HOKKAIDO SUMMER INSTITUTE 2024

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Magnetic spectroscopy experiments as a probe of the microscopic electronic properties of materials

https://hokkaidosummerinstitute.oia.hokudai.ac.jp/en/courses/CourseDetail=G006

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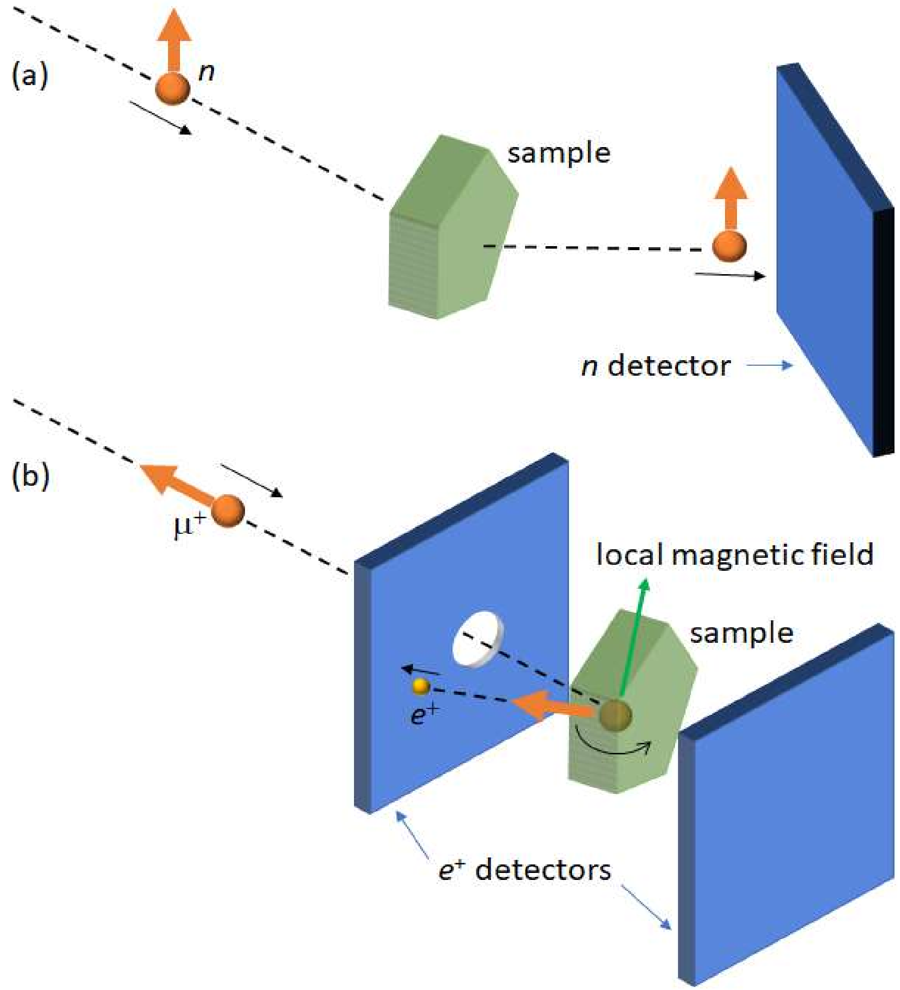
Sapporo, 29. July – 2. August 2024

Outline

- ❑ Introduction to magnetism
- ❑ Probing magnetism: conventional bulk and scattering techniques
- ❑ Local probes of magnetism
- ❑ Electron spin resonance (ESR)
- ❑ Nuclear magnetic resonance (NMR)
- ❑ Muon spectroscopy (μSR)
- ❑ Summary: strengths, limitations and complementarity of local probes



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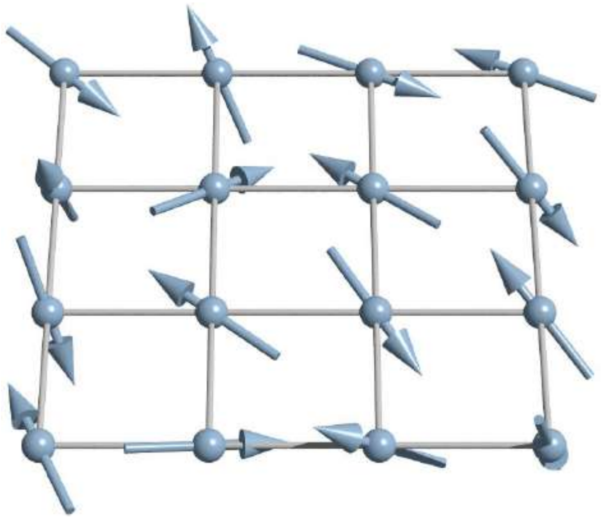
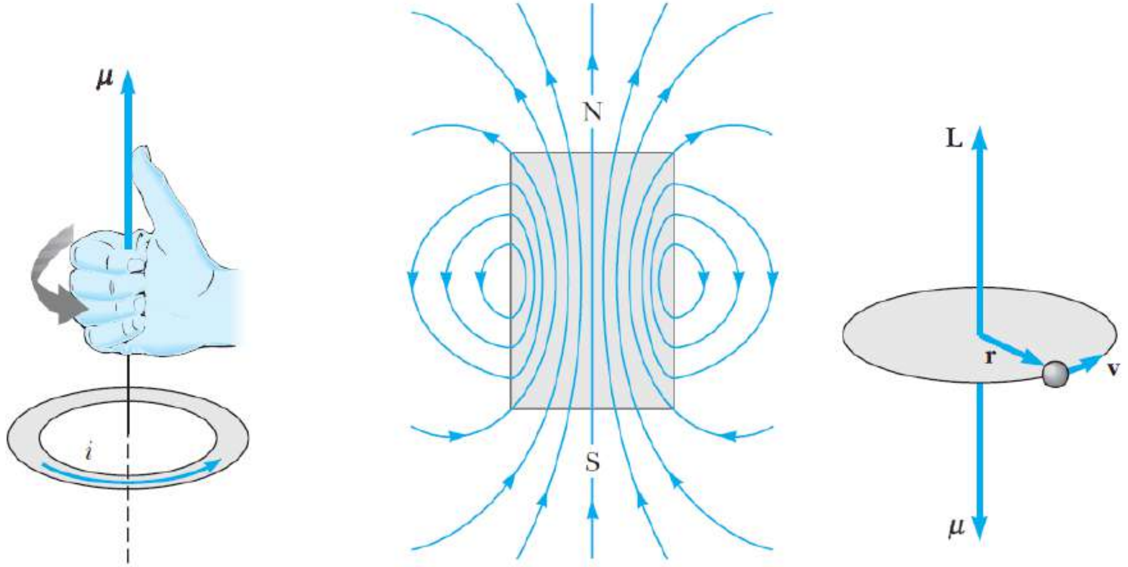


Introduction to Magnetism

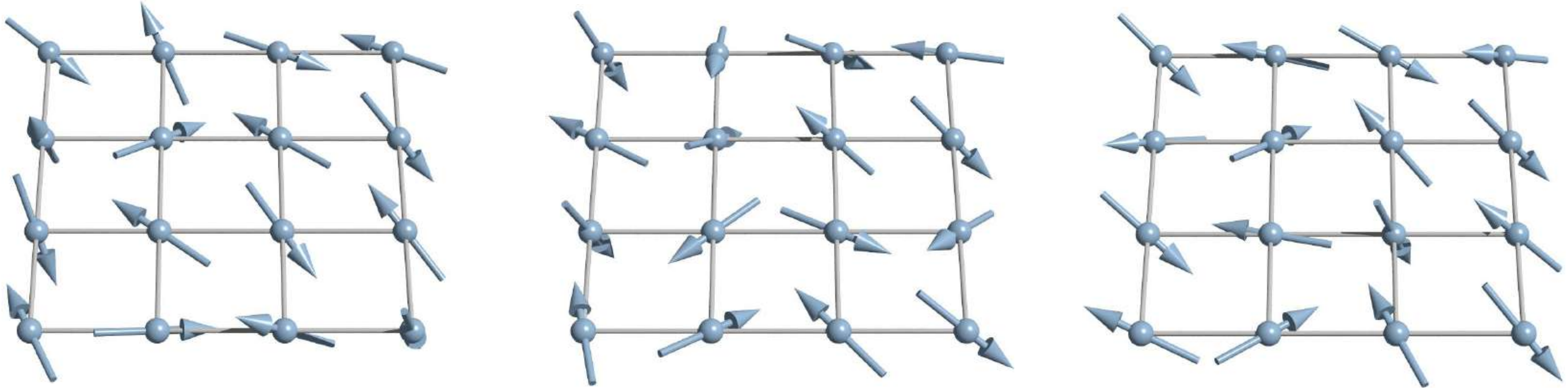
- Magnetic moments:

$$\vec{\mu} = \vec{\mu_o} + \vec{\mu_s} = -\frac{\mu_B}{\hbar}(\vec{L} + g\vec{S})$$

$$\mu_B = \frac{e_0\hbar}{2m_e} = 9{,}27 \times 10^{-24}\ \mathrm{Am}^2$$



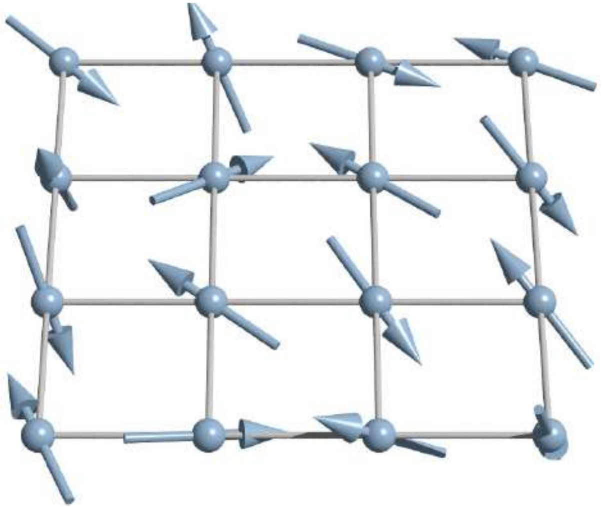
- Electric insulators: localized moments



The Many Faces of Magnetism

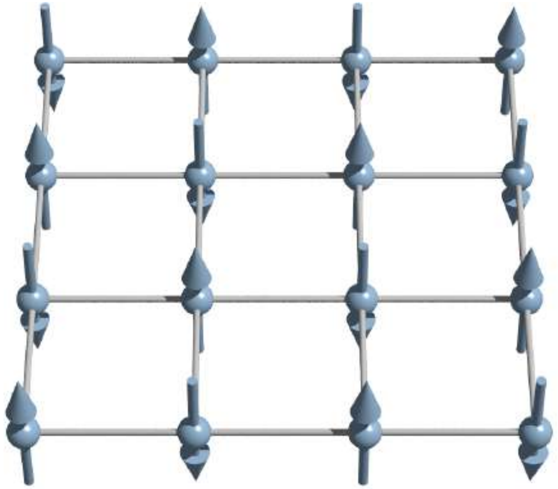
- Exchange interactions: $\mathcal{H} = J \sum_{(i,j)} \vec{S}_i \cdot \vec{S}_j$

$T > T_c, T_N$



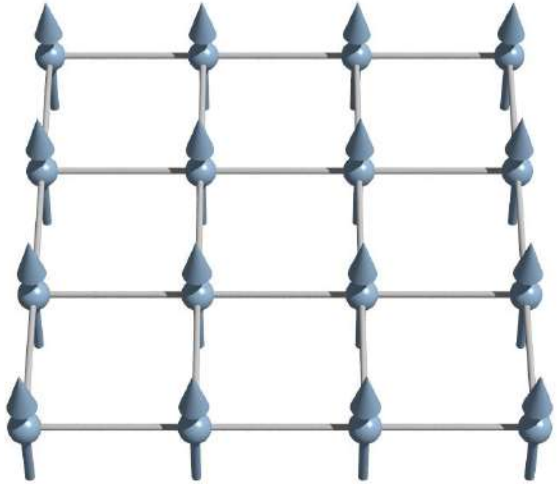
PARAMAGNET

$T < T_N$



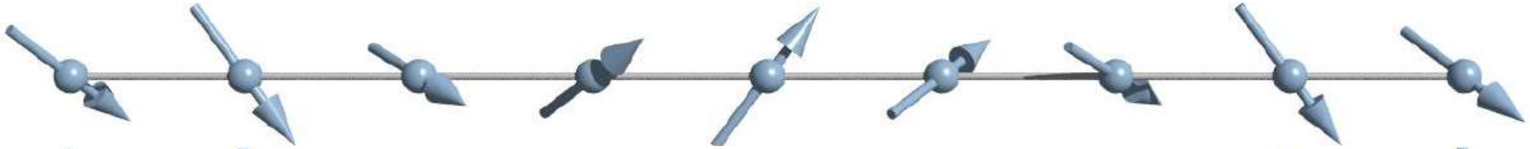
ANTIFERROMAGNET: $J > 0$

$T < T_c$

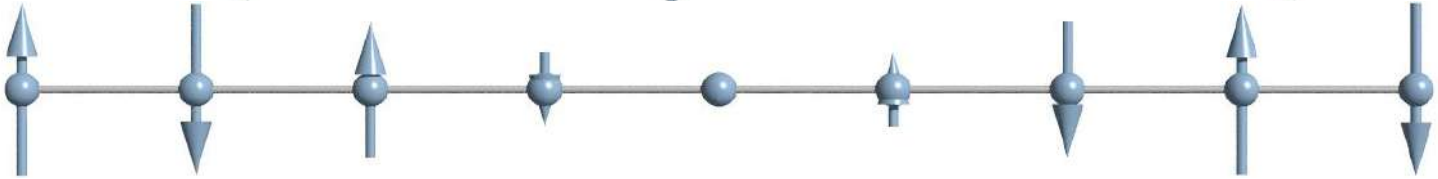


FERROMAGNET: $J < 0$

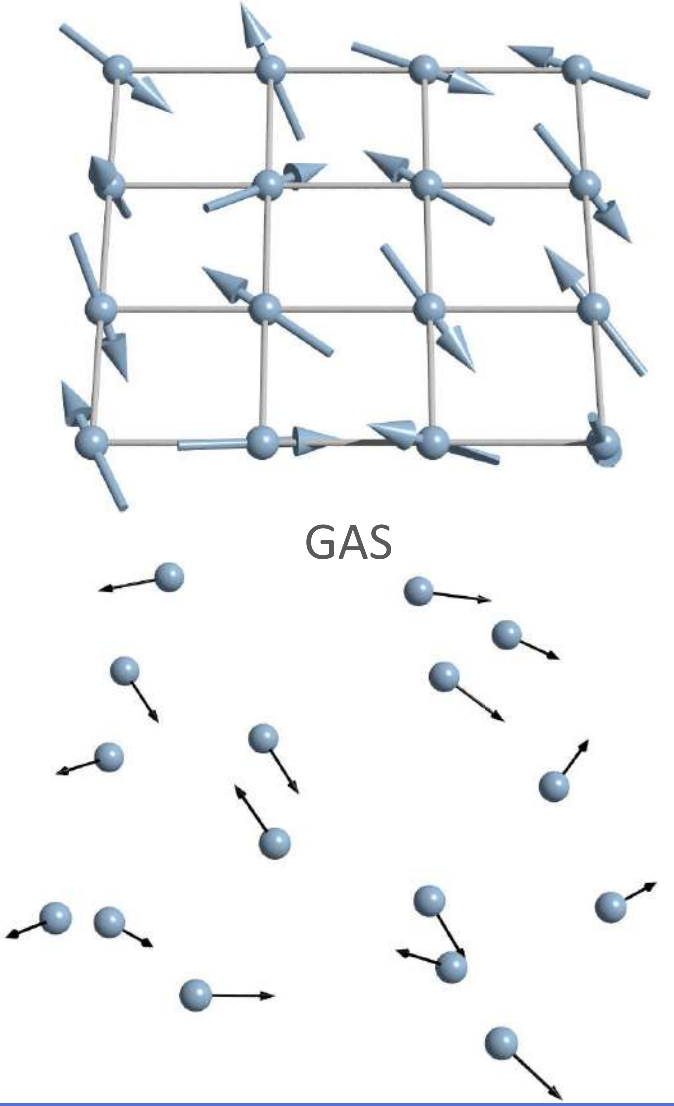
SPIRAL

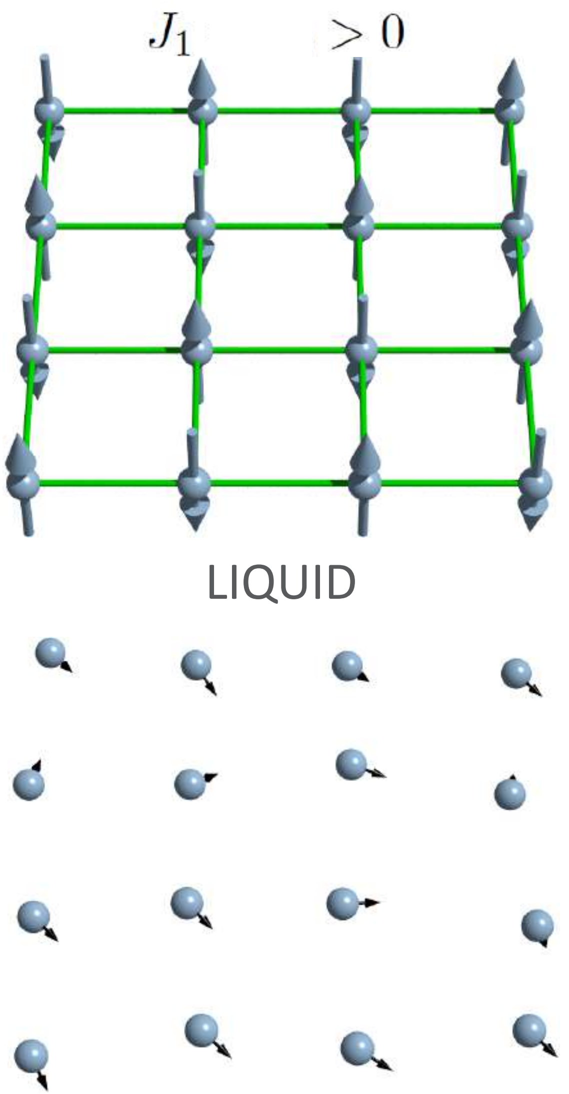


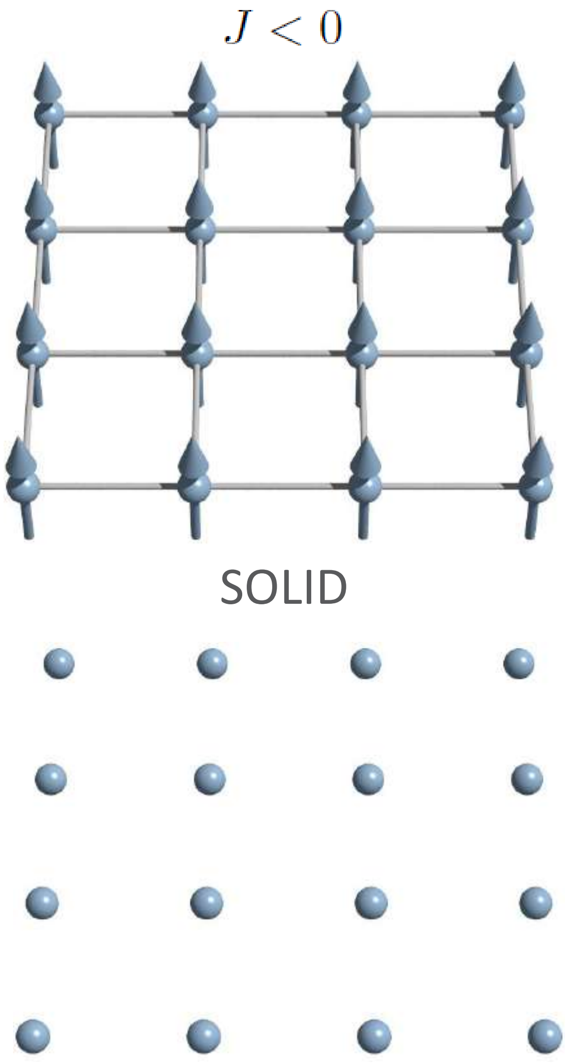
AMPLITUDE-MODULATED



Analogy with States of Matter







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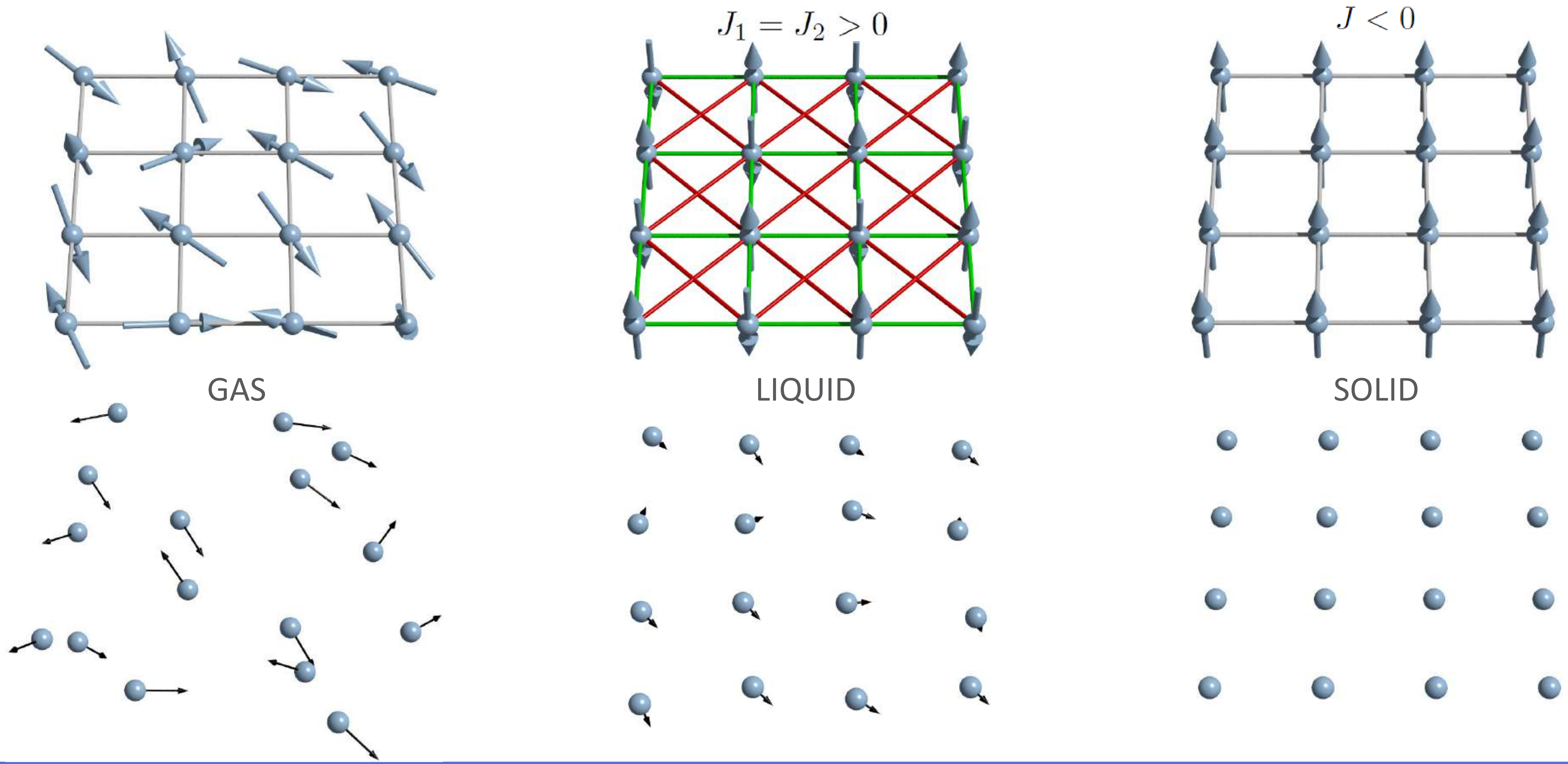

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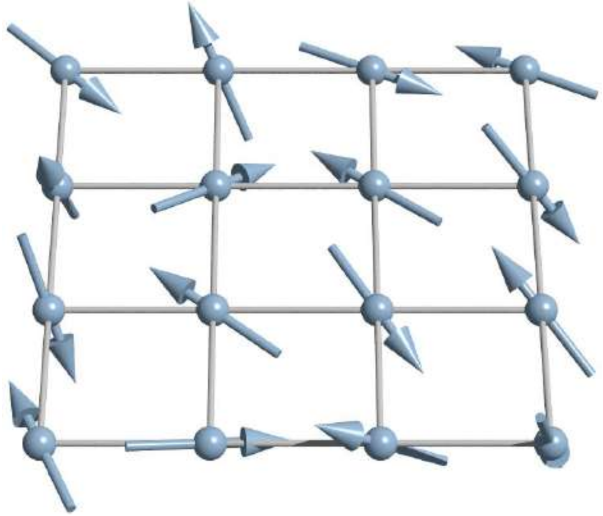
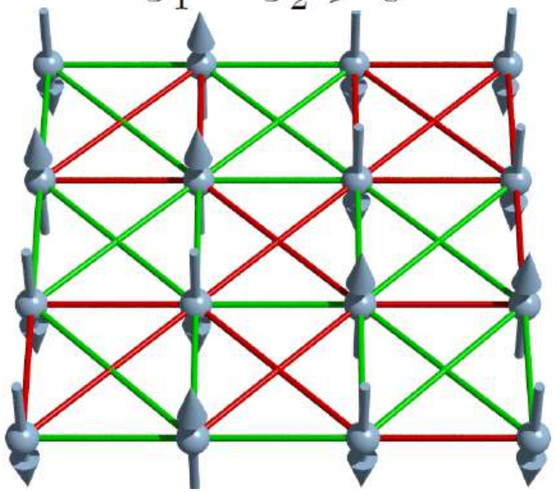
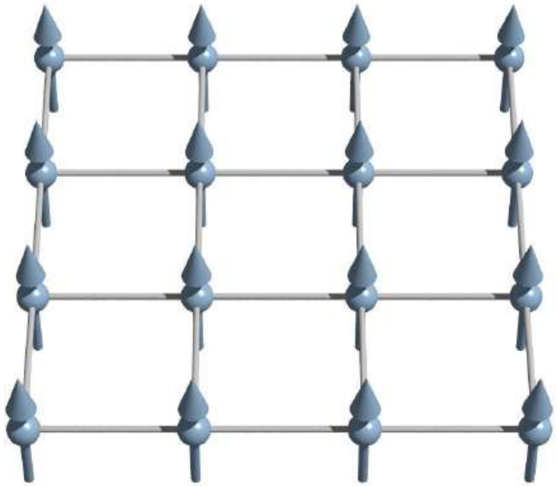


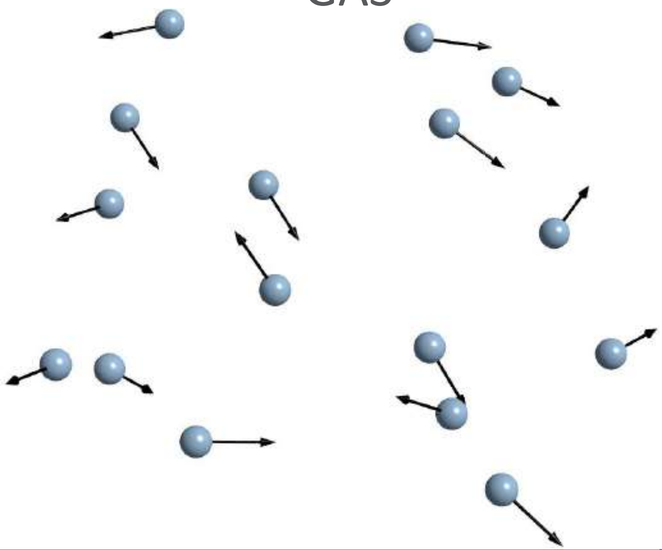


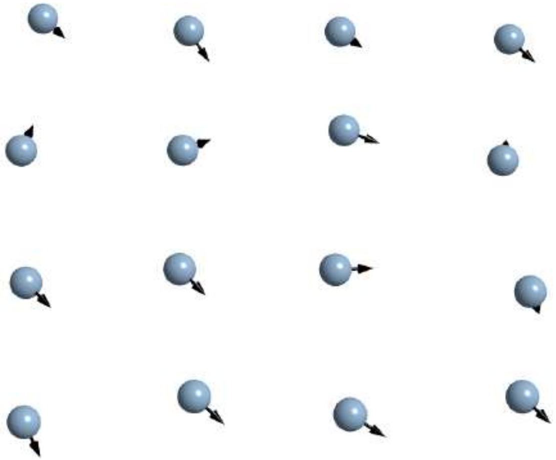


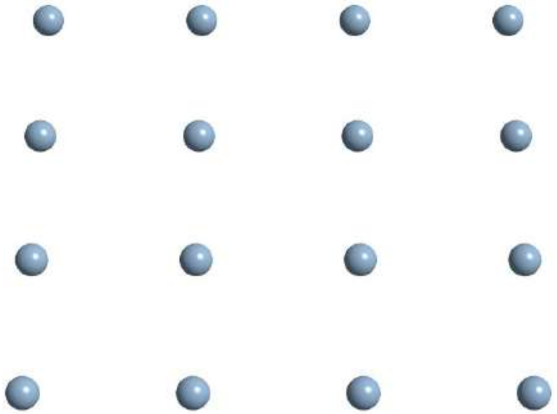
GAS

LIQUID

SOLID







Analogy with States of Matter

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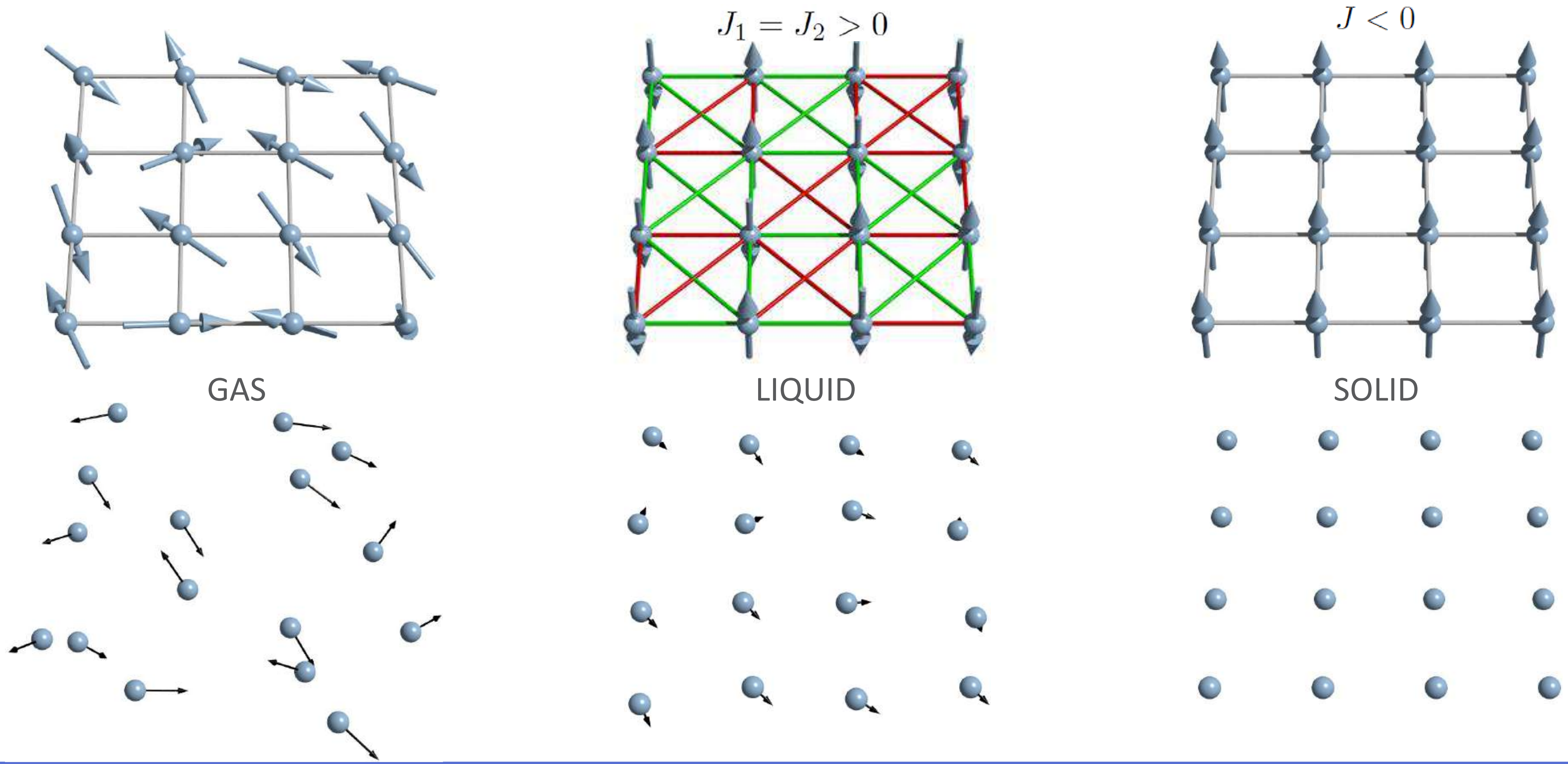
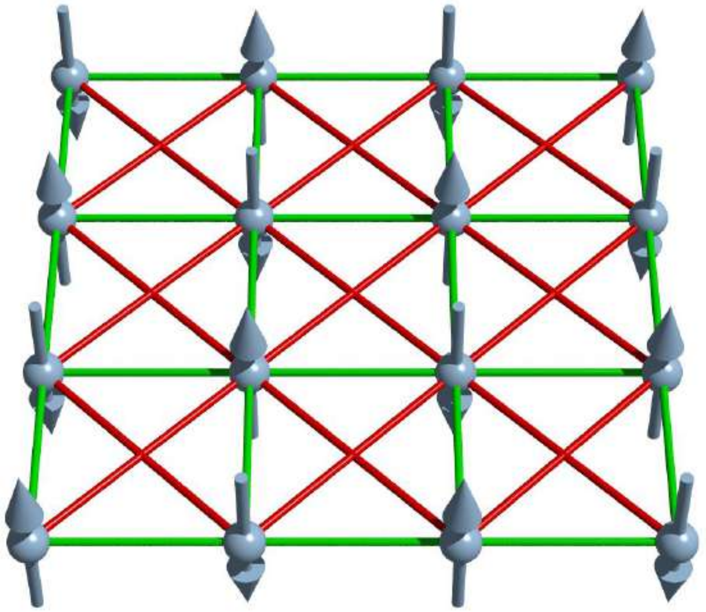


Frustration in Magnetism

- Geometrical frustration: an inability to simultaneously minimize all local interactions as a consequence of the frustration of the forces or geometry.



$$\mathcal{H} = \sum_{(i,j)} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

Frustration in Magnetism

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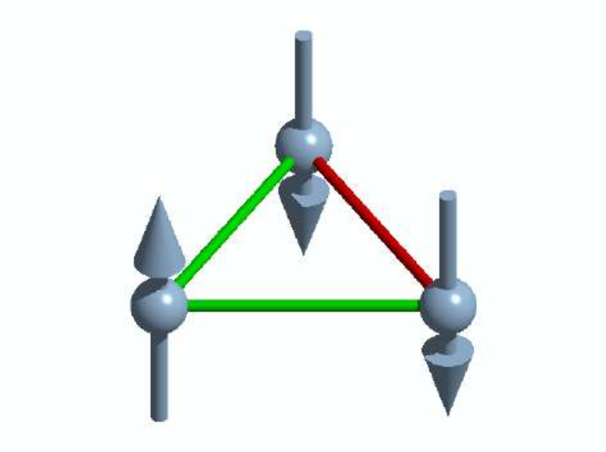
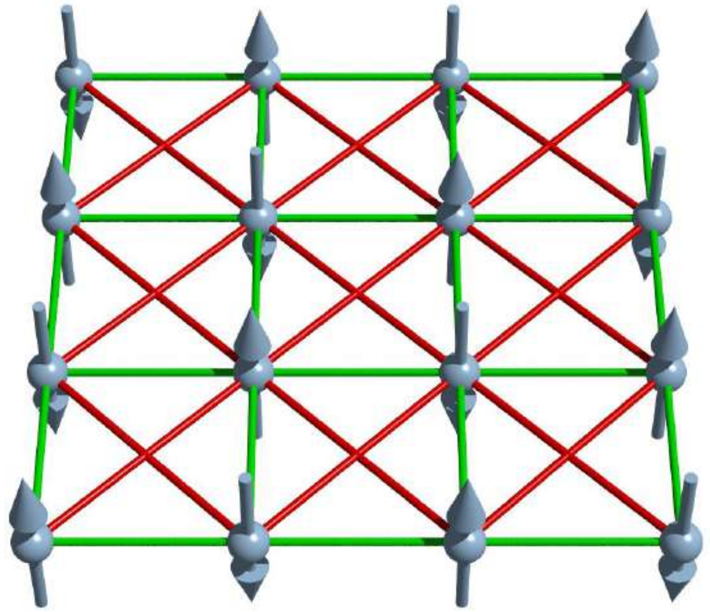
- Generic example: Ising AFM triangle



$$\mathcal{H} = J \sum_{\Delta} S_i^z S_j^z$$



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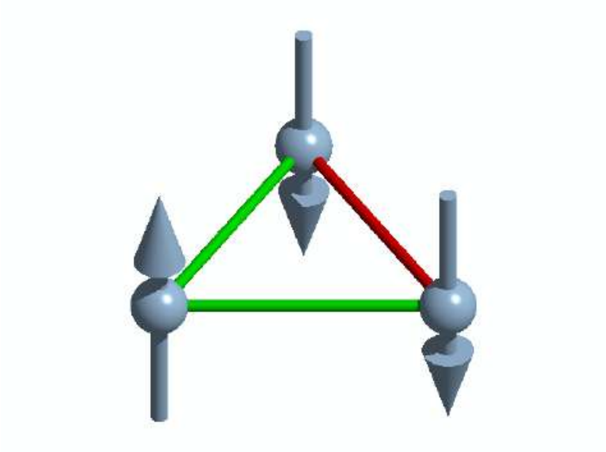
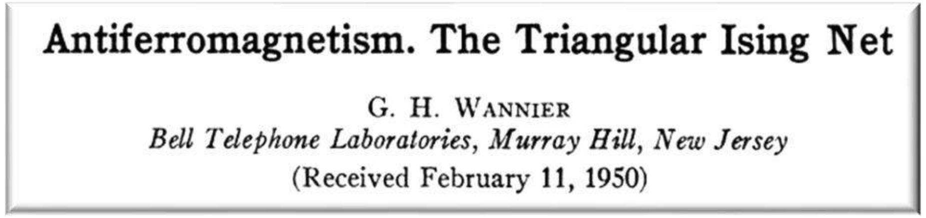


$$\mathcal{H} = J \sum_{\Delta} S_i^z S_j^z$$

- Macroscopic degeneracy: disordered state



Antiferromagnetism. The Triangular Ising Net

G. H. Wannier
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received February 11, 1950)

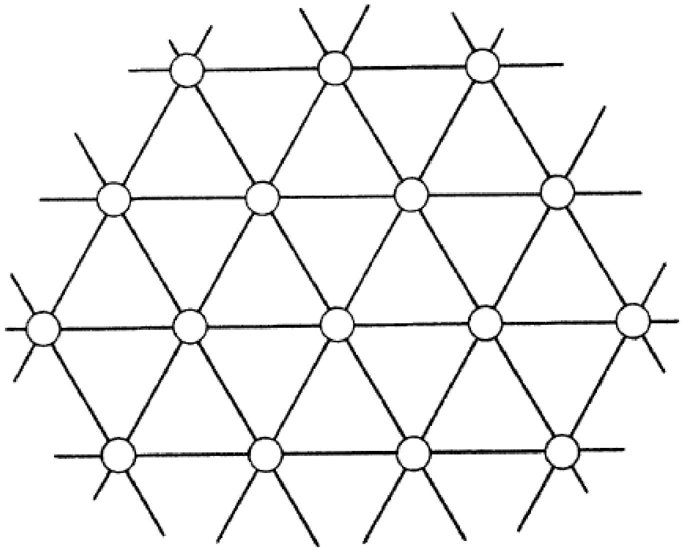


Fig. 2. Triangular Ising net. No perfectly regular antiferromagnetic arrangement can be fitted into this structure.

Wannier, Phys. Rev. **79**, 357 (1950)

Frustration in Magnetism

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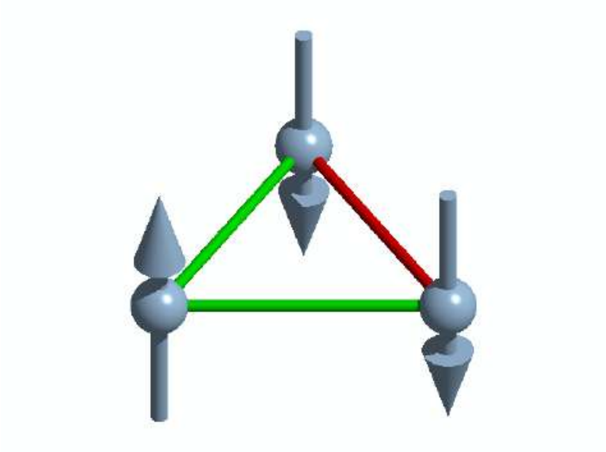

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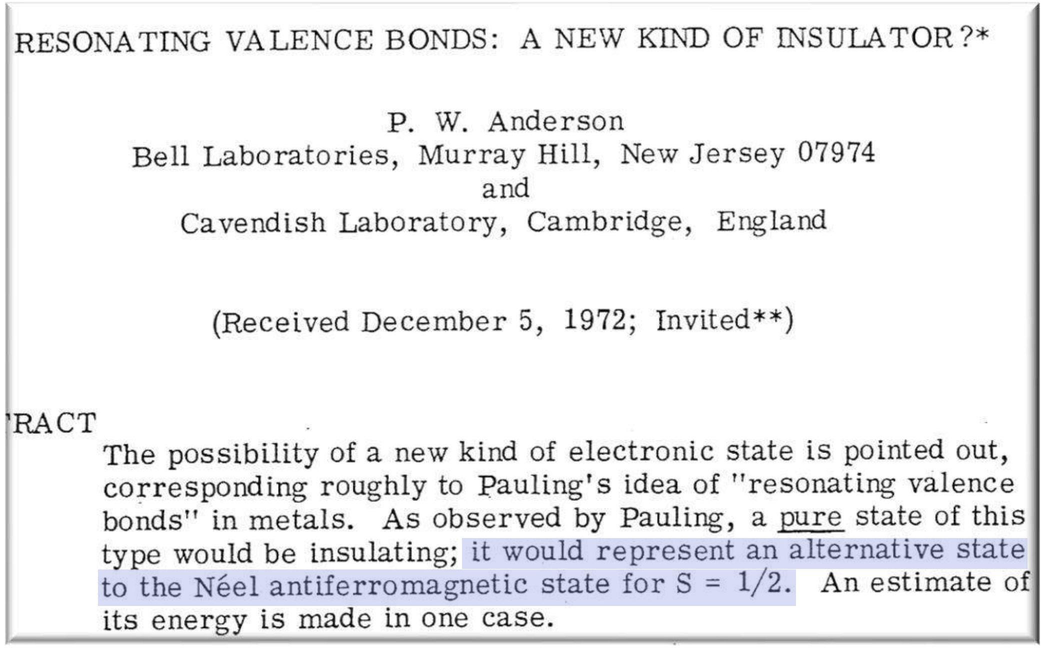


RESONATING VALENCE BONDS: A NEW KIND OF INSULATOR?*

P. W. Anderson
Bell Laboratories, Murray Hill, New Jersey 07974
and
Cavendish Laboratory, Cambridge, England

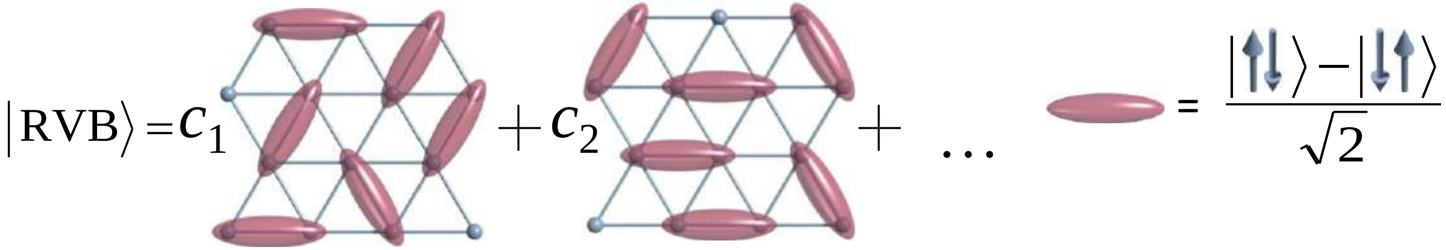
(Received December 5, 1972; Invited**)

RACT

The possibility of a new kind of electronic state is pointed out, corresponding roughly to Pauling's idea of "resonating valence bonds" in metals. As observed by Pauling, a pure state of this type would be insulating; it would represent an alternative state to the Néel antiferromagnetic state for S = 1/2. An estimate of its energy is made in one case.

Anderson, Mat. Res. Bull. **8**, 153 (1973)

- Many-body entanglement: novel excitations



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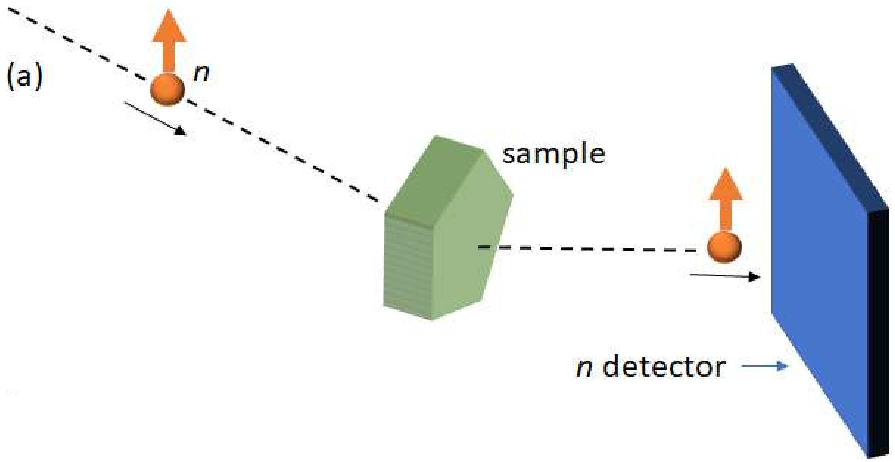
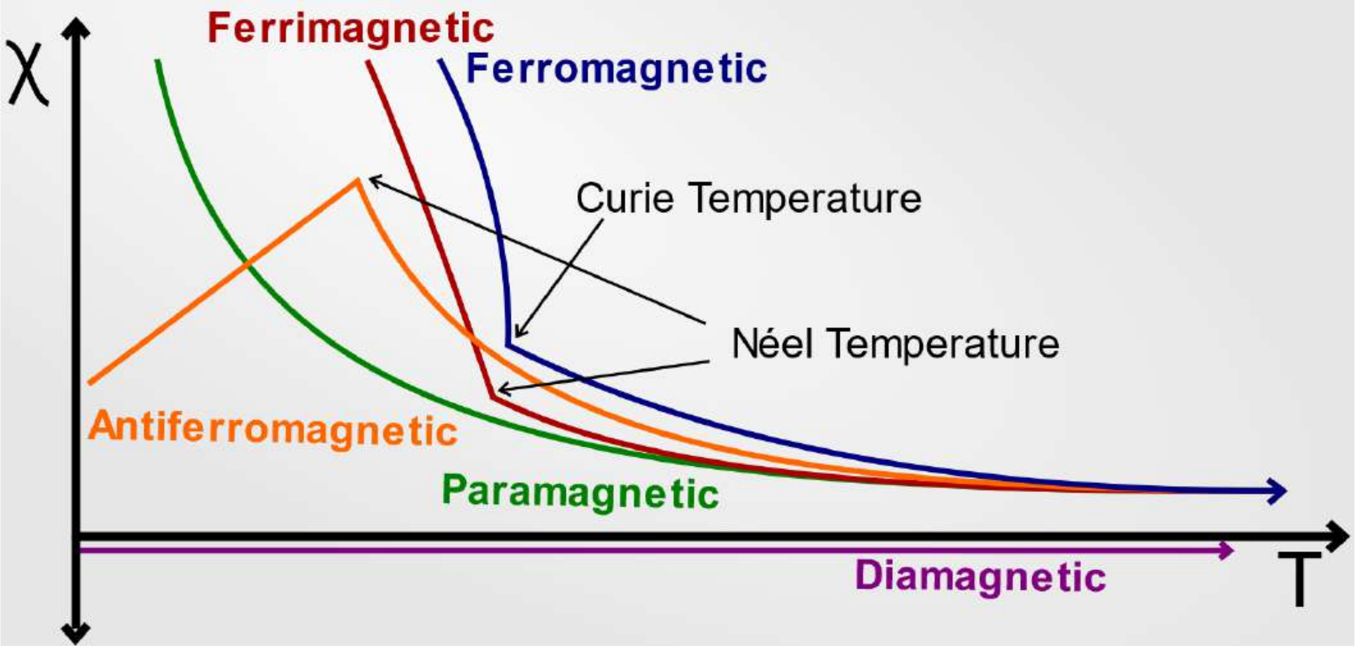


Bulk Magnetization/Susceptibility

- Detecting phase transitions:

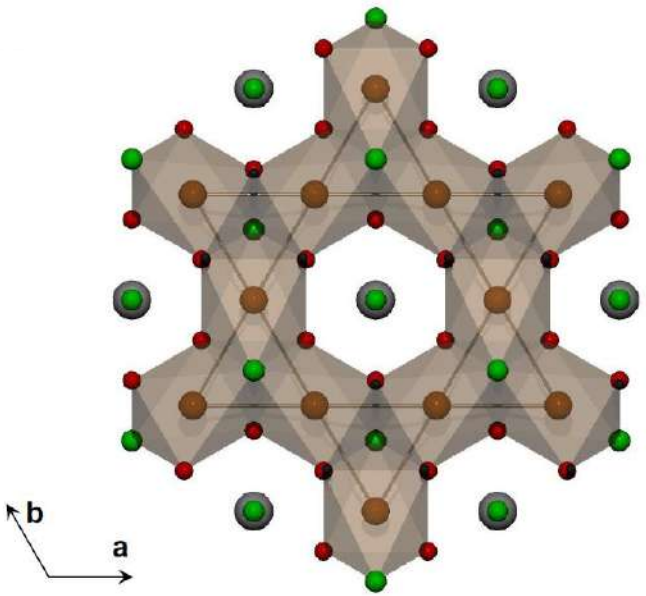


https://msestudent.com

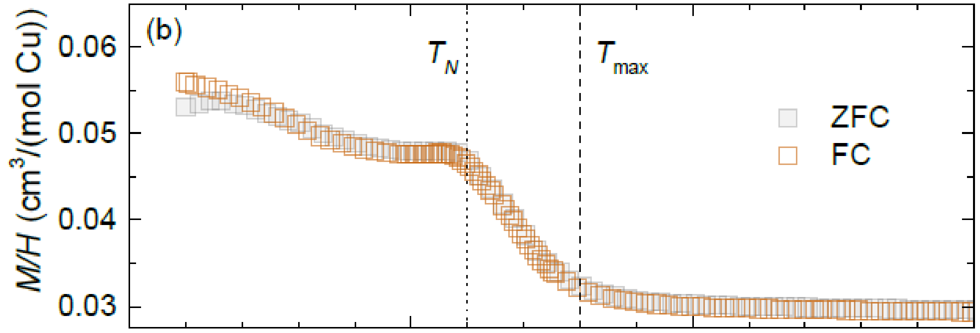
Bulk Magnetization/Susceptibility

- Averaging over the sample (constant *B*): uniform response

$$\chi(q=0,\omega)$$



$YCu_3(OH)_6Cl_3$: kagome AFM



Arh *et al.*, Phys. Rev. Lett. **125**, 027203 (2020)

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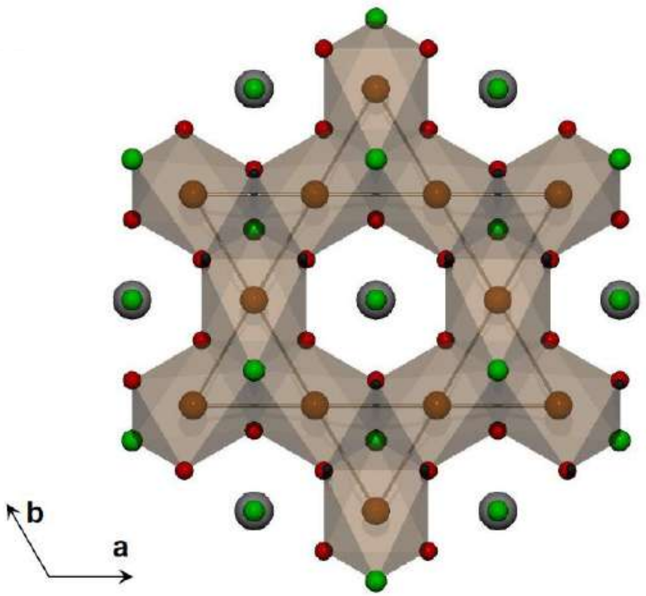

