Title: NMR and Frustrated Magnetism

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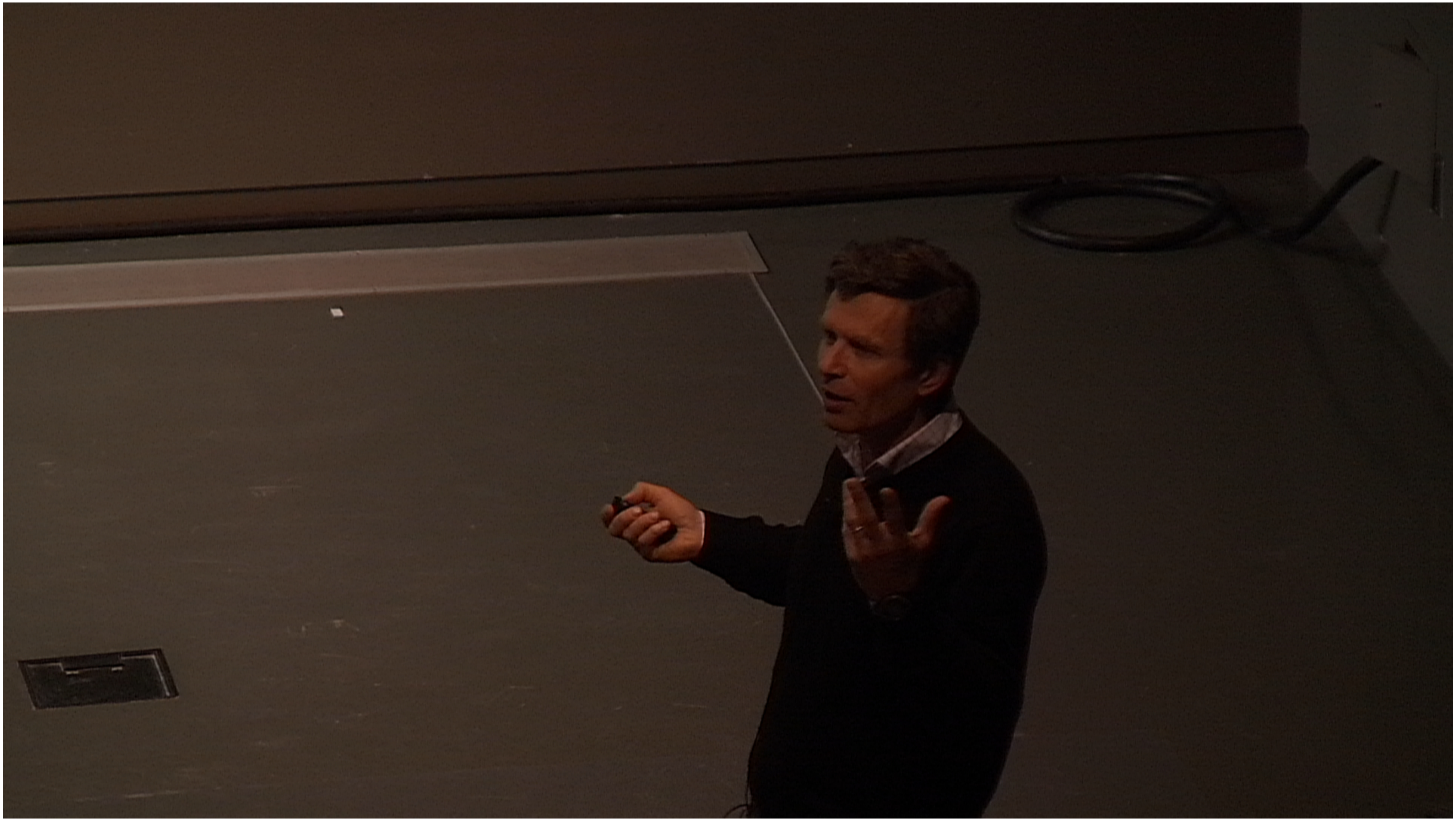
Abstract:



# NMR and Frustrated Magnetism

P. Mendels
Lab. Physique des solides
Univ. Paris-Sud Orsay

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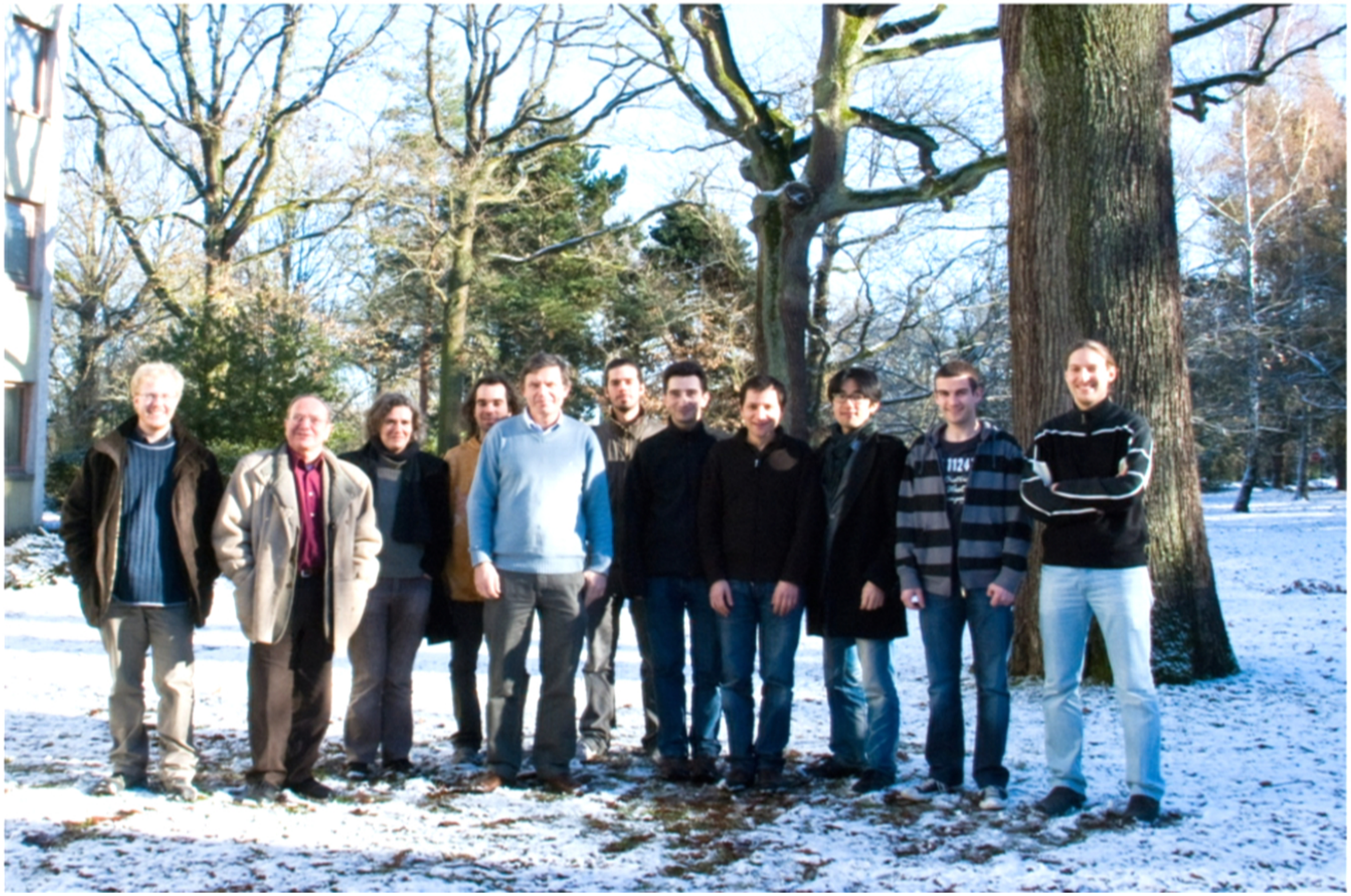

# NMR and Frustrated Magnetism

# NMR, in the world of resonance techniques: Mössbauer, µSR, ESR

(for solid- state physics ⊕ magnetism)

- All probes are resonant bulk, local probes: integrate over q, similar coupling formalism for NMR, Mössbauer and µSR
- Difference through (i) the coupling to the environment

  (ii) the time window, the field range

  (iii) sensitivity and pulsed versus continuum

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Zeeman,
Nobel Physics 1902

Rabi,
Nobel Physics 1944

Nuclear spin
Electronic spin

- Field induced splitting of the levels: transition $\nu_{res} \sim H_0 + \delta H_{local}$
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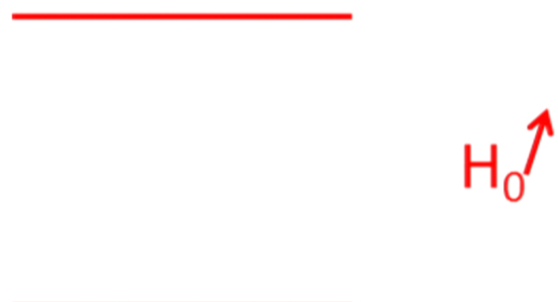


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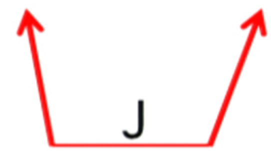
- *ESR: acts on the electronic spin*

  More involved treatment

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  - ✓ Sweep the frequency at a fixed external field
  - ✓ Sweep the field at a constant frequency
  - ✓ Sometimes, no need of an applied field

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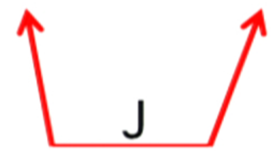


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# Outline of the presentation

- Basics: energy levels, coupling Hamiltonian, quadrupolar effects
- Static local studies: shift, site-resolved, magnetic ordering, structural effects, spin textures...
- Dynamical studies: $T_1$, ($T_2$), wipe out
- Comparison with μSR

Selected examples

What do we look at ~ what we see in papers

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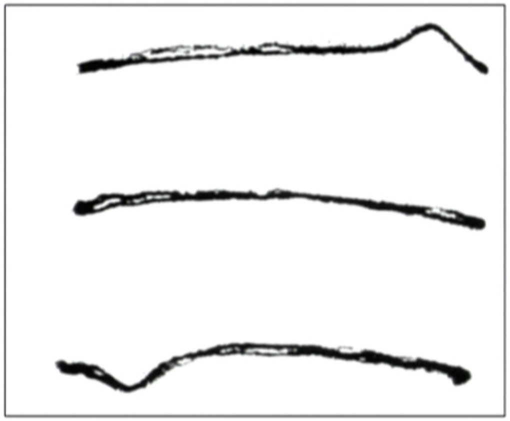
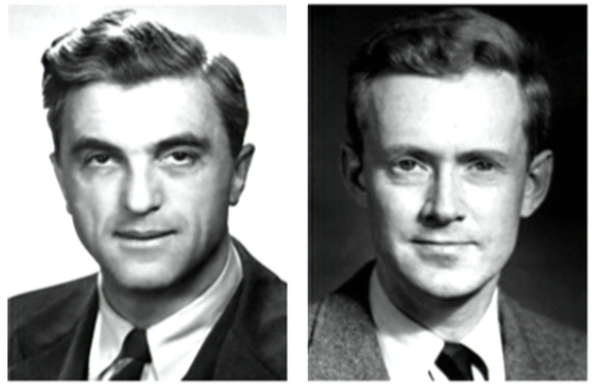
# NMR: milestones (1)





Bloch & Purcell,
Nobel Physique 1952

Ernst,
Nobel Chemistry 1991

Wuthrich,
Nobel Chemistry 2002

Lauterbur & Mansfeld,
Nobel Medecine 2003

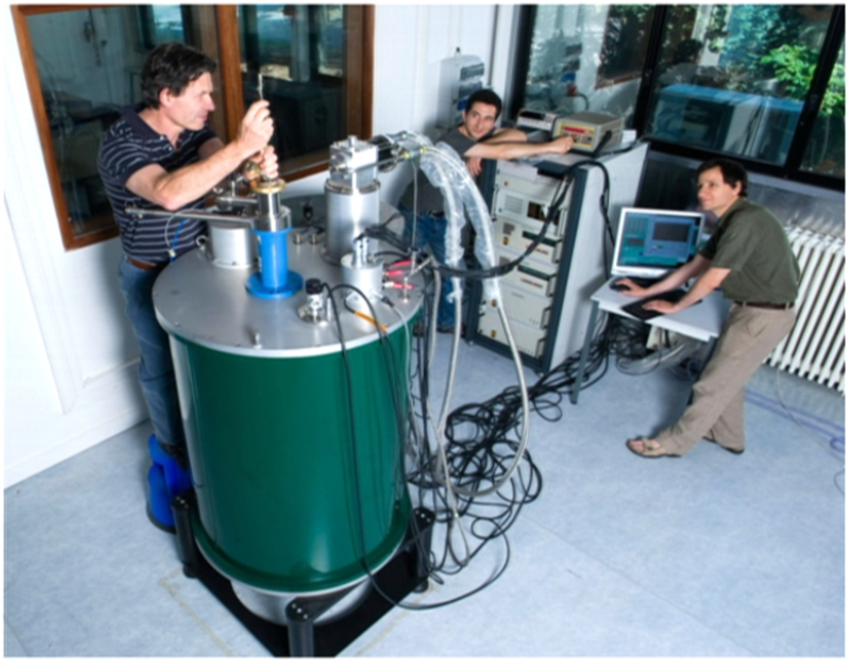
# NMR: milestones (2)

# NMR for chemistry


7 Tesla


23 Tesla

# Our cryofree 14 T magnet; room-T bore



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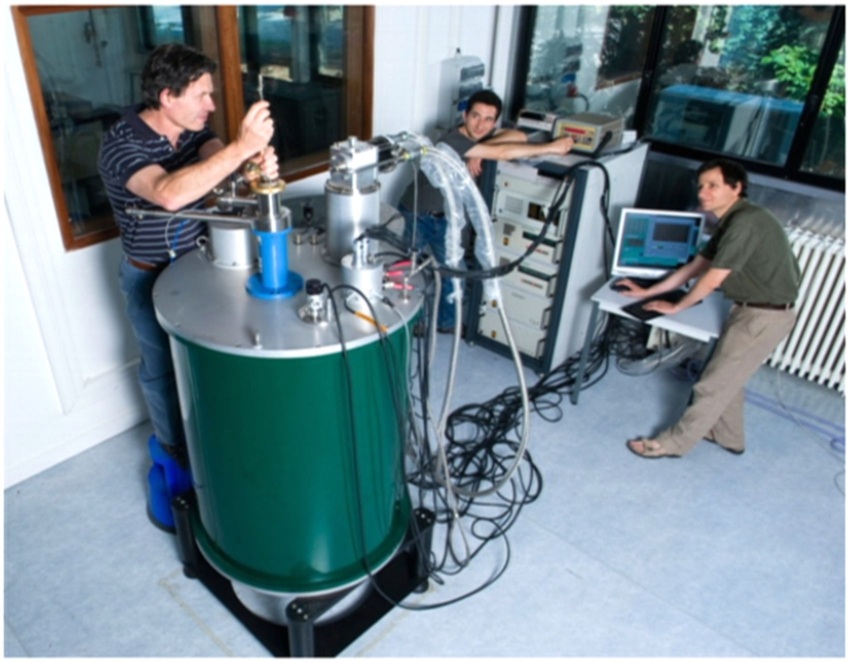
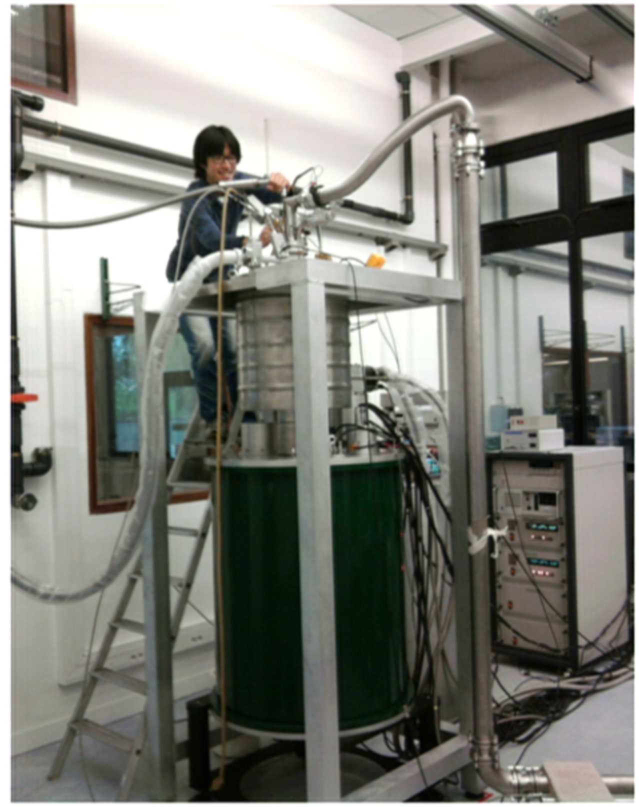
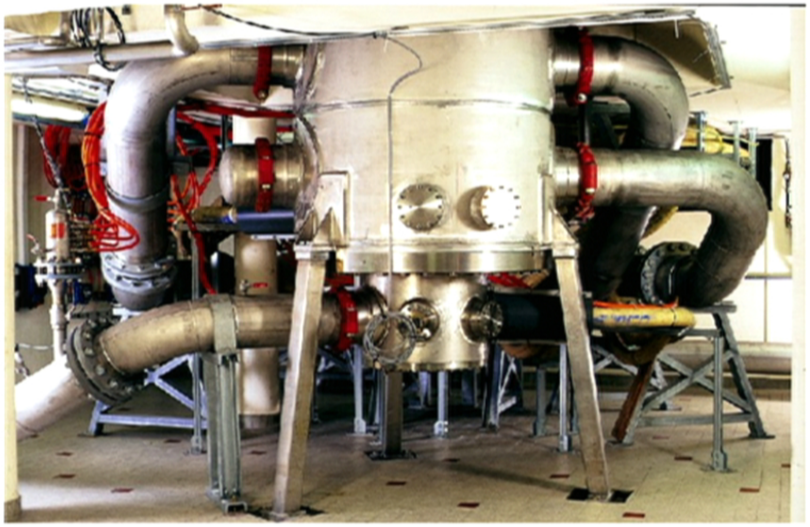




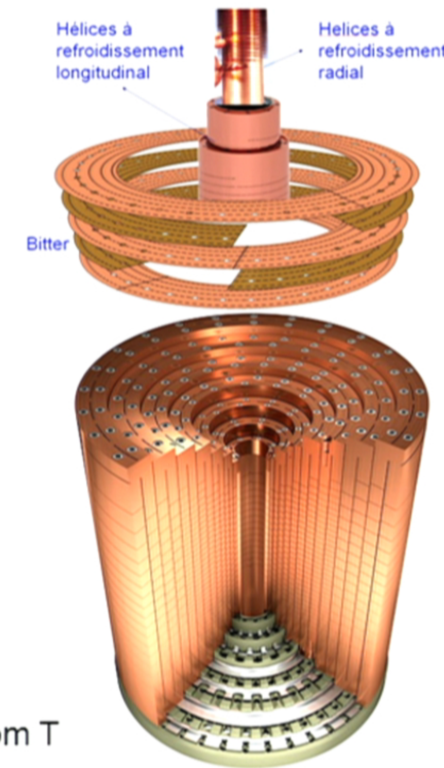
# NMR in High Magnetic Fields

## Grenoble

**$H_{max}$ = 35 Tesla (steady, 24 MW)**



M9 magnet, 34 mm bore :
$\Delta B/B$ = 700 ppm within 1 $cm^3$ sphere (radius = 6.2 mm)
time fluctuations can be stabilized by NMR spin-lock at room T




## Tallahassee: 45 T

# NMR basic principles (1)

Nuclear spin I in a magnetic field $H_0$

*Zeeman effect* : $H = - \mu.\mathbf{H_0} = - \gamma \hbar \; H_0 \; I_z$

Energy levels $E = - m \gamma \hbar H_0$ , $m=-I, -I+1 \ldots I-1, I$

ZFNMR: impossible, not common, also NQR

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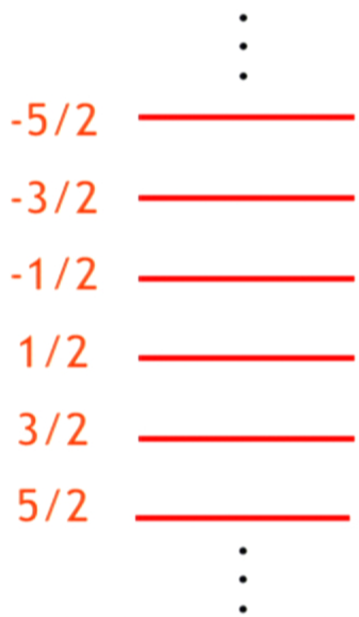


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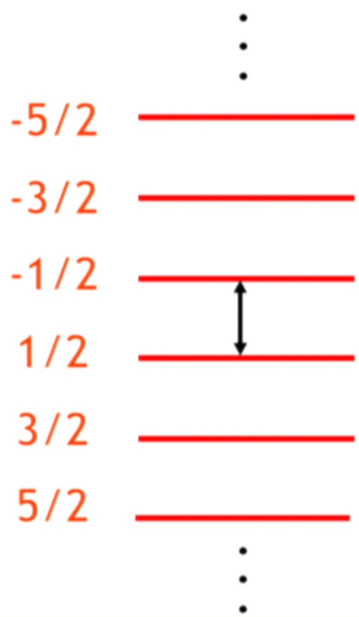


$\Delta E = \hbar\gamma H_0 = h\nu$

Need for r.f. field $h_1(\nu)$

$h_1 \perp H_0$

$H = -\mu.(\mathbf{H_0} + \mathbf{h_1})$

$= -\gamma\hbar\ (H_0 I_z + h_1 I_x)$

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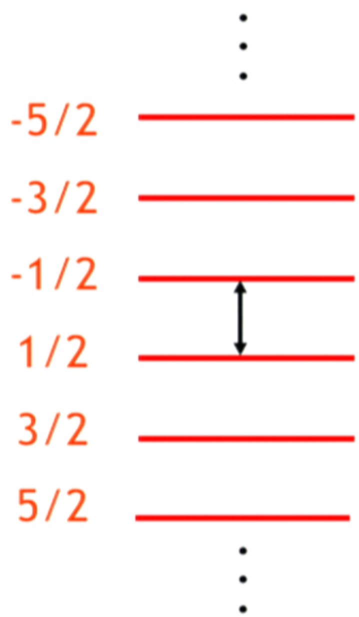


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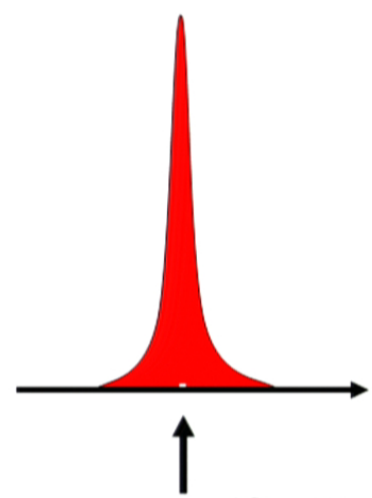

$\nu_{NMR} = \gamma/2\pi\ H_0$

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# NMR basic principles (2)

Nuclear spin I in a magnetic field $H_0$ ⊕ r.f. field $h_1$

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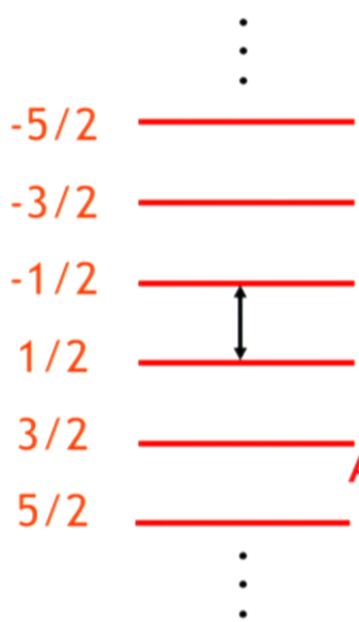
Energy levels $E = -m\gamma\hbar H_0$ , $m=-I, -I+1 \ldots I-1, I$

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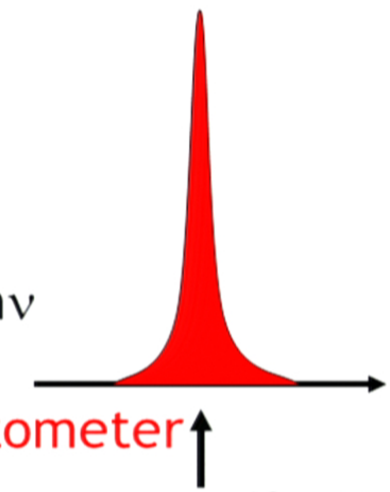

An accurate magnetometer

$\nu_{NMR} = \gamma/2\pi\, H_0$

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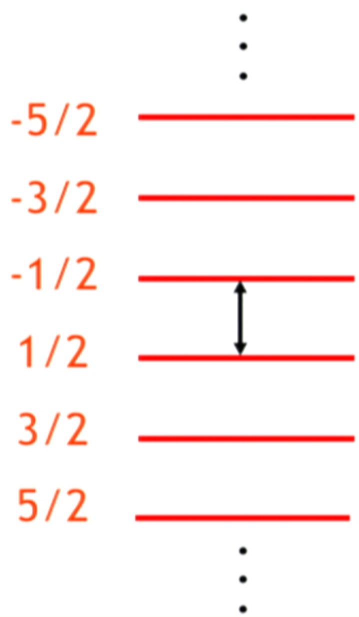
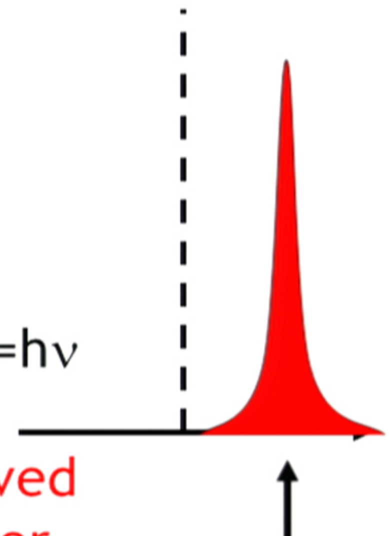



$\Delta E = \hbar\,\gamma\, H_{local} = h\nu$

Spatially resolved magnetometer



$\nu_{NMR} = \gamma/2\pi\,(H_0 + \delta H_{local})$

ZFNMR: impossible, not common, also NQR

# Which nuclei ?

Nuclear magnetic moment $\vec{M}=\gamma\hbar\vec{I}$

## Common NMR Active Nuclei

| Isotope | Spin $I$ | %age abundance | $\gamma$ MHz/T |
|---|---|---|---|
| $^{1}H$ | 1/2 | 99.985 | 42.575 |
| $^{2}H$ | 1 | 0.015 | 6.53 |
| $^{13}C$ | 1/2 | 1.108 | 10.71 |
| $^{14}N$ | 1 | 99.63 | 3.078 |
| $^{15}N$ | 1/2 | 0.37 | 4.32 |
| $^{17}O$ | 5/2 | 0.037 | 5.77 |
| $^{19}F$ | 1/2 | 100 | 40.08 |
| $^{23}Na$ | 3/2 | 100 | 11.27 |
| $^{31}P$ | 1/2 | 100 | 17.25 |

1 – 40 MHz / Tesla

Resonance are in the EM (radiofrequency) range!

# Which nuclei ?

***eNMR***

**NMR Periodic Table**

| Group | I | II | | IIIa | IVa | Va | VIa | VIIa | VIIIa | VIIIb | VIIIc | IB | IIB | III | IV | V | VI | VII | VIII |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Period | | | | | | | | | | | | | | | | | | | |
| 1 | 1 H | | | | | | | | | | | | | | | | | | 2 He |
| 2 | 3 Li | 4 Be | | | | | | | | | | | | 5 B | 6 C | 7 N | 8 O | 9 F | 10 Ne |
| 3 | 11 Na | 12 Mg | | | | | | | | | | | | 13 Al | 14 Si | 15 P | 16 S | 17 Cl | 18 Ar |
| 4 | 19 K | 20 Ca | | 21 Sc | 22 Ti | 23 V | 24 Cr | 25 Mn | 26 Fe | 27 Co | 28 Ni | 29 Cu | 30 Zn | 31 Ga | 32 Ge | 33 As | 34 Se | 35 Br | 36 Kr |
| 5 | 37 Rb | 38 Sr | | 39 Y | 40 Zr | 41 Nb | 42 Mo | 43 Tc | 44 Ru | 45 Rh | 46 Pd | 47 Ag | 48 Cd | 49 In | 50 Sn | 51 Sb | 52 Te | 53 I | 54 Xe |
| 6 | 55 Cs | 56 Ba | * | 71 Lu | 72 Hf | 73 Ta | 74 W | 75 Re | 76 Os | 77 Ir | 78 Pt | 79 Au | 80 Hg | 81 Tl | 82 Pb | 83 Bi | 84 Po | 85 At | 86 Rn |
| 7 | 87 Fr | 88 Ra | ** | 103 Lr | 104 Unq | 105 Unp | 106 Unh | 107 Uns | 108 Uno | 109 Mt | 110 Uun | 111 Uuu | 112 Uub | 113 Uut | 114 Uuq | 115 Uup | 116 Uuh | 117 Uus | 118 Uuo |
| | | | | | | | | | | | | | | | | | | | |
| *Lanthanides | | | * | 57 La | 58 Ce | 59 Pr | 60 Nd | 61 Pm | 62 Sm | 63 Eu | 64 Gd | 65 Tb | 66 Dy | 67 Ho | 68 Er | 69 Tm | 70 Yb | | |
| **Actinides | | | ** | 89 Ac | 90 Th | 91 Pa | 92 U | 93 Np | 94 Pu | 95 Am | 96 Cm | 97 Bk | 98 Cf | 99 Es | 100 Fm | 101 Md | 102 No | | |

| Nuclear Spins | 1/2 | 1 | 3/2 | 5/2 | 7/2 | 9/2 |
|---|---|---|---|---|---|---|

Many resident nuclei sensitivity detection pbs

# Experimental set-ups

Field range: 1T – 45 T (homogeneity tens ppm → ppm)

T-range: 10 mK – 1000 K

Sensitivity: 1 mMole... depends on sensitivity: $\gamma$, $H^2$

Misc: pressure (few GPa), in-situ rotation

# NMR basics (3): the chemistry side

***With NMR we study the time evolution of nuclear magnetization, driven by the hyperfine interactions…***

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{n-n} + \mathcal{H}_{n-e} + \mathcal{H}_{EFG}$$

$$\mathcal{H}_Z = -\gamma\hbar \sum_i I_z^i H_0 \ .$$

$$\mathcal{H}_{n-n} = \sum_{j<k} \frac{\hbar^2\gamma^2}{r^3}\Big(A + B + C + D + E + F\Big)_{jk}$$

A very useful tool to determine the chemical bonding

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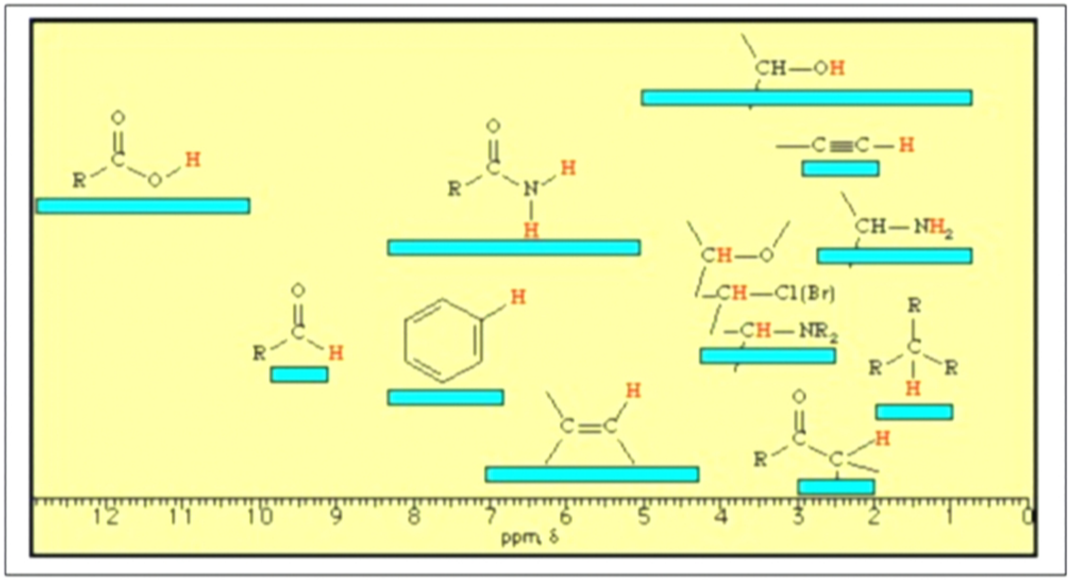
Indirect interaction between nuclear moments (electrons)

