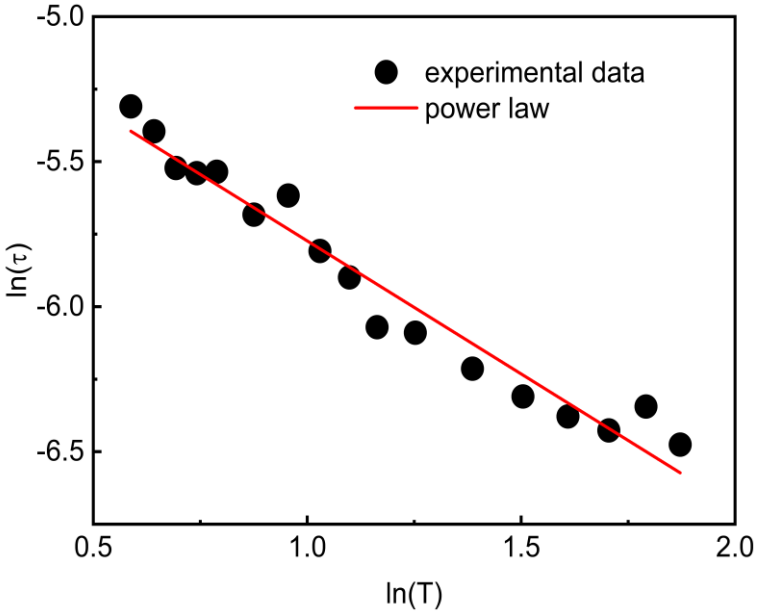
AFM dimerized chain with soliton qubits - $(Et\text{-}2,6\text{-}diMe\text{-}Pz)(TCNQ)_2$

Spin-Lattice Relaxation

Isolated spin defects – solitons



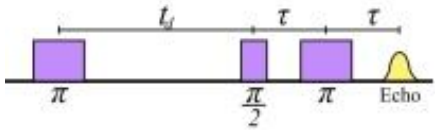
Power law model
(Direct / Raman relaxation mechanism)

n – coefficient of relaxation

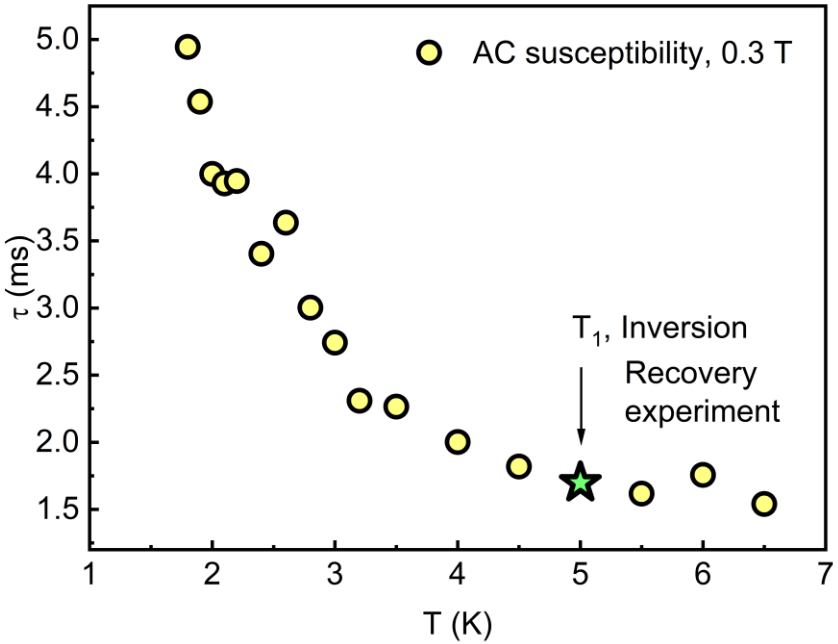
$\tau = CT^{-n}$

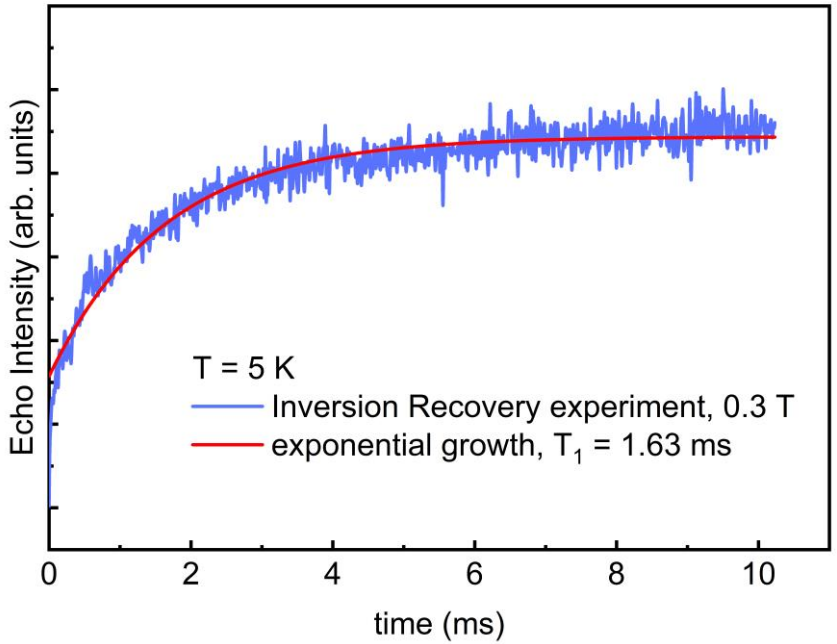
$n = 0.92$

Inversion Recovery, T_1



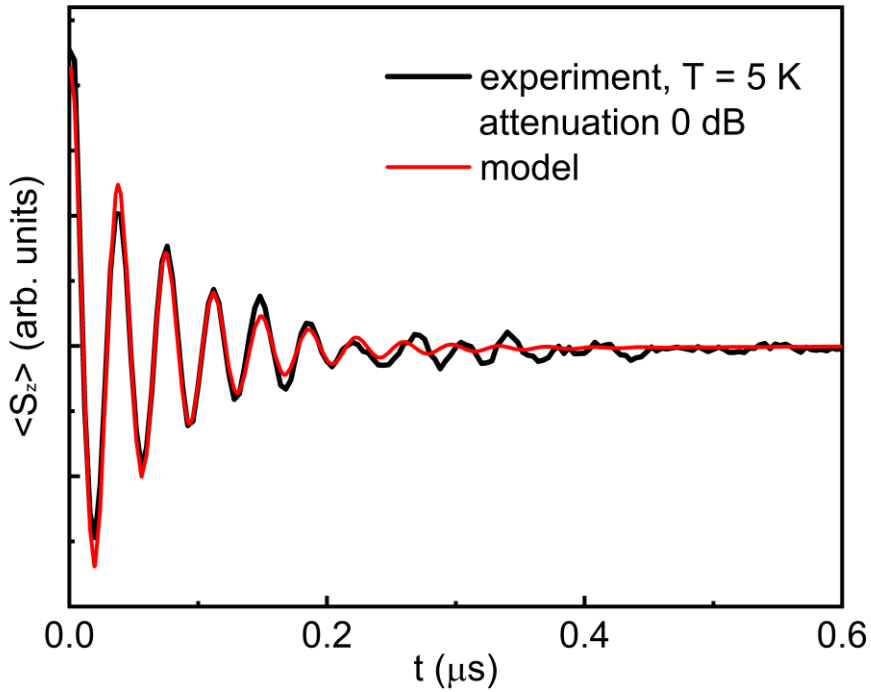
AC susceptibility – spin-lattice relaxation time $\tau = T_1$





AFM dimerized chain with soliton qubits - $(Et\text{-}2,6\text{-}diMe\text{-}Pz)(TCNQ)_2$

Rabi oscillations – quantum coherence



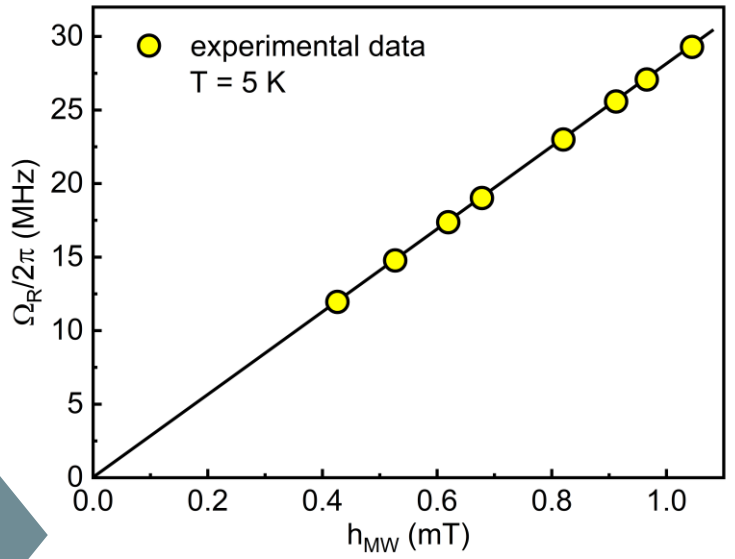
Exponentially damped sinusoidal function