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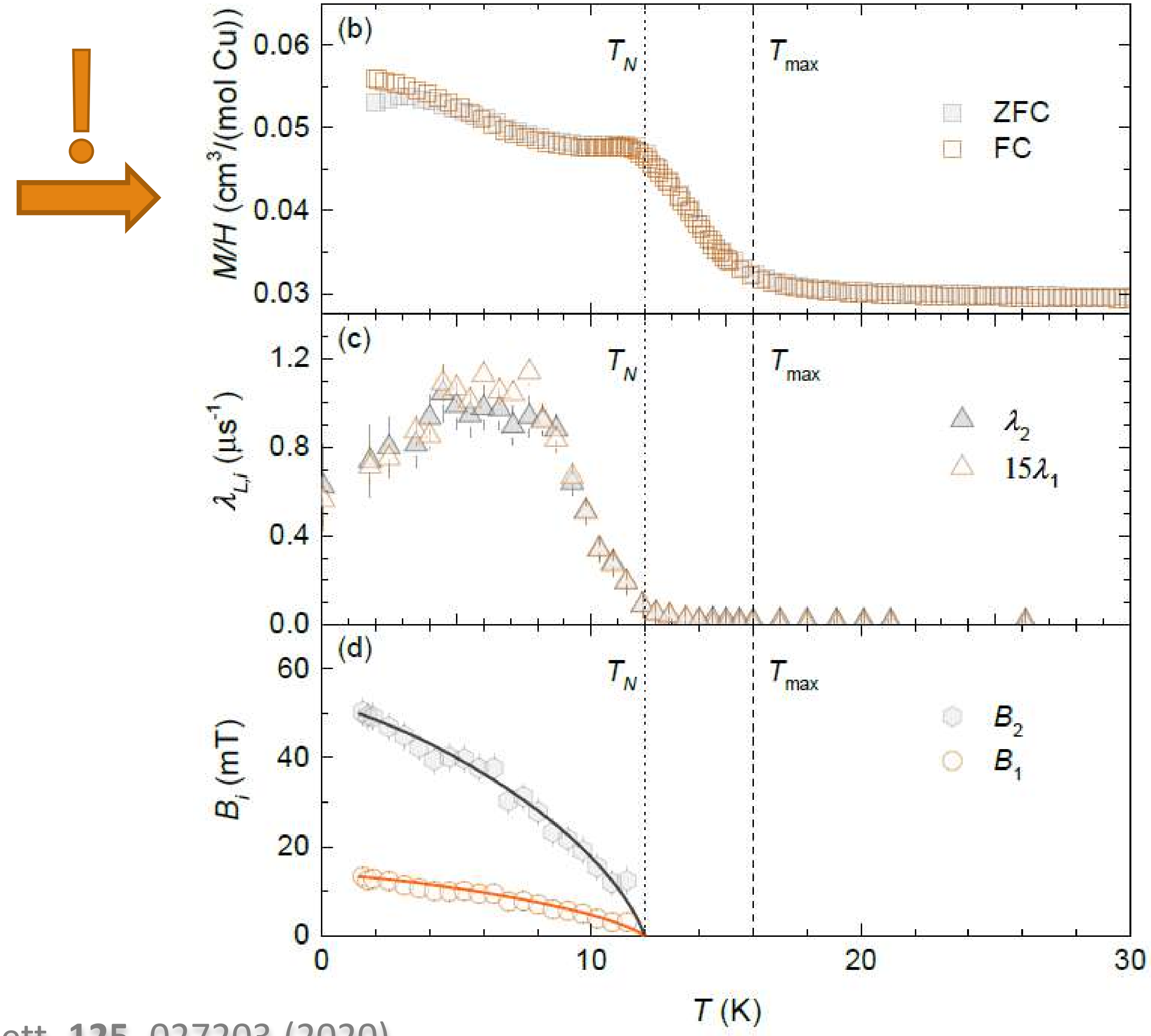
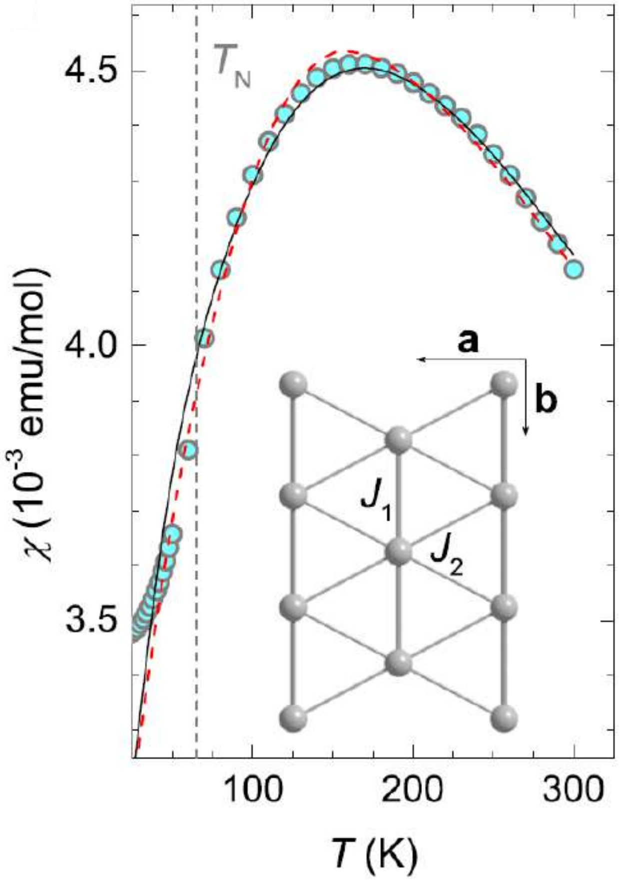
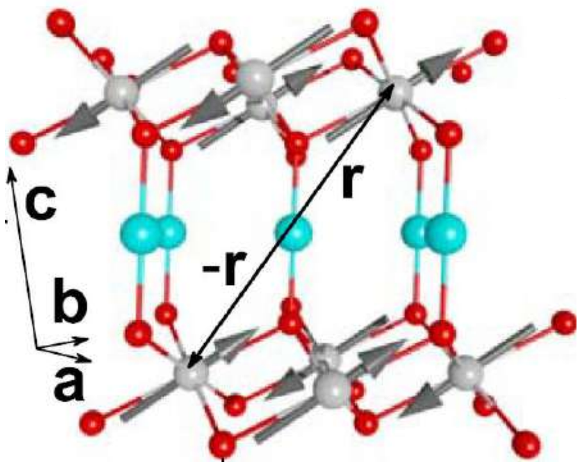


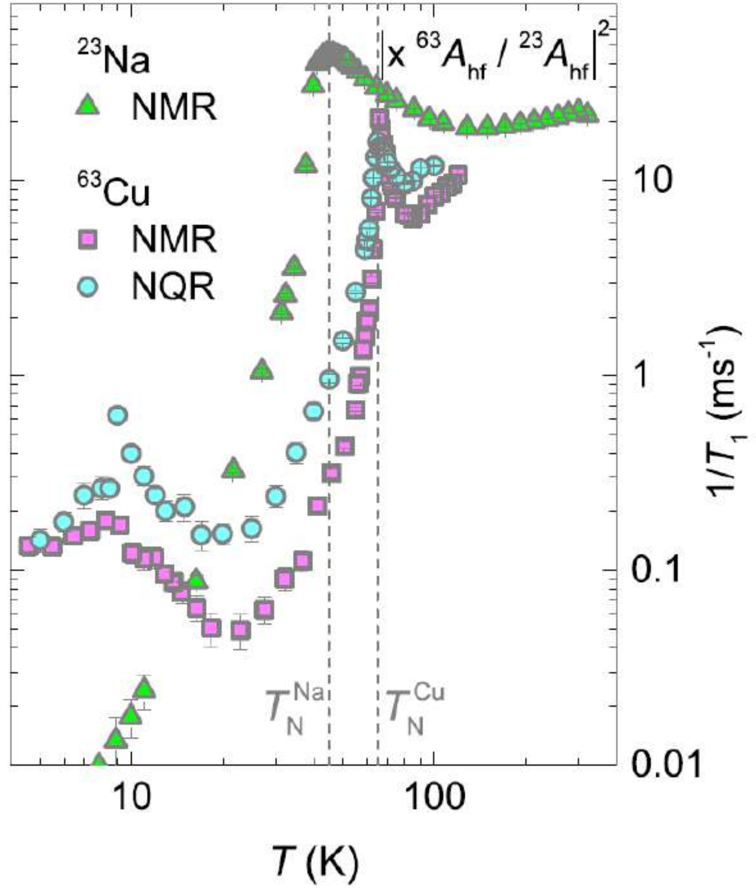
Arh *et al.*, Phys. Rev. Lett. **125**, 027203 (2020)

Bulk Magnetization/Susceptibility

- Small bulk response at T_N:





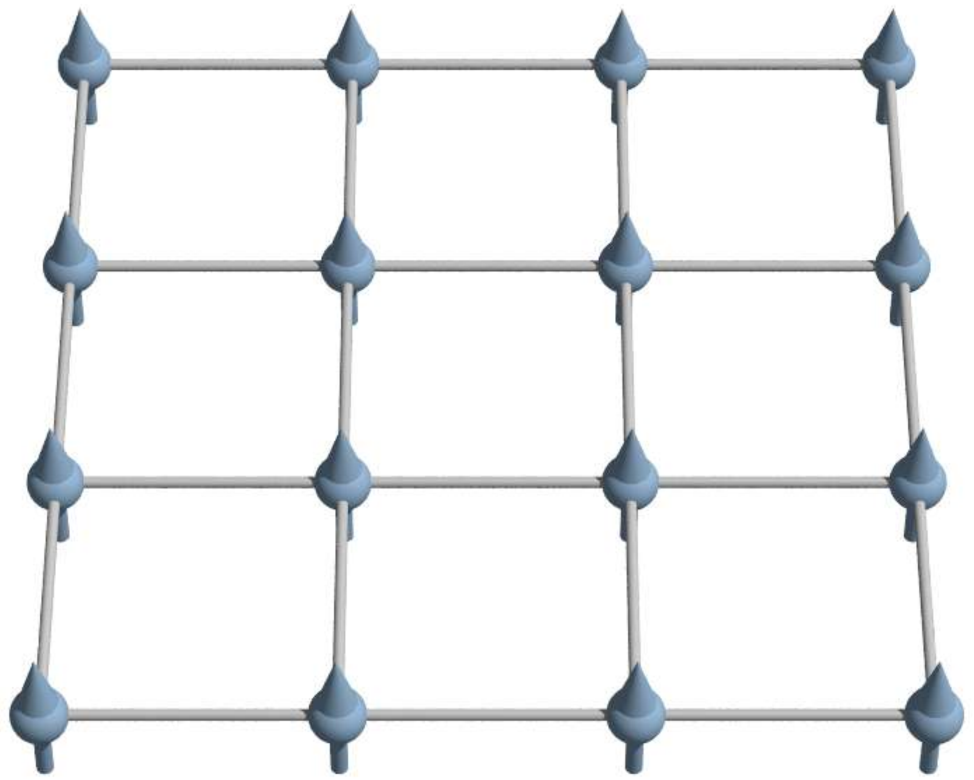


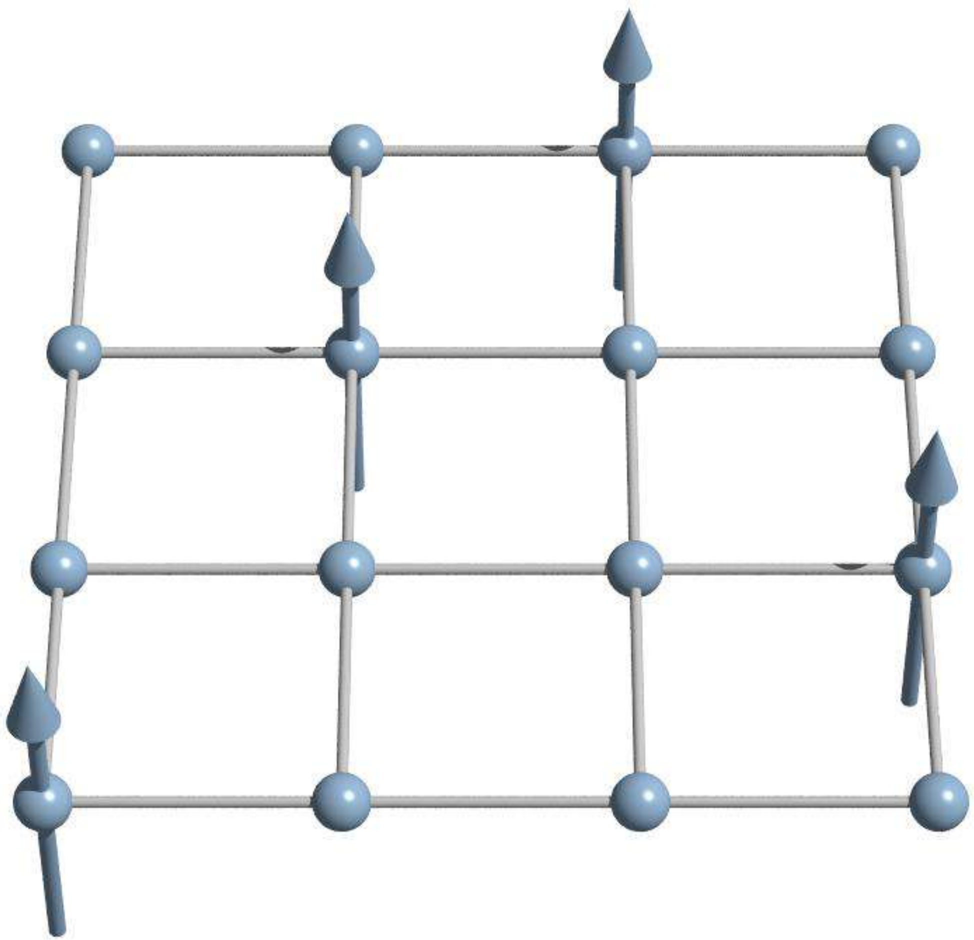
$NaMnO_2$ & $CuMnO_2$:
triangular AFM

Zorko *et al.*, Sci. Rep. **5**, 9272 (2015)

Bulk Magnetization/Susceptibility

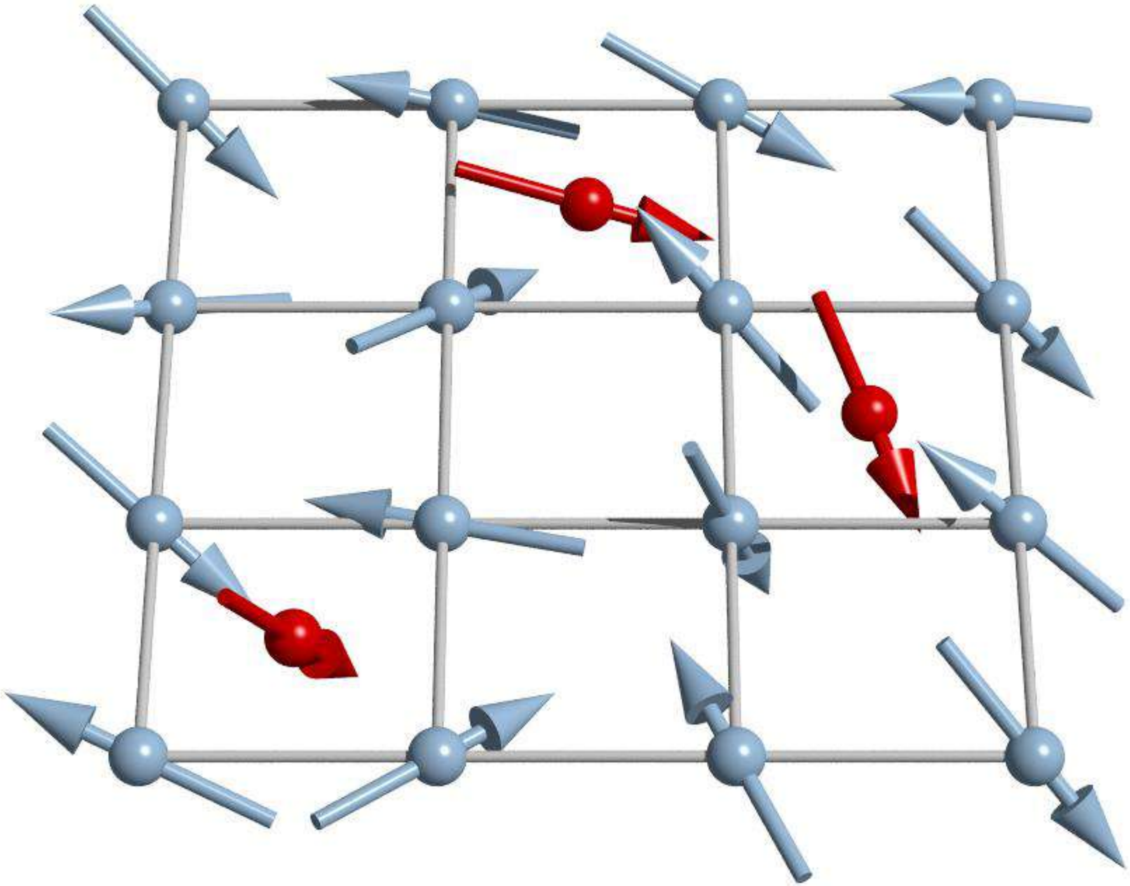
- Small ordered moments *vs.* diluted moments:

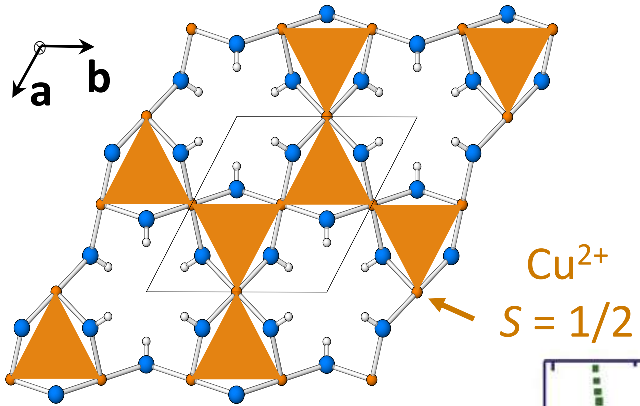




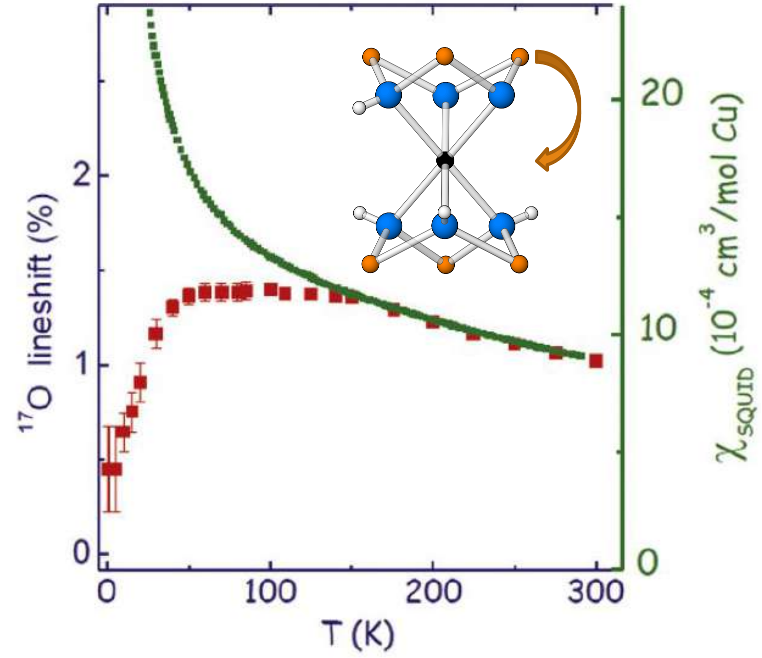
Bulk Magnetization/Susceptibility

- Averaging over different contributions:





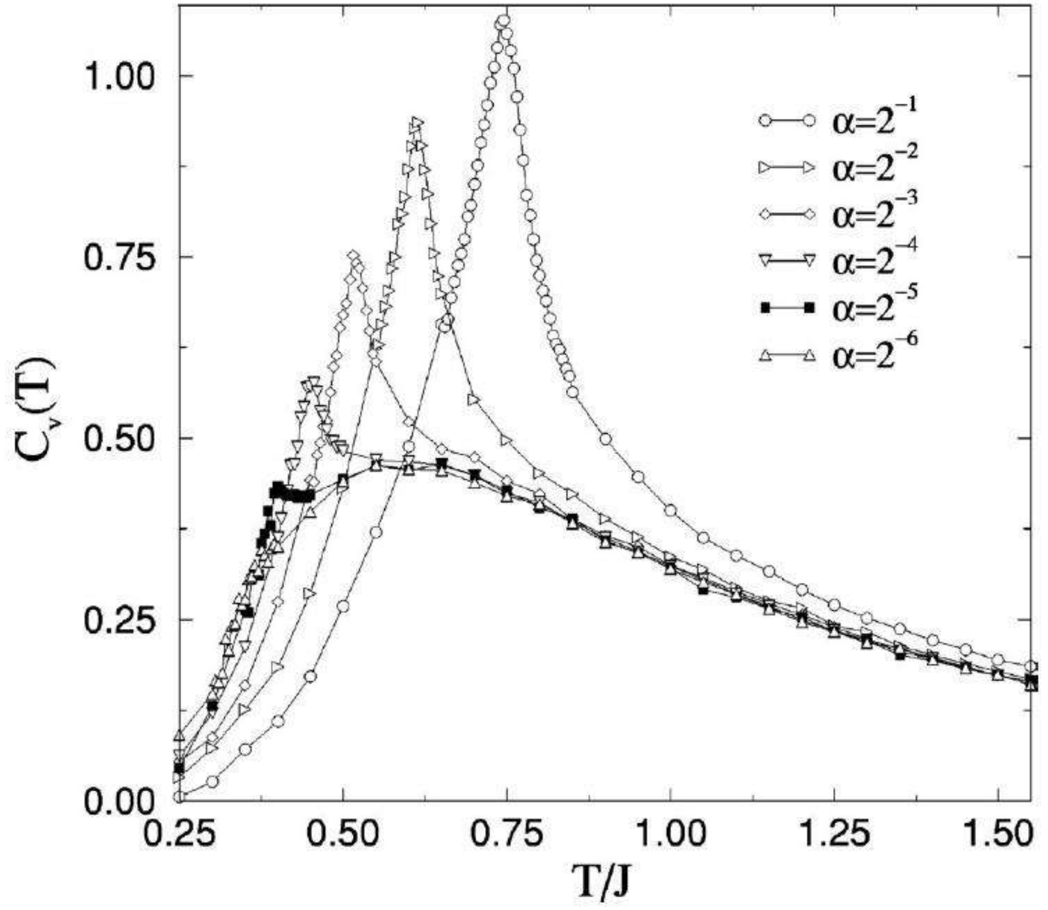
$ZnCu_3(OH)_6Cl_2$:
kagome AFM



Olariu *et al*., Phys. Rev. Lett. **100**, 087202 (2008)

Bulk Heat Capacity

- Detecting phase transitions:

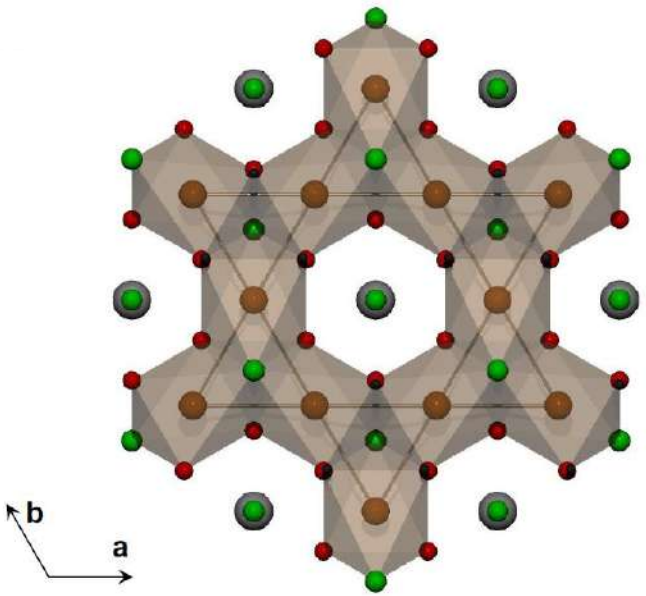


Sengupta *et al.*, Phys. Rev. B **68**, 094423 (2003)

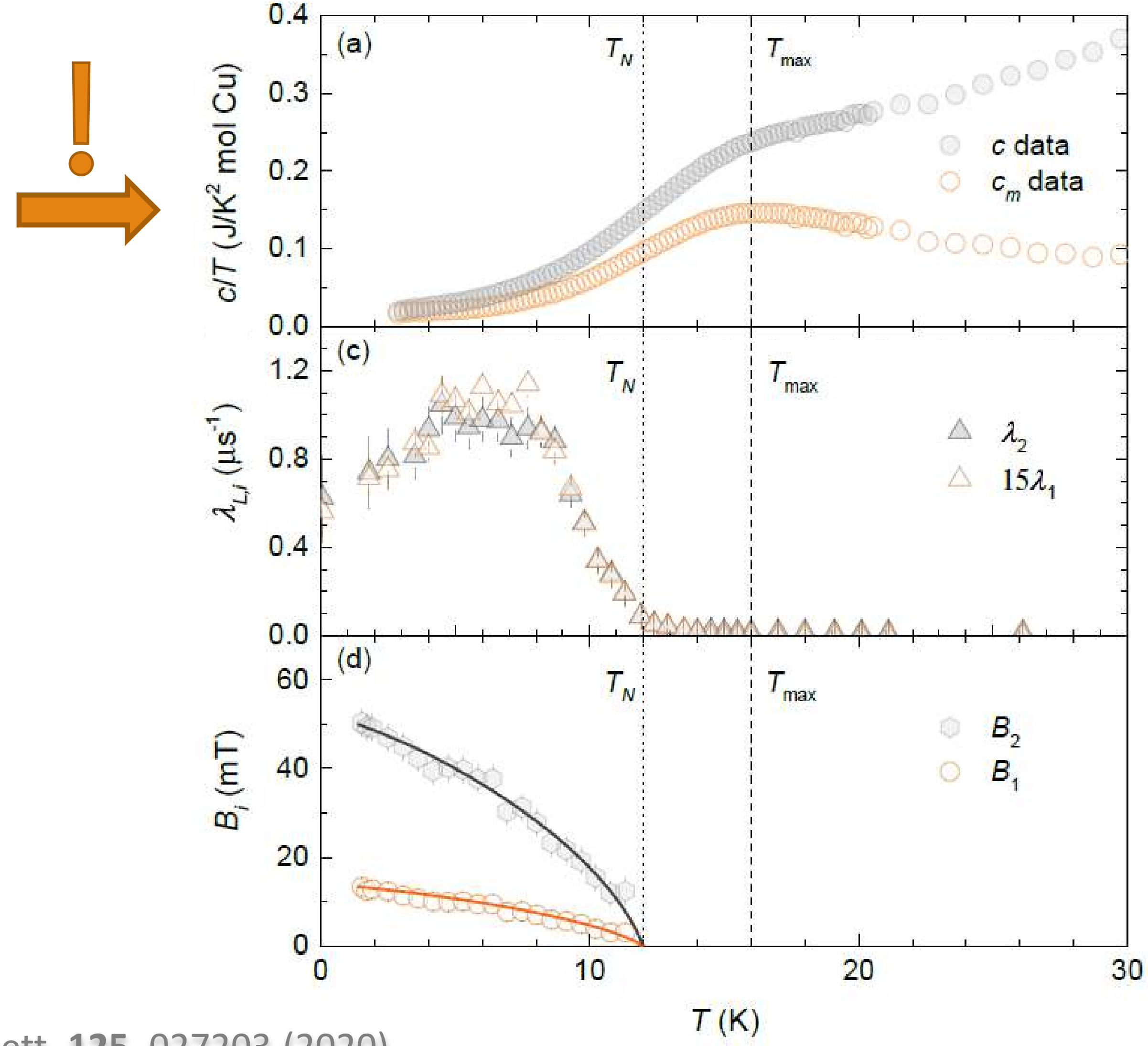
low-D magnets:
correlations far above T_N

Bulk Heat Capacity

- Small entropy release at T_N:



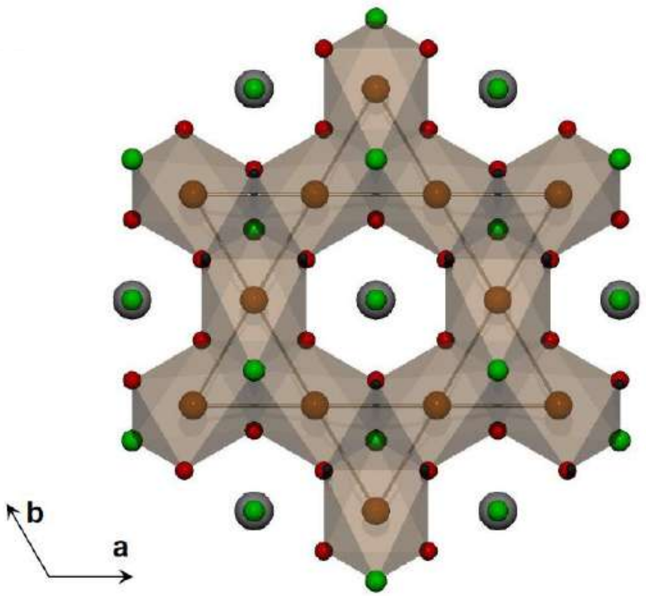
$YCu_3(OH)_6Cl_3$: kagome AFM



Arh *et al.*, Phys. Rev. Lett. **125**, 027203 (2020)

Bulk Heat Capacity

- Magnetic c_p hard to extract:



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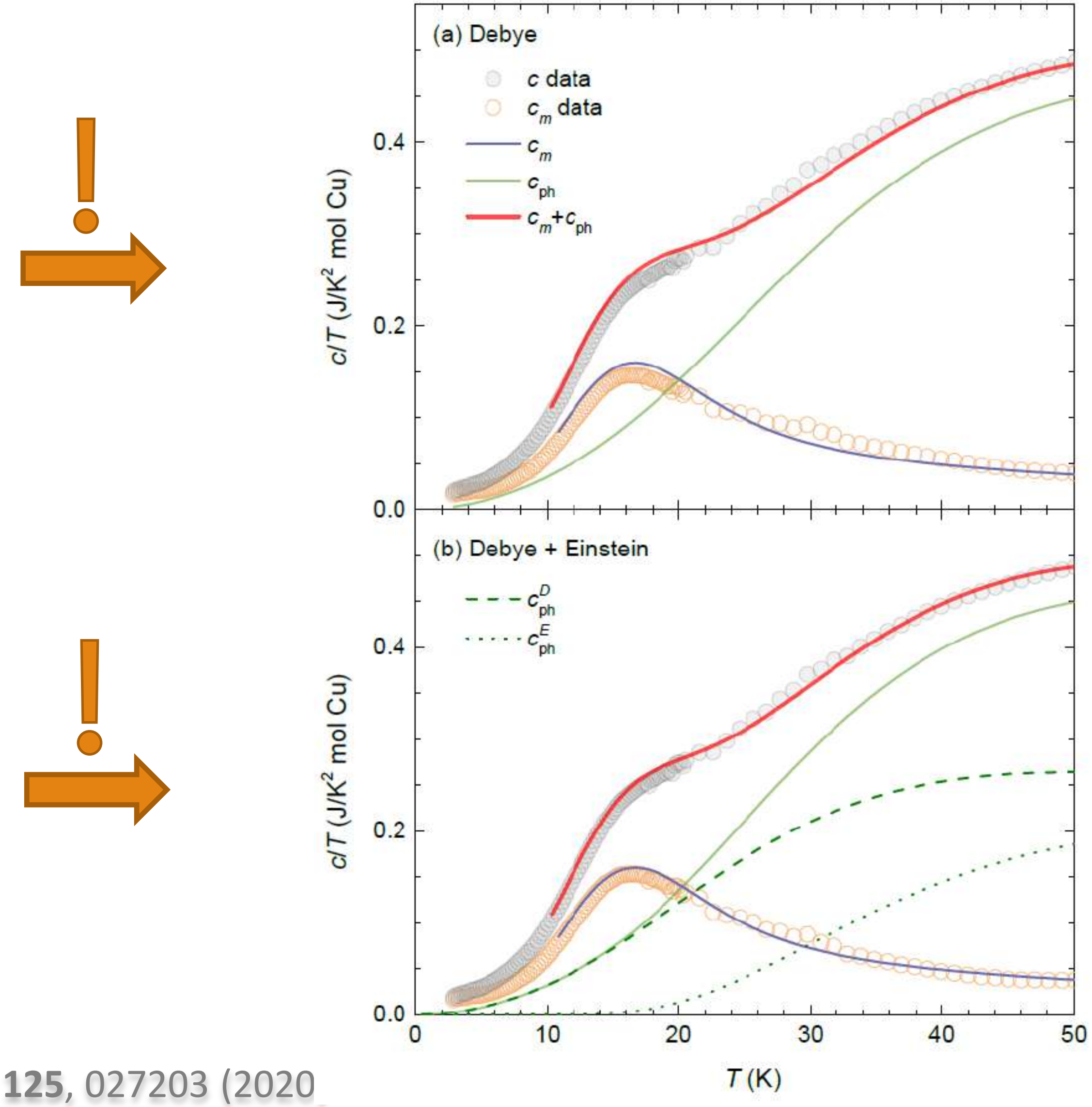


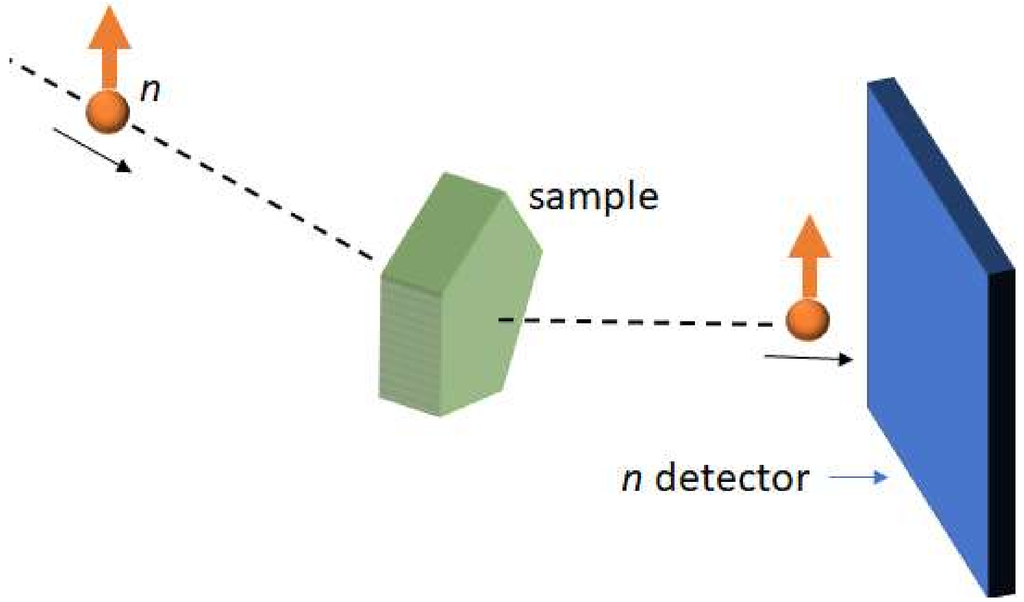
Arh *et al.*, Phys. Rev. Lett. **125**, 027203 (2020

Magnetic Neutron Scattering

- Properties of a neutron:
  - zero electric charge: weak interaction with matter
  - magnetic moment: magnetic interaction

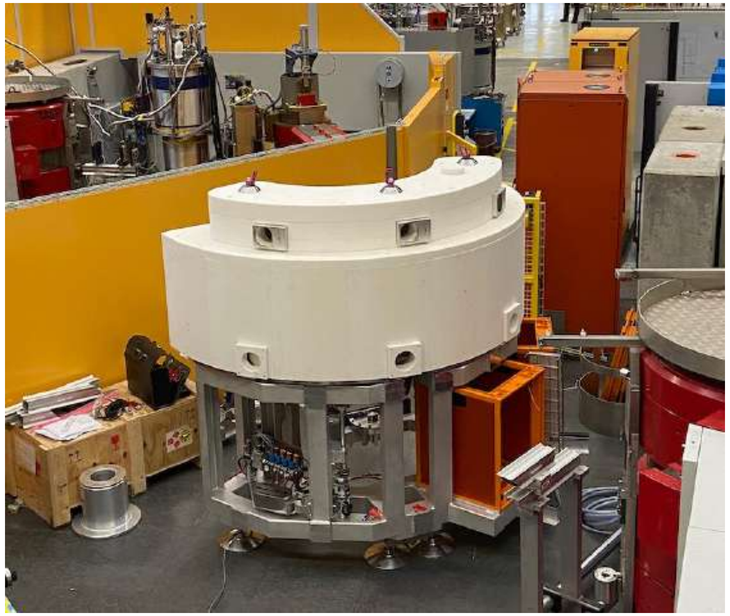
$$\mu = -1.913\mu_N = -9.663 \times 10^{-27}\ \mathrm{Am}^2$$

  - wavelengths comparable to interatomic distances: 0.3 – 15 Å
  - energies comparable to structural and magnetic excitations: 1 – 1000 meV

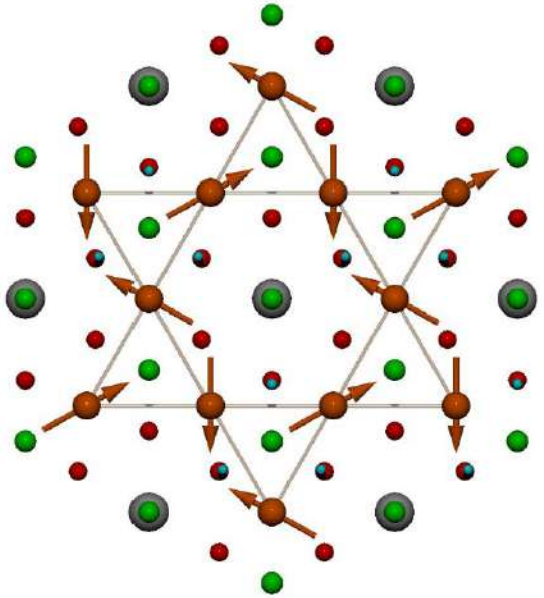


Magnetic Neutron Scattering

❑ Magnetic long-range order: momentum-resolved insight



DMC, PSI, Switzerland



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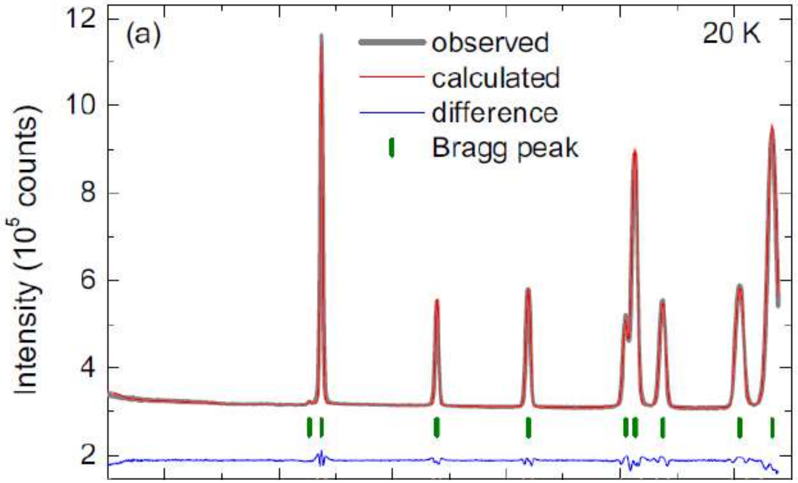

Zorko *et al.*, Phys. Rev. B **100**, 144420 (2019)

Magnetic Neutron Scattering

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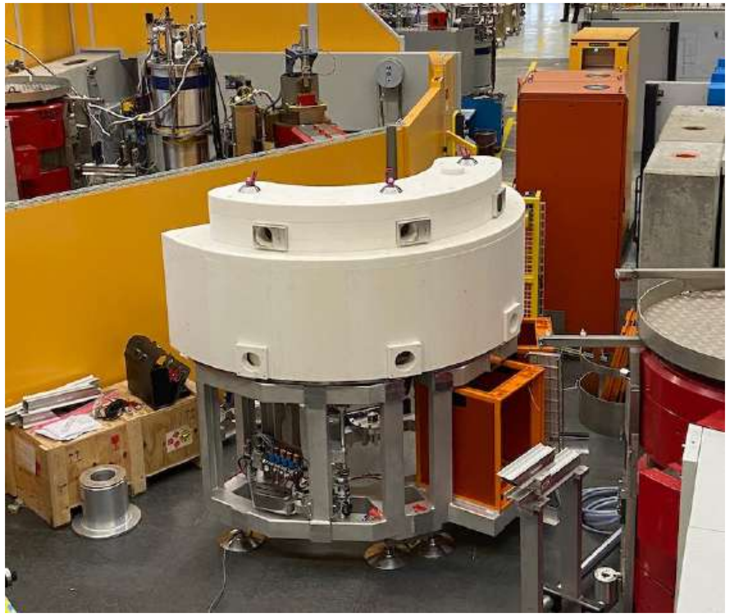

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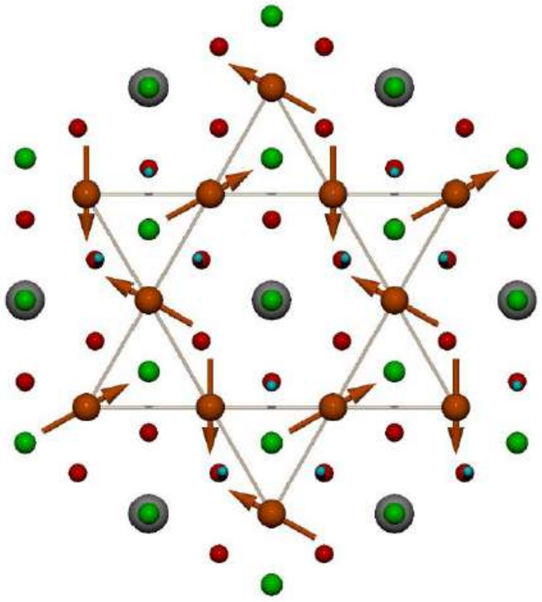

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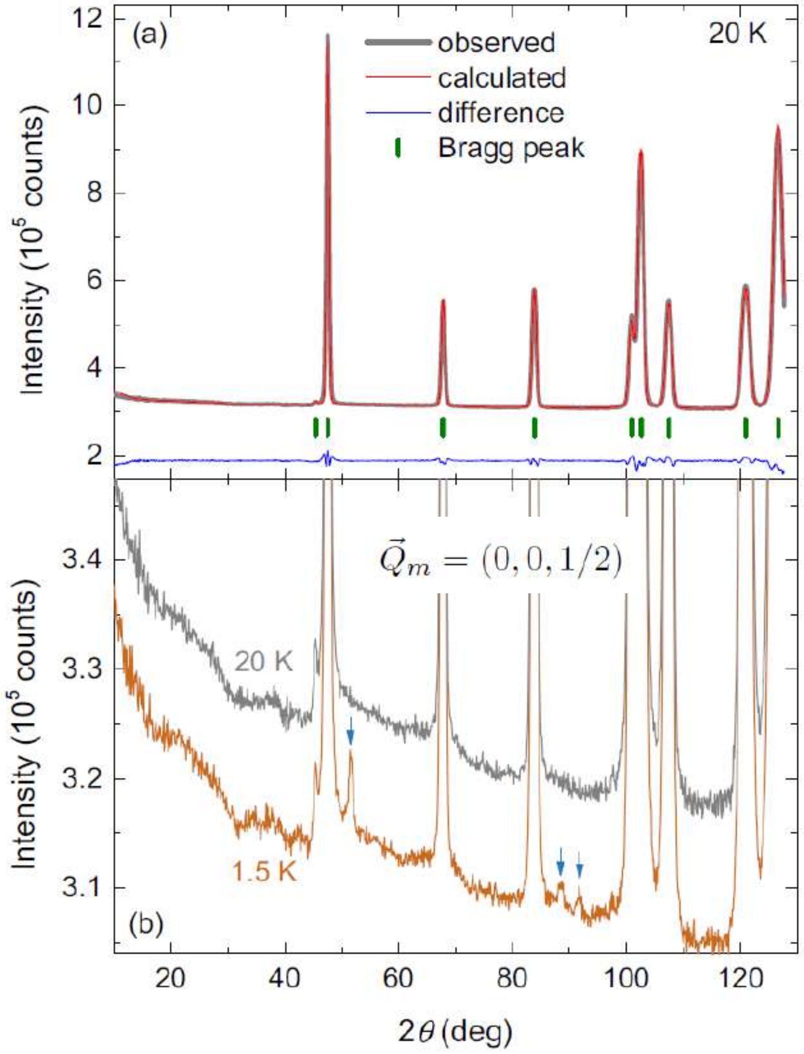
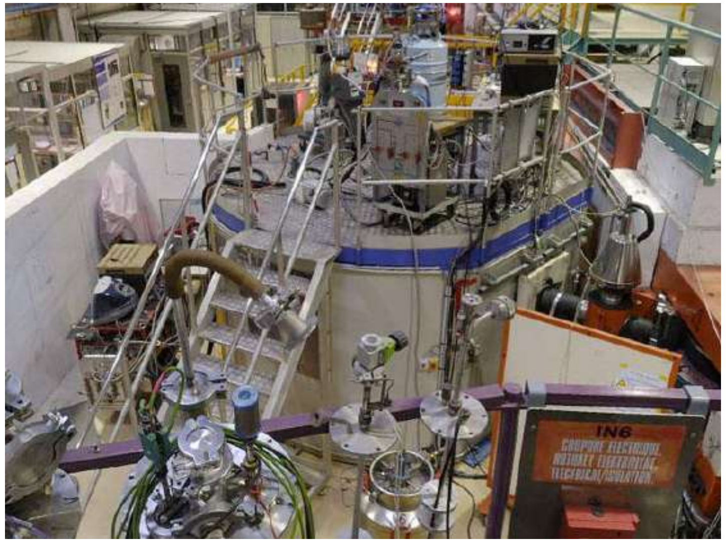


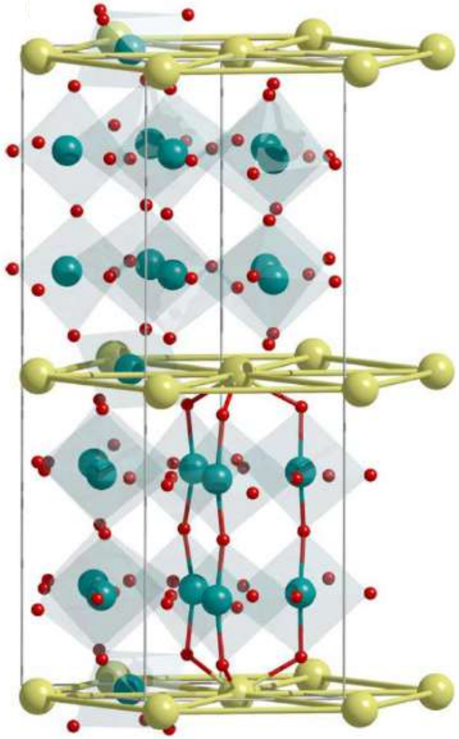
Zorko *et al.*, Phys. Rev. B **100**, 144420 (2019)

Magnetic Neutron Scattering

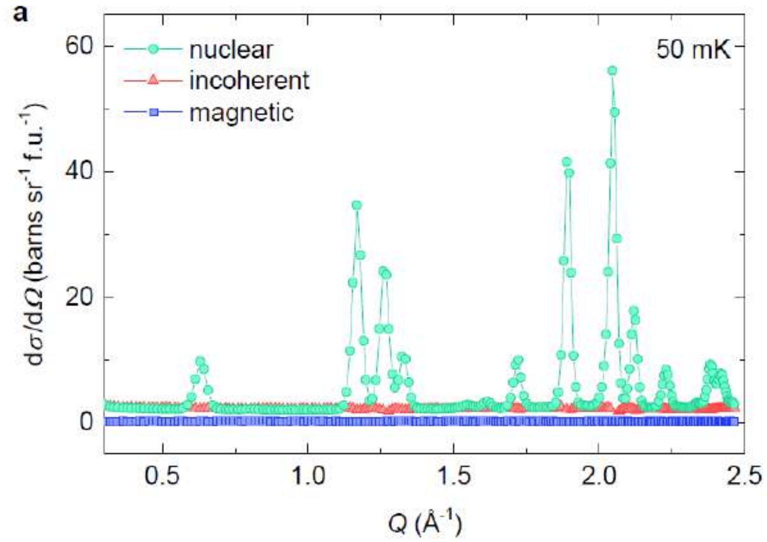
- Polarized neutrons:



D7, ILL, France



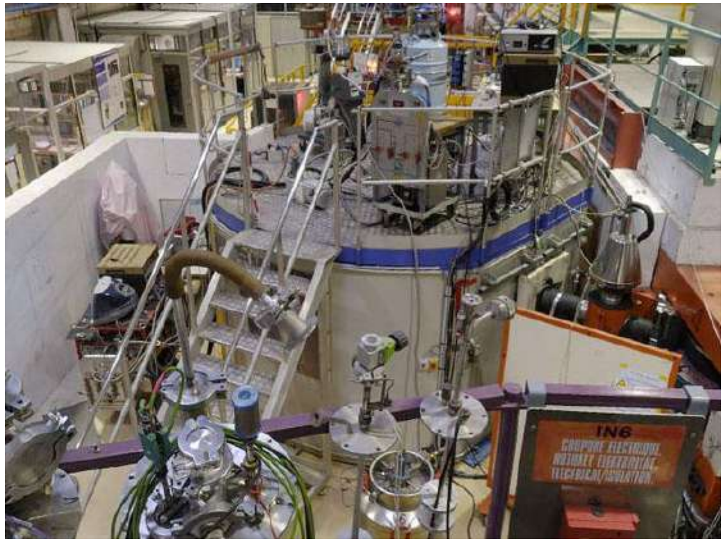
$NdTa_7O_{19}$:
triangular AFM



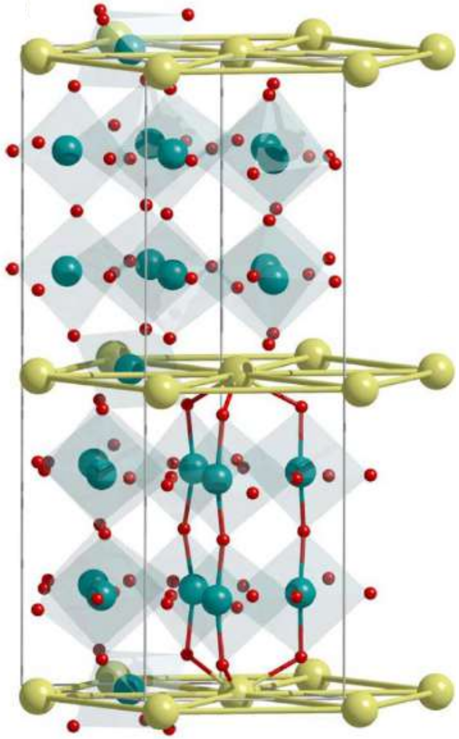
Arh *et al.*, Nat. Mater. **21**, 416 (2022).