Fine structure

A very useful tool to determine the chemical bonding

# Chemical shift (ppm)



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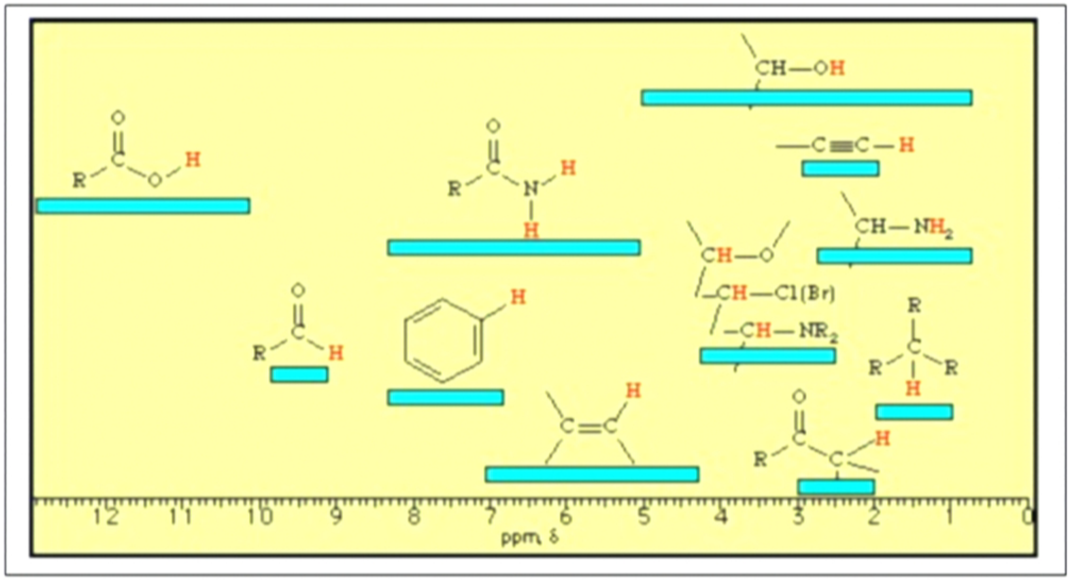

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$$\mathcal{H}_{n-e} = -\gamma\hbar \sum_{i,k} \boldsymbol{I}_i \tilde{A}_{ik} \boldsymbol{S}_k$$

$$\mathcal{H}_{EFG} = \sum_i \frac{e^2 Q V_{ZZ}}{4I(2I-1)} \Big( 3(I_z^i)^2 - I(I+1) + \frac{\eta}{2}[(I_+^i)^2 + (I_-^i)^2] \Big)$$

A very involved Hamiltonian…coupling to electronic moments

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A very involved Hamiltonian…coupling to electronic moments and surrounding charges

# Nucleus – electron coupling

$$H_{hf} = -\hbar^2 \gamma_e \gamma_n \frac{\vec{I}.\vec{l}}{r^3} + \hbar^2 \gamma_e \gamma_n \left[ \frac{\vec{I}.\vec{s}}{r^3} - 3 \frac{\left(\vec{I}.\vec{r}\right)\left(\vec{s}.\vec{r}\right)}{r^5} \right] - \hbar^2 \gamma_e \gamma_n \frac{8\pi}{3} \vec{I}.\vec{s}\, \delta\left(\vec{r}\right)$$

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Orbital effect

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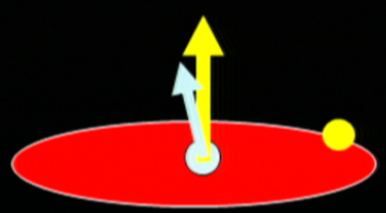

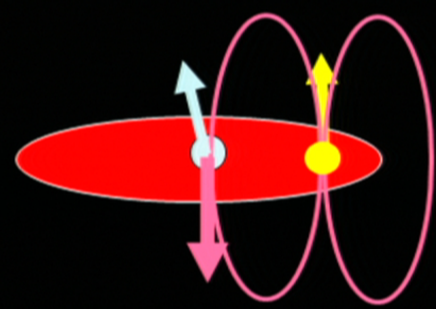

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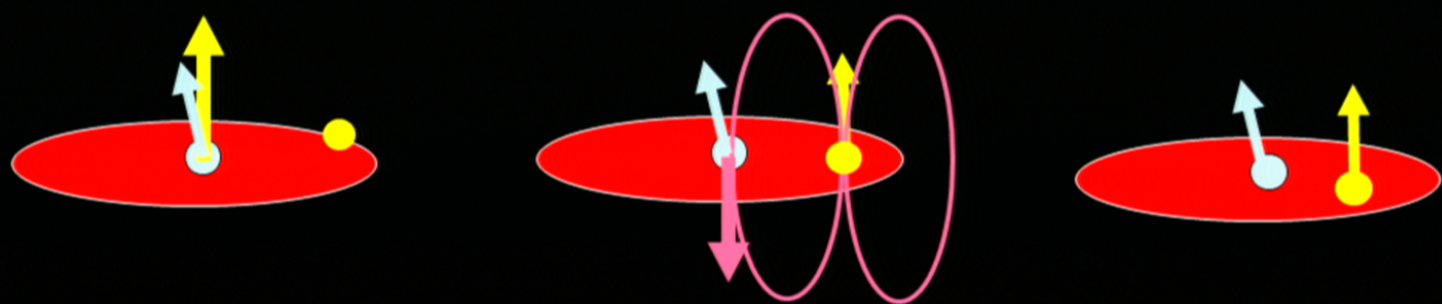
Contact contribution from an
unpaired spin on a s orbital



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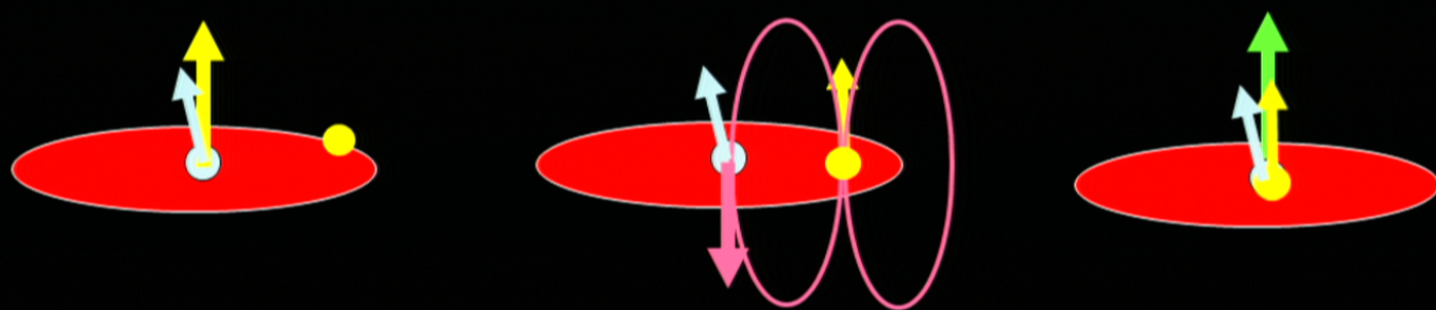


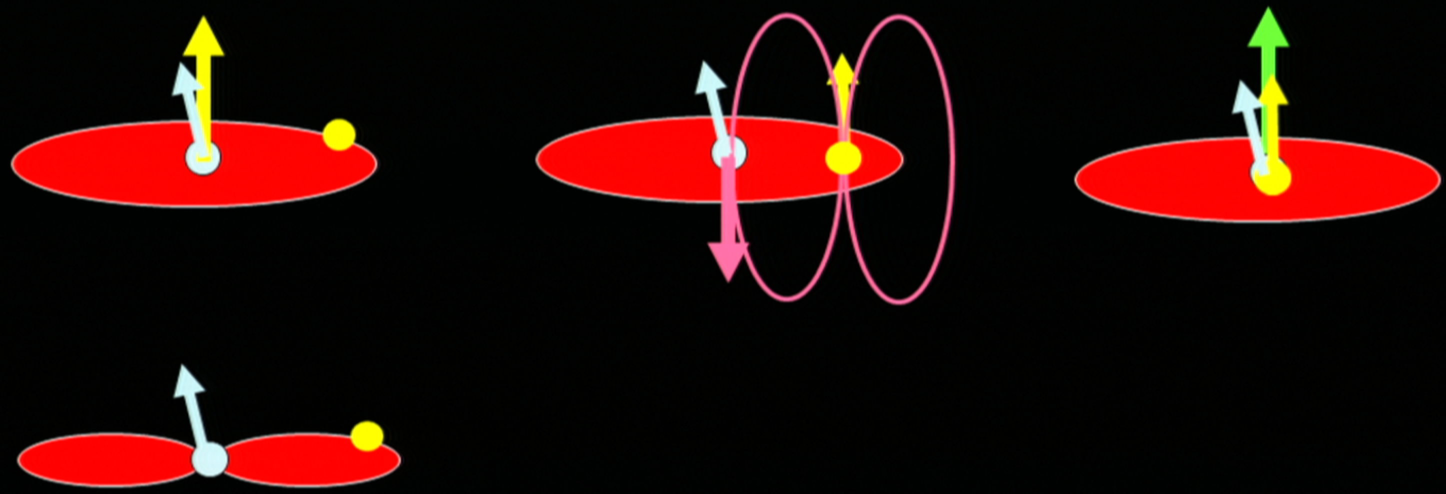
# Nucleus – electron coupling

$$H_{hf} = -\hbar^2 \gamma_e \gamma_n \frac{\vec{I}.\vec{l}}{r^3} + \hbar^2 \gamma_e \gamma_n \left[ \frac{\vec{I}.\vec{s}}{r^3} - 3\frac{\left(\vec{I}.\vec{r}\right)\left(\vec{s}.\vec{r}\right)}{r^5} \right] - \hbar^2 \gamma_e \gamma_n \frac{8\pi}{3} \vec{I}.\vec{s}\,\delta\left(\vec{r}\right)$$

Orbital effect

Dipolar effect from
An unpaired spin

Contact contribution from an
unpaired spin on a s orbital



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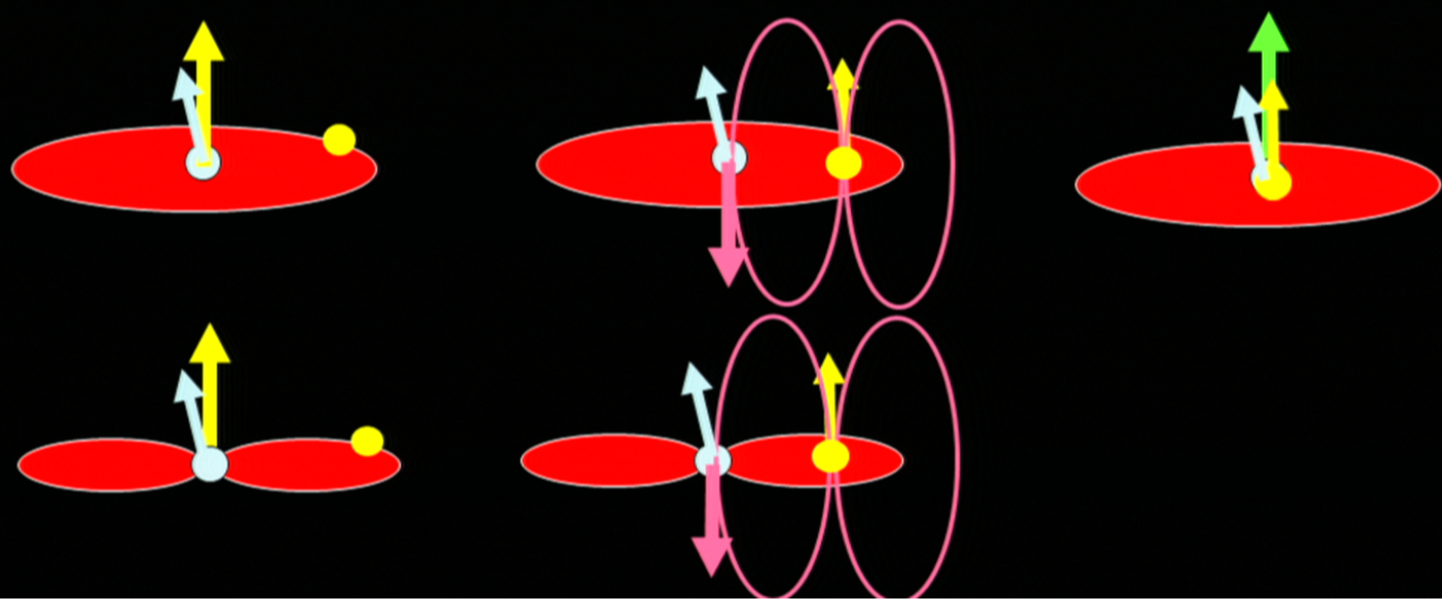

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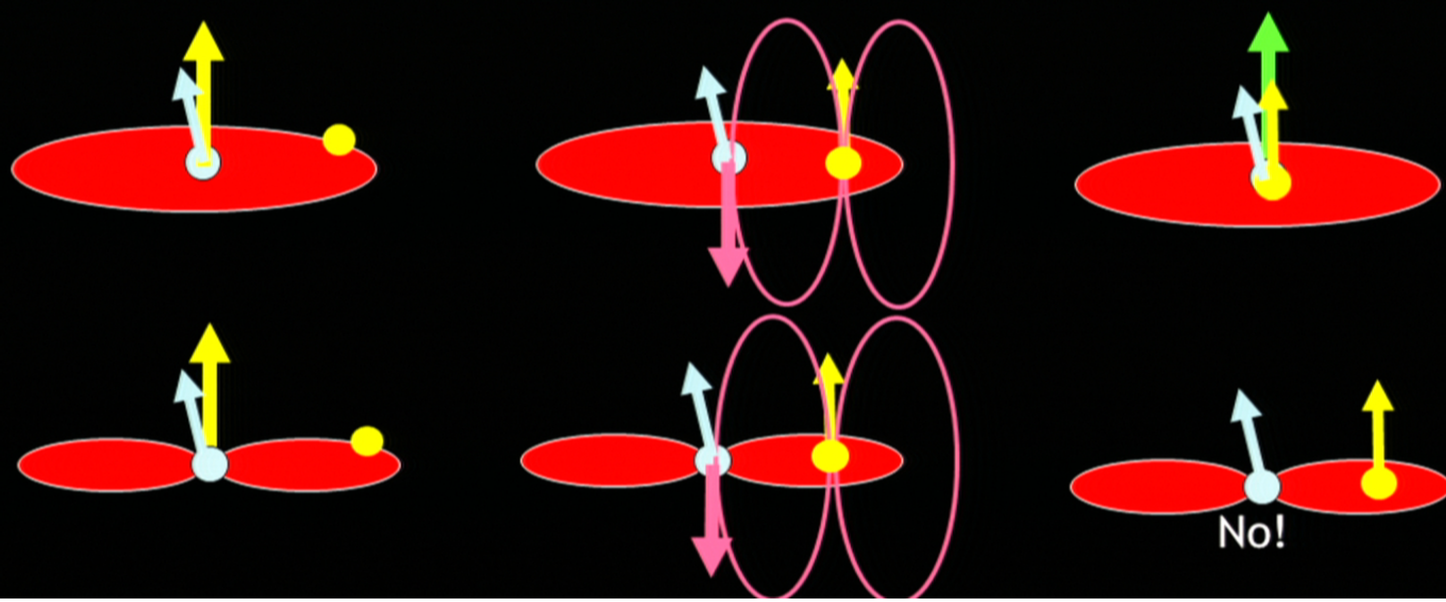

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Orbital effect

Dipolar effect from
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Contact contribution from an
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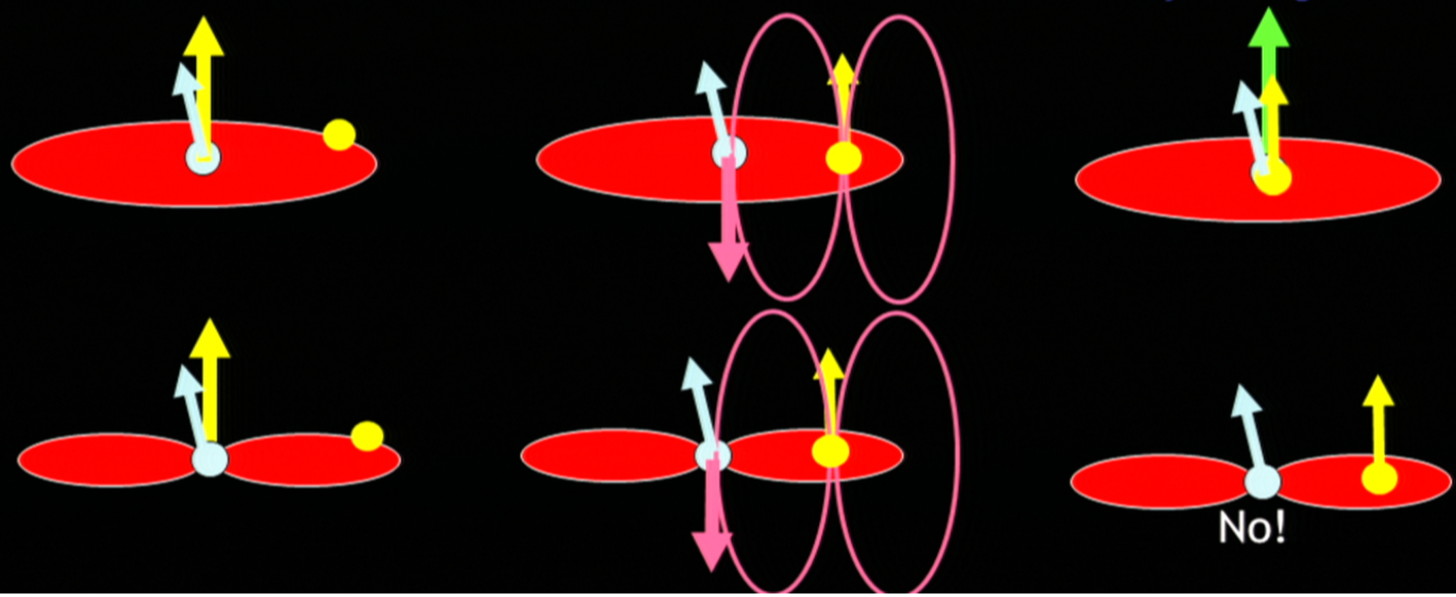
*Very strong - Isotropic*



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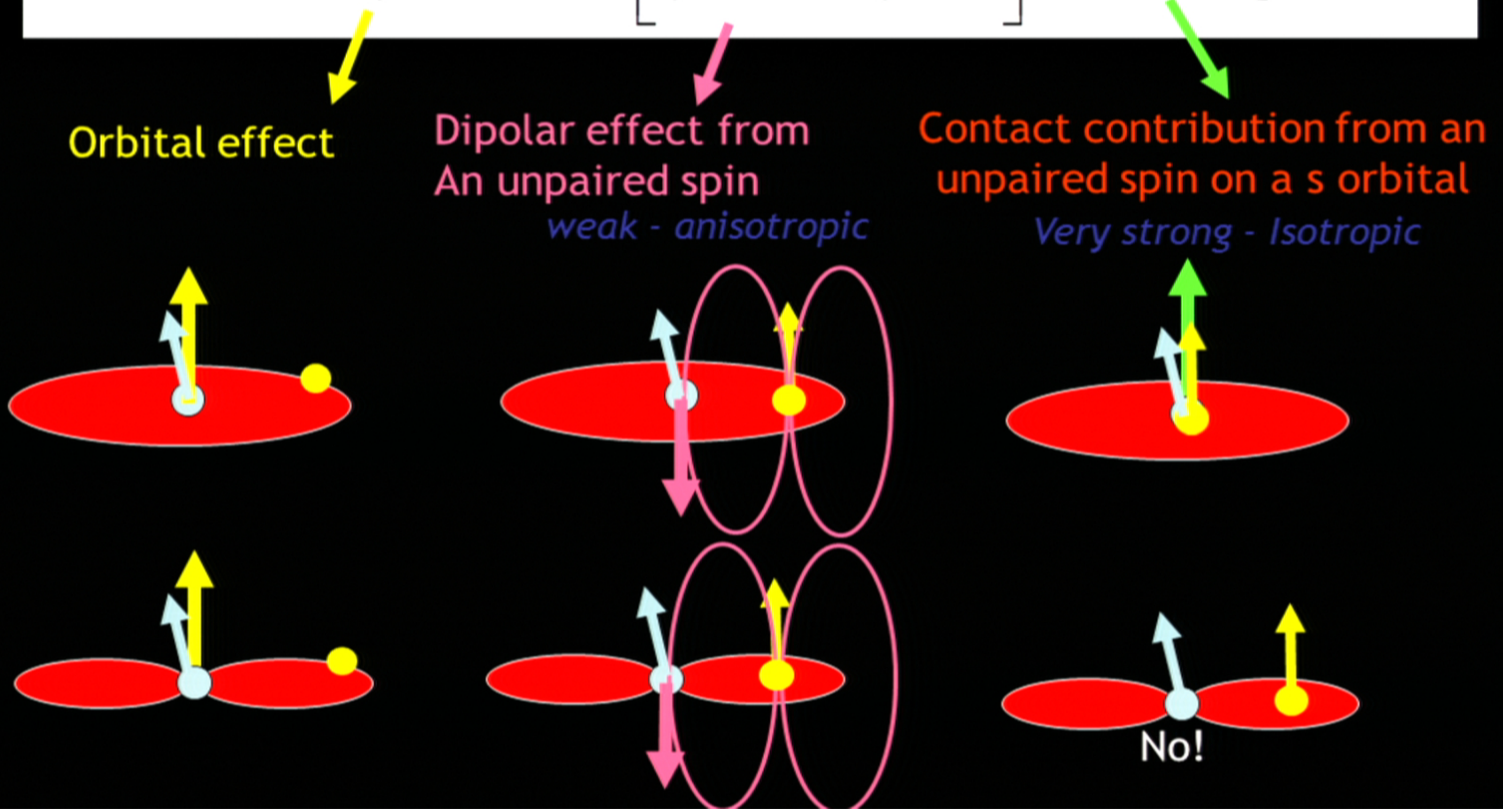

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Orbital effect

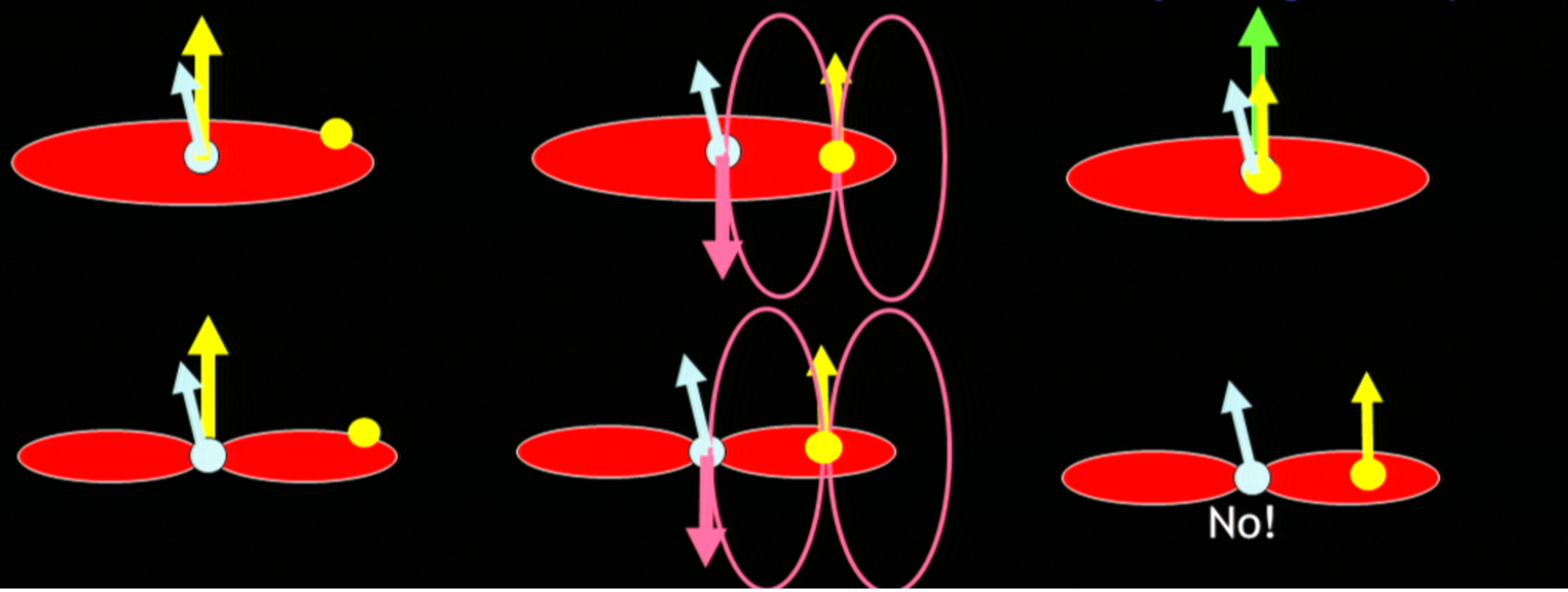
*weak - anisotropic*

Dipolar effect from
An unpaired spin

*weak - anisotropic*

Contact contribution from an
unpaired spin on a s orbital

*Very strong - Isotropic*



# NMR basics (5): nucleus-electron coupling

*(hyperfine interaction)*

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Orbital effect

Spin-dipolar effect from an unpaired spin s

Contact contribution from an unpaired spin on a **s orbital**

$$\nu^i = \frac{\gamma}{2\pi} H_0$$

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$$\nu^{i=x,y,z} = \frac{\gamma}{2\pi}\left(1 + K_{orb}^i + K_{dip}^i + K_{contact} + K_{core-polarization}\right)$$

Gyromagnetic ratio: depends on the nucleus

Orbital shift

Spin shift

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*(hyperfine interaction)*

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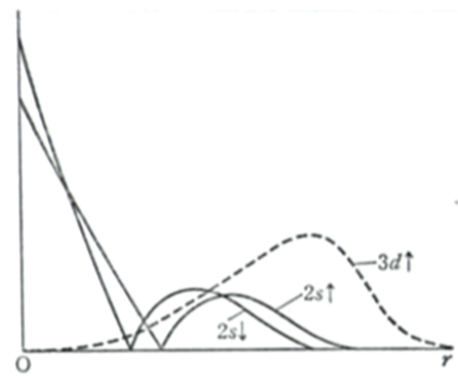
Orbital shift



# Outline of the presentation

- Basics: energy levels, coupling Hamiltonian, quadrupolar effects
- Static local studies: shift, site-resolved, magnetic ordering, structural effects, spin textures...
- Dynamical studies: $T_1$, ($T_2$), wipe out
- Comparison with µSR

# Orbital shift

$$H = -\hbar^2 \gamma_{e^-} \gamma_{nucleus} \frac{\mathbf{I}.\mathbf{L}}{r^3}$$

Orbital shift

- Filled shells
- Unpaired electrons

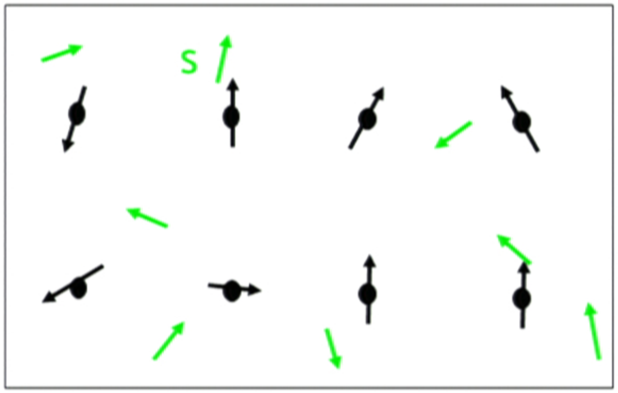
Main features

- **T-independent**
- Tensor: linear response in field, orientation dependent

Information

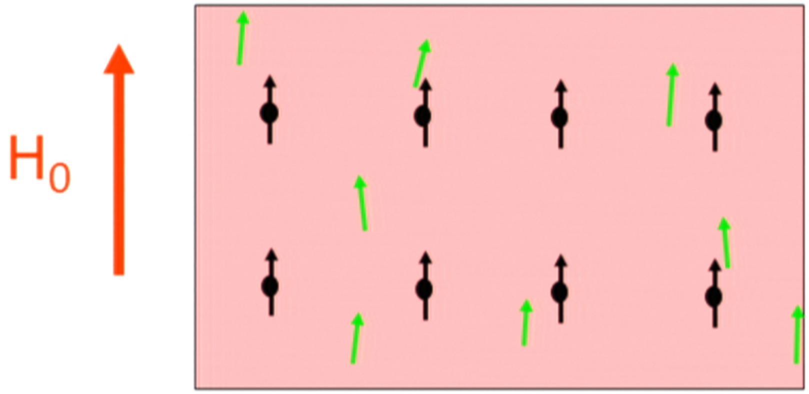
- Nature of **orbitals** (e.g. spin state for 3d elements)
- → **Orbital susceptibility**

# Spin shift




Knight shift = Spin shift for metals

# Spin shift




$$M=\chi H_0$$

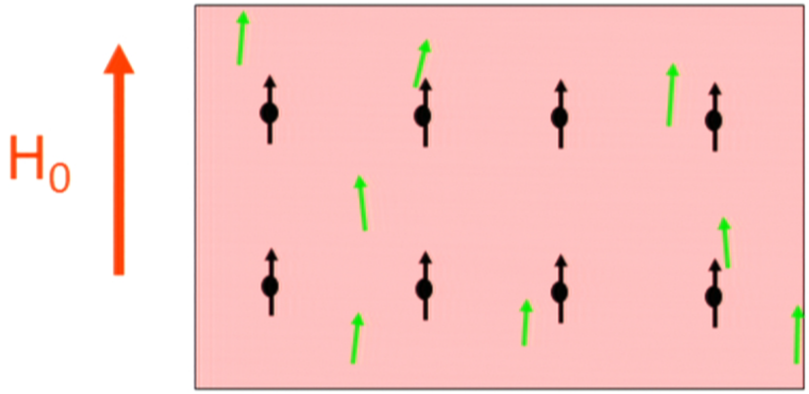
$$H_{loc}=H_0+a\chi_{loc}H_0$$

$$H = A_{hf}\,\vec{I}.\vec{s}$$

$$K_{spin} = A_{hf}\,\frac{1}{\hbar^2\gamma_n\gamma_e}\,\chi_{electron}$$

Knight shift = Spin shift for metals

# Spin shift

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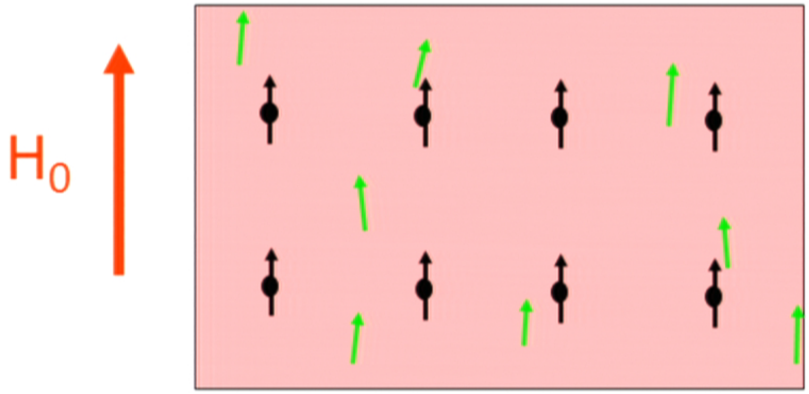



