Complementarity between NMR and μSR

(for solid- state physics)

P. Mendels

Lab. Physique des solides

Univ. Paris-Sud Orsay

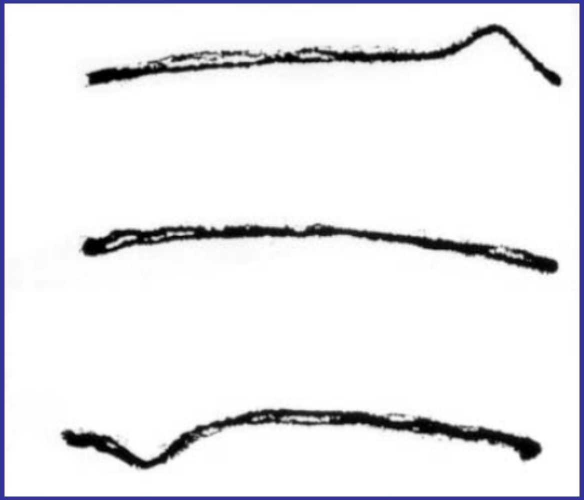
- Both probes are bulk, local probes: integrate over q, same formalism

- Difference through (i) the coupling to the environment

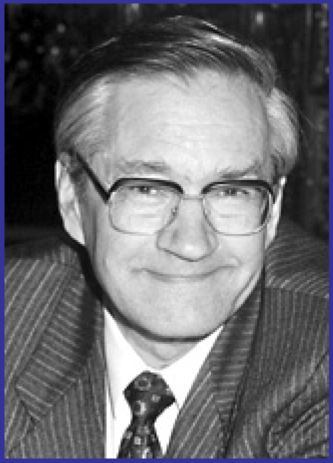
  (ii) the time window, the field range

  (iii) sample details

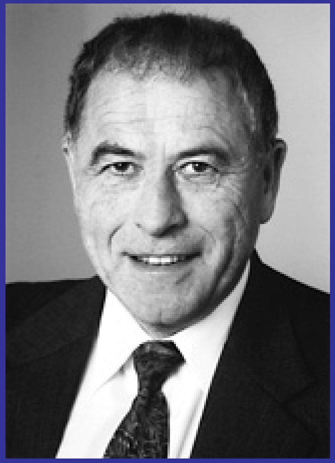
µSR and NMR: milestones (1)



Bloch & Purcell,
Nobel Physique 1952



Ernst,
Nobel Chimie 1991

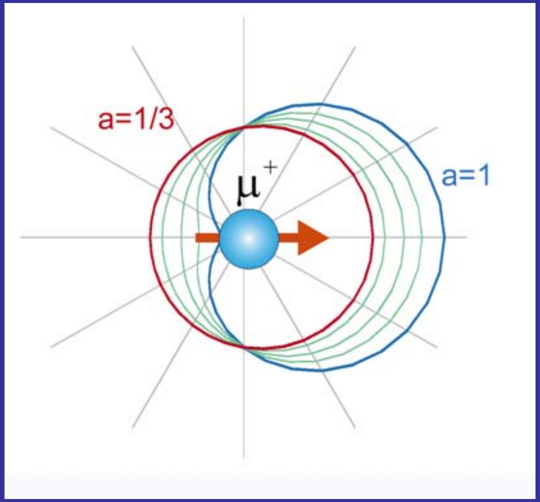


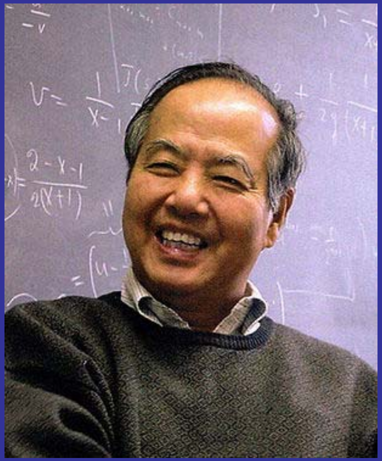
Wuthrich,
Nobel Chimie 2002

Lauterbur & Mansfeld,
Nobel Medecine 2003

μSR and NMR: milestones (2)

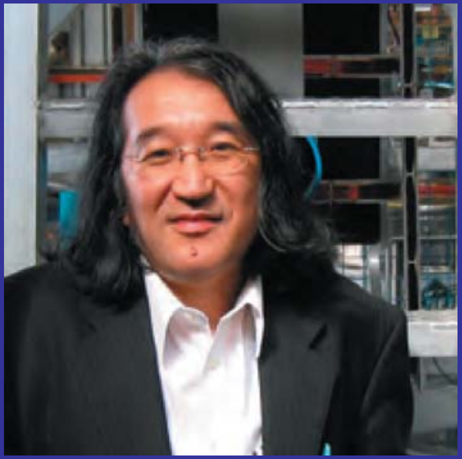
μSR and NMR: milestones (3)