Magnetic Neutron Scattering

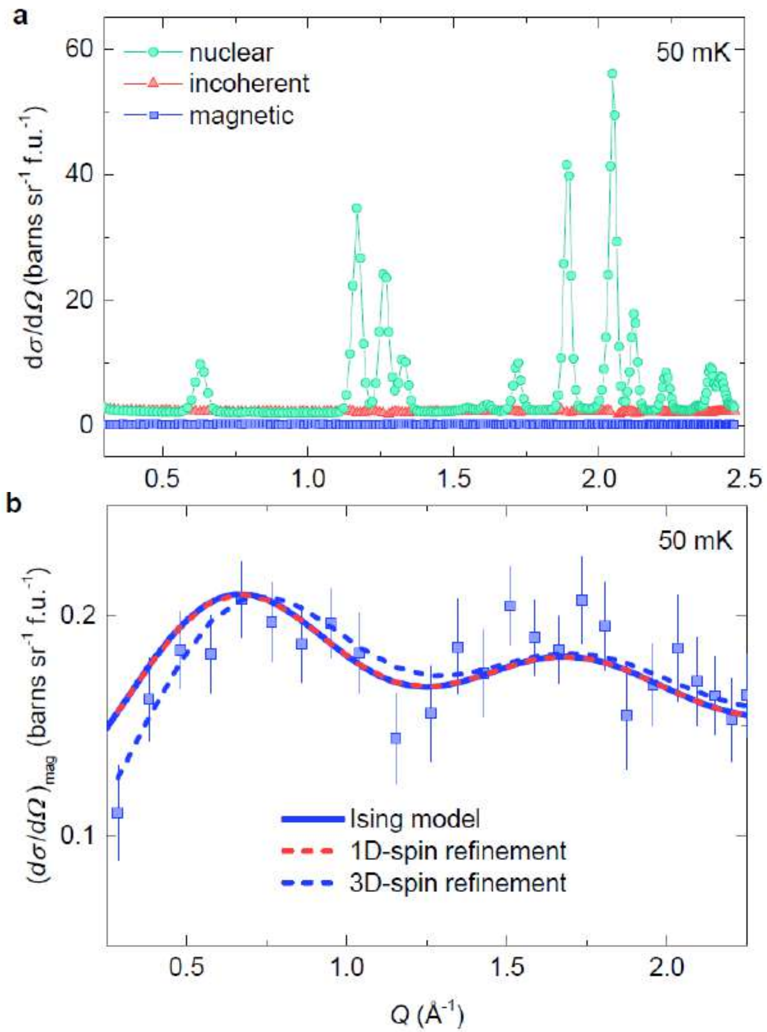
- Polarized neutrons:



D7, ILL, France



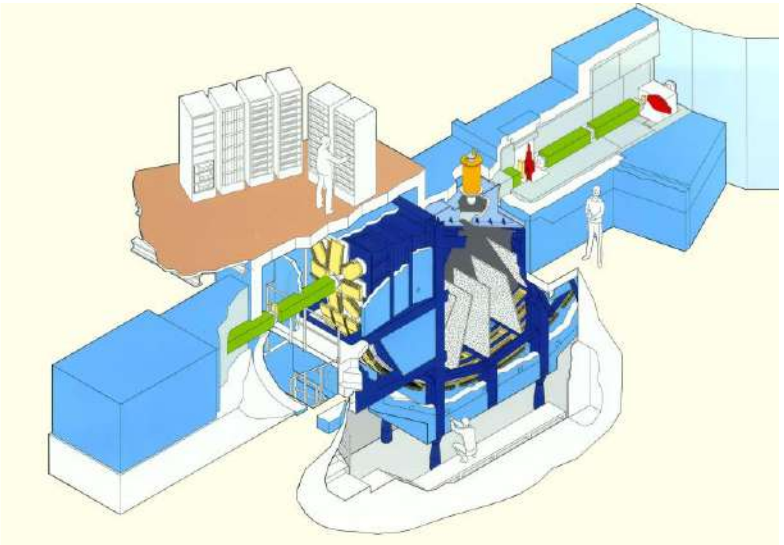
$NdTa_7O_{19}$:
triangular AFM



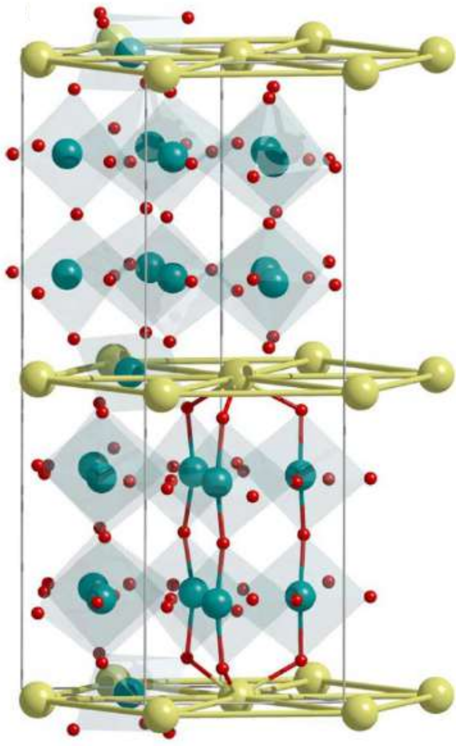
Arh *et al.*, Nat. Mater. **21**, 416 (2022).

Magnetic Neutron Scattering

- Energy-resolved insight:



MARI, ISIS, UK



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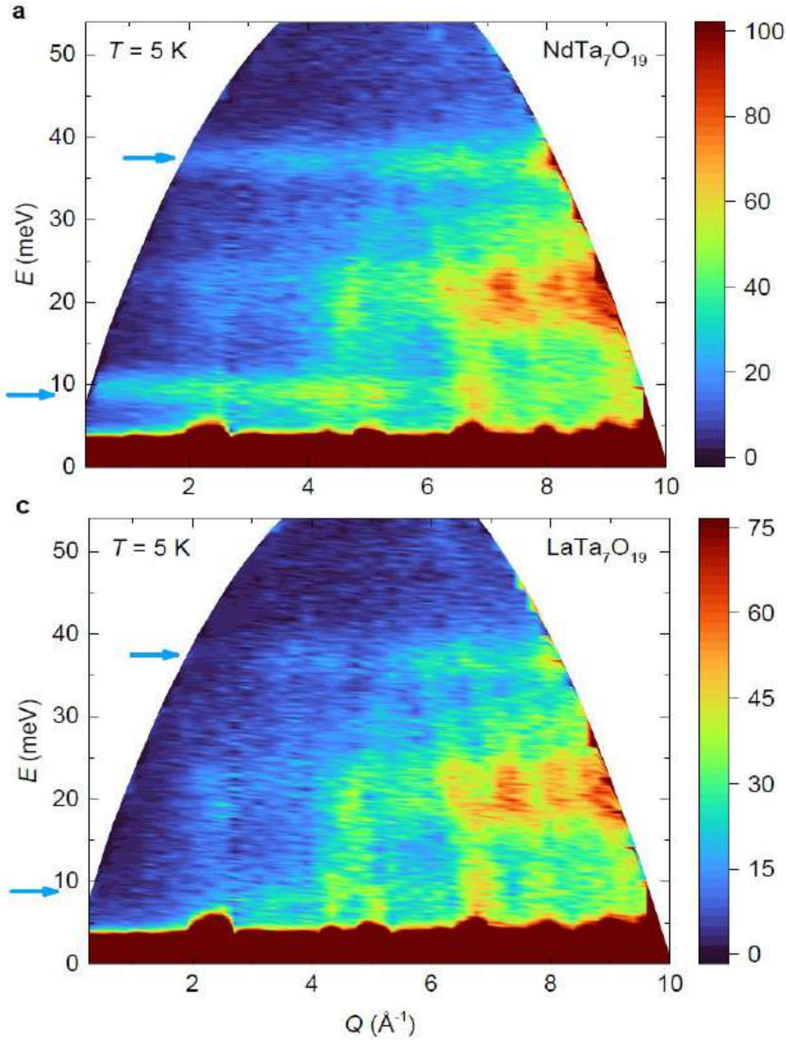
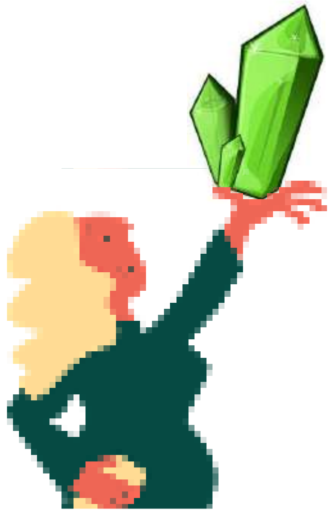


Arh *et al.*, Nat. Mater. **21**, 416 (2022).

Magnetic Neutron Scattering

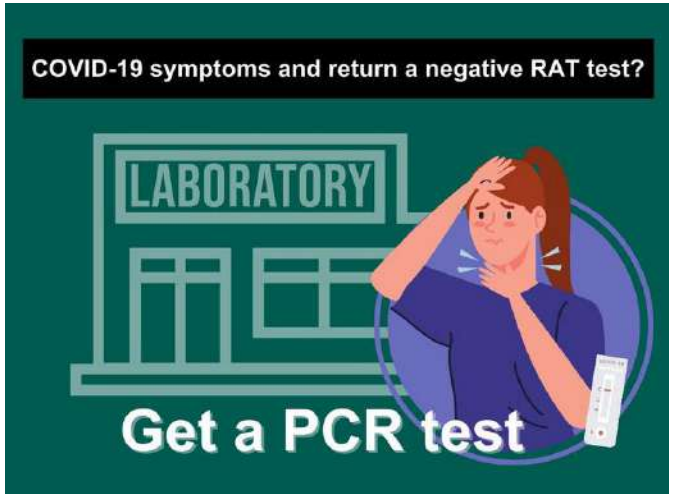
- Gives direct *Q*-space information but requires:
  - large samples (magnetic scattering and INS are weak)
  - large enough ordered moments (magnetic scattering and INS are weak)
  - no strong incoherent scattering (H)
  - no strong neutron absorption (Cd, Ir, B, …)
  - long counting times



Bulk Techniques

❑ Provide necessary preliminary characterisation but have drawbacks:

➢ sensitivity

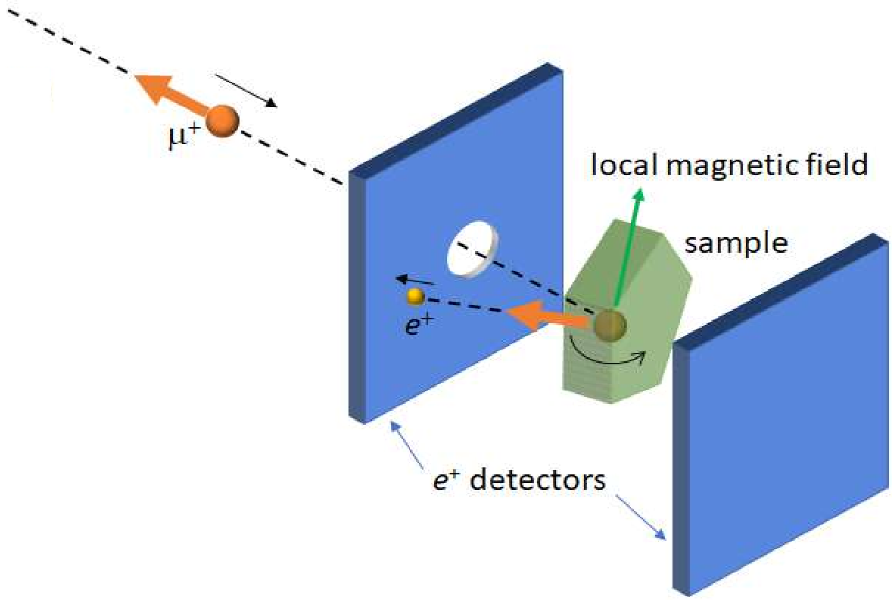


➢ average response

➢ no insight on the microscopic scale

Outline

- ❑ Introduction to magnetism
- ❑ Probing magnetism: conventional bulk and scattering techniques
- ❑ Local probes of magnetism
- ❑ Electron spin resonance (ESR)
- ❑ Nuclear magnetic resonance (NMR)
- ❑ Muon spectroscopy (μSR)
- ❑ Summary: strengths, limitations and complementarity of local probes



Local Probes of Magnetism

- Local probes: intrinsic (direct or indirect)

Probe	Charge	Spin	Mass	$\gamma/2\pi$ (MHz T^{-1})	Lifetime (μs)	Method
e	$-e_0$	$\frac{1}{2}$	m_e	28.03×10^3	∞	ESR
p	e_0	$\frac{1}{2}$	$1836 m_e$	42.58	∞	NMR

Local Probes of Magnetism

- Local probes: intrinsic (direct or indirect) or extrinsic

Probe	Charge	Spin	Mass	$\gamma/2\pi$ (MHz T^{-1})	Lifetime (μs)	Method
e	$-e_0$	$\frac{1}{2}$	m_e	28.03×10^3	∞	ESR
μ^+	e_0	$\frac{1}{2}$	$207m_e$	135.5	2.197	μSR
p	e_0	$\frac{1}{2}$	$1836m_e$	42.58	∞	NMR

- Measuring principles: induction (in cavity or coil) or particle counting

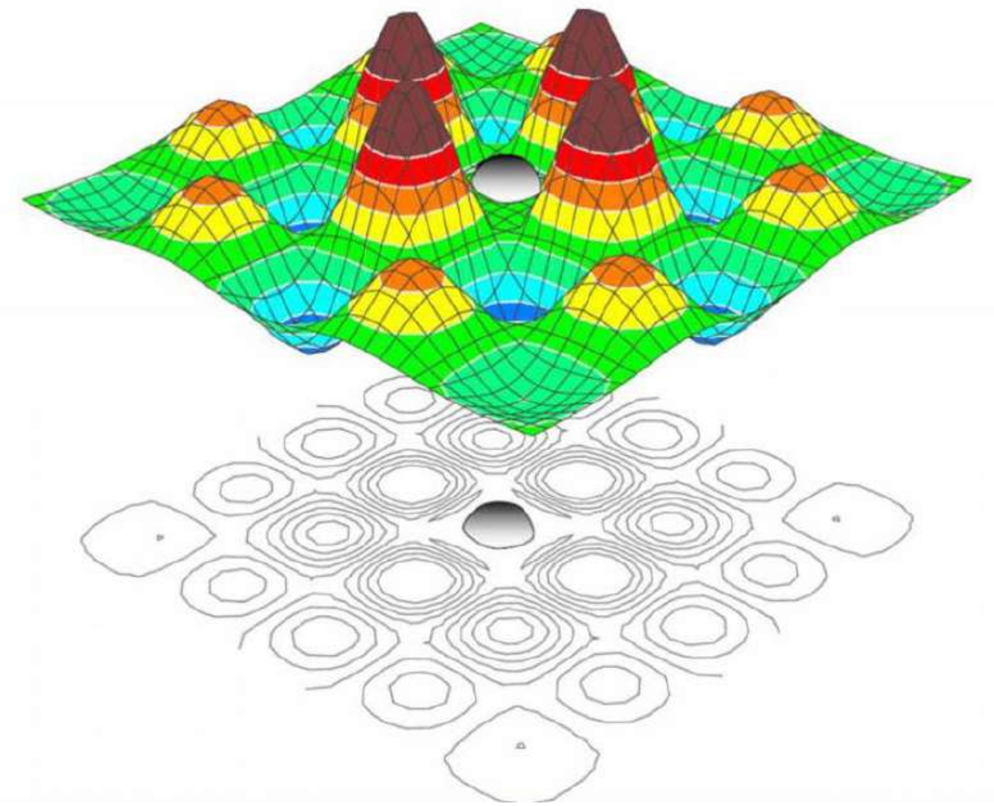


Local Probes of Magnetism

- ❑ Local field: $\vec{B}(t) = \sum_j A_j \vec{S}_j(t) = \sum_{j,\vec{q}} A_j \mathrm{e}^{i\vec{q}\cdot\vec{r}_j} S_{\vec{q}}$

  - ➢ *q*-integrated response
  - ➢ selective (no extrinsic contributions)
  - ➢ measurements of sublattice magnetization (AFM)
  - ➢ measurements of phase separation/segregation

- ❑ Detection of static and fluctuating local fields to study spin polarization



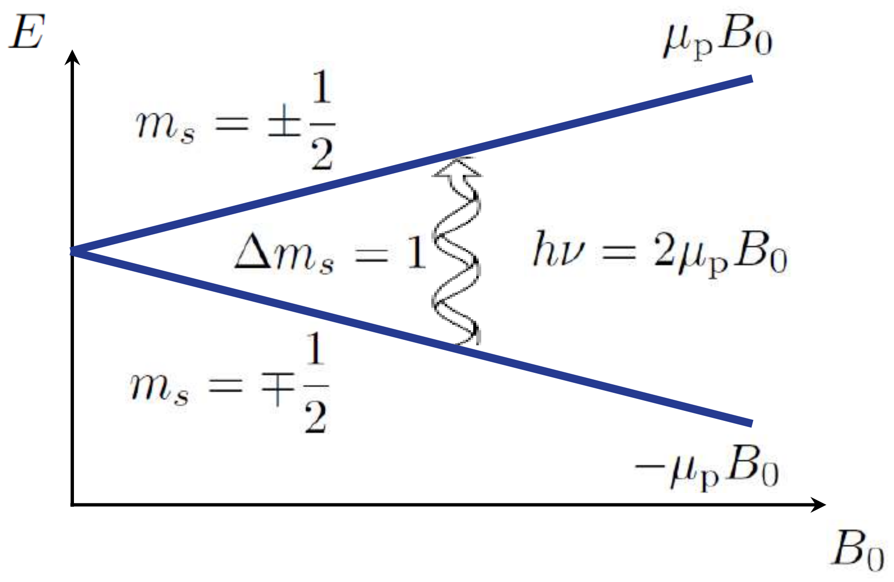
Alloul *et al.*, Rev. Mod. Phys. **81**, 45 (2009)

Local Probes of Magnetism

- Hamiltonian:

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{\rm pe} + \mathcal{H}_{\rm pn}$$

- Zeeman interaction: $\mathcal{H}_Z = -\vec{\mu}_{\rm p} \cdot \vec{B}_0$
- probe – electronic-spins interaction
- probe – nuclear-spins interaction



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Confusion with the name…

- How many different techniques are there?

  - EPR: Electron Paramagnetic Resonance
  - ESR: Electron Spin Resonance
  - EMR: Electron Magnetic Resonance

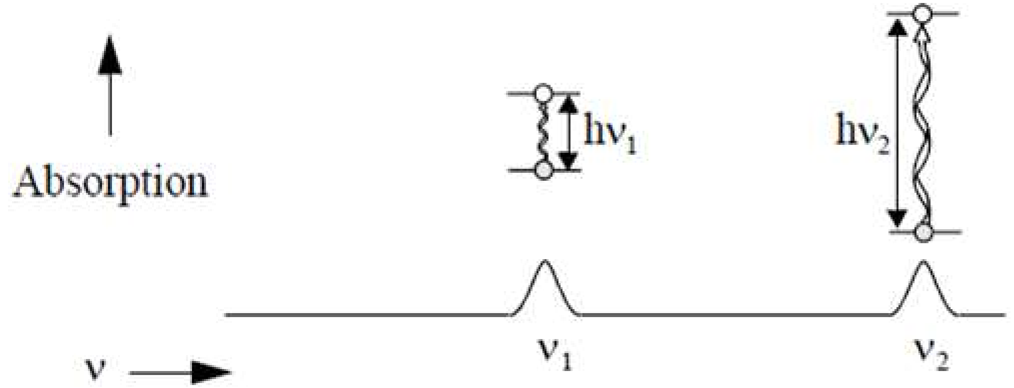
  - AFMR/FMR: AntiFerroMagnetic Resonance/FerroMagnetic Resonance
  - CESR: Conduction Electron Spin Resonance

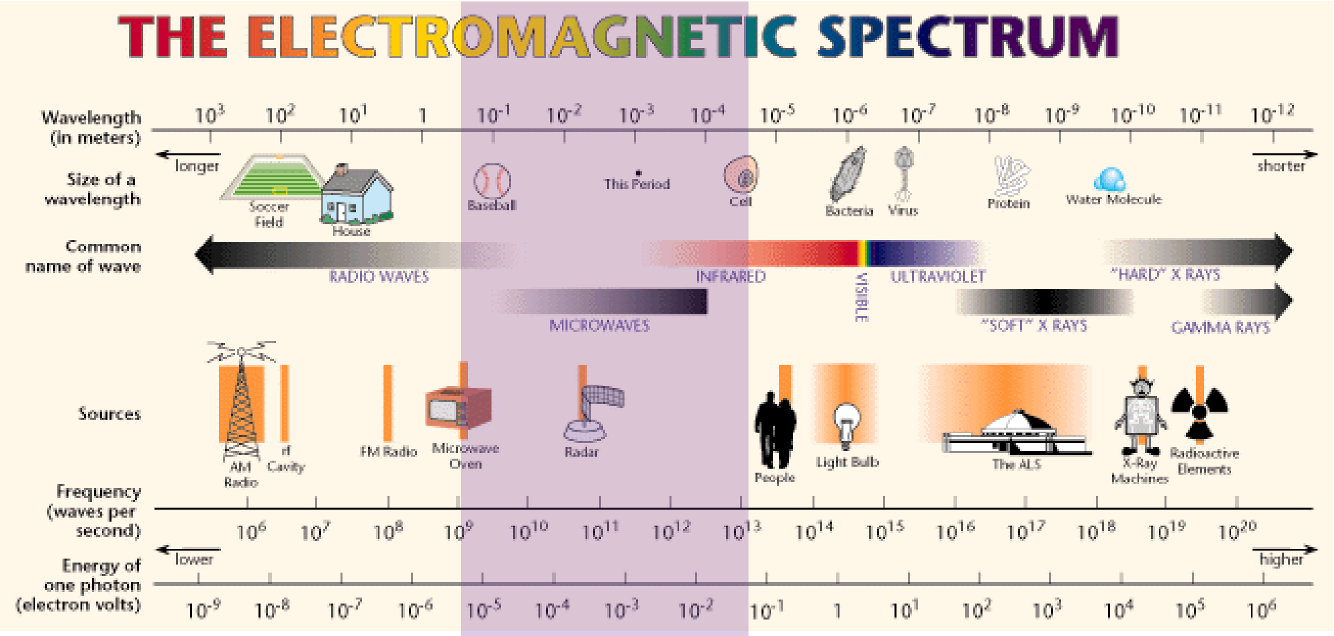
Motivation for ESR Measurements

- ❑ Direct detection of the electron spins:

$$I(\omega) = \frac{1}{2}\omega H_0^2 \chi''(\mathbf{q}=0,\omega)$$

- ❑ High sensitivity: $10^{9} – 10^{15}$ spins (a few mg of sample)
- ❑ High spectral resolution: $10^{-4} – 10^{-5}$
- ❑ Broad range of available frequencies: $10^{9} – 10^{13}$ Hz
- ❑ CW and pulsed techniques





Motivation for ESR Measurements

- Broad range of applications:
  - kinetics of radical reactions
  - oxidation and reduction processes
  - catalytic reactions
  - petroleum research
  - …

  CHEMISTRY

  - spin labeling
  - free radicals in living tissues and fluids
  - drug detection, metabolism, and toxicity
  - spin trapping
  - …

  BIOLOGY/ MEDICINE

  - magnetic properties of TM and RE
  - conduction electrons in conductors and semiconductors
  - defects in crystals
  - excited states of molecules
  - crystal fields in crystalline solids
  - …

  PHYSICS/ MATERIALS RESEARCH

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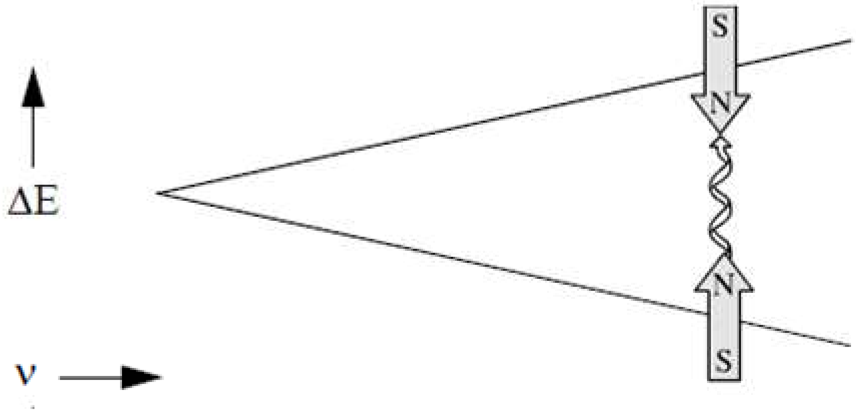
  - …

PHYSICS/
MATERIALS
RESEARCH

A Brief History of ESR

- 1896: discovery of the Zeeman effect



$$\mathcal{H}_Z = -\vec{\mu}_{\mathrm{p}} \cdot \vec{B}_0$$

The Nobel Prize in Physics 1902

Photo from the Nobel Foundation archive.
Hendrik Antoon Lorentz
Prize share: 1/2

Photo from the Nobel Foundation archive.
Pieter Zeeman
Prize share: 1/2

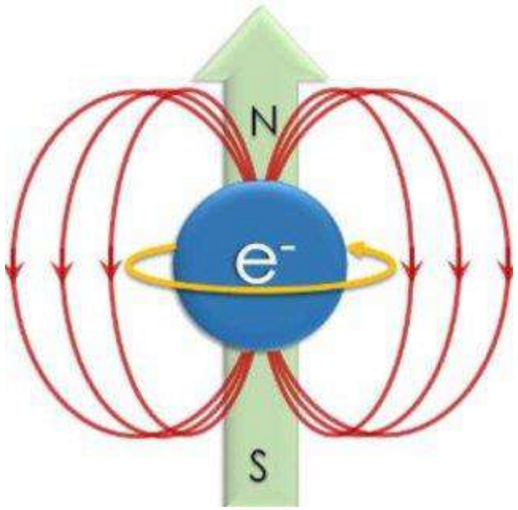
The Nobel Prize in Physics 1902 was awarded jointly to Hendrik Antoon Lorentz and Pieter Zeeman "in recognition of the extraordinary service they rendered by their researches into the influence of magnetism upon radiation phenomena."

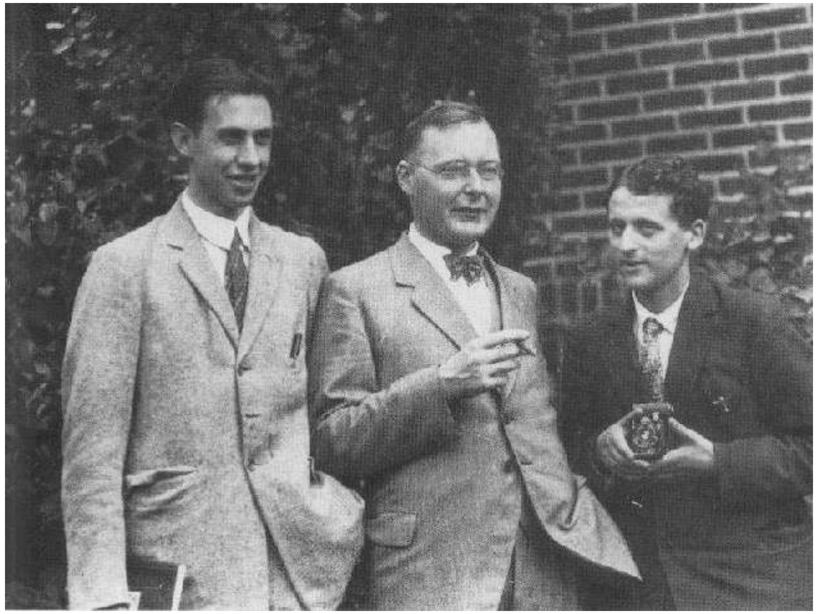
https://www.nobelprize.org

A Brief History of ESR

❑ 1925: discovery of the electron spin

$$\vec{\mu} = -g_J \mu_B \vec{J}$$

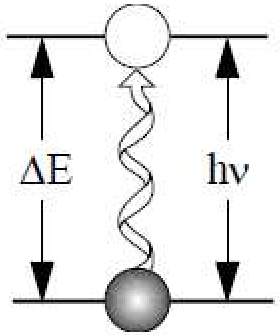


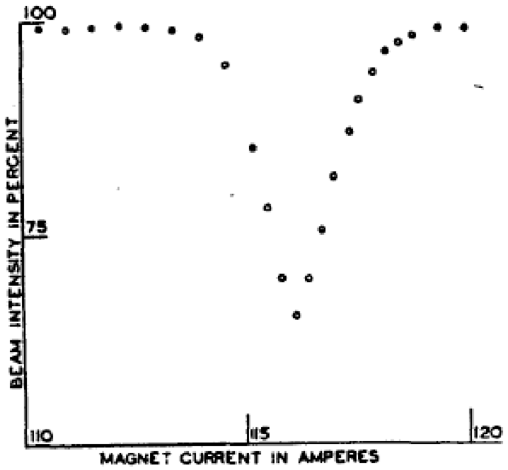


G. E. Uhlenbeck S. Goudsmit

A Brief History of ESR

- 1938: interactions of LiCl molecular beams with EM waves in a static magnetic field





The Nobel Prize in Physics 1944

Photo from the Nobel Foundation archive.

Isidor Isaac Rabi

Prize share: 1/1

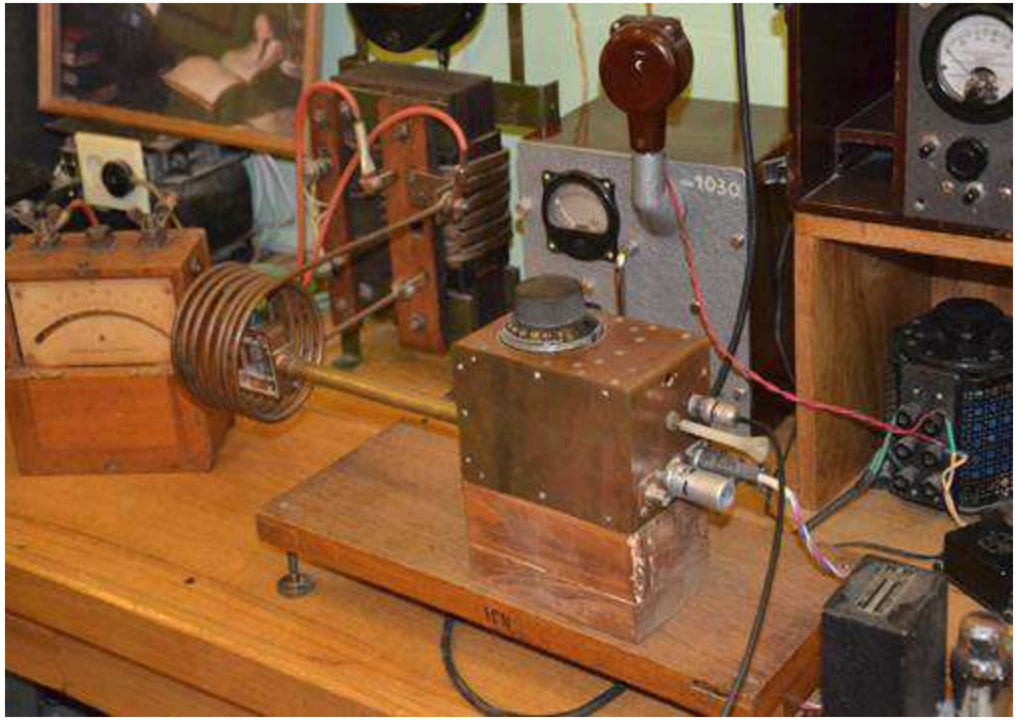
The Nobel Prize in Physics 1944 was awarded to Isidor Isaac Rabi "for his resonance method for recording the magnetic properties of atomic nuclei."

https://www.nobelprize.org

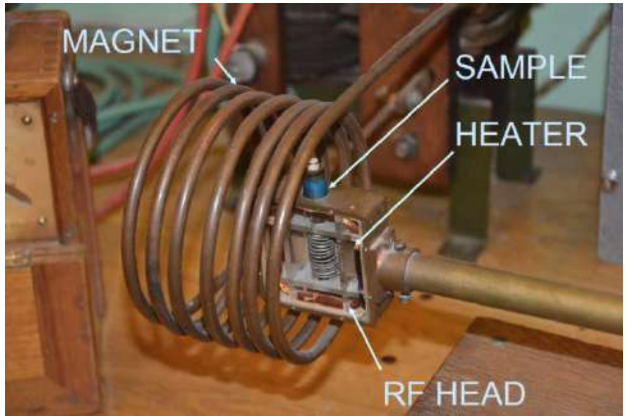
A Brief History of ESR

- 1944: discovery of ESR (first ESR spectrometer at the Kazan University, USSR)

Yevgeny Zavoisky

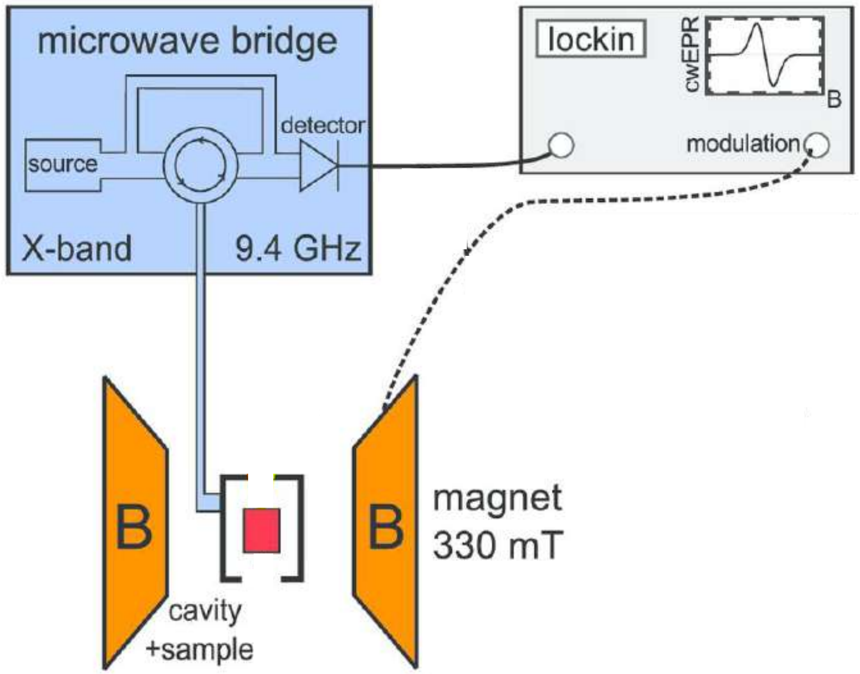


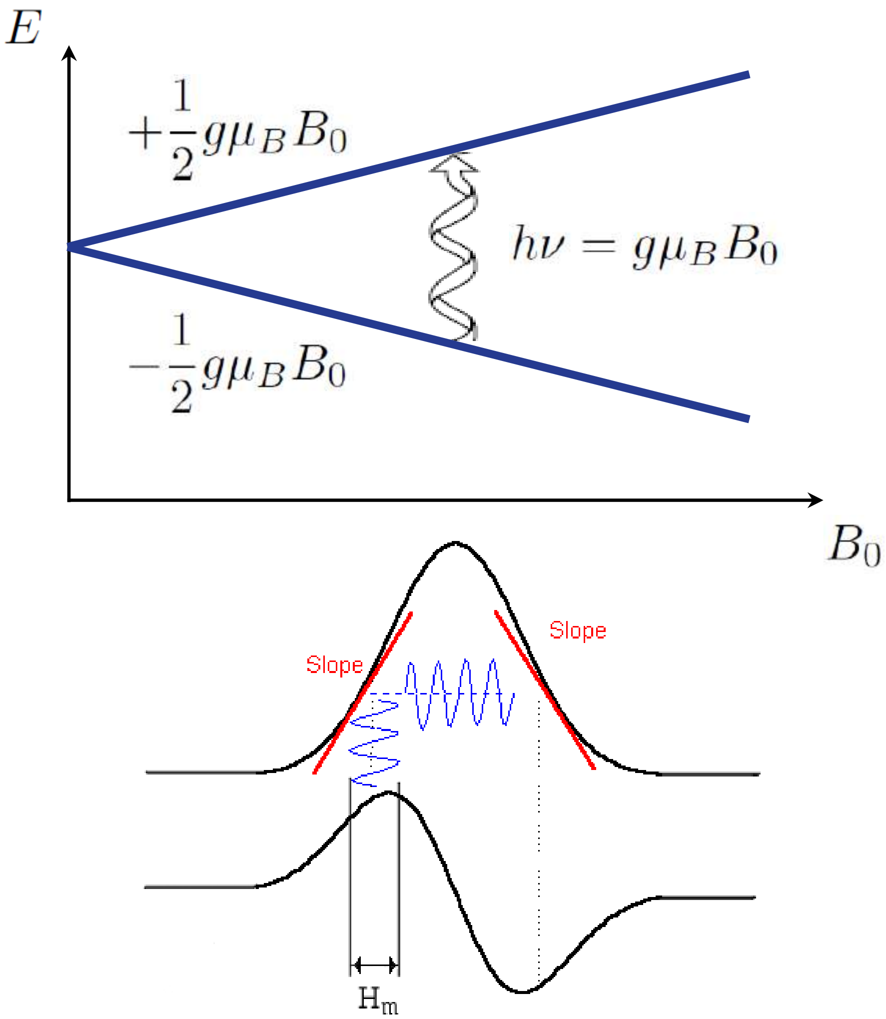
Cu-based salts
20 MHz (7.5 Oe)



ESR Apparatus

- ❑ magnet (static + modulation)
- ❑ MW source
- ❑ detector

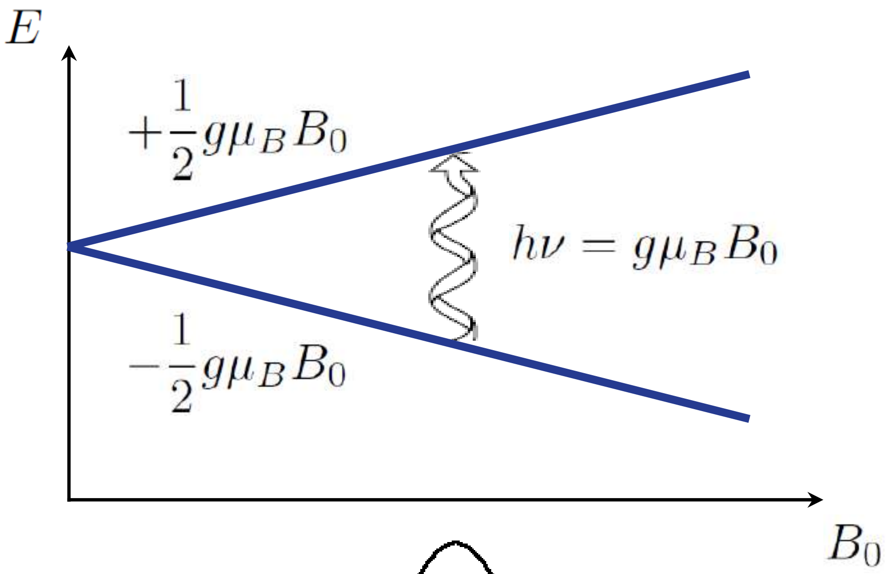


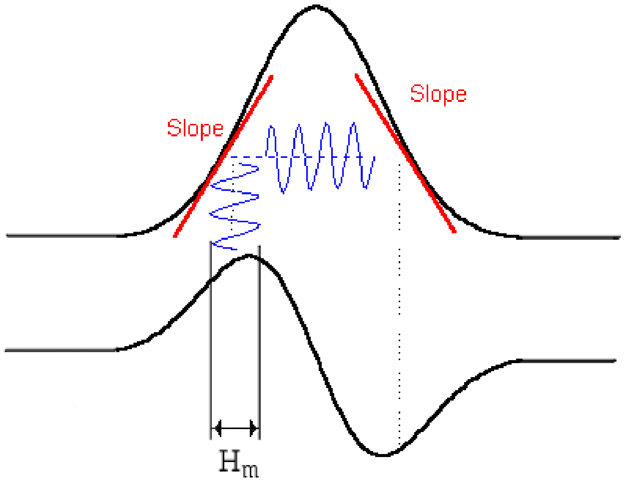


ESR Apparatus

- ❑ magnet (static + modulation)
- ❑ MW source
- ❑ detector

Bruker Elexsys E580 CW/FT EPR spectrometer





ESR Spectrum

- ESR absorption:

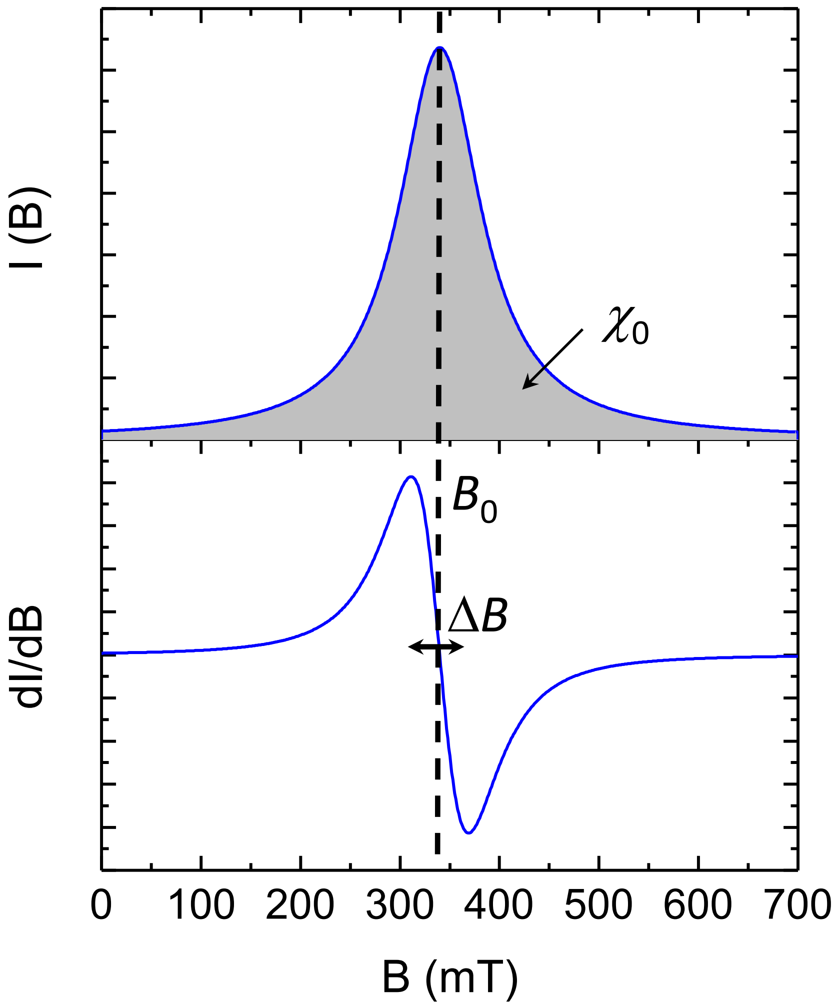
$$I(\omega) = \frac{1}{2}\omega H_0^2 \chi''(\mathbf{q}=0,\omega)$$

$$\chi''(\omega) = \frac{\omega V}{2k_B T}\int_{-\infty}^{\infty}\langle M^+(t)M^-(0)\rangle \mathrm{e}^{-i\omega t}\mathrm{d}t$$

- ESR parameters:
  - **ESR intensity:** local static susceptibility
  - **ESR resonance field:** interaction with CF

$$\Delta g = g - 2.0023$$

  - **ESR linewidth:** magnetic anisotropy, inhomogeneities, interaction with phonons



Spin Hamiltonian

$$\chi''(\omega) = \frac{\omega V}{2k_B T}\int_{-\infty}^{\infty}\langle M^+(t)M^-(0)\rangle e^{-i\omega t}dt \qquad \frac{d}{dt}M^{\pm}(t) = \frac{i}{\hbar}\left[\mathcal{H}, M^{\pm}(t)\right]$$

- The effective spin Hamiltonian: $\mathcal{H} = \mathcal{H}_{eZ} + \mathcal{H}_{cf} + \mathcal{H}_{hf} + \mathcal{H}_{ee} + \mathcal{H}_{nZ}$

electron Zeeman interaction | zero-field splitting in crystal field | hyperfine coupling | electron-electron interaction | nuclear Zeeman interaction

- Magnetic systems: $\mathcal{H} = \mathcal{H}_{eZ} + \mathcal{H}_{ex} + \mathcal{H}'$

exchange interaction | magnetic anisotropy

$$\mathcal{H}_{ex} = \sum_{(i,j)} J_{ij}\vec{S}_i\cdot\vec{S}_j$$

complicated 4-spin correlation function !

- 2-spin coupling: $\vec{S}_i \cdot \underline{J}_{ij} \cdot \vec{S}_j$

$$\underline{J}_{ij} = J_{ij}\begin{bmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix} + \begin{bmatrix}E & 0 & 0\\ 0 & -E & 0\\ 0 & 0 & D\end{bmatrix} + \begin{bmatrix}0 & d_z & -d_y\\ -d_z & 0 & d_x\\ d_y & -d_x & 0\end{bmatrix}$$

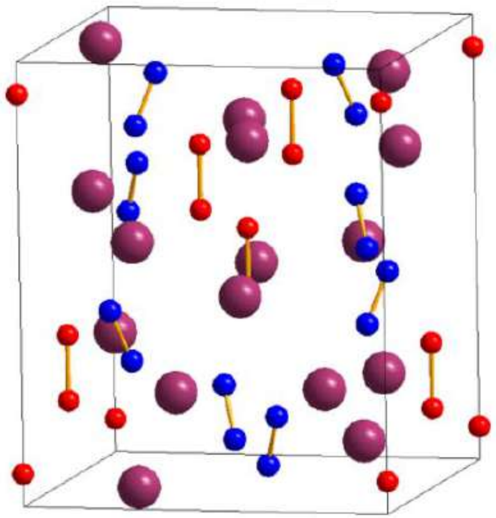
isotropic exchange | symmetric anisotropy | Dzyaloshinskii-Moriya

ESR Intensity

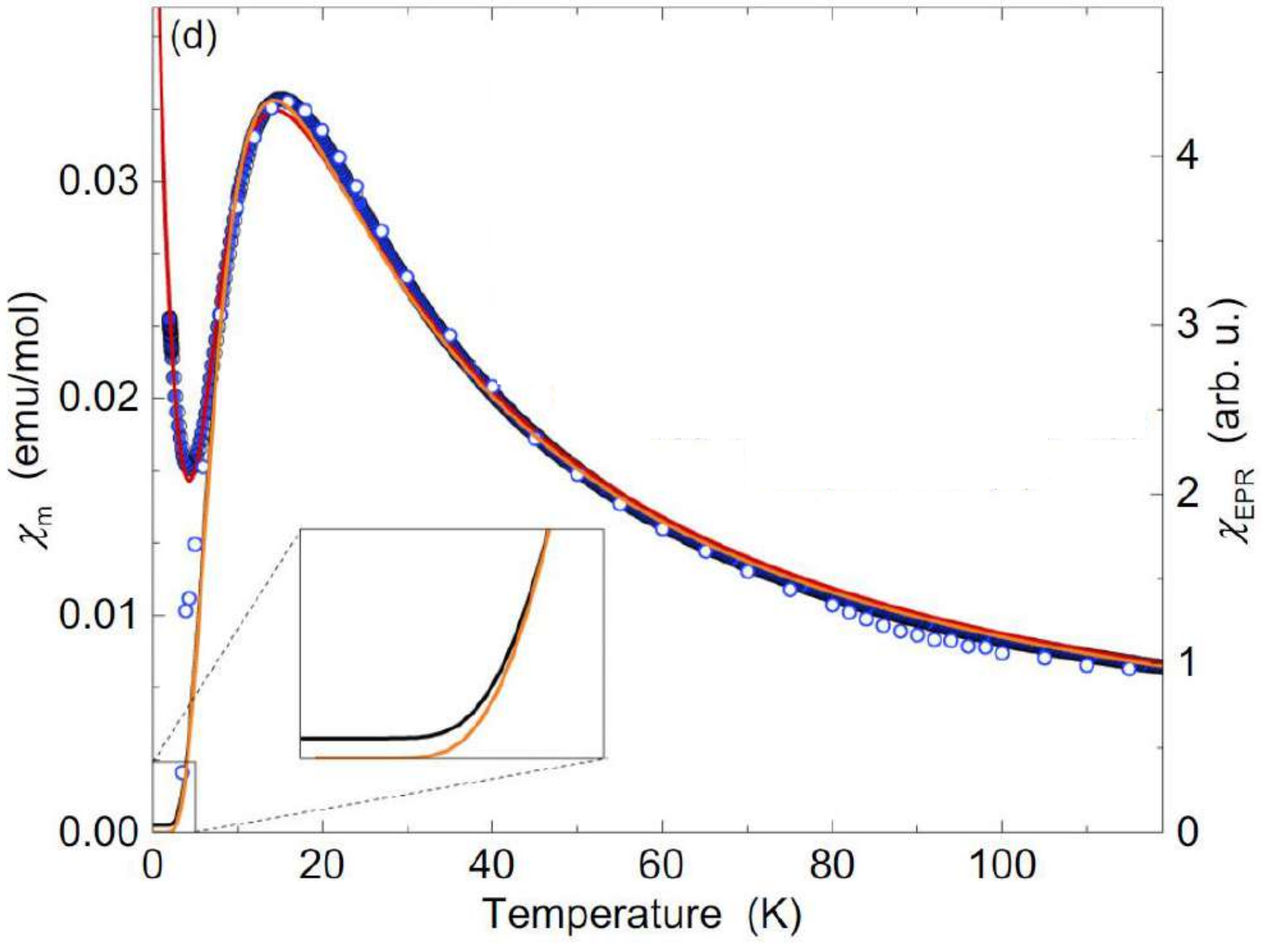
- Kramers-Kronig relations:

$$\chi'(\omega=0)=\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\chi''(\omega')}{\omega'}\mathrm{d}\omega'$$

$$I(\omega)=\frac{1}{2}\omega H_0^2\chi''(\mathbf{q}=0,\omega) \xrightarrow{\Delta B \ll B_0} \int_{-\infty}^{\infty} I(\omega)\mathrm{d}\omega \propto \chi_0$$



- Dimerization of molecular O_2^- anions : mixed-valance compound Rb_4O_6



Knafljič *et al.*, Phys. Rev. B **101**, 024419 (2020)

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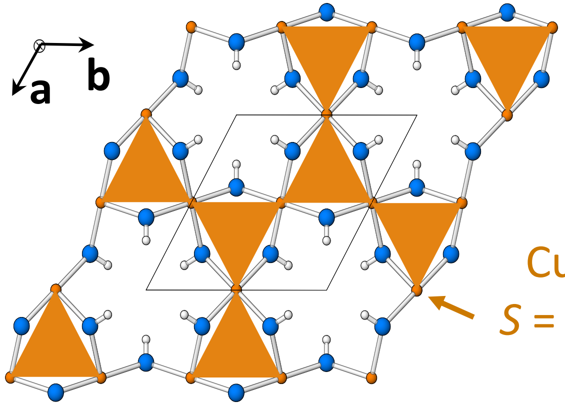
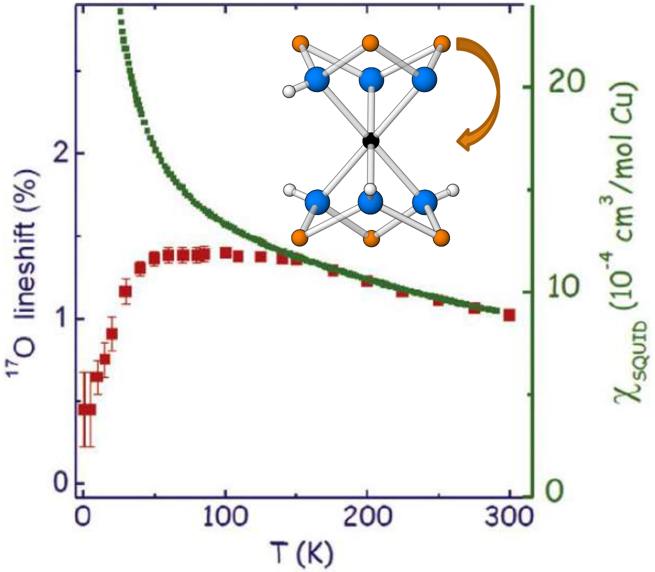


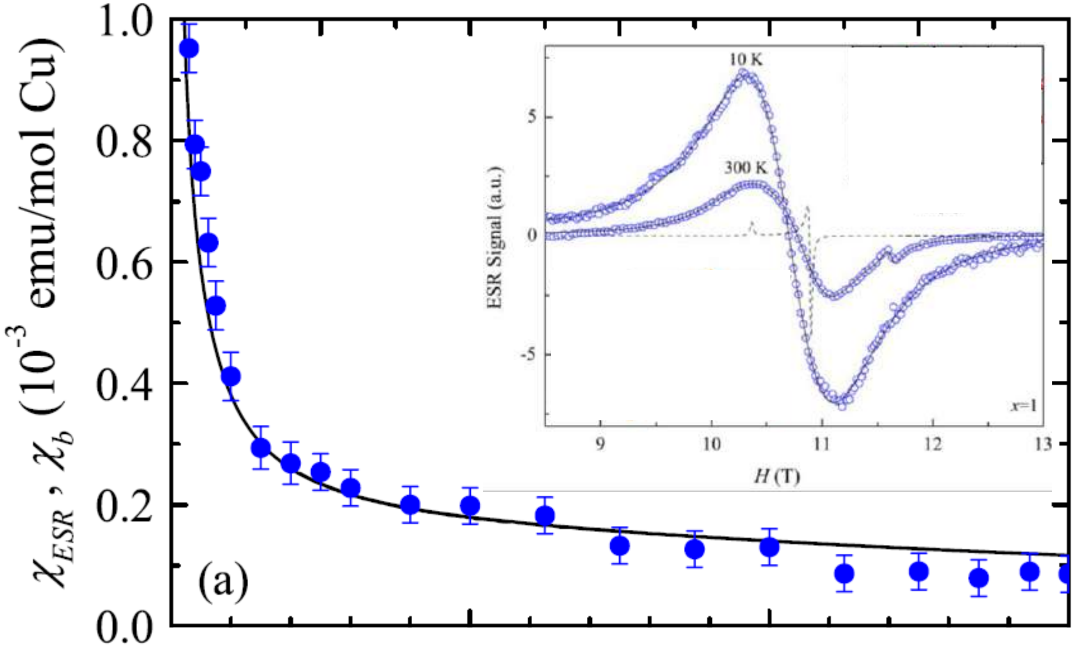
Cu^{2+}
S = 1/2

$ZnCu_3(OH)_6Cl_2$:
kagome AFM



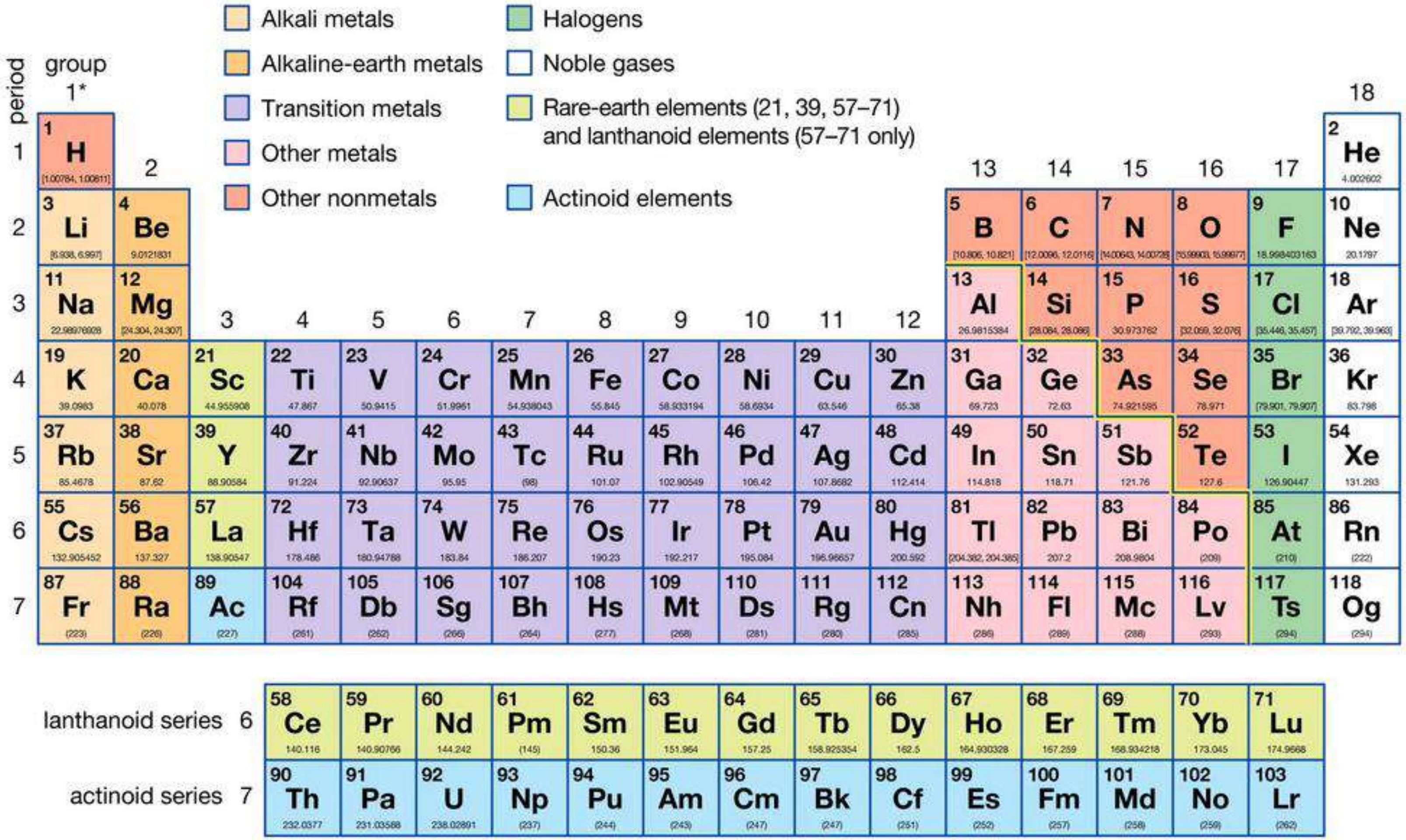
coupling between impurity and intrinsic spins