$M=\chi H_0$

$H_{loc}=H_0+a\chi_{loc}H_0$

The spin shift yields the local susceptibility near the nucleus: « atomic » resolved susceptibility susceptibility

$$H = A_{hf}\,\vec{I}.\vec{s}$$

$$K_{spin} = A_{hf}\,\frac{1}{\hbar^2\gamma_n\gamma_e}\,\chi_{electron}$$

Knight shift = Spin shift for metals

# Spin shift

$$H = A_{hf} \vec{I} . \vec{s}$$

Spin shift

- Unpaired electrons

Main features

- **T-dependent**
- Can be anisotropic (susceptibility, hyperfine tensor)

Information

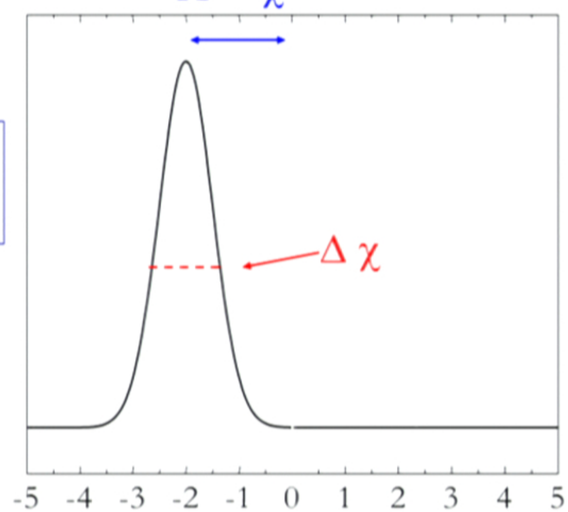
- **Measures the local susceptibility**
- $\rightarrow$ histogram of local environments
- $\rightarrow$ site selective

Knight shift = Spin shift for metals

# Spin shift

$$H = A_{hf} \vec{I} . \vec{s}$$

Line shift **K** : **susceptibility** $\chi_{frustr}$

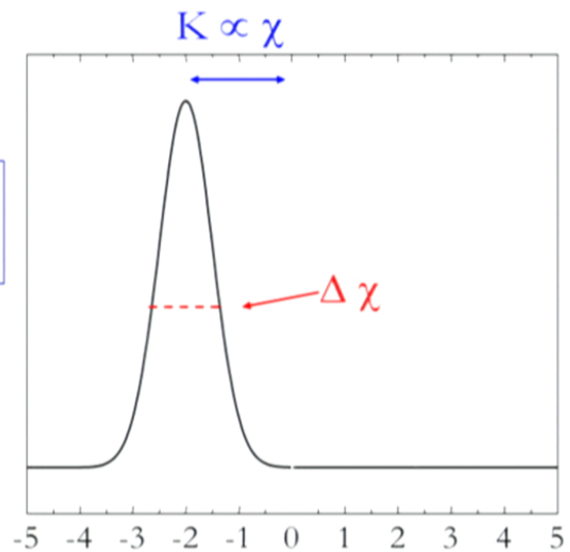



Linewidth ΔH : **spatially inhomogeneous susceptibility** **(spin defects, spin freezing)**

# Spin shift

$$H = A_{hf}\, \vec{I} \cdot \vec{s}$$

Line shift **K** :
**susceptibility** $\chi_{frustr}$

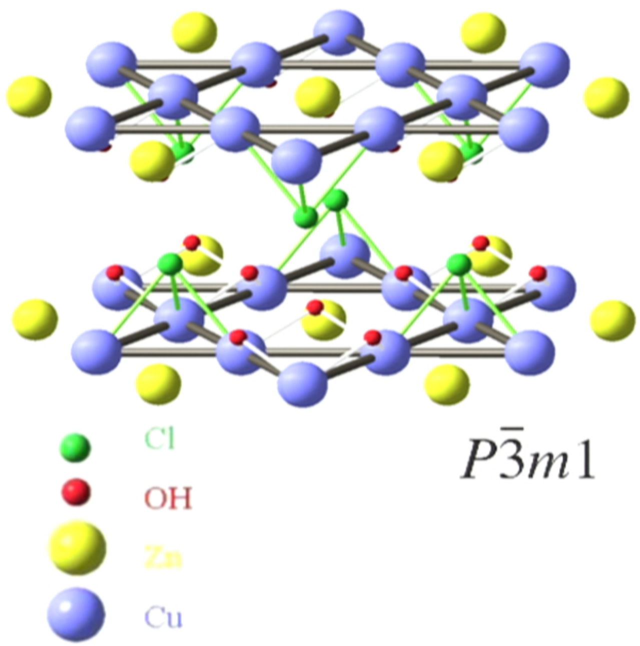


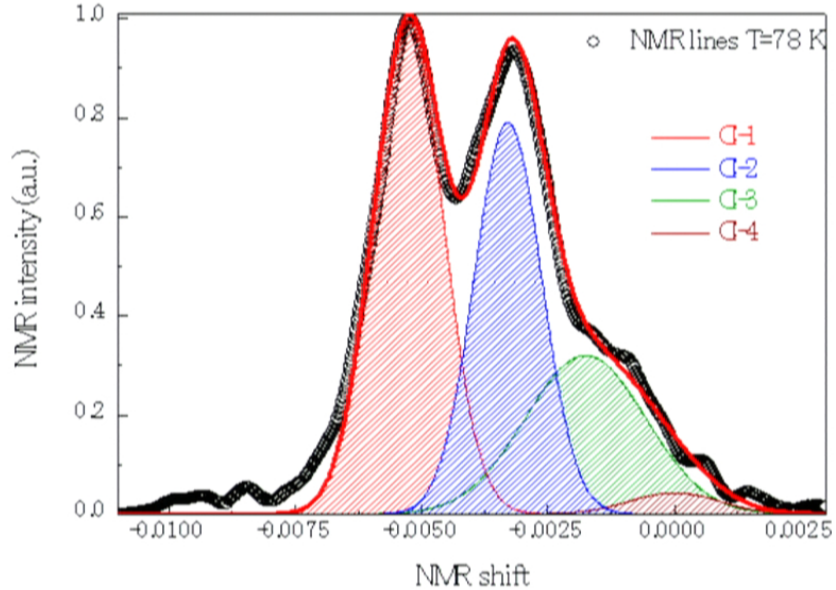

Linewidth $\Delta H$ :
**spatially inhomogeneous susceptibility (spin defects, spin freezing)**

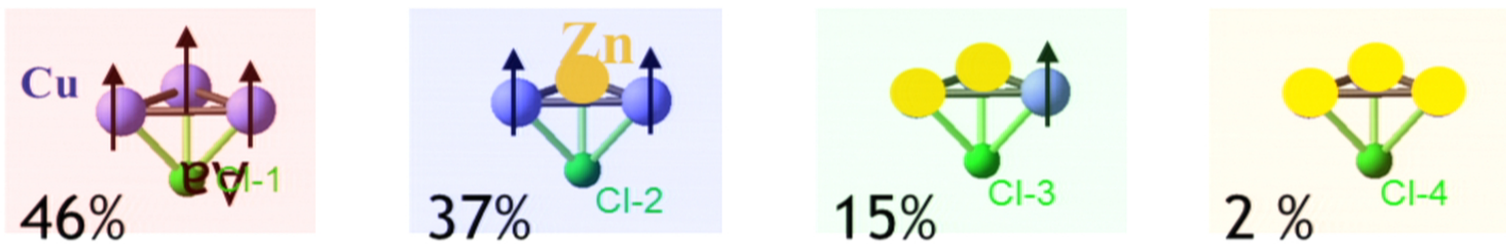
Line shift **K** :
**More advanced**

$$K = \frac{\left(\sum_k \tilde{A}_k \langle \boldsymbol{S}_k \rangle\right)_z}{H_0}.$$

# $^{35}$Cl NMR in Kapellasite




F. Kermarrec (thursday) HFM 2012

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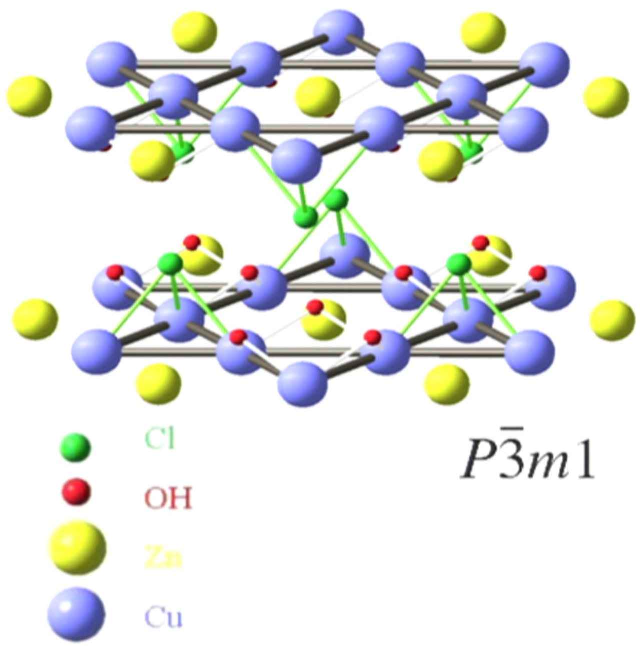


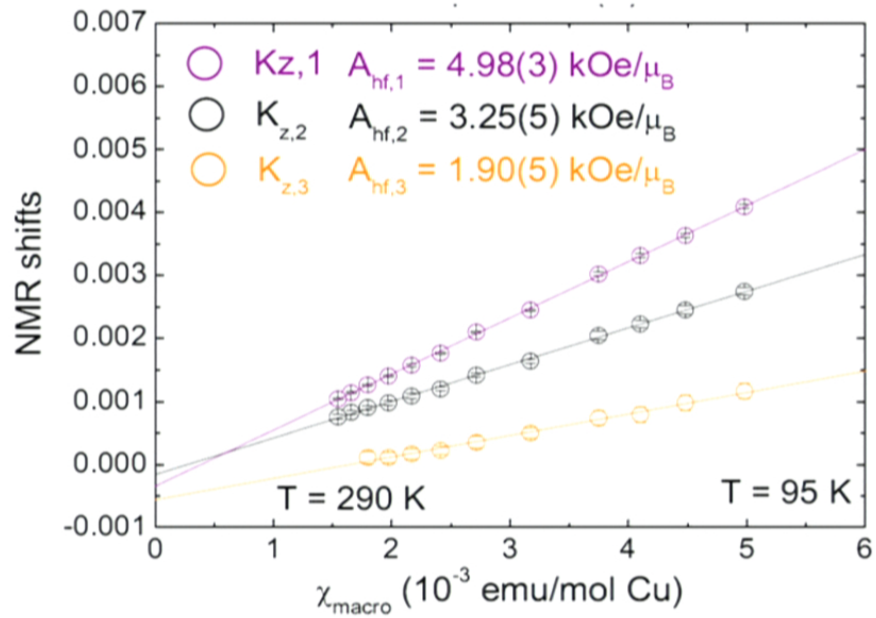


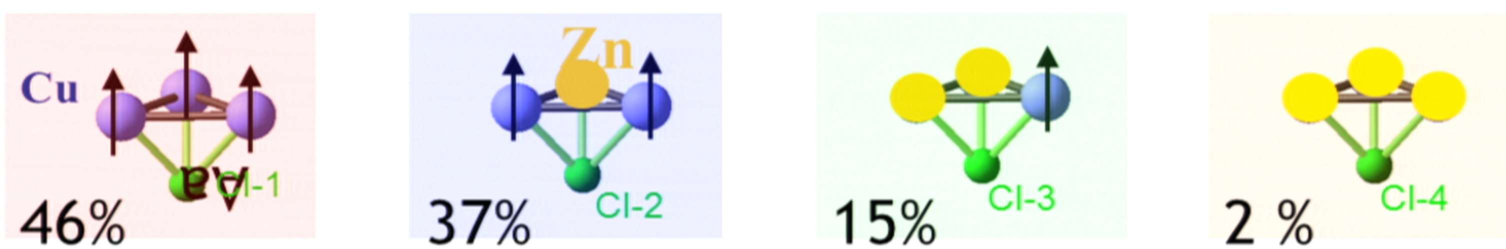


F. Kermarrec (thursday) HFM 2012

# NMR basics (6): nucleus-charges coupling

***With NMR we study the time evolution of nuclear magnetization, driven by the hyperfine interactions…***

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{n-n} + \mathcal{H}_{n-e} + \mathcal{H}_{EFG}$$

$$\mathcal{H}_Z = -\gamma\hbar \sum_i I_z^i H_0 \ .$$

$$\mathcal{H}_{n-n} = \sum_{j<k} \frac{\hbar^2\gamma^2}{r^3} \Big( A + B + C + D + E + F \Big)_{jk}$$

$$\mathcal{H}_{n-e} = -\gamma\hbar \sum_{i,k} \boldsymbol{I}_i \tilde{A}_{ik} \boldsymbol{S}_k$$

$$\mathcal{H}_{EFG} = \sum_i \frac{e^2 Q V_{ZZ}}{4I(2I-1)} \Big( 3(I_z^i)^2 - I(I+1) + \frac{\eta}{2}[(I_+^i)^2 + (I_-^i)^2] \Big)$$

A very involved Hamiltonian, quite rewarding

# Outline of the presentation

- Basics: energy levels, coupling Hamiltonian, quadrupolar effects
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- Comparison with μSR

# NMR basics (6): quadrupole interaction

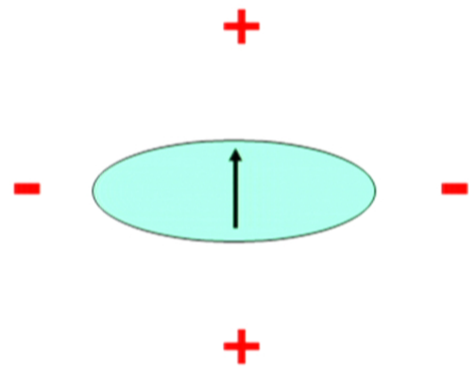
If I>1/2, nuclear spin I is sensitive to any Electric Field Gradient from the lattice (non-sphericity of the nucleus)


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

$\nu_Q$ $\eta$

I=1/2: cubic local symmetry: no quadrupolar effect

# NMR basics (6): quadrupole interaction

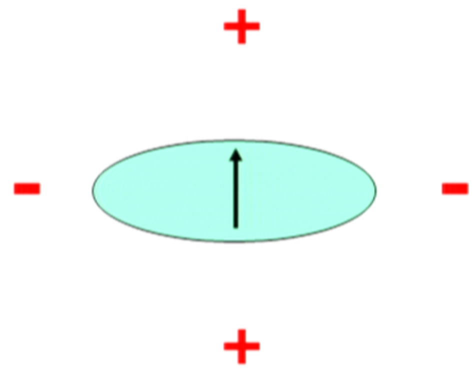


$$V(r) = V(0) + \sum_{i=3\_directions} x_i \left.\frac{\partial V}{\partial x_i}\right)_{r=0} + \frac{1}{2} \sum_{i=3\_directions} x_i x_j \left.\frac{\partial^2 V}{\partial x_i \partial x_j}\right)_{r=0} + \ldots$$

- $V(0)$ → cst
- First-order term → 0 since center of mass and charge coincides
- Second-order term → Quadrupole term → We express it in principal axes where V is diagonal :

Quadrupolar moment of the nucleus $eQ = \frac{1}{2}\int (3z^2 - r^2)\rho d^3 R$

# NMR basics (6): quadrupole interaction



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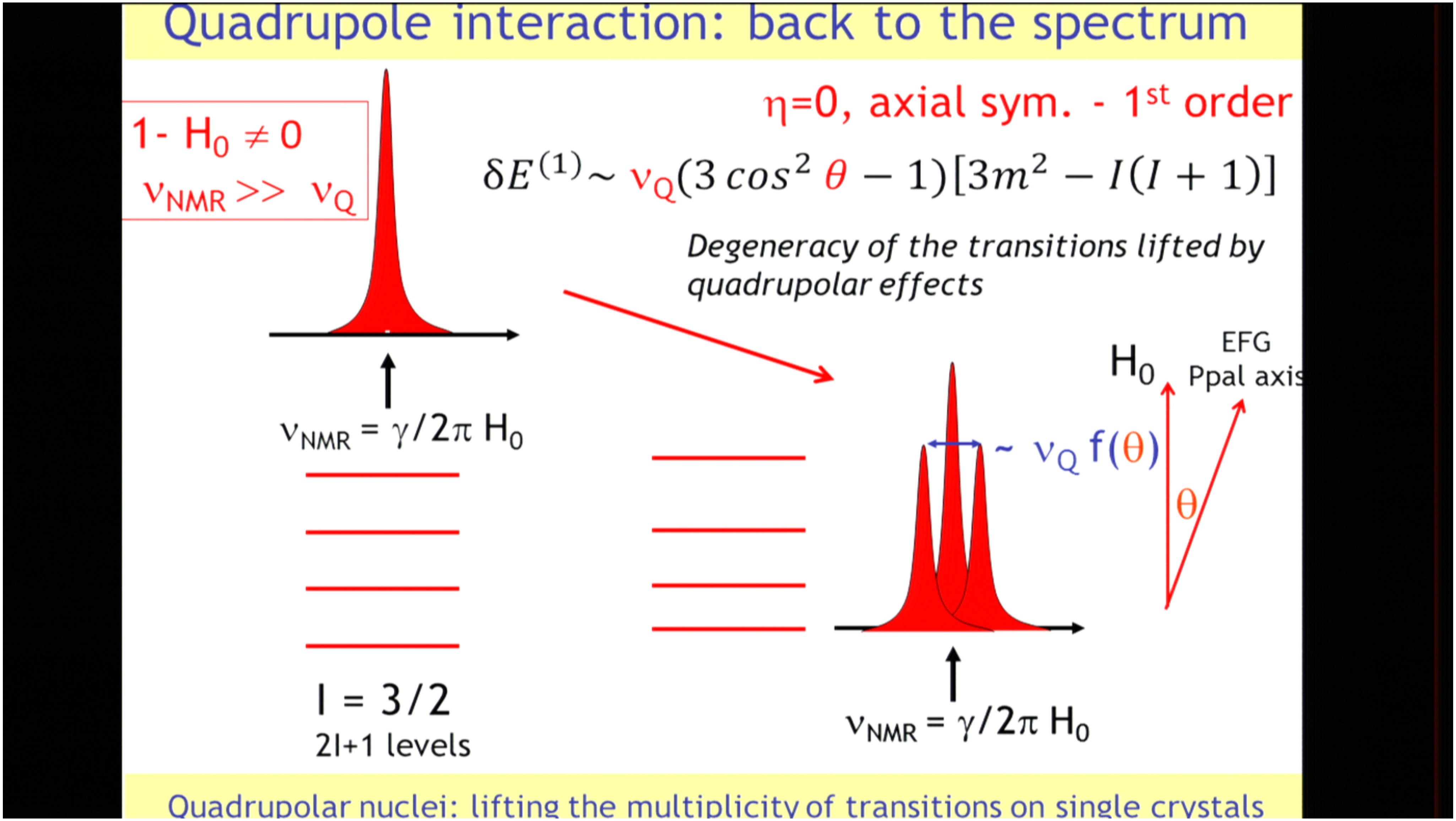
$$H_Q = \int \rho_n(\vec{r}) V(\vec{r}) d\vec{r}$$

Wigner-Eckart theorem

$$H_Q = \frac{eQ}{4I(2I-1)}\left\{\left(\frac{\partial^2 V}{\partial x^2} - \frac{\partial^2 V}{\partial y^2}\right)(I_x^2 - I_y^2) + \frac{\partial^2 V}{\partial z^2}(3I_z^2 - I^2)\right\}$$

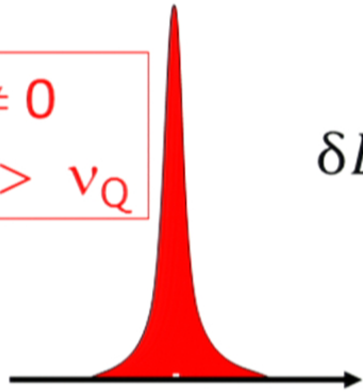
Quadrupolar moment of the nucleus $eQ = \frac{1}{2}\int (3z^2 - r^2)\rho d^3 R$


Quadrupole interaction: back to the spectrum
1- H0 ≠ 0
νNMR >> νQ
η=0, axial sym. - 1st order
δE(1) ~ νQ(3 cos2 θ − 1)[3m2 − I(I + 1)]
Degeneracy of the transitions lifted by quadrupolar effects
νNMR = γ/2π H0
~ νQ f(θ)
H0
EFG
Ppal axis
θ
I = 3/2
2I+1 levels
νNMR = γ/2π H0
Quadrupolar nuclei: lifting the multiplicity of transitions on single crystals

# Quadrupole interaction: back to the spectrum

1- $H_0 \neq 0$

$\nu_{NMR} >> \nu_Q$



$\nu_{NMR} = \gamma/2\pi\, H_0$

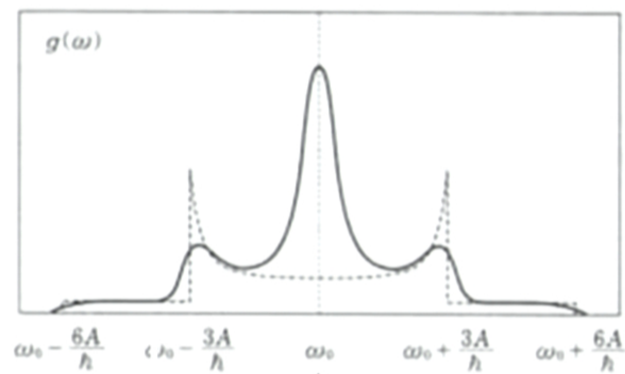
$I = 3/2$

2I+1 levels

$\eta$=0, axial sym. - 1st order

$$\delta E^{(1)} \sim \nu_Q (3\cos^2\theta - 1)[3m^2 - I(I+1)]$$

*Degeneracy of the transitions lifted by quadrupolar effects*




$\nu_{NMR} = \gamma/2\pi\, H_0$

Quadrupolar nuclei: distribution of angles → powder average

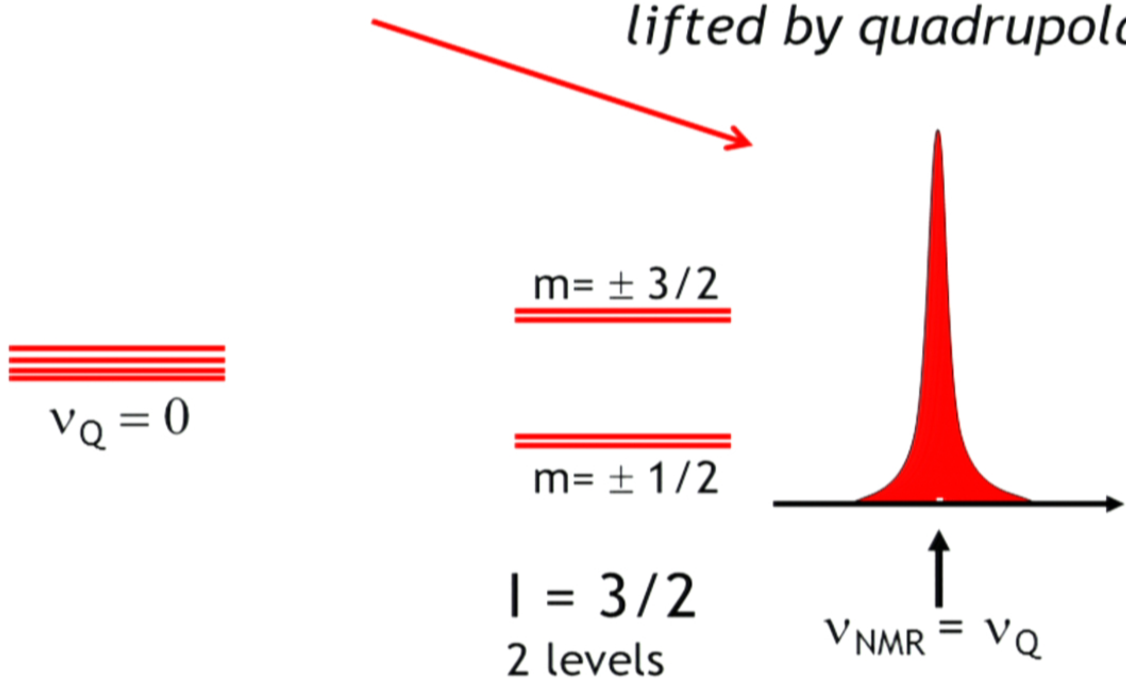
# Quadrupole interaction only: NQR

2- H = 0

$\eta$=0, axial sym. - 1st order

$$\delta E^{(1)} \sim \nu_Q / 6[3m^2 - I(I+1)]$$

*Degeneracy of the transitions lifted by quadrupolar effects*




Quadrupolar resonance: powders = single crystals

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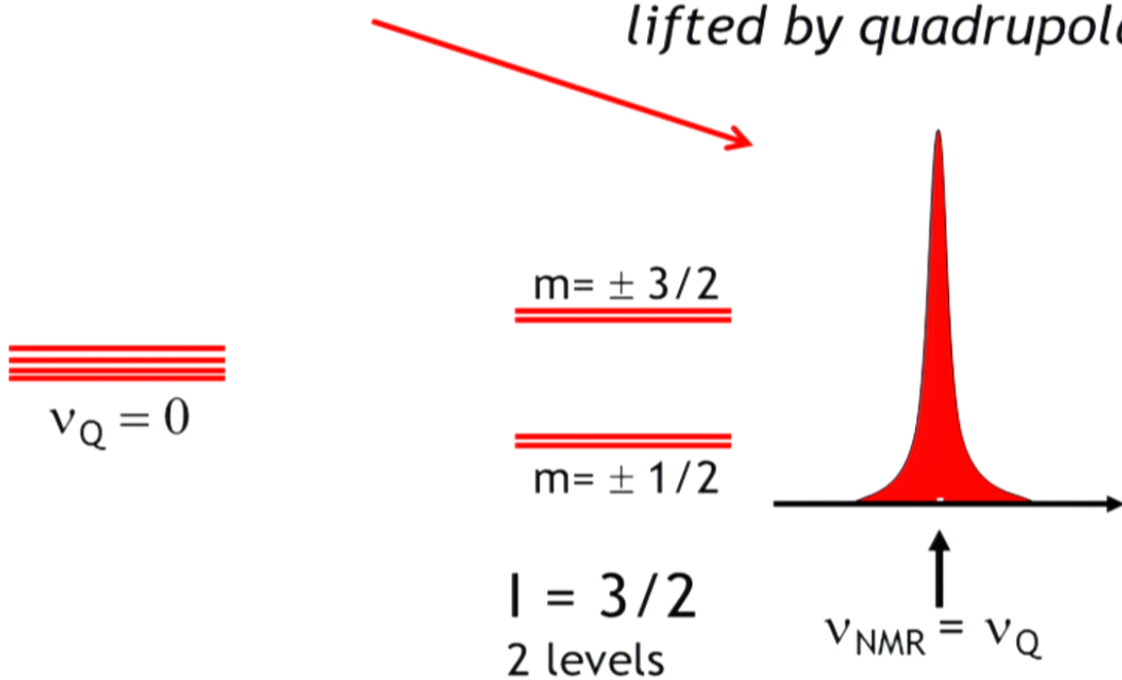
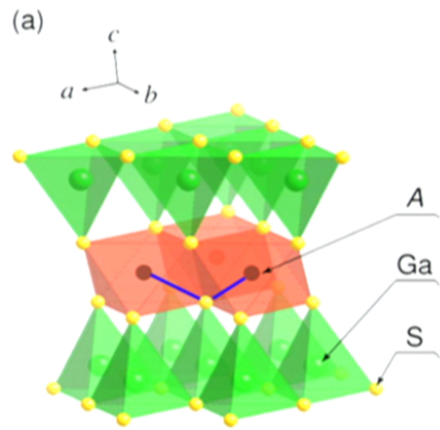
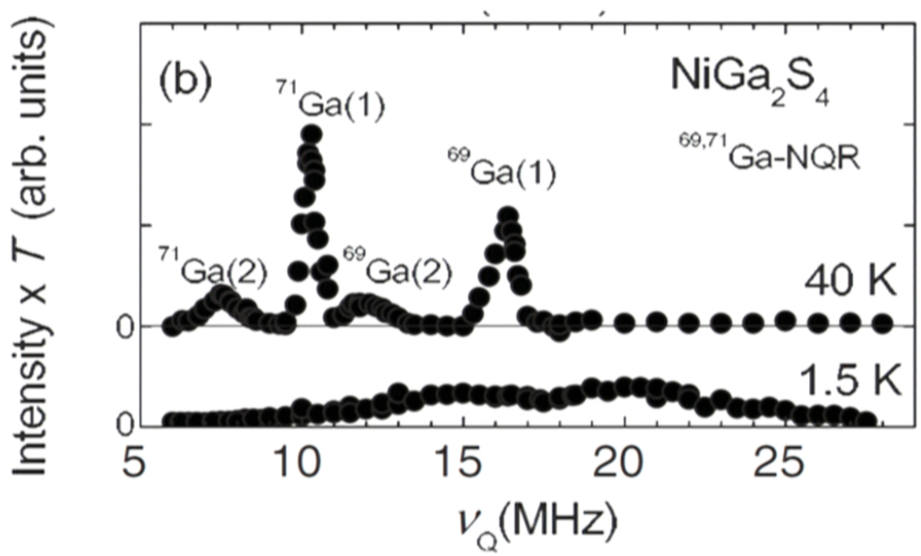



Quadrupolar resonance: powders = single crystals

# Ga NQR in $NiGa_2S_4$

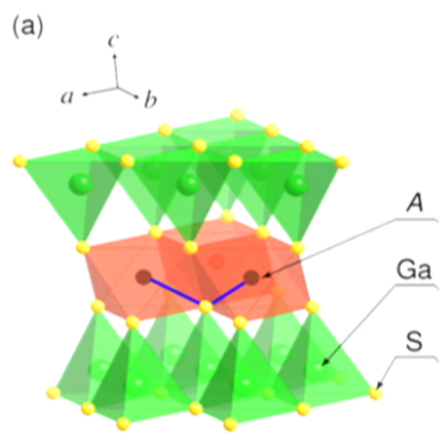


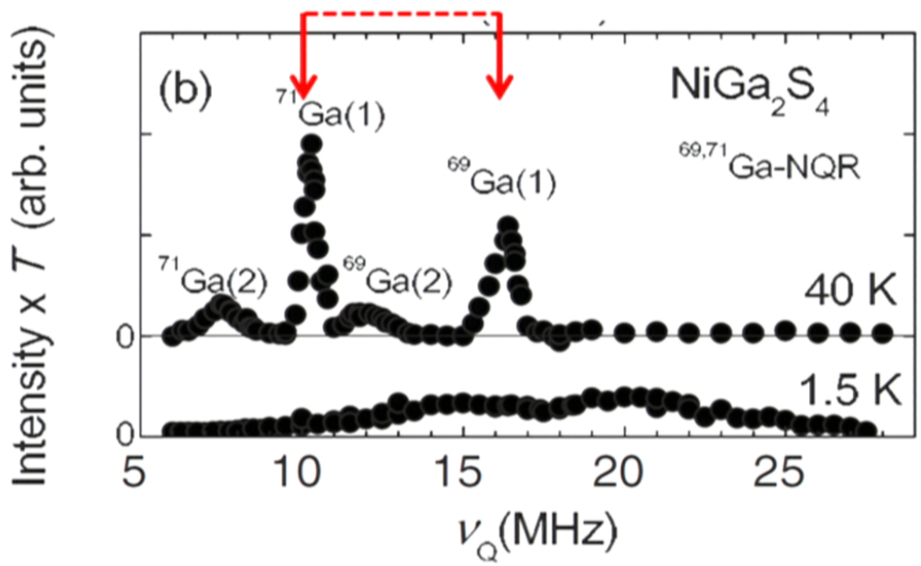




*H. Takeya et al., Phys. Rev. B (2008)*

2 isotopes, 2 sites (only one expected from structure)

# Ga NQR in $NiGa_2S_4$




*H. Takeya et al., Phys. Rev. B (2008)*

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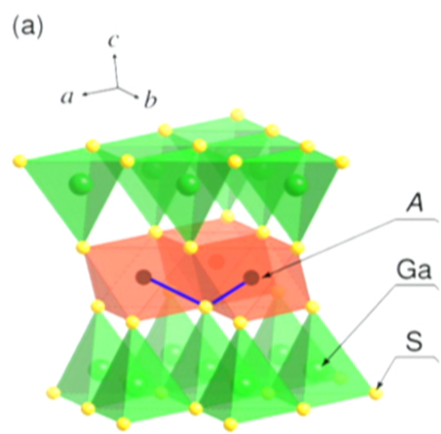
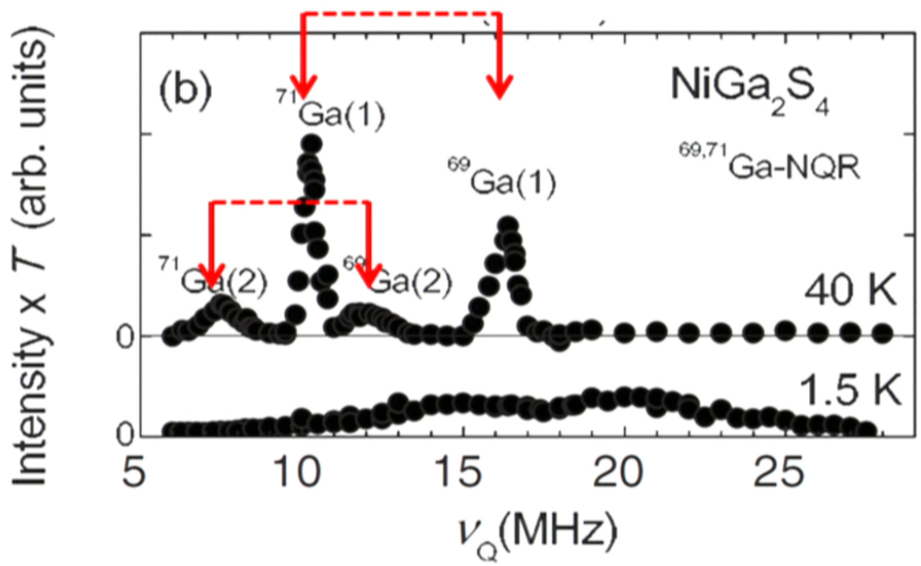


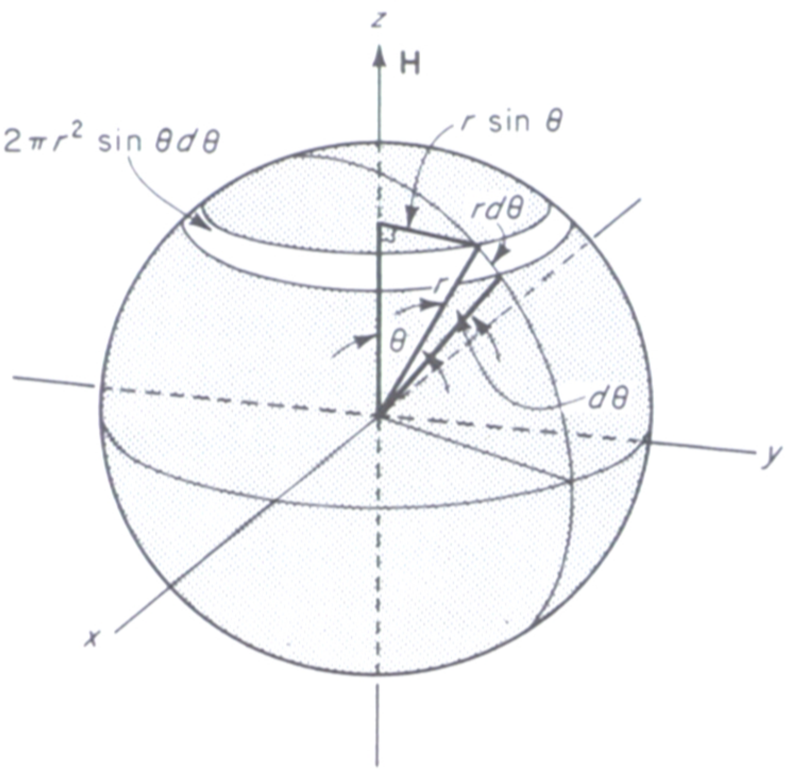




*H. Takeya et al., Phys. Rev. B (2008)*

2 isotopes, 2 sites (only one expected from structure)

# Averaging on angles: EFG, hyperfine tensor

The EFG and hyperfine tensors may not have the same principal axis! One can manage, playing with isotopes, field ...