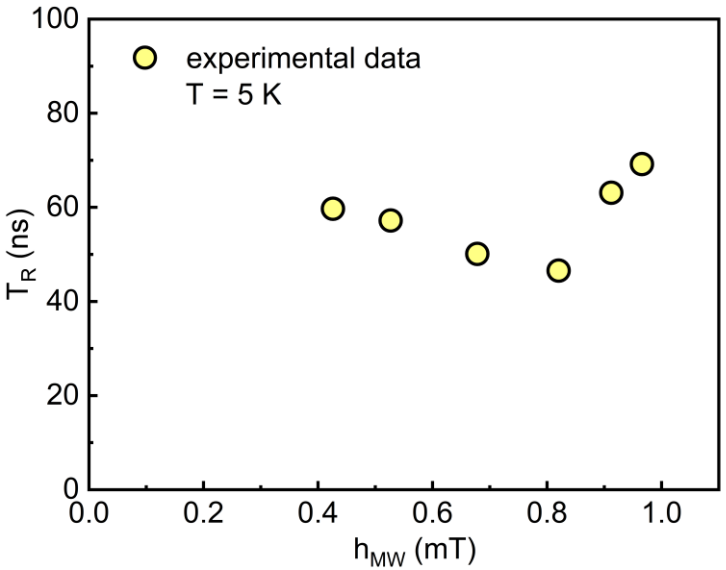
$$\langle S_x(t)\rangle = \langle S_x(0)\rangle \sin(\Omega_R t + \varphi)\, exp^{(-t/T_R)} + bt$$

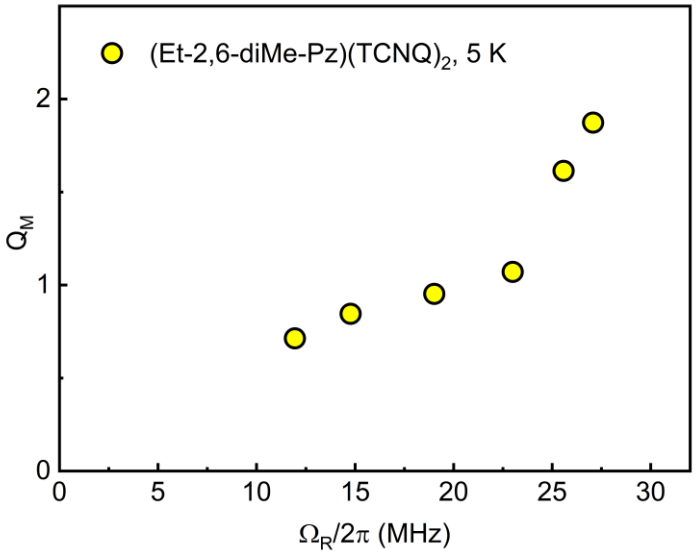
characteristic coherence time T_R

- can be affected, e.g., by microwave field inhomogeneities due to sample size.

T_2^*, T_R transient nutation experiment





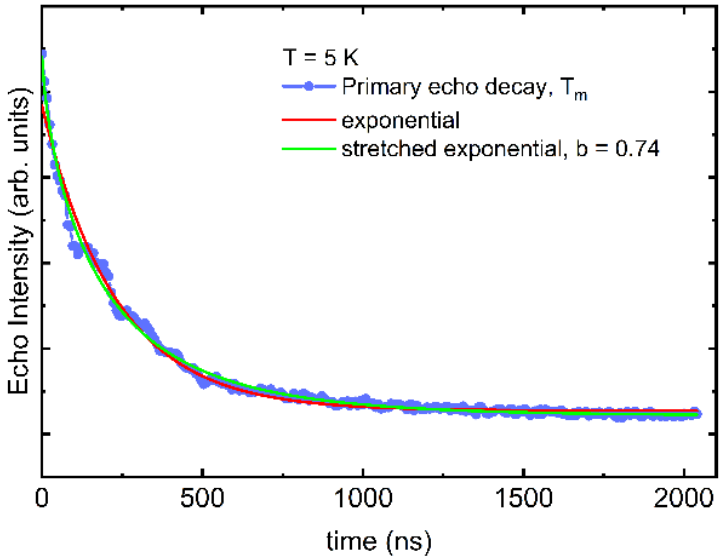


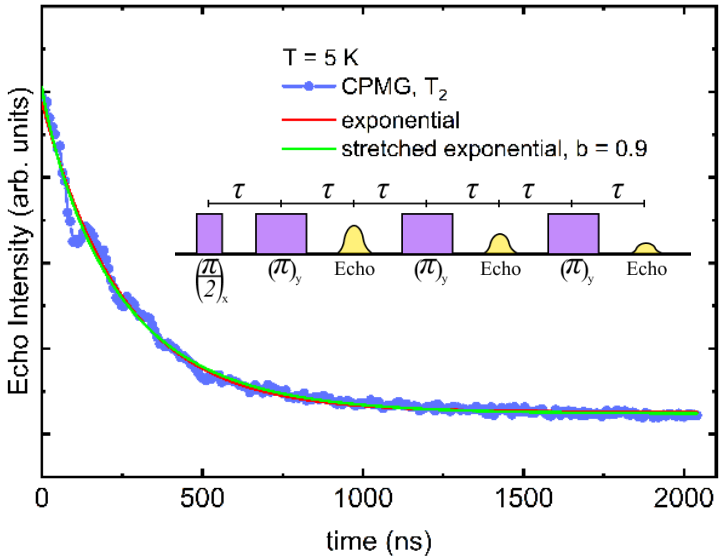
Merit factor corresponds to the quantities of possible quantum operations for qubit at certain frequencies.

$$Q_M = \frac{\Omega_R}{2\pi} \cdot T_R$$

$\frac{\Omega_R}{2\pi}$ – Rabi frequency of the oscillation

AFM dimerized chain with soliton qubits - $(Et\text{-}2,6\text{-}diMe\text{-}Pz)(TCNQ)_2$





T_m - phase-memory time

primary echo decay (Hahn echo)

Includes the influence of inhomogeneous broadening due to local internal field inhomogeneities (e.g., generated by nuclear spin fluctuations)

exponential decay function

$$I = I_0 exp^{-(t/T)^b} + y_0$$

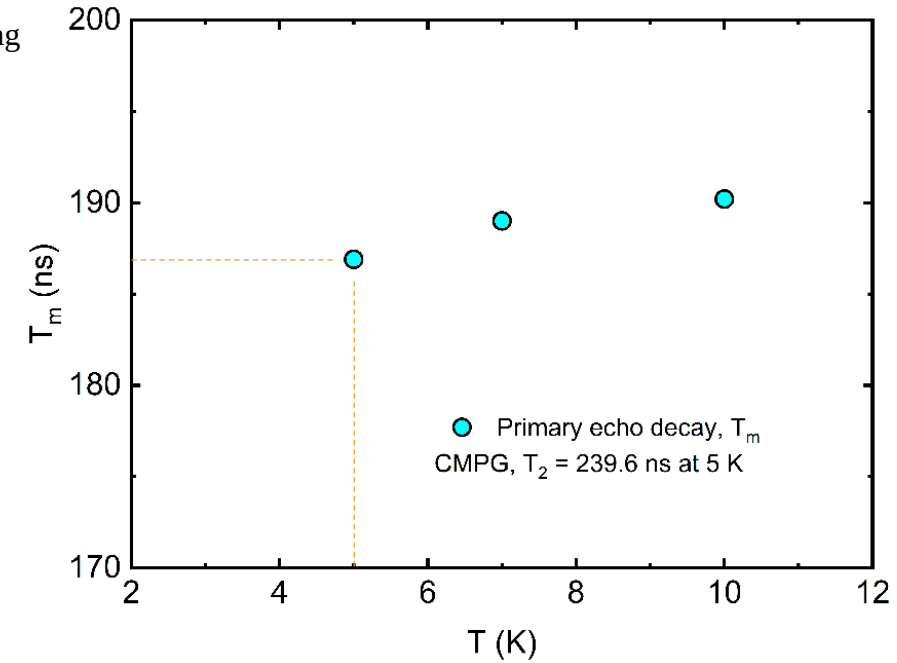
T_2 – spin-spin relaxation time,

Carr-Purcell-Meiboom-Gill (CPMG)