Lee & Yang
Nobel Prize Physics 1953

J. Brewer
Brockhouse Medal, 2008



Y. Uemura
Yamazaki Prize, 2005

E. Morenzoni
Yamazaki Prize, 2008

μSR: some key features

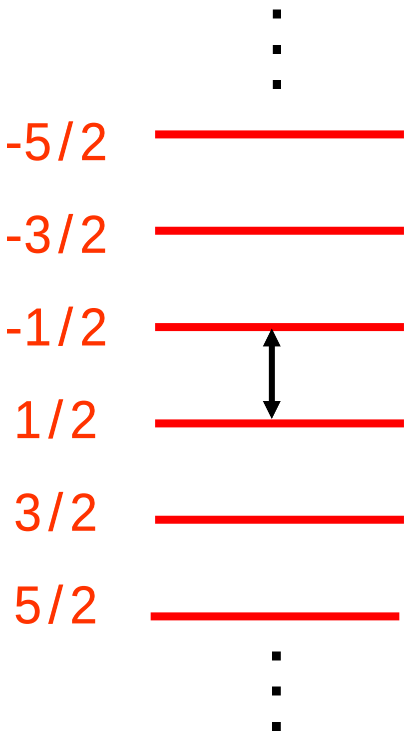
- $S_\mu = 1/2$. No quadrupolar effect
- LIFETIME $\tau_\mu = 2.2$ μs
- Implantation in all materials.
- Material and temperature independent sensitivity.
- Bulk probe (200 μm penetration, 150 mg/cm^2)... LEM!
- Implantation in one well-defined (or several) site(s):
  $O\mu^-$, 0.1 nm bond in oxides
- 100% spin polarized probe
- Diluted probe
- $m_\mu = 1/9\ m_p$: Possible diffusion of the muon: T > 150-200 K
- $\mu_\mu = 3.2\ \mu_p$; $\gamma_\mu = 13.55$ MHz/kG
- Beam spot: 7 to 30 mm. Reduced in background free setups
- H < 7 Teslas

From NMR basics (1)

Nuclear spin I in a magnetic field H_0

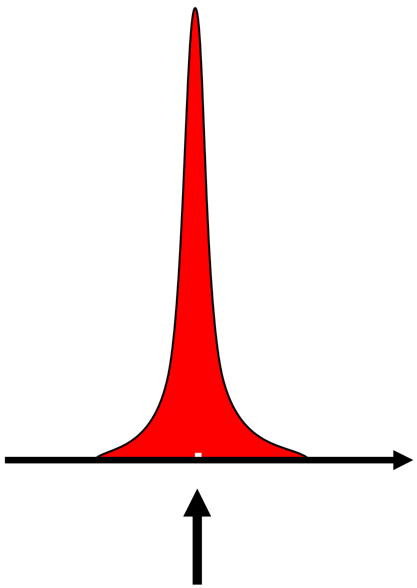
Zeeman effect : $H = -\,\mu.\mathbf{H_0} = -\,\gamma\,\hbar\,H_0\,I_z$

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



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

Need for r.f. field



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

ZFNMR: impossible...not common, also NQR

From NMR basics (2)

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

Common NMR Active Nuclei

Isotope	Spin I	%age abundance	γ 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

γ_μ = 135.5 MHz/T

μ^+ is a very sensitive probe

From NMR basics (3)

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 but... sensitivity, detection pbs...

From NMR basics (4)

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

NMR basics (5): nucleus-electron coupling

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

Orbital effect

Dipolar effect from an unpaired spin s

Contact contribution from an unpaired spin on a s orbital

$$\nu^i = \frac{\gamma}{2\pi}H_0 + \frac{\gamma}{2\pi}H_{hf}^{orb} + \frac{\gamma}{2\pi}H_{hf}^{dip} + \frac{\gamma}{2\pi}H_{hf}^{contact}$$

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

Gyromagnetic ratio: depends on the nucleus

Orbital or chemical shift

Spin shift

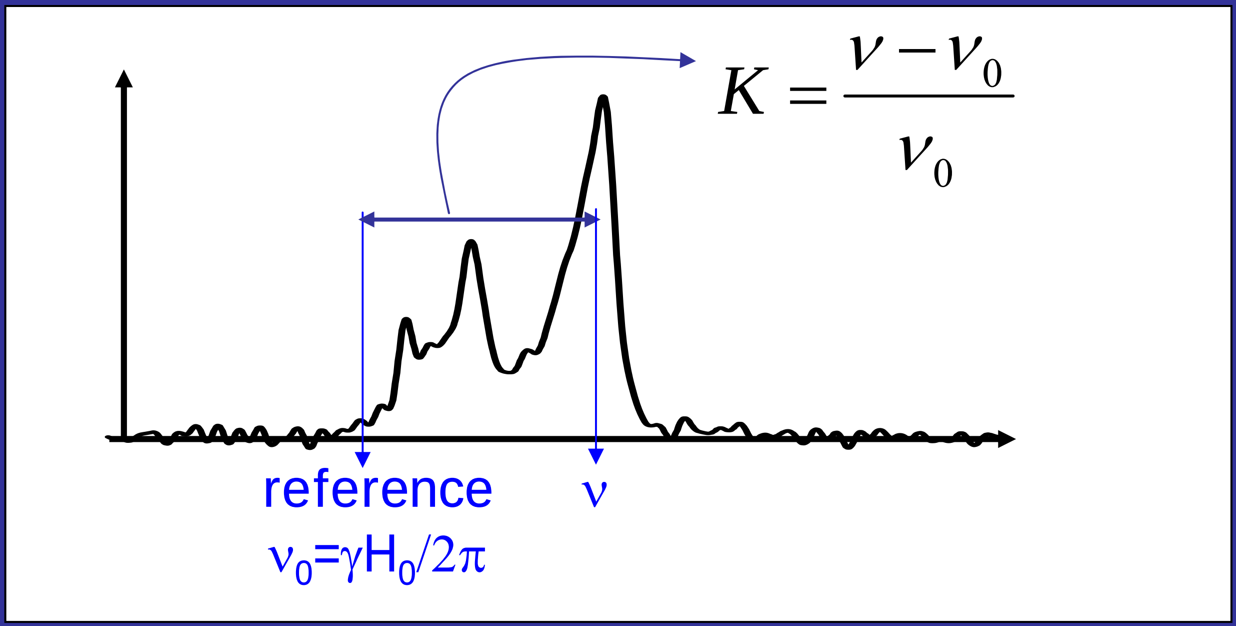
The equations are the same!

$$\tilde{\Delta K} = \frac{\sum_k \tilde{A}_k < \boldsymbol{S}_k >}{H_0}$$

$$\frac{1}{T_1} = \frac{\gamma^2}{2} \int_{-\infty}^{+\infty} e^{i\omega_0 t} < h_+(t) h_-(0) > dt$$

A_k, h: coupling to the neighbourhood is what matters!