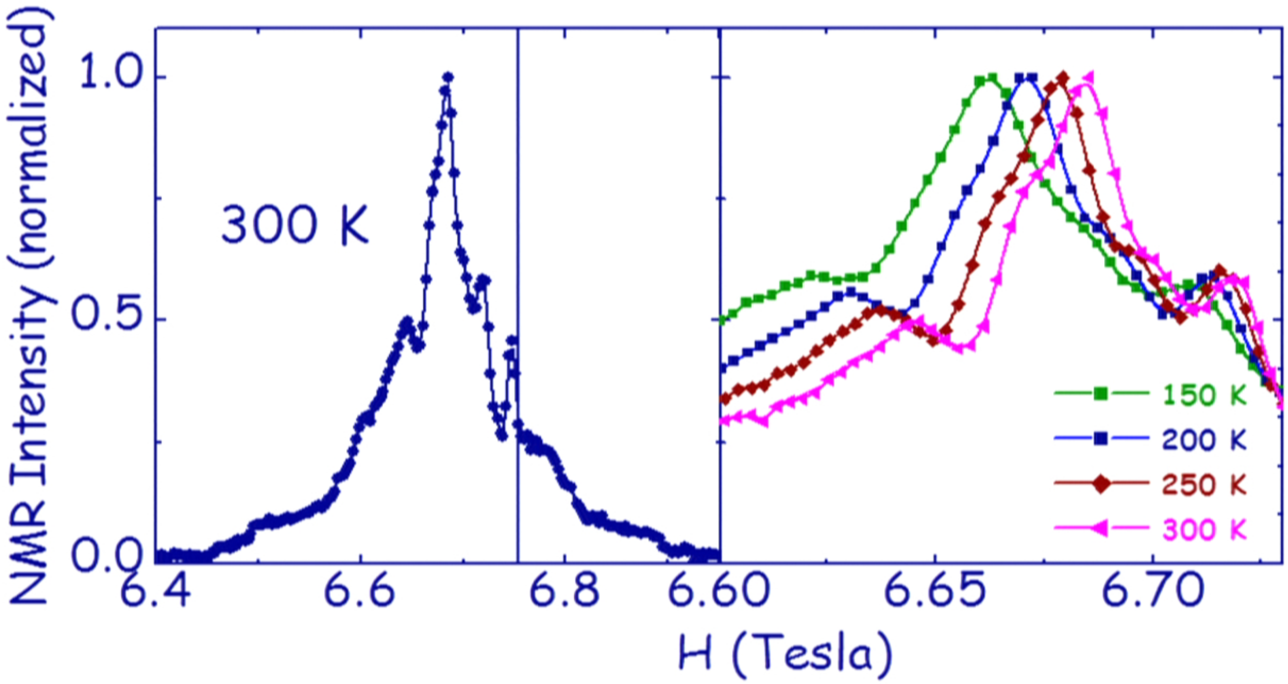

Single crystals are best. Fitting routines for powders ...

# Outline of the presentation

- Basics: energy levels, coupling Hamiltonian, quadrupolar effects
- Static local studies: shift, site-resolved, magnetic ordering, structural effects, spin textures...
- Dynamical studies: $T_1$, ($T_2$), wipe out
- Comparison with μSR

# $^{17}$O-NMR in Herbertsmithite: site selection

If I>1/2, nuclear spin I is sensitive to any Electric Field Gradient from the lattice




$\eta \neq 0$, unoriented powders

M.I.T., 2005

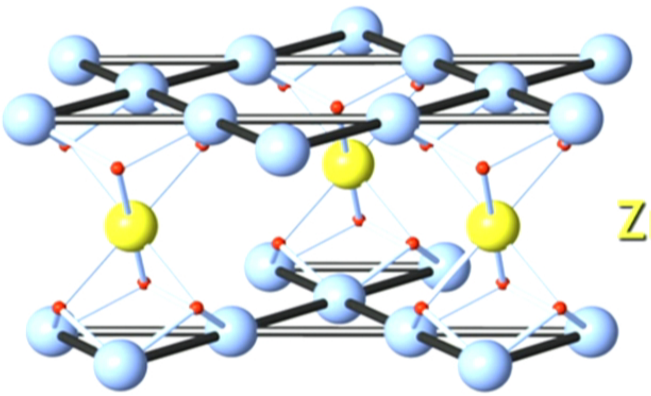
J|A|C|S
COMMUNICATIONS

Published on Web 09/09/2005

## A Structurally Perfect $S = {}^1/_2$ Kagomé Antiferromagnet

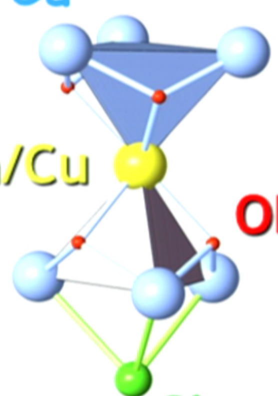
Matthew P. Shores, Emily A. Nytko, Bart M. Bartlett, and Daniel G. Nocera*

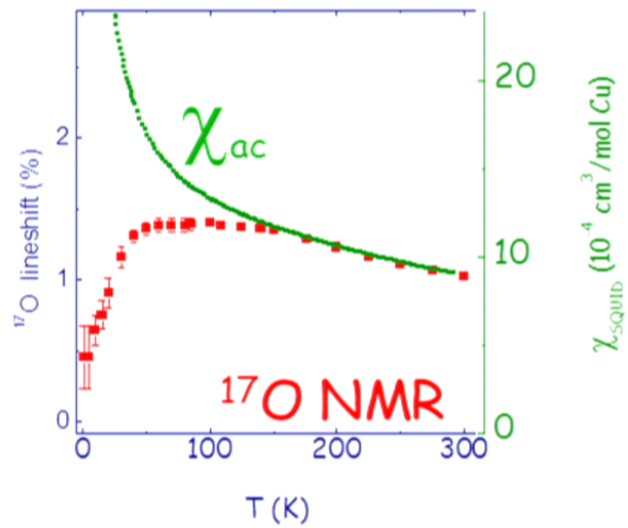
*Department of Chemistry, 6-335, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139-4307*



Herbertsmithite
$ZnCu_3(OH)_6Cl_2$

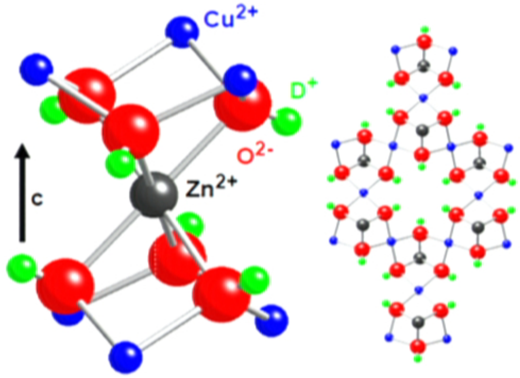
$Cu^{2+}$, S=1/2

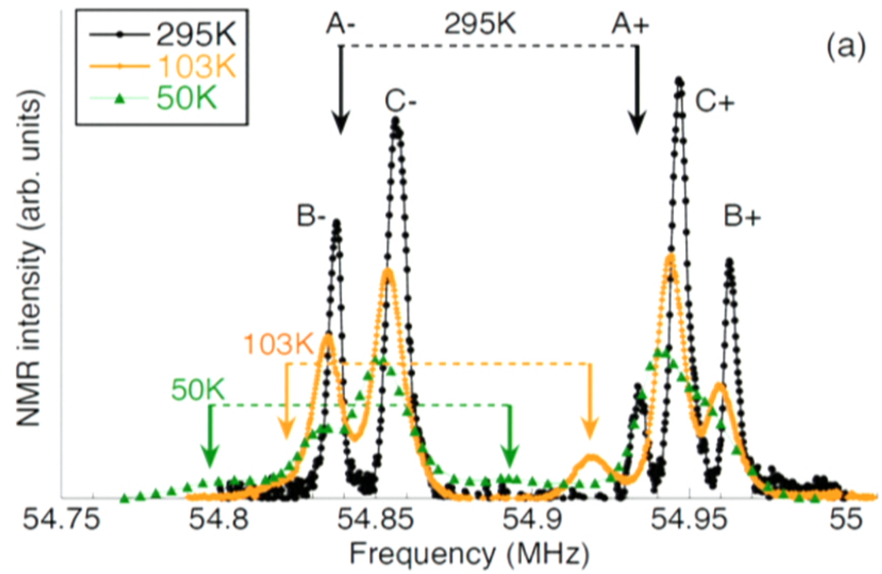



A. Olariu et al., Phys. Rev. Lett (2008)

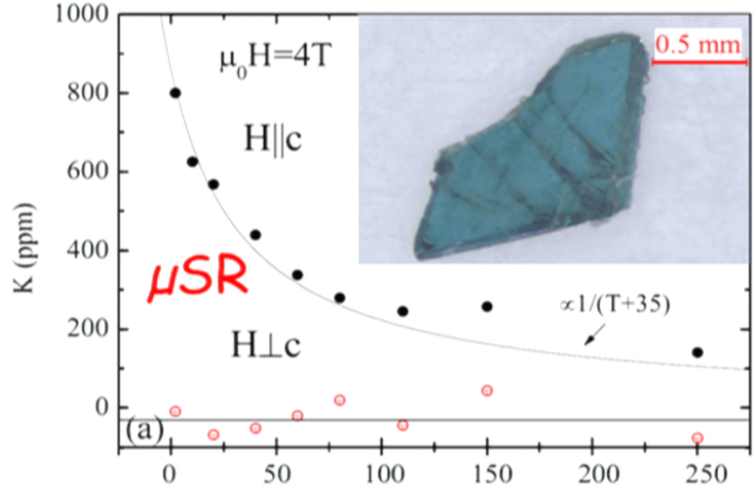
# $^2$D-NMR in Herbertsmithite

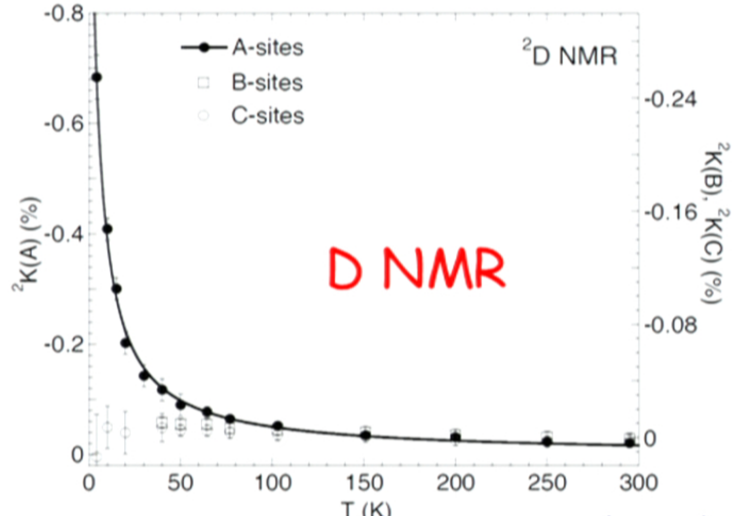



I = 1: Single crystal: H//c: 3 different D environments

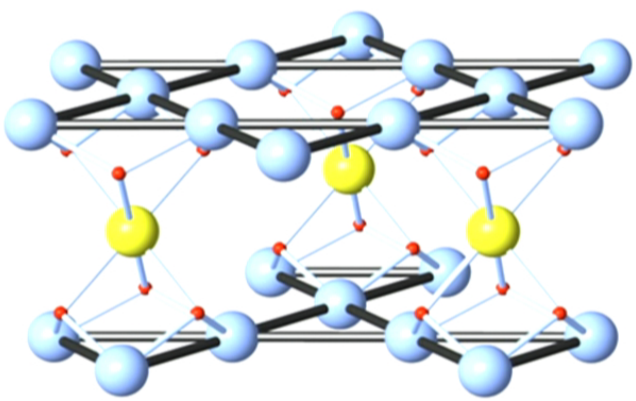
# local susceptibility: site selection

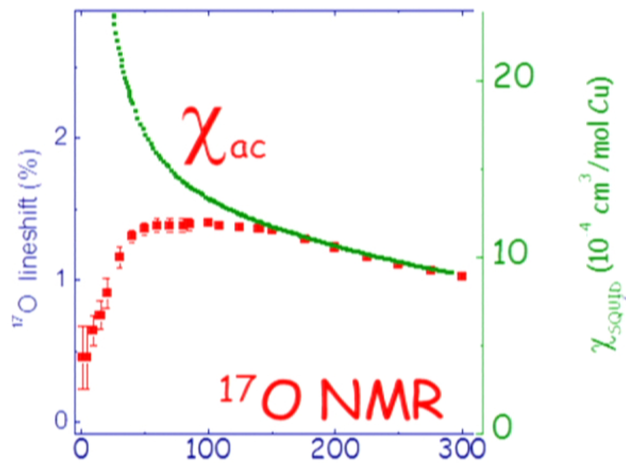


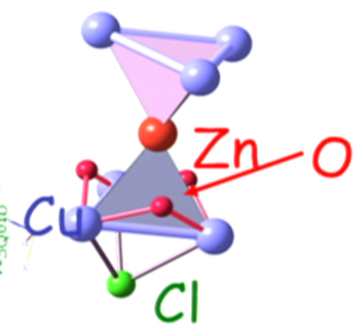




O. Ofer et al., ArXiv (2010)

T. Imai, Phys. Rev. B (2011)





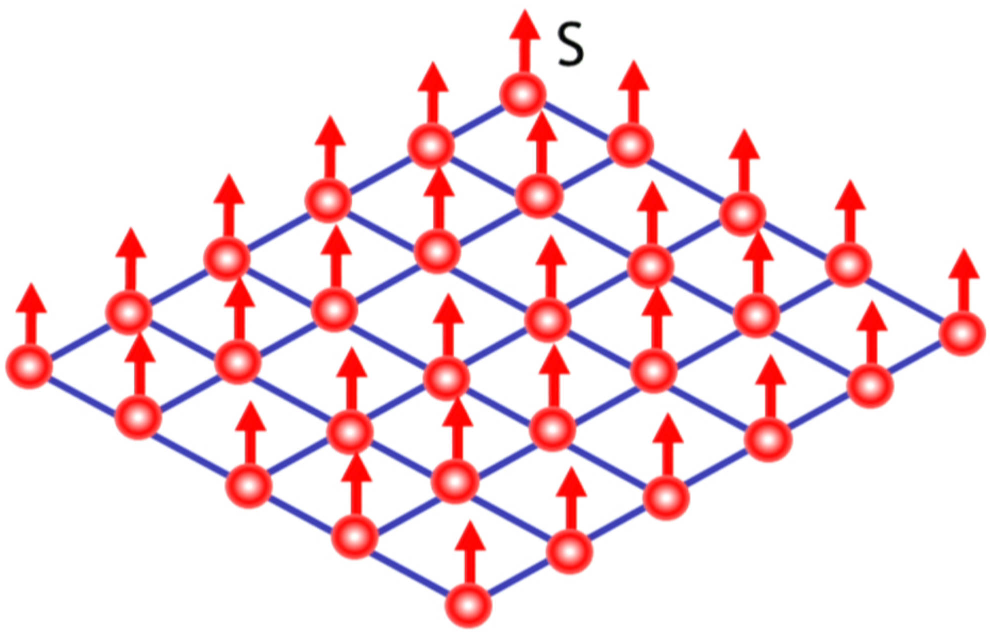



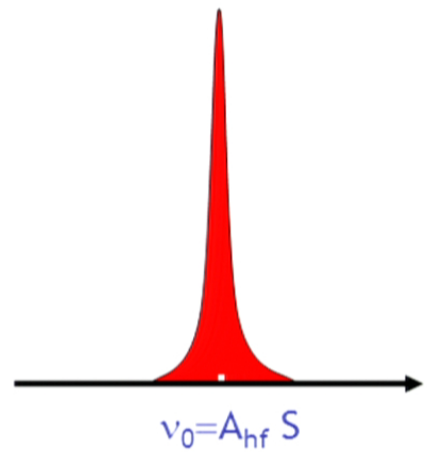

A. Olariu et al., Phys. Rev. Lett. (2008)

# Magnetic ordering

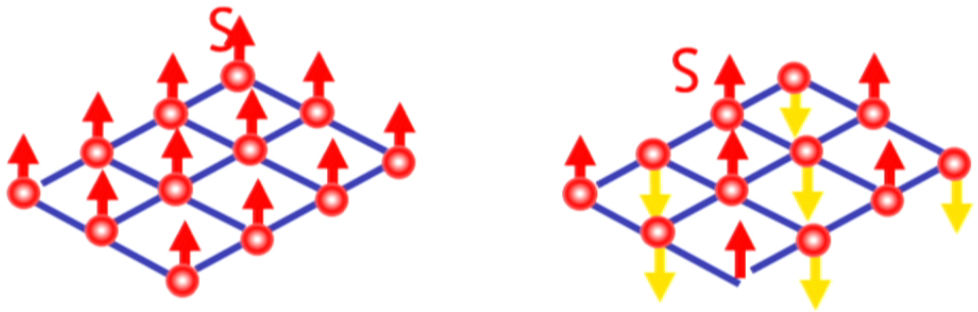
•very strong local fields : in the paramagnetic phase, need of a field $H_0$ so that $\langle S \rangle \neq 0$; in an ordered phase $H \sim A_{hf} \langle S \rangle$, $\langle S \rangle \neq 0$

• ZERO FIELD NMR : if hyperfine field is strong enough, *no need of an applied field*; lineshape depends on the distribution of the modulus of fields

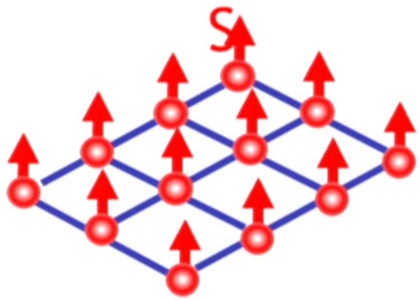


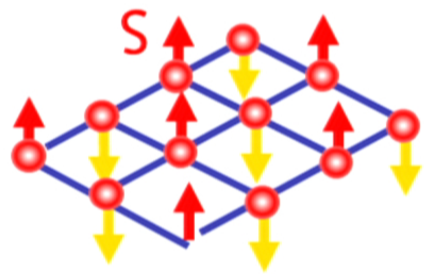



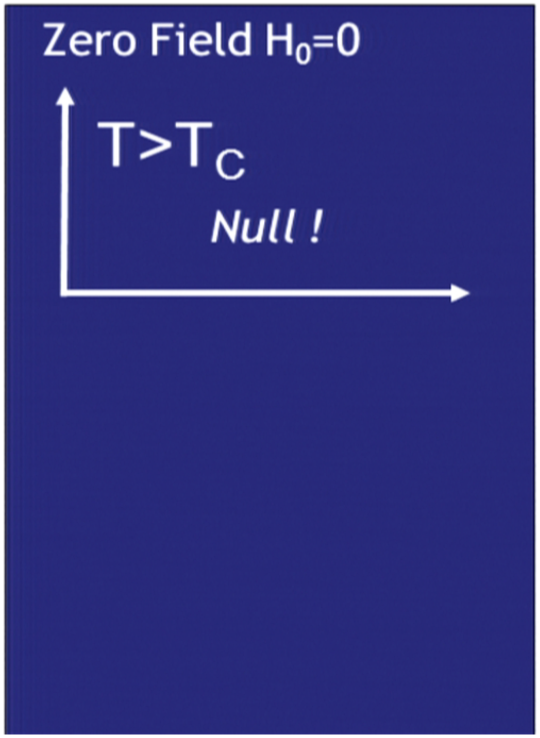
# Magnetic ordering



# Magnetic ordering



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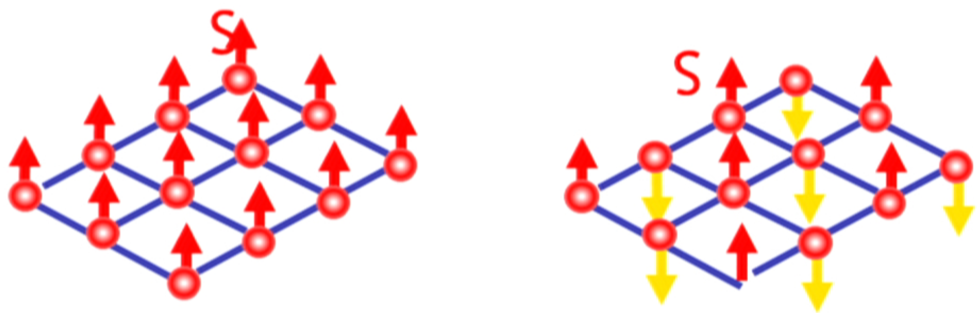
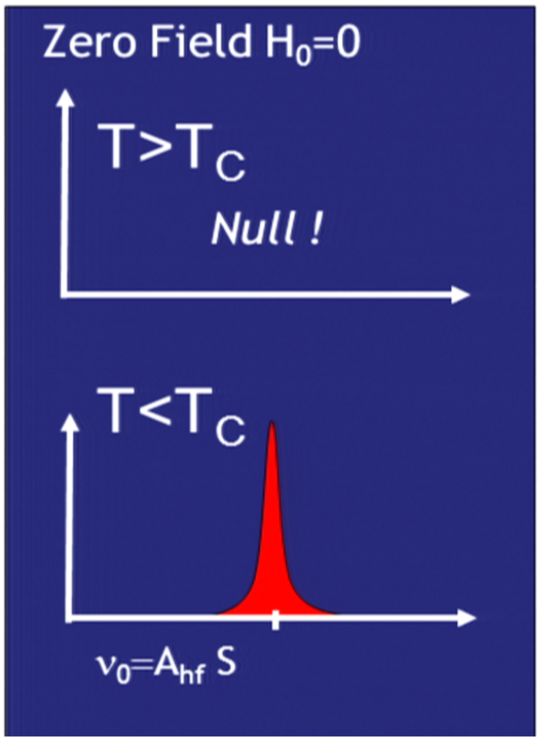
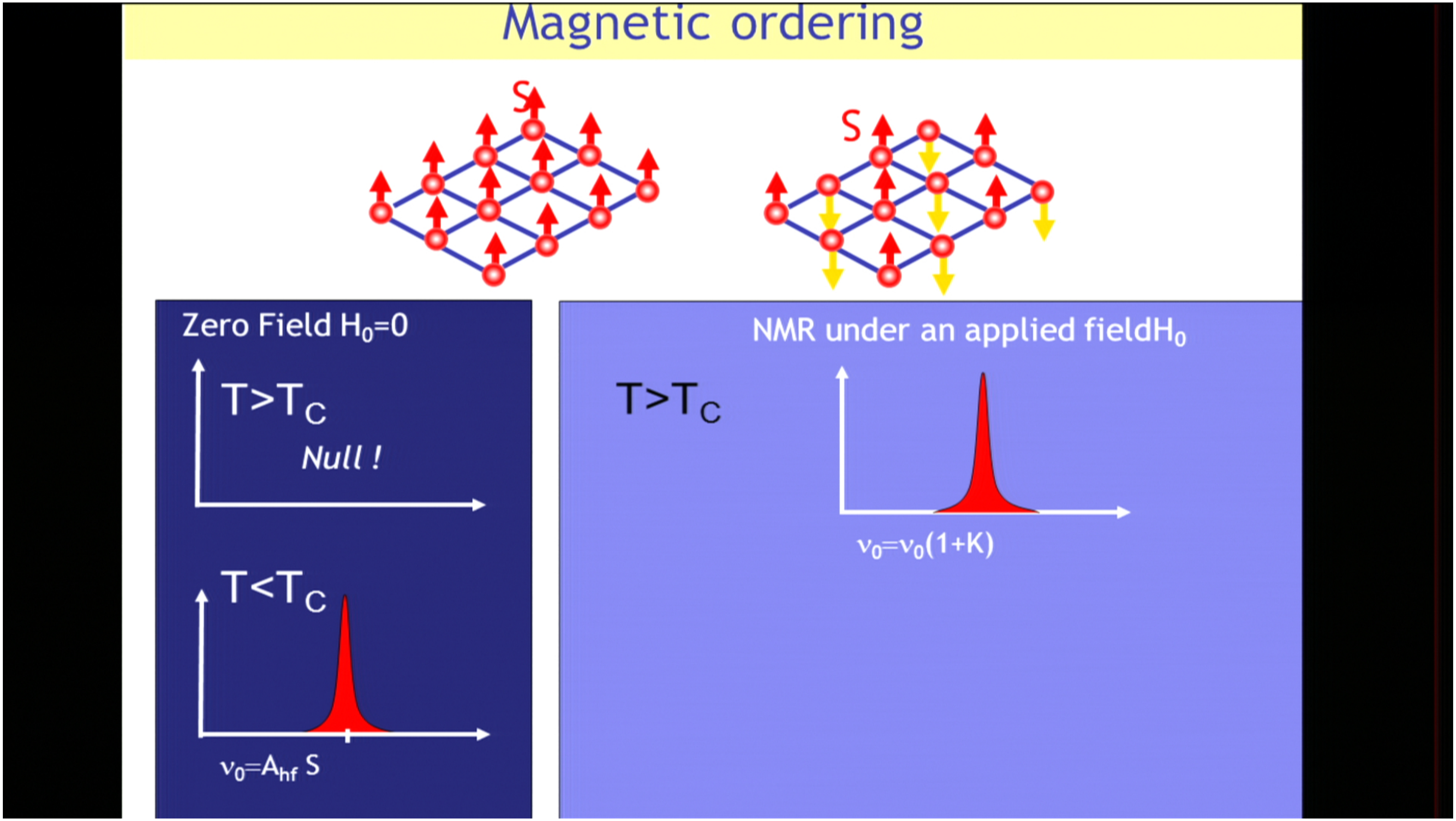
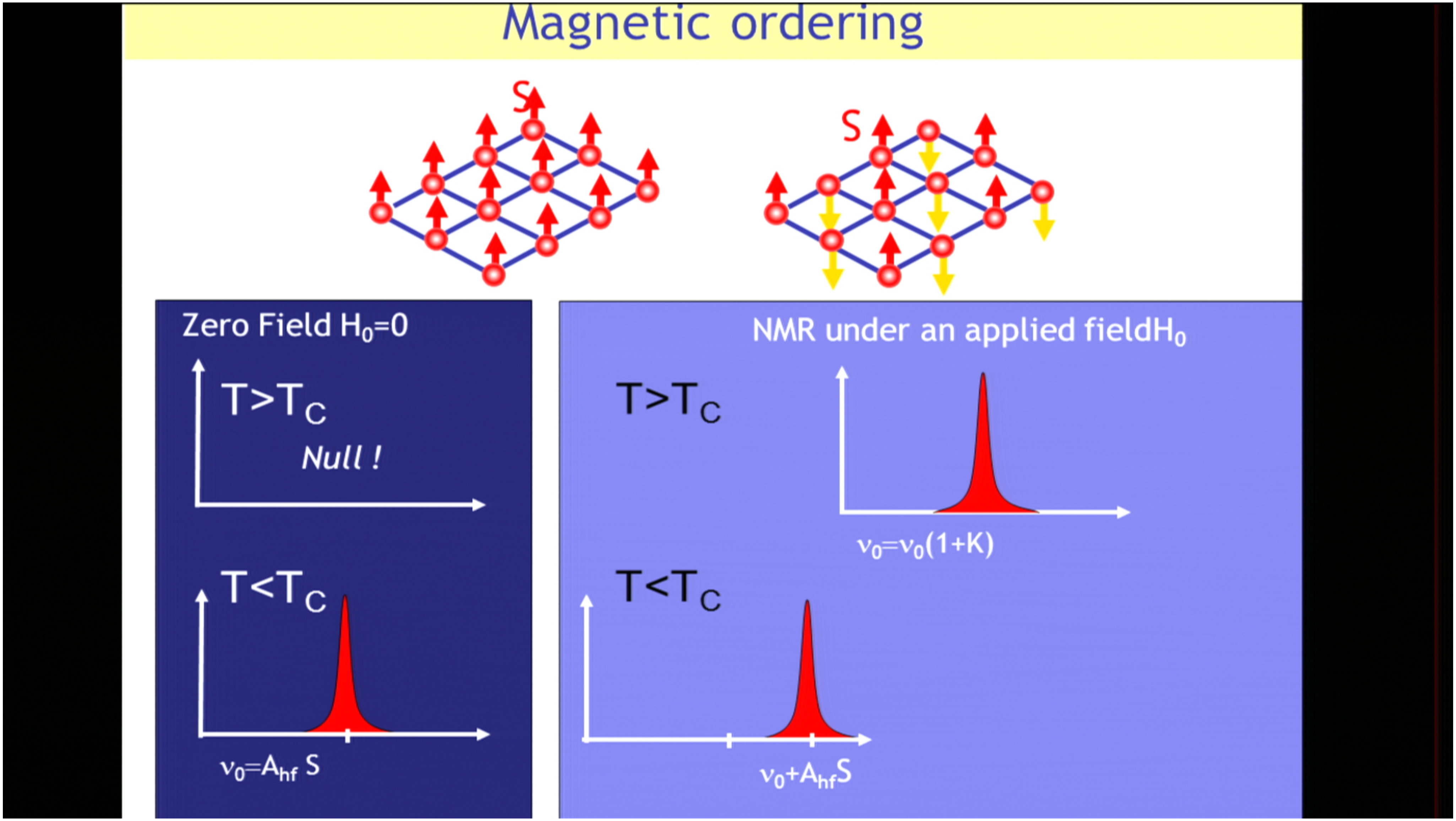