Repeated refocusing pulses reduce the influence of inhomogeneous broadening; the relaxation – dephasing - governed by homogeneous broadening effects, e.g., mutual spin-spin interactions yielding random spin flips

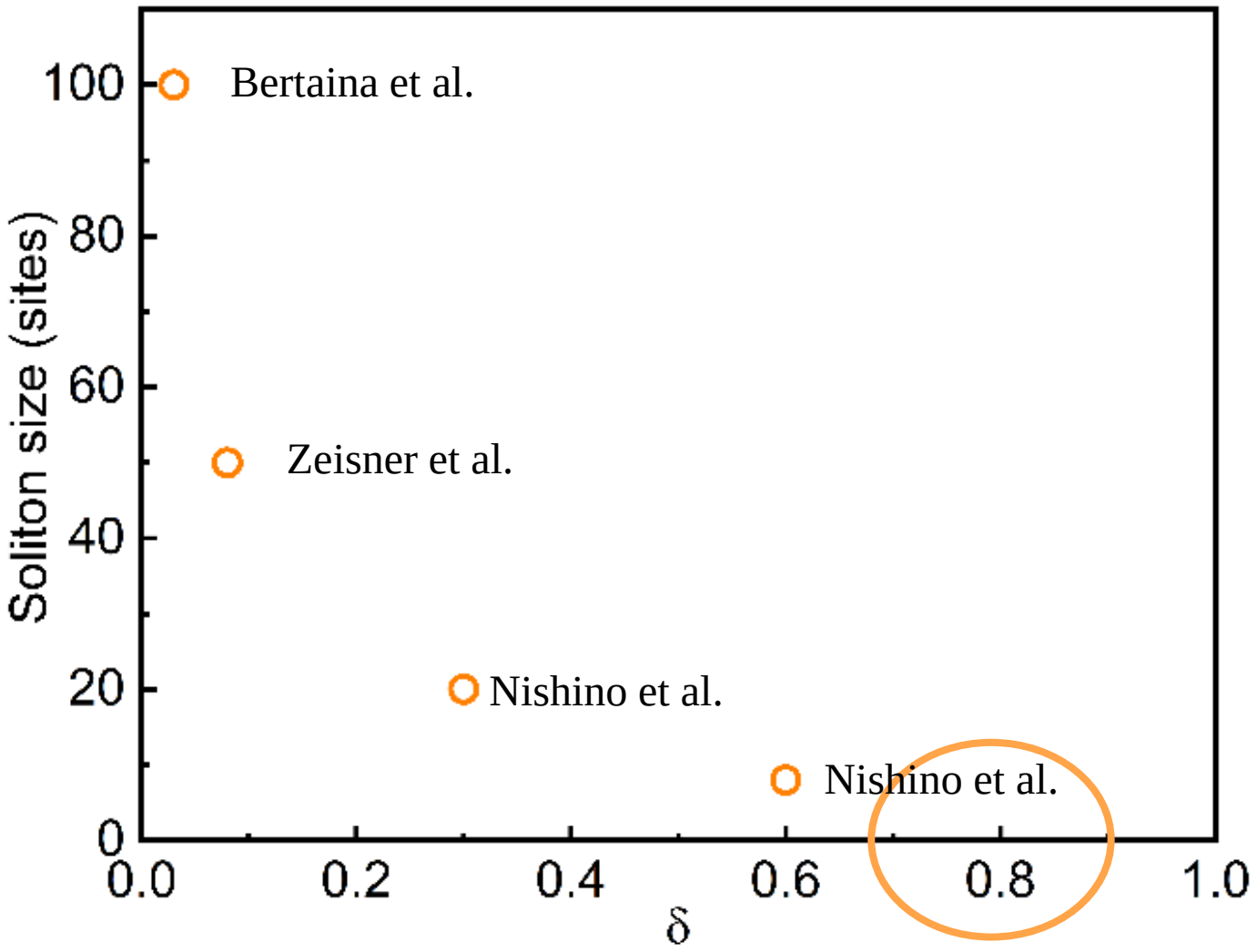
relation between T_m and T_2

$$\frac{1}{T_m} = \frac{1}{T_2} + \frac{1}{T_2'}$$



	5 K	7 K	10 K
T_m, b = 1	229.5 ns	223 ns	223 ns
T_m	187 ns, b = 0.741	189 ns, b = 0.767	190 ns, b = 0.775
T_2, b = 1	254 ns		
T_2	240 ns, b =0.898		

AFM dimerized chain with soliton qubits - $(Et\text{-}2,6\text{-}diMe\text{-}Pz)(TCNQ)_2$



(Et-2,6-diMe-Pz)(TCNQ)₂

$(TMTTF)_2PF_6$

$\delta \sim 0.03$ 100 sites

$(o\text{-}DMTTF)_2X$

$\delta \sim 0.08 \div 0.1$ 50 sites

theoretical prediction

$\delta \sim 0.3$ 20 sites

$\delta \sim 0.6$ 10 sites

$(ET\text{-}2,6\text{-}diMe\text{-}Pz)(TCNQ)_2$

$\delta \sim 0.75$ 5 sites ?

dimerization parameter

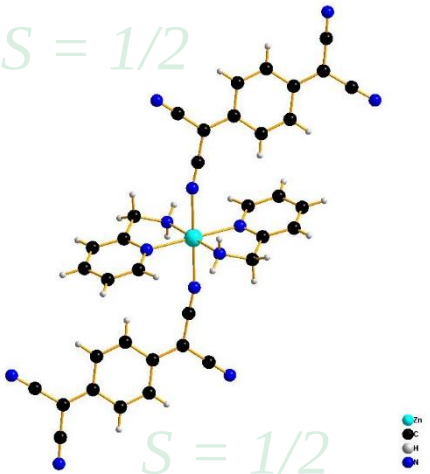
$$\delta = \frac{1-\alpha}{1+\alpha}$$

Magnetic interactions in hybrid complexes - $M(2ampy)_2(TCNQ)_2$, M=Ni, Zn

Hybrid transition metal – ARS complexes – a route to create spin- and bond-alternating chains

Zn complex

shortest C-C distances 3.159 Å



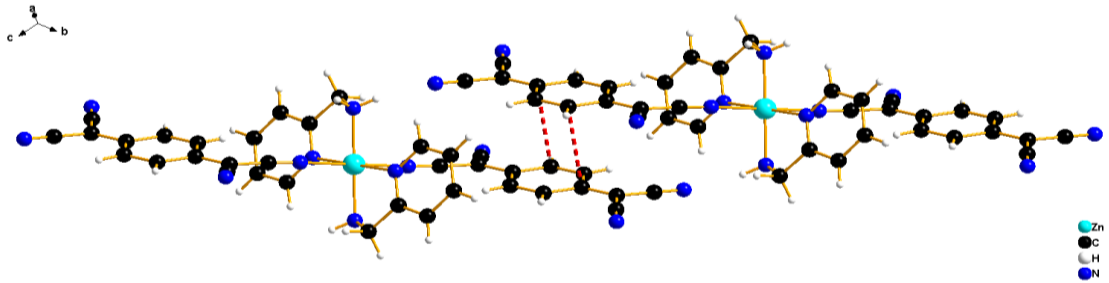
100 K

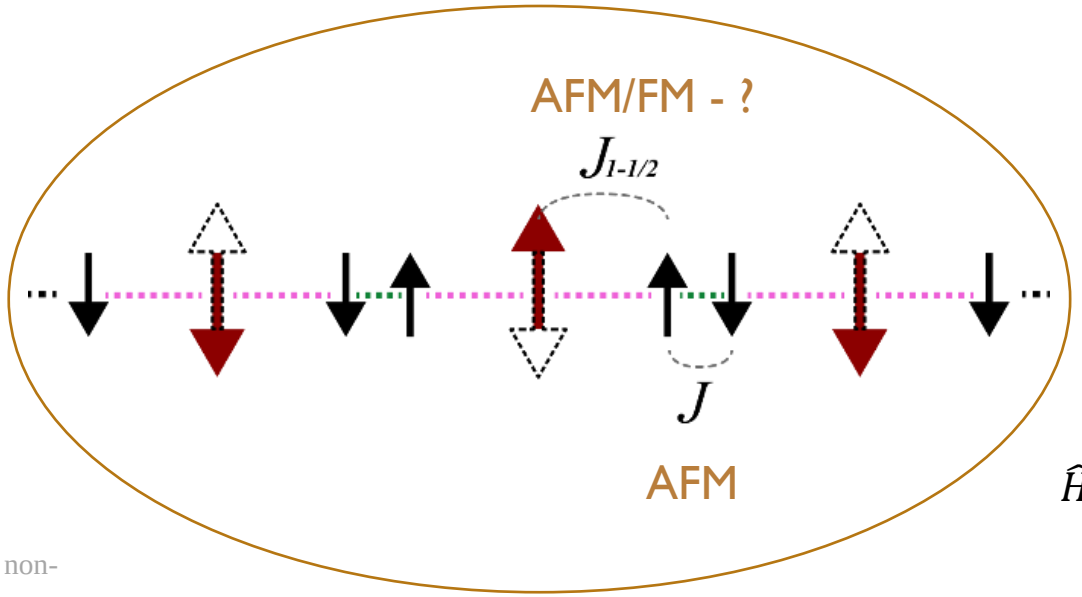
$\hat{H}_{dimer} = J\hat{S}_1\hat{S}_2$

$\chi = 2(1-c)\chi_{Curie} + C\chi_{dimer}$

$c = 0.995$ (only 0.5% of TCNQ ARs pairs are non-interacting, contributing to the paramagnetic susceptibility)