Olariu *et al.*, Phys. Rev. Lett. **100**, 087202 (2008)



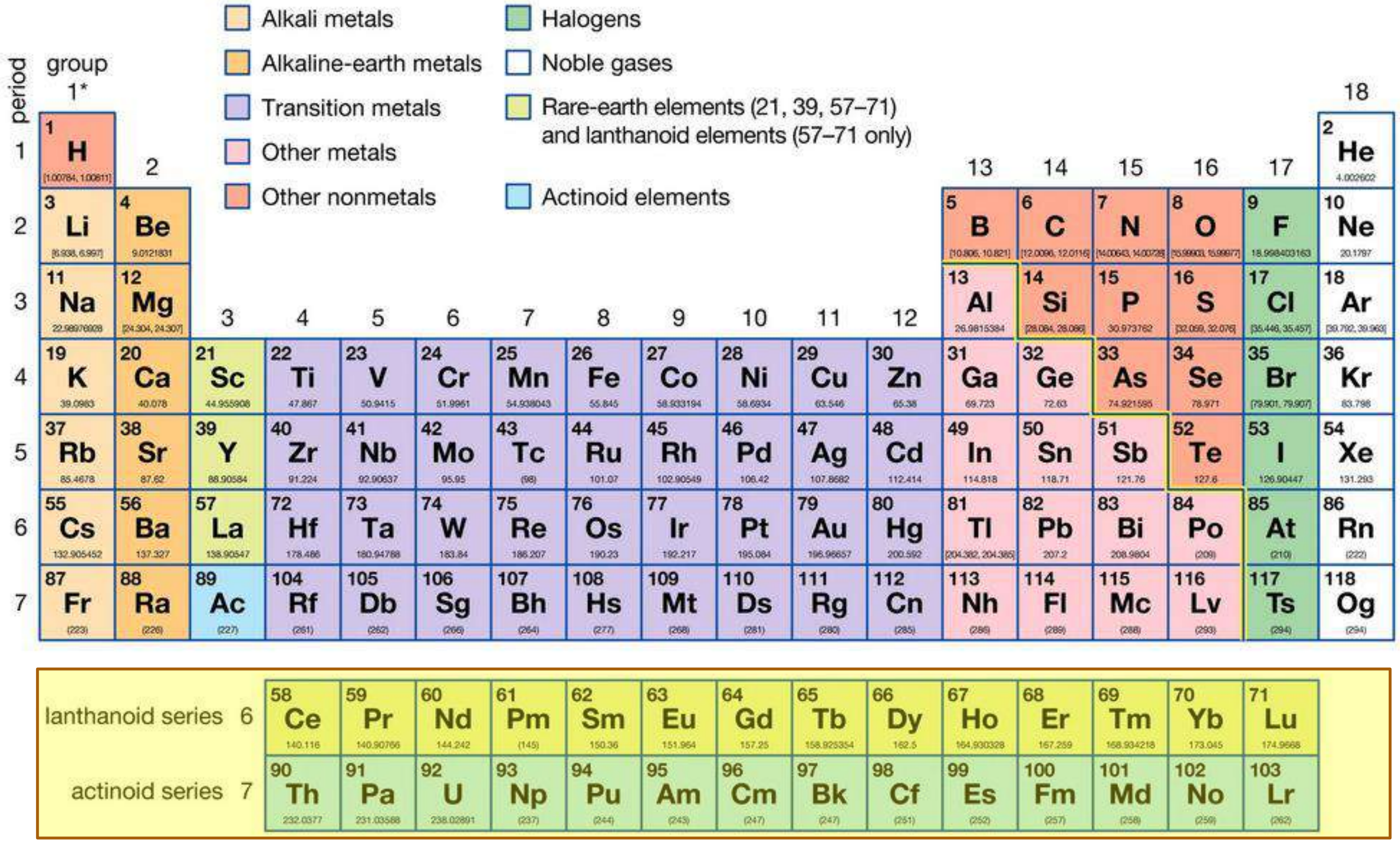
Zorko *et al.*, Phys. Rev. Lett. **101**, 024419 (2008)

ESR Resonance Field



ESR Resonance Field

- Rare-earths: $\mathcal{H}_{cf} \ll \mathcal{H}_{LS} = \lambda \vec{L} \cdot \vec{S}$ → $\vec{J} = \vec{L} + \vec{S}$



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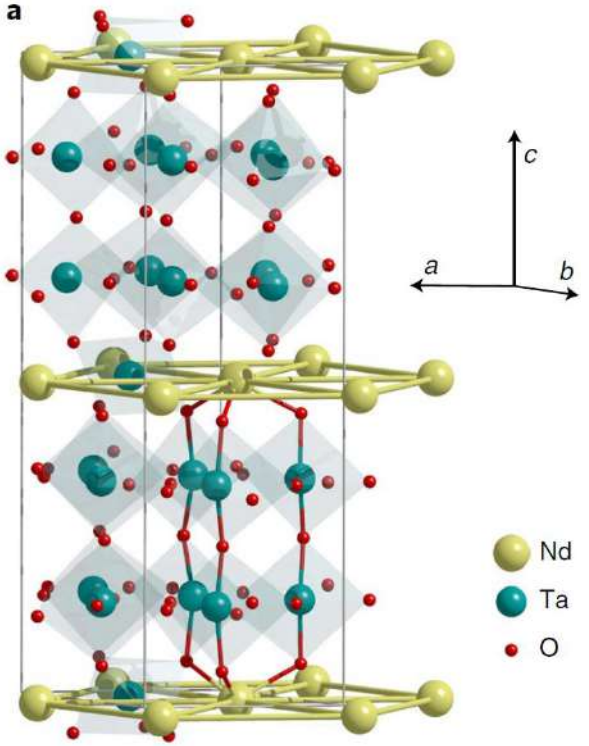
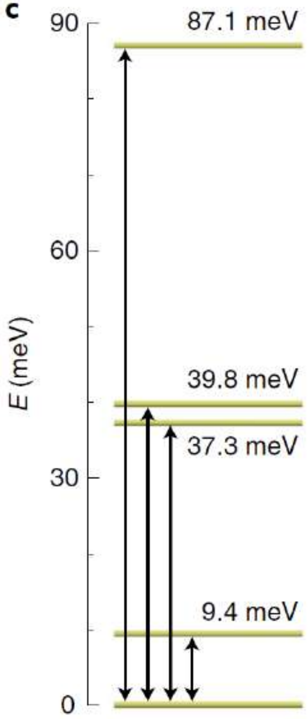
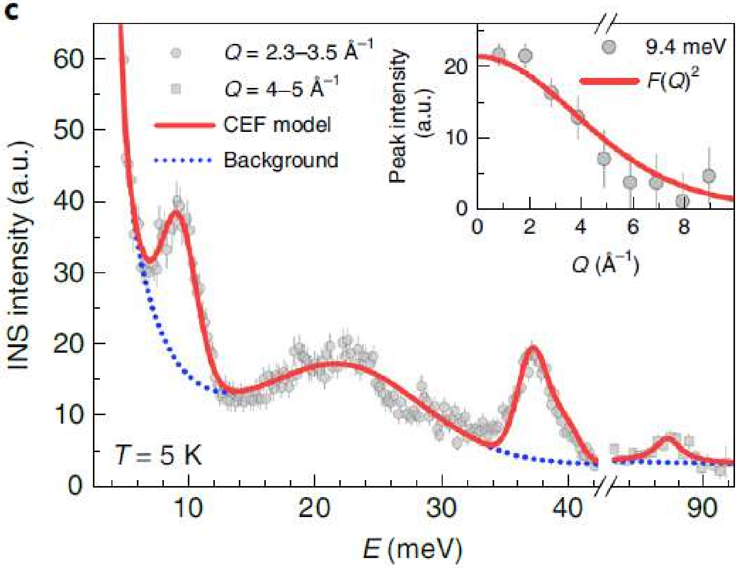
- CF splitting: $NdTa_7O_{19}$
  (triangular AFM with J = 9/2)





GS doublet:

$\vert \pm m_J \rangle$	$\pm\omega_0$
$\vert \pm 9/2 \rangle$	0
$\vert \pm 7/2 \rangle$	0
$\vert \pm 5/2 \rangle$	0.933
$\vert \pm 3/2 \rangle$	0
$\vert \pm 1/2 \rangle$	0
$\vert \mp 1/2 \rangle$	$\mp$0.244
$\vert \mp 3/2 \rangle$	0
$\vert \mp 5/2 \rangle$	0
$\vert \mp 7/2 \rangle$	0.263
$\vert \mp 9/2 \rangle$	0
E(meV)	0



Arh *et al.*, Nat. Mater. **21**, 416 (2022).

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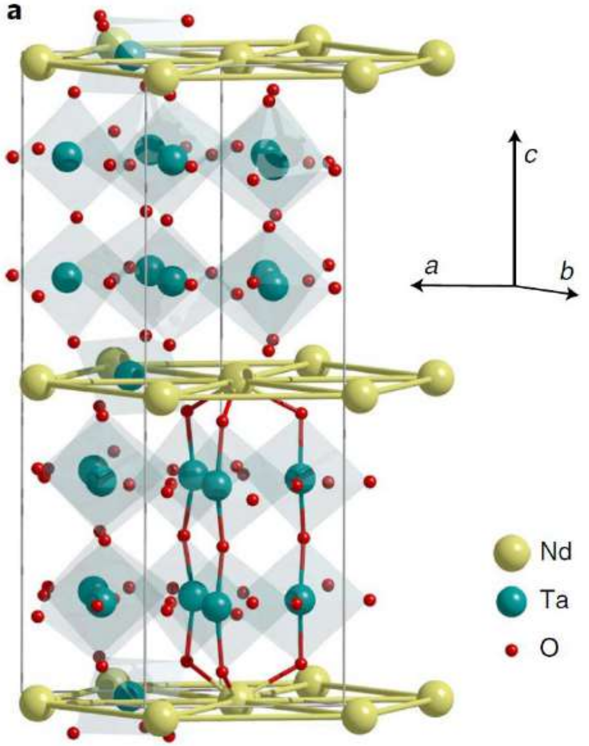

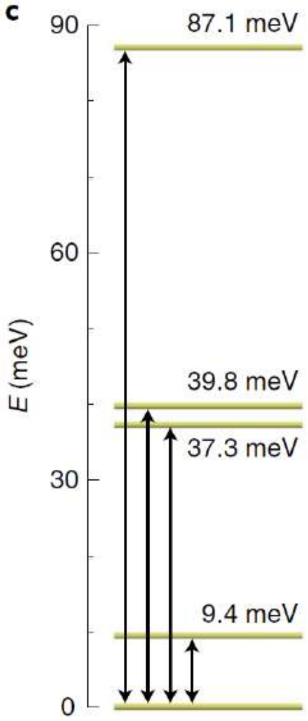

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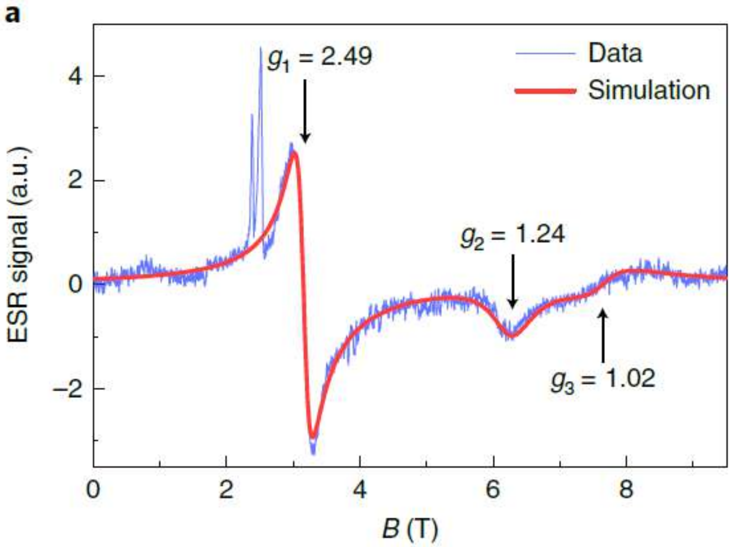
$\lvert \mp 7/2 \rangle$	0.263
$\lvert \mp 9/2 \rangle$	0
$E(\mathrm{meV})$	0



$$\mathcal{H}_{\mathrm{ex}} = \sum_{\langle i,j \rangle} \mathcal{J}_z S_i^z S_j^z + \mathcal{J}_{xy} \left(S_i^x S_j^x + S_i^y S_j^y \right)$$

$$\mathcal{J}_\alpha = \mathcal{J}_0 g_\alpha^2 (g_J - 1)^2 / g_J^2$$

$$\mathcal{J}_z = 0.90(2)\ \mathrm{K}$$
$$\mathcal{J}_{xy} = 0.16(2)\ \mathrm{K}$$

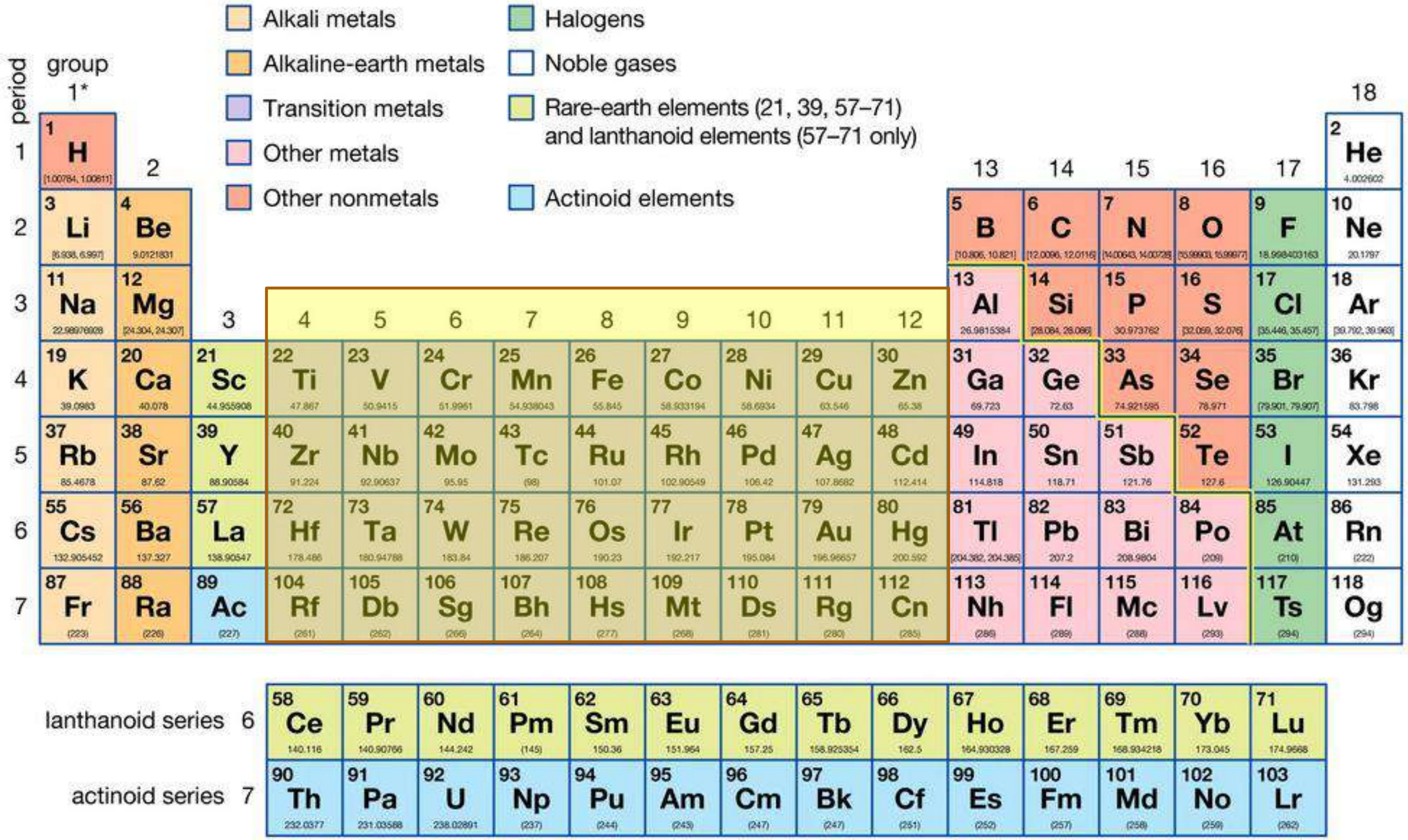
Ising TAFM

Arh *et al.*, Nat. Mater. **21**, 416 (2022).

ESR Resonance Field

HOKKAIDO UNIVERSITY

- Transition metals:



ESR Resonance Field

- Transition metals: $\mathcal{H}_{cf} \gg \mathcal{H}_{LS} = \lambda \vec{L} \cdot \vec{S}$ → $\langle \hat{\vec{L}} \rangle = 0$ (quenching of the orbital momentum)

- CF levels mixing: $\mathcal{H}_{LS} = \lambda \mathbf{L} \cdot \mathbf{S}$

$$\Lambda_{\mu,\nu} = \frac{\langle 0|L_\mu|n\rangle\langle n|L_\nu|0\rangle}{E_n - E_0}$$

  - Zeeman term:

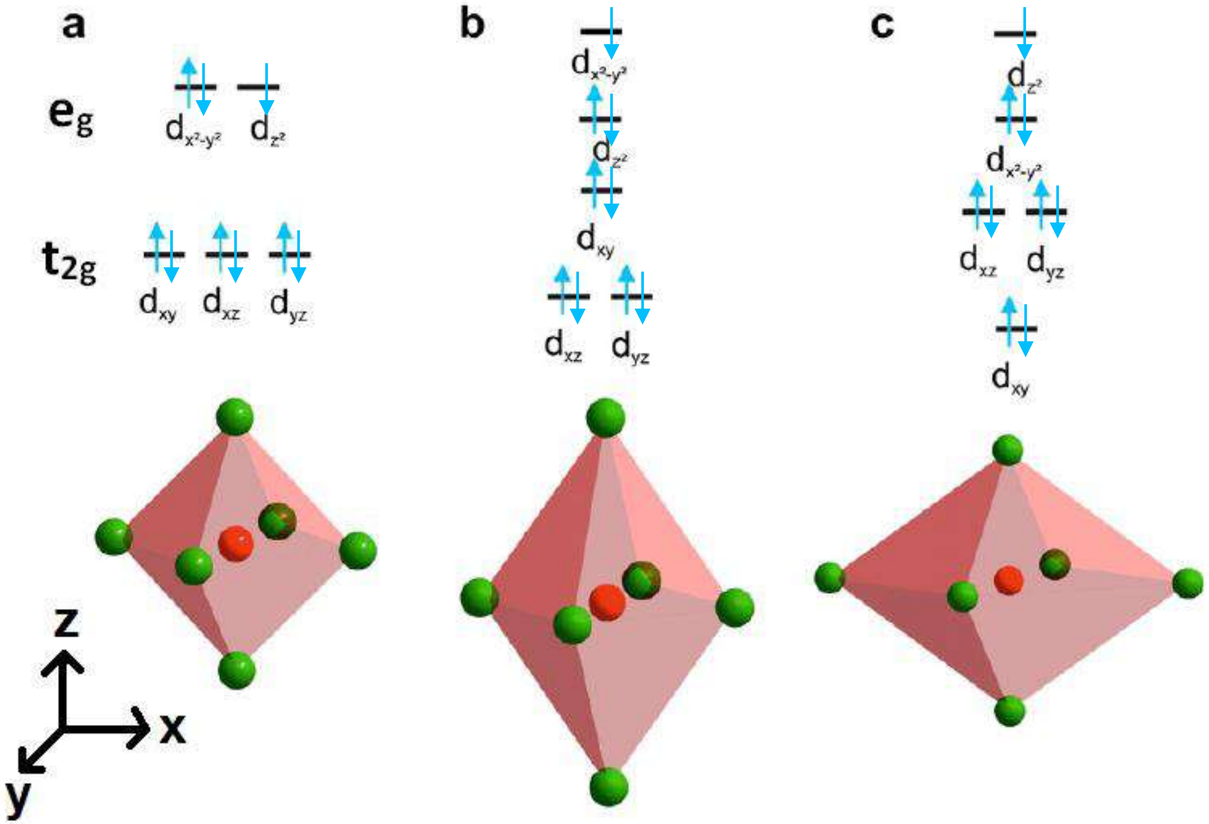
$$\mathcal{H}_{eZ} = \mu_B \mathbf{B} \cdot \underline{\mathbf{g}} \cdot \mathbf{S}$$

$$\underline{\mathbf{g}} = g_0(\underline{\mathbf{g}} - \lambda \underline{\mathbf{\Lambda}})$$

  - CF term:

$$\mathcal{H}_{cf} = -\lambda^2 \mathbf{S} \cdot \mathbf{\Lambda} \cdot \mathbf{S} = \\ = D\left(S_z^2 - \frac{1}{3}S(S+1)\right) + E\left(S_x^2 - S_y^2\right)$$

$L = 2$

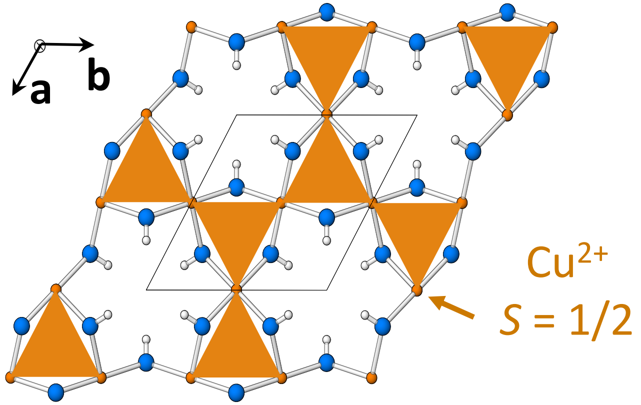


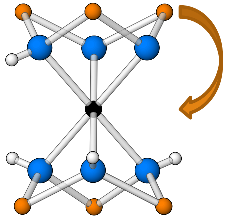
octahedral CF

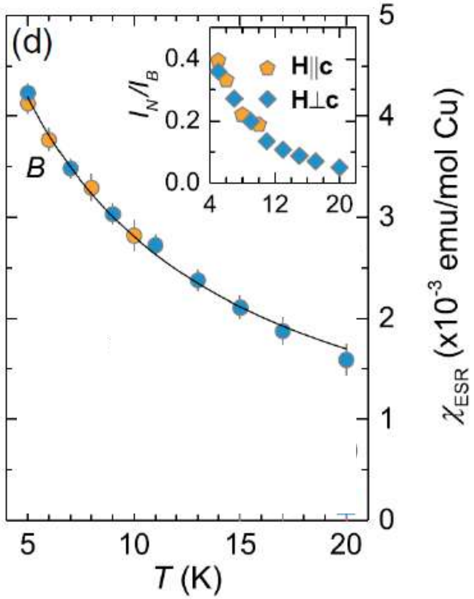
tetrahedral CF

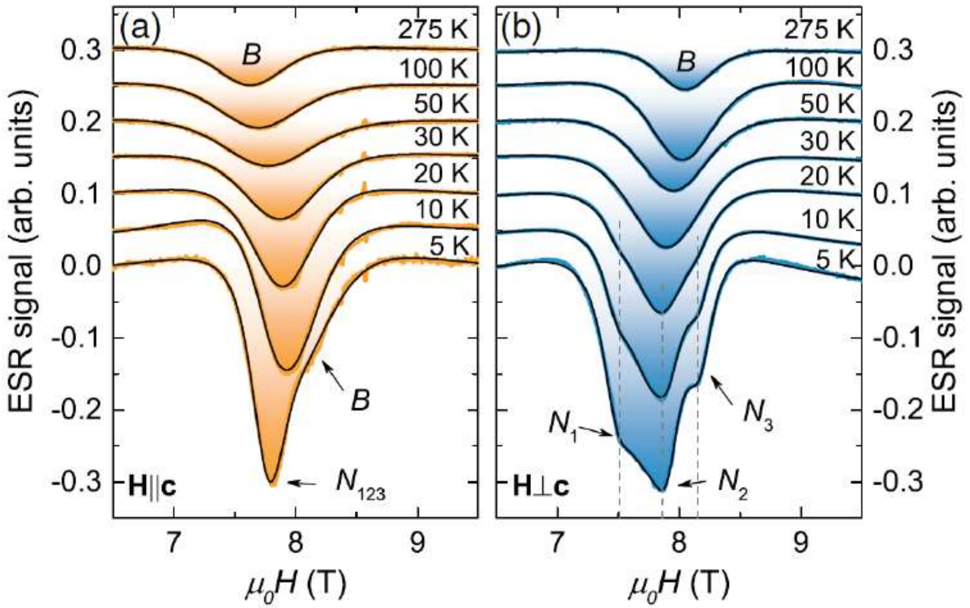
ESR Resonance Field

- Defects in herbertsmithite:









Zorko *et al.*, Phys. Rev. Lett. **118**, 017202 (2017)

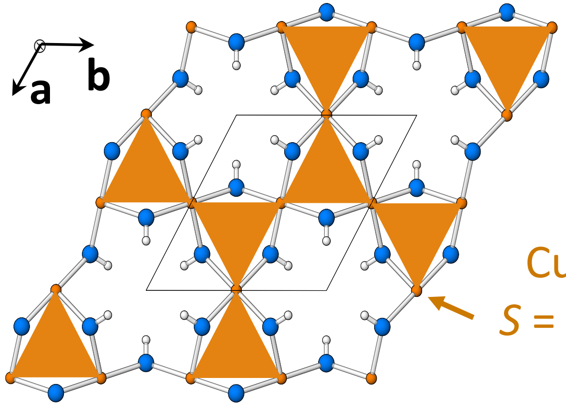
ESR Resonance Field

- Defects in herbertsmithite:
  - defect site 1: broad lines

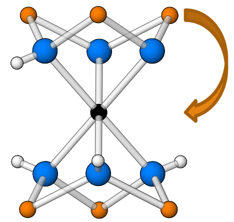
    $$J^{d_I} > J_H = \Delta g \mu_B \mu_0 H / k_B \approx 2\ \mathrm{K}$$

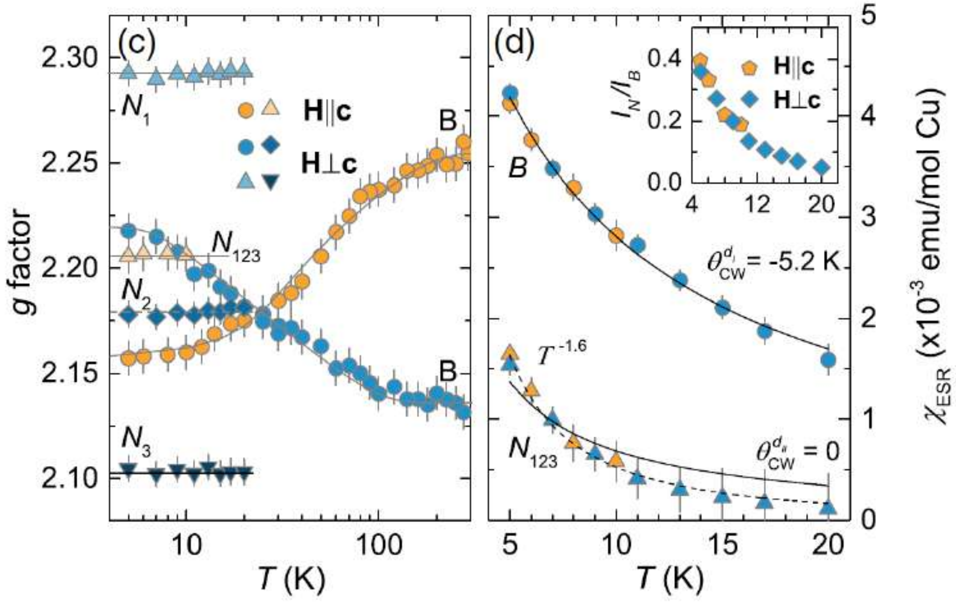
  - defect site 2: narrow lines

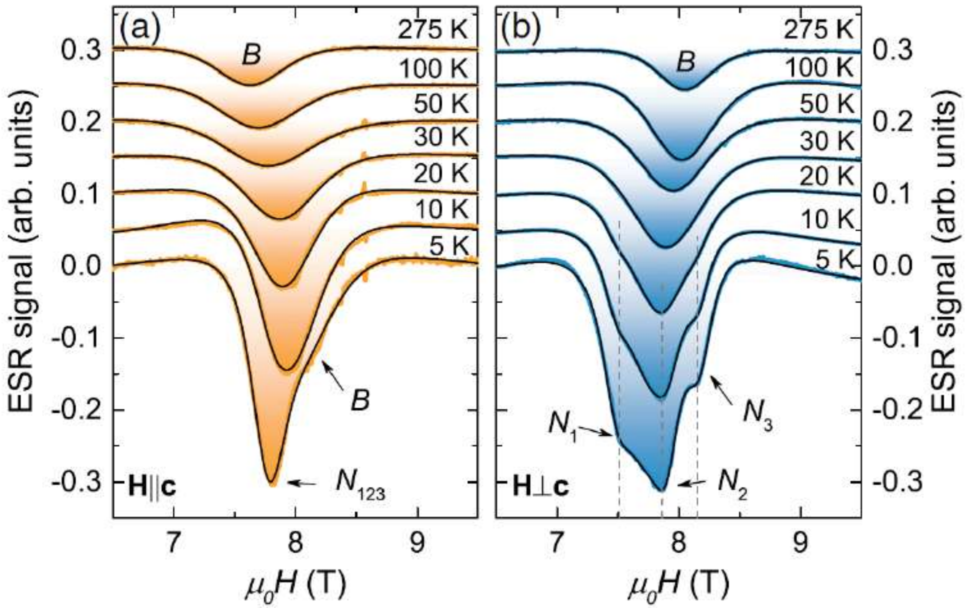
    $$\left| J^{d_{II}} \right| \ll J_H$$



Cu^{2+}
$S = 1/2$







Zorko *et al.*, Phys. Rev. Lett. **118**, 017202 (2017)

ESR Resonance Field

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  - **defect site 1**: broad lines

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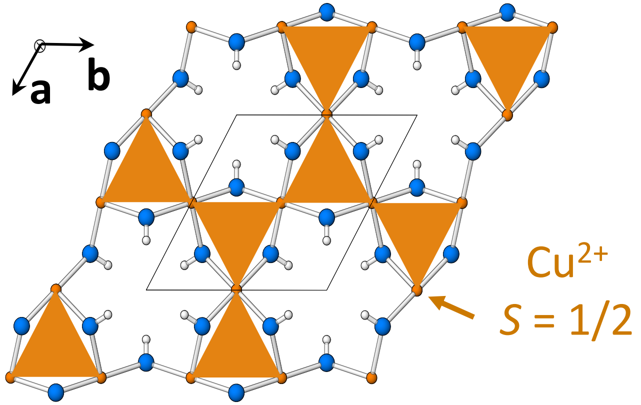
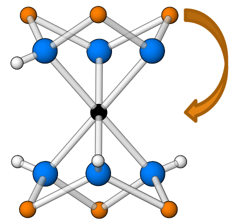
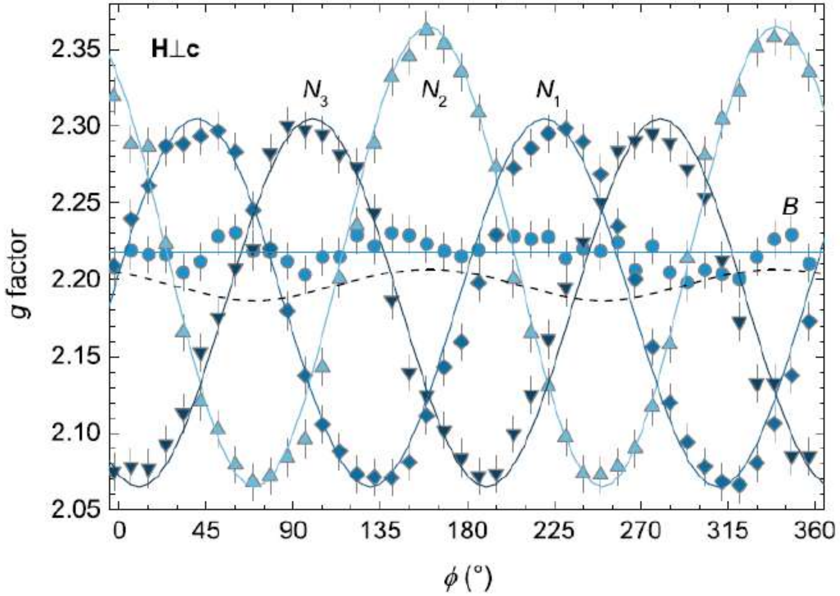


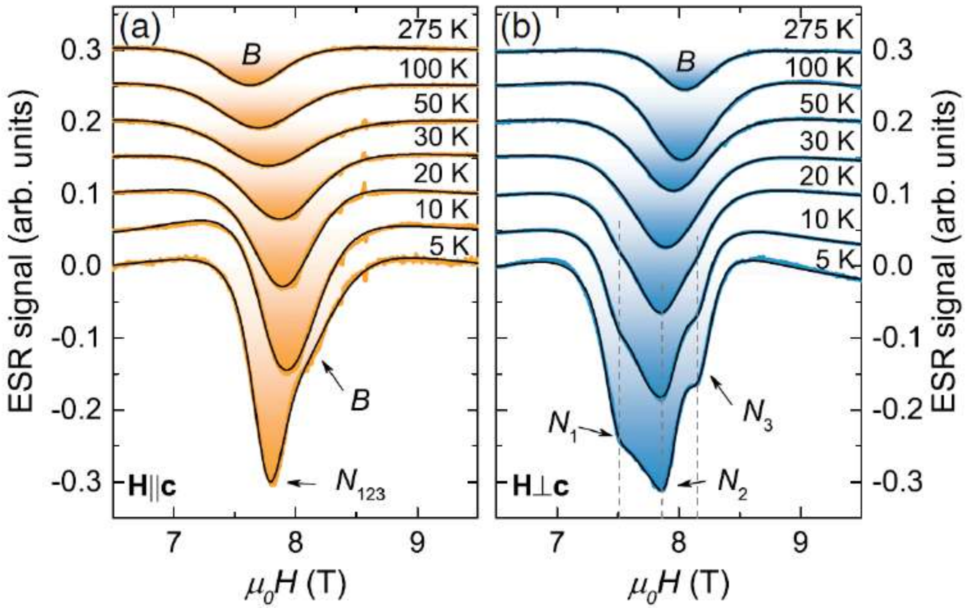




broken axial symmetry:

$\Delta g_{ab}^{d_{II}} = 0.02$

$|\Delta g_{ab}^{d_I}| \sim 0.003(1)$



Zorko *et al.*, Phys. Rev. Lett. **118**, 017202 (2017)

ESR Resonance Field

- Temperature dependent line shift: $\mathcal{H}' \ll \mathcal{H}_{ex}, \mathcal{H}_Z$

$$\delta B = \frac{1}{g\mu_B}\left(\frac{M_1}{M_0} - B_0\right) = \frac{\langle [S^-, [S^+, \mathcal{H}']] \rangle}{2g\mu_B \langle S^z \rangle}$$

$$\mathcal{H}' = \frac{1}{2}\sum_{i,j\neq i} \mathbf{S}_i \cdot \underline{K}_{ij} \cdot \mathbf{S}_j \qquad \underline{K}_{ij} = \underline{\delta}_{ij} + \underline{D}_{ij}$$

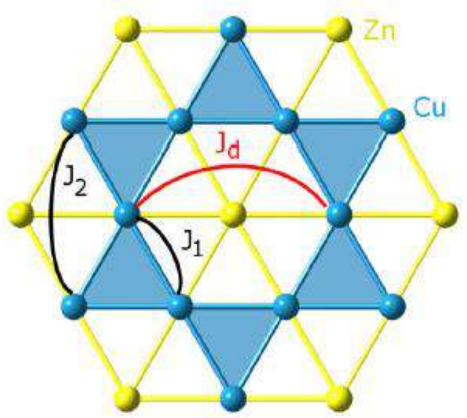
dipolar interaction

symmetric AE

$$\Delta g^z(T) = \frac{\langle S^z \rangle}{2\mu_B B_0} \sum_{j \neq i} \left(2K_{ij}^{zz} - K_{ij}^{xx} - K_{ij}^{yy}\right)$$

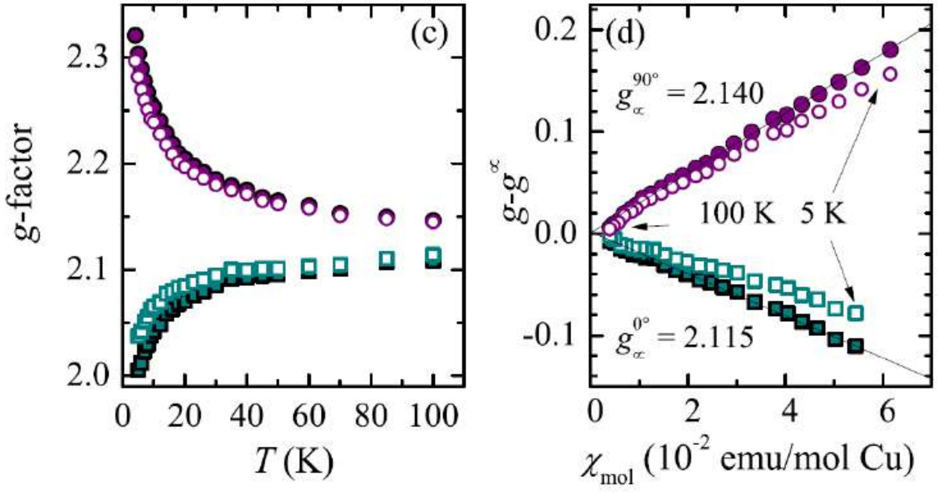
$$\langle S^z \rangle = \sum_i \langle S_i^z \rangle = \frac{\chi_{mol}(T) B_0}{N_A g \mu_0 \mu_B}$$

Nagata *et al.*, JPSJ **32**, 337 (1972)



$ZnCu_3(OH)_6Cl_2$ kapellasite: 27%-depleted kagome AFM

$|D'^{cc}/J_1| = 3\%$



Kermarrec *et al.*, Phys. Rev. B **90**, 205103 (2014)

ESR Linewidth

$\omega_0 = g\mu_B B_0/\hbar$

- Relaxation Function (Kubo-Tomita approach): $\mathcal{H}' \ll \mathcal{H}_0 = \mathcal{H}_Z + \mathcal{H}_{ex}$

$$\varphi(t) = \left\langle \tilde{S}^+(t)S^-(0)\right\rangle / \langle S^+(0)S^-(0)\rangle \quad \longrightarrow \quad I(\omega) \propto \int_{-\infty}^{\infty} \varphi(t) e^{i(\omega-\omega_0)t} \mathrm{d}t$$

- slow spin fluctuations: $\omega_0\tau_c \gg 1$ ($\tau_c \approx h/J$) $\longrightarrow$ $\varphi(t) = \exp\left(-\frac{1}{2}\frac{M_2}{\hbar^2}t^2\right)$ $\longrightarrow$ Gaussian line shape

- fast spin fluctuations: $\omega_0\tau_c \ll 1$ ($\tau_c \approx h/J$) $\longrightarrow$ $\varphi(t) = \exp\left(-\sqrt{\frac{\pi}{2}}\frac{M_2}{\hbar^2}\tau_c t\right)$ $\longrightarrow$ Lorentzian line shape

$$\Delta B = C\frac{k_B}{g\mu_B}\sqrt{\frac{M_2^3}{M_4}} \propto \frac{M_2}{J}$$

$$M_2 = \frac{\langle[\mathcal{H}', S^+][S^-, \mathcal{H}']\rangle}{\langle S^+S^-\rangle},$$

$$M_4 = \frac{\langle[\mathcal{H} - \mathcal{H}_Z, [\mathcal{H}', S^+]][\mathcal{H} - \mathcal{H}_Z, [\mathcal{H}', S^-]]\rangle}{\langle S^+S^-\rangle}$$

A. Zorko, Determination of Magnetic Anisotropy by EPR, in *Topics From EPR Research* (ed. Ahmed Maghraby), IntechOpen, 2018.

ESR Linewidth

$\omega_0 = g\mu_B B_0/\hbar$

❑ Relaxation Function (Kubo-Tomita approach): $\mathcal{H}' \ll \mathcal{H}_0 = \mathcal{H}_Z + \mathcal{H}_{ex}$

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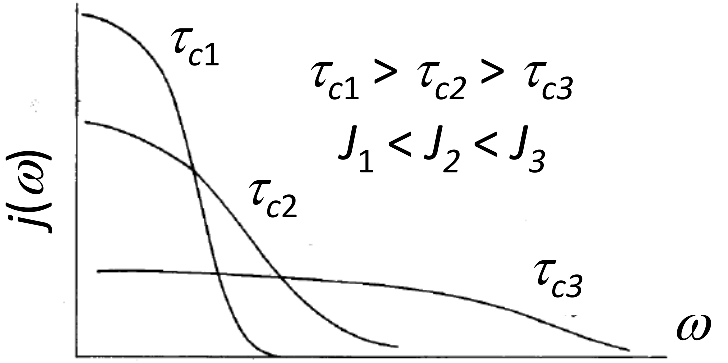
$$\Delta B = C\frac{k_B}{g\mu_B}\sqrt{\frac{M_2^3}{M_4}} \propto \frac{M_2}{J}$$

! $\Rightarrow$

❖ exchange narrowing

❖ finite linewidth due to $\mathcal{H}'$

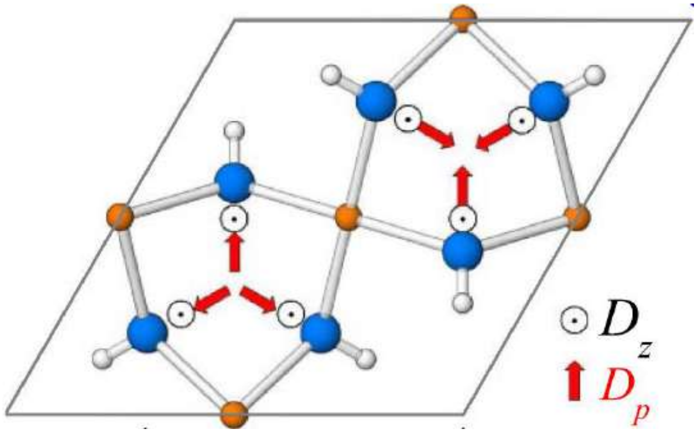


Zorko, Determination of Magnetic Anisotropy by EPR, in *Topics From EPR Research* (ed. Ahmed Maghraby), IntechOpen, 2018.

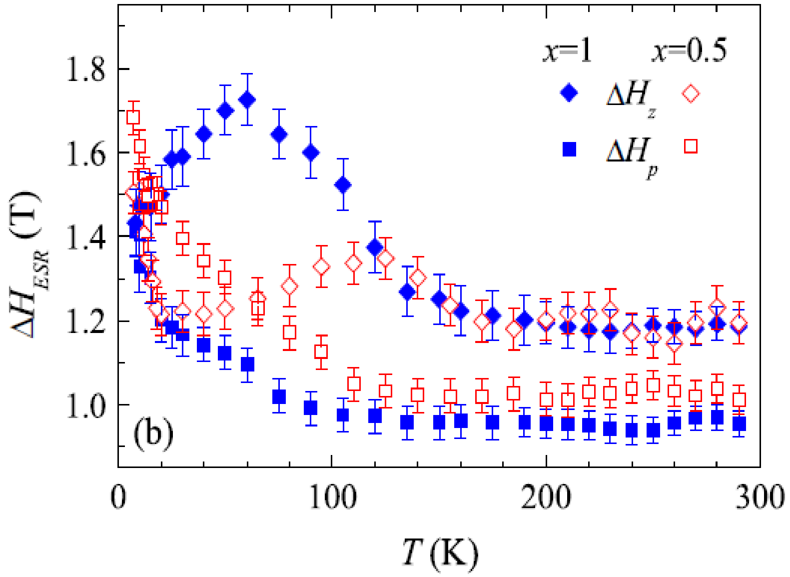
ESR Linewidth

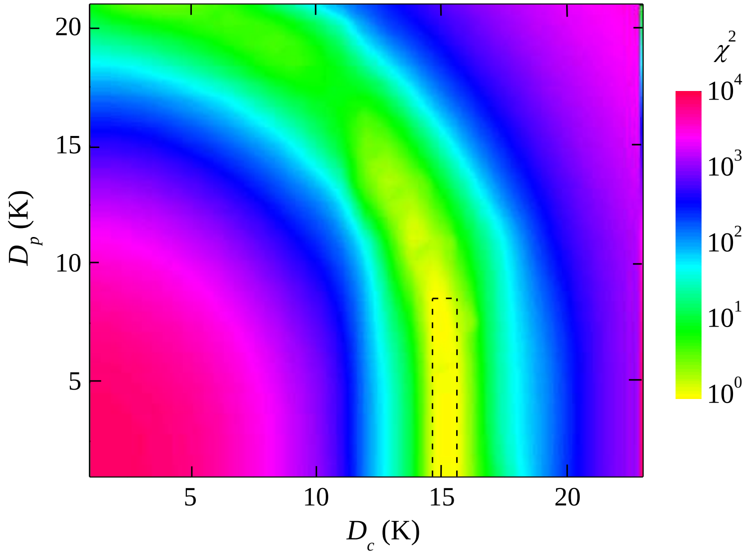
- ESR linewidth on the kagome lattice: $\mathcal{H}_{\rm DM} = \vec{D}\cdot\sum_{(i,j)}\vec{S}_i\times\vec{S}_j$

$$\Delta B(\theta) = \sqrt{2\pi}\frac{k_b}{2g(\theta)\mu_B J}\sqrt{\frac{\left(2d_z^2+3d_p^2+\left(2d_z^2-d_p^2\right)\cos^2\theta\right)^3}{16d_z^2+78d_p^2+\left(16d_z^2-26d_p^2\right)\cos^2\theta}}$$

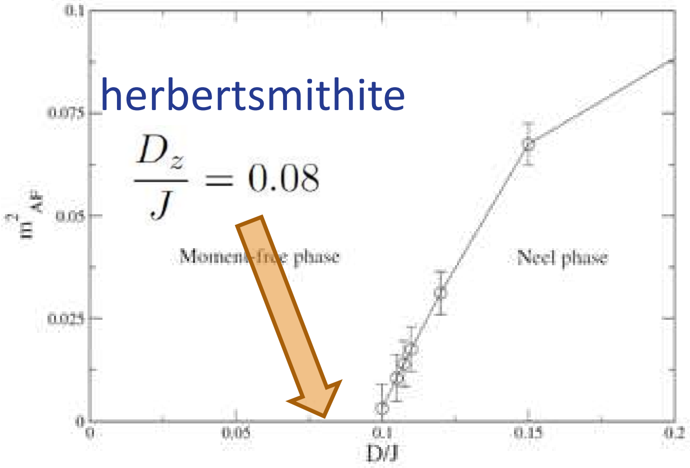


- Herbertsmithite: kagome AFM





Zorko *et al.*, Phys. Rev. Lett. **101**, 026405 (2008)



Cepas *et al.*, Phys. Rev. B **78**, 140405(R) (2008)

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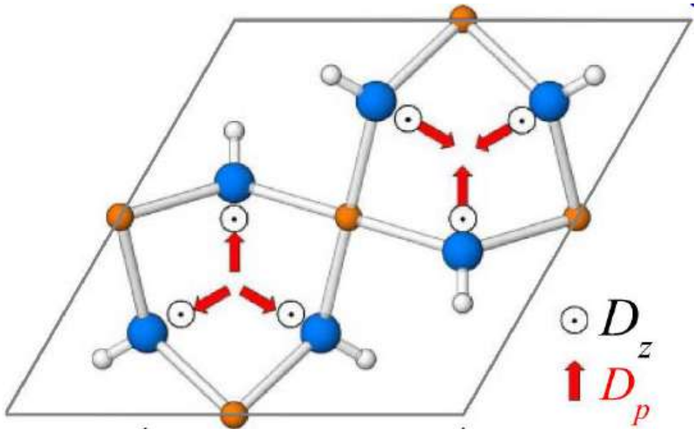
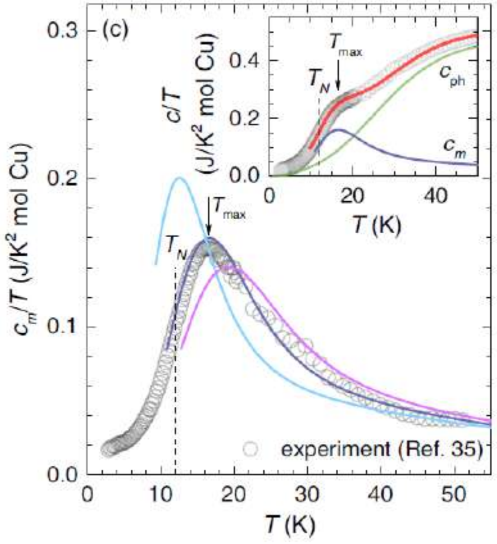
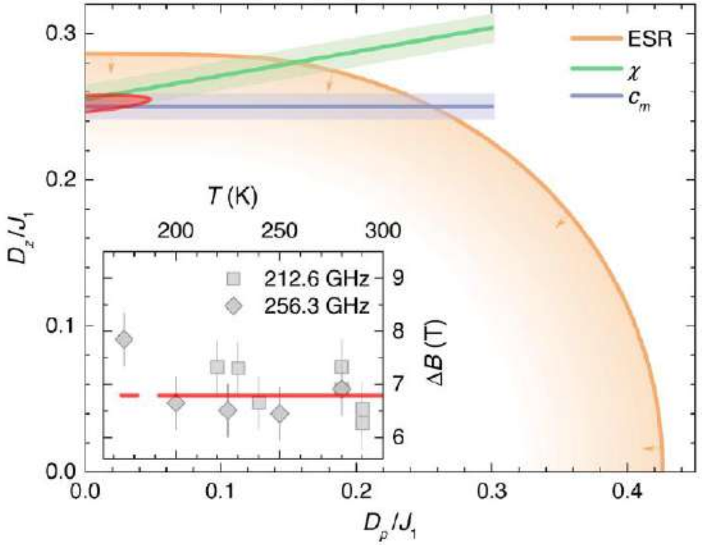
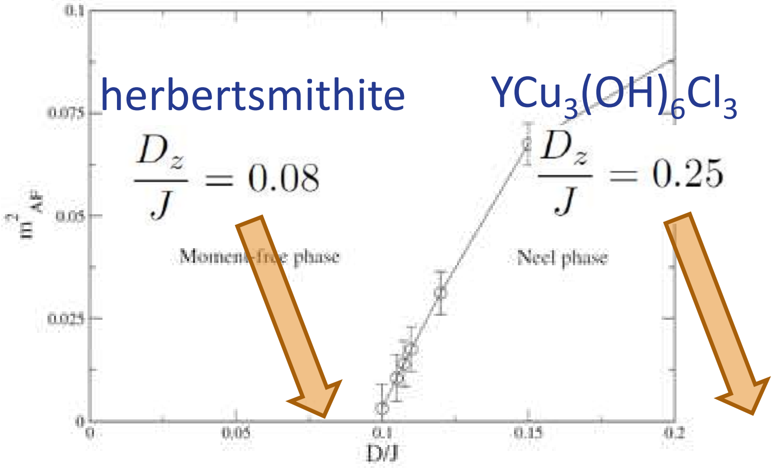


- $YCu_3(OH)_6Cl_3$: kagome AFM





Arh *et al.*, Phys. Rev. Lett. **125**, 027203 (2020)