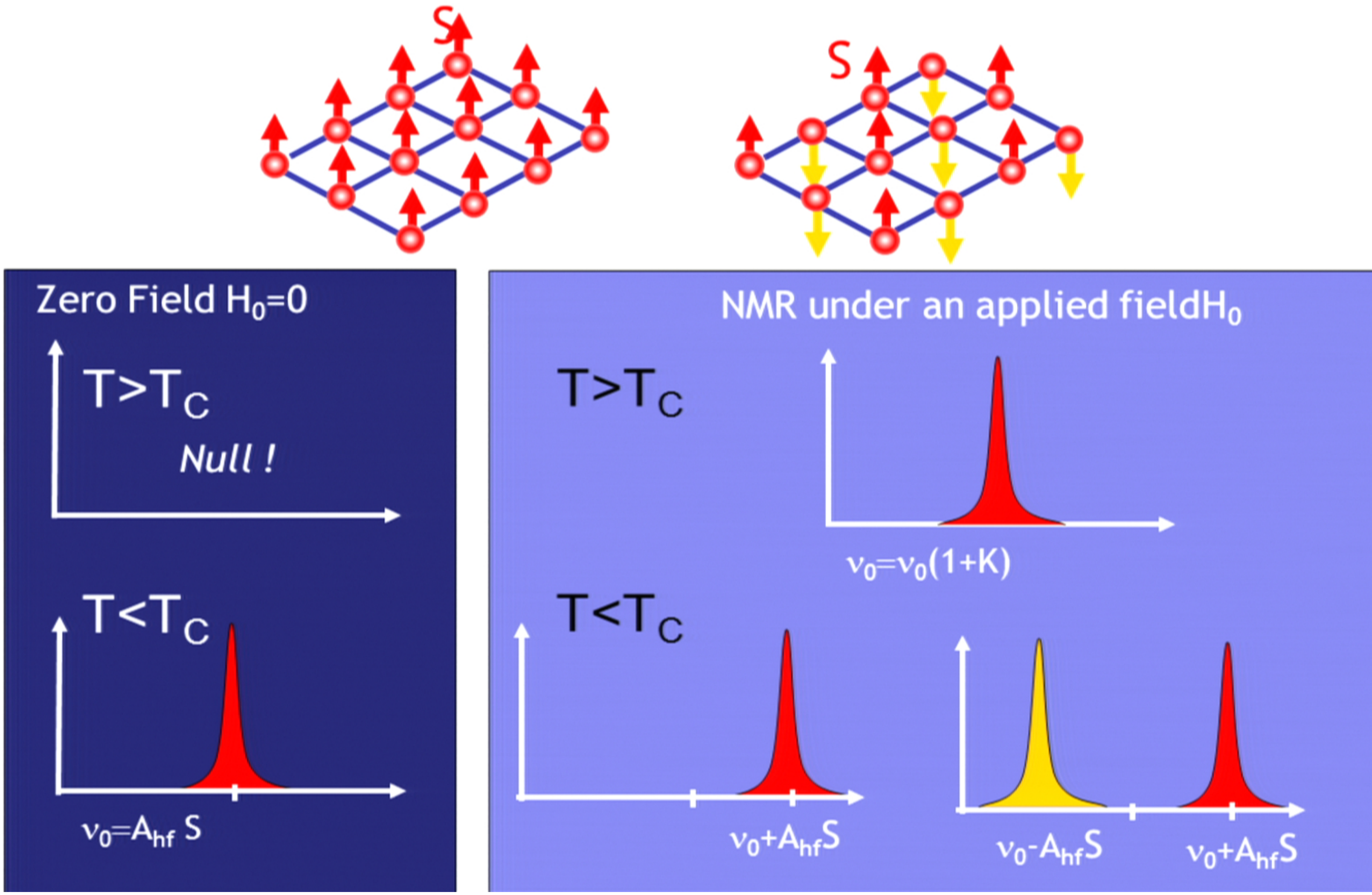

$T>T_C$


Magnetic ordering
S
S
Zero Field $H_0$=0
$T>T_C$
Null !
$T<T_C$
$\nu_0=A_{hf}\,S$
NMR under an applied field$H_0$
$T>T_C$
$\nu_0=\nu_0(1+K)$

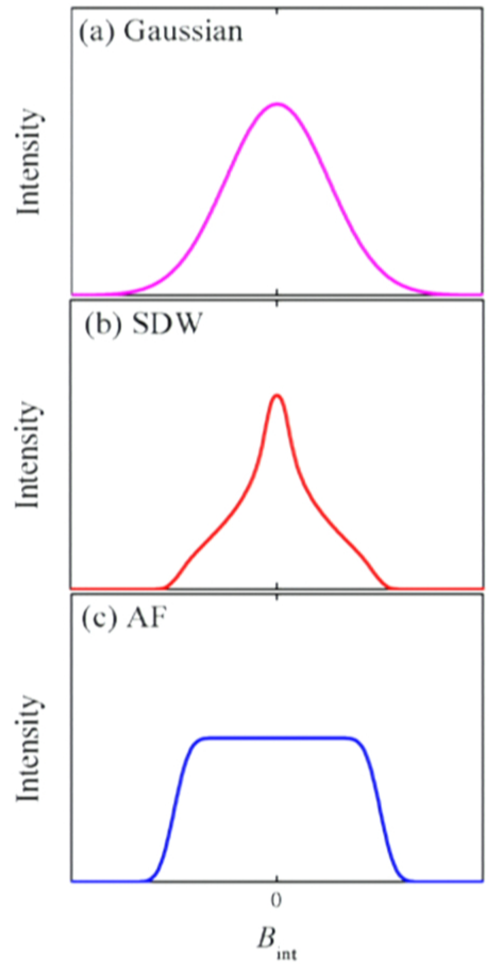


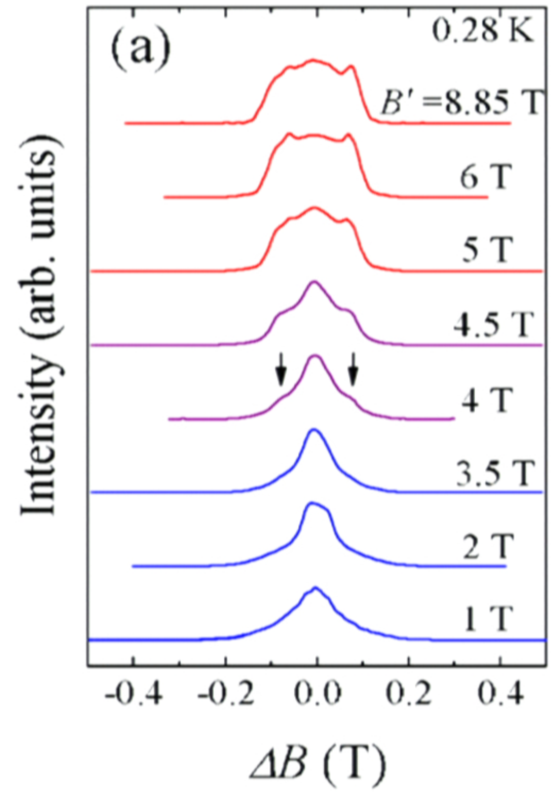
Magnetic ordering
S
S
Zero Field H0=0
T>TC
Null !
T<TC
ν0=Ahf S
NMR under an applied fieldH0
T>TC
ν0=ν0(1+K)
T<TC
ν0+AhfS

# Magnetic ordering



# Powder line shape: applied field ⊕ internal field




*M. Yoshida et al., JPSJ (2012), Phys. Rev. Lett (2009)*

NMR can elucidate magnetic structures: invaluable for high fields

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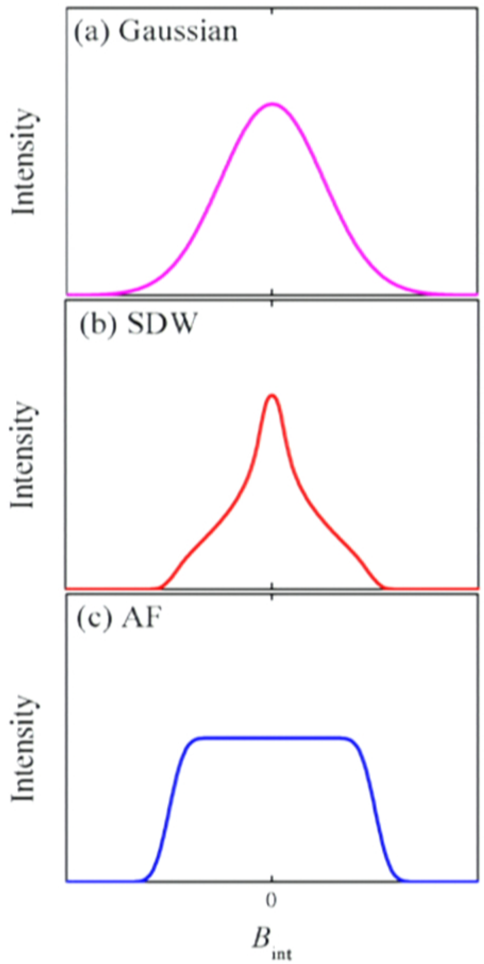


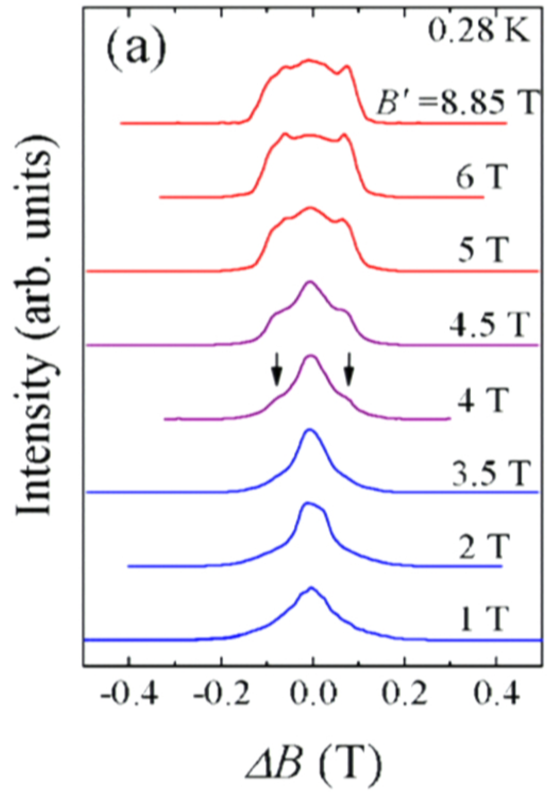


M. Yoshida et al., JPSJ (2012), Phys. Rev. Lett (2009)

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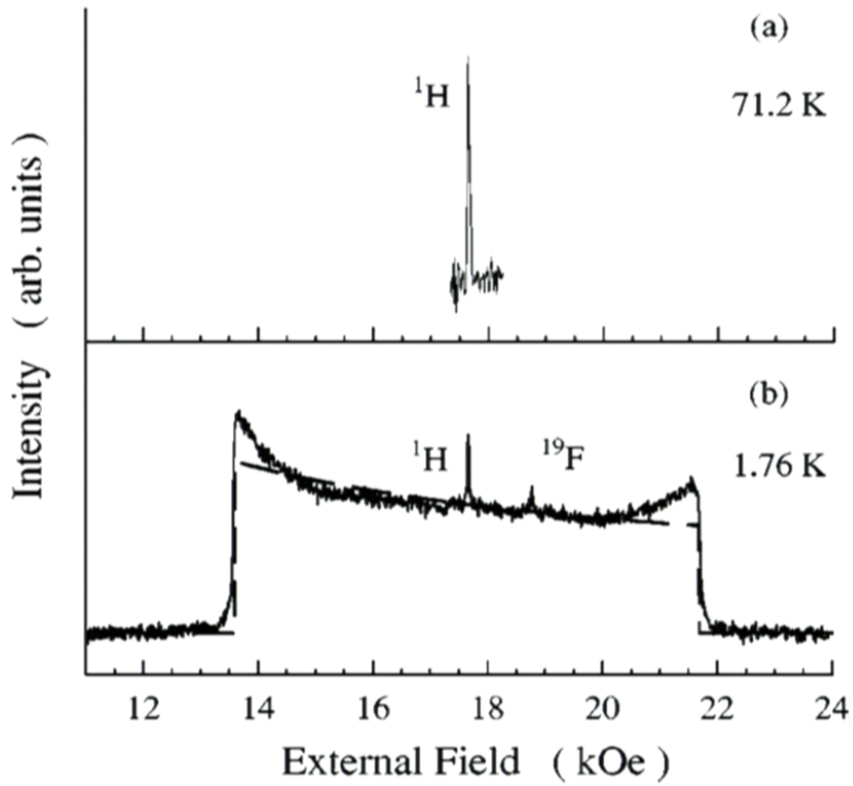
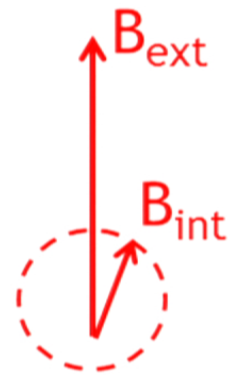
# Jarosite: $KFe_3(OH)_6(SO_4)_2$




*M. Nishiyama, Phys. Rev. B (2003)*

B >> B Dipolar coupling of H to moments

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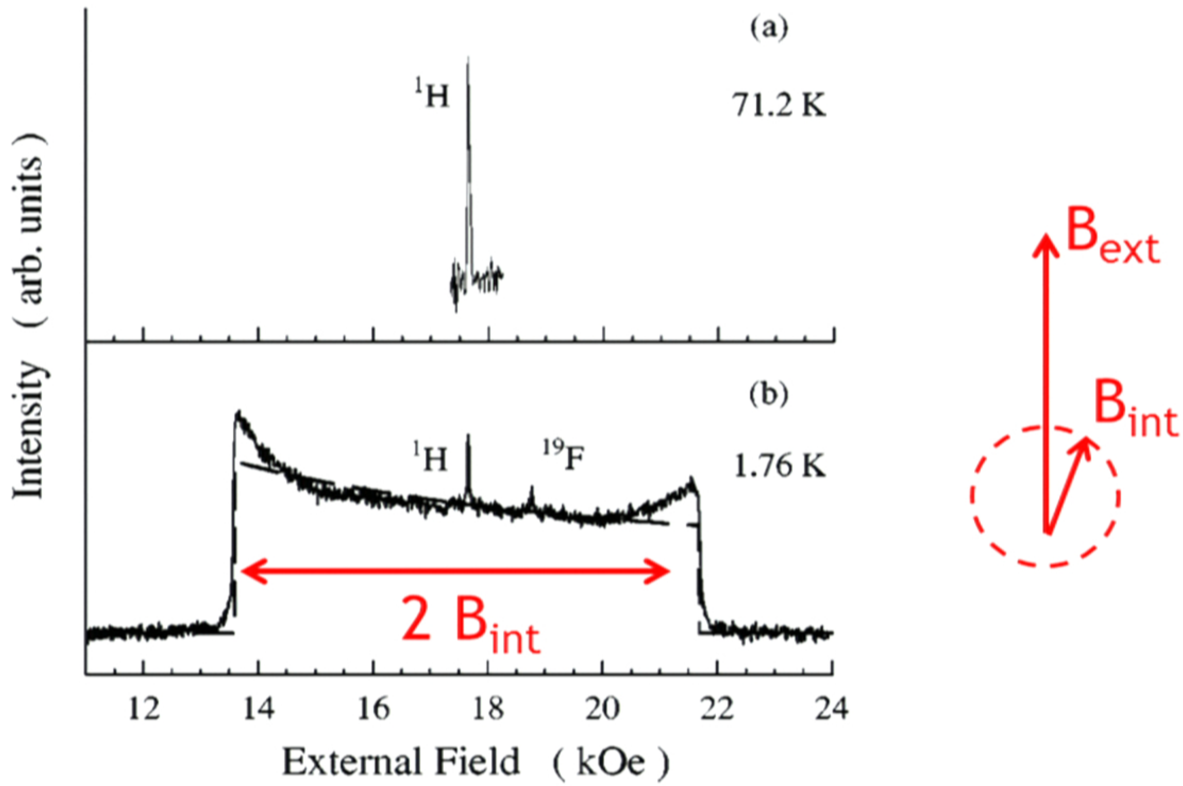


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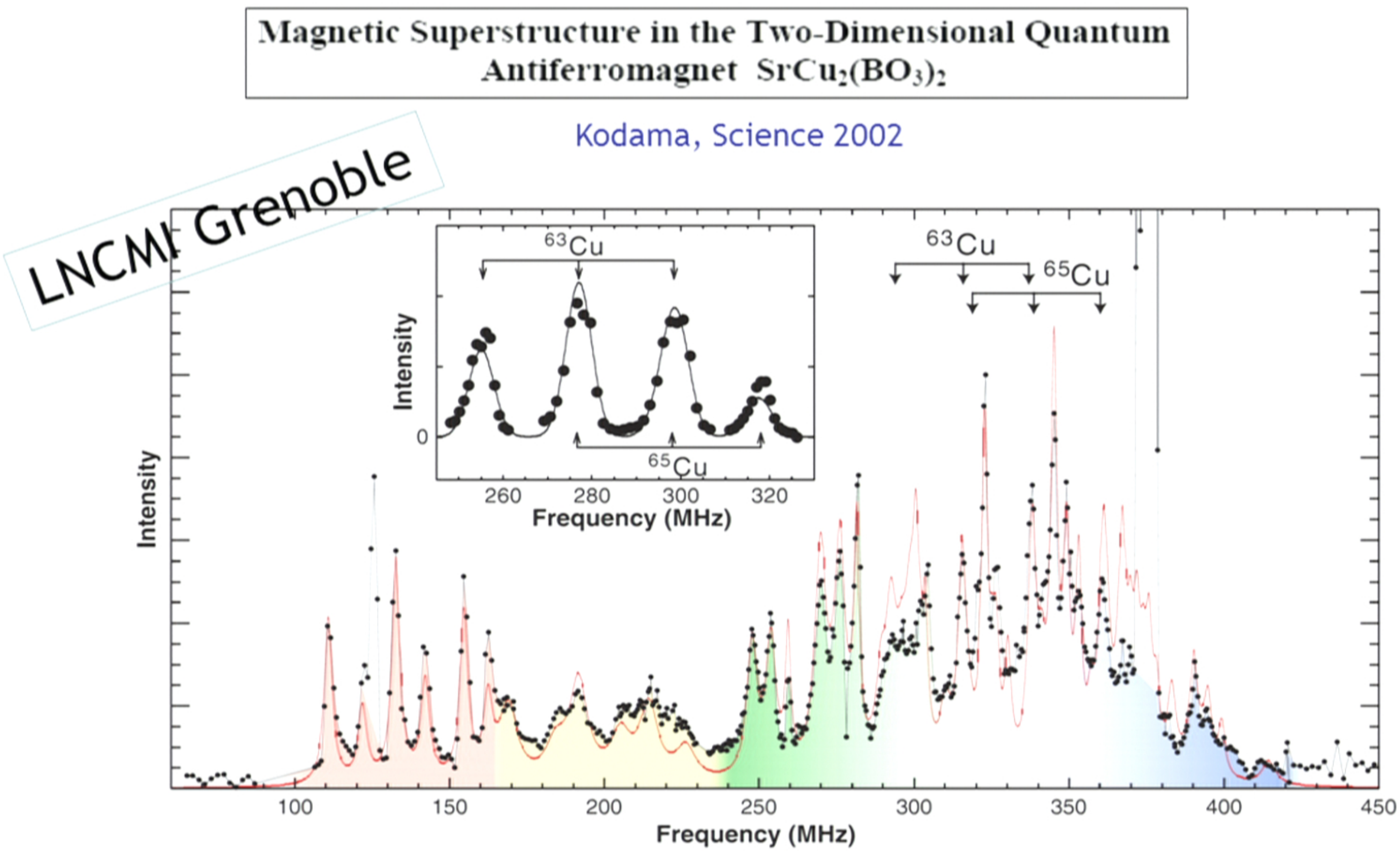
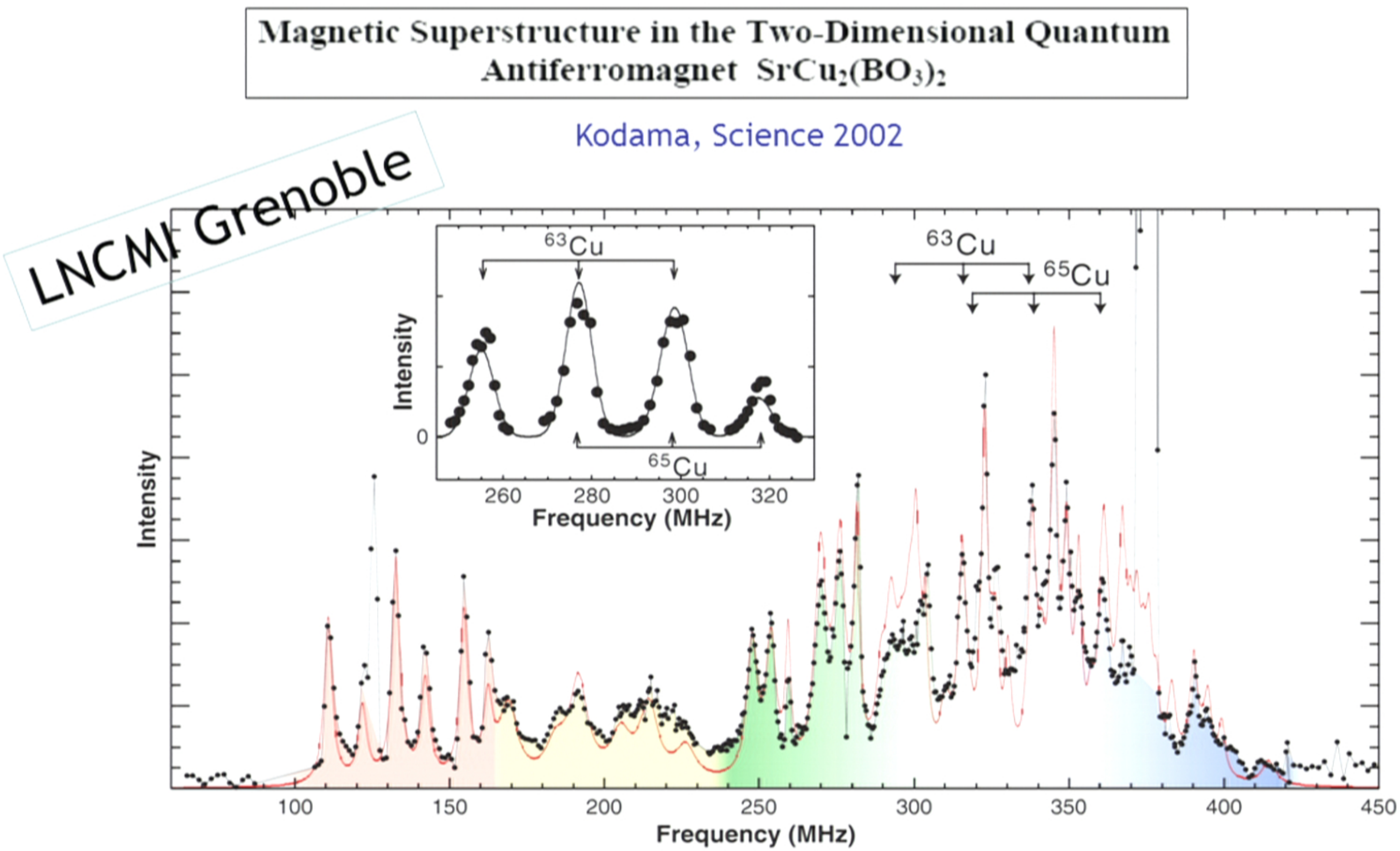
# NMR in High Magnetic Fields: large scale facilities




Magnetization plateau ~28 T: superstructure of triplet state

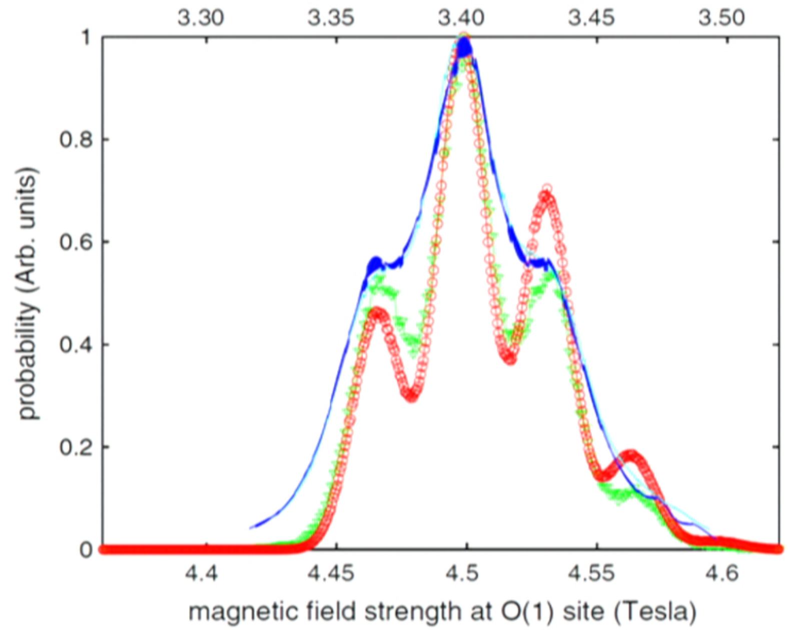
# NMR in High Magnetic Fields: large scale facilities




Magnetization plateau ~28 T: superstructure of triplet state

# $^{17}O$ in spin-ice $Dy_2Ti_2O_7$ : ZFNMR

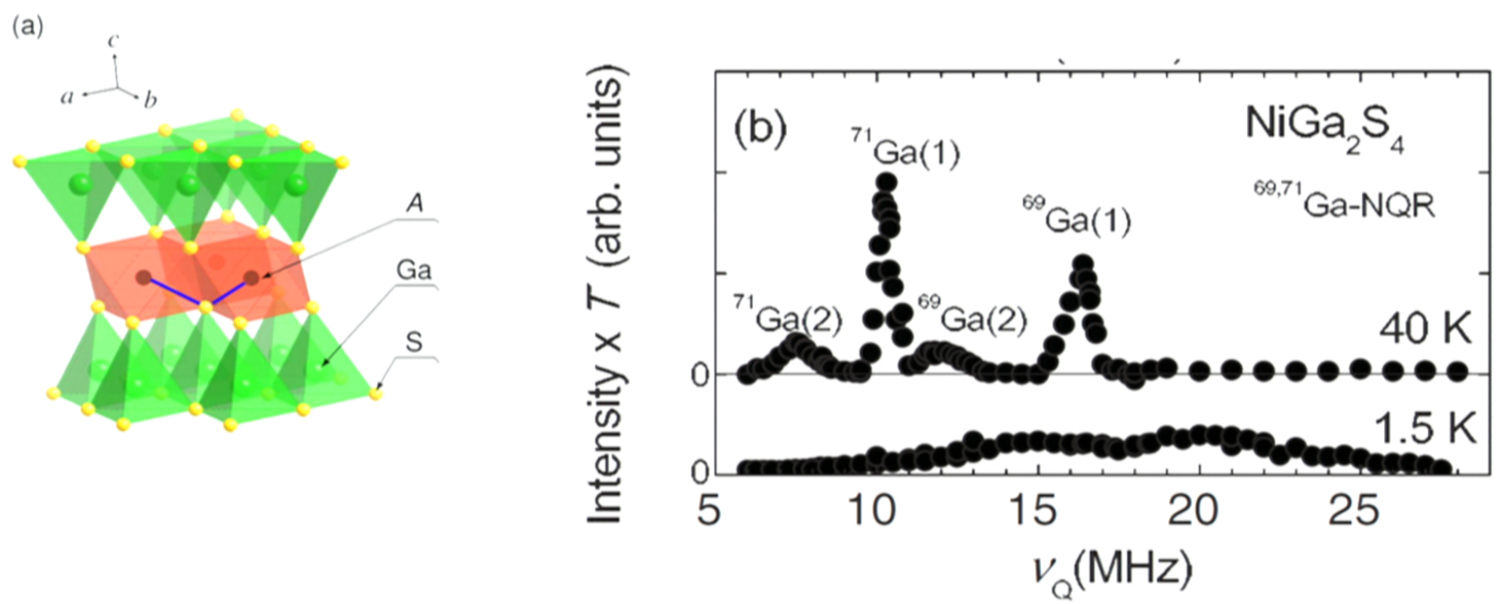
- 2 in – 2 out spin-ice rule → a single field value at the O site
- Sub-Kelvin experiments




*G. Sala et al., Phys. Rev. Lett. (2012)*

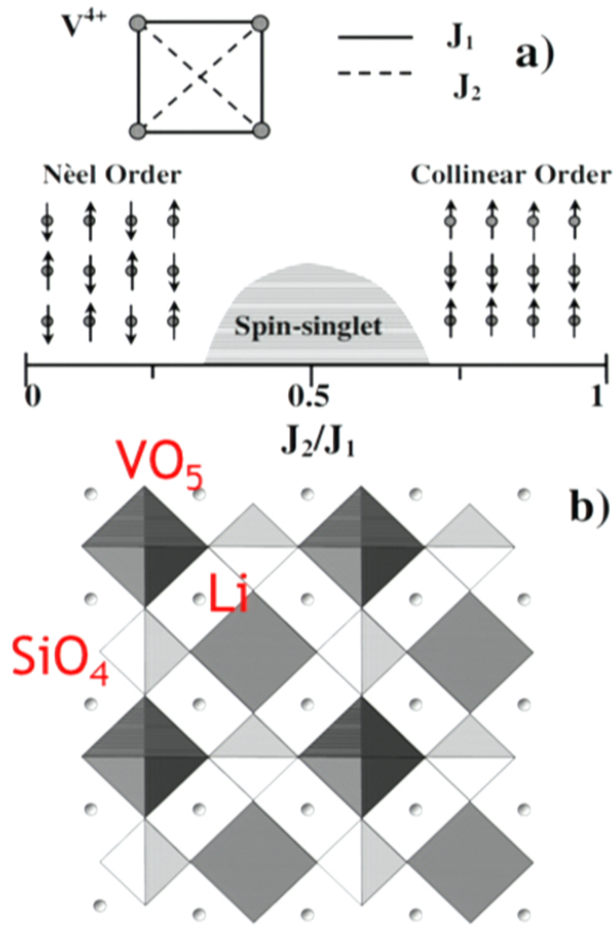
- Detect excitations (monopoles): int. field 25% smaller