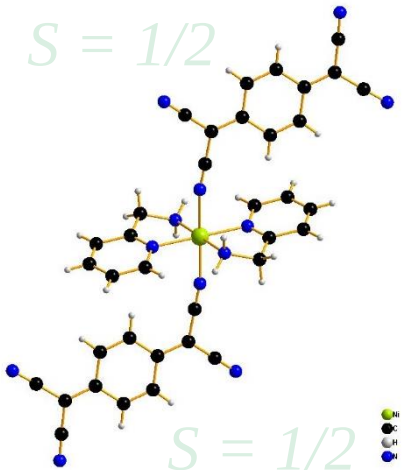
$\frac{J}{k_B} = 1369$ K AFM dimers





Ni complex

shortest C-C distances 3.160 Å



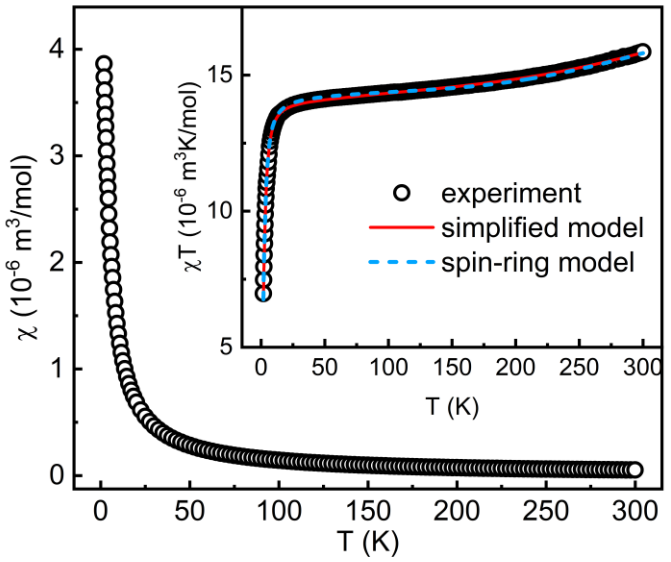
100 K

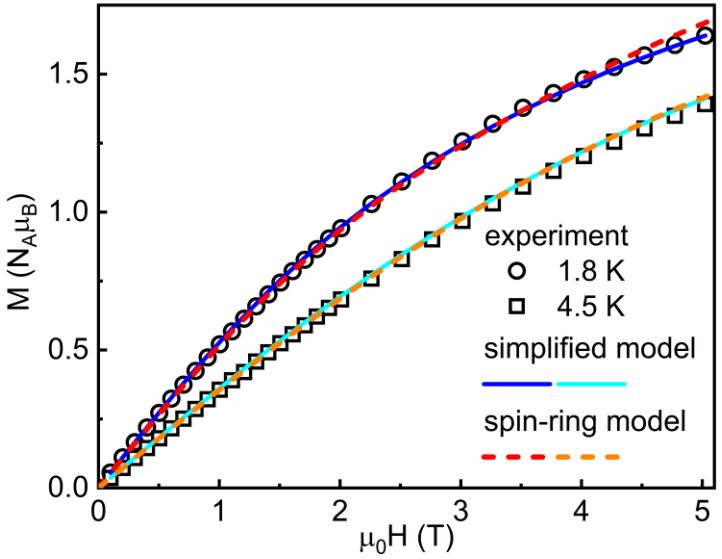
$\chi = \chi_{Ni} + \chi_{dimer} + \chi_0$

$\hat{H}_{Ni} = D\left[\hat{S}_Z^2 - \frac{S(S+1)}{3}\right] + E\left[\hat{S}_x^2 - \hat{S}_y^2\right]$

?

Magnetic interactions in hybrid complexes - $M(2ampy)_2(TCNQ)_2$, M=Ni, Zn





Magneto-structural correlations

D/k_B = 4.9 K at 296 K
D/k_B = -5.4 K at 173 K
D/k_B = -4.3 K at 100 K

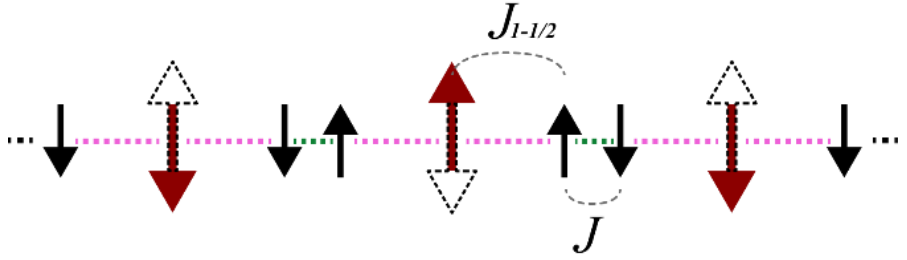
Simplified model of ARS AFM dimers and isolated Ni sites

$$\chi = \chi_{Ni} + \chi_{dimer} + \chi_0$$

$$\chi_{Ni} = \frac{\chi_{ZFS}}{1 - \frac{zJ'}{N_A g^2 \mu_B^2}\chi_{ZFS}}$$

D/k_B = -8.5 K
E/D = 0.28
g_{Ni} = 2.11
J'/k_B = 0.6 K
J/k_B = 1206 K

Spin-ring model approach includes interaction between ARS and Ni sites

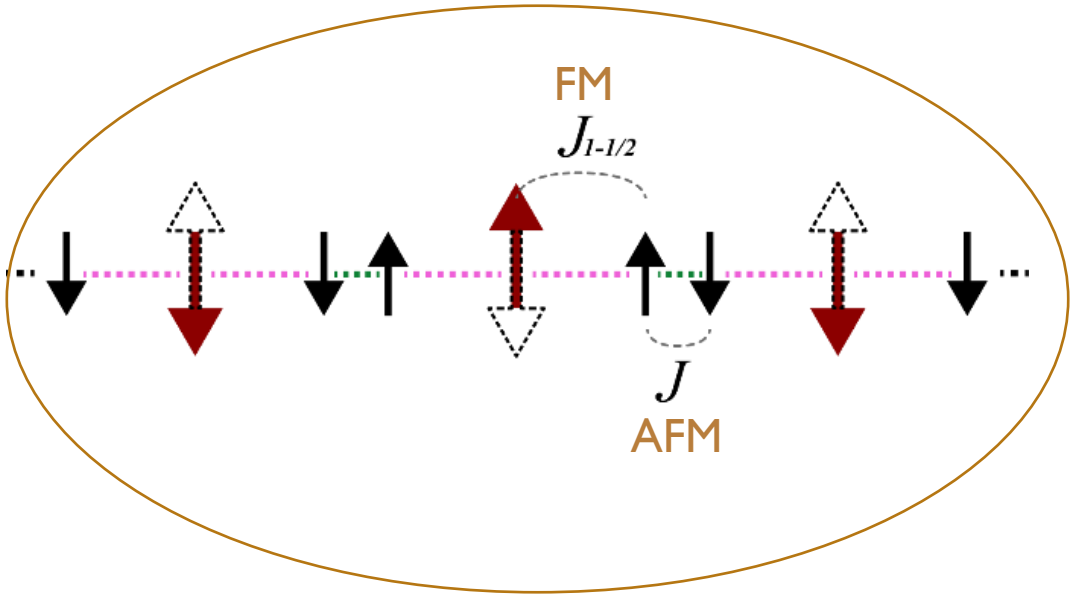


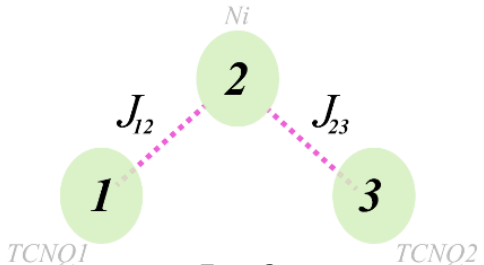
D/k_B = -6.5 K
E/D = 0.2
g_{Ni} = 2.12
$J_{1\text{-}1/2}/k_B$ = -22 K **FM - ?**
J/k_B = 1105 K