Electron-nucleus interaction



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

Gyromagnetic ratio

Orbital or chemical shift

« Knight shifts »

From NMR basics (6)

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

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

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

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

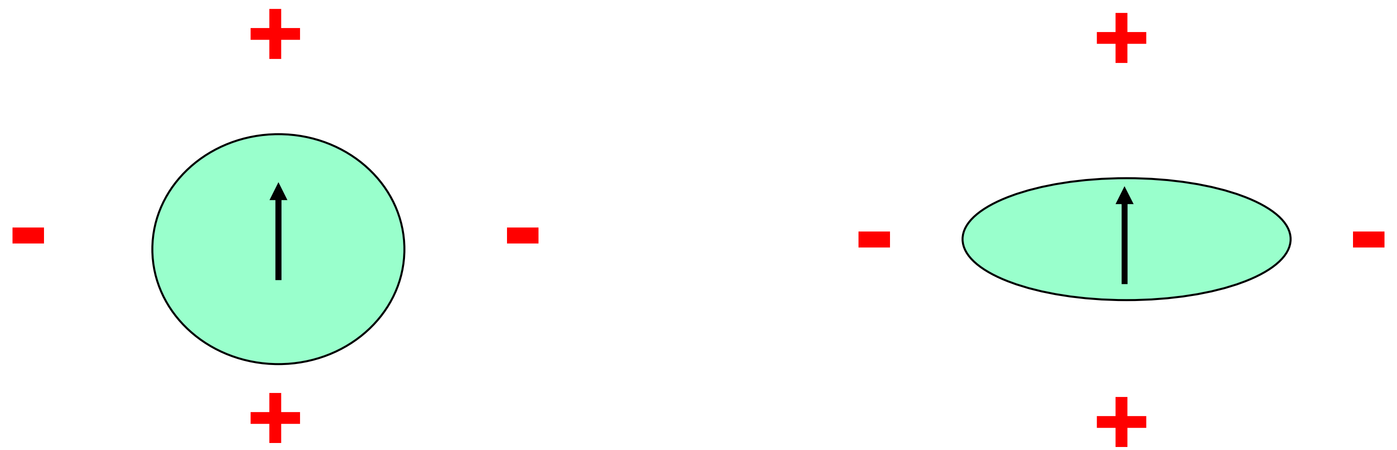
$$\mathcal{H}_{n-e} = -\gamma\hbar \sum_{i,k} \boldsymbol{I}_i \tilde{A}_{ik} \boldsymbol{S}_k$$

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

A very involved Hamiltonian…quite rewarding

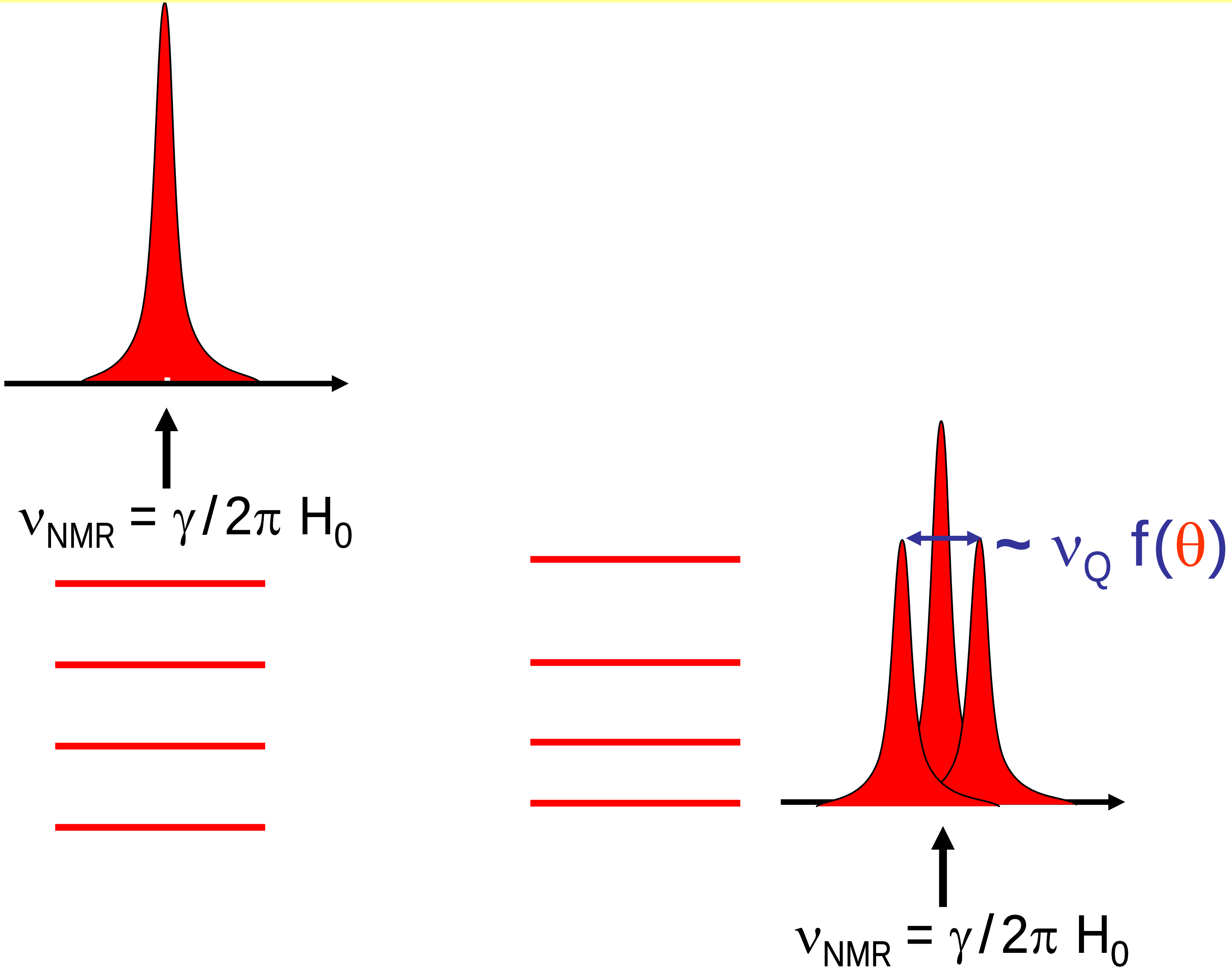
From NMR basics: quadrupole interaction (7)