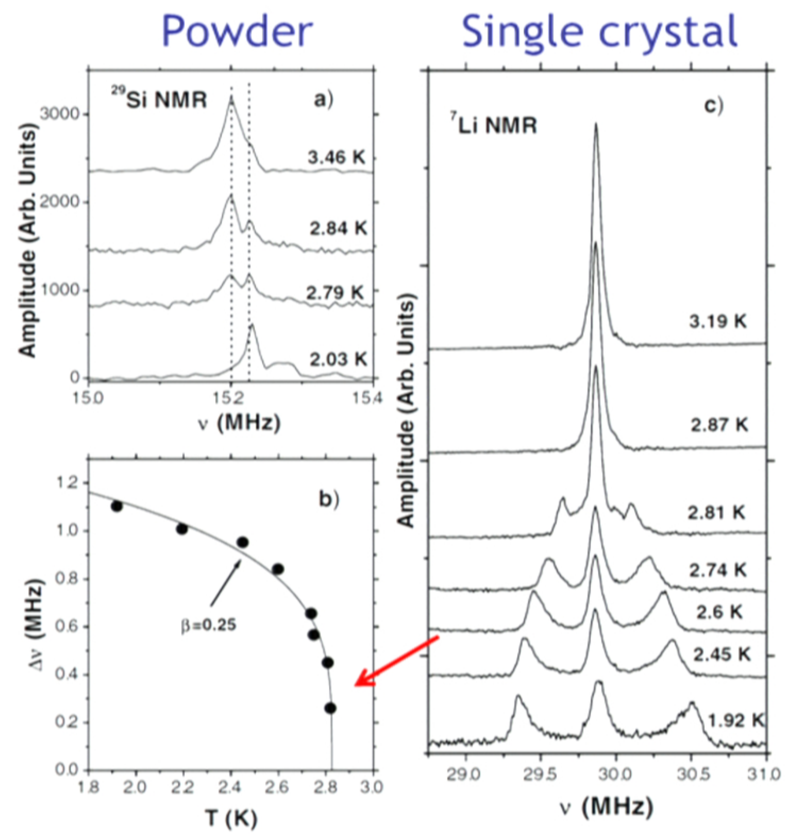
# Ga NQR in $NiGa_2S_4$




2 isotopes, 2 sites (only one expected from structure)

# J1-J2 model in Vanadates




*Melzi et al, PRL 2000*

Note: change in Si spectrum above $T_N$, structural distortion

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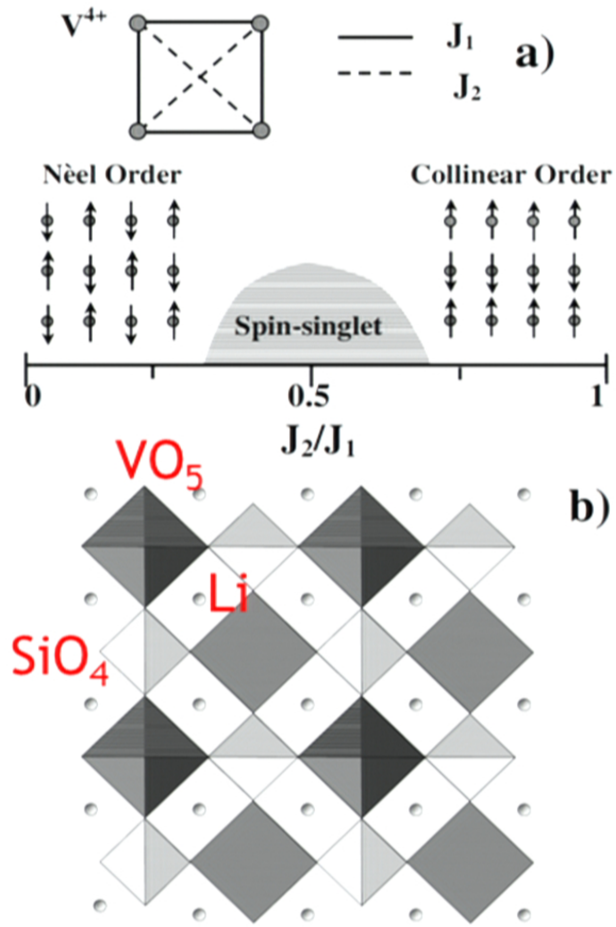
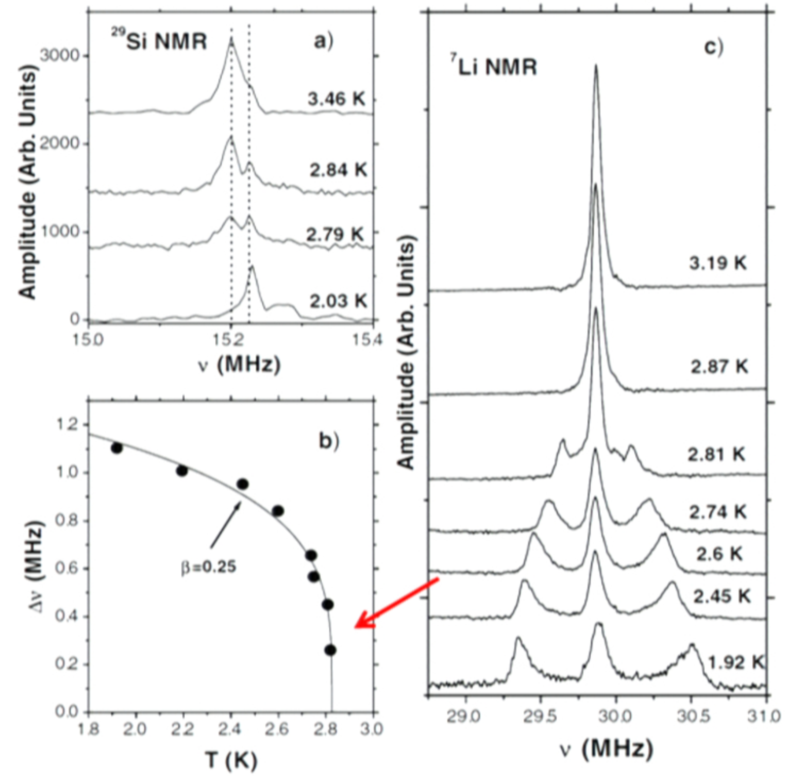



Powder

Single crystal

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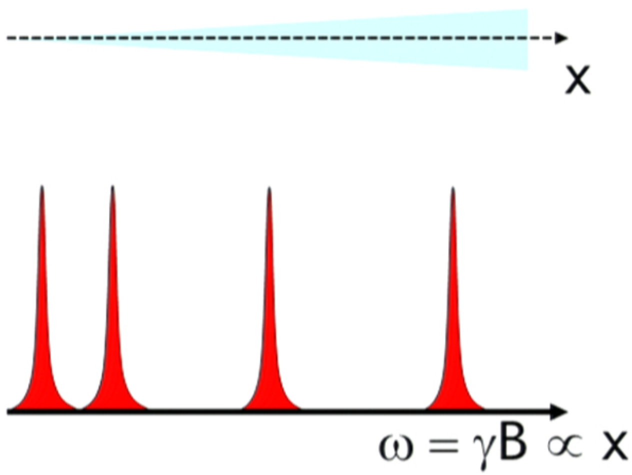
# Probing spin textures

## MRI

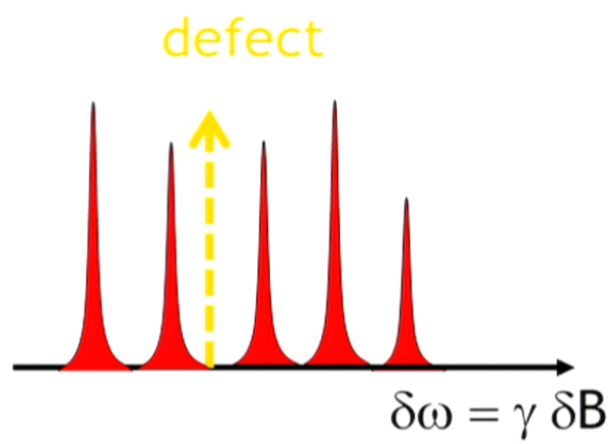
- Coding space with a field gradient




- Contrast experiments using relaxation times

## Electronic / Magnetic systems

- Magnetic / spin vacancies generate a distribution of magnetic moments *ie* a distribution of local fields under an applied field



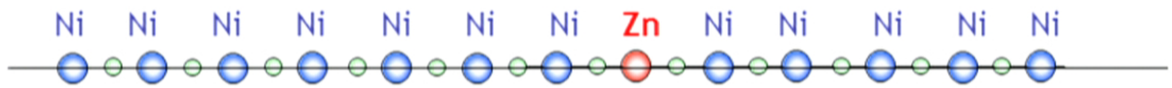

- Intensity depends on relaxation times Contrast experiment

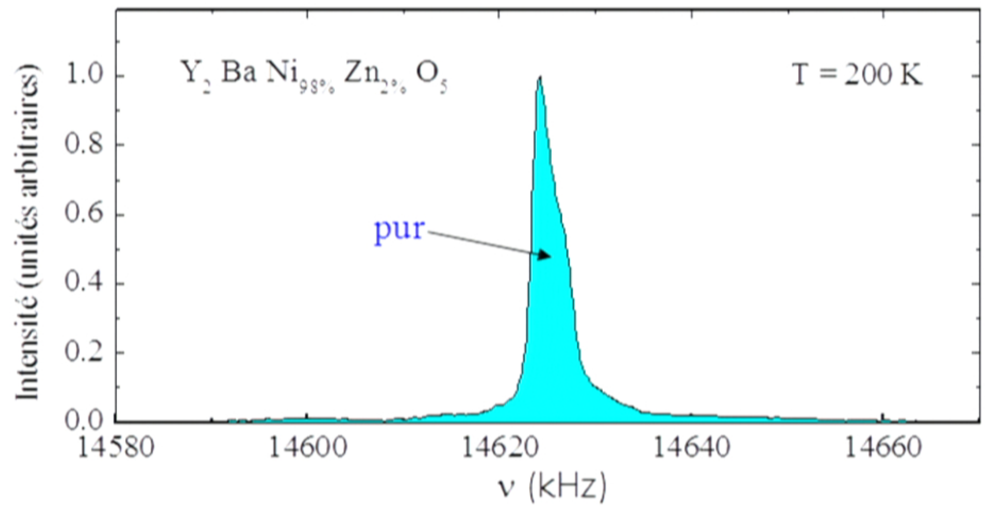
Variation of static and dynamical electronic/magnetic properties around

# Spin textures

$K_{spin}$ yields a histogram of $\chi$ values, not a sum

One impurity in a Haldane chain, $YBa_2NiO_5$ (S=1) with Zn impurities on Ni site




Tedoldi *et al.*, PRL 99; Das *et al.*PRB 04

Spatially resolved probe of susceptibility $\chi$

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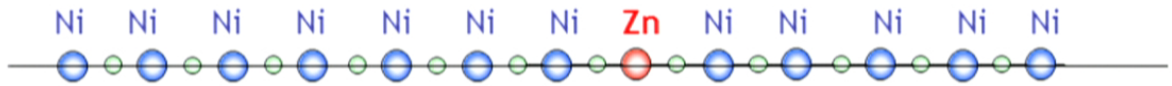


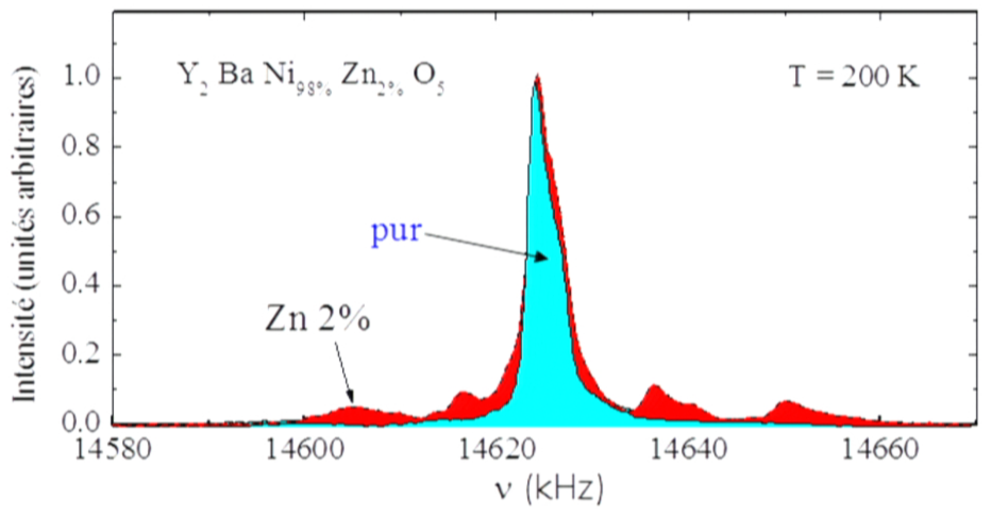


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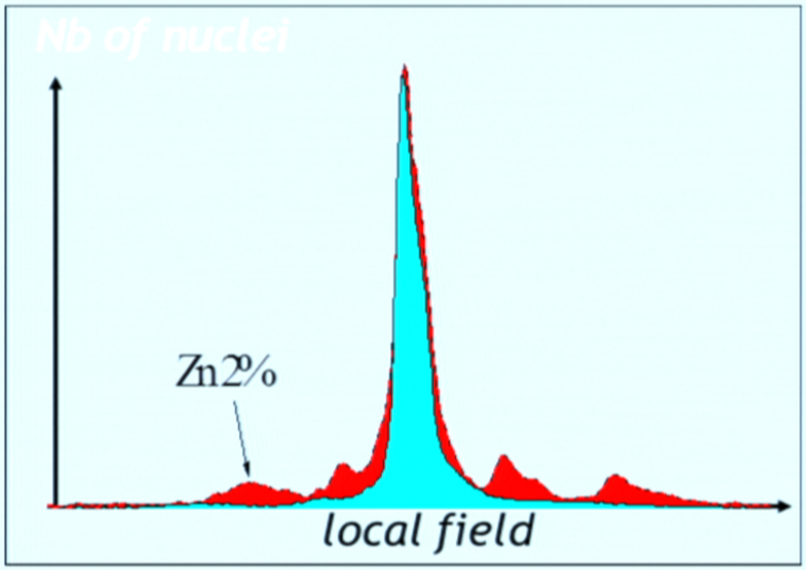
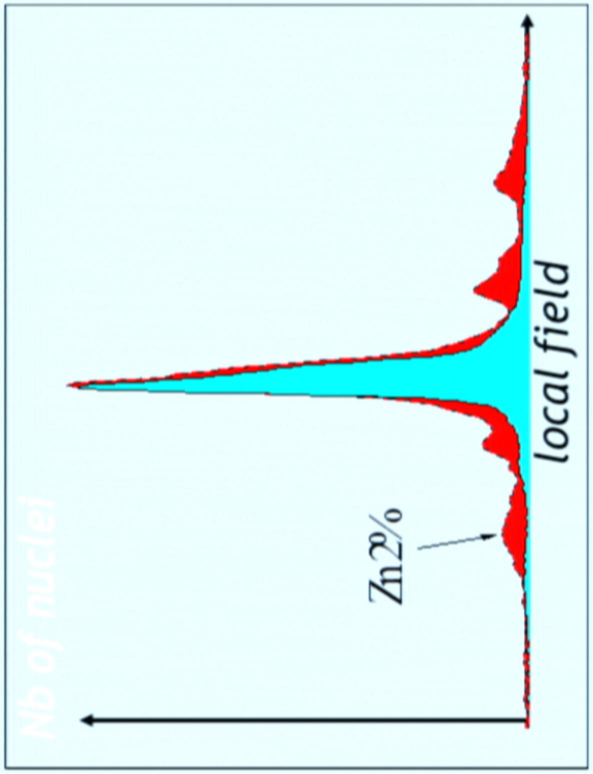
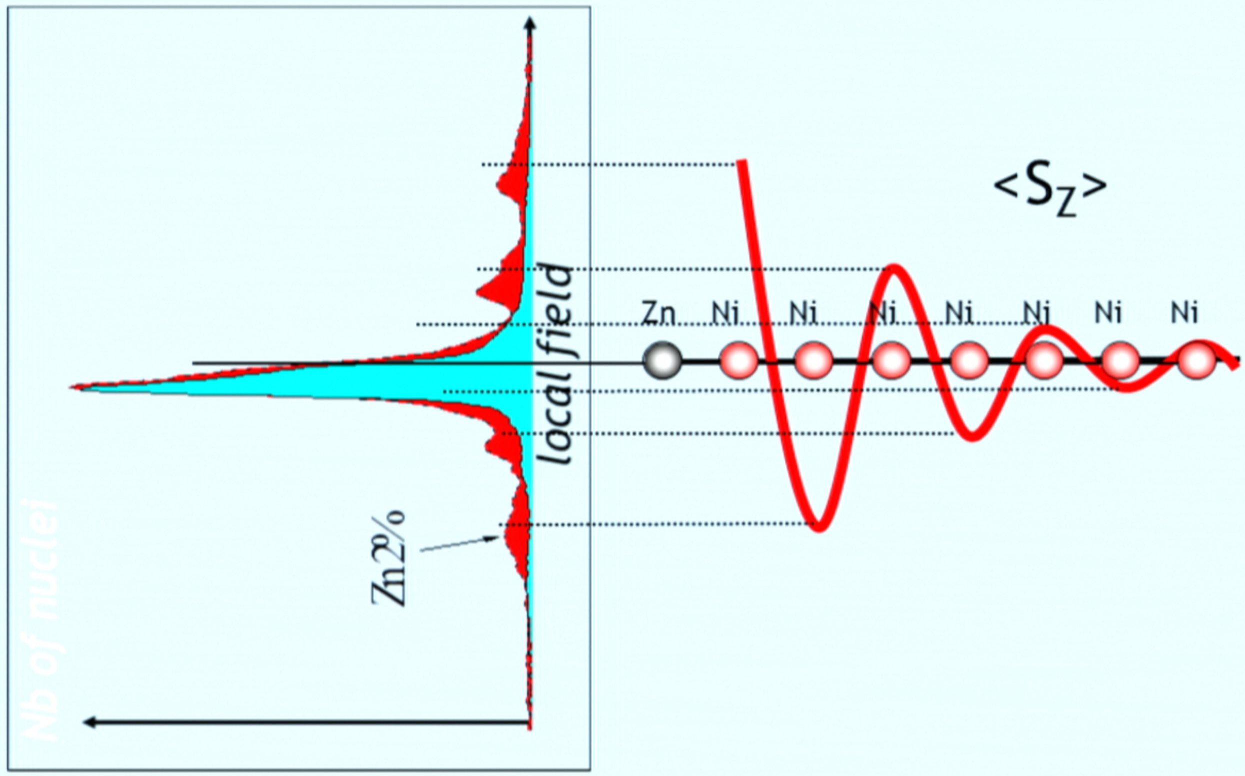



## Measurement of the correlation length $\xi$

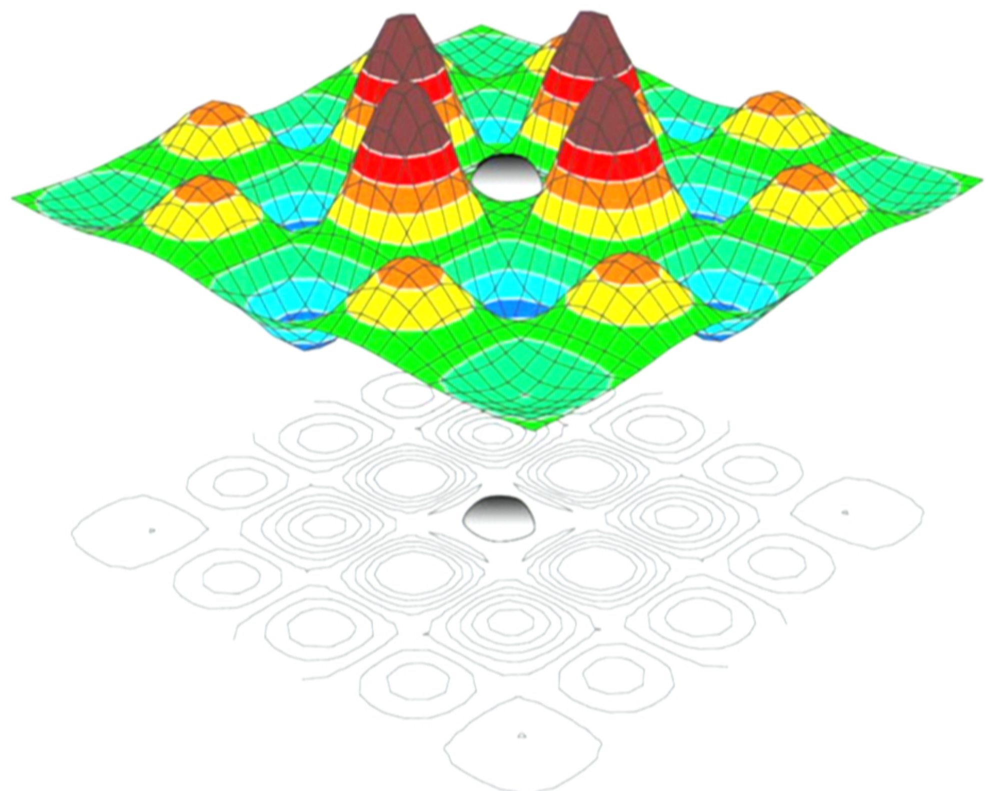



# Measurement of the correlation length ξ




# Measurement of the correlation length ξ

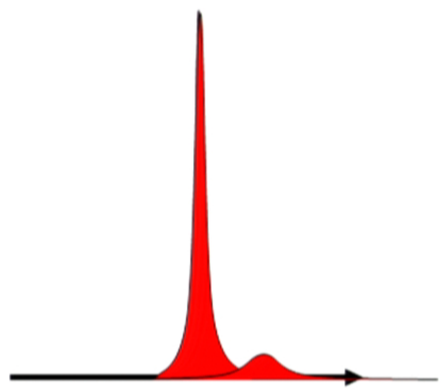
# Zn (Ni): a spinless (magnetic) defect in HTSC



*Alloul et al., Rev. Mod.Phys. 2009*

Staggered response peaked on the neighbors

# What is the ideal case?



$$\nu_{NMR} = \gamma/2\pi\, H_0 + \delta H_{loc}$$

Either specific lines or line broadening, (a)symmetry of the NMR line

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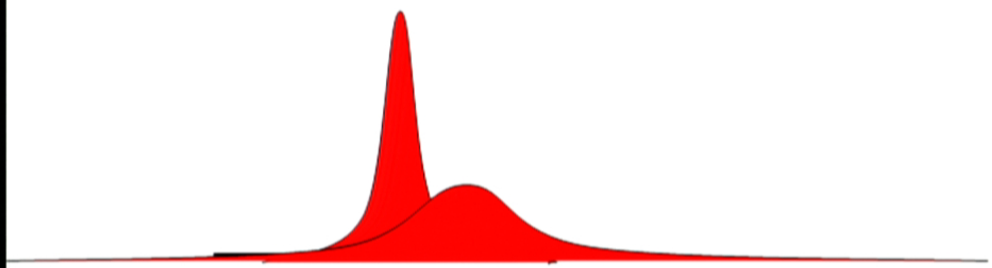

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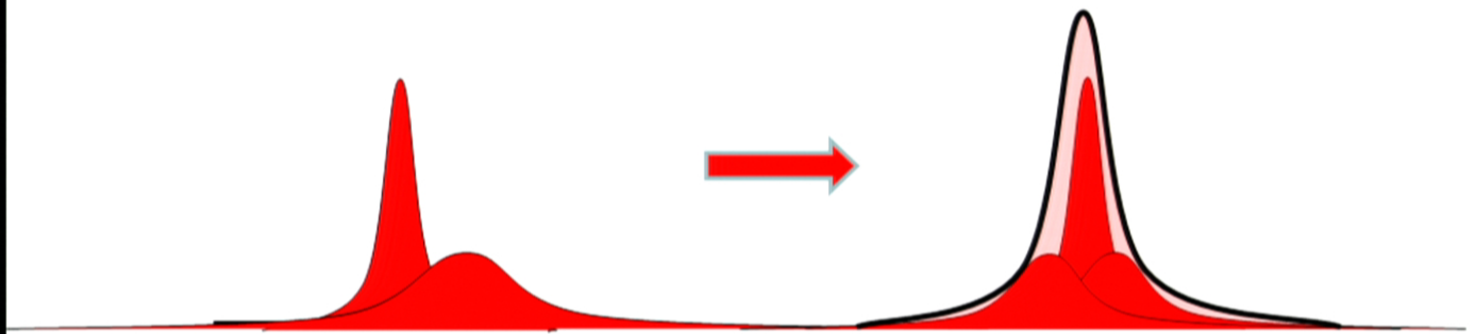

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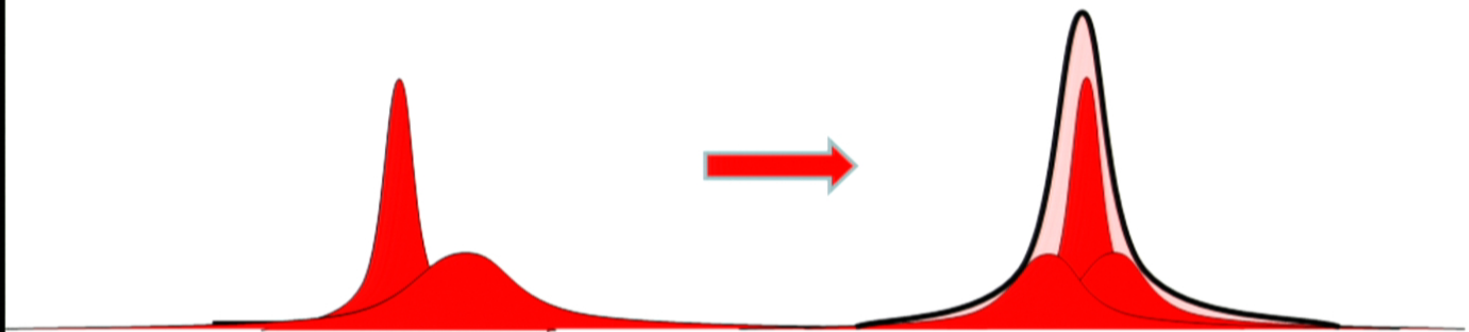
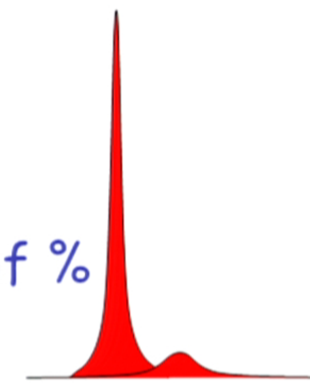


$\nu_{NMR} = \gamma/2\pi\ H_0 + \delta H_{loc}$

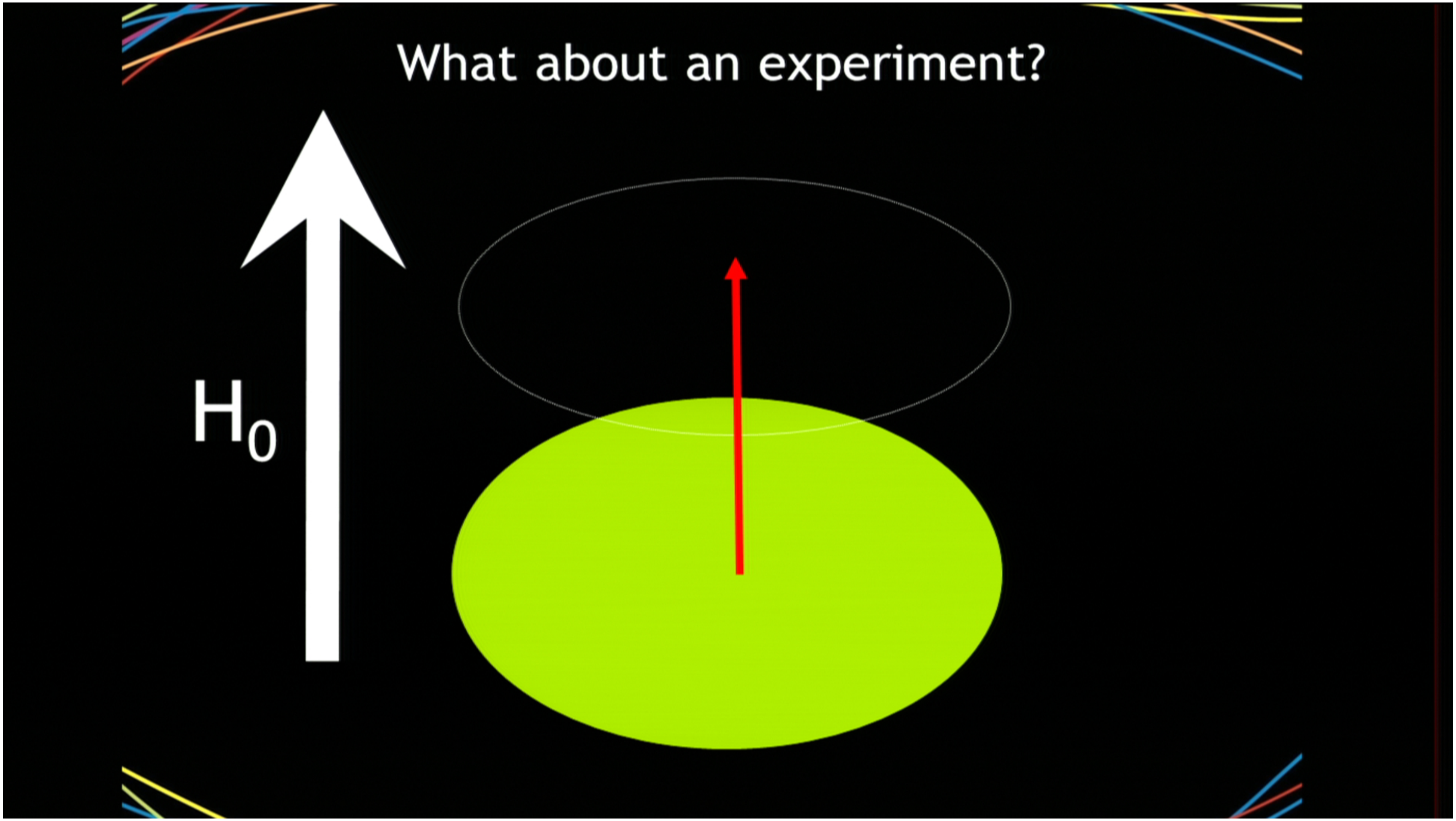
Typical goal: impurity at level of ~ fraction of %

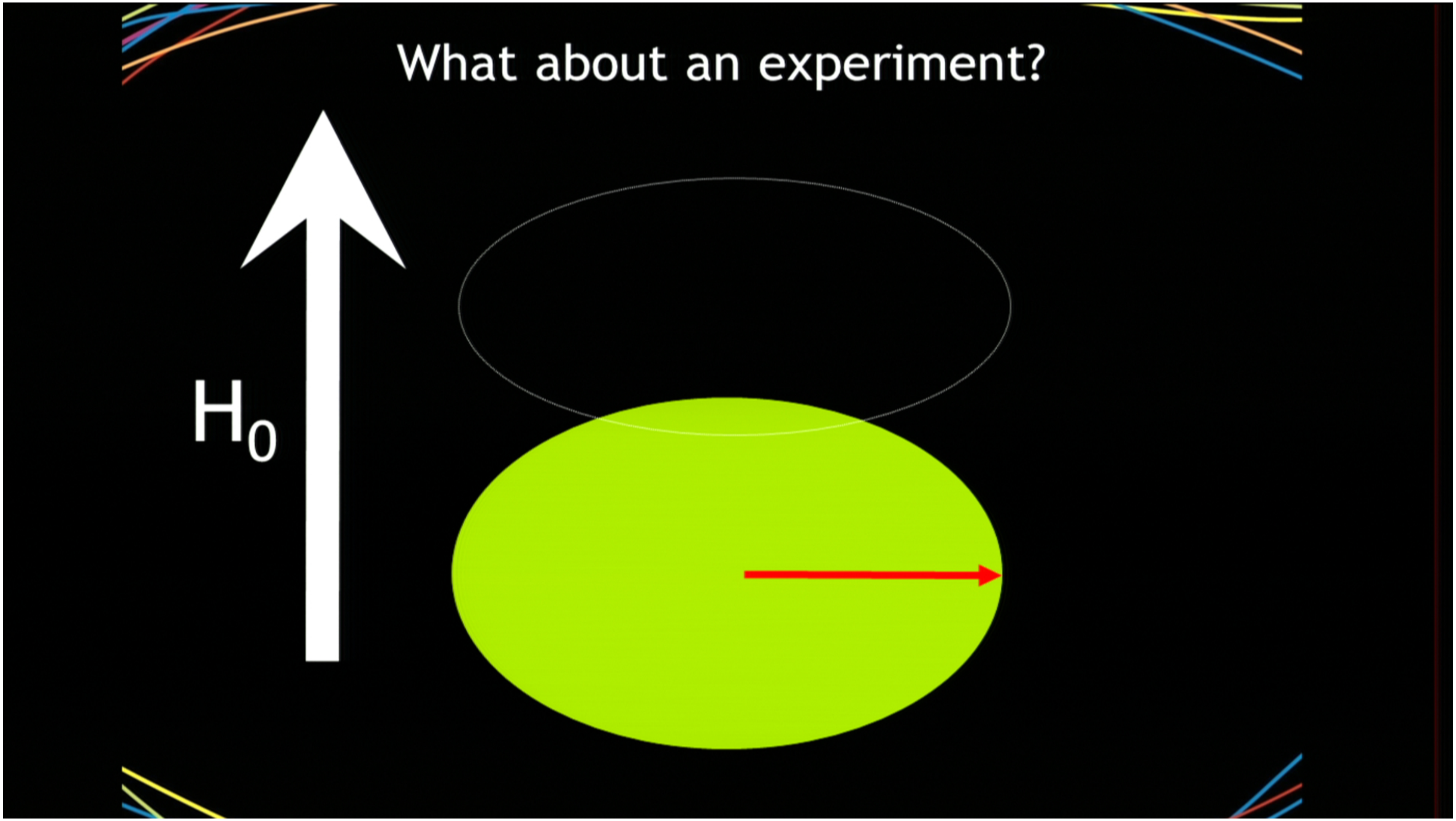


Either specific lines or line broadening, (a)symmetry of the NMR line

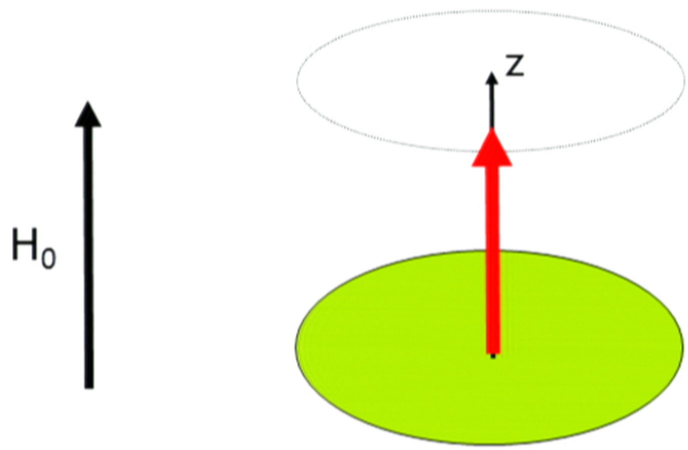
# Defects ≡ perturb to reveal: what can we learn?