Titiš J., Boča R., *Inorganic Chemistry (2010) 49(9) 3971-3973*

Magnetic interactions in hybrid complexes - $M(2ampy)_2(TCNQ)_2$, M=Ni, Zn

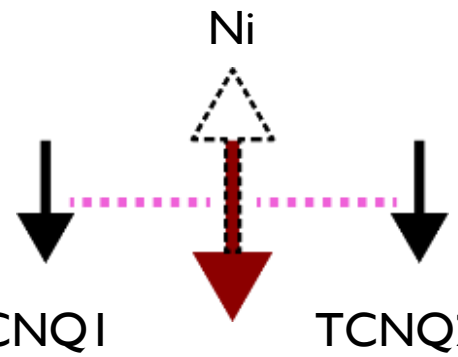
Check the exchange interaction by BS DFT method





$J_{13}=0$

$J_{12}=J_{23}$



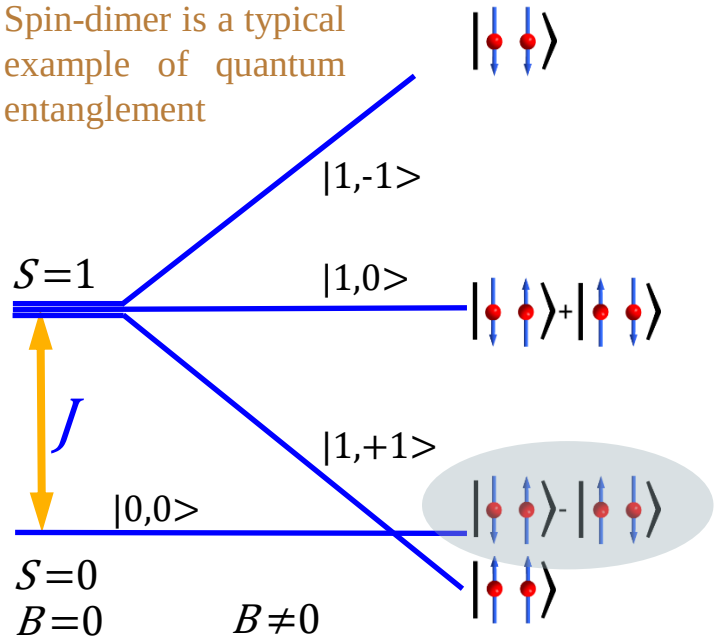
$HS\frac{\uparrow\uparrow\uparrow}{1\,2\,3}$	$J_{13}=0$
$BS1\frac{\uparrow\downarrow\uparrow}{1\,2\,3}$	$J_{12}=J_{23}=-\frac{E_{HS}-E_{BS1}-E_{BS2}+E_{BS3}}{\langle S^2\rangle_{HS}-\langle S^2\rangle_{BS1}-\langle S^2\rangle_{BS2}+\langle S^2\rangle_{BS3}}$
$BS2\frac{\downarrow\uparrow\uparrow}{1\,2\,3}$	if $BS2=BS3, \langle S^2\rangle_{BS2}=\langle S^2\rangle_{BS3}$, then
$BS3\frac{\uparrow\uparrow\downarrow}{1\,2\,3}$	$J_{12}=J_{23}=-\frac{E_{HS}-E_{BS1}}{\langle S^2\rangle_{HS}-\langle S^2\rangle_{BS1}}$

	100 K	173 K	296 K
$J_{1-\frac{1}{2}}/k_B$ (K)	-66.24	-69.75	-71.71

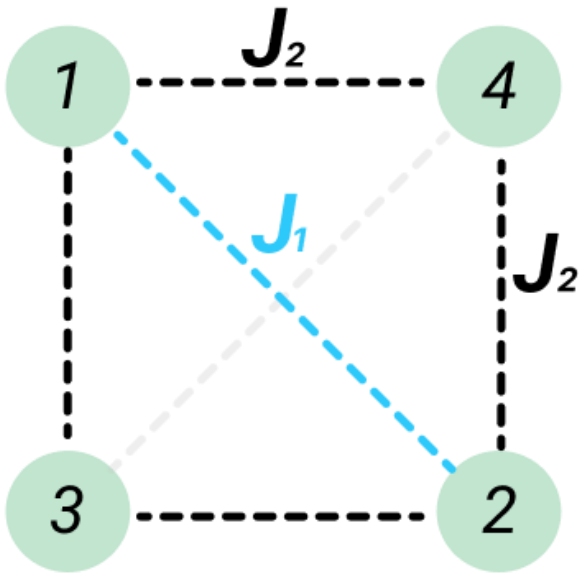
Based on approach of Arczyński M., Pinkowicz D., *Inorganic Chemistry (2020) 59(18) 13489-13501*

Quantum entanglement in diamond spin clusters - $[Ni_4(ClQ)_6Cl_2(H_2O)_2]\cdot 2DMF$

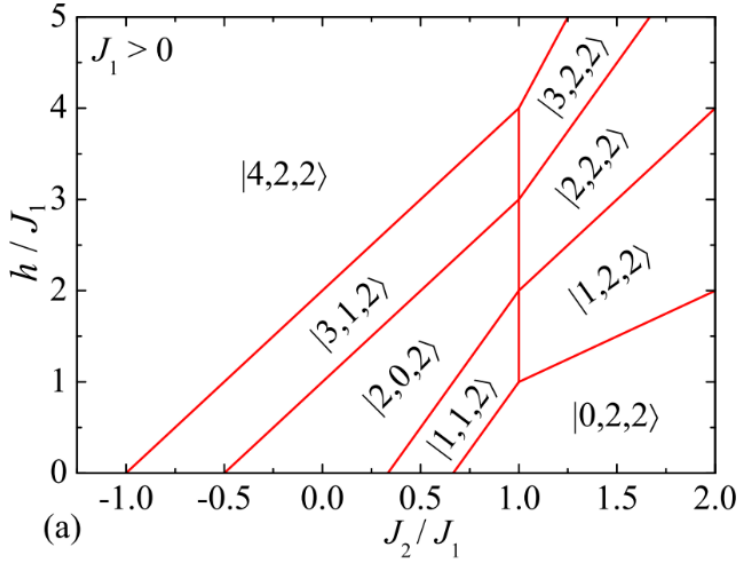
Spin-dimer is a typical example of quantum entanglement



$[Ni_2(Medpt)_2(\mu\text{-}ox)(H_2O)_2](ClO_4)_2$

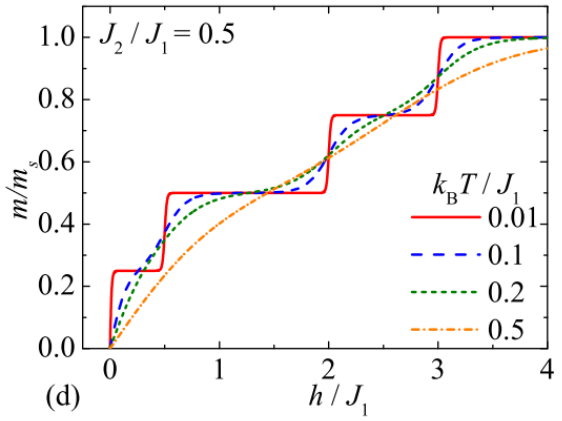


Ground-state phase diagram

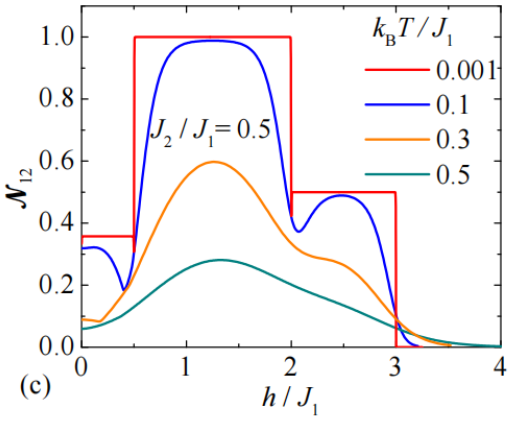


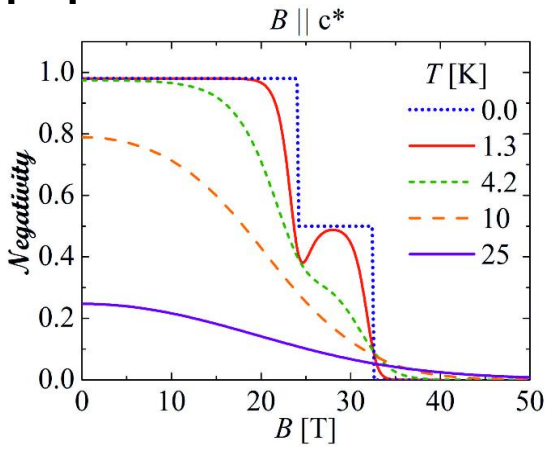
A. Ghannadan and J. Strečka, Molecules **26**, 3420 (2021)