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



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

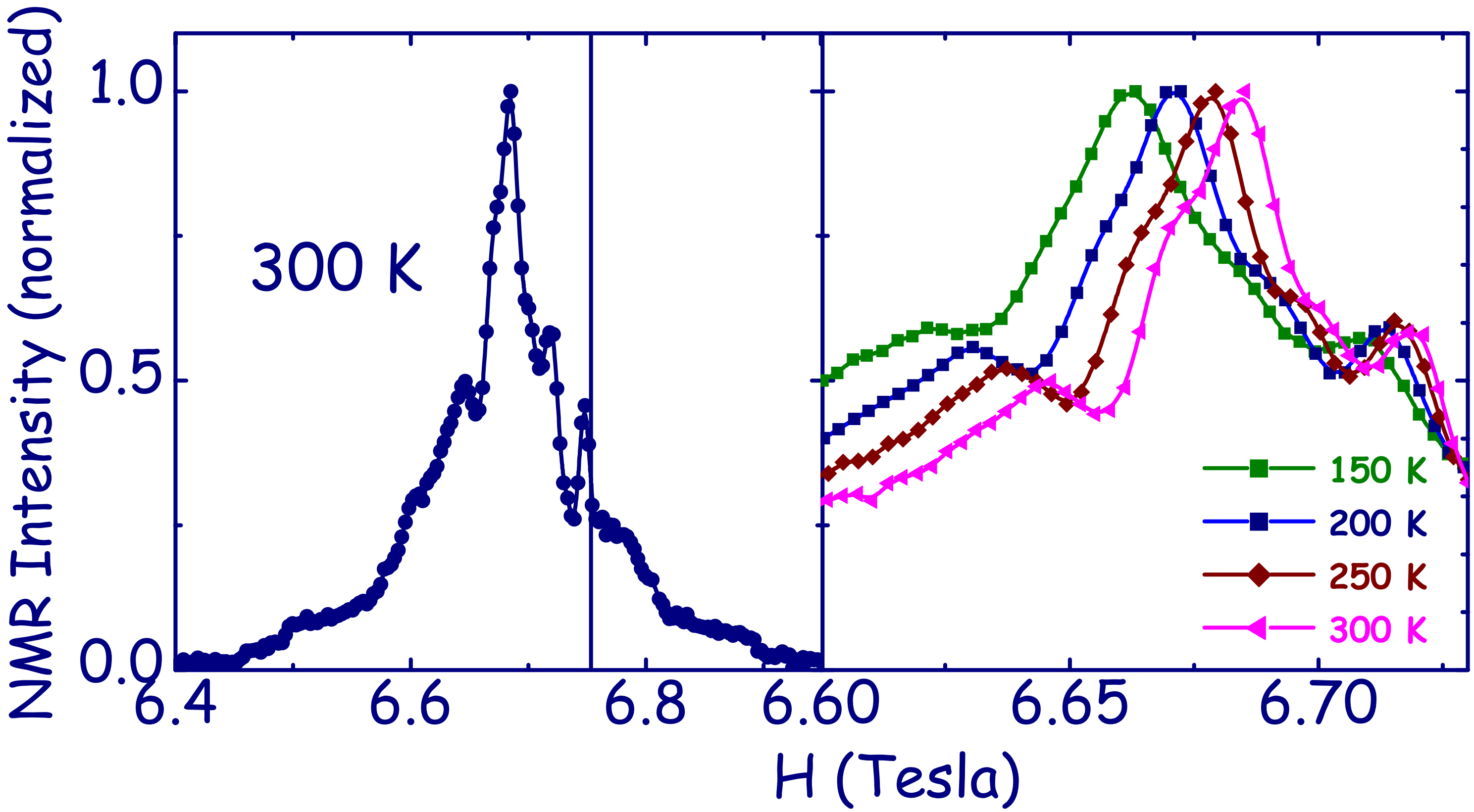
From NMR basics: quadrupole interaction (8)