Cepas *et al.*, Phys. Rev. B **78**, 140405(R) (2008)

ESR Linewidth

❑ Limitations of the Kubo-Tomita approach:

- high temperatures

- transformation of the DM term to higher-order terms due to hidden symmetry

  - staggered DM in spin chains

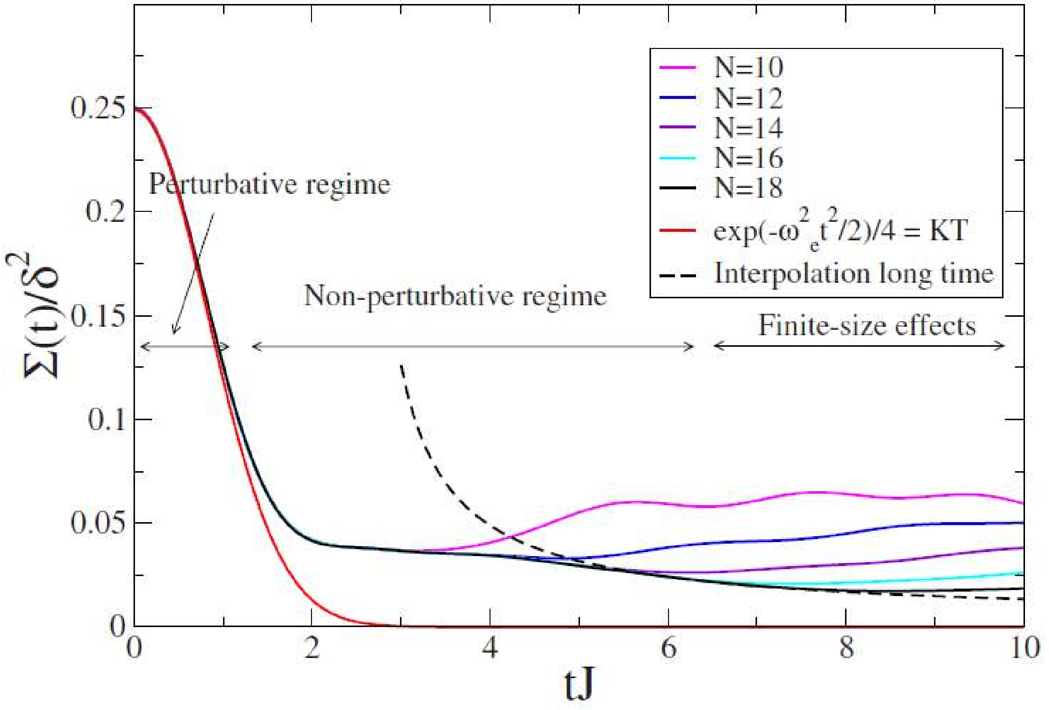
    Choukround *et al.*, Phys. Rev. Lett. **87**, 127207 (2001)

  - reducible DM components in 2D

    Cheng *et al.*, Phys. Rev. B **75**, 144422 (2007)

- slower decay of spin correlations in low-D magnets

➡ overestimation of magnetic anisotropy



El Shawish *et al.*, Phys. Rev. B **81**, 224421 (2010)

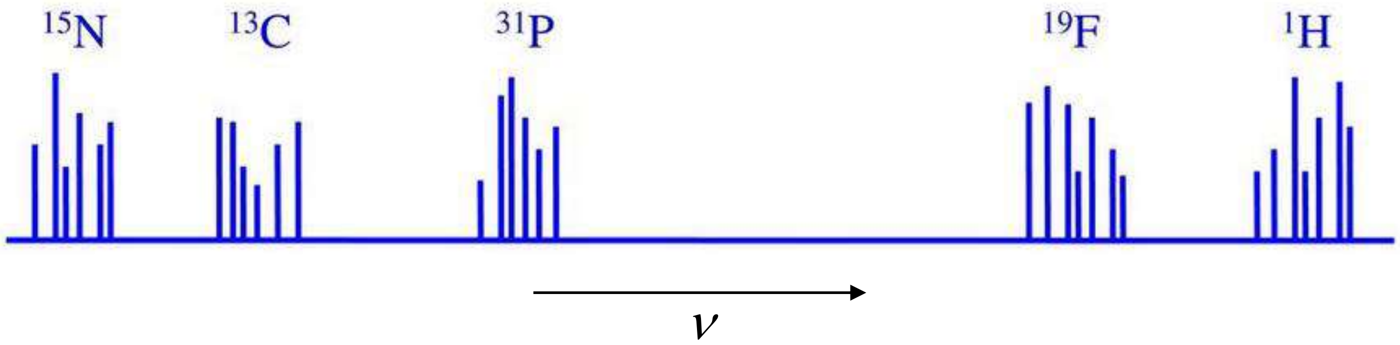
Outline

- ❑ Introduction to magnetism
- ❑ Probing magnetism: conventional bulk and scattering techniques
- ❑ Local probes of magnetism
- ❑ Electron spin resonance (ESR)
- ❑ Nuclear magnetic resonance (NMR)
- ❑ Muon spectroscopy (μSR)
- ❑ Summary: strengths, limitations and complementarity of local probes

Motivation for NMR Measurements

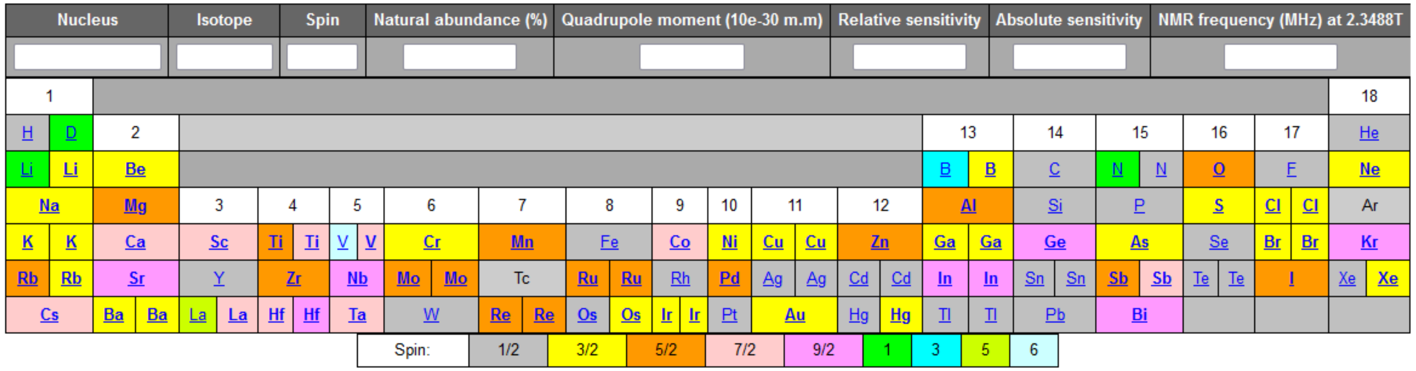
HOKKAIDO UNIVERSITY

- Possibility of detecting a broad variety of nuclei



- High spectral resolution: $<10^{-6}$

- Broad frequencies range: 10 – 1000 MHz



https://www.pascal-man.com

Motivation for NMR Measurements

- Most common nuclei:

Isotope	Occurrence in nature (%)	Spin number I	Magnetic moment μ (μ_N)	Electric quadrupole moment ($e \times 10^{-24}$ cm^2)	Operating frequency at 7 T (MHz)	Relative sensitivity
^{1}H	99.984	$\frac{1}{2}$	2.79628	0	300.13	1
^{2}H	0.016	1	0.85739	0.0028	46.07	0.0964
^{10}B	18.8	3	1.8005	0.074	32.25	0.0199
^{11}B	81.2	$\frac{3}{2}$	2.6880	0.026	96.29	0.165
^{12}C	98.9	0	0	0	0	0
^{13}C	1.1	$\frac{1}{2}$	0.70220	0	75.47	0.0159
^{14}N	99.64	1	0.40358	0.071	21.68	0.00101
^{15}N	0.37	$\frac{1}{2}$	−0.28304	0	30.41	0.00104
^{16}O	99.76	0	0	0	0	0
^{17}O	0.0317	$\frac{5}{2}$	−1.8930	−0.0040	40.69	0.0291
^{19}F	100	$\frac{1}{2}$	2.6273	0	282.40	0.834
^{28}Si	92.28	0	0	0	0	0
^{29}Si	4.70	$\frac{1}{2}$	−0.5548	0	59.63	0.0785
^{31}P	100	$\frac{1}{2}$	1.1205	0	121.49	0.0664
^{35}Cl	75.4	$\frac{3}{2}$	0.92091	−0.079	29.41	0.0047
^{37}Cl	24.6	$\frac{3}{2}$	0.68330	−0.062	24.48	0.0027

https://en.wikipedia.org

Motivation for NMR Measurements

HOKKAIDO UNIVERSITY

- Broad range of application s:

  - analysis of chemicals and chemical compositions
  - molecular structure
  - molecular physics/dynamics
  - purity determination
  - process control (pharmaceutical industry, polymer production, cosmetics, food manufacturing, study of batteries,…)
  - …

CHEMISTRY/ INDUSTRY

  - biochemical studies of tissues
  - magnetic resonance imaging (MRI)
  - …

BIOLOGY/ MEDICINE

  - magnetic properties of materials
  - structural properties of materials
  - …

PHYSICS/ MATERIALS RESEARCH

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CHEMISTRY/ INDUSTRY

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  - …

BIOLOGY/ MEDICINE

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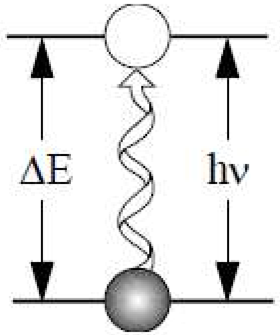
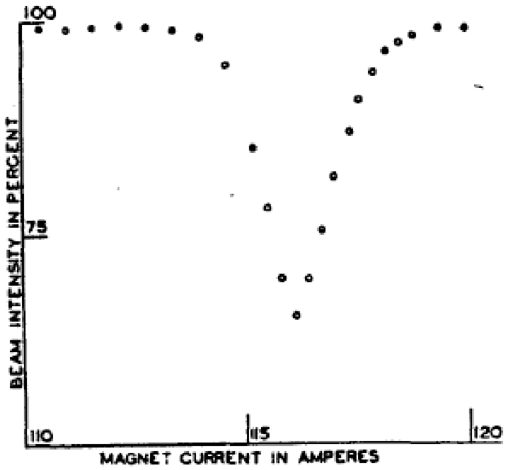
  - structural properties of materials
  - …

PHYSICS/ MATERIALS RESEARCH

A Brief History of NMR

- 1938: interactions of LiCl molecular beams with EM waves in a static magnetic field





The Nobel Prize in Physics 1944

Photo from the Nobel Foundation archive.

Isidor Isaac Rabi

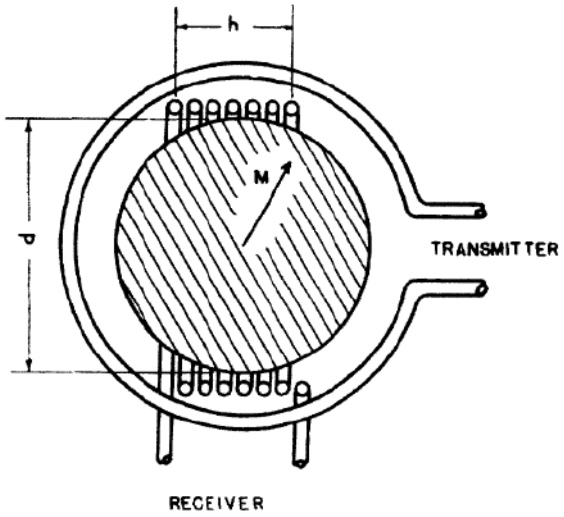
Prize share: 1/1

The Nobel Prize in Physics 1944 was awarded to Isidor Isaac Rabi "for his resonance method for recording the magnetic properties of atomic nuclei."

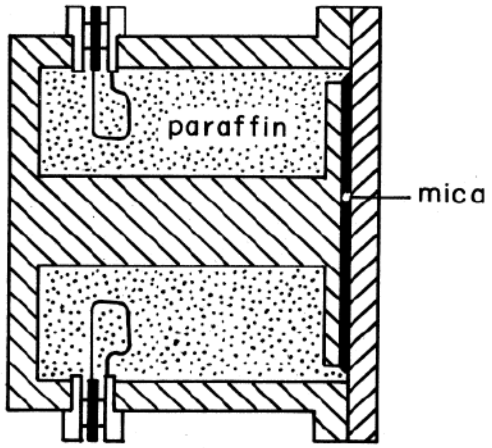
https://www.nobelprize.org

A Brief History of NMR

- 1945: NMR in condensed matter



in water



in paraffin

The Nobel Prize in Physics 1952

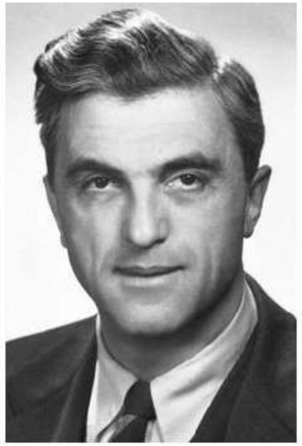


Photo from the Nobel Foundation archive.
Felix Bloch
Prize share: 1/2

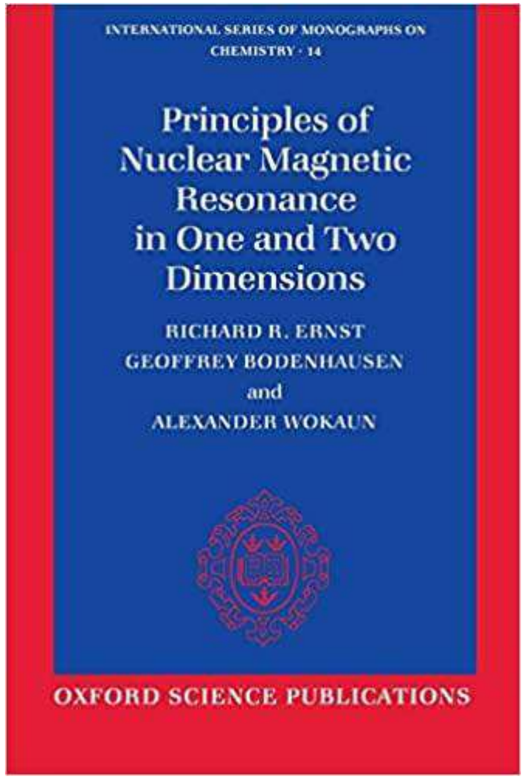
Photo from the Nobel Foundation archive.
Edward Mills Purcell
Prize share: 1/2

The Nobel Prize in Physics 1952 was awarded jointly to Felix Bloch and Edward Mills Purcell "for their development of new methods for nuclear magnetic precision measurements and discoveries in connection therewith."

https://www.nobelprize.org

A Brief History of NMR

- 1950’s and 1960’s: high resolution NMR (FT NMR, noise decoupling, novel pulse techniques, 2D NMR,…)



The Nobel Prize in Chemistry 1991

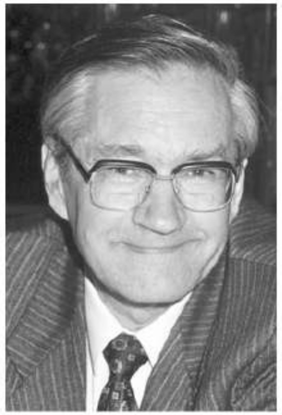


Photo from the Nobel Foundation archive.

Richard R. Ernst

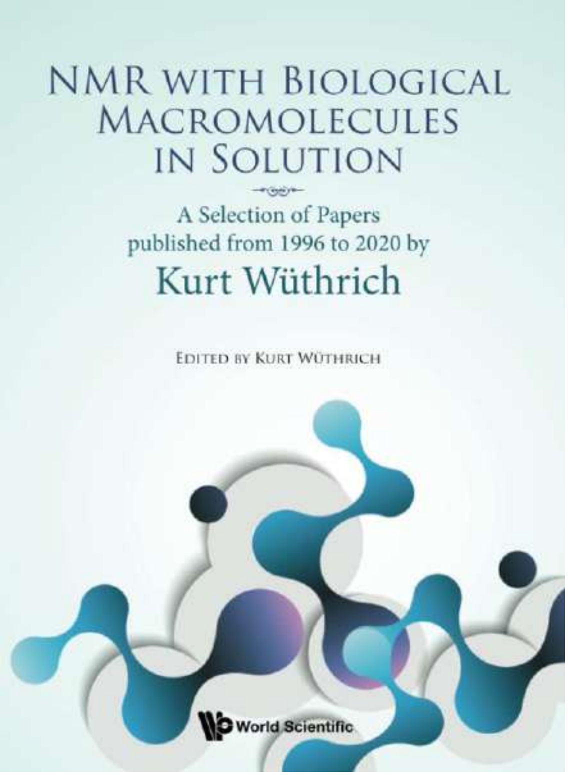
Prize share: 1/1

The Nobel Prize in Chemistry 1991 was awarded to Richard R. Ernst "for his contributions to the development of the methodology of high resolution nuclear magnetic resonance (NMR) spectroscopy."

https://www.nobelprize.org

A Brief History of NMR

- 1970's and 1980's: 3D structure of biological macromolecules in solution with NMR



The Nobel Prize in Chemistry 2002

Photo from the Nobel Foundation archive.
John B. Fenn
Prize share: 1/4

Photo from the Nobel Foundation archive.
Koichi Tanaka
Prize share: 1/4

Photo from the Nobel Foundation archive.
Kurt Wüthrich
Prize share: 1/2

The Nobel Prize in Chemistry 2002 was awarded "for the development of methods for identification and structure analyses of biological macromolecules" with one half jointly to John B. Fenn and Koichi Tanaka "for their development of soft desorption ionisation methods for mass spectrometric analyses of biological macromolecules" and the other half to Kurt Wüthrich "for his development of nuclear magnetic resonance spectroscopy for determining the three-dimensional structure of biological macromolecules in solution."

https://www.nobelprize.org

A Brief History of NMR

- 1970's: magnetic resonance imaging (MRI)

The Nobel Prize in Physiology or Medicine 2003

Photo from the Nobel Foundation archive.

Paul C. Lauterbur

Prize share: 1/2

Photo from the Nobel Foundation archive.

Sir Peter Mansfield

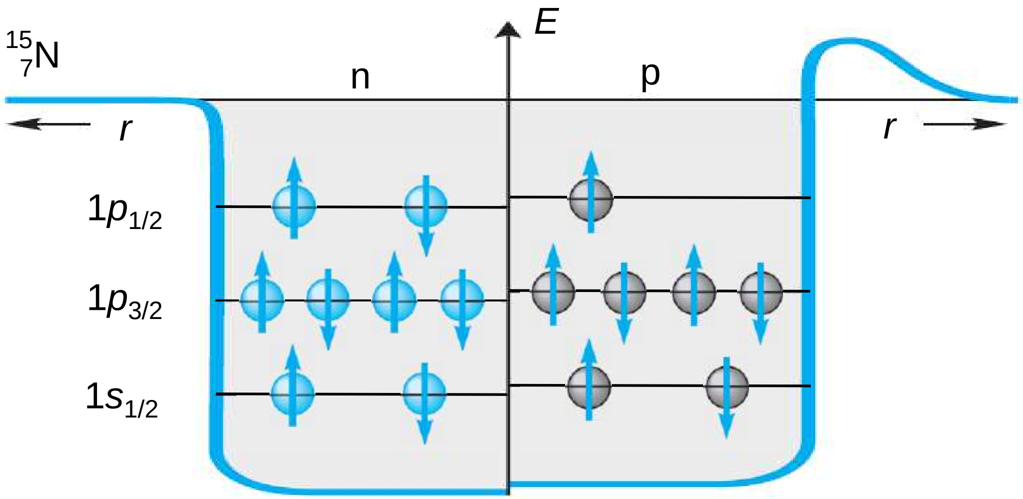
Prize share: 1/2

The Nobel Prize in Physiology or Medicine 2003 was awarded jointly to Paul C. Lauterbur and Sir Peter Mansfield "for their discoveries concerning magnetic resonance imaging."

https://www.nobelprize.org

Nuclear Magnetism

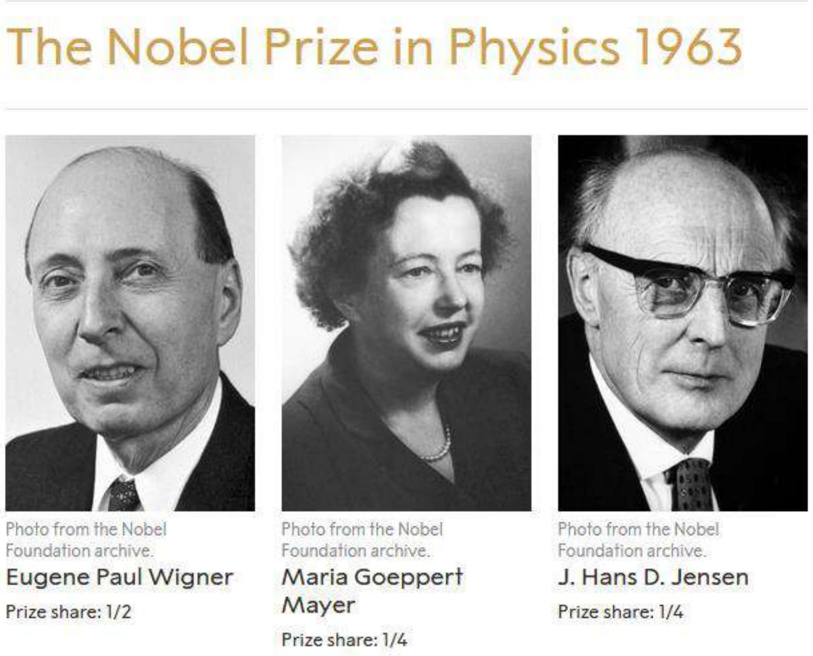
- Shell model: nuclear spin I



- Nuclear magnetic moment:

$$\vec{\mu} = g\mu_n \vec{I} = \hbar\gamma_n \vec{I}$$

$$\mu_n = \frac{e_0\hbar}{2m_p} = 5.05 \times 10^{-27}\ \mathrm{Am}^2$$

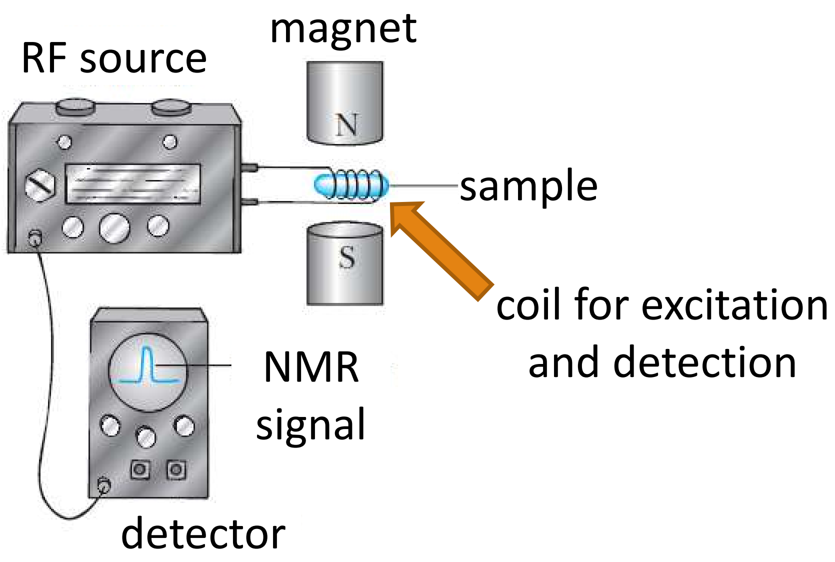


The Nobel Prize in Physics 1963 was divided, one half awarded to Eugene Paul Wigner "for his contributions to the theory of the atomic nucleus and the elementary particles, particularly through the discovery and application of fundamental symmetry principles", the other half jointly to Maria Goeppert Mayer and J. Hans D. Jensen "for their discoveries concerning nuclear shell structure."

https://www.nobelprize.org

NMR Apparatus

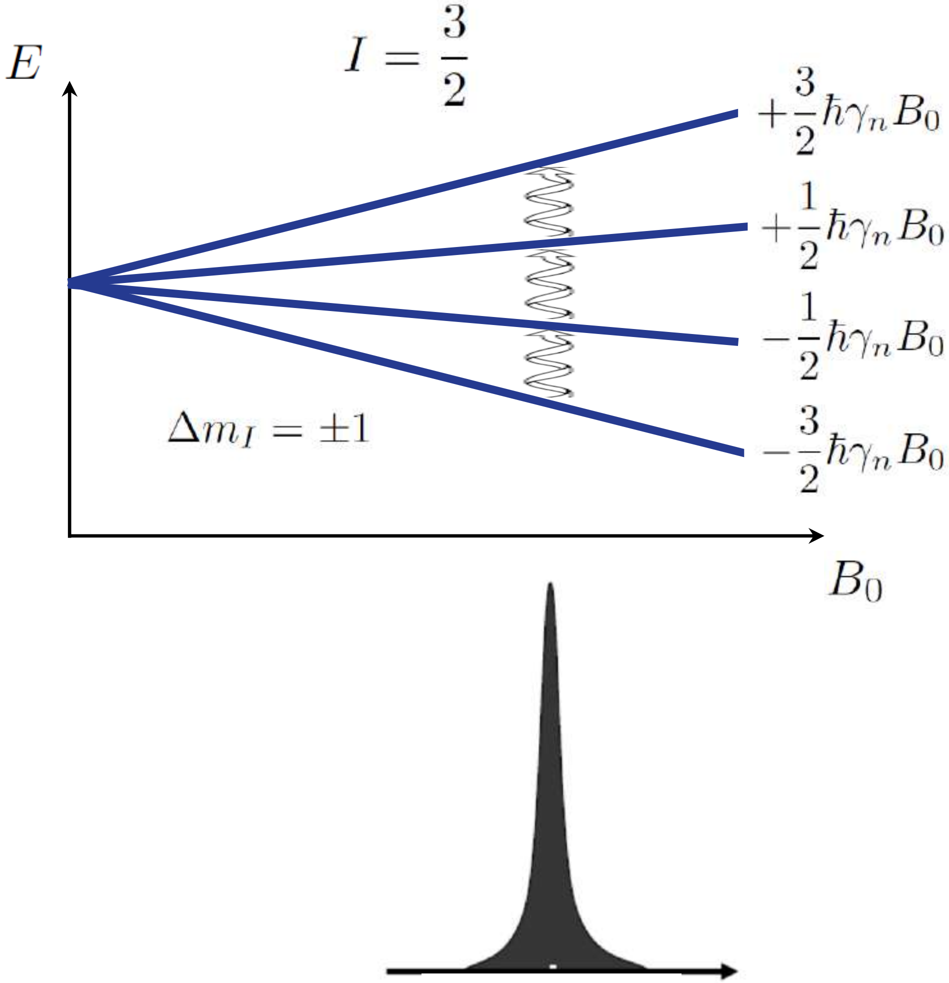
- magnet
- RF source
- detector



NMR Apparatus

- ❑ magnet
- ❑ RF source
- ❑ detector

Bruker NMR spectrometer

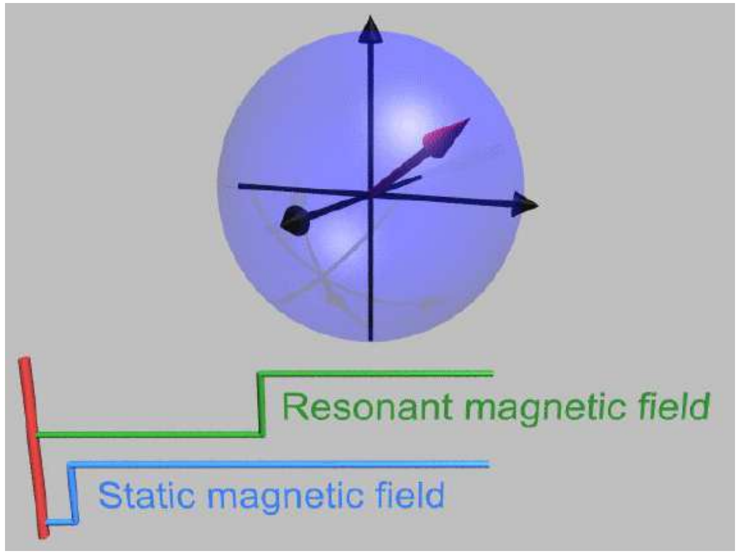


Larmor frequency: $\nu_L = \frac{\gamma_n}{2\pi} B_0$

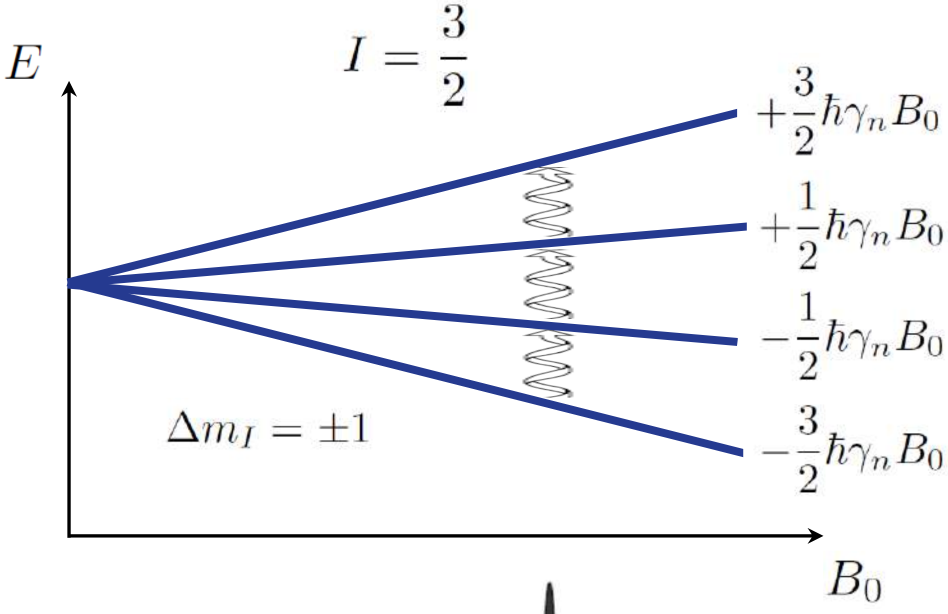
NMR Apparatus

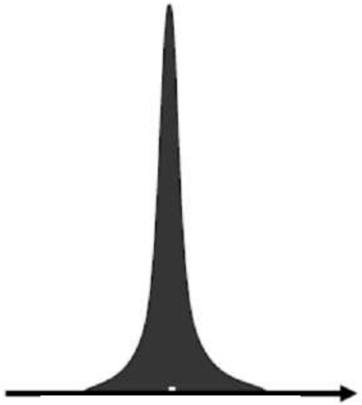
- magnet
- RF source
- detector

$$\frac{d\vec{\mu}}{dt} = \gamma_n \vec{\mu} \times \vec{B}$$



Wikimedia Commons

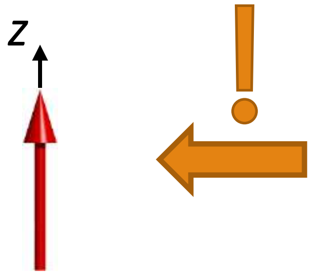




Larmor frequency: $\nu_L = \frac{\gamma_n}{2\pi} B_0$

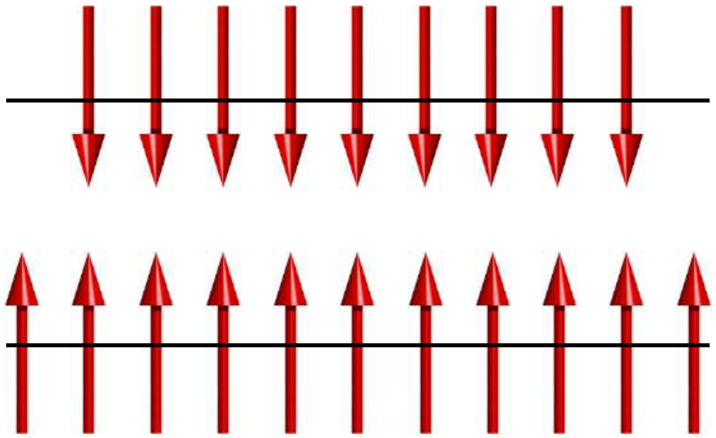
Nuclear Magnetization

- External field: $\vec{B}_0 \| z$



equilibrium magnetization at 1 K and 1 T

$$\frac{\hbar \gamma_n B_0}{k_B} \sim 100\,\mu\mathrm{K}$$

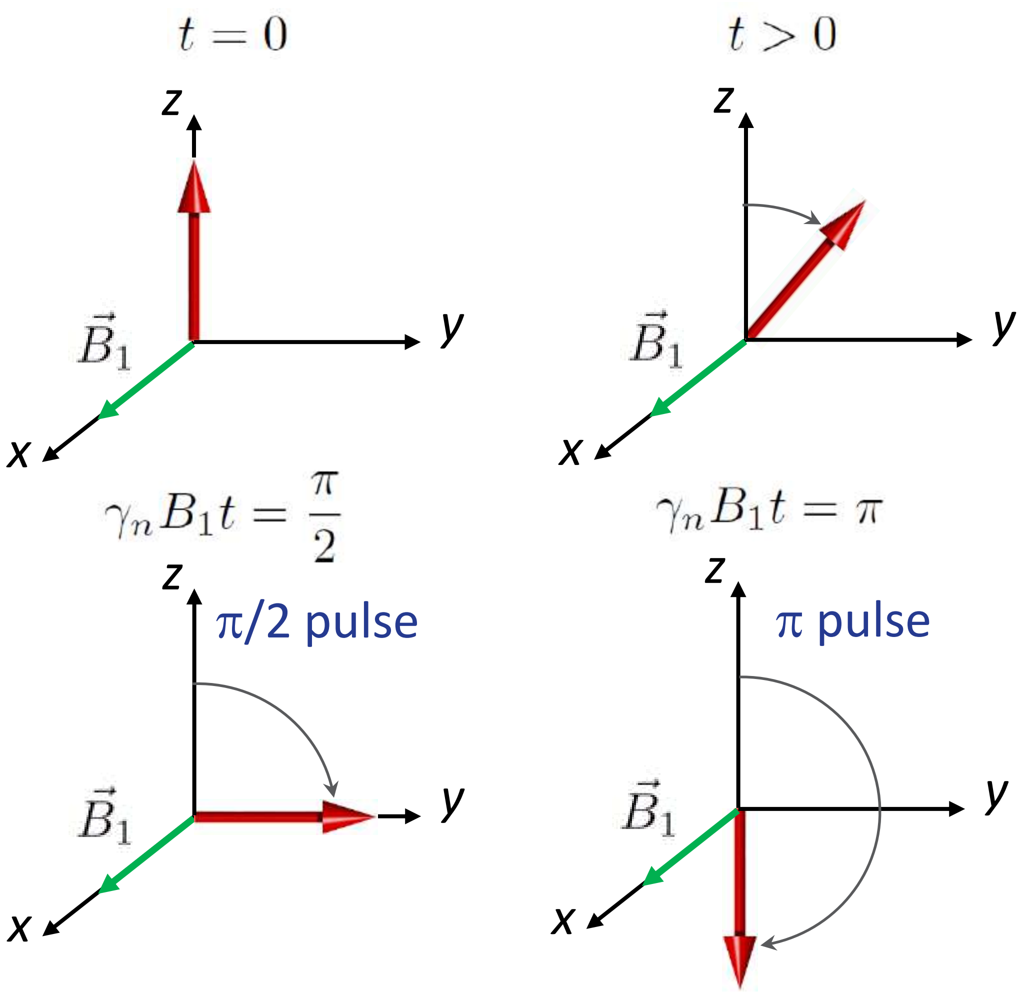


$$M_{mol} = \frac{N_A \mu^2}{3 k_B T} B_0 \sim 10^{-4} \mu N_A \sim 10^{-7}\,\mathrm{Am}^2$$

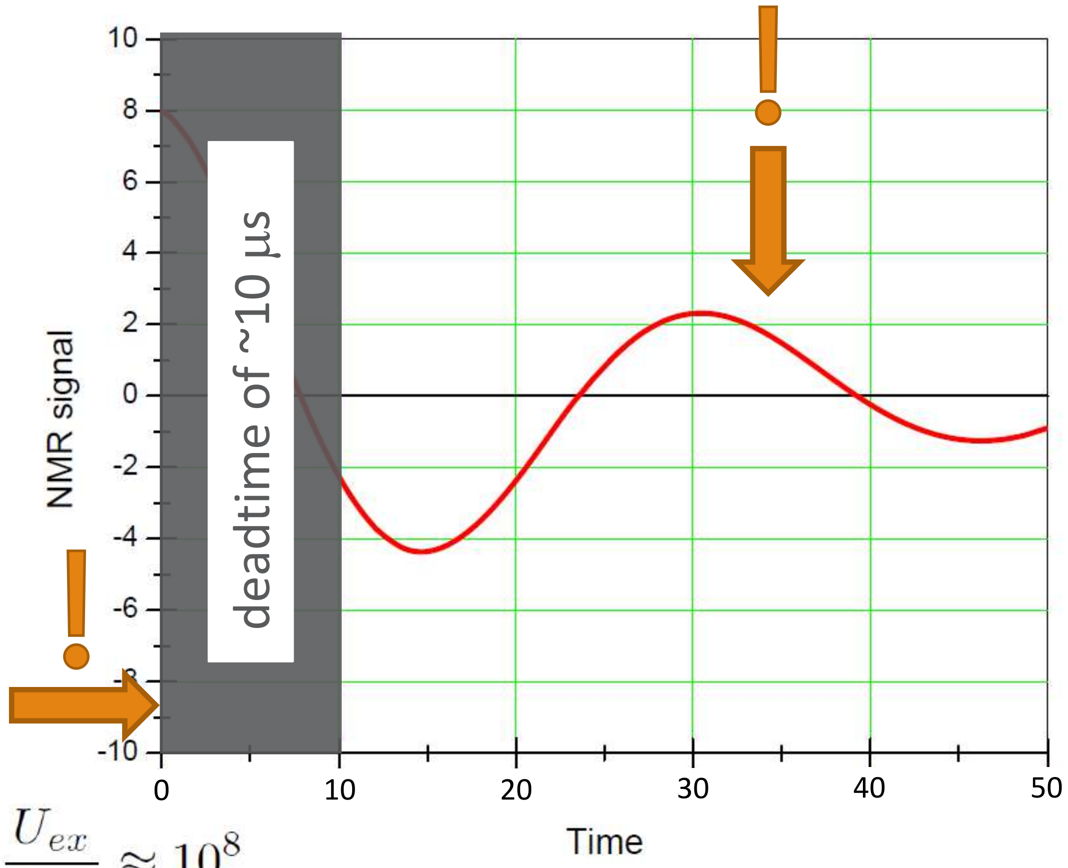
- Requirements:
  - high magnetic field (> 1 T)
  - (low temperature helps)

Pulsed NMR

- Pulsed RF field: $\vec{B}_1 \perp \vec{B}_0 \| z$



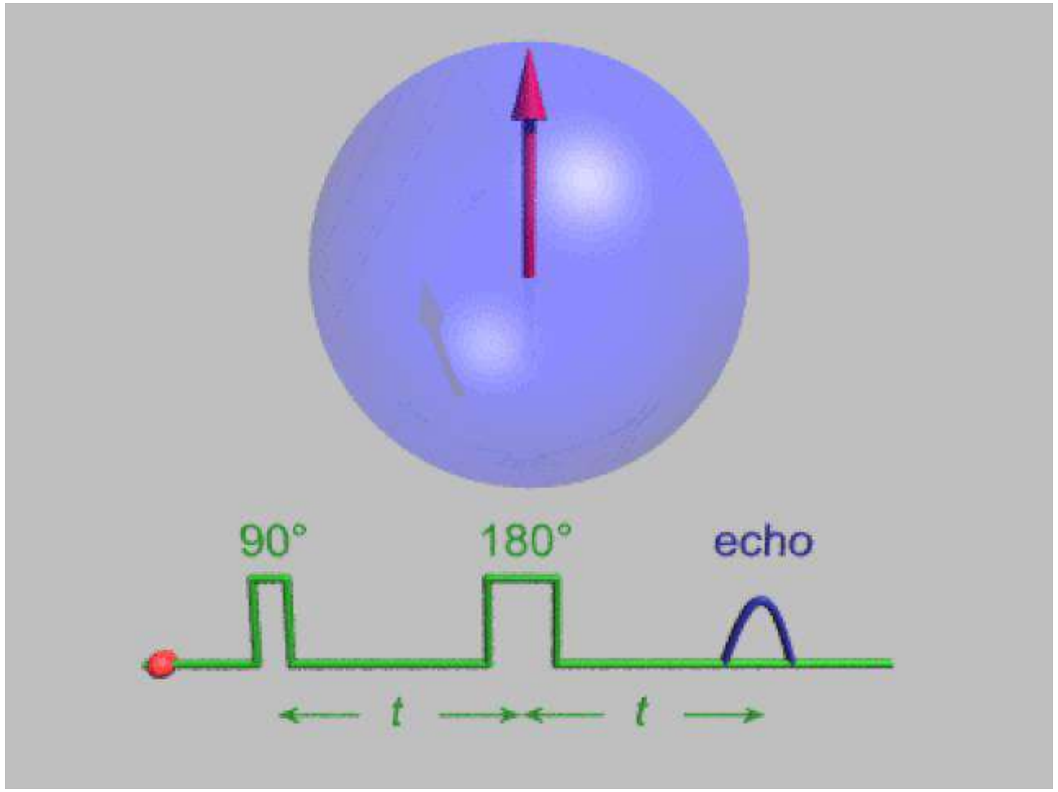
- FID after π/2 pulse:



$\frac{U_{ex}}{U_{det}} \approx 10^8$

Pulsed NMR

- Spin (Hahn) echo: $\pi/2 - \pi -$ ECHO



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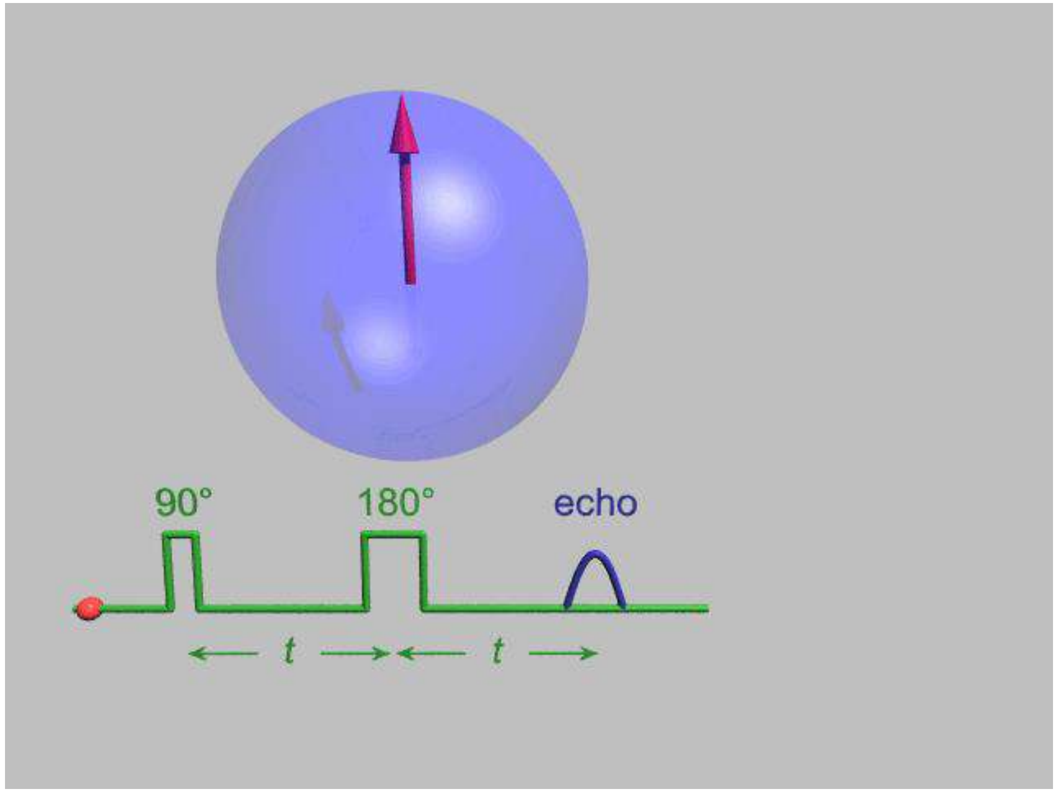
Nuclear Spin Relaxation

- Spin-spin relaxation: T_2 relaxation



Wikimedia Commons

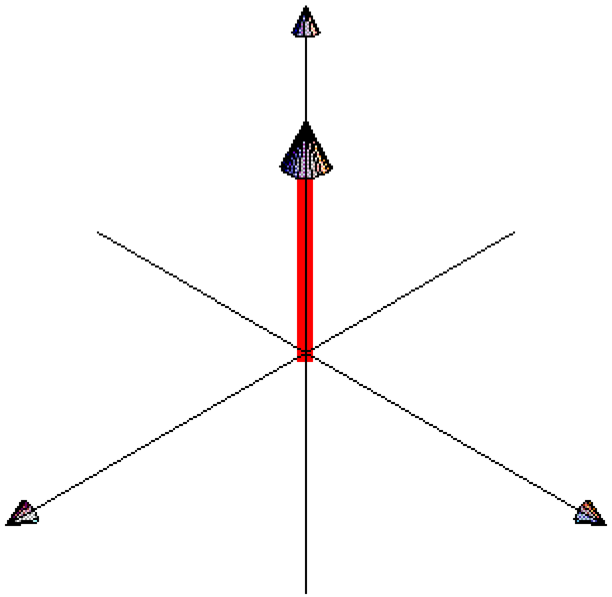
Bloch equations:

$$\frac{\mathrm{d}M_x}{\mathrm{d}t} = \gamma_n M_y B_0 - \frac{M_x}{T_2}$$

$$\frac{\mathrm{d}M_y}{\mathrm{d}t} = -\gamma_n M_x B_0 - \frac{M_y}{T_2}$$

Nuclear Spin Relaxation

❑ Spin-lattice relaxation: T_1 relaxation



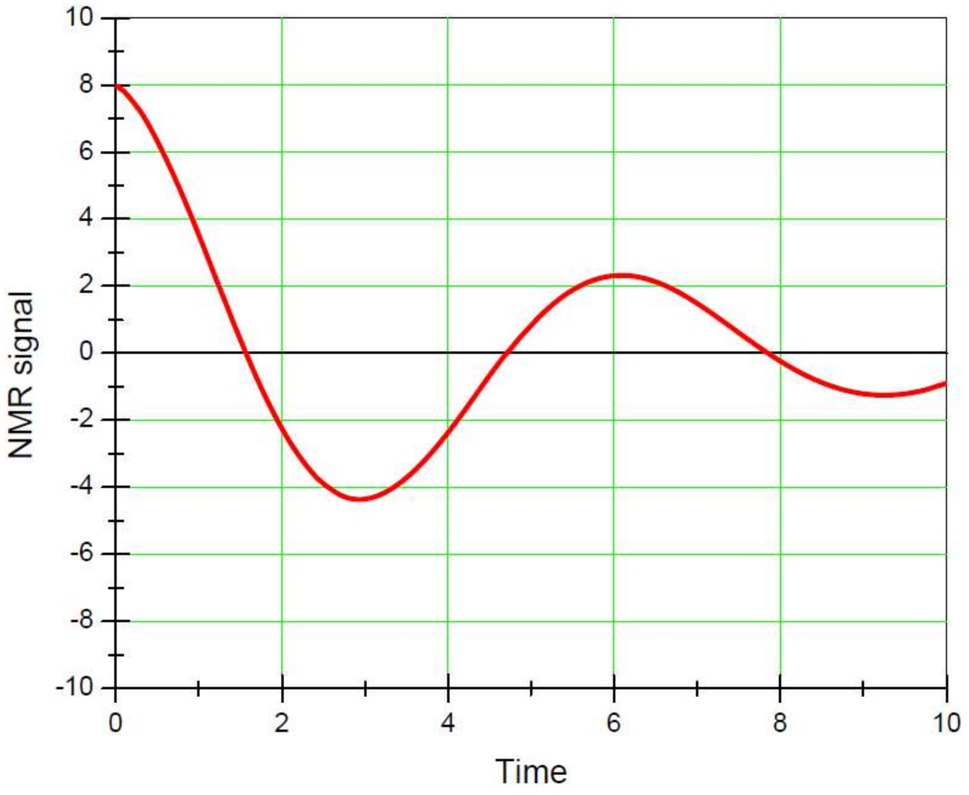
Bloch equations:

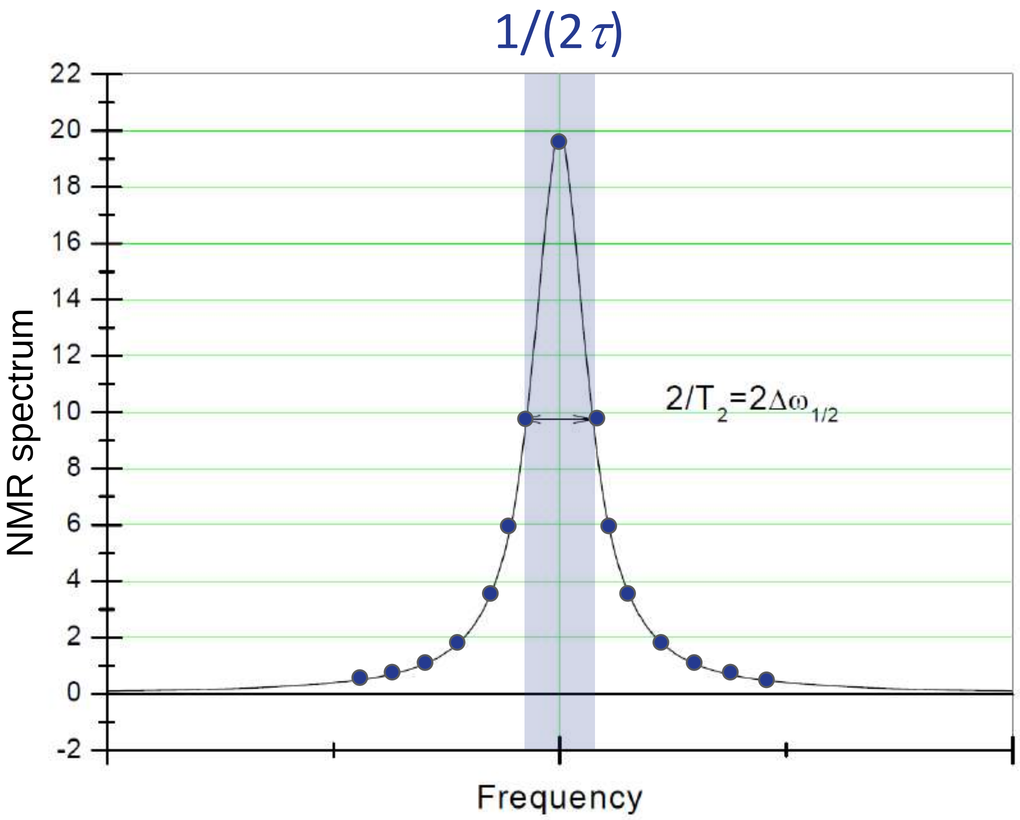
$$\frac{\mathrm{d}M_z}{\mathrm{d}t} = \frac{M_0 - M_z}{T_1}$$

https://gifimage.net

NMR spectrum

- Fourier transform: excitation width $1/(2\tau)$





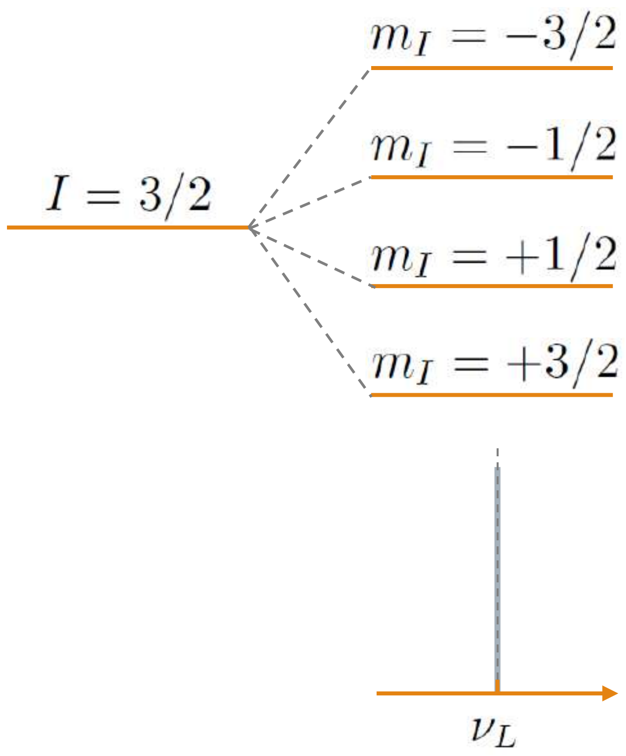
combining FTs

NMR Hamiltonian

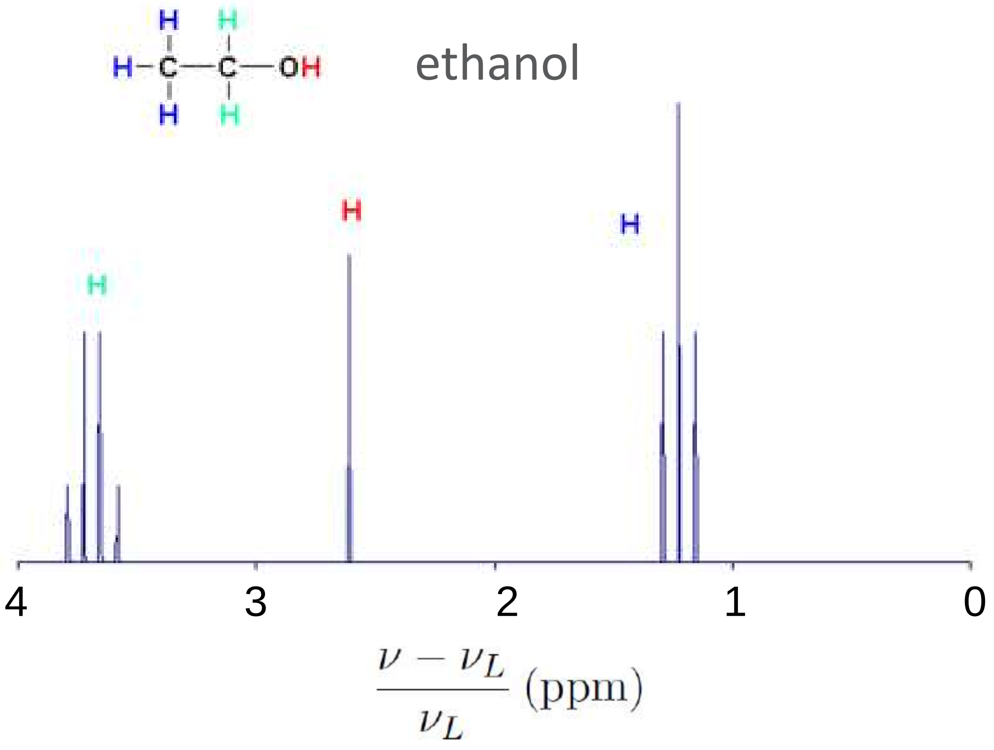
- The Hamiltonian:

$$\mathcal{H} = \mathcal{H}_{nZ} + \mathcal{H}_{nn} + \mathcal{H}_{ne} + \mathcal{H}_{EFG}$$

nuclear Zeeman interaction | nuclear-nuclear interaction | hyperfine coupling | quadrupole interaction



chemical shift:
electron
screening



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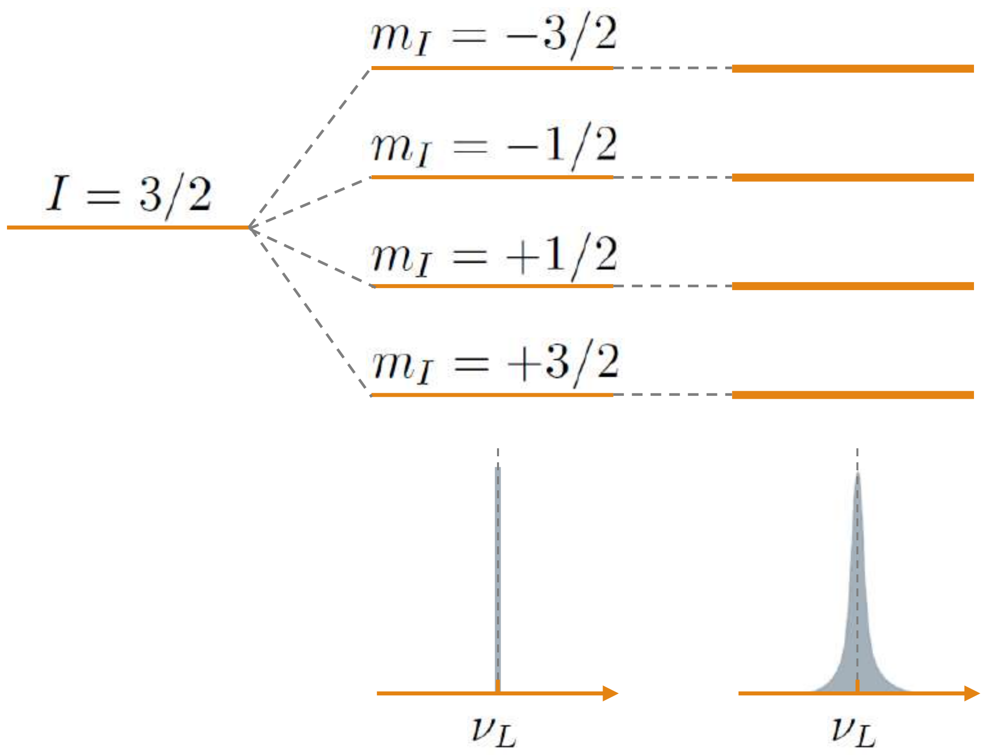