Magnetization

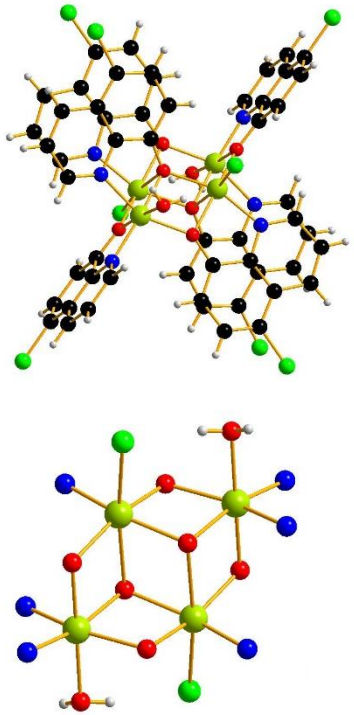


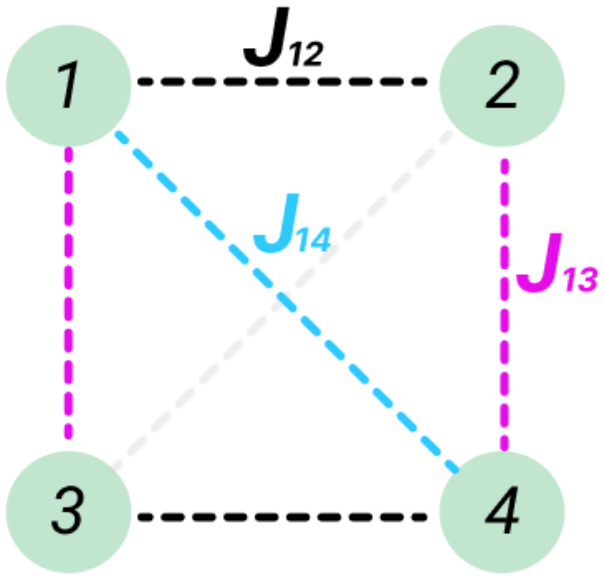
Negativity – Quantum superposition state

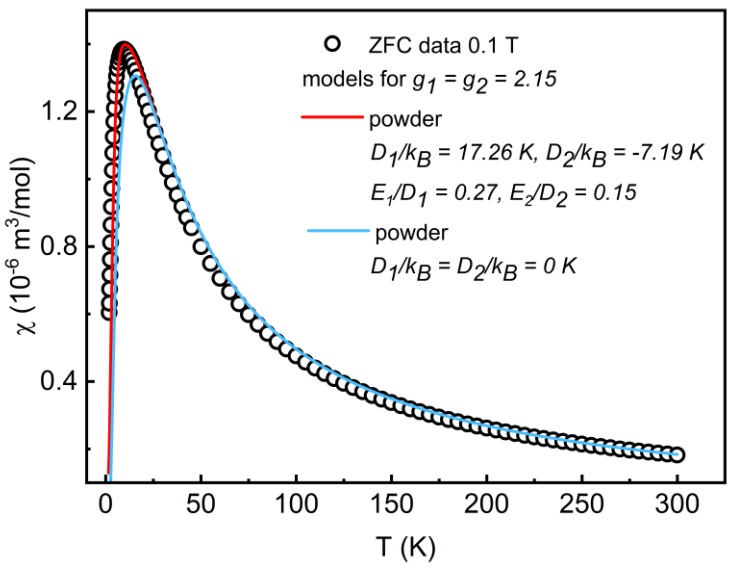


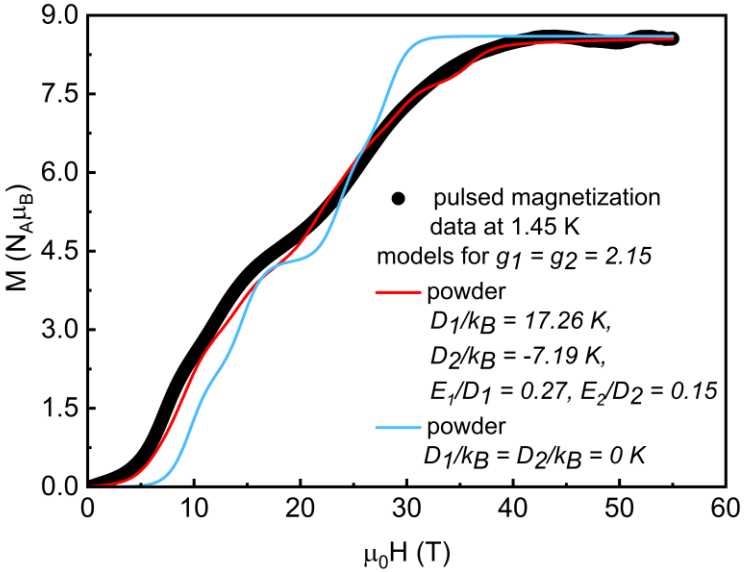


Quantum entanglement in diamond spin clusters - $[Ni_4(ClQ)_6Cl_2(H_2O)_2]\cdot 2DMF$









BS DFT calculations

4Ni	B3LYP (K)
$J_{12} = J_{34}$	11.77
$J_{13} = J_{24}$	3.15
J_{14}	8.45
J_{23}	0.072

$g_1 = 2.25$, $g_2 = 2.23$

$D_1 = D_4 = 17.1$ K

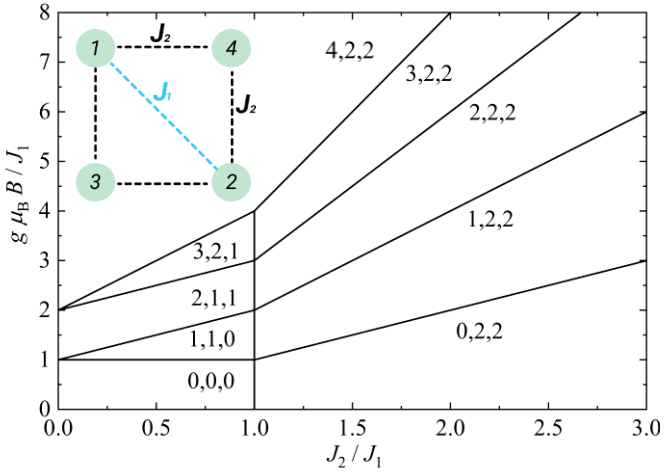
$D_2 = D_3 = -7.3$ K

$E_1/D_1 = 0.27$, $E_1/D_2 = 0.15$

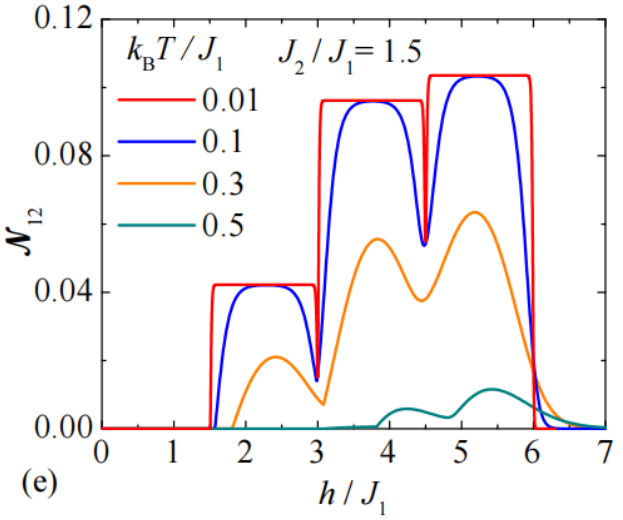
set of exchange interactions

J_{12}	J_{13}	J_{14}	J_{23}	J_{24}	J_{34}
15.8	4.3	5.7	0	4.3	15.8

Ground-state phase diagram



Negativity



Mariia Holub

Conclusions

- **AFM *S* = 1/2 bond-alternating (dimerized) chain based on TCNQ ARS – prototype of a complex qubit system**

(Et-2,6-diMe-Pz)(TCNQ)$_2$ It consists of a small number of spin sites in the chain, which are more susceptible to the influence of inhomogeneous effects, yielding shorter coherence as in other studied ARS.