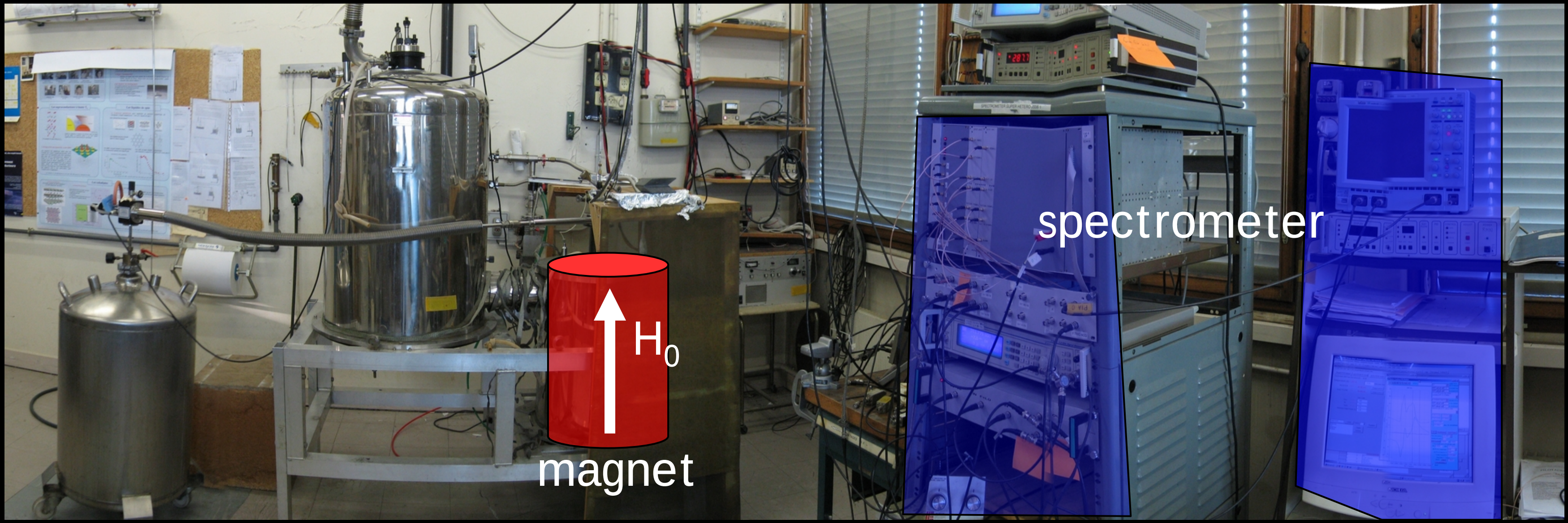
Quadrupolar nuclei: rich but involved on powders

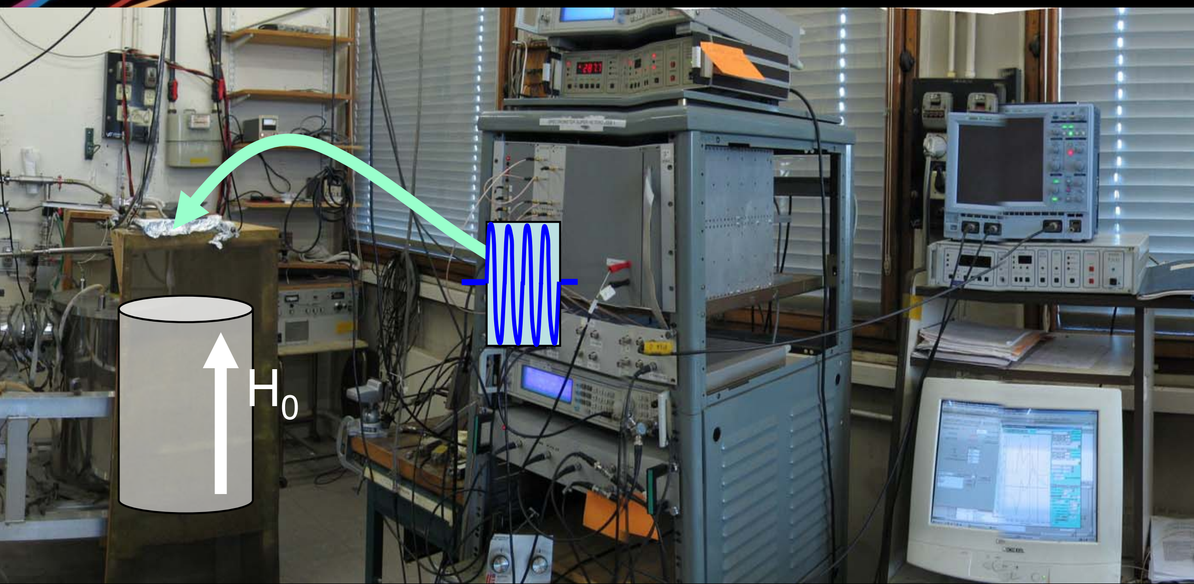
From NMR basics: quadrupole interaction (9)