- ✓ Susceptibility in the vicinity of the defect
  (*shift of satellites, defect = local probe itself*)
- ✓ Nature of spin texture and correlation length
  ( intrinsic vs extrinsic)
- ✓ Link of the response with concentration of defects
- ✓ Modeling the response and discriminating between models


What about an experiment?
$H_0$


What about an experiment?
H0

# Dynamics as probed by NMR: relaxation times



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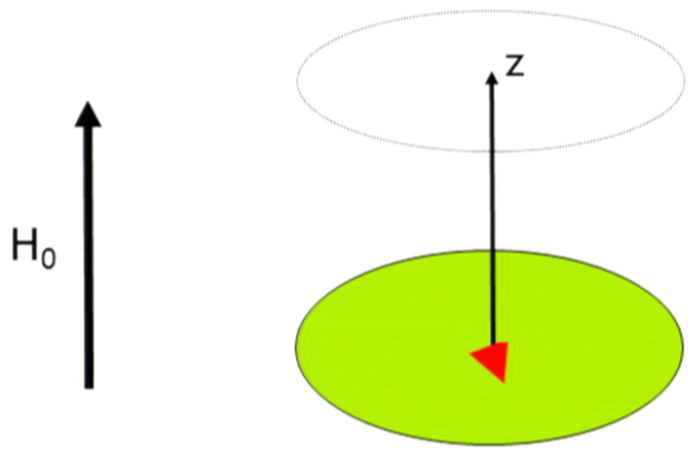
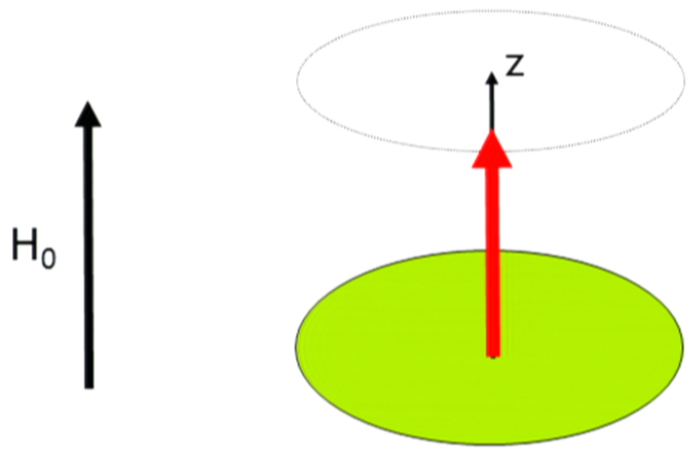



$T_2$

# Dynamics as probed by NMR: relaxation times




$T_1$

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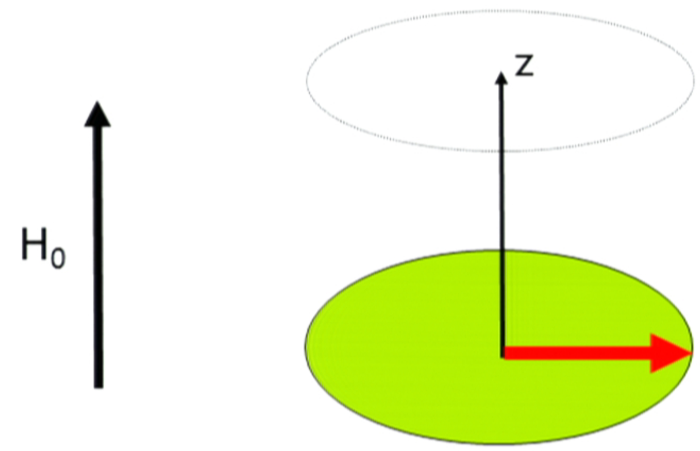

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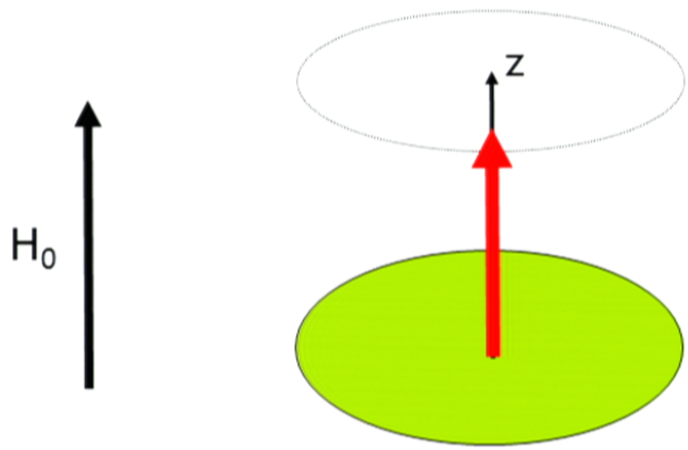


$T_1$

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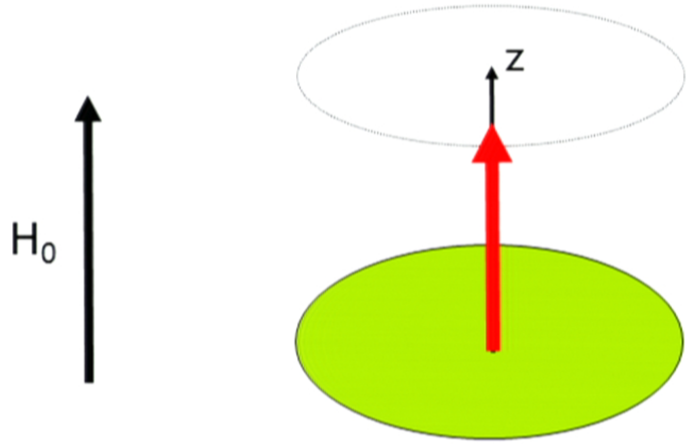



transverse relaxation : $T_2$

Enegy is conserved

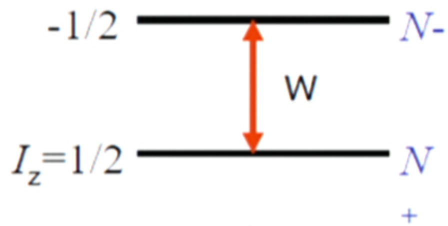
$$\frac{dM_{X,Y}}{dt} = \frac{-M_{X,Y}}{T_2} + \gamma\left(\vec{M} \times \vec{H}\right)_{X,Y}$$

Longitudinal relaxation : $T_1$

Energy exchange
with the lattice

$$\frac{dM_Z}{dt} = \frac{M_{equilibrium} - M_Z}{T_1} + \gamma\left(\vec{M} \times \vec{H}\right)_Z$$

# Relaxation time $T_1$




Transition probability due to fluctuating local field

$$H' = -\gamma_N \hbar \vec{I} \cdot \vec{H}_{hf}(t) \qquad -\frac{\gamma_N \hbar}{2}\left(I^+ H^-_{hf}(t) + I^- H^+_{hf}(t)\right)$$

$$1/T_1 = 2W \qquad I^\pm = I_x \pm i I_y, \quad H^\pm_{hf} = H^x_{hf} \pm i H^y_{hf}$$

Local magnetic fluctuations at $\omega_n$ (Fermi golden rule)

$$\frac{1}{T_1} \sim \int_{-\infty}^{\infty} < B_L^+(t) B_L^-(0) > \exp(-i\omega_n t) dt$$

$$B(t) = \sum_{coupled\,nuclei\,r_i} A_{hf}(r_i) \vec{I}.\vec{S}(r_i, t)$$

Fourier transform

$$\frac{1}{T_1} \sim \int_{-\infty}^{\infty} \sum_q \left|A_{hf}(q)\right|^2 < s^+(q,t) s^-(q,0) > \exp(-i\omega_n t) dt$$

Fluctuation

-

Dissipation

⇨

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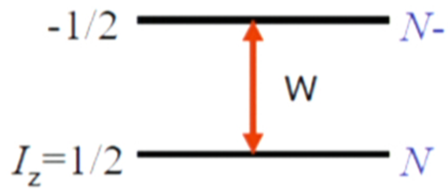


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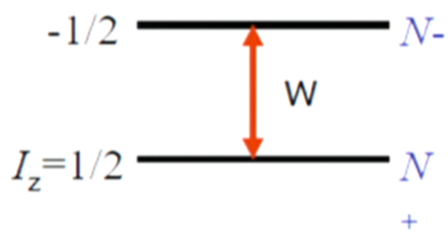


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Fluctuation - Dissipation

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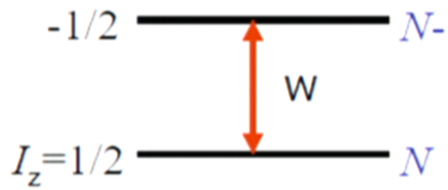
⇨

# Relaxation time $T_1$

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$$\hbar\omega_n << k_B T \;\Rightarrow\; \frac{1}{T_1} = \frac{1}{\hbar^2}\frac{k_B T}{(g\mu_B)^2}\sum_q |A(q)|^2 \frac{\chi_t''(q,\omega_n)}{\omega_n}$$

# Filtering factor

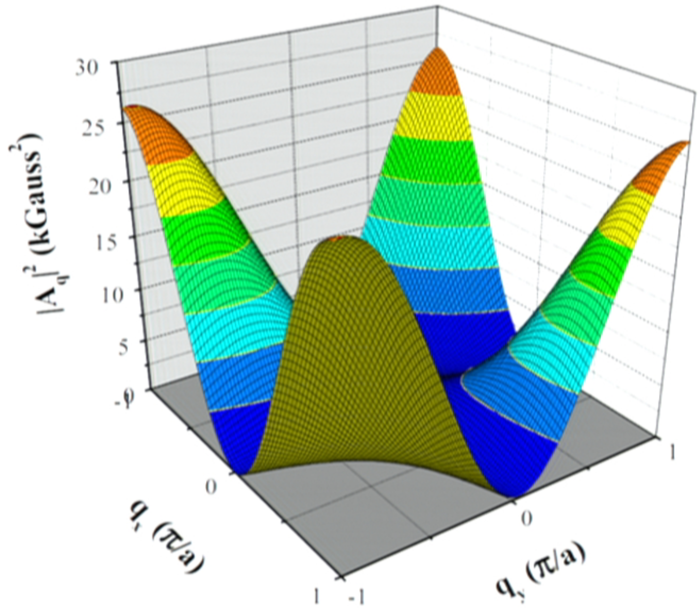


**Fig. 3.** $^{29}$Si form factor in the first Brillouin zone of the two-dimensional frustrated antiferromagnet $Li_2VOSiO_4$. Excitations at wave vectors $(\pm\pi/a, 0)$ or $(0, \pm\pi/a)$ are filtered out, *i.e.* $^{29}$Si $1/T_1$ is not sensitive to these modes.

*P. Carretta, A. Keren, chapter in*
*Introduction to Frustrated Magnetism, Springer (2011), Ed. C. Lacroix, P. Mendels, F. Mila*

Note: no filtering factor in a uniform phase (para...)

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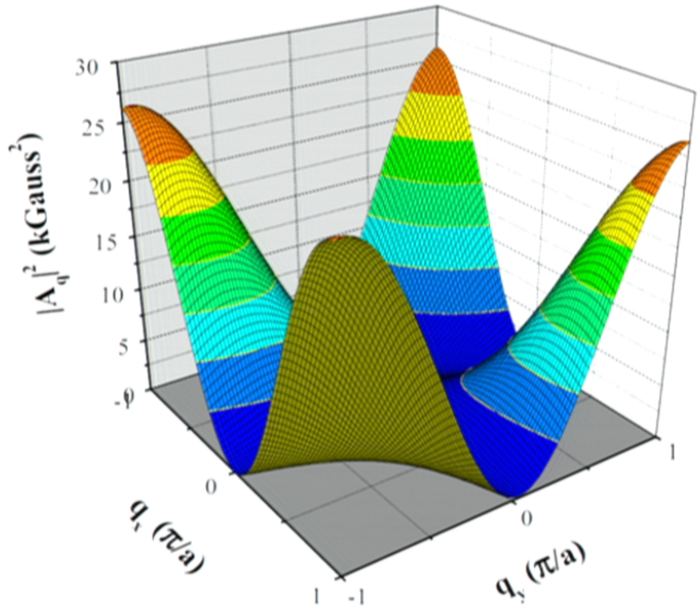


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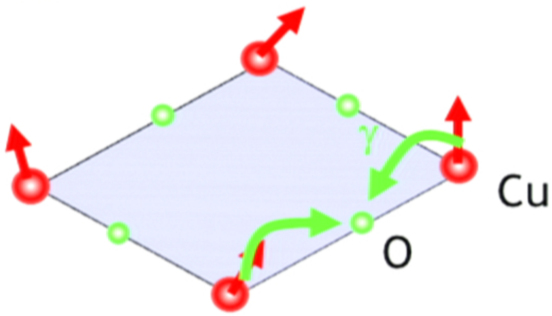
# Relaxation time $T_1$: electronic spins

$$\frac{1}{T_1} = \frac{1}{\hbar^2} \frac{k_B T}{(g\mu_B)^2} \sum_q |A(q)|^2 \frac{\chi_t''(q,\omega_n)}{\omega_n} \qquad A(\vec{q}) = \sum_{r_i} A(\vec{r_i}) e(-i\vec{q}.\vec{r_i})$$

A(q) form factor and favours some q.




Cu

O

Underdoped cuprate

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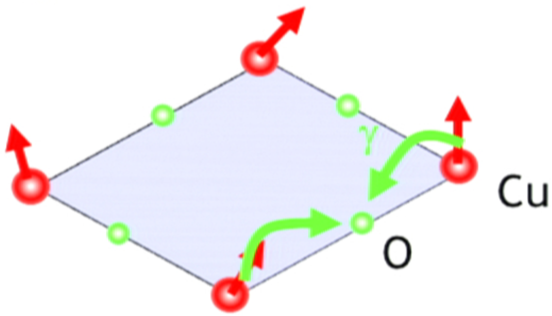
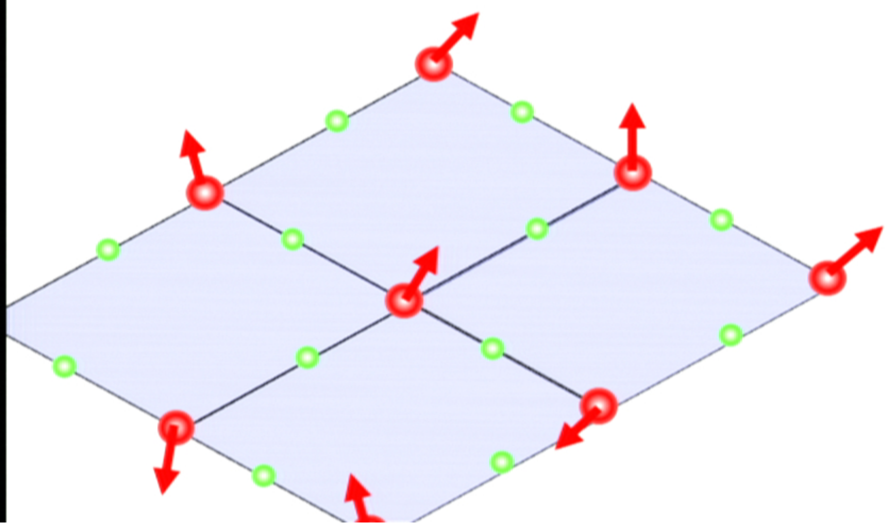



$$|A(\vec{q})|^2 \sim 2\gamma\left[1+\frac{1}{2}\left(\cos(q_x a)+\cos(q_y b)\right)\right]$$

favours q=0, ferromagnetic fluctuations between Cu



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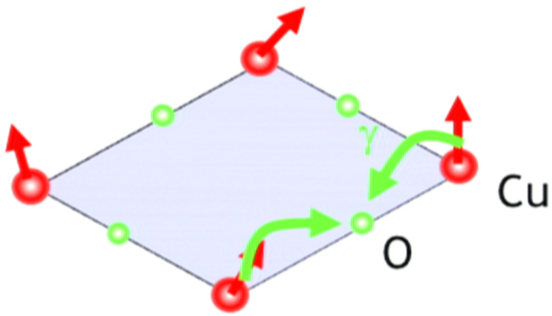


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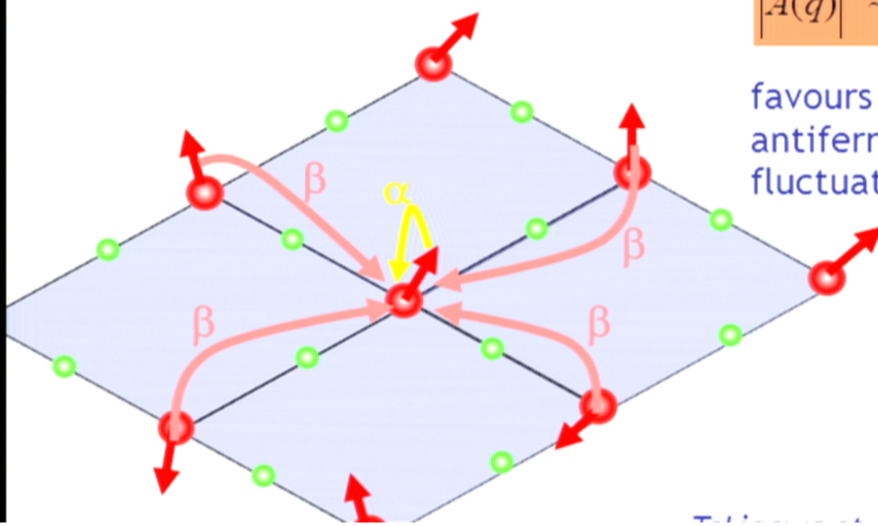
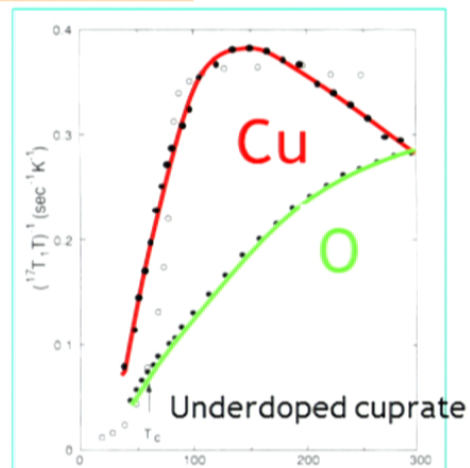
$$|A(\vec{q})|^2 \sim \left[\alpha + 2\beta\left(\cos(q_x a)+\cos(q_y b)\right)\right]^2$$




favours q=π,π, antiferromagnetic fluctuations

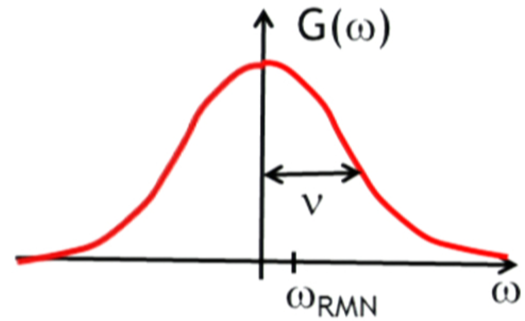



Takigawa et al., PRB (1991)

# Longitudinal relaxation $T_1$: fast fluctuaions

Frequency spectrum of local field fluctuation

$$G(\omega) = \int_{-\infty}^{\infty} < B_L^+(t) B_L^-(0) > \exp(-i\omega t) dt$$




a useful and simple expression: case of one single frequency dynamics

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

$$B_{loc} \approx A_{hf} S$$

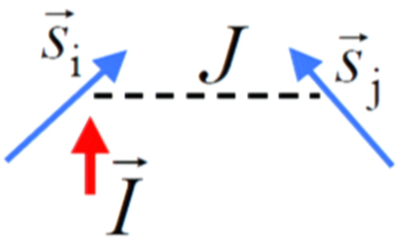
$$\frac{1}{T_1} = \gamma_n^2 G(\omega_{RMN}) = \gamma_n^2 B_{loc}^2 \frac{2\nu}{\nu^2 + \omega_{RMN}^2}$$

Fast fluctuation $\omega_{RMN} << \nu$
« *motional narrowing* »

$$\frac{1}{T_1} \approx \frac{\gamma_n^2 B_{loc}^2}{\nu} = \frac{A_{hf}^2 S^2}{\hbar^2 \nu}$$

## $T_1$: Paramagnetic regime for an insulator ⊕ exchange (J)

High temperature, paramagnetic limit $\nu >> \omega_{RMN}$ : $\dfrac{1}{T_1} \approx \dfrac{A_{hf}^2 S^2}{\hbar^2 \nu}$




$S_i$ fluctuates because of the effective Instantaneous field from the *z* neighbors

$$\nu \approx \frac{J\sqrt{z}S}{\hbar} \Rightarrow \boxed{\frac{1}{T_1} \approx \frac{A_{hf}^2 S}{\hbar J \sqrt{z}}}$$

1/$T_1$ is T-independent

# Magnetic transition: divergence of $T_1$

## Slowing down of fluctuations

### In a weak metallic antiferromagnet

- Above $T_{Neel}$ : $T_1TK$=cst
- At $T_{Neel}$ : divergence of $1/T_1$

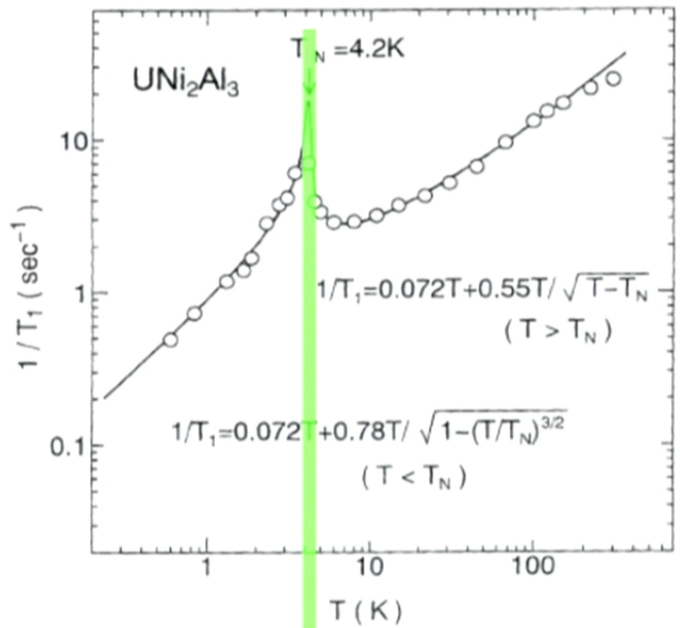
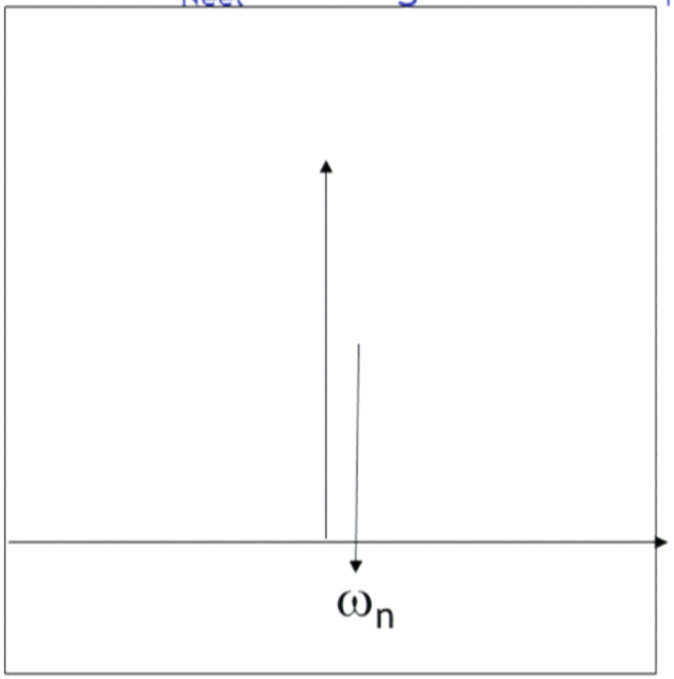



Fig. 3. Temperature dependence of $1/T_1$ of $^{27}Al$ at $H=12.1$ kOe and 2.9 kOe ($H \perp c$) in the $T$-range of 1.5–300 K and 0.6–1.5 K, respectively. Solid line is a calculation based on the SCR theory for weak itinerant antiferromagnets.[15]




Kyogaku et al., JPSJ (1993)

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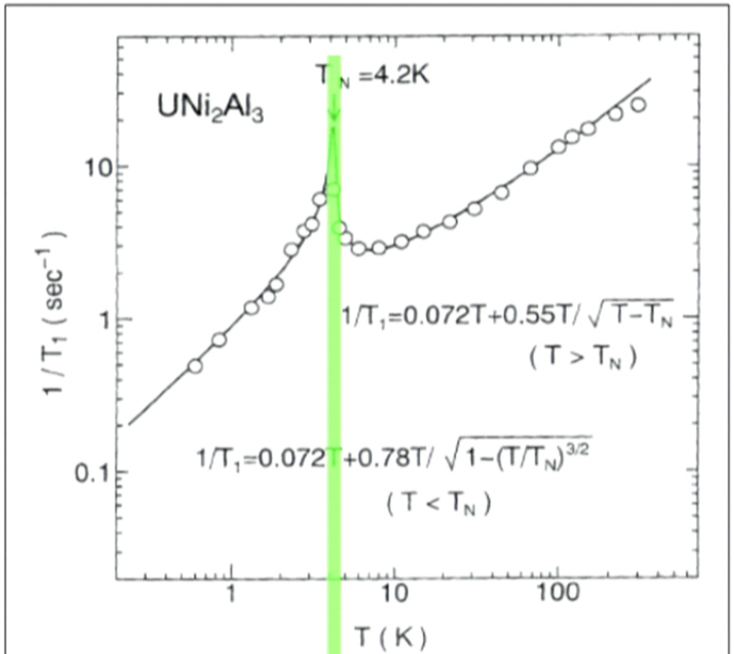


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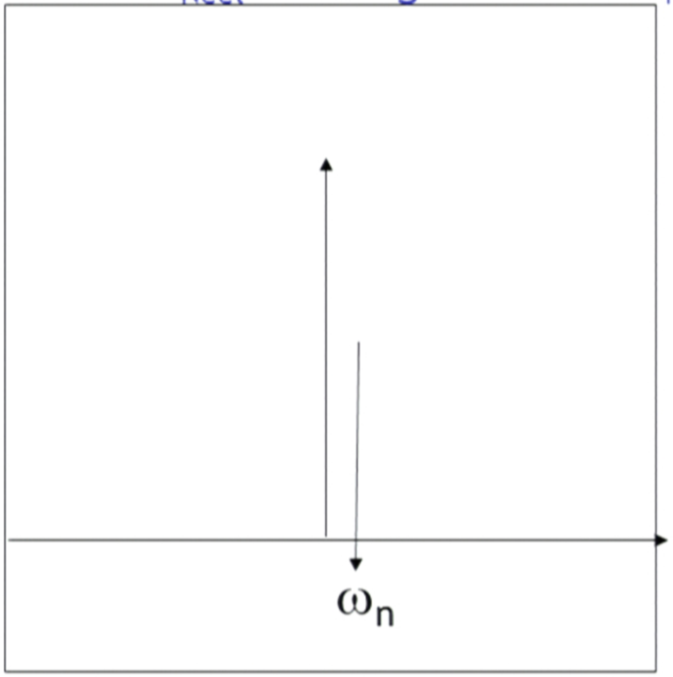

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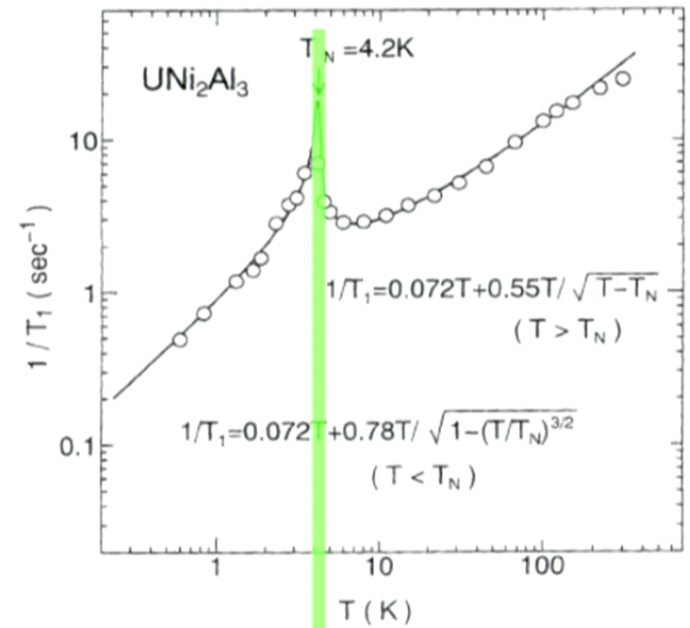