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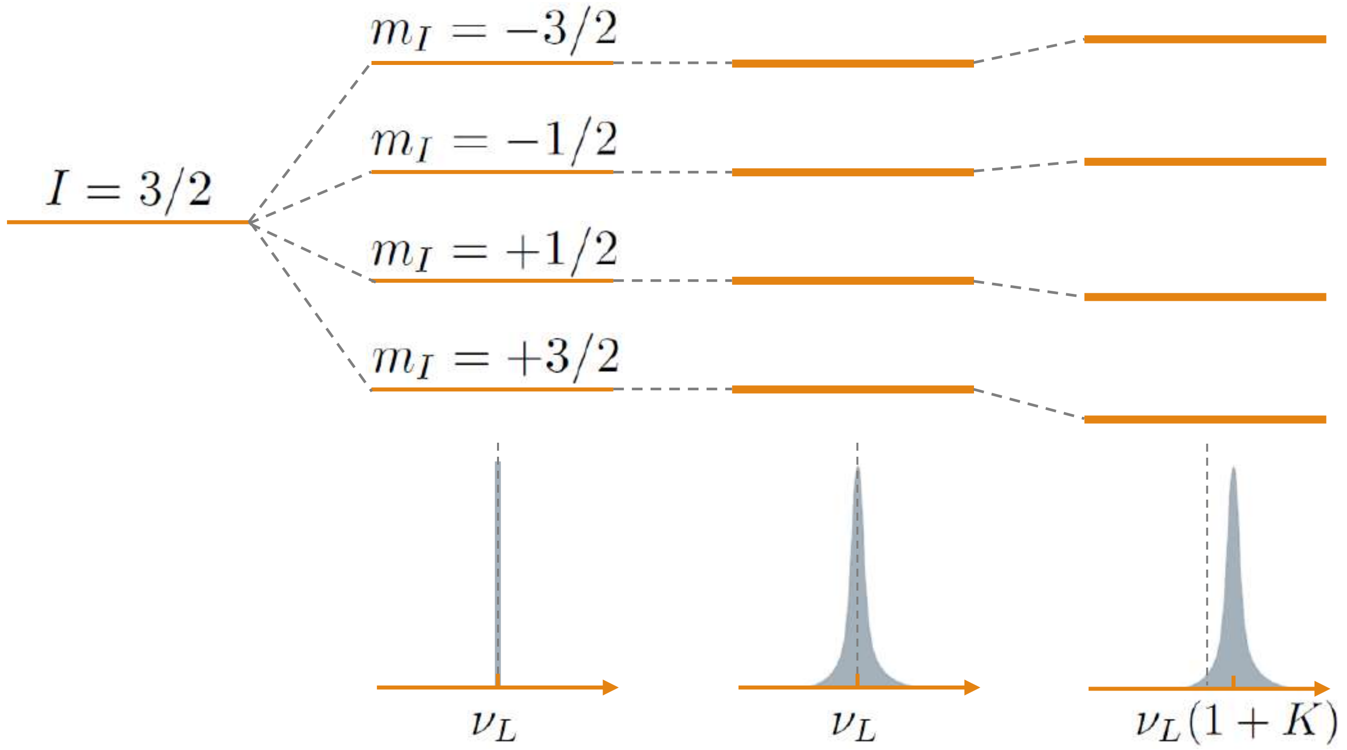

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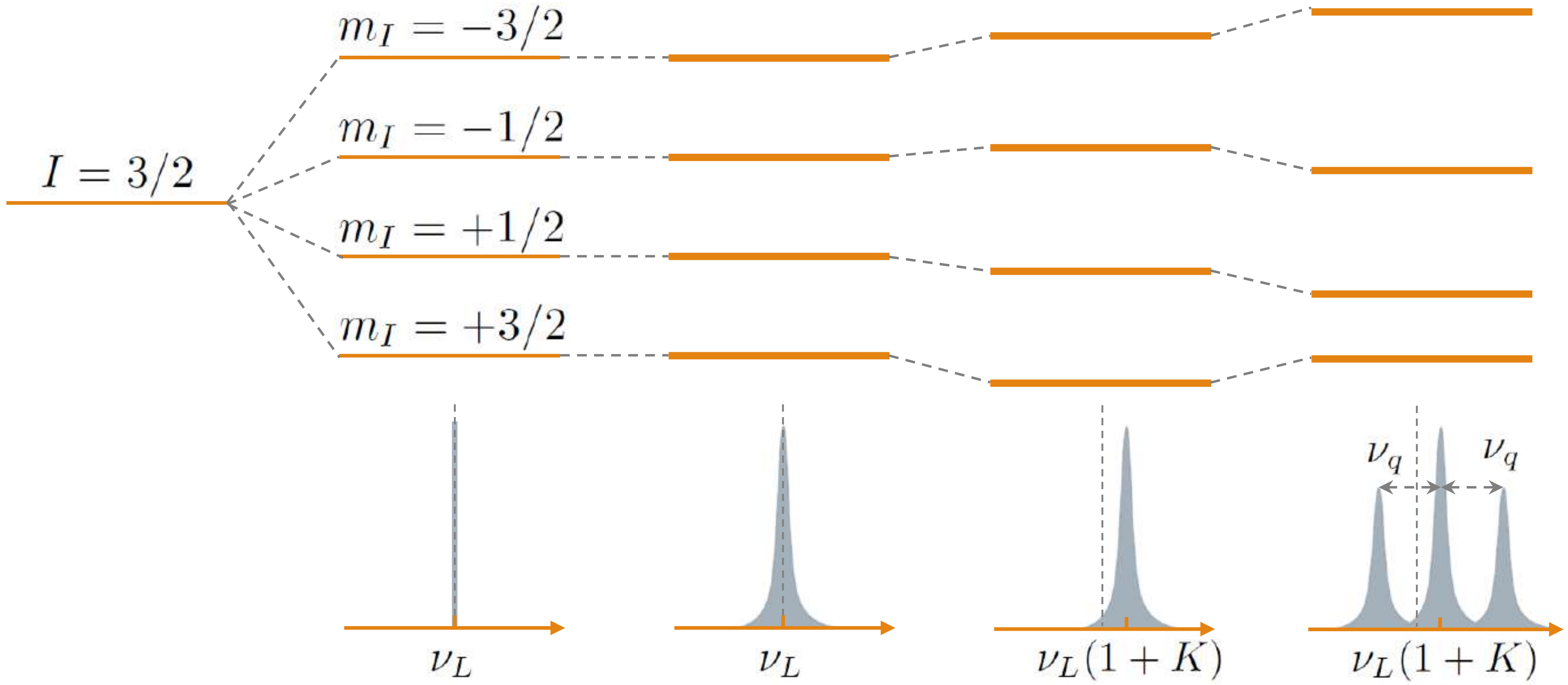

NMR Hamiltonian

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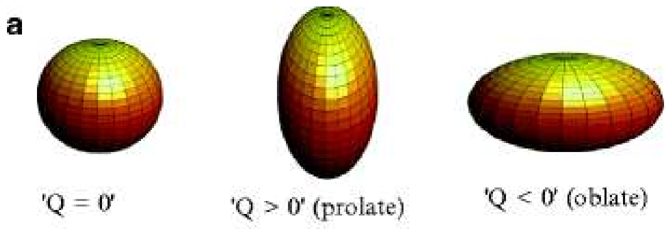
- Quadrupole interaction: *I* > 1/2



- nuclear quadrupole moment:

$$eQ_{\alpha\beta} = e \sum_{i \in \mathrm{protons}} \left(3x_i^\alpha x_i^\beta - \delta_{\alpha\beta} r_i^2 \right)$$

Fernandez, Probing Quadrupolar Nuclei by Solid-State NMR Spectroscopy: Recent Advances

NMR Hamiltonian

- The Hamiltonian:

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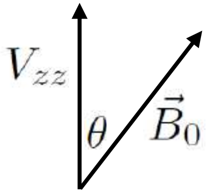

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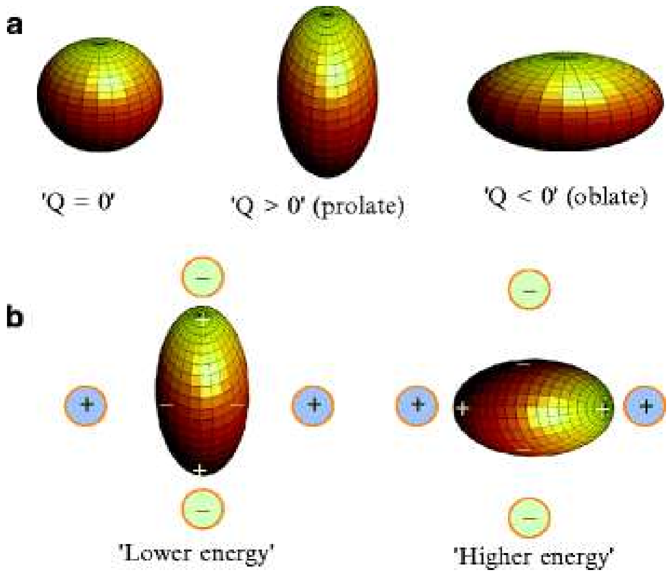


Fernandez, Probing Quadrupolar Nuclei by Solid-State NMR Spectroscopy: Recent Advances

- nuclear quadrupole moment:

$$eQ_{\alpha\beta} = e \sum_{i \in \text{protons}} \left(3x_i^\alpha x_i^\beta - \delta_{\alpha\beta} r_i^2\right)$$

- electric field gradient: $V_{\alpha\beta} = \frac{\partial^2 V}{\partial x^\alpha \partial x^\beta}$

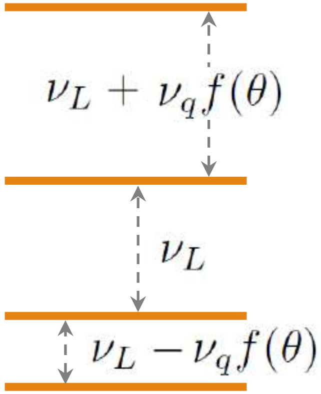
$$V(\vec{r}) = V(0) + \frac{1}{2} \sum_{\alpha,\beta=x,y,z} x^\alpha x^\beta \frac{\partial^2 V}{\partial x^\alpha \partial x^\beta}$$

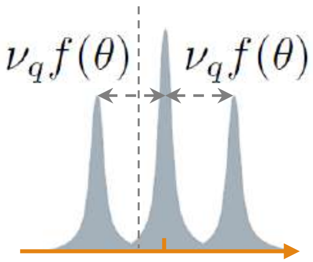
- Hamiltonian:

$$\mathcal{H}_{EFG} = \frac{e^2 qQ}{4I(2I-1)} \left[3I_z^2 - I(I+1) + \frac{\eta}{2}(I_+^2 + I_-^2)\right]$$

$$eq = V_{zz} \qquad \eta = \frac{V_{yy} - V_{xx}}{V_{zz}} \qquad V_{zz} \geq V_{yy} \geq V_{xx}$$

$$\eta = 0 \qquad \Delta E^{(1)} = \nu_q \left(3\cos^2\theta - 1\right) \left[3m_I^2 - I(I+1)\right]$$



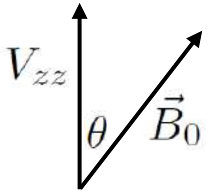


single crystal

NMR Hamiltonian

- ❑ The Hamiltonian:

$$\mathcal{H} = \mathcal{H}_{nZ} + \mathcal{H}_{nn} + \mathcal{H}_{ne} + \mathcal{H}_{EFG}$$



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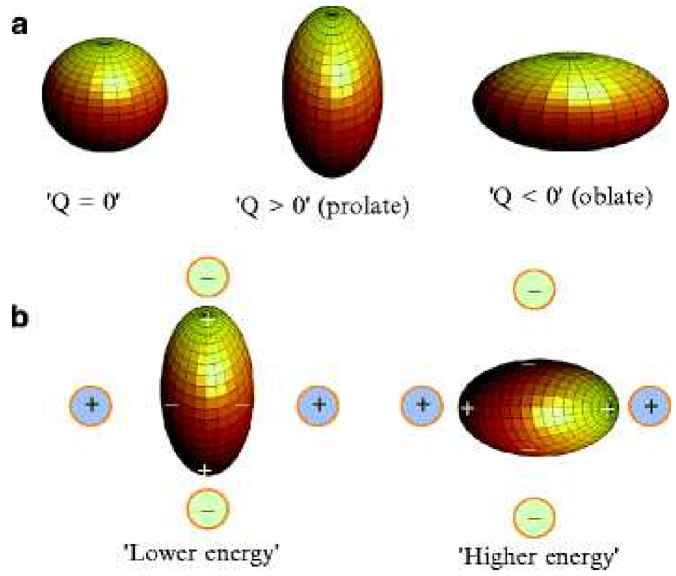

Fernandez, Probing Quadrupolar Nuclei by Solid-State NMR Spectroscopy: Recent Advances

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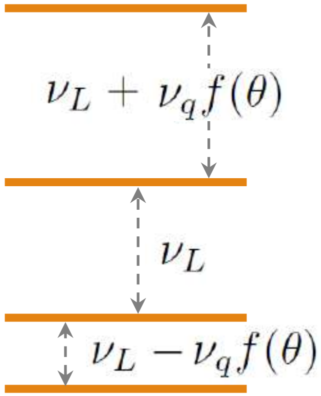
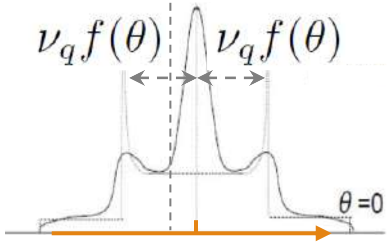




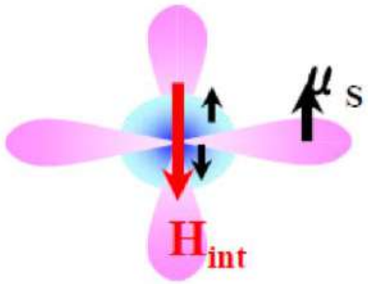
powder

andrej.zorko@ijs.si

NMR: the Probe of Static Magnetism

- Nucleus-electron (hyperfine) interaction:
  - on-site hyperfine
  - transferred hyperfine
  - dipolar interaction
  - contact interaction (metals)

$$\mathcal{H}_{ne}^{i} = -\hbar\gamma_n \vec{I}_i \cdot \sum_j \underline{A}_{ij} \cdot \vec{S}_j = -\hbar\gamma_n \vec{I}_i \cdot \vec{B}_i^{loc}$$



- LRO: internal field (order parameter)
- Fast spin fluctuations: $B_{loc} = \left\langle \vec{B}_i^{loc} \right\rangle_z = \sum_j \underline{A}_{ij} \cdot \left\langle \vec{S}_j \right\rangle_z$

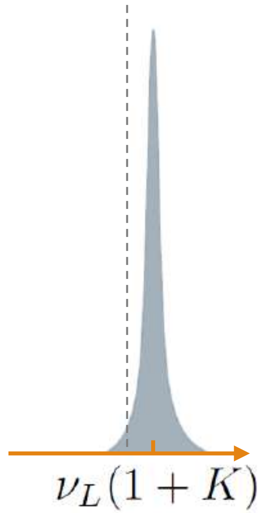
$$K = \frac{B_{loc} - B_0}{B_0} = \frac{\nu - \nu_L}{\nu_L}$$

hyperfine shift

$$B_{loc} \ll B_0 \quad \Rightarrow \quad \nu = \gamma_n (B_0 + B_{loc}) = \nu_L (1 + K)$$

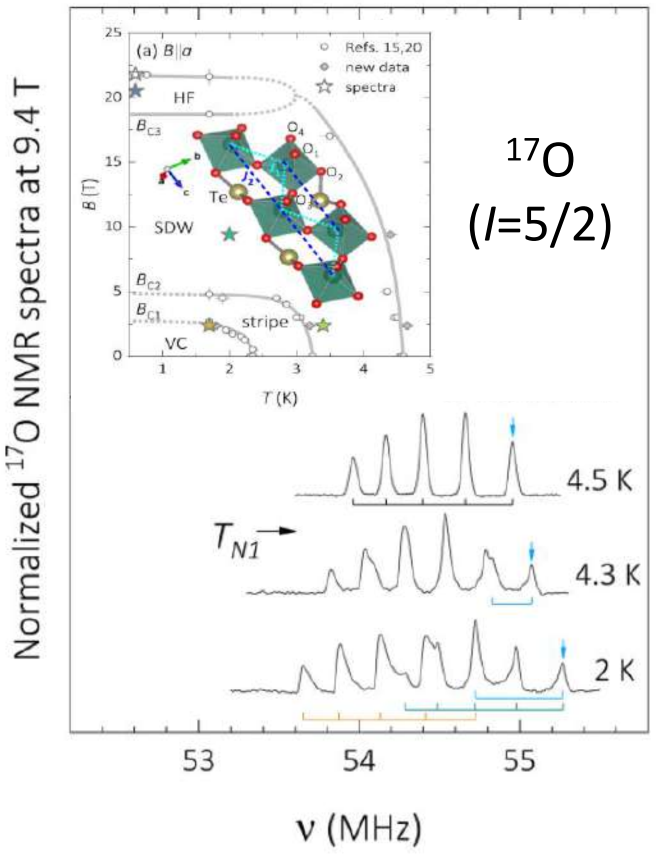
- Paramagnet: uniform static susceptibility $\chi(q=0, \omega=0) = \mu_0 \frac{N g \mu_B \left\langle \vec{S}_j \right\rangle_z}{V B_0}$

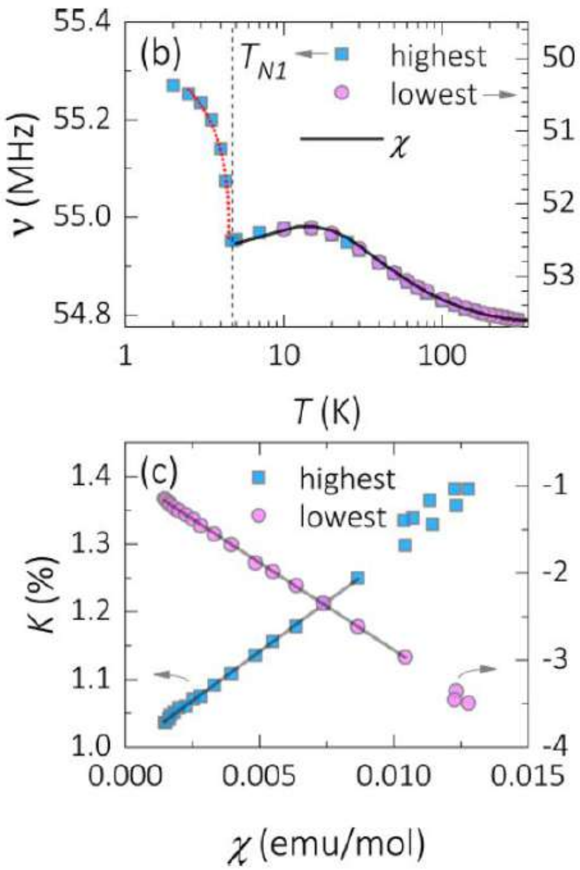
$$K = \sum_j \tilde{A}_{ij} \chi(q=0, \omega=0)$$



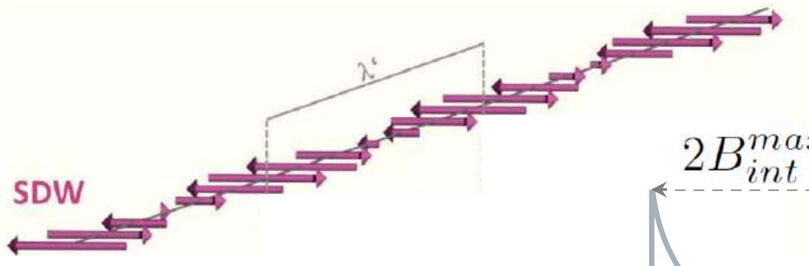
NMR: the Probe of Static Magnetism

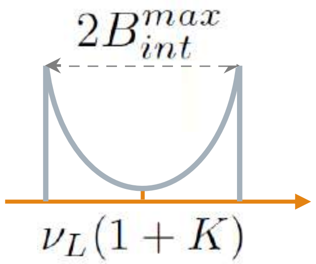
- Frustrated zig-zag spin chain: β-$TeVO_4$





- $T < T_{N1}$: line splitting + field distribution





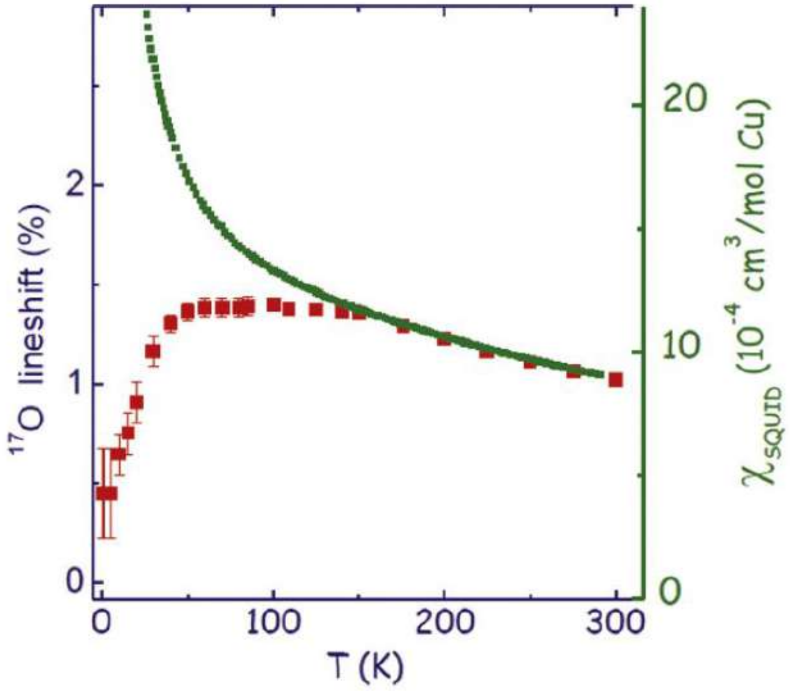
- $T > T_{N1}$: $K \propto \chi$

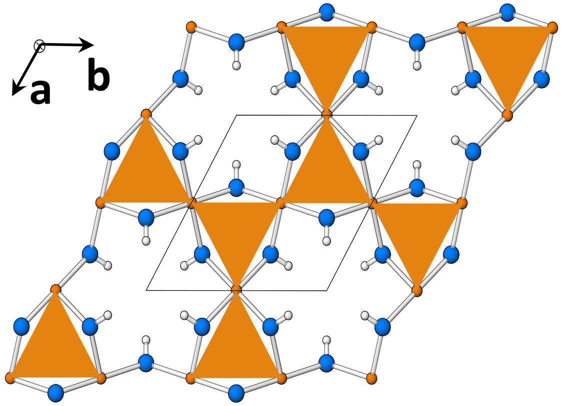
Clogston-Jaccarino plot

Pregelj *et al*., Phys. Rev. B **105**, 035145 (2022)

NMR: the Probe of Static Magnetism

❑ Intrinsic spin susceptibility in a QSL: kagome AFM $ZnCu_3(OH)_6Cl_2$





- **bulk susceptibility:** dominated by impurities
- **local susceptibility:** maximum due to spin correlations

Olariu *et al.*, Phys. Rev. Lett. **100**, 087202 (2008)

NMR: the Probe of Static Magnetism

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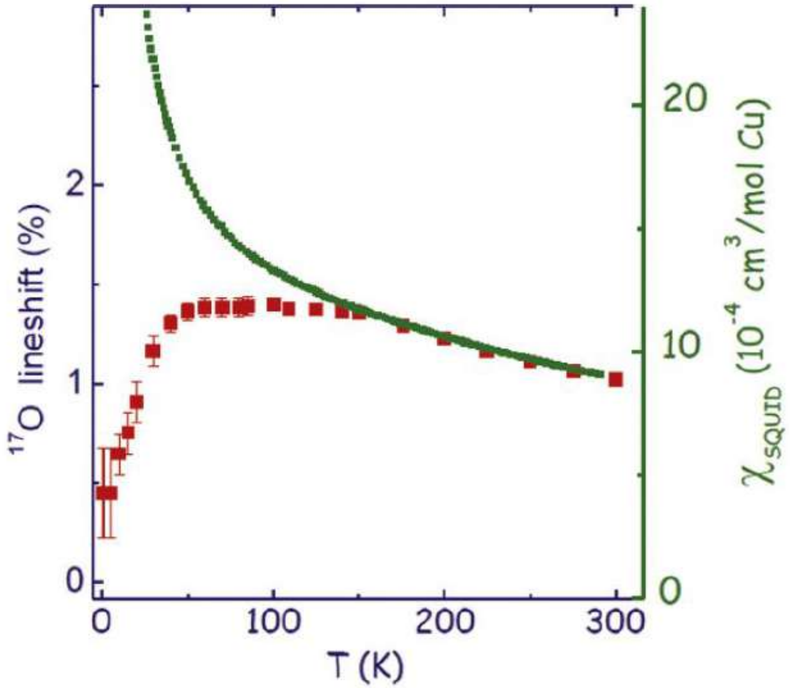
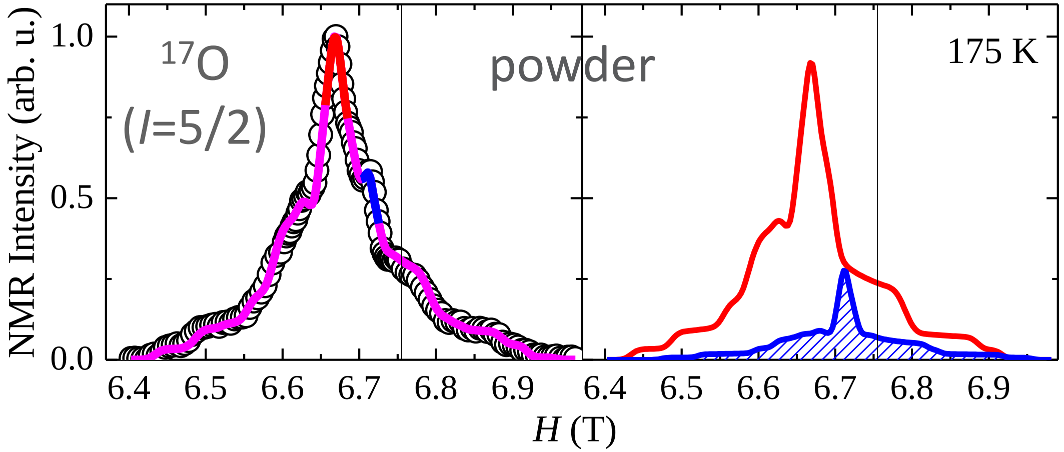




- bulk susceptibility: dominated by impurities
- local susceptibility: maximum due to spin correlations

Olariu *et al.*, Phys. Rev. Lett. **100**, 087202 (2008)

NMR: the Probe of Static Magnetism

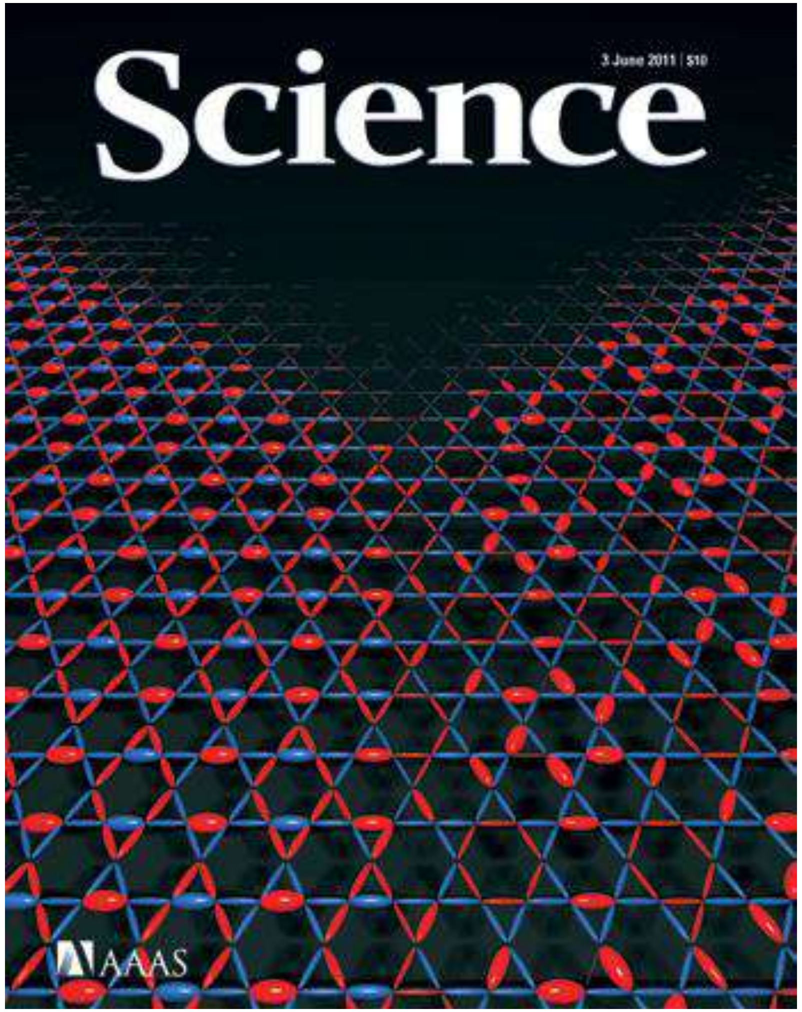
- The nature of the GS:

gapped

topological QSL

$$c_v \propto \mathrm{e}^{-\Delta/T}$$

$$\chi \propto \mathrm{e}^{-\Delta/T}$$



https://www.science.org

gapless

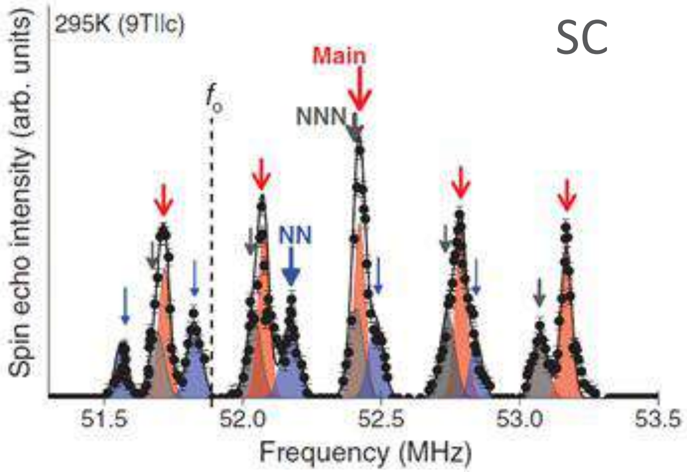
algebraic Dirac QSL

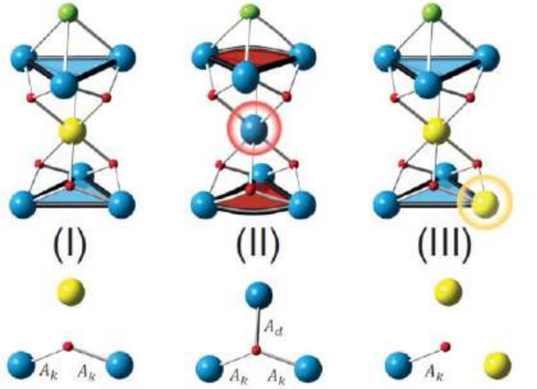
$$c_v \propto T^2$$

$$\chi \propto T$$

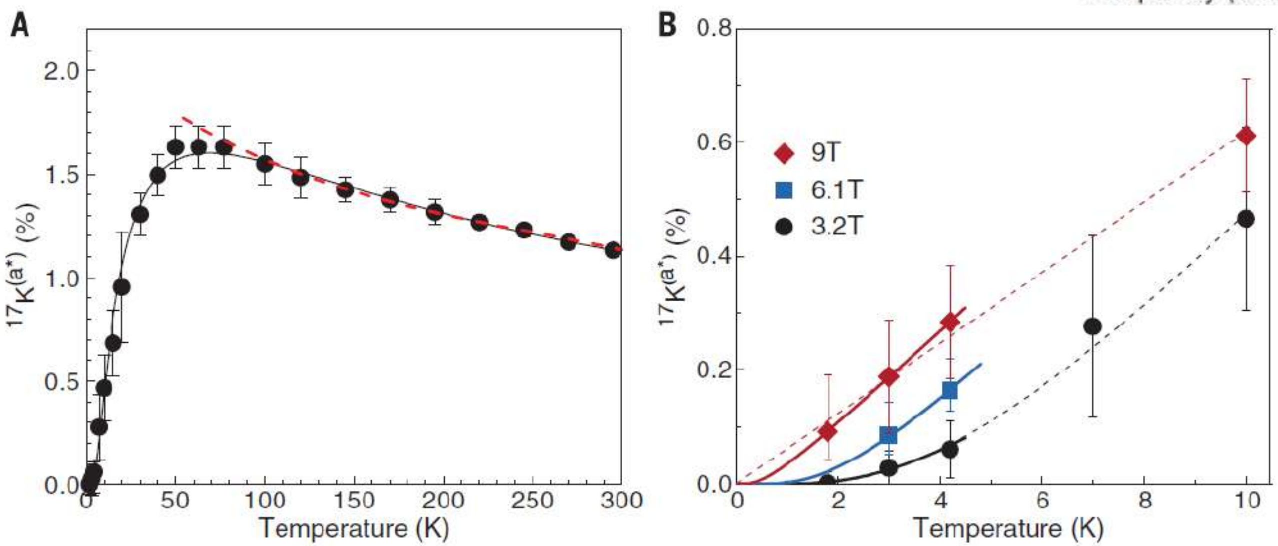
NMR: the Probe of Static Magnetism

- The nature of the GS: the problem of defects





gapped



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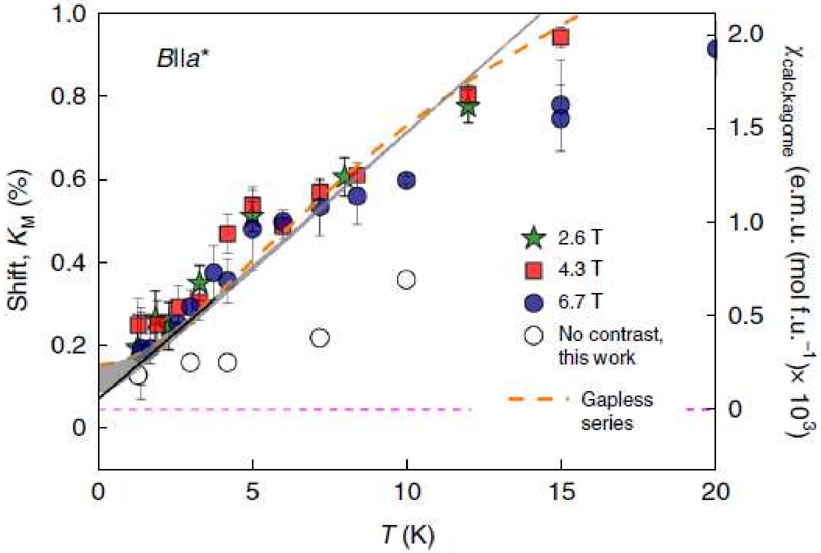
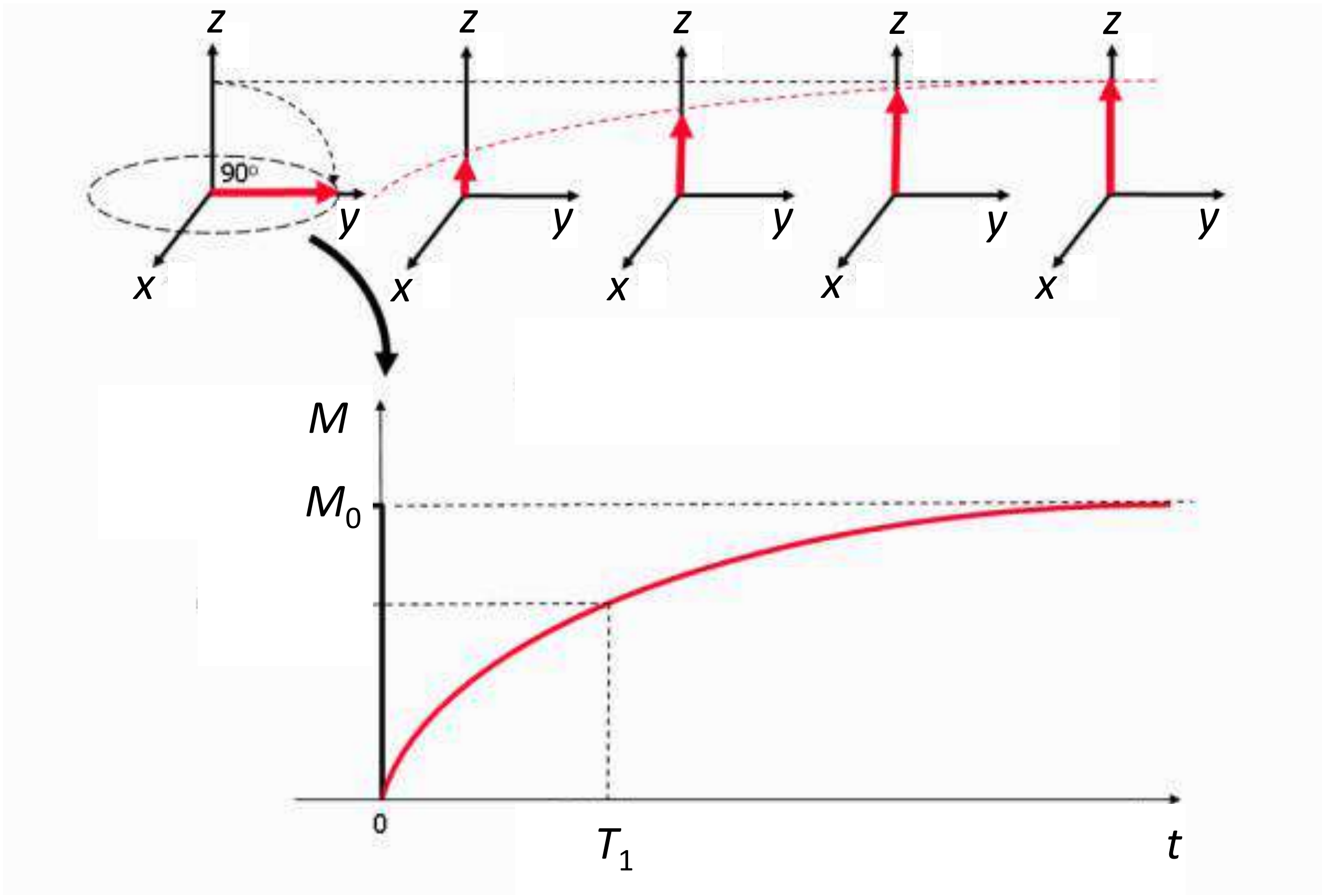


Fu *et al.*, Science **350**, 655 (2015)

Khuntia et al., Nat. Phys. **16**, 469 (2020)

NMR: the Probe of Spin Fluctuations

❑ Fluctuations of local fields at frequency ω induce transitions between Zeeman-split levels – T_1 relaxation:



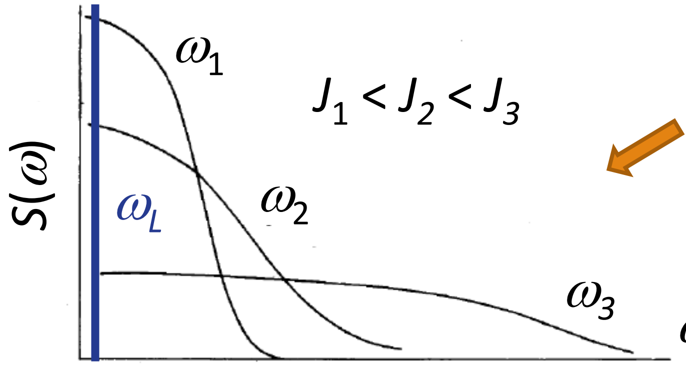
➢ exponential recovery towards equilibrium

➢ Fermi golden rule: $B_{loc}(t) \ll B_0$

$$\frac{1}{T_1} = \frac{\gamma_n^2}{2} \int_{-\infty}^{\infty} \langle B_{loc}^+(t) B_{loc}^-(0) \rangle \, e^{-i\omega_L t} dt$$

❖ transverse fluctuations

❖ spectral density at the Larmor frequency



sum rule

NMR: the Probe of Spin Fluctuations

- Fluctuations of local fields at frequency ω induce transitions between Zeeman-split levels – T_1 relaxation:

➢ reciprocal space: $\vec{S}(\vec{q},t) = \frac{1}{\sqrt{N}} \sum_j e^{i\vec{q}\cdot\vec{r}_j} \vec{S_j}(t)$

$$\frac{1}{T_1} = \frac{\gamma_n^2}{2}\frac{1}{N}\sum_{\vec{q},\alpha=x,y,z}\left[|A_{\vec{q}}|^2 S_{\alpha\alpha}(\vec{q},\omega_L)\right]_\perp$$

$$S_{\alpha\beta}(\vec{q},\omega_L) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\left\langle B^\alpha_{-\vec{q}}(t) B^\beta_{\vec{q}}(0)\right\rangle e^{-i\omega_L t} dt$$

❖ q-integrated DSF over 1BC

❖ form factor: $|A_{\vec{q}}|^2$ $\quad A_{\vec{q}} = \sum_j A_j e^{i\vec{q}\cdot\vec{r}_j}$ (scalar)

➢ imaginary dynamical spin susceptibility (FD theorem): $k_B T \gg \hbar\omega_L$

$$\frac{1}{T_1} = \frac{\gamma_n^2}{2}\frac{k_B T}{\hbar}\frac{1}{N}\sum_{\vec{q},\alpha=x,y,z}\left[|A_{\vec{q}}|^2 \frac{\chi''_{\alpha\alpha}(\vec{q},\omega_L)}{\omega_L}\right]_\perp$$

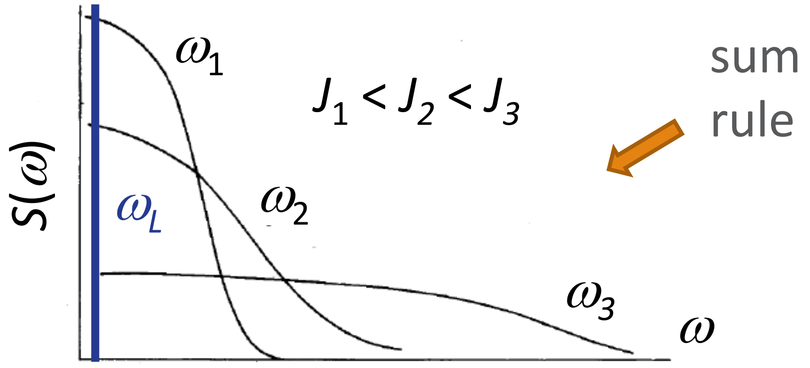
➢ exponential recovery towards equilibrium

➢ Fermi golden rule: $B_{loc}(t) \ll B_0$

$$\frac{1}{T_1} = \frac{\gamma_n^2}{2}\int_{-\infty}^{\infty}\left\langle B^+_{loc}(t) B^-_{loc}(0)\right\rangle e^{-i\omega_L t} dt$$

❖ transverse fluctuations

❖ spectral density at the Larmor frequency



NMR: the Probe of Spin Fluctuations

- Redfield formula (BPP): exponentially decaying local-field correlations

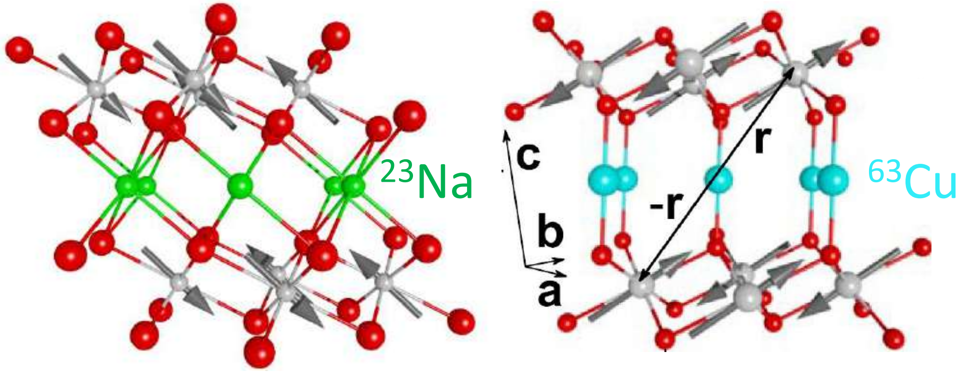
$$\langle B_{loc}^{+}(t)B_{loc}^{-}(0)\rangle = \Delta^2 \mathrm{e}^{-\nu t}$$

$$\frac{1}{T_1} = \frac{\gamma^2\Delta^2\nu}{\nu^2+\gamma^2 B_0^2}$$

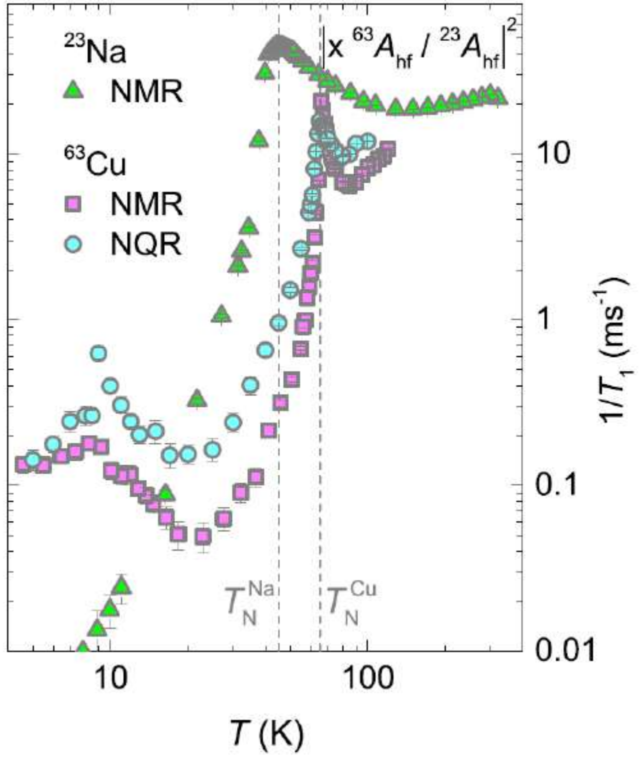
  - critical slowing down of spin fluctuations: $T > T_N$
  - phase transition: drastic change of excitations
  - filtering by the form factor:

$$A_{\vec{q}} = \sum_j A_j \mathrm{e}^{i\vec{q}\cdot\vec{r}_j}$$

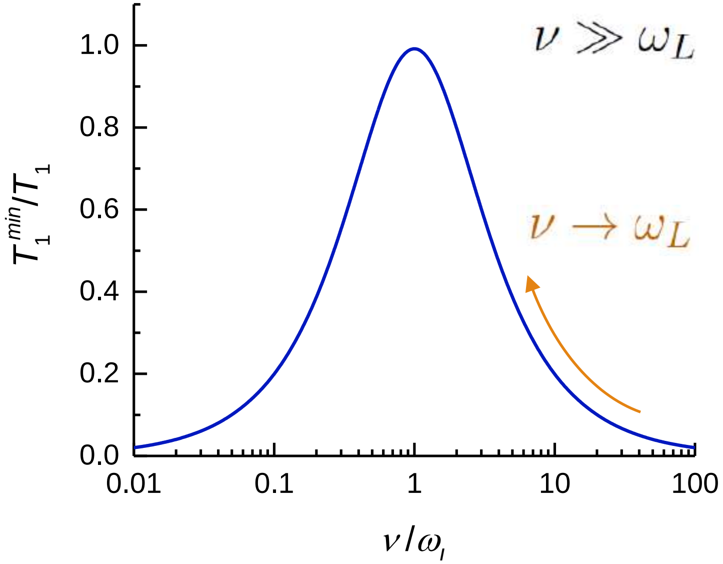
$A_{\vec{q}_{AFM}} = 0$ $\qquad$ $A_{\vec{q}_{AFM}} \neq 0$