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

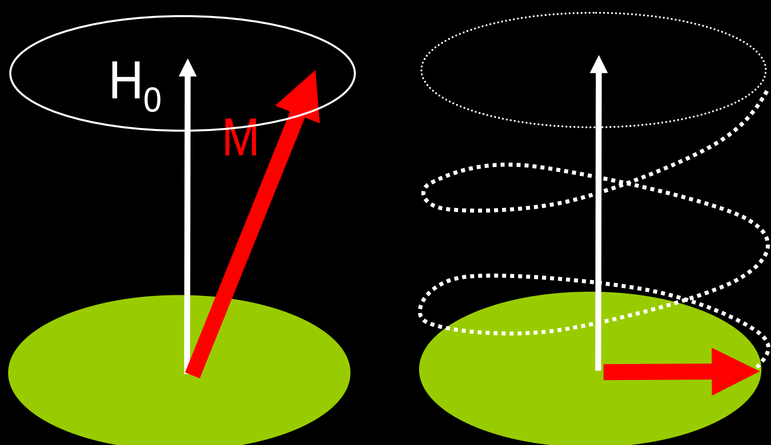


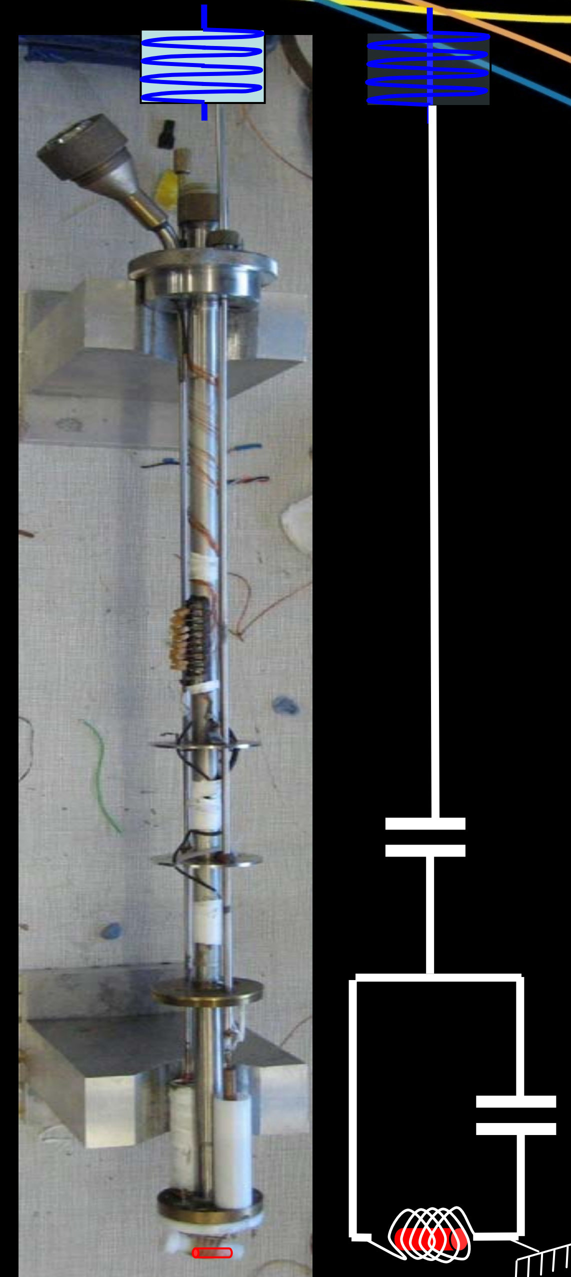
An NMR lab



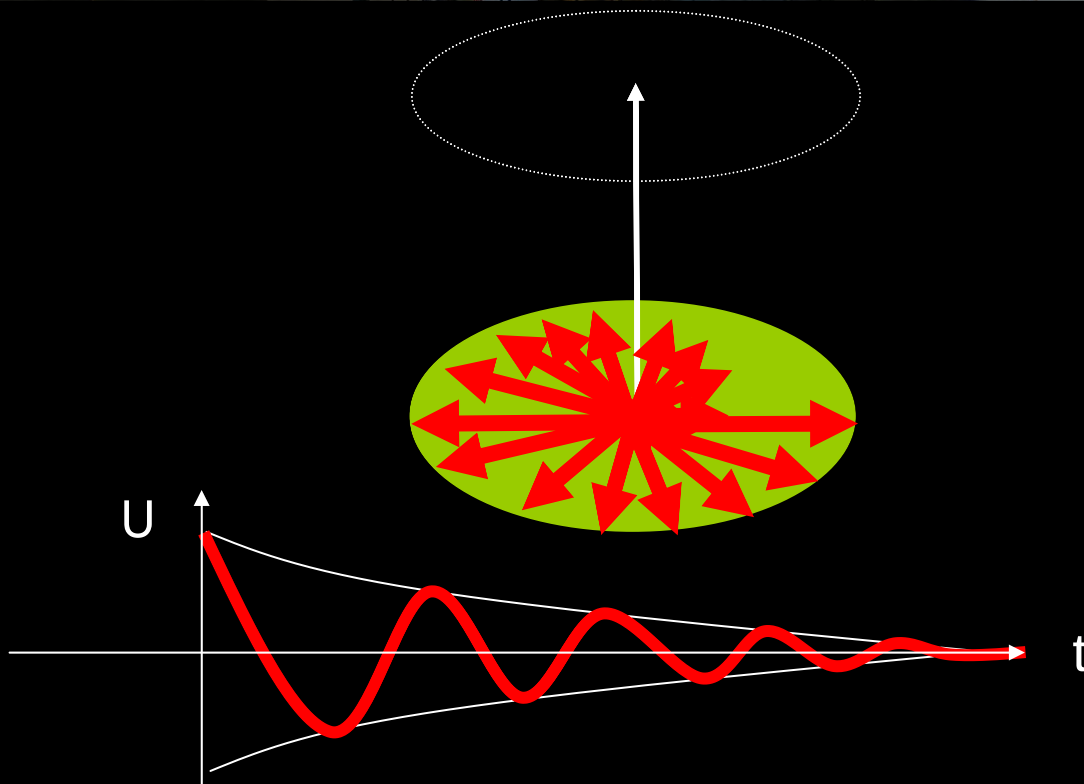


Radiofrequency pulse ~ few μsec






H_0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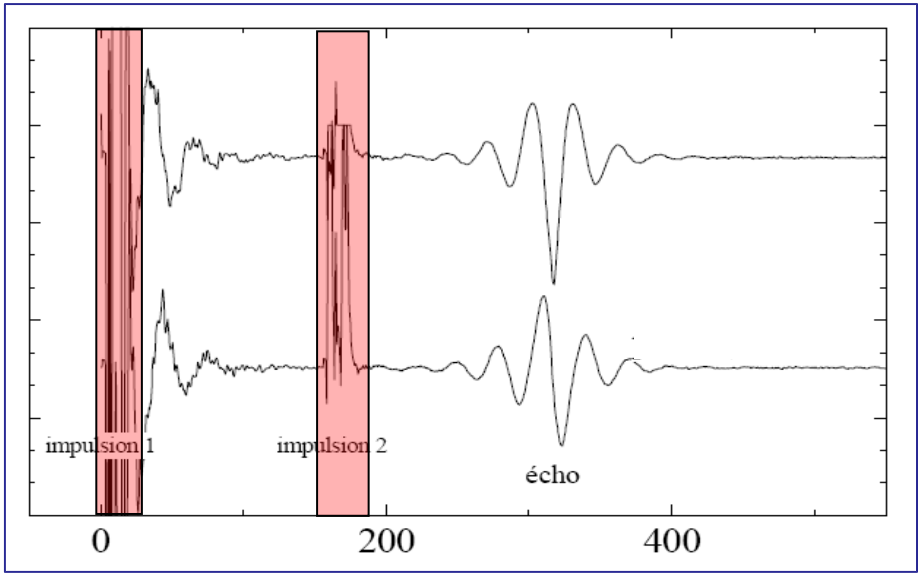
From NMR technique: time window



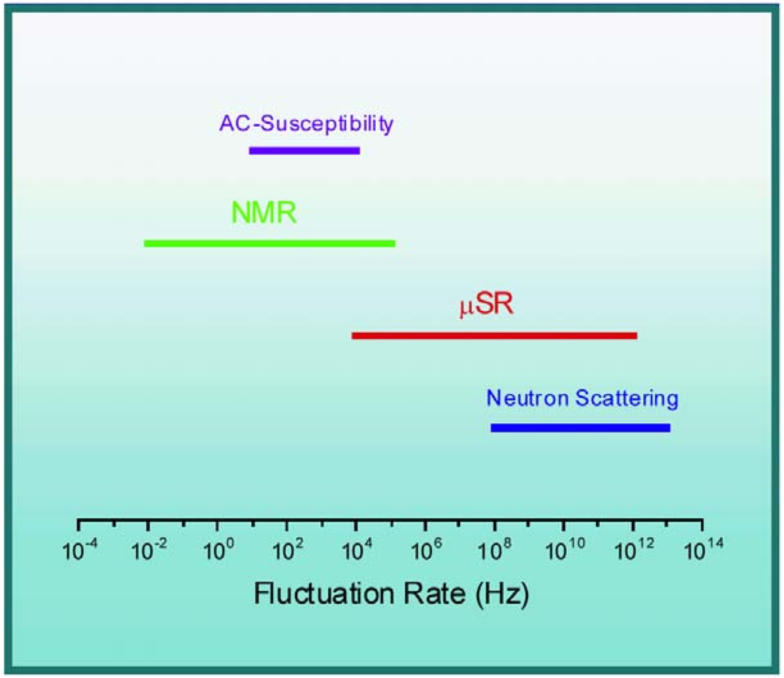
Time window: 10 µs ... mn

Orders of magnitude NMR vs μSR

- Local field 10 – 100 times larger in NMR → Accurate measurement of χ → Sometimes too broad lines when frozen moments
- γ 10 times smaller in NMR
- Time window start 1000 time larger in NMR
- Time window end infty in NMR

One example: fast fluctuations

$$1/T_1 = (\gamma B)^2 \tau$$



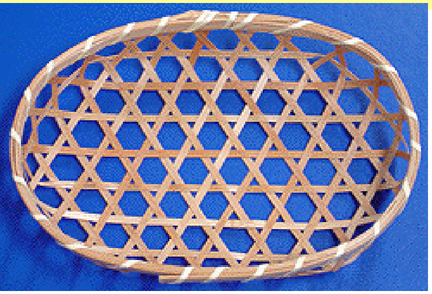
μ+: smaller couplings, shorter times

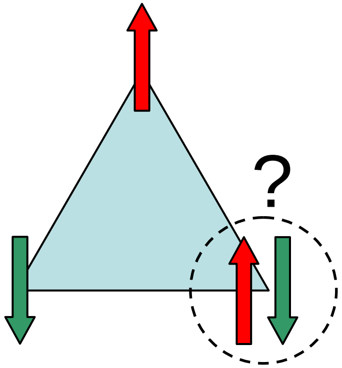
NMR/μSR: a comparative summary

	μSR	NMR
Which sample?	All, easy	Many…needs time
Time window	Few ns…20 μs	10 μs…mn
Location/coupling	Interstitial, where??? 0.1 T/ μ_B	At. Site, hyperfine 0.1 T – 10 T/ μ_B
Sensitivity	Magnetic transitions Small moments Background	Magnetic susceptibilities Whole sample?
Temperature range	10 mK – 800 K	10 mK – 1000 K
Field range	0 – 6 T	1 – 45 T
Dynamics	Fast dynamics	Slow dynamics
Intrinsic drawback	Additional charge and moment	r.f. field needed, field needed Tuning of the probe

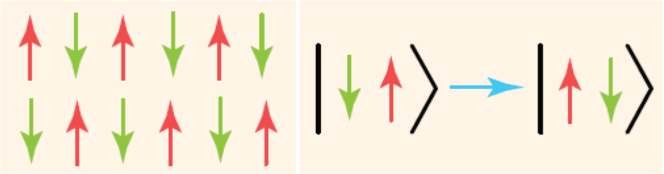
Think and select the best: μSR, a front tool but…

ZF Phase diagrams in a family of samples





An End to the Drought of Quantum Spin Liquids



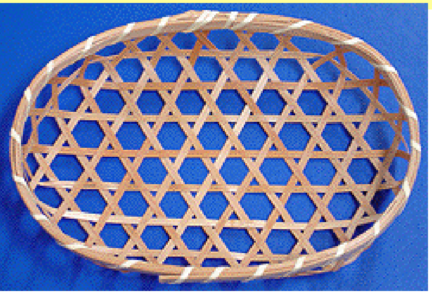
Patrick A. Lee

After decades of searching, several promising examples of a new quantum state of matter have now emerged.