- **Hybrid transition metal - ARS complexes – alternating spin and exchange interaction chain - understanding of magneto-structural correlations for design of gapped spin systems**

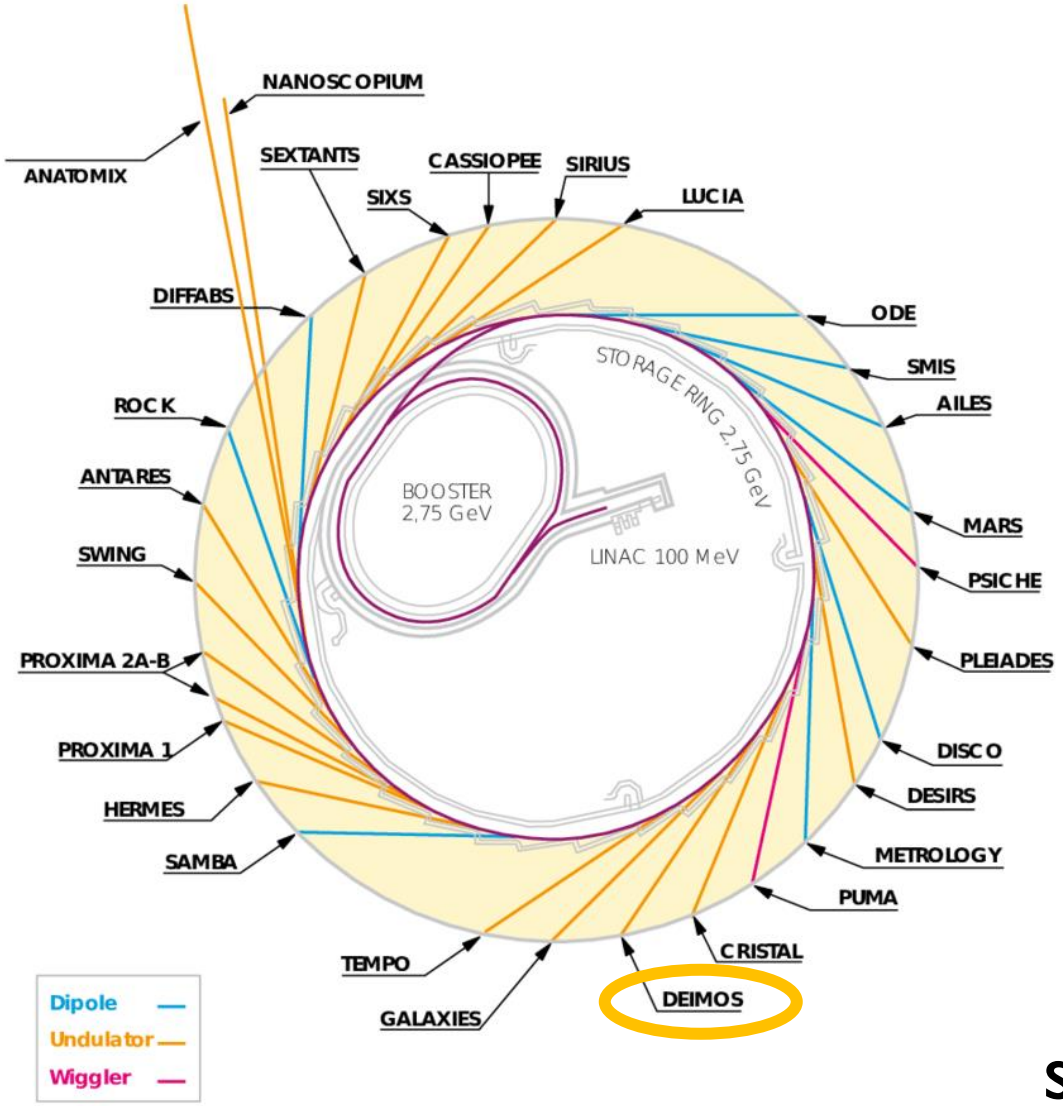
M(2ampy)$_2$(TCNQ)$_2$, M=Zn, Ni. It was suggested FM exchange interaction $J_{1\text{-}1/2}/k_B$ = -22 K between Ni(II) and ARs, effectively reducing the TCNQ-TCNQ interaction compared to Zn(II) analogue.

[Ni(bpy)$_3$]$_2$(TCNQ-TCNQ)(TCNQ)$_2$·6H$_2$O. Even seemed on the first view like uniform chain, structure has minor planar deviations at ARs stacking what leads to dimerization.

[Ni(bpy)(Bz)$_2$]. The intermolecular interactions were analyzed and calculated by ORCA package. Unfortunately, our attempts to detect a non-zero out of phase AC susceptibility, how was observed in some octahedral Ni-based complexes, were unsuccessful.

- **AFM diamond spin cluster systems based on *S* = 1 Ni(II) ions as model system for the understanding and tuning of quantum entanglement**

[Ni$_4$(ClQ)$_6$Cl$_2$(H$_2$O)$_2$]·2DMF identified as a diamond spin cluster; the model system proposed to study the field-controlled quantum entanglement. The *ab initio* and BS DFT calculations predicted strong exchange couplings and two types of ZFS splitting in the spin cluster. The pulsed-field magnetization measured at low temperatures in magnetic fields up to 55 T was essential for constructing a ground-state phase diagram suggesting four magnetization plateaus in the system. In comparison with theoretical predictions, we can expect the field-induced increase of negativity, the measure of quantum entanglement, if the ZFS splitting can be reduced by proper chemical design.



SOLEIL
synchrotron

TECHNIQUES

- **X**-ray **A**bsorption **S**pectroscopy (**XAS**)
- **X**-ray **M**agnetic **C**ircular **D**ichroism (**XMCD**)
- **X**-ray **N**atural **C**ircular **D**ichroism (**XNCD**)
- **X**-ray (**M**agnetic) **L**inear **D**ichroism (**XMLD**)

SCIENTIFIC COMMUNITIES

PHYSICS

Condensed matter, material science, surface and interface magnetism…

CHEMISTRY

Molecular magnet and nanomagnet, hybrid magnetic material, spintronics…

BIOLOGY

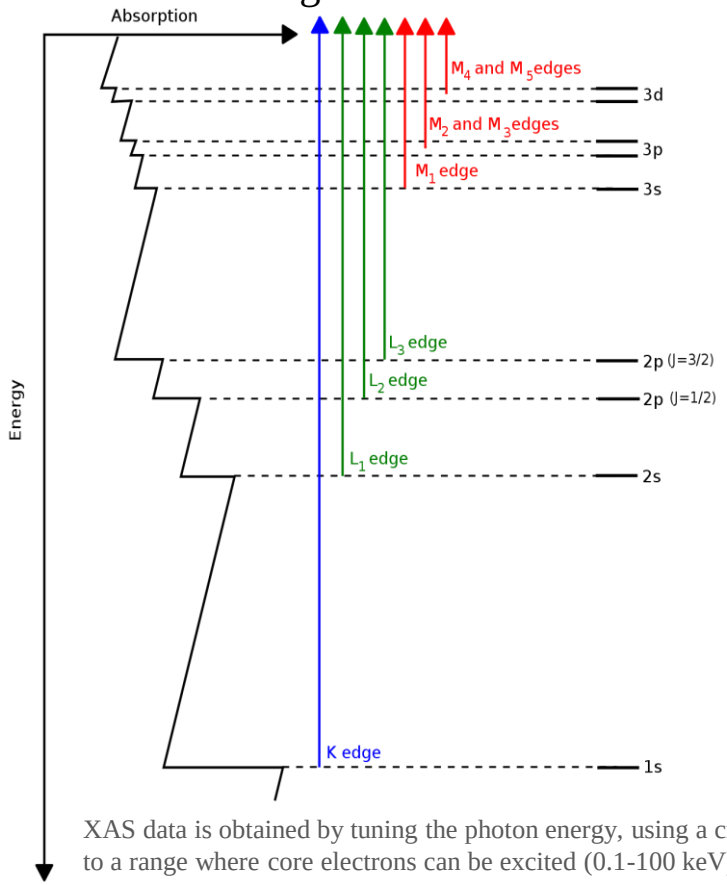
Metalloenzyme, biocompatible magnet…

MINERALOGY

Environmental science, paleo-magnetism…

XAS

- for the local geometric and/or electronic structure of matter.