$NaMnO_2$ & $CuMnO_2$:
triangular AFM

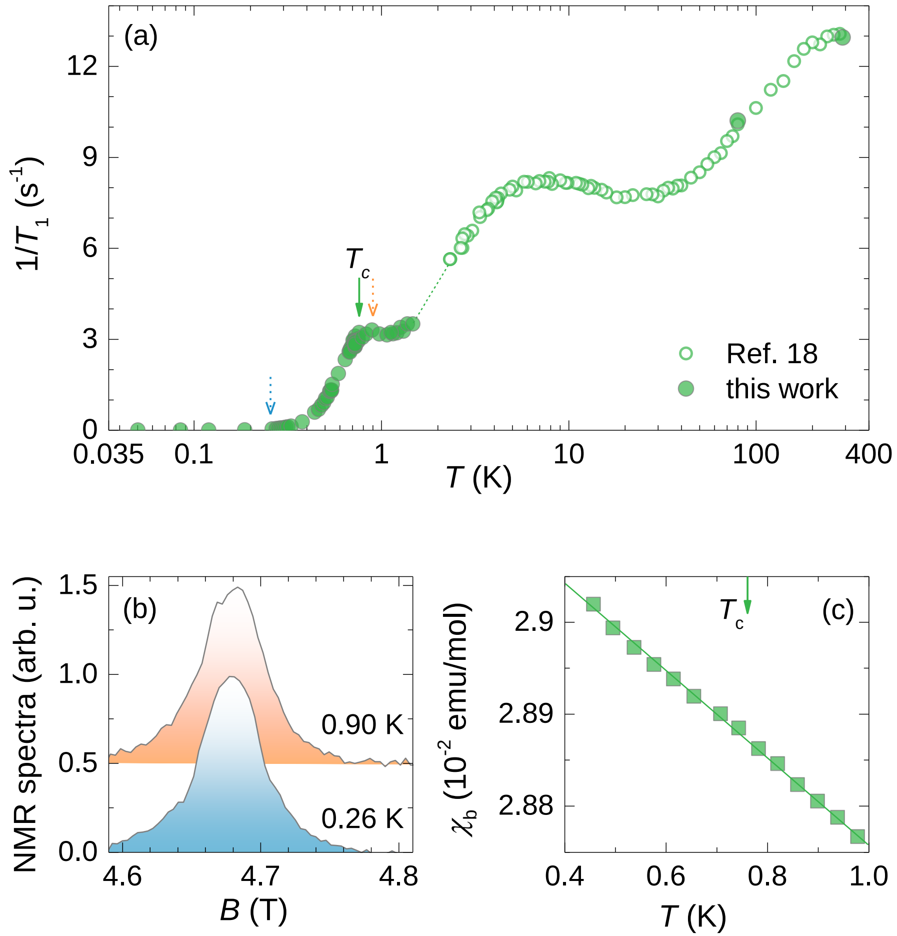


Zorko *et al*., Sci. Rep. **5**, 9272 (2015)



NMR: the Probe of Spin Fluctuations

❑ Zn-brochantite: distorted kagome-lattice AFM with a spinon-Fermi-surface QSL GS

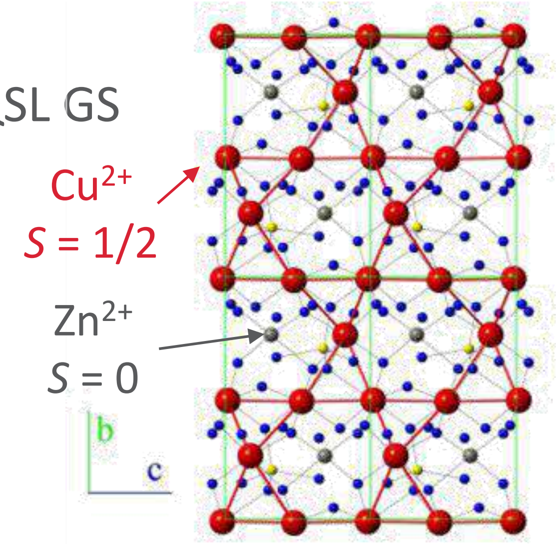


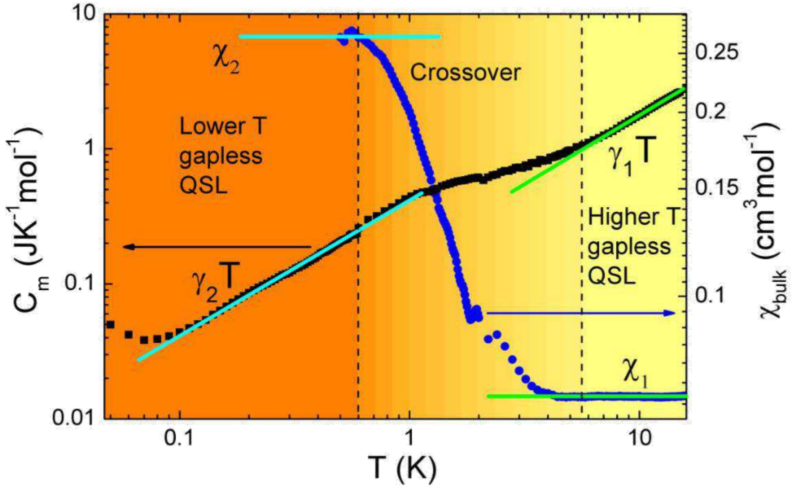
Gomilšek *et al.*, Phys. Rev. Lett. 119, 137205 (2017)

➢ NO magnetic order at T_c = 0.76 K
- ❖ no divergence in $1/T_1$
- ❖ no NMR broadening
- ❖ no thermodynamic anomaly

⬇

- ❖ QSL state at $T < T_c$
- ❖ fundamental modification of the excitation spectrum

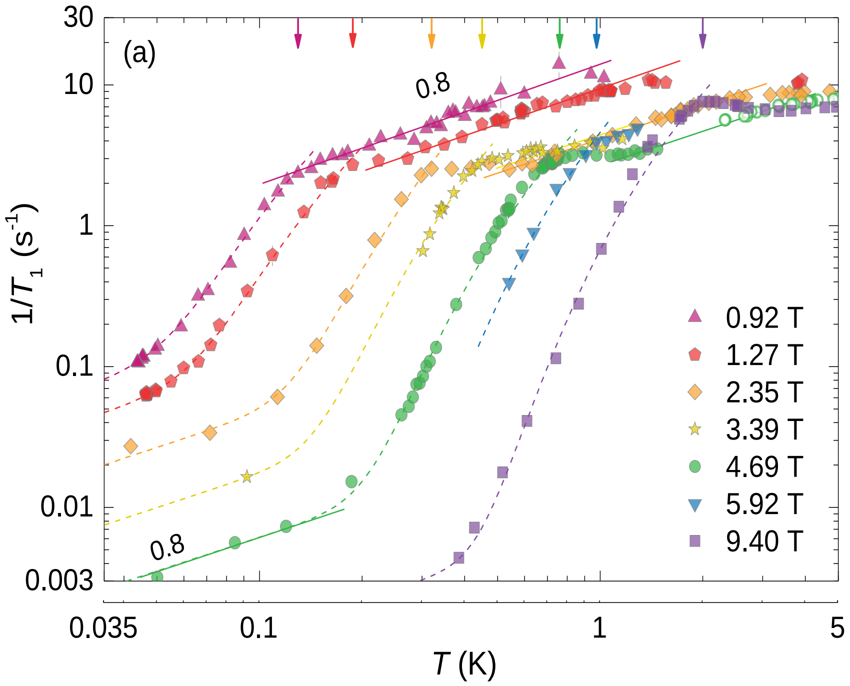




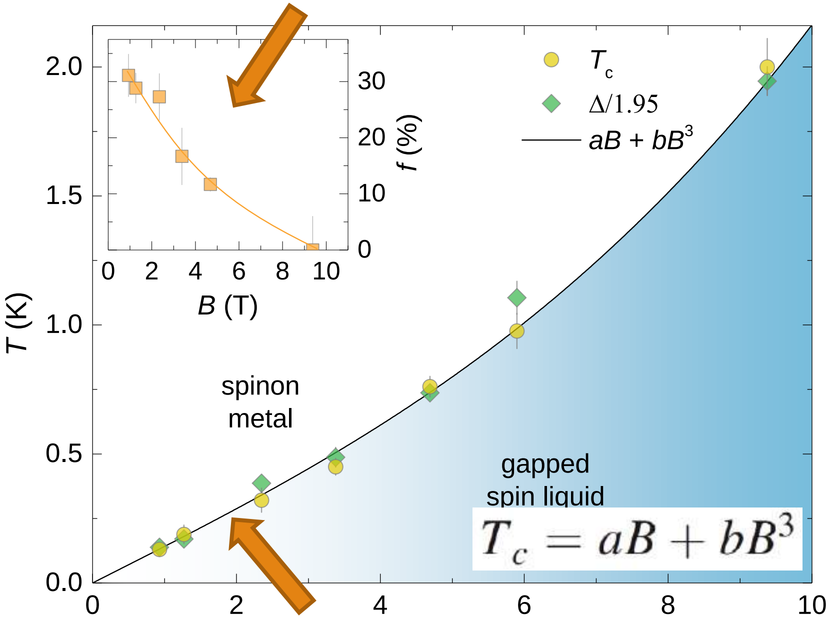
Li *et al.*, New J. Phys. **16**, 093011 (2014)

NMR: the Probe of Spin Fluctuations

- Zn-brochantite: distorted kagome-lattice AFM with a spinon-Fermi-surface QSL GS
- Field-induced modification of the spinon Fermi surface below T_c

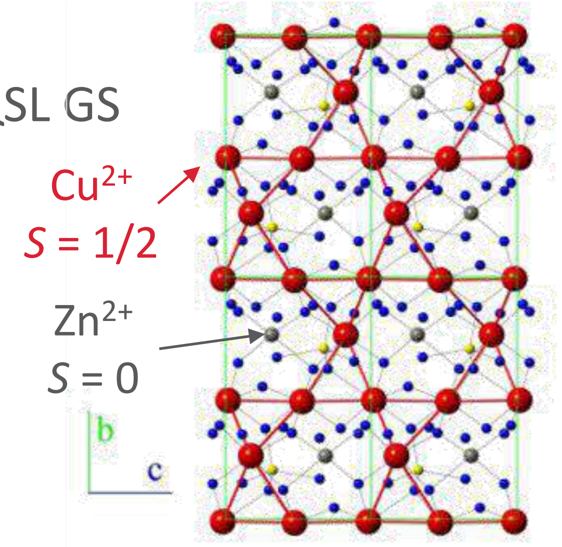


residual spinon metal



$T_c = aB + bB^3$

"g" = 0.2



$$\frac{1}{T_1} = dT e^{-\Delta/T} + f^2 c T^\eta$$

gapped QSL

residual spinon metal

Gomilšek *et al.*, Phys. Rev. Lett. 119, 137205 (2017)

NMR: the Probe of Spin Fluctuations

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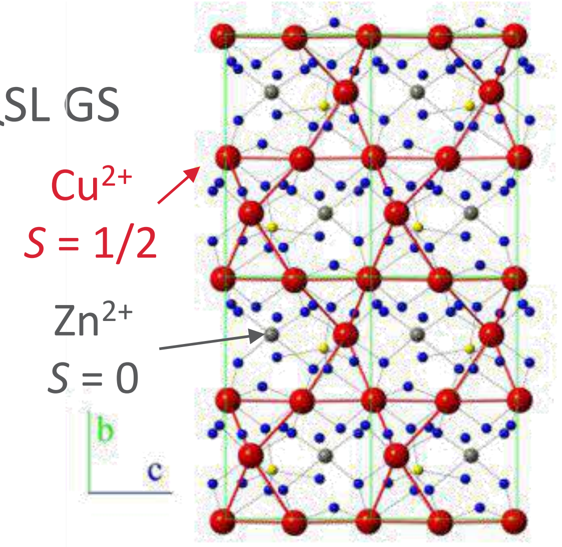
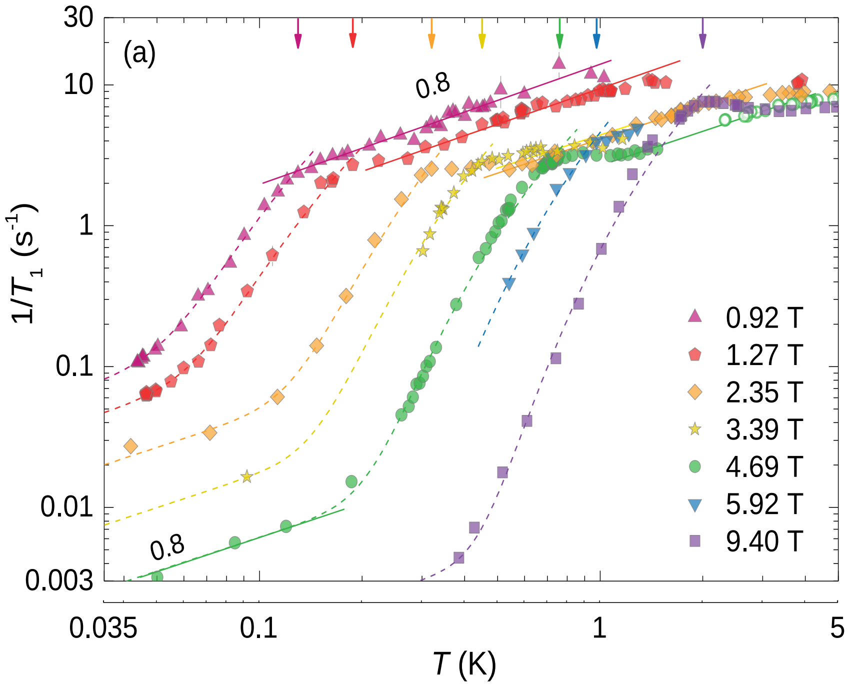
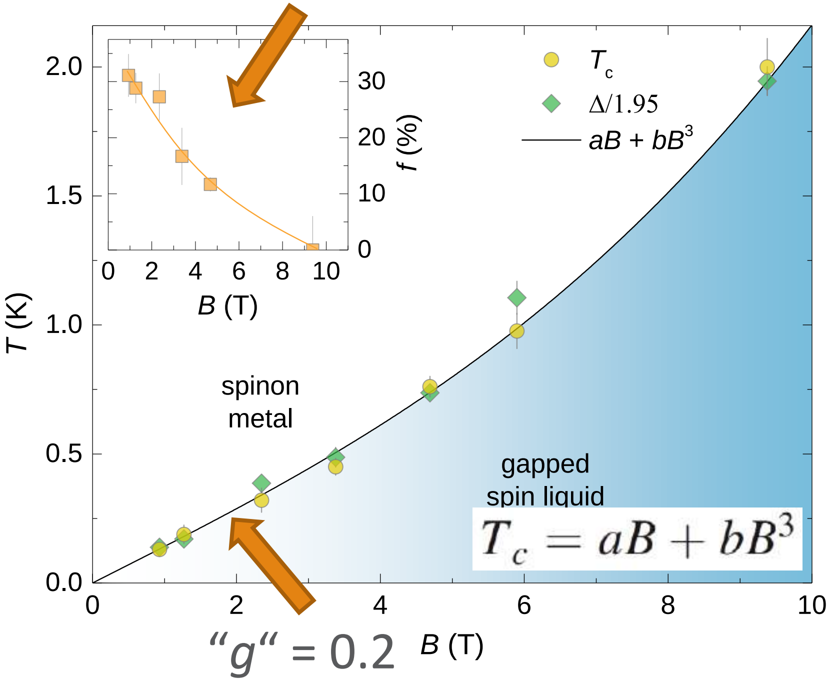
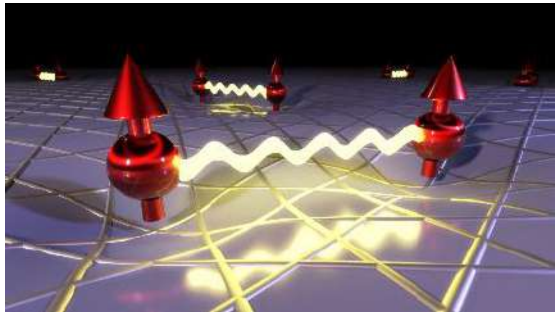






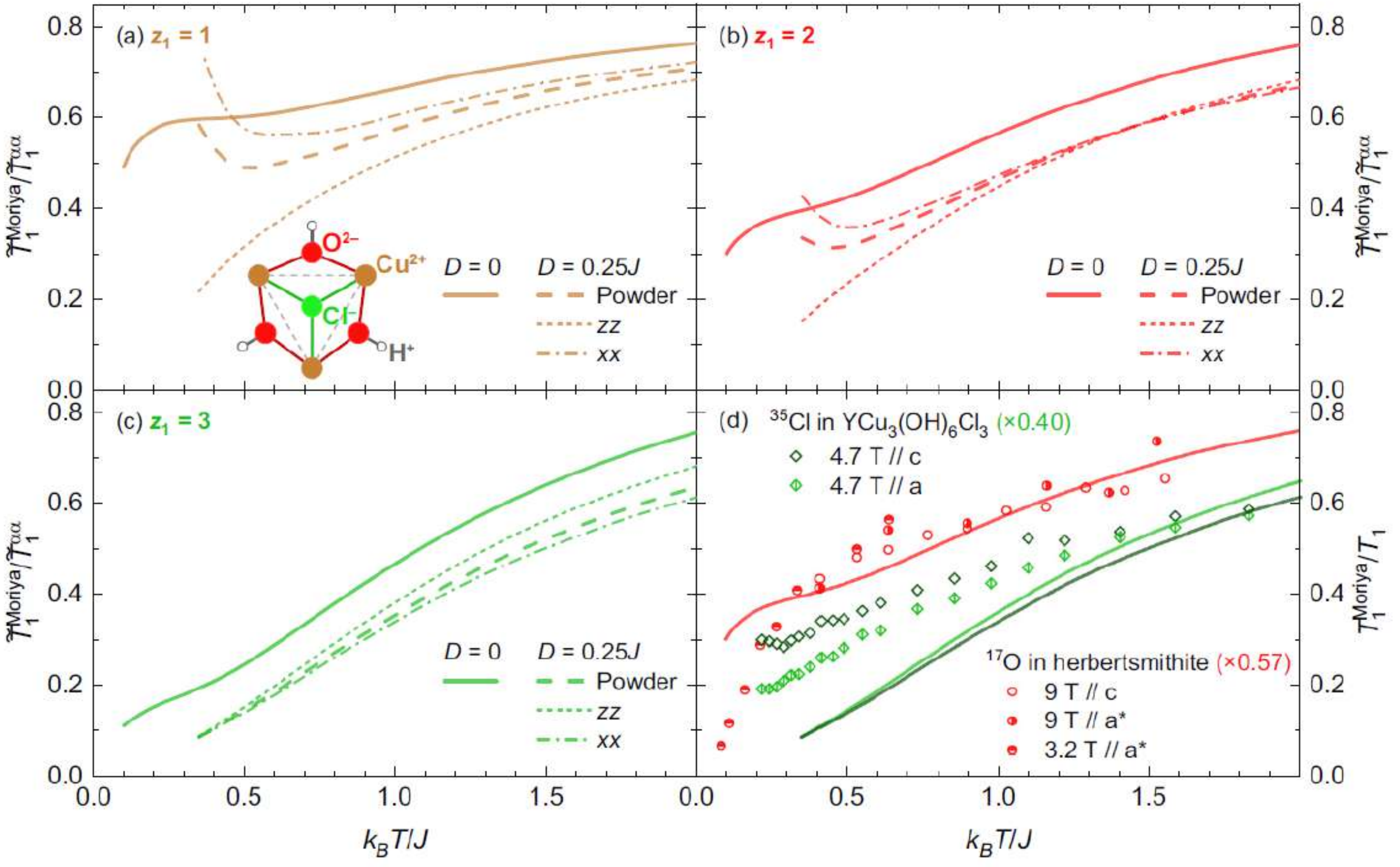
spinon pairing



Gomilšek *et al.*, Phys. Rev. Lett. 119, 137205 (2017)

NMR: the Probe of Spin Fluctuations

- Kagome AFM + DM interaction: T_1-relaxation in the correlated “paramagnetic” state by FTLM



Prelovšek *et al.*, Phys. Rev. B **103**, 014431 (2021)

- Deviations from the Moriya limit: high temperatures

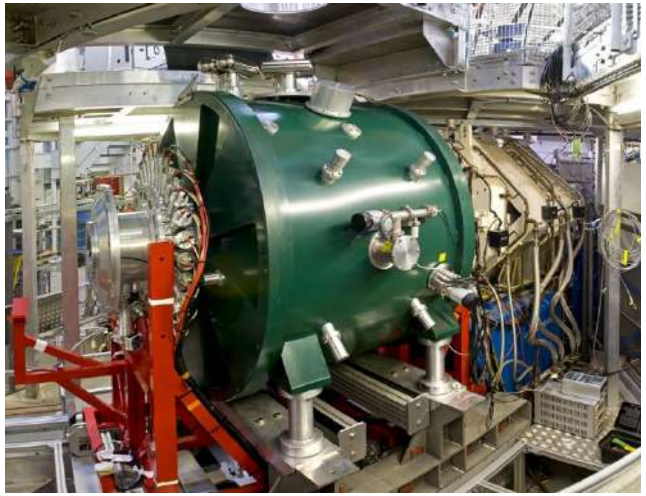
$$\frac{1}{T_1} = \sqrt{\frac{\pi}{3}}\frac{A^2\sqrt{S(S+1)}}{\hbar J\sqrt{z}}$$

- anisotropic fluctuations due to DM interaction
- site-specific anisotropy

filtering of dominant chiral fluctuations by form factor

Outline

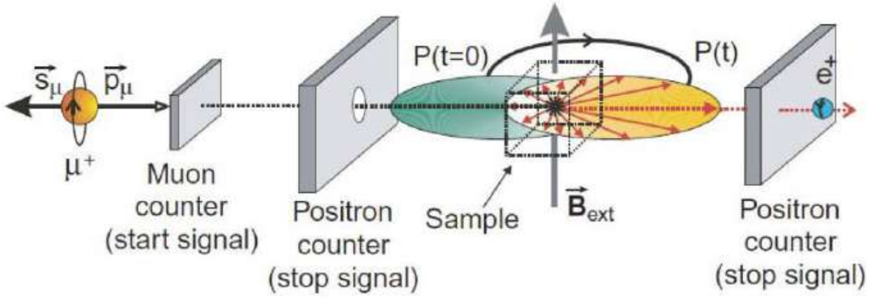
- ❑ Introduction to magnetism
- ❑ Probing magnetism: conventional bulk and scattering techniques
- ❑ Local probes of magnetism
- ❑ Electron spin resonance (ESR)
- ❑ Nuclear magnetic resonance (NMR)
- ❑ Muon spectroscopy (μSR)
- ❑ Summary: strengths, limitations and complementarity of local probes



HIFI, ISIS, UK

Motivation for Muon Spectroscopy

- ❑ Extreme sensitivity to static and dynamic internal fields: ~0.1 G
- ❑ Measures fluctuations in a broad frequency range: $10^4 - 10^{12}$ Hz
- ❑ Muon can be implanted into any material
- ❑ A non-destructive technique that does not active samples
- ❑ Allows zero-field measurements



https://www.psi.ch

Motivation for Muon Spectroscopy

❑ Range of applications:

- study of ionic diffusion in battery materials
- study of energy-storage materials
- study of reactions kinetics
- study of free-radical chemistry
- …

CHEMISTRY/
INDUSTRY

- study of cultural heritage artefacts
- …

OTHER AREAS

- magnetic properties of materials
- electronic properties of superconductors
- study of functional materials
- impurities in semiconductors
- …

PHYSICS/
MATERIALS
RESEARCH

Motivation for Muon Spectroscopy

- Range of applications:

  - study of ionic diffusion in battery materials
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  - study of reactions kinetics
  - study of free-radical chemistry
  - …

CHEMISTRY/ INDUSTRY

  - study of cultural heritage artefacts
  - …

OTHER AREAS

  - magnetic properties of materials
  - electronic properties of superconductors
  - study of functional materials
  - impurities in semiconductors
  - …

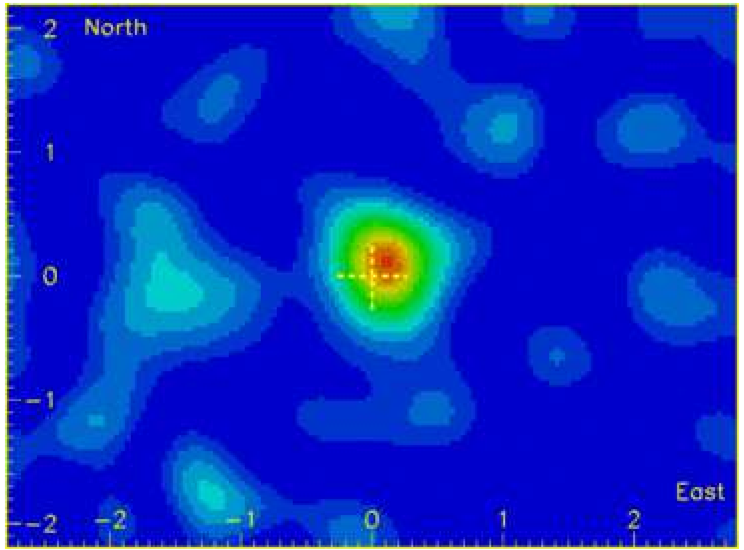
PHYSICS/ MATERIALS RESEARCH

A Brief History of μSR

- 1936: discovery of the muon as secondary radiation of cosmic rays

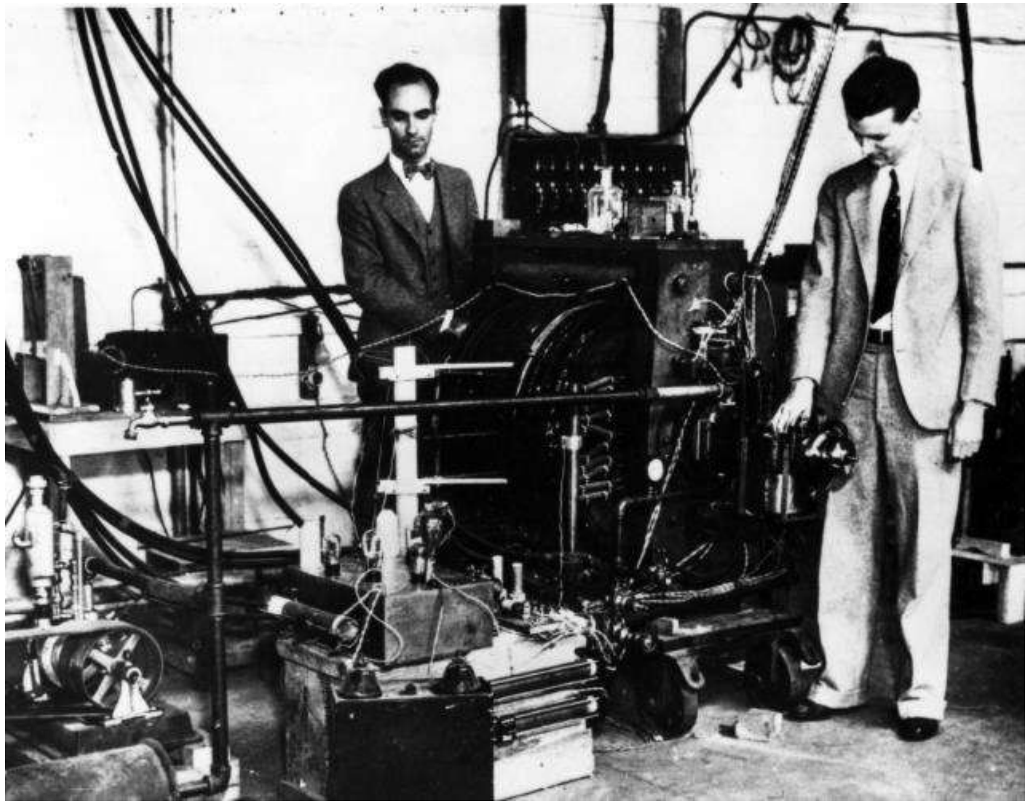
I. I. Rabi: “Who ordered that?”

cosmic ray shadow



https://en.wikipedia.org

Carl Anderson and Seth Neddermeyer with magnet cloud chamber

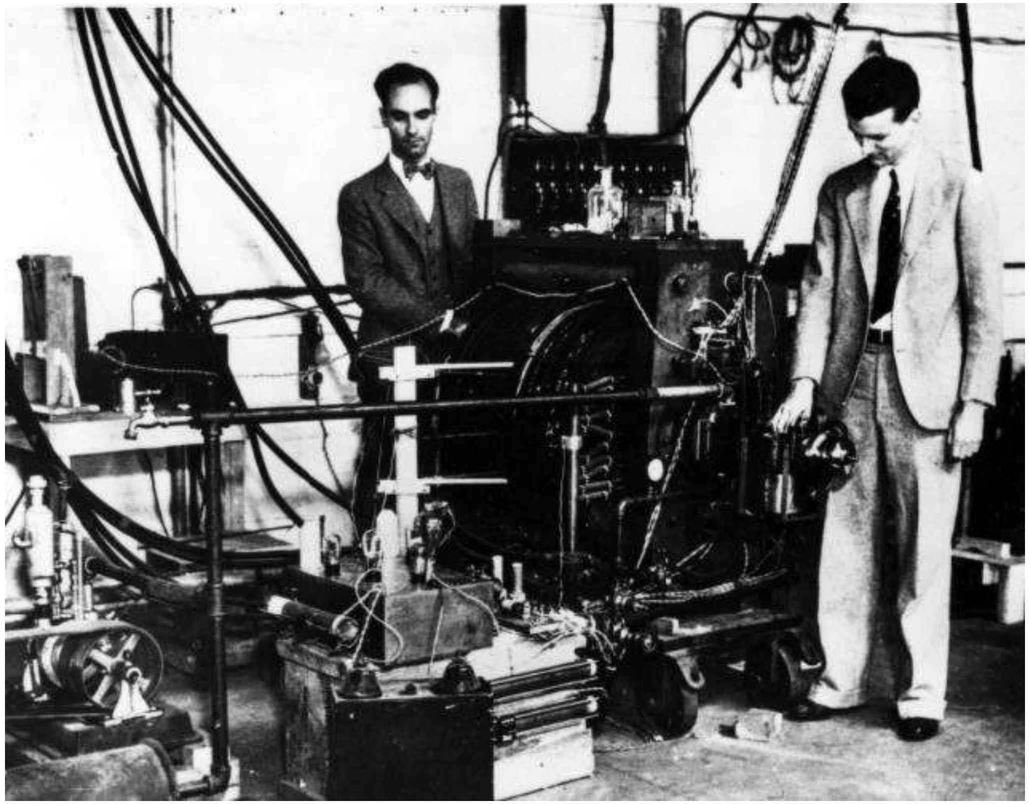


https://digital.archives.caltech.edu

A Brief History of μSR

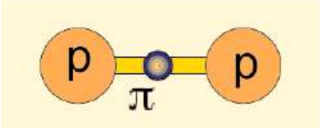
- 1936: discovery of the muon as secondary radiation of cosmic rays

Carl Anderson and Seth Neddermeyer with magnet cloud chamber



https://digital.archives.caltech.edu

Initially labeled "mesotron"



$\Delta E \sim 100\,\mathrm{MeV}$

Anderson/Neddermayer particle

✕

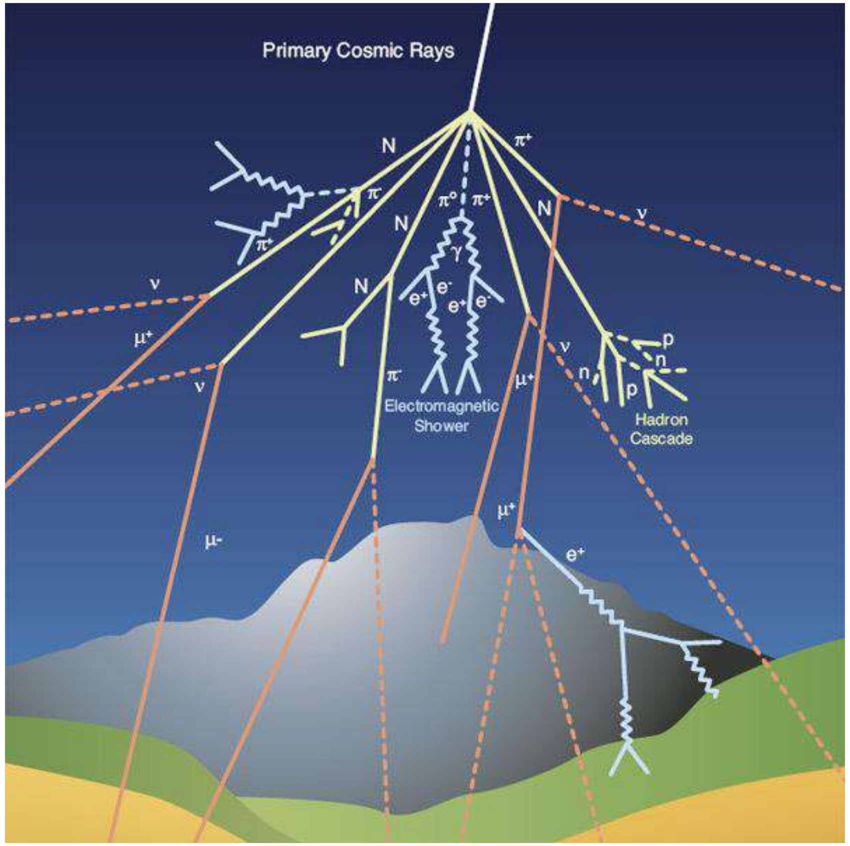
Yukawa particle

Hideki Yukawa

https://en.wikipedia.org

A Brief History of μSR

- 1947: discovery of pions



https://home.cern

$$\pi^+ \rightarrow \mu^+ + \nu_\mu$$
$$\pi^- \rightarrow \mu^- + \bar{\nu}_\mu$$

$$m_\pi c^2 = 139.6\,\mathrm{MeV}$$
$$m_\mu c^2 = 105.7\,\mathrm{MeV}$$

$$\tau = 27\,\mathrm{ns}$$

The Nobel Prize in Physics 1950

Photo from the Nobel Foundation archive.

Cecil Frank Powell

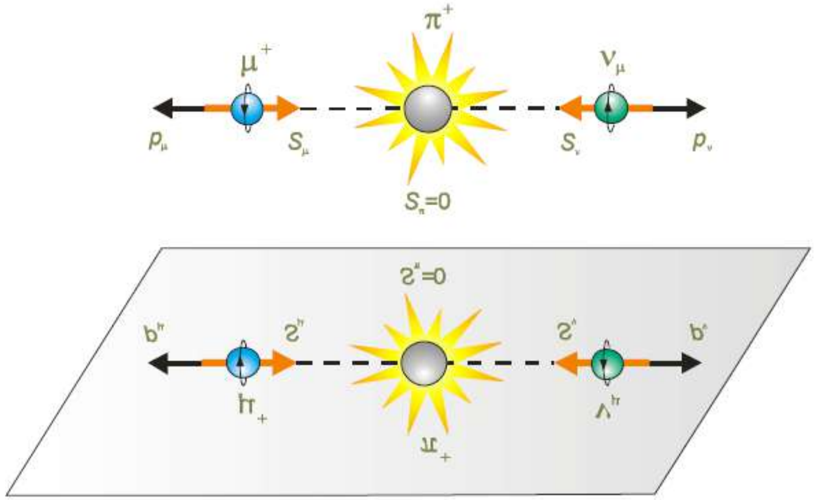
Prize share: 1/1

The Nobel Prize in Physics 1950 was awarded to Cecil Frank Powell "for his development of the photographic method of studying nuclear processes and his discoveries regarding mesons made with this method."

https://www.nobelprize.org

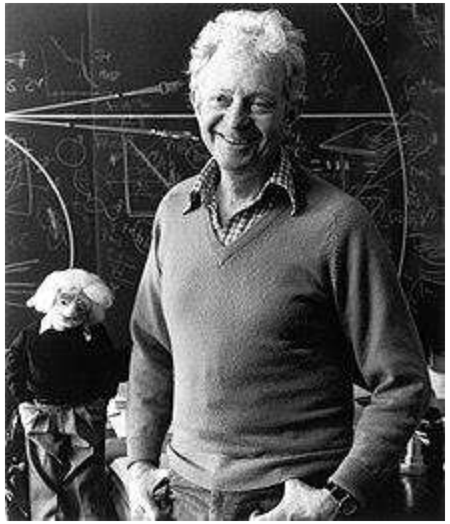
A Brief History of μSR

- 1957: discovery of parity violation in weak decay

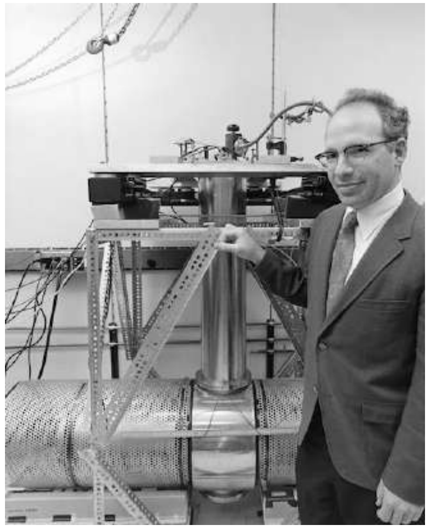


http://cmms.triumf.ca

muon's spin antiparallel to its momentum



Leon M. Lederman



Richard L. Garwin

Various other materials were investigated for μ^+ mesons. Nuclear emulsion as a target was found to have a significantly weaker asymmetry (peak-to-valley ratio of 1.40±0.07) and it is interesting to note that this did not increase with reduced delay and gate width. Neither was there any evidence for an altered moment. It seems possible that polarized positive and negative muons will become a powerful tool for exploring magnetic fields in nuclei (even in Pb, 2% of the μ^- decay into electrons[9]), atoms, and interatomic regions.

Observations of the Failure of Conservation of Parity and Charge Conjugation in Meson Decays: the Magnetic Moment of the Free Muon*

RICHARD L. GARWIN,† LEON M. LEDERMAN, AND MARCEL WEINRICH

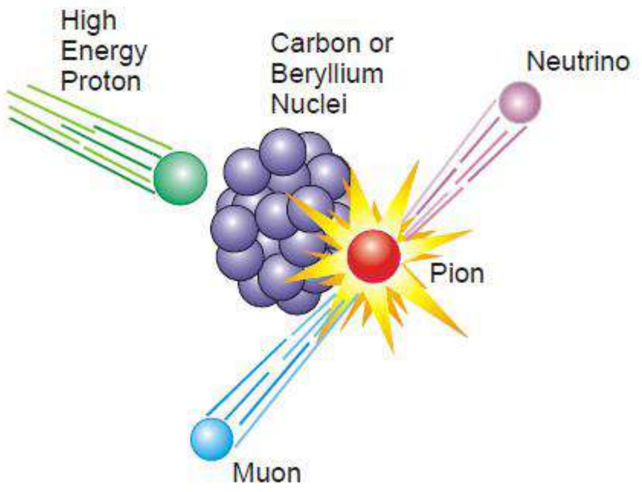
Physics Department, Nevis Cyclotron Laboratories, Columbia University, Irvington-on-Hudson, New York, New York

(Received January 15, 1957)

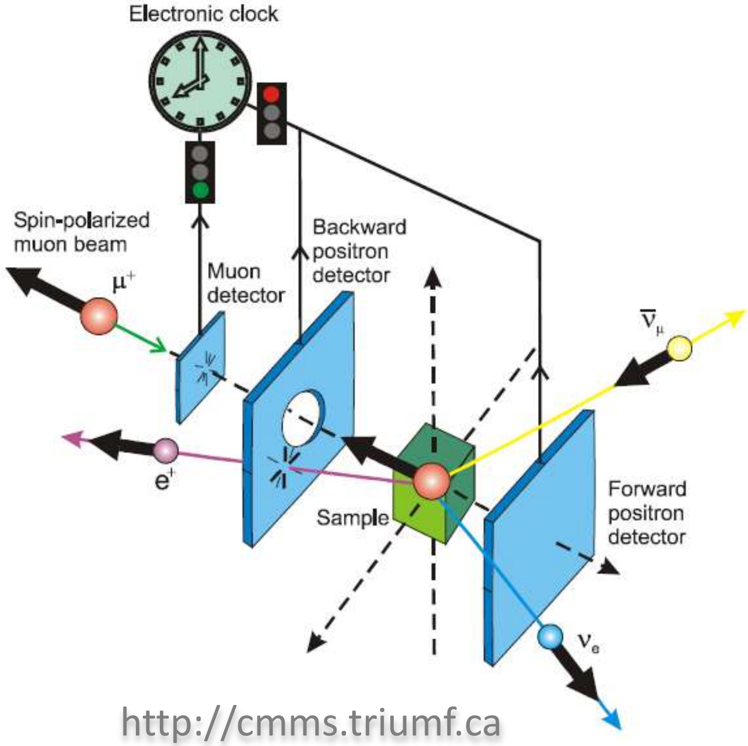
μSR Apparatus

- How does it work?

1. **muon production (accelerator):** surface muons (p = 29.8 MeV/c)



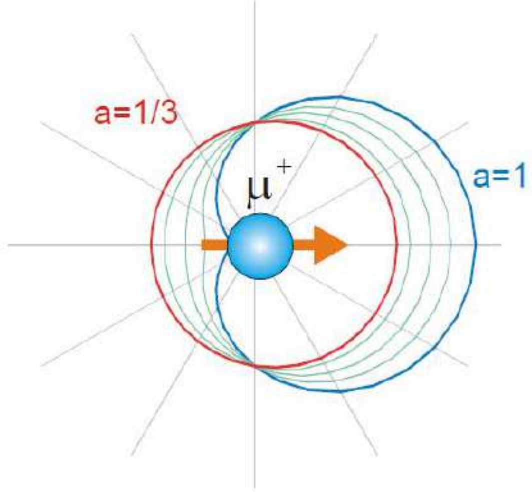
2. **muon implantation:** in about 100 ps up to a few tenths of mm (polarization preserved)



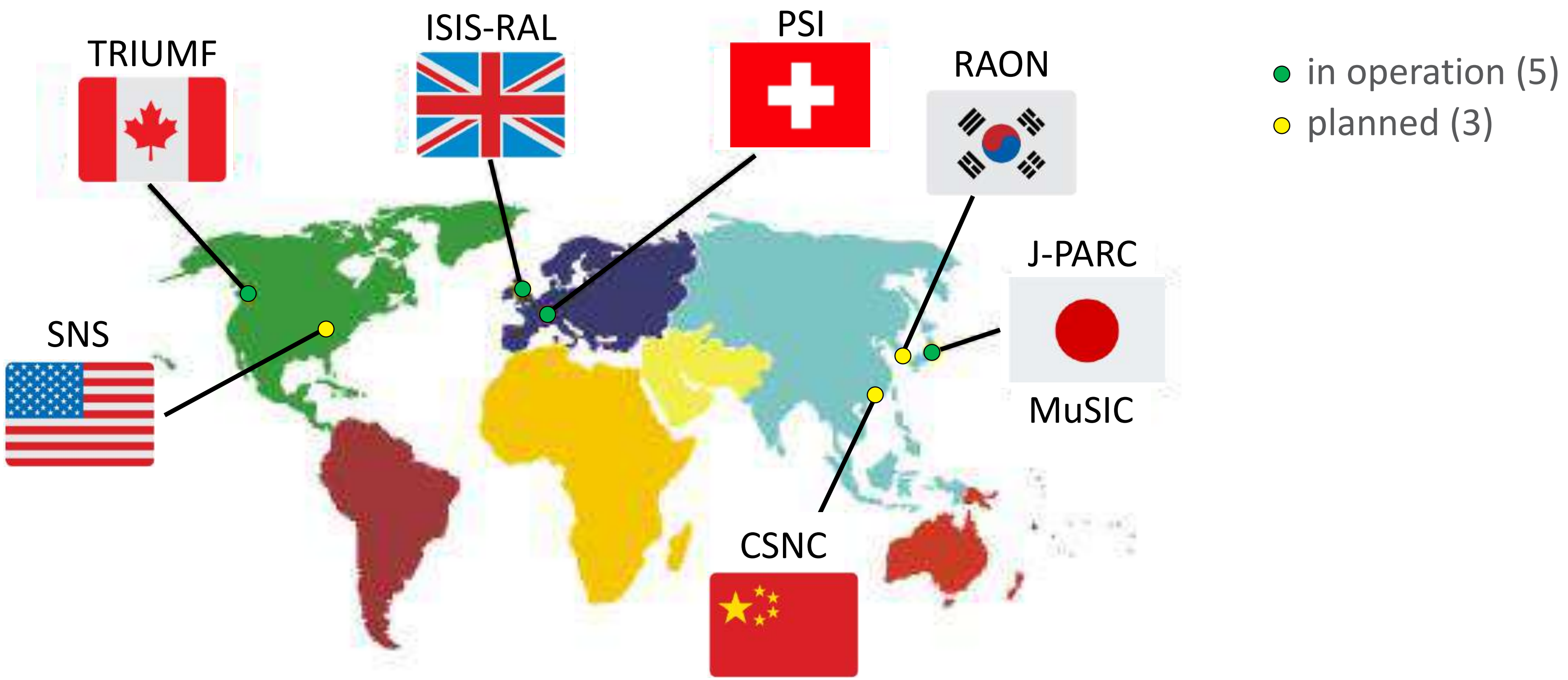
http://cmms.triumf.ca

3. **muon decay:** $\tau = 2.2\,\mu s$ (parity violation)

$$\mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu$$



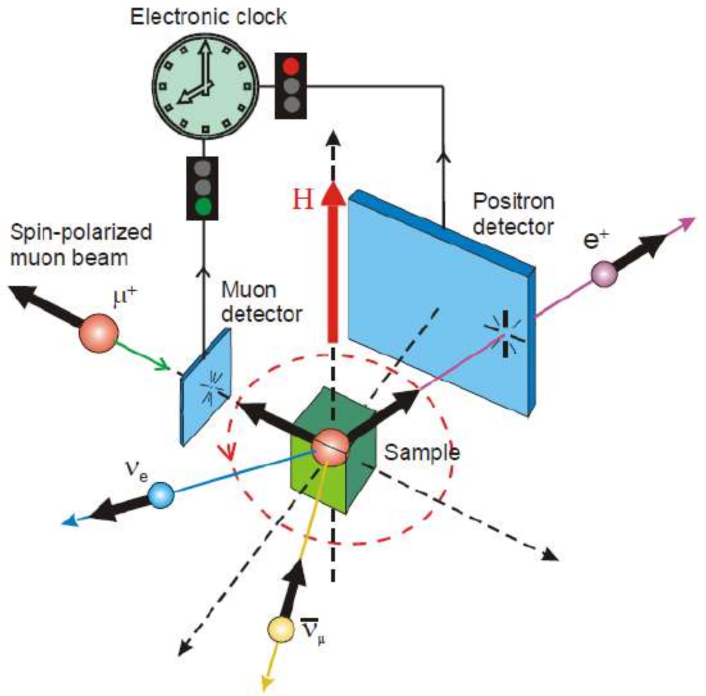
μSR User Facilities



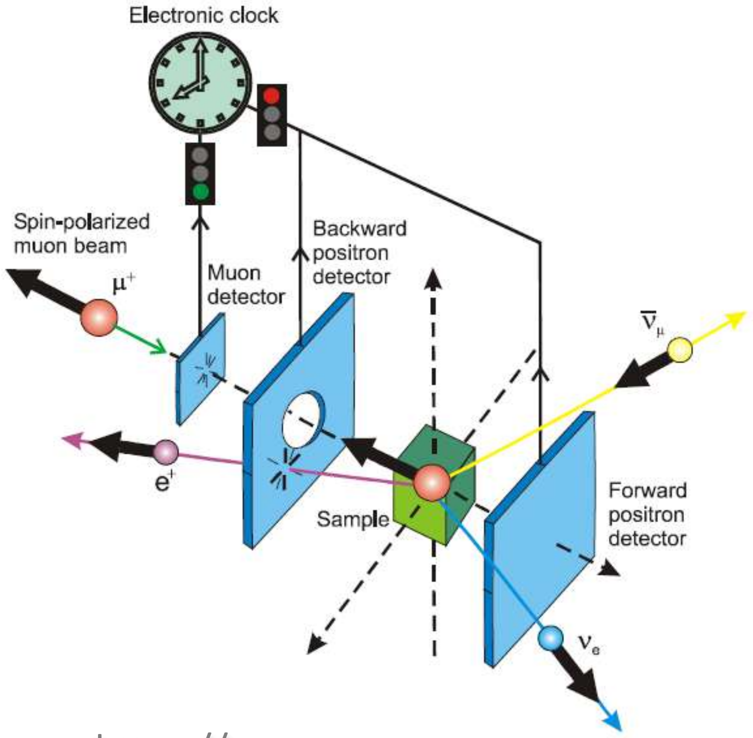
μSR Experiments

- μSR = muon spin rotation/relaxation/resonance (research)

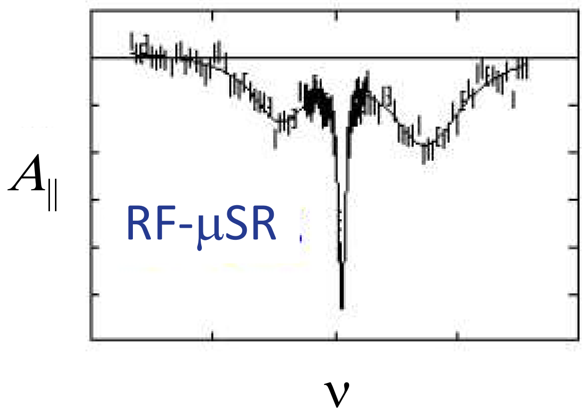
1. rotation: TF-μSR



2. relaxation: LF-μSR and ZF-μSR



3. resonance: RF-μSR, μLCR, μSE



https://muonsources.org

μSR Hamiltonian

- The Hamiltonian:

$$\mathcal{H} = \mathcal{H}_{\mu Z} + \mathcal{H}_{\mu n} + \mathcal{H}_{\mu e}$$

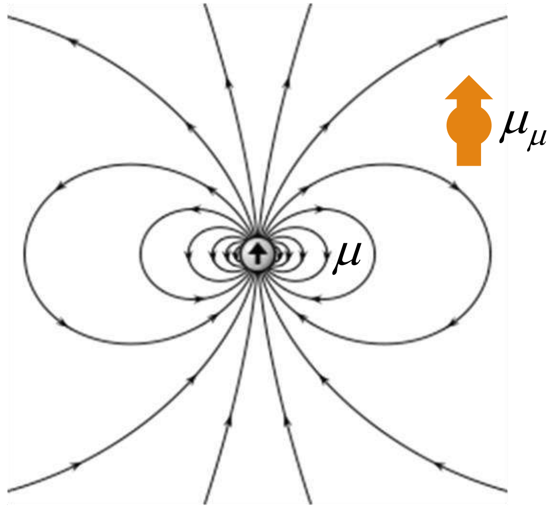
muon Zeeman interaction → not required

muon-nuclear coupling

muon-electron coupling

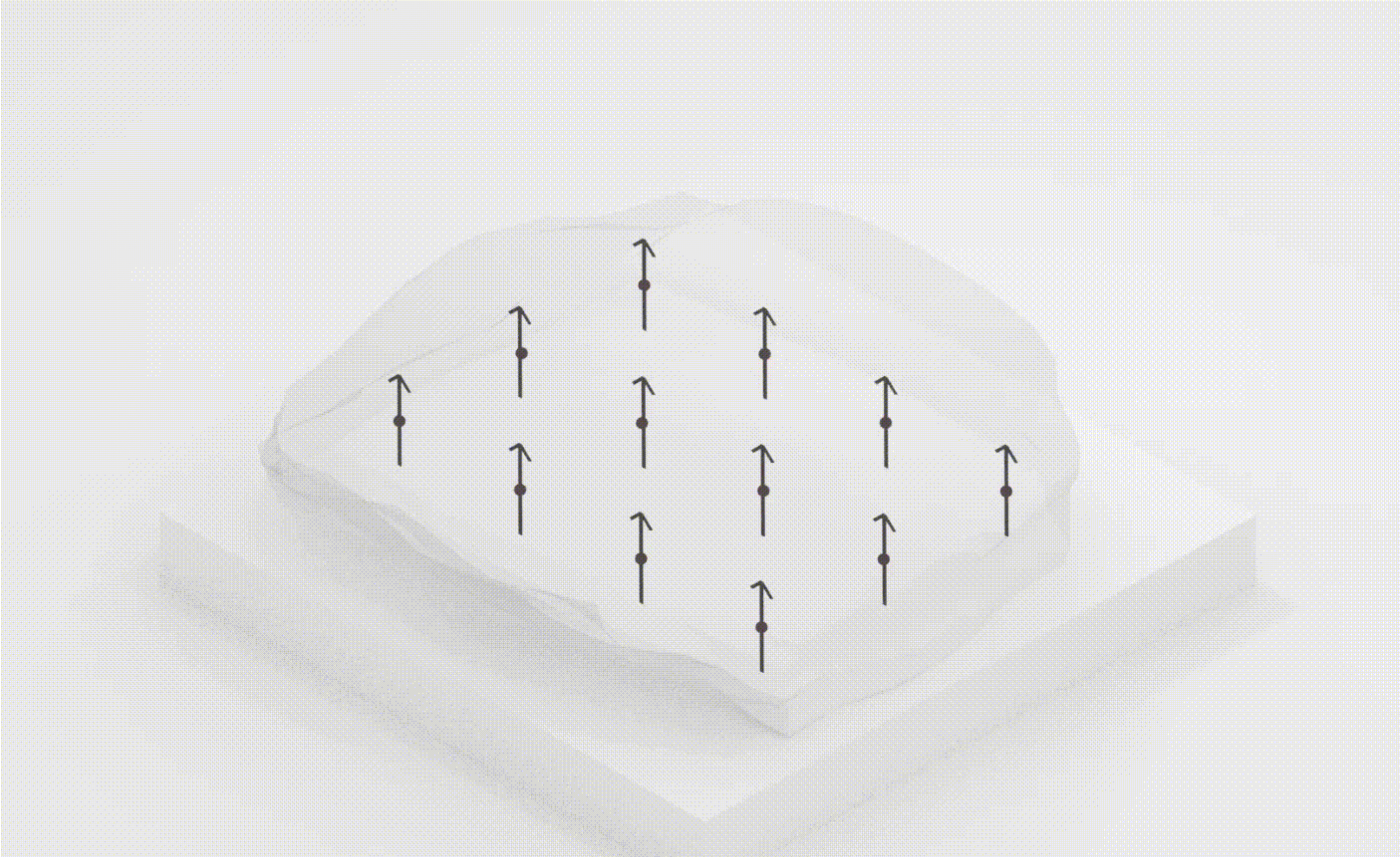
$$\mathcal{H}_{dip} = \frac{\mu_0}{4\pi}\left(\frac{\vec{\mu}_\mu \cdot \vec{\mu}}{r^3} - \frac{3(\vec{\mu}_\mu \cdot \vec{r})(\vec{\mu} \cdot \vec{r})}{r^5}\right)$$

dipole field



μSR: Static Field

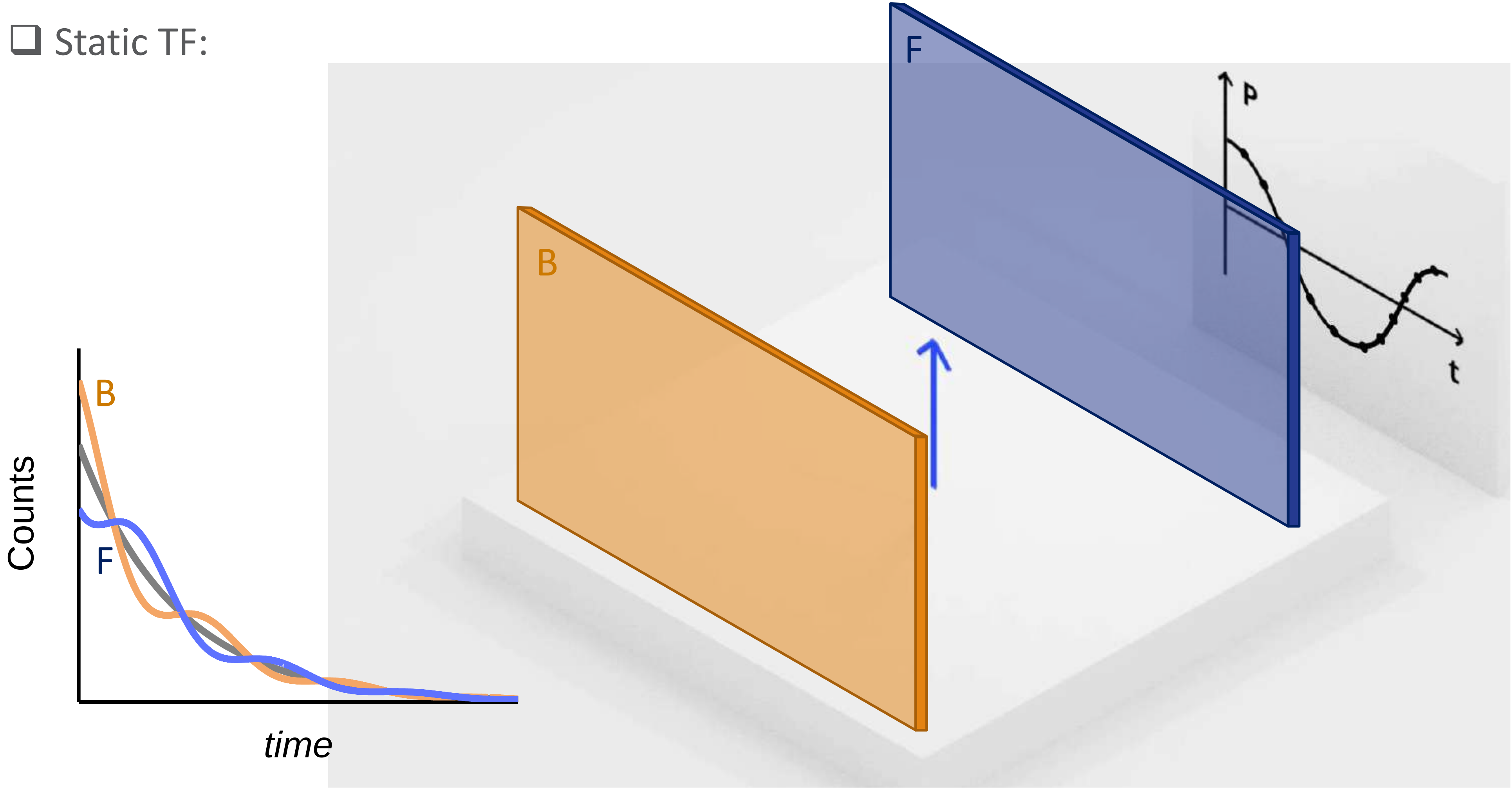
- Static TF:



https://upload.wikimedia.org/wikipedia/commons/8/87/Muon_Spin_Resonance_%28Musr%29.webm