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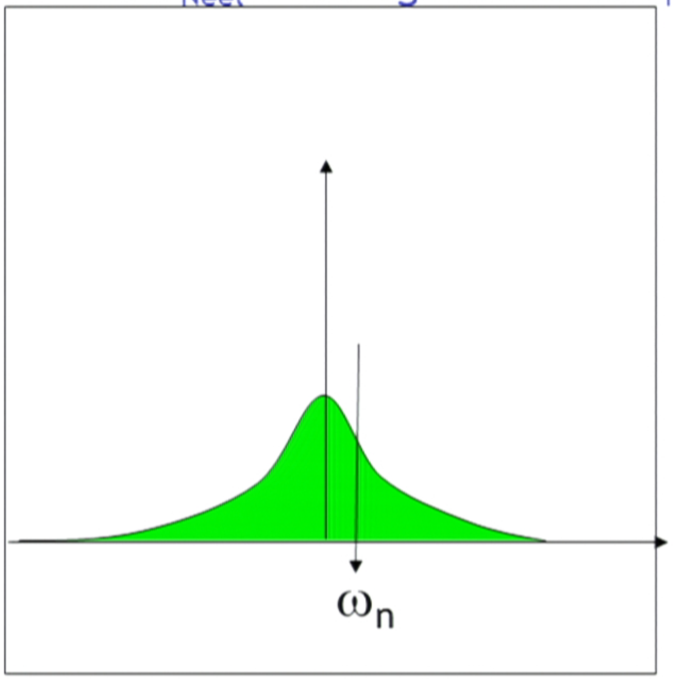

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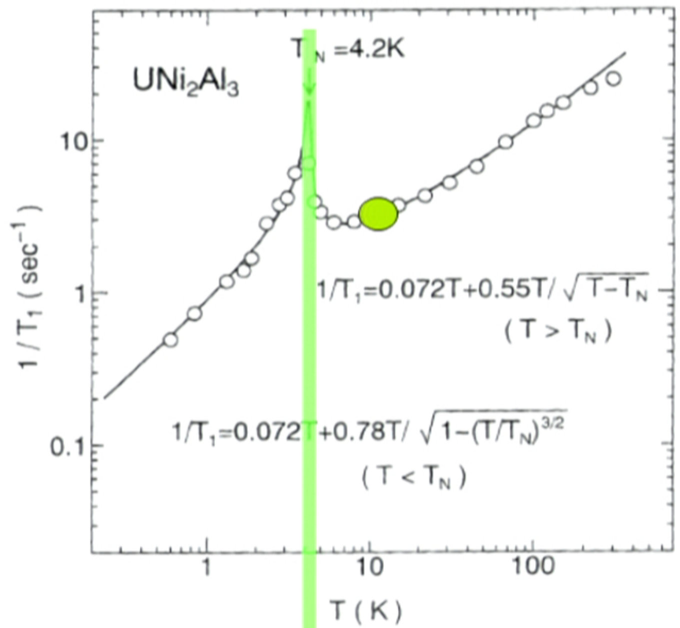


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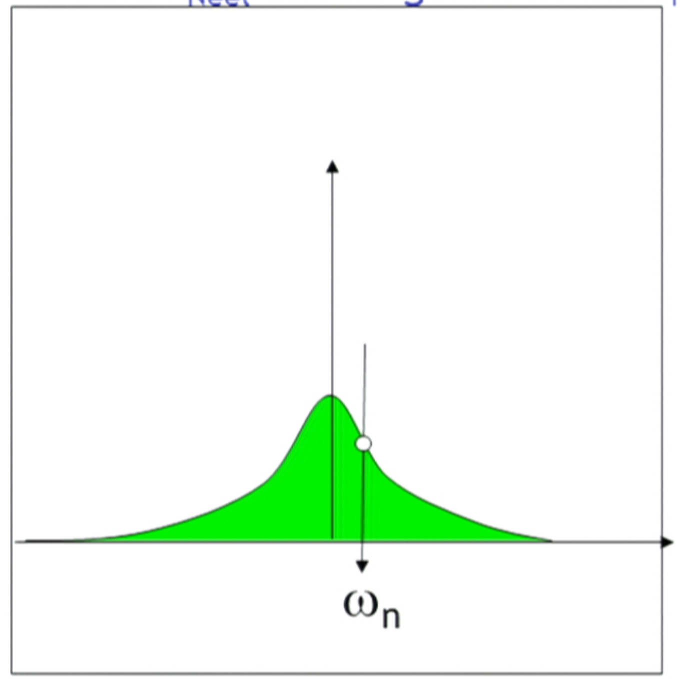

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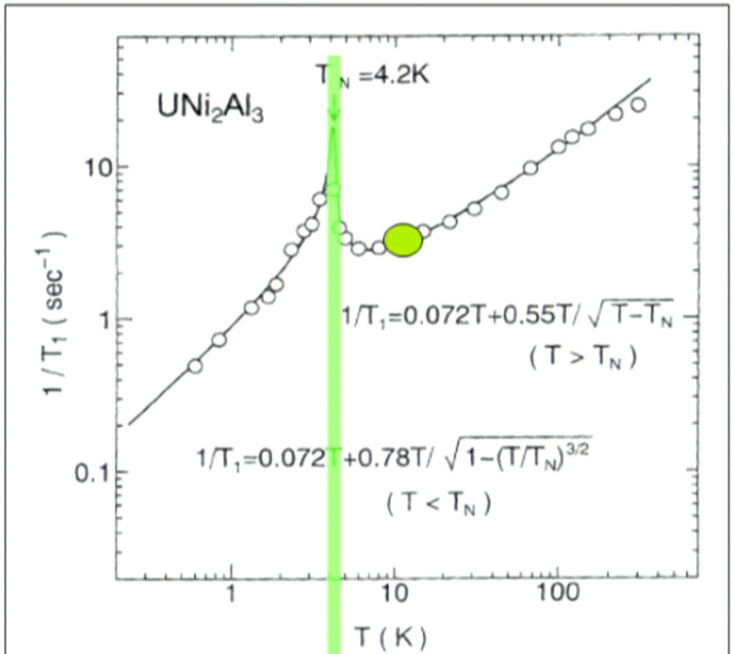


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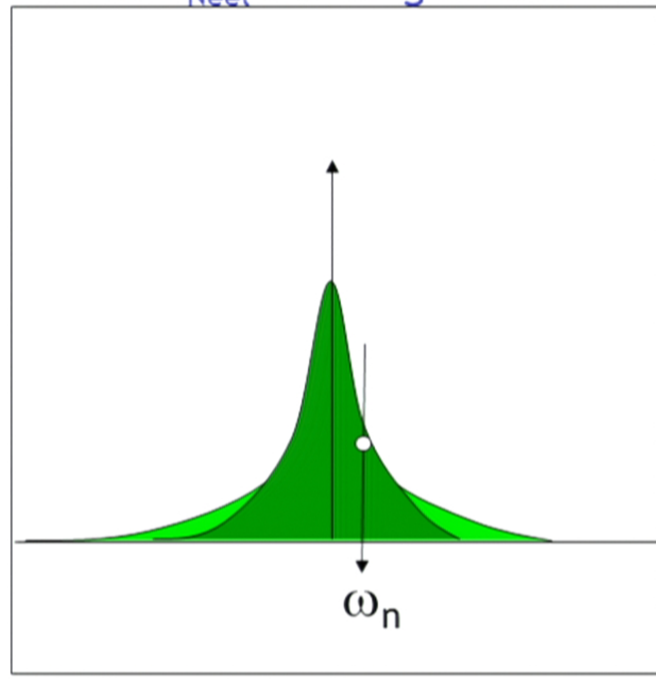

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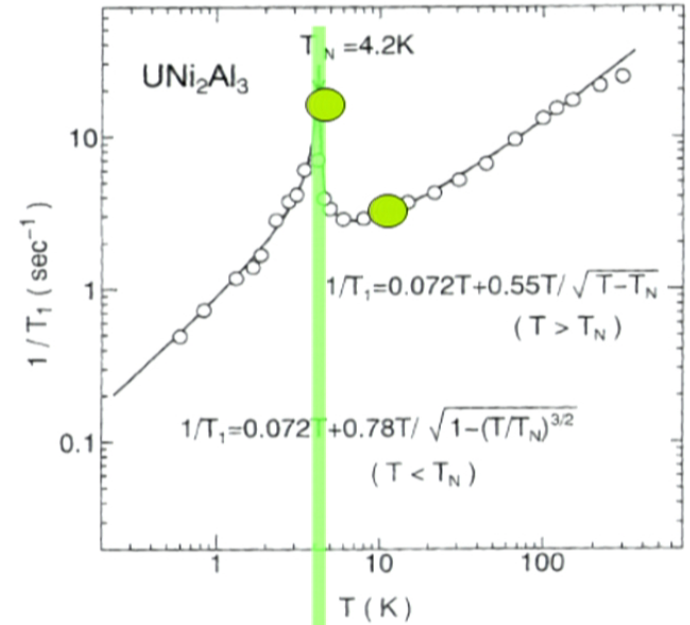


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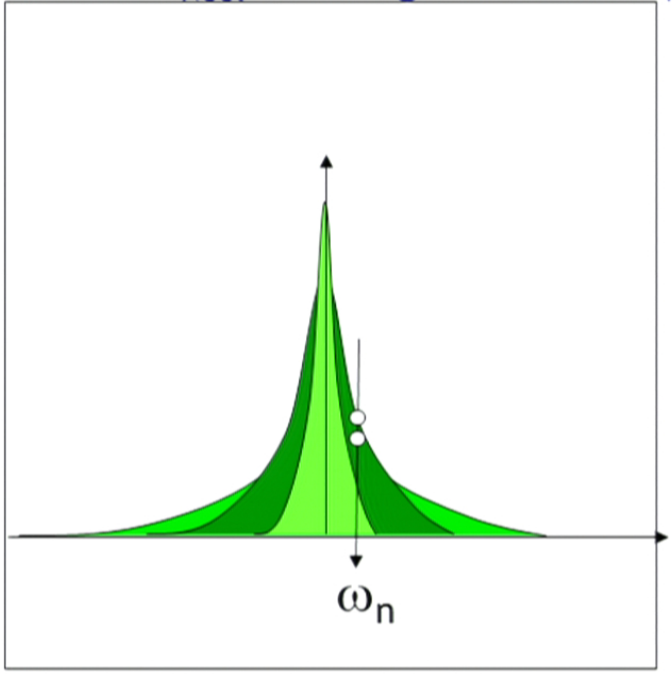
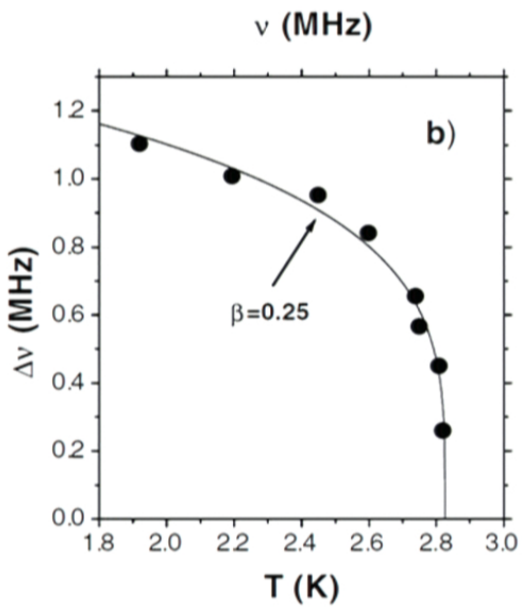
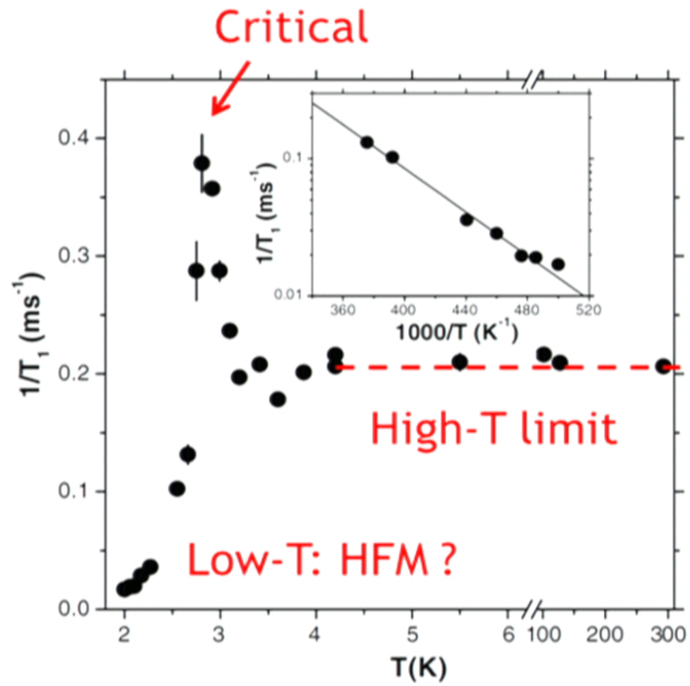


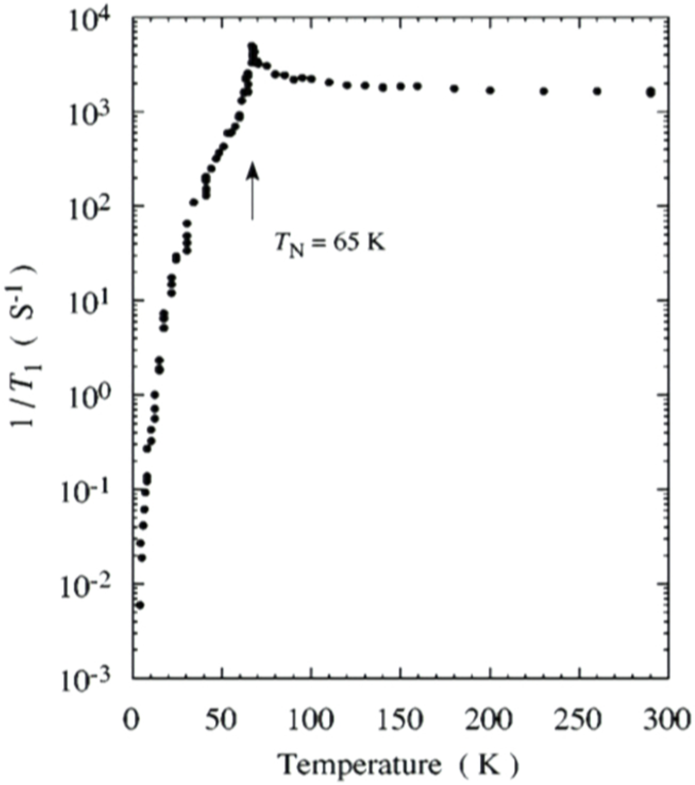
# J1-J2 model in Vanadates



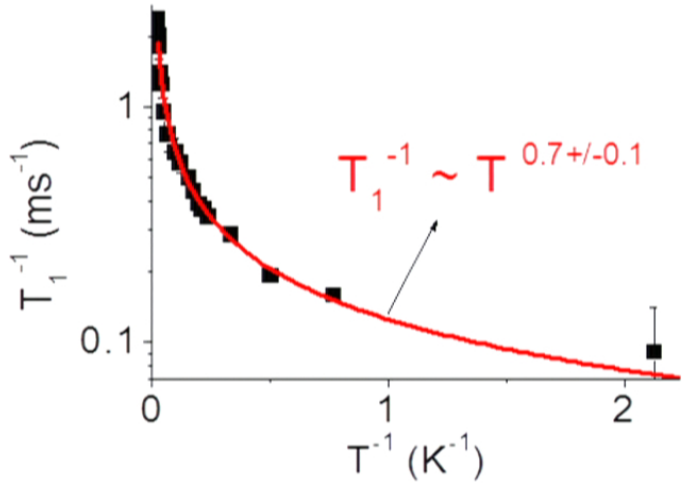

*Melzi et al. PRL 2000*

# Gapped versus non-gapped dynamics




Jarosite: $KFe_3(OH)_6(SO_4)_2$

*M. Nishiyama, Phys. Rev. B (2003)*

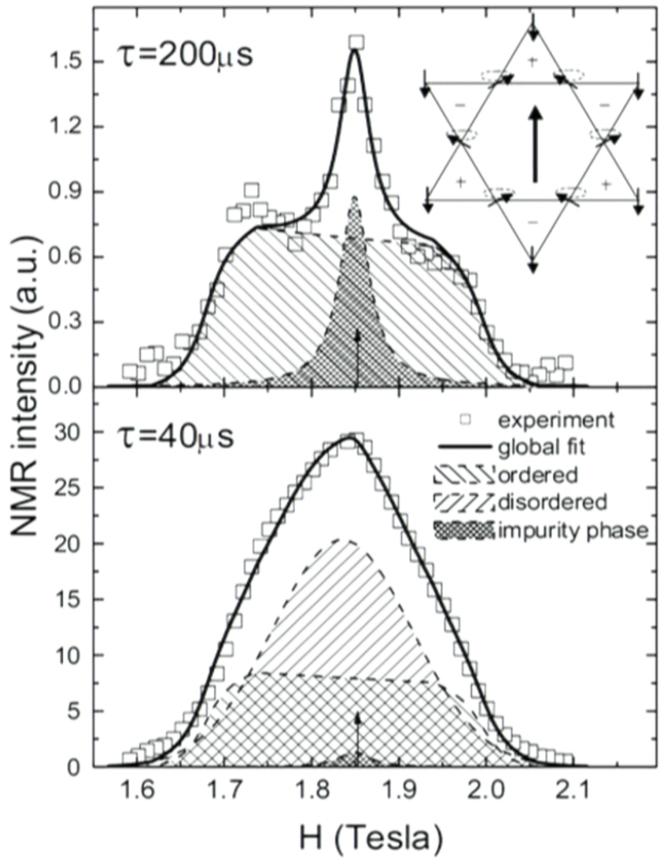



Herbertsmithite: $Cu_3Zn(OH)_6Cl_2$

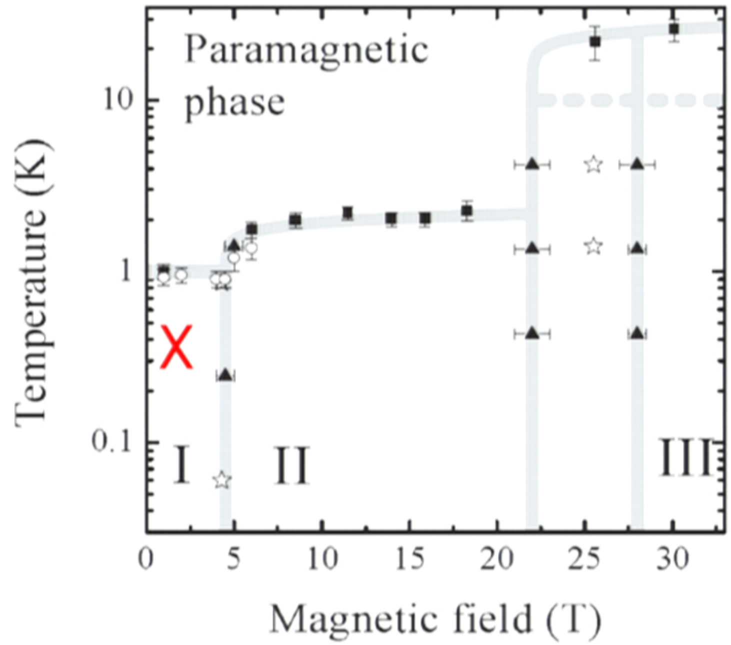
*A. Olariu et al., Phys. Rev. Lett (2008)*

Note: homogeneous (Σ exp) vs inhomogeneous relaxation (stretched)

# Contrast experiment (~MRI)



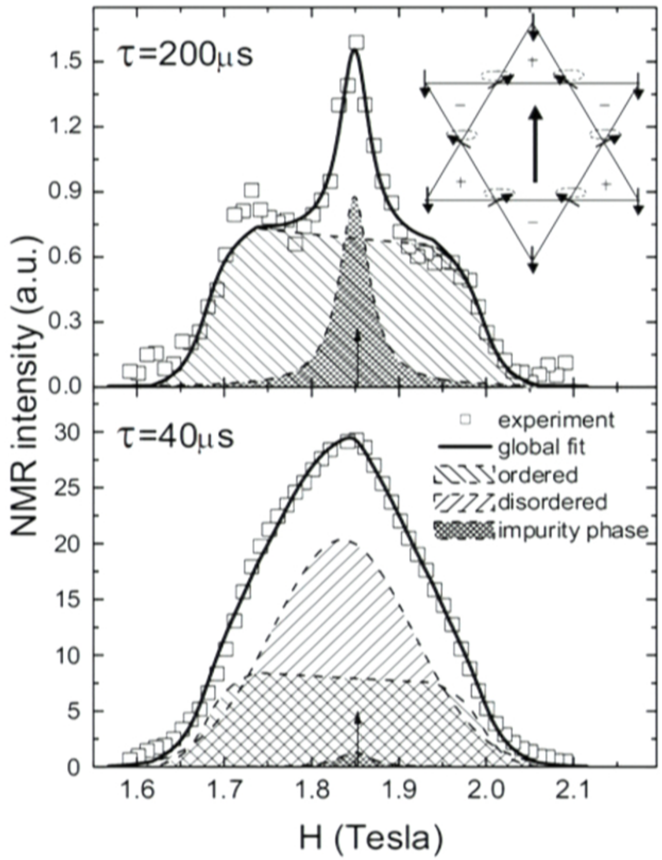

## Volborthite



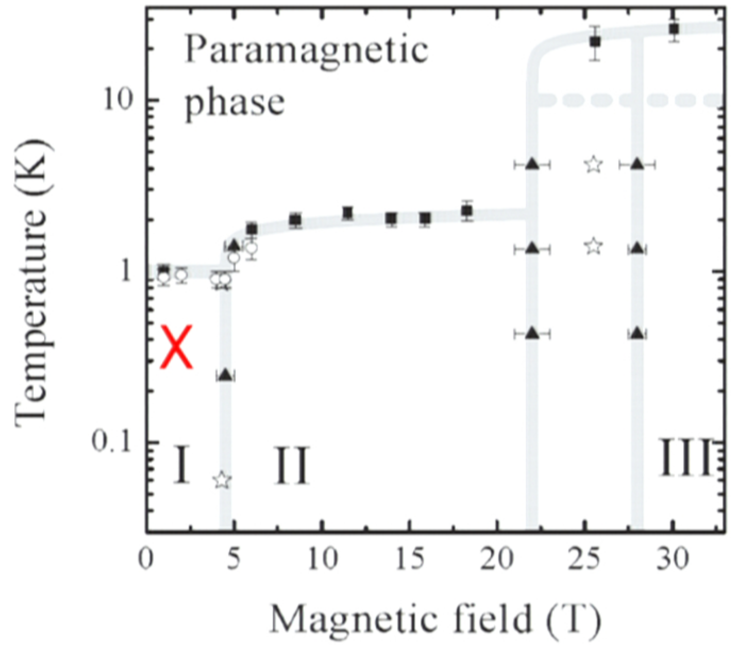

*F. Bert, Phys. Rev. Lett. (2005); Takigawa, Yoshida et al.*

Need for single crystals (~10 years)

# Contrast experiment (~MRI)




## Volborthite

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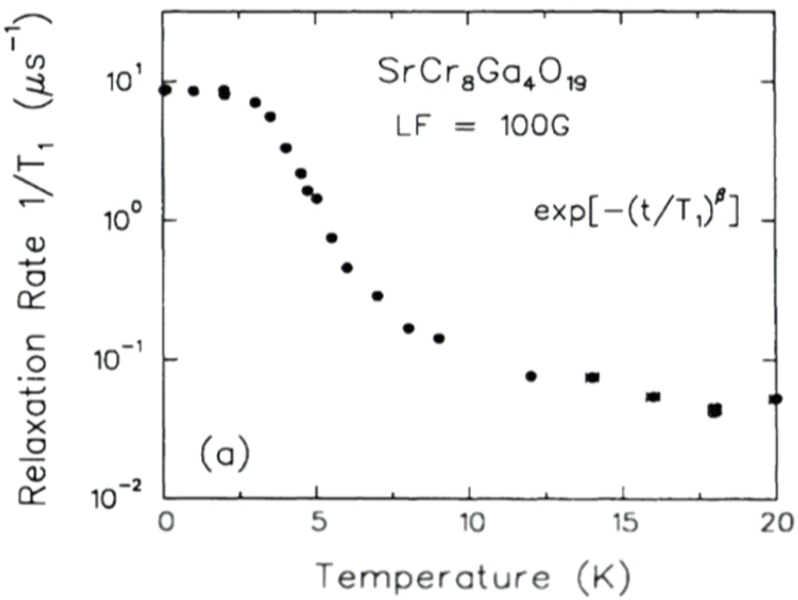
# Frustrated magnets: spin liquid like states

**Spin Fluctuations in Frustrated Kagomé Lattice System $SrCr_8Ga_4O_{19}$ Studied by Muon Spin Relaxation**

Y.J. Uemura et al., PRL 1994




Persistent relaxation!

NMR: wipe-out when slowing down of fluctuations

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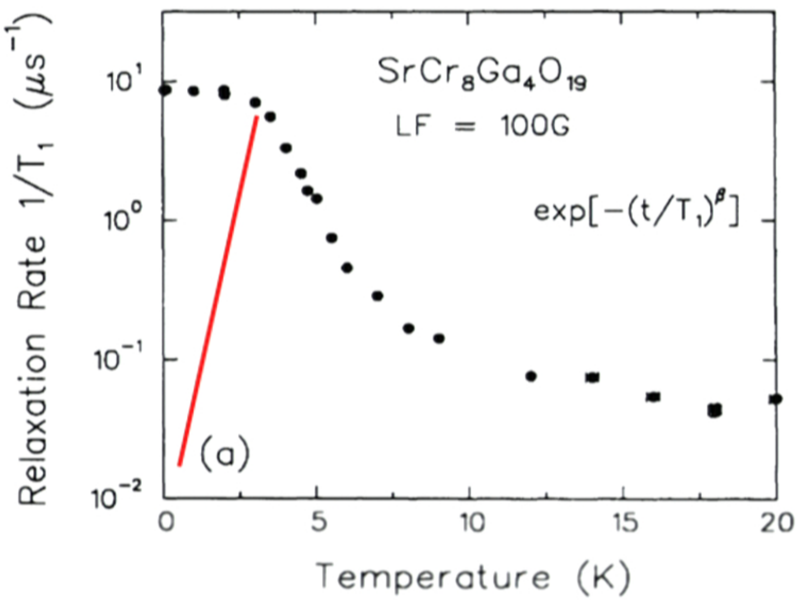


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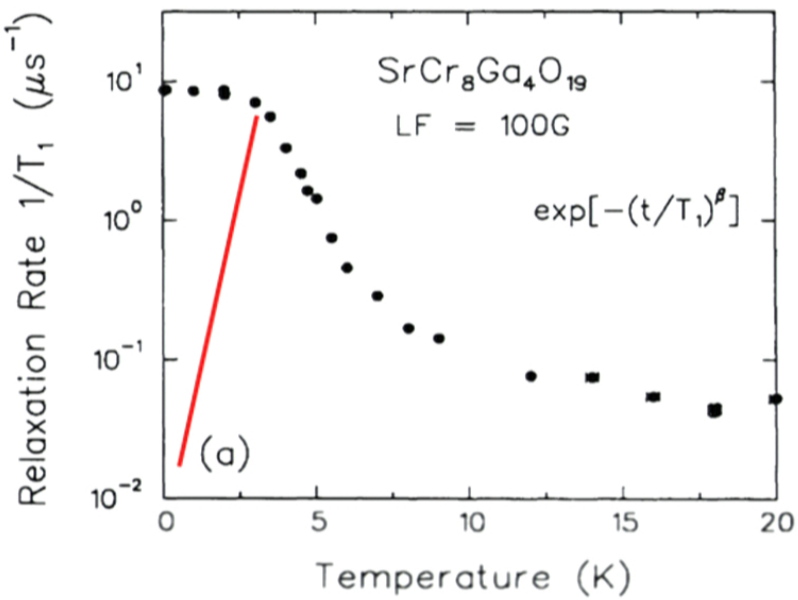


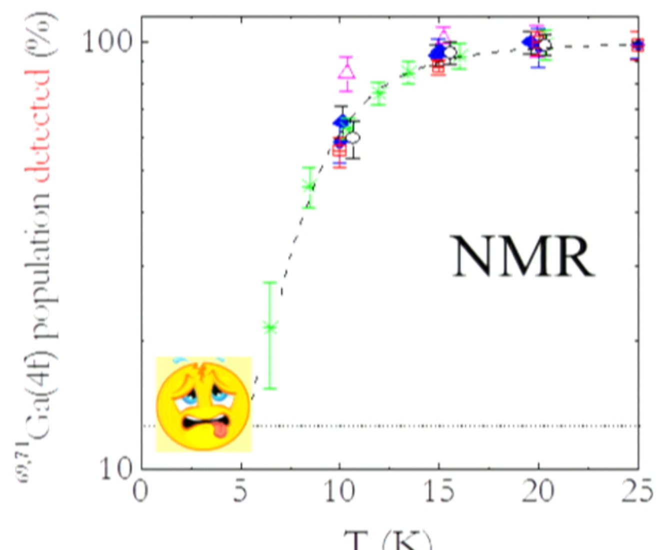


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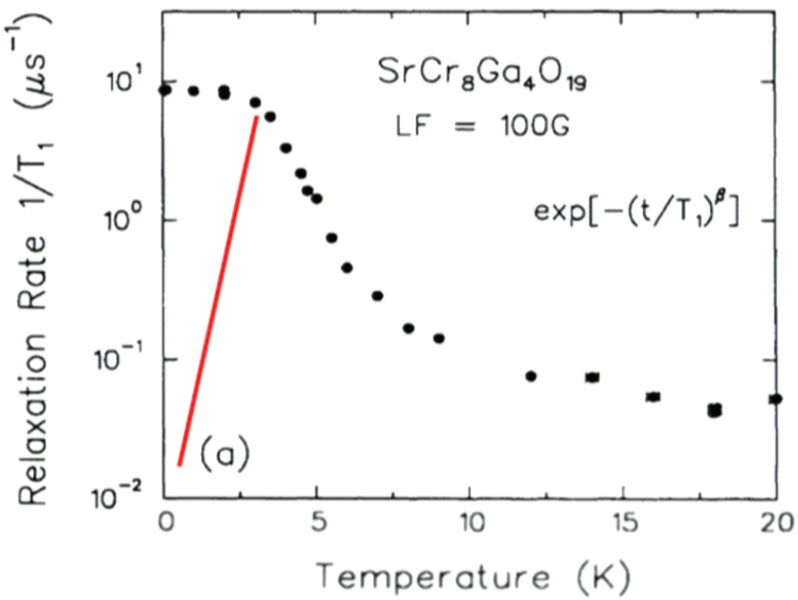


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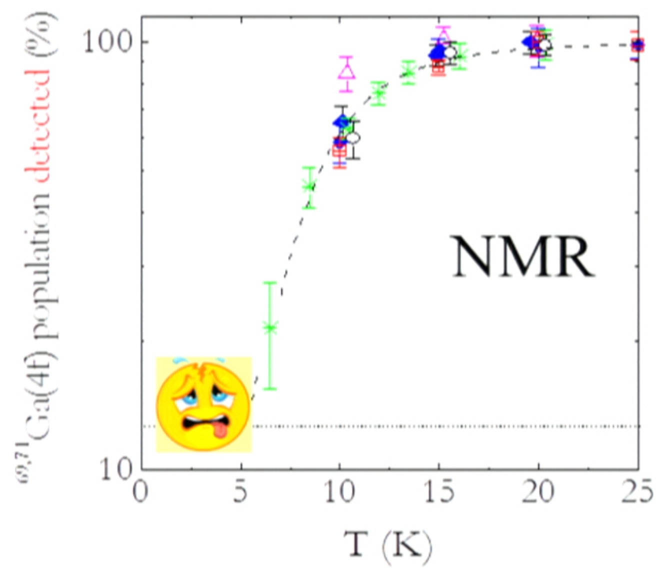


Wipe-out!

NMR: wipe-out when slowing down of fluctuations

# Summary: observables

## Static

- Orbital susceptibility
- Spatially resolved static susceptibility
- Inhomogeneities, distribution of local fields
- Charge effects
- Ordered phases (charge or magnetic order)

## Techniques

- In applied field: NMR: easy for I=1/2 on powders
  For I>1/2, quadrupolar effects, much better with single crystals
- Zero applied field: NQR (no probe of $\chi$), ZFNMR
  ~ single crystals

## Dynamics $\langle h^{+}_{loc}(t)\, h^{-}_{loc}(0)\rangle$

- Magnetic correlations $\xi(T)$
- Excitations (gapped or not gapped) $\Delta$
- Critical regime

Compare timescales of the probes vs coupling constant

# References

http://hebergement.u-psud.fr/rmn/


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