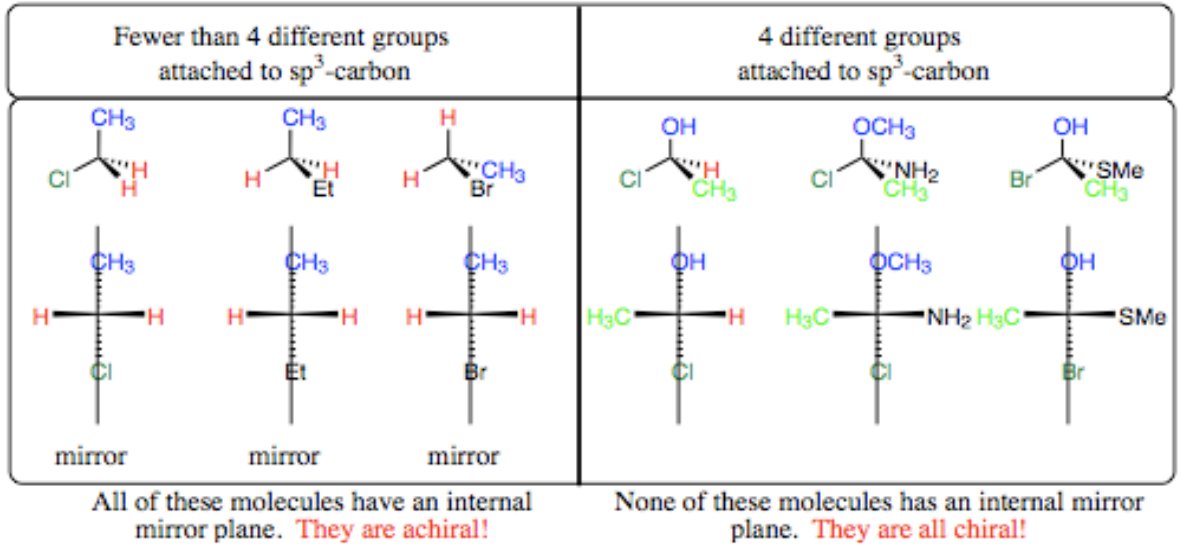


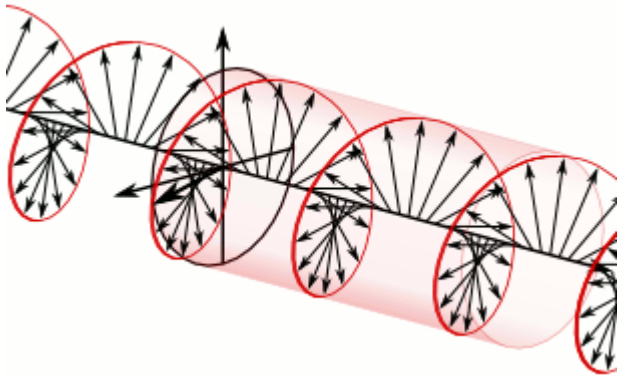
XAS data is obtained by tuning the photon energy, using a crystalline monochromator, to a range where core electrons can be excited (0.1-100 keV).

The edges **K-, L-, and M-edges** correspond to **n = 1, 2, and 3** orbitals

XNCD

- for optical **isomerism** and secondary structure of molecules.
- for chiral molecules (has a non-superposable mirror image).

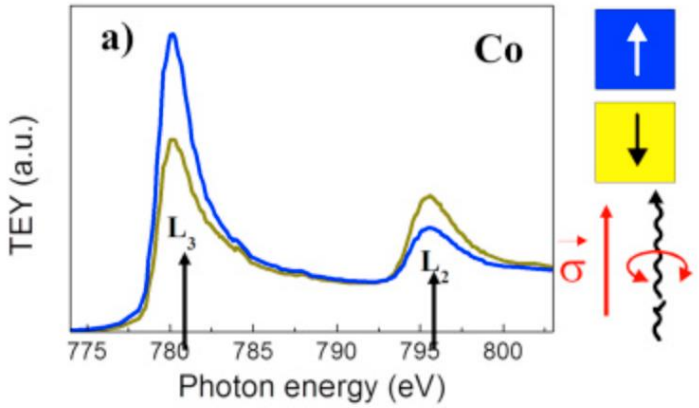


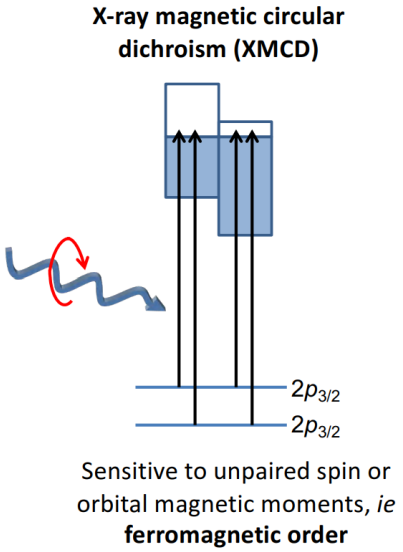


To convert circularly polarized light to the other handedness, one can use a **half-waveplate.**
A half-waveplate shifts a given linear component of light one half of a wavelength relative to its orthogonal linear component.

XMCD

is a difference spectrum of two X-ray absorption spectra (**XAS**) taken in a magnetic field, one taken with left circularly polarized light, and one with right circularly polarized light.



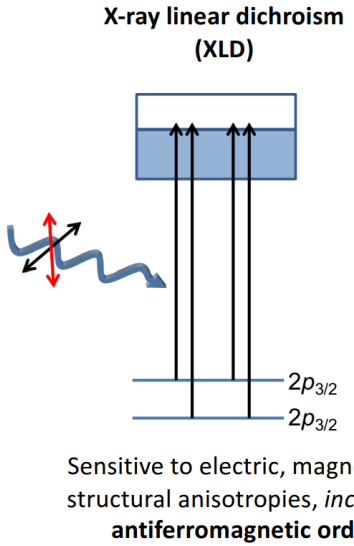


Sensitive to unpaired spin or orbital magnetic moments, *ie* **ferromagnetic order**

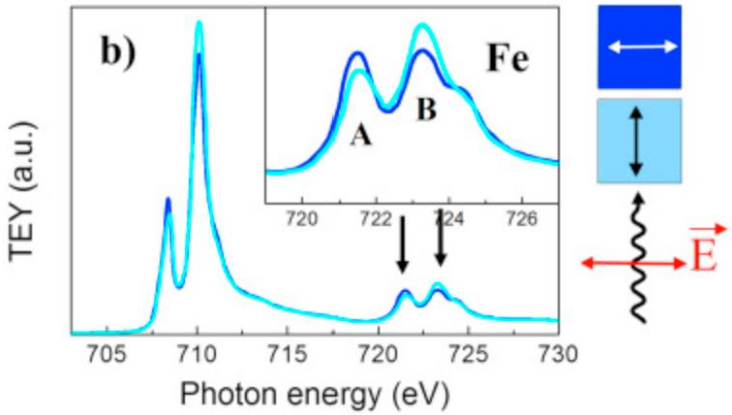
In the case of transition metals such as iron, cobalt, and nickel, the absorption spectra for XMCD are usually measured at the L-edge.

XMLD

is defined as the difference in absorbance found when linearly polarized light with the electric vectors in two directions, perpendicular to each other.



Sensitive to electric, magnetic or structural anisotropies, *including* **antiferromagnetic order**



used for imaging domains and domain walls in magnetic and magnetoelectric materials, investigating surface and interface effects.

Scientific opportunities

SURFACE AND INTERFACE MAGNETISM, MATERIALS FOR SPIN ELECTRONICS	Magnetic properties of low dimensional structures – size effects; correlation between magnetic properties, morphology and structure - magnetoelastic effects, contributions in the magnetic anisotropy; magnetic moments and anisotropy of isolated atoms - tunneling surface diffusion at very low temperatures; ferromagnetic-antiferromagnetic interfaces – origin of the exchange coupling; magnetic tunnel junctions; etc.
MOLECULAR MAGNETS, LANGMUIR-BLODGETT FILMS, HYBRID MAGNETIC MATERIALS, HIGH SPIN MOLECULES	Magnetic and electronic properties of pure molecular magnets (dichroism of small magnetic polarization of the NO groups, with site selectivity); organo-metallic compounds and supramolecular assemblies – large variety of magnetic structures tuning chemical properties, "exotic" magnetic structures and mechanisms; lamellar compounds – ferrimagnetism, magnetic frustration; polynuclear molecules with monodisperse magnetic properties (moments and anisotropy) – molecular electronics, q-bits.
SUPERPARAMAGNETIC NANOPARTICLES, EARTH SCIENCE, PALEOMAGNETISM	Magnetic properties of variously synthesized particles of magnetite (Fe_3O_4), maghemite ((γ-Fe_2O_3), hematite (α-Fe_2O_3), pyrrhotite ($Fe_{1-x}S$) or greigite (Fe_3S_4) - magnetic surface canting, chemical and magnetic disorder, vacancies ordering.

THANK YOU
FOR YOUR ATTENTION