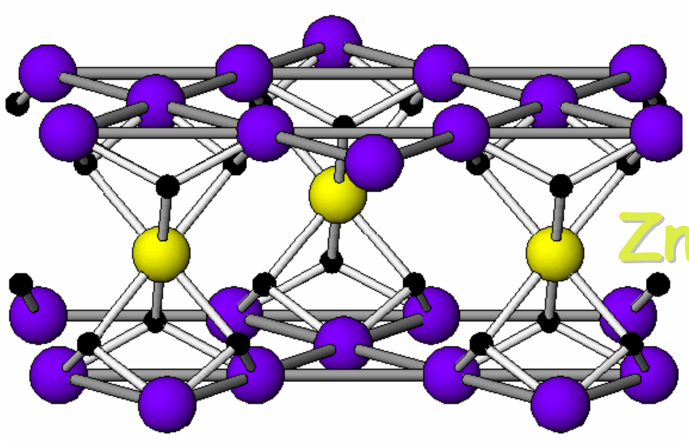
Science, perspectives sept 2008

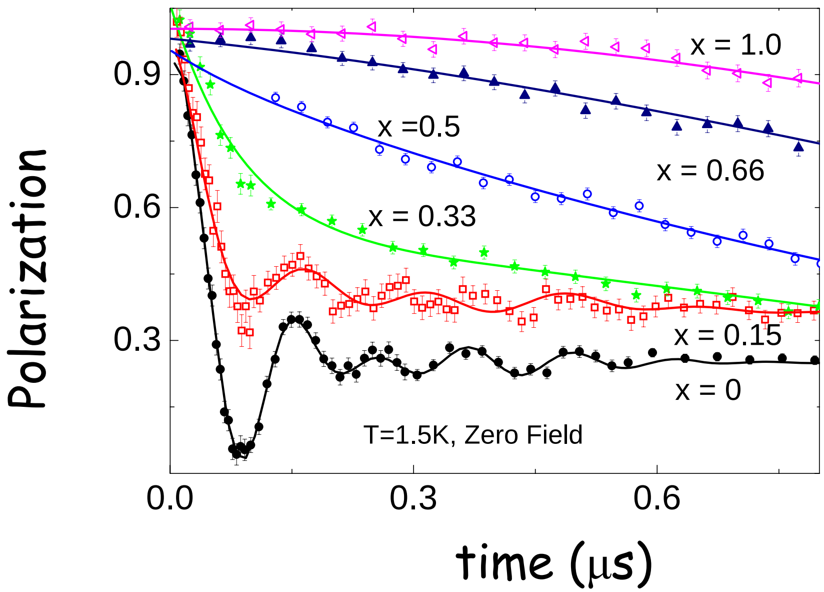
μSR: direct comparison, easiness to track transitions, ZF

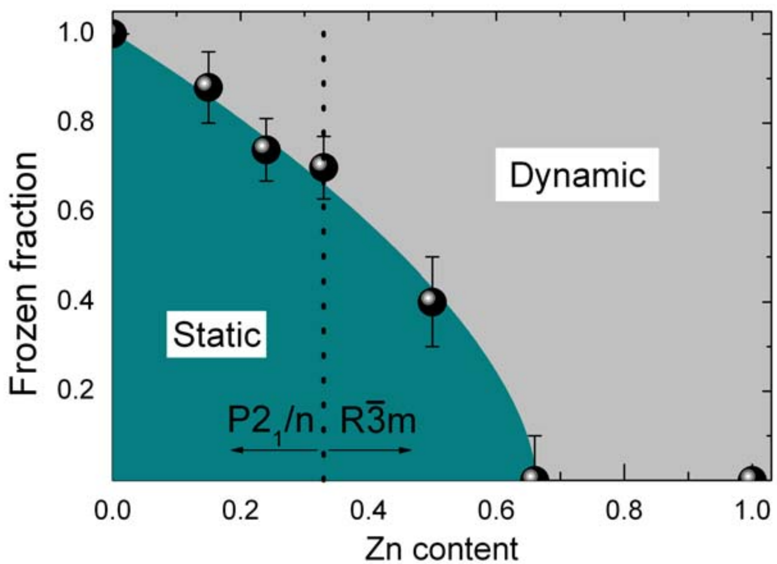
ZF Phase diagrams in a family of samples



$Zn_xCu_{4-x}(OH)_6Cl_2$ atacamite family

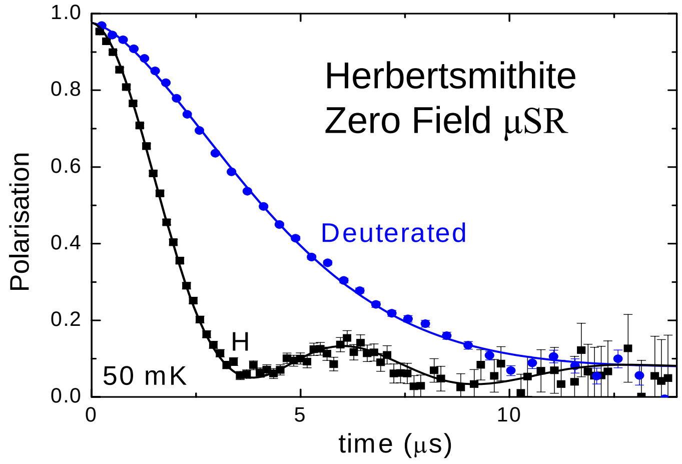