μSR: Static Field

- Static TF:



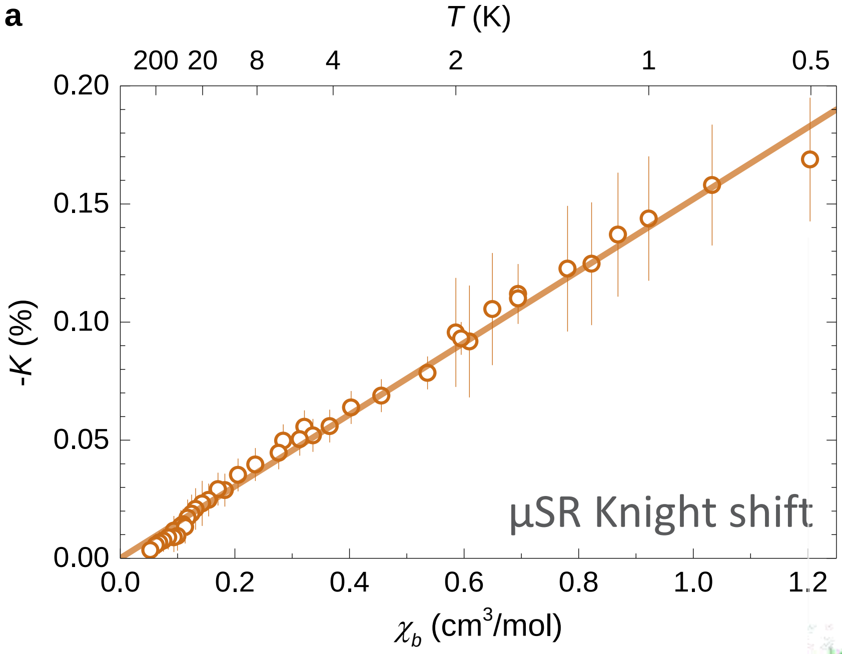
$$\nu = \frac{\gamma_\mu}{2\pi} B_{loc}$$

https://upload.wikimedia.org/wikipedia/commons/8/87/Muon_Spin_Resonance_%28Musr%29.webm

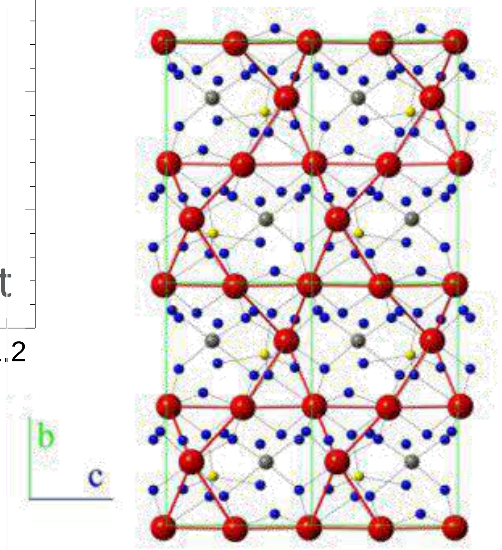
µSR: Static Field

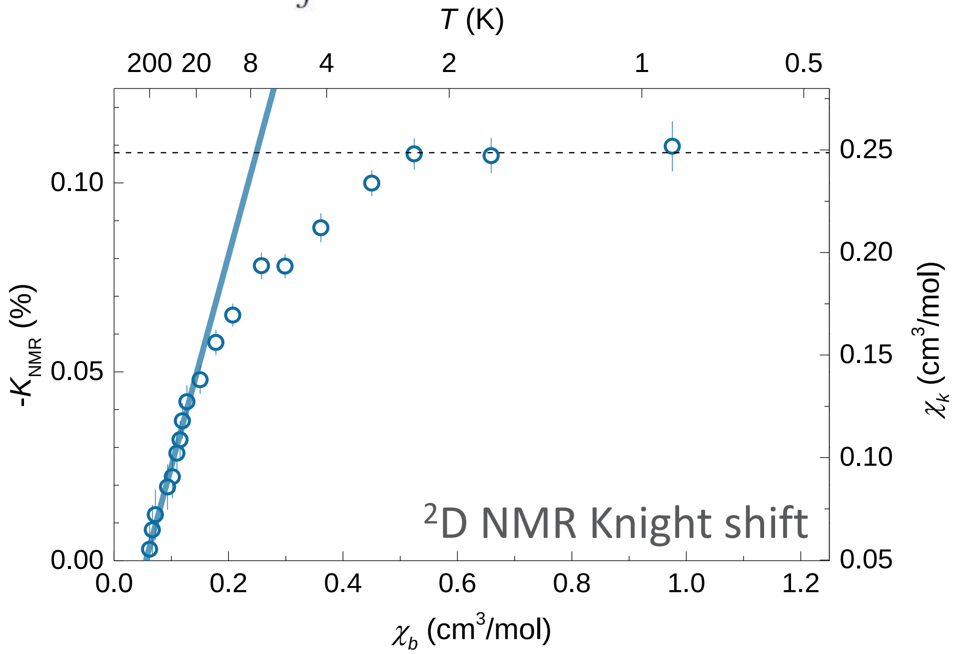
- Static TF: frequency shift

$$B_{loc} \ll B_0 \quad \Rightarrow \quad K = \frac{B_{loc} - B_0}{B_0} = \frac{\nu - \nu_L}{\nu_L} \qquad K = \sum_j \tilde{A}_{ij}\chi(q=0,\omega=0)$$



Zn-brochantite:
distorted KAFM
(spinon FS QSL)





⇒ coupling to intrinsic and impurity spins

⇒ coupling to only intrinsic spins

Gomilšek *et al*., Nat. Phys. **15**, 754 (2019)

μSR: Static Field

- Static TF: frequency shift

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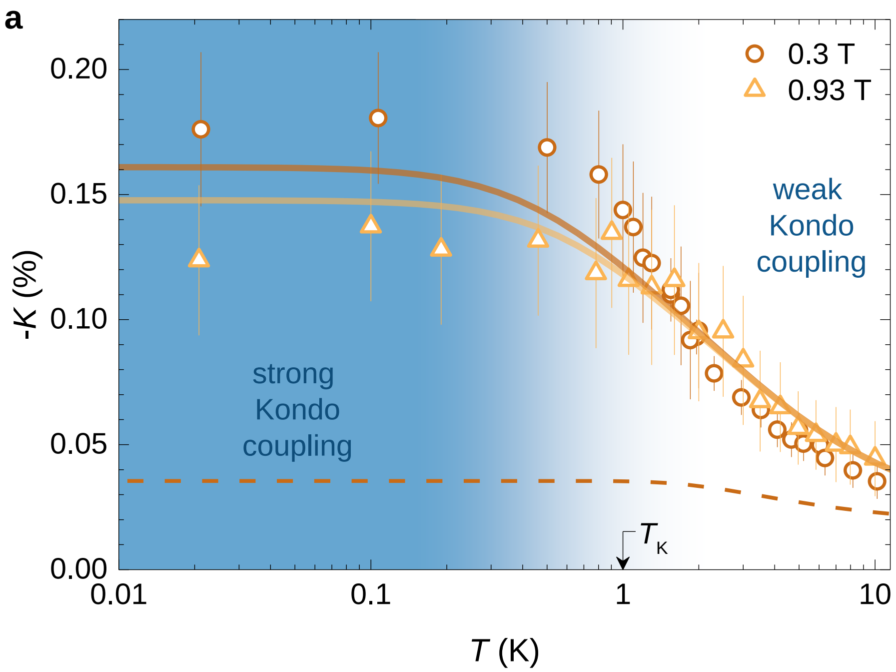

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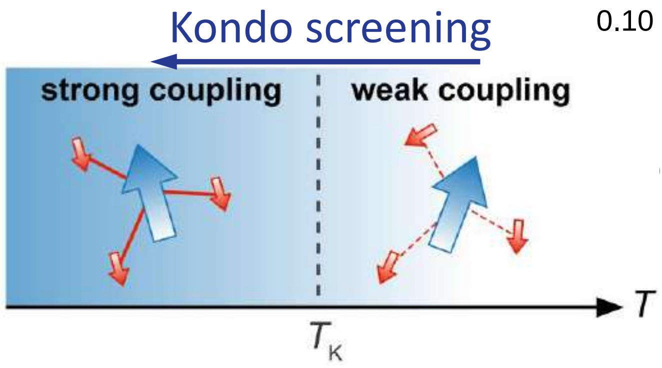
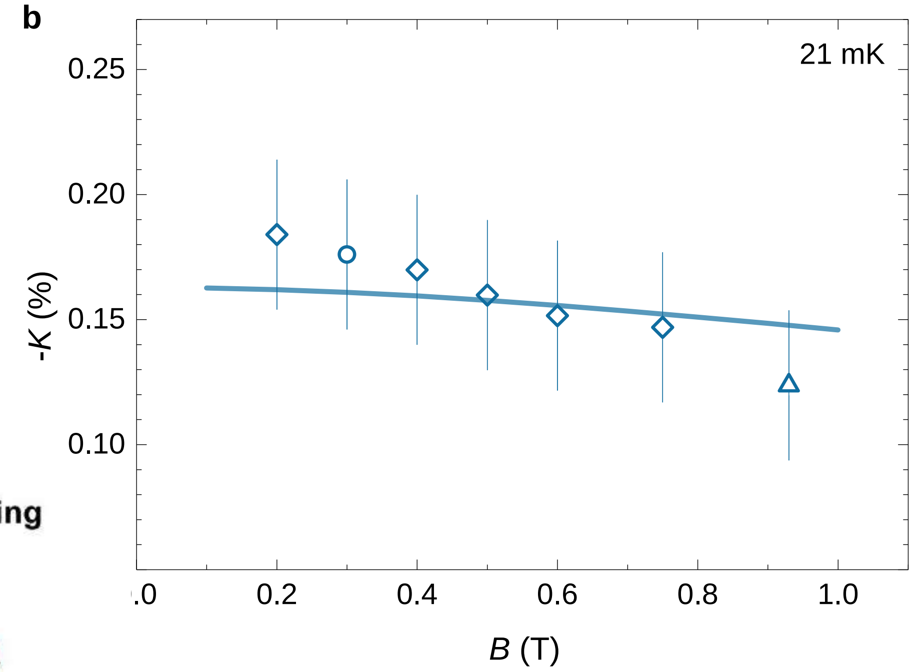




→ spinon Kondo effect

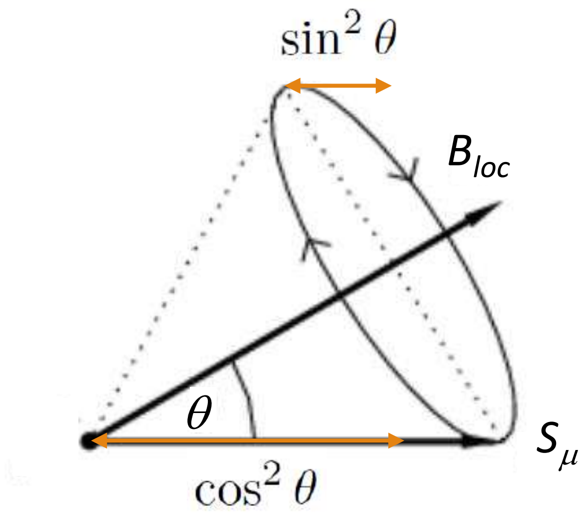
→ coupling of spinons

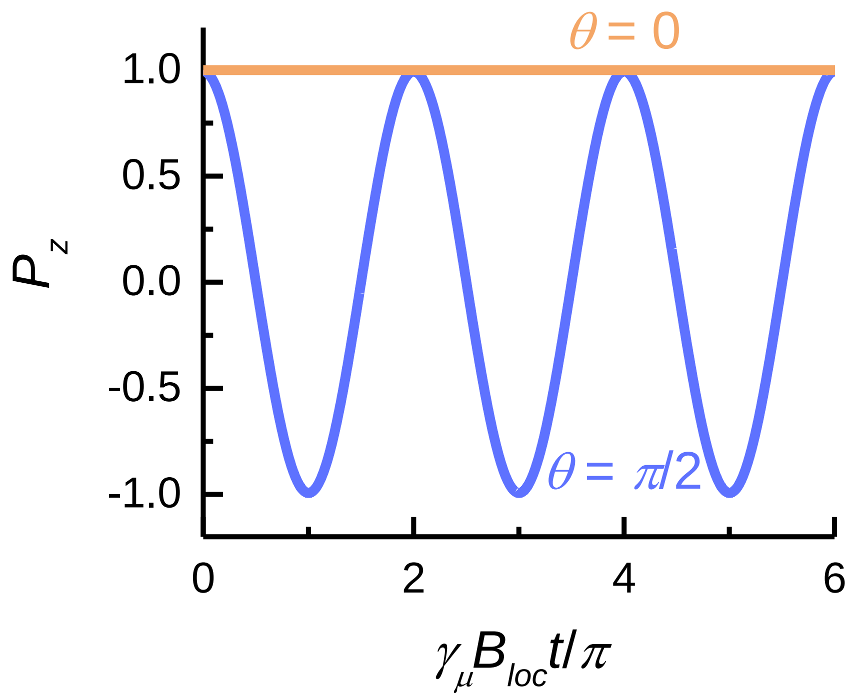
Gomilšek, AZ et al., Nat. Phys. **15**, 754 (2019)

μSR: Static Field

- Static local field:

$$P_z(t) = \cos^2\theta + \sin^2\theta\cos(\gamma_\mu B_{loc} t)$$

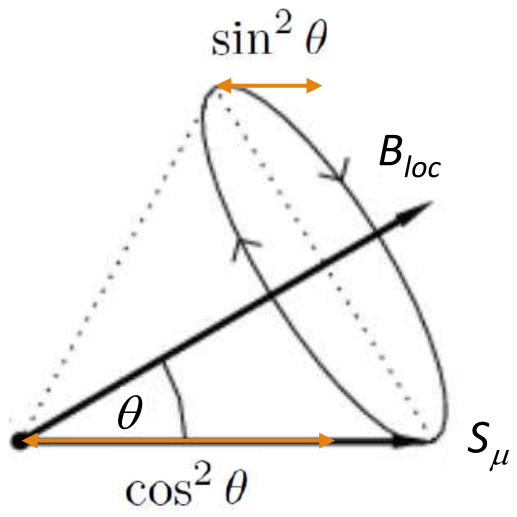


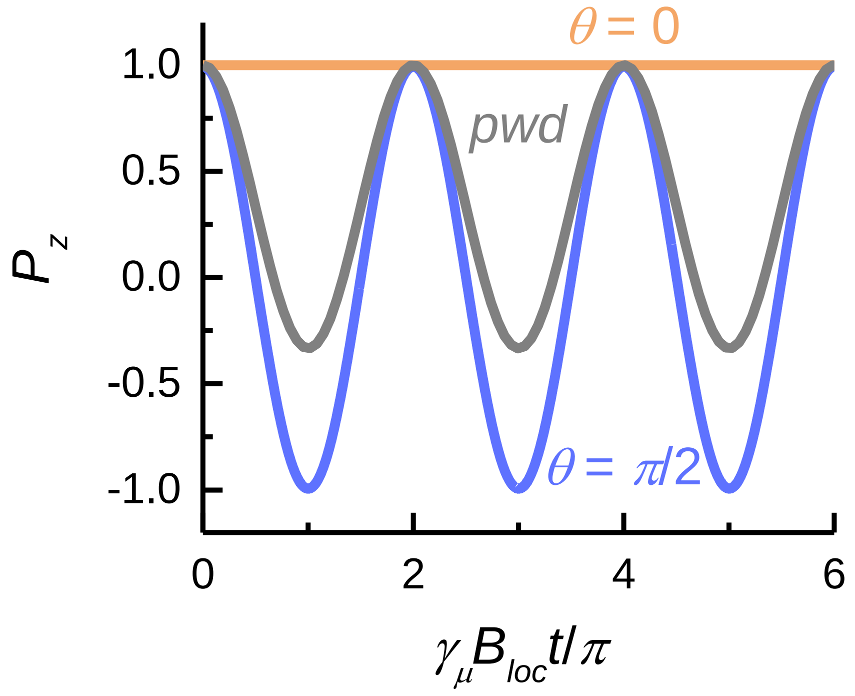


μSR: Static Field

- Static local field: $$P_z(t) = \cos^2\theta + \sin^2\theta \cos(\gamma_\mu B_{loc} t)$$

powder → $$P_z(t) = \frac{1}{3} + \frac{2}{3}\cos(\gamma_\mu B_{loc} t)$$





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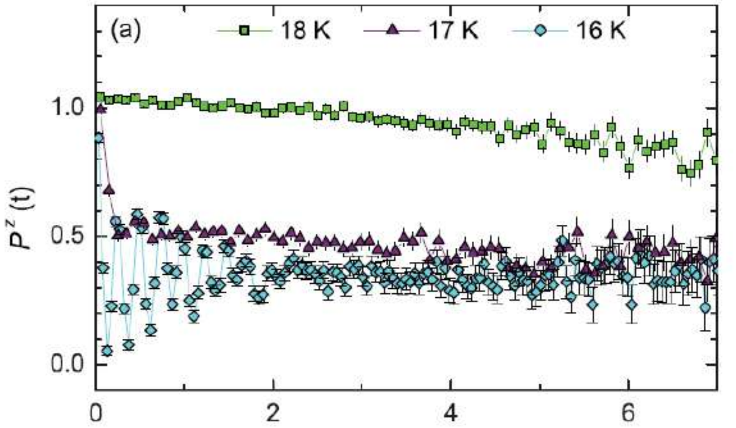
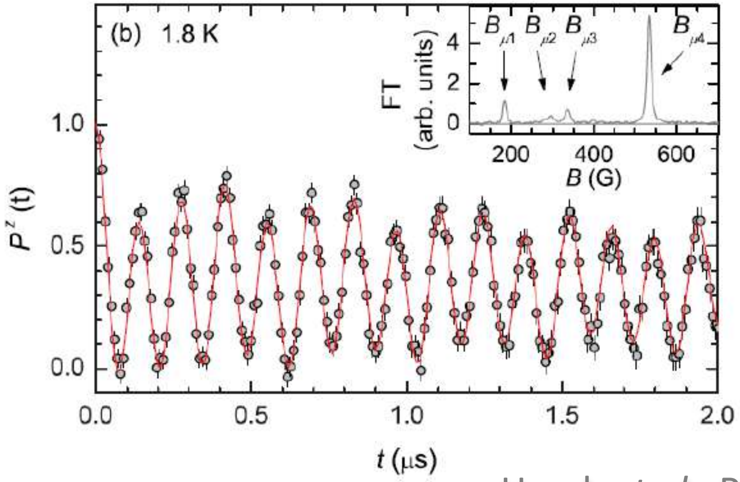
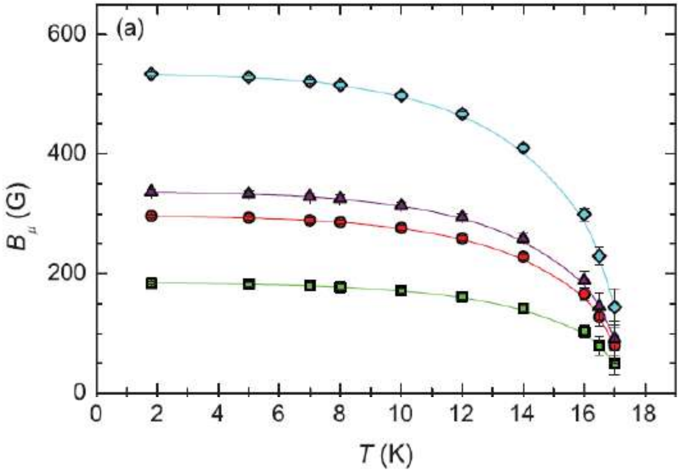
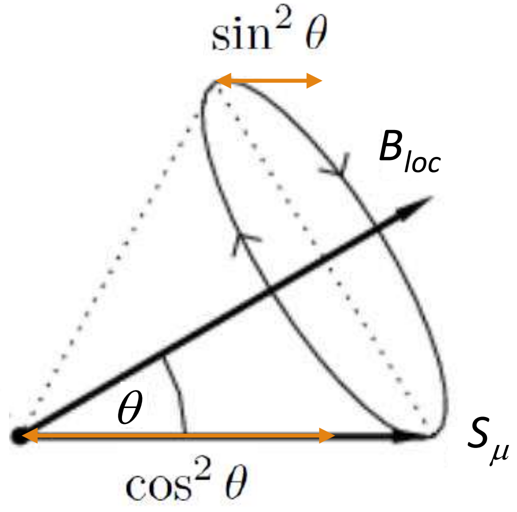








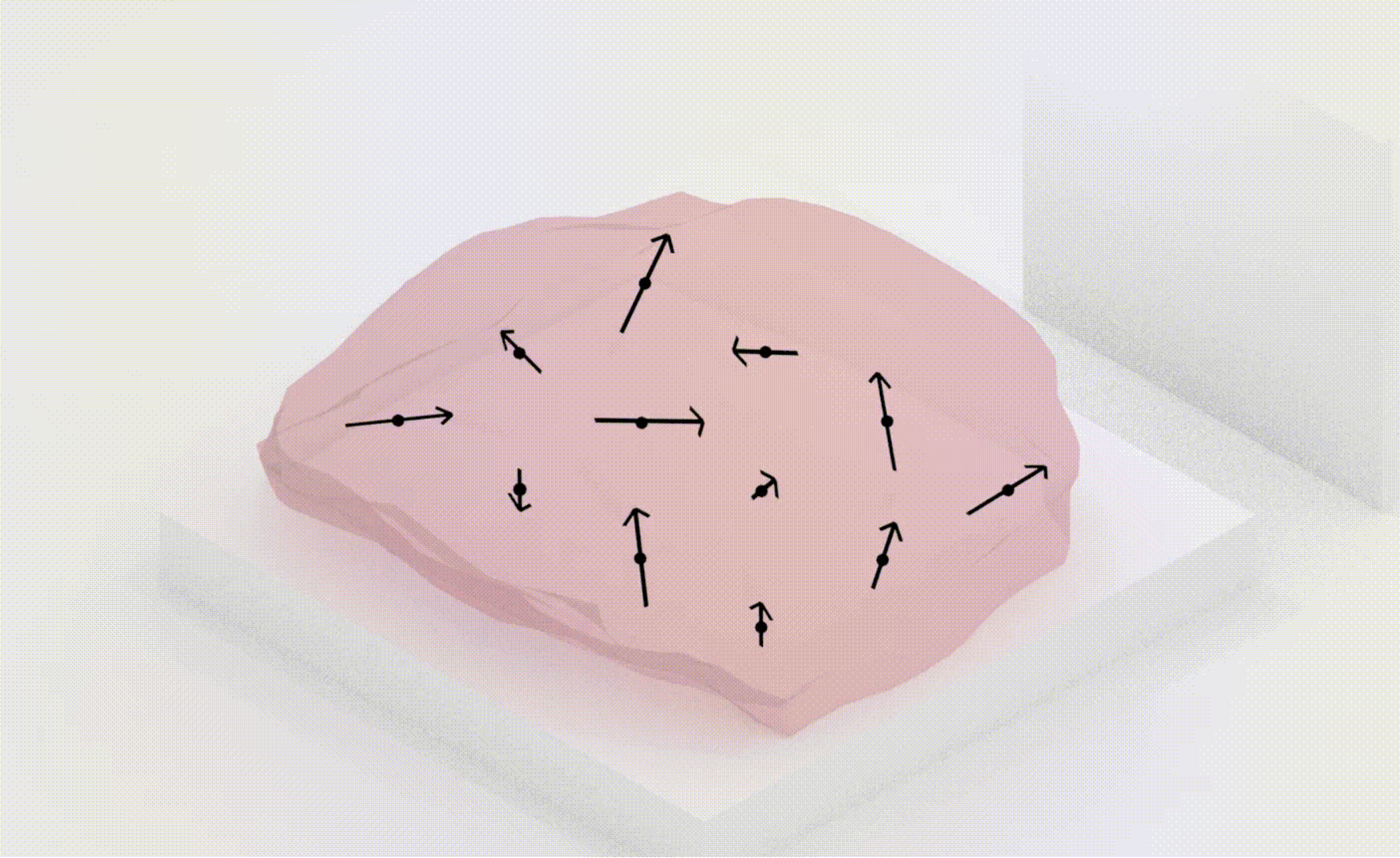
Herak *et al*., Phys. Rev. B **87**, 104413 (2013)

quasi-1D: $CuSe_2O_5$

- order parameter
- volume fraction
- FT analysis

μSR: Static Field

- Static-field (random) distribution:



$$\nu = \frac{\gamma_\mu}{2\pi} B_{loc}$$

https://upload.wikimedia.org/wikipedia/commons/8/87/Muon_Spin_Resonance_%28Musr%29.webm

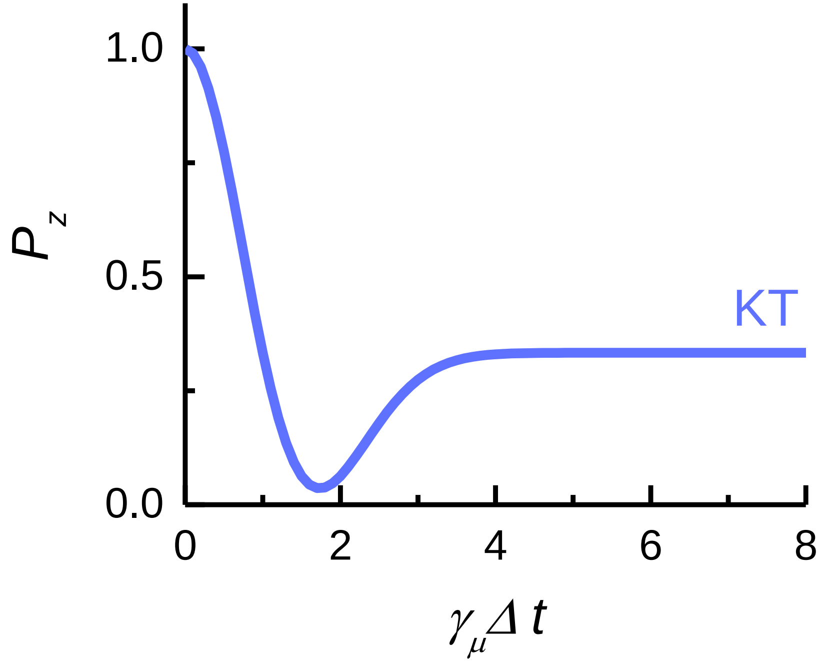
μSR: Static Field

- Static-field (random) distribution: Gaussian

$$\mathrm{prob}(B) \propto B^2 e^{-B^2/2\Delta^2}$$

ZF Kubo-Toyabe function

$$P_z(t) = \frac{1}{3} + \frac{2}{3} e^{-\frac{1}{2}\gamma_\mu^2 \Delta^2 t^2}(1 - \gamma_\mu^2 \Delta^2 t^2)$$

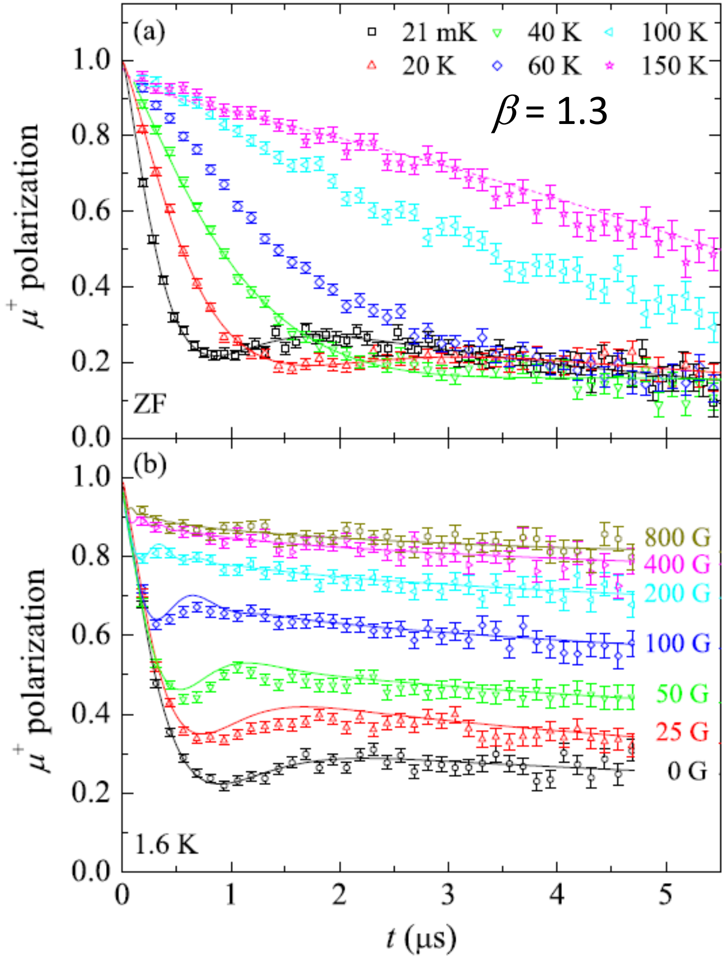


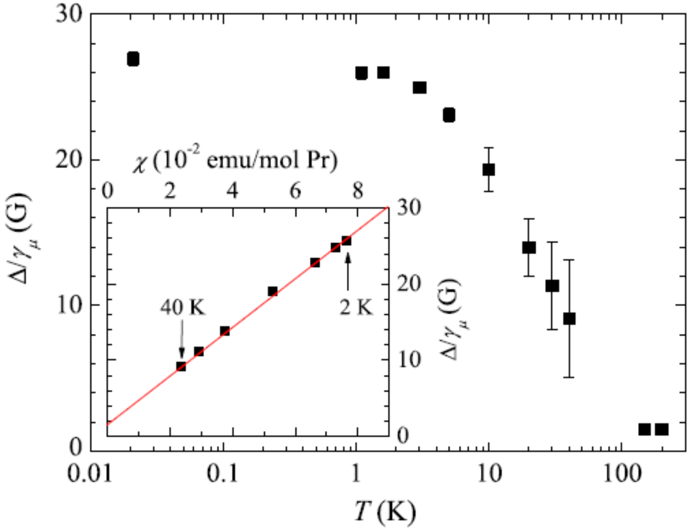
Ryogo Kubo

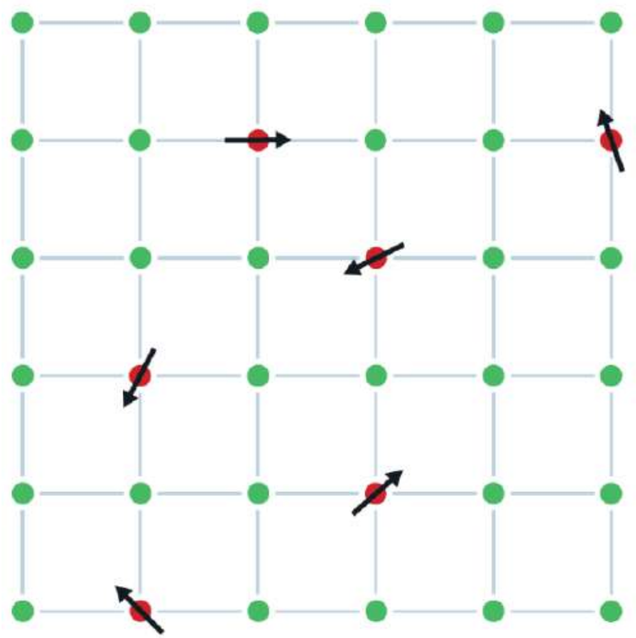
μSR: Static Field

- Voightian Kubo-Toyabe: $$P_z(t) = \frac{1}{3} + \frac{2}{3} e^{-\frac{1}{\beta}(\gamma_\mu^2 \Delta^2 t^2)^\beta} \left[1 - (\gamma_\mu^2 \Delta^2 t^2)^\beta\right]$$

Lorentzian (β = 1) for diluted moments: spin glass







kagome lattice: $Pr_3Ga_5SiO_{14}$

- hyperfine-enhanced ^{141}Pr magnetism
- Van-Vleck paramagnet

Zorko *et al*., Phys. Rev. Lett. **104**, 057202 (2010)

https://www.forbes.com

μSR: Dynamic Fields

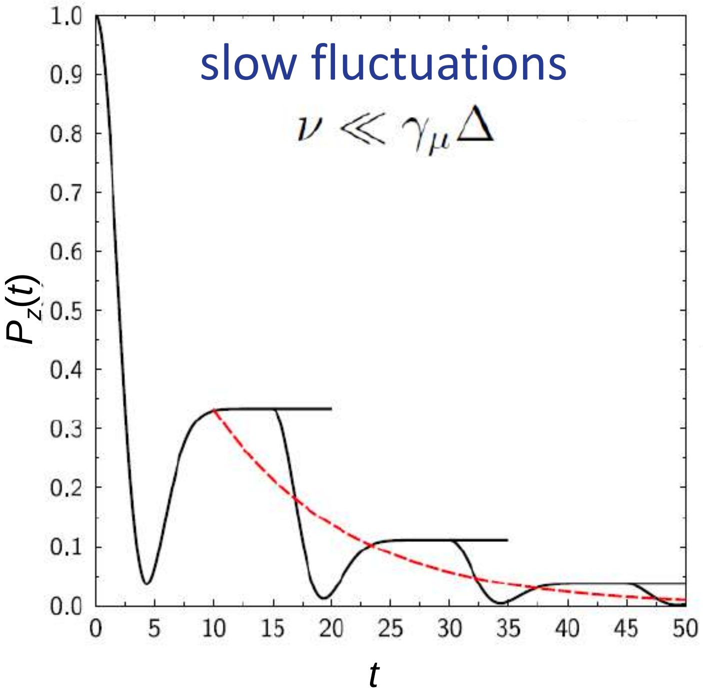
- Change of the local field at frequency ν:
  - random oscillations
  - muon hopping
  - elementary excitations

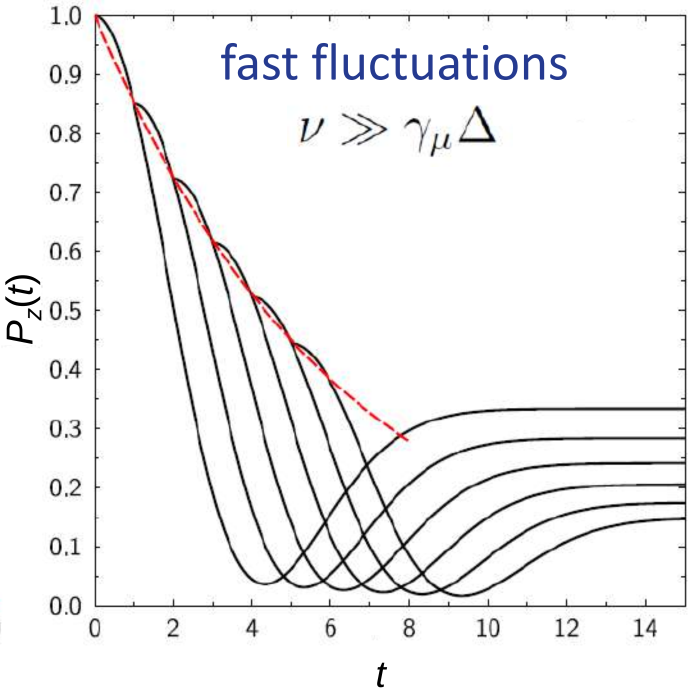
$$\lambda = \gamma_\mu^2 \int_0^\infty \langle B_{loc}^+(t) B_{loc}^-(0) \rangle \, \mathrm{e}^{-i\omega_L t} \mathrm{d}t$$

spectral density

$$\langle B_{loc}^+(t) B_{loc}^-(0) \rangle = \Delta^2 \mathrm{e}^{-\nu t} \quad \Rightarrow \quad \lambda = \frac{\gamma^2 \Delta^2 \nu}{\nu^2 + \gamma^2 B_0^2}$$

relaxation of the "tail"





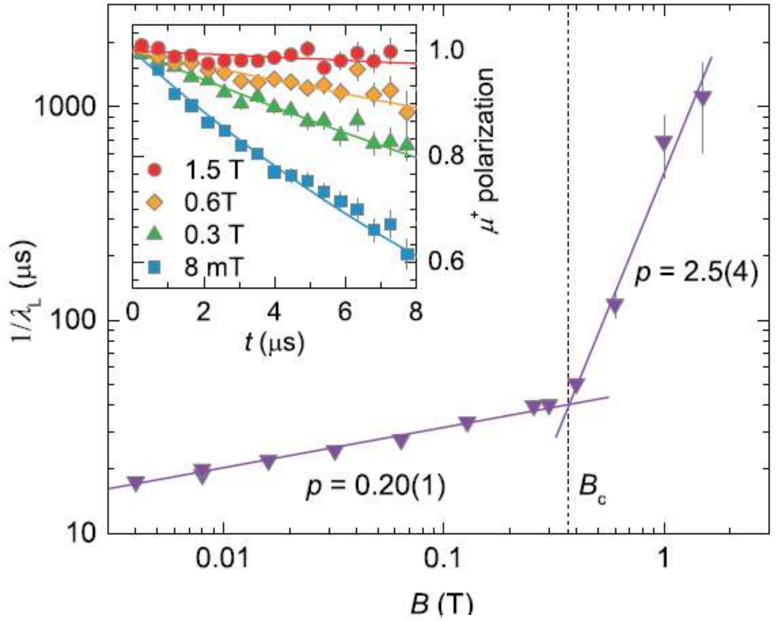
exchange narrowing

$$P_z(t) = \mathrm{e}^{-\lambda t}$$

μSR: Dynamic Fields

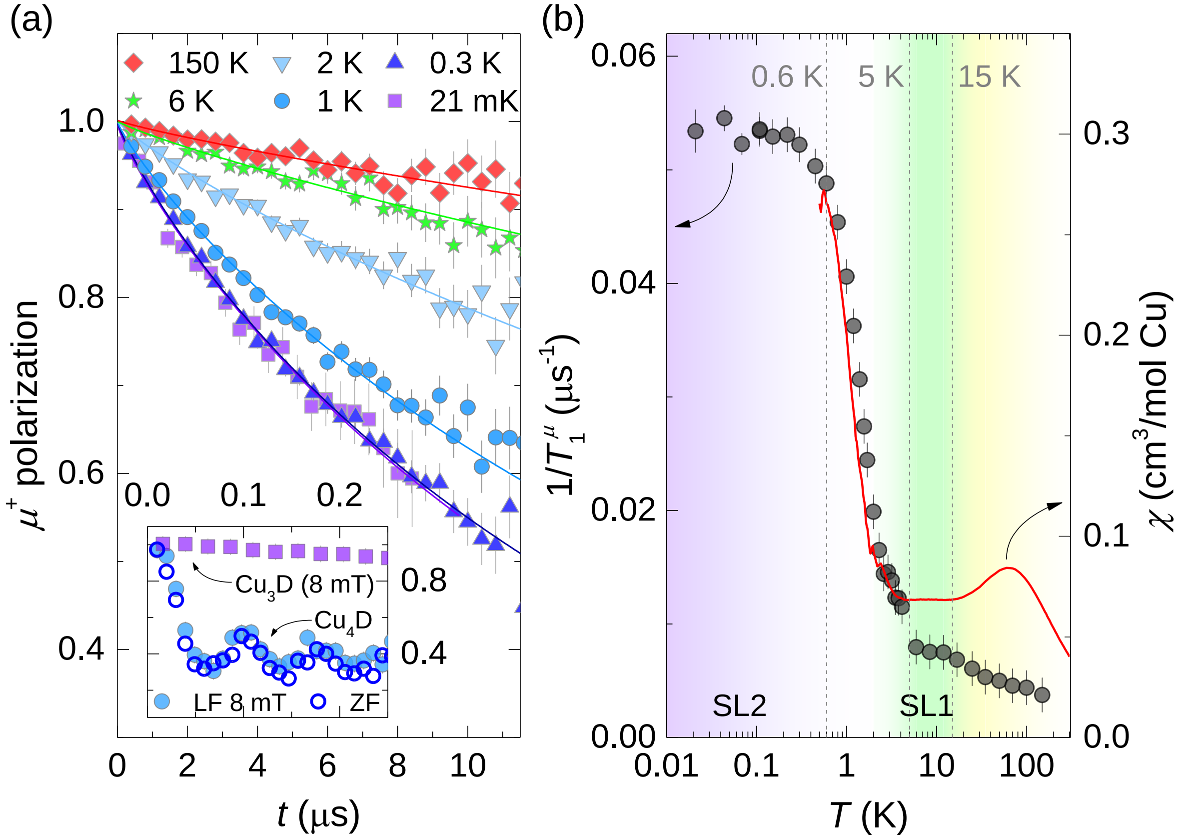
- Monotonic $P_z(t)$: fingerprint of a dynamical state (e.g., QSL)
- Field dependence of λ: energy dependence of the spectral density of fluctuations

Zn-brochantite: distorted KAFM (spinon FS QSL)



$$S(\omega) \propto \omega^{-0.2} \;\Rightarrow\; \langle B(t)B(0)\rangle \propto t^{-0.8}$$

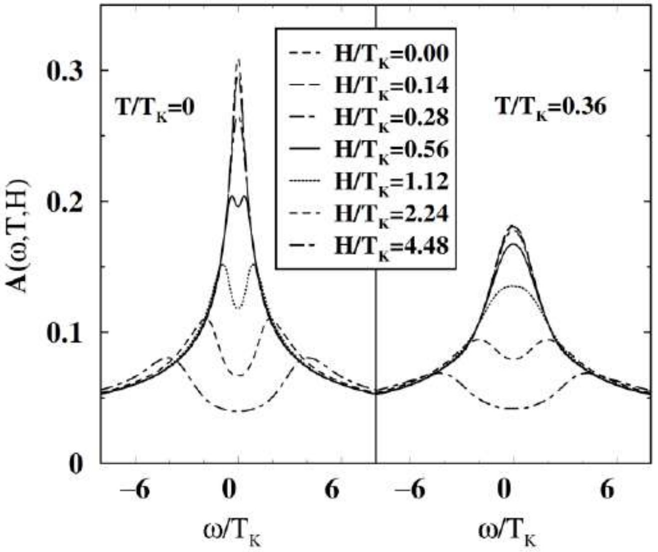
Gomilšek *et al.*, Phys. Rev. B **94**, 024438 (2016)



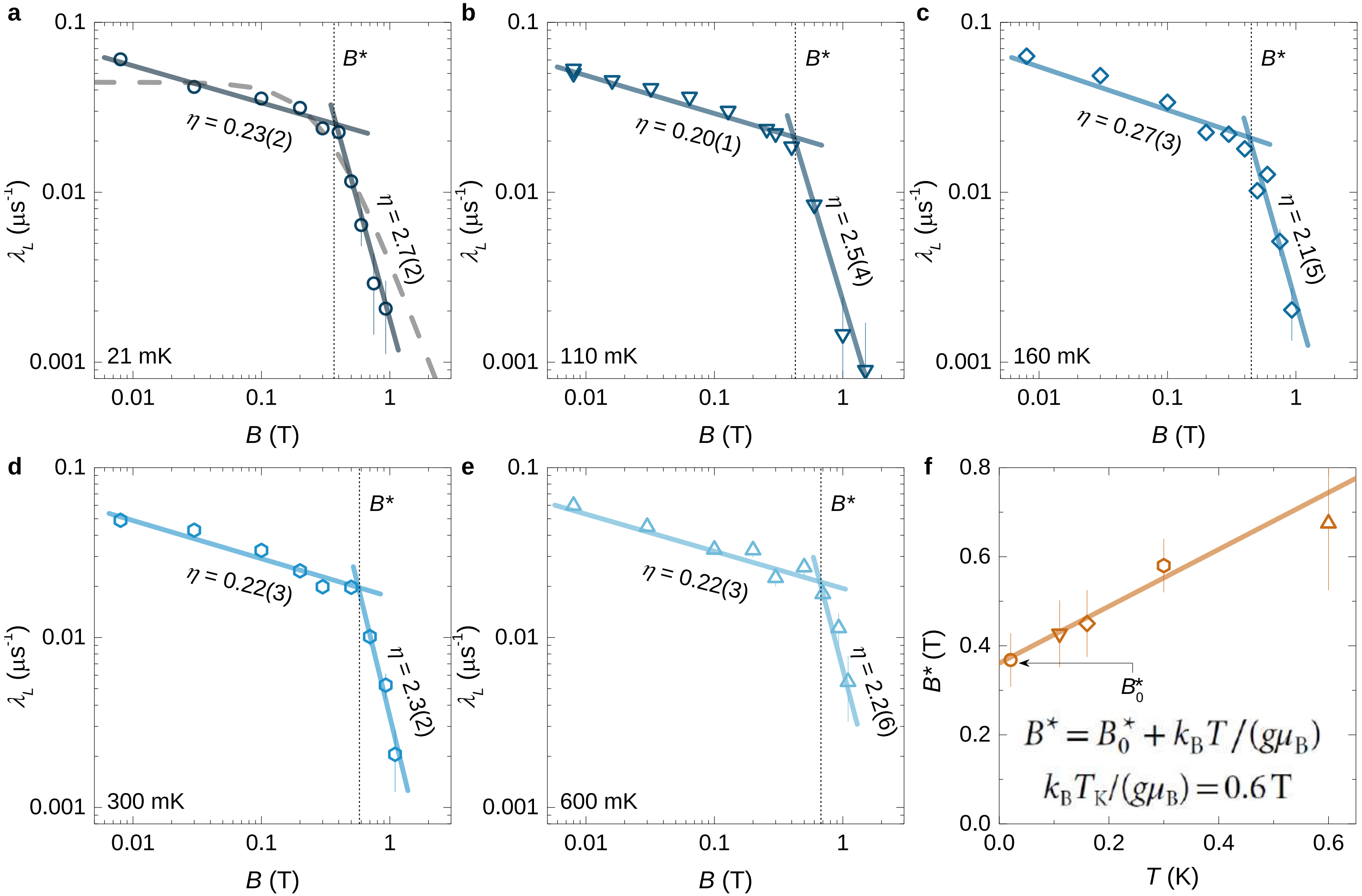
Gomilšek *et al.*, Phys. Rev. B **93**, 060405(R) (2016)

μSR: Dynamic Fields

- Changes in spin excitations: Kondo-resonance splitting
  - ➢ decrease of local DOS at the Fermi level
  - ➢ finite critical field linear in *T*



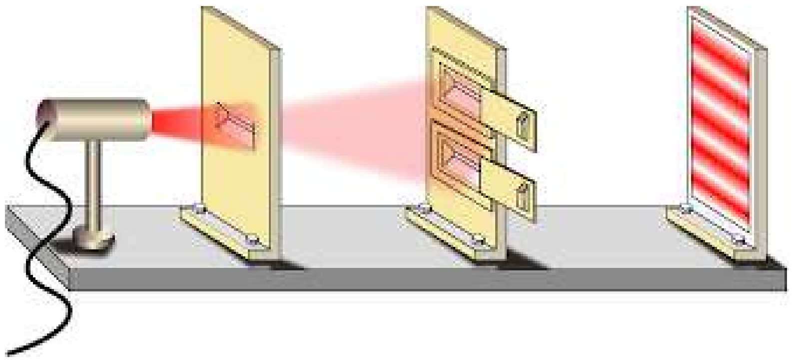
Costi *et al.*, PRL **85**, 1504 (2000)



Gomilšek *et al.*, Nat. Phys. **15**, 754 (2019)

Outline

- ❑ Introduction to magnetism
- ❑ Probing magnetism: conventional bulk and scattering techniques
- ❑ Local probes of magnetism
- ❑ Electron spin resonance (ESR)
- ❑ Nuclear magnetic resonance (NMR)
- ❑ Muon spectroscopy (μSR)
- ❑ Summary: strengths, limitations and complementarity of local probes



Summary: STRENGTHS and LIMITATIONS

	ESR	NMR	μSR
Sample	ESR lines not too broad (bulk samples)	many available nuclei (bulk samples)	any sample (thin-films possible, ~0.01μ_B)
Acquisition	a few minutes	a few hours	tens of minutes
Probe location	on magnetic site	close-far from magnetism	not exactly known
Probe coupling	direct (?)	hyperfine, 0.1-10 T/μ_B	dipolar, 0.01-0.1 T/μ_B
Signal relaxation	only extremely "slow" relaxa-tions can be measured	slow relaxation (infinite acq.) fast relaxation (deadtime μs)	slow relaxation (muon decay) fast relaxation (deadtime ns)
T-range	0.35 – 1000 K (polarization decreases with *T*)	0.02 – 1000 K (polarization decreases with *T*)	0.02 – 800 K constant polarization
B-range	0.1 – 45 T finite B_0 might affect physics	1 – 45 T finite B_0 might affect physics	0 – 9.5 T inherent polarization (ZF exp.)
Perturbation	non-perturbative	non-perturbative	muon = charge defect
Cost	low cost	low cost	large-scale facilities (high cost)

Summary: Complementarity

❑ Time windows: spin dynamics

- slow fluctuations: $\frac{1}{T_1} \propto \nu$
- fast fluctuations: $\frac{1}{T_1} \propto \frac{(\gamma A)^2}{\nu}$

$$\frac{A_{\mathrm{NMR}}}{A_{\mu\mathrm{SR}}} \sim 10 - 100 \qquad \frac{\gamma_{\mathrm{NMR}}}{\gamma_{\mu\mathrm{SR}}} \sim \frac{1}{10}$$

- ESR: $\Delta B > 0.3\,\mathrm{mT}$

$$\frac{1}{T_1^{\mathrm{ESR}}} < 100\,\mathrm{ns}$$

- Combination of techniques: complementary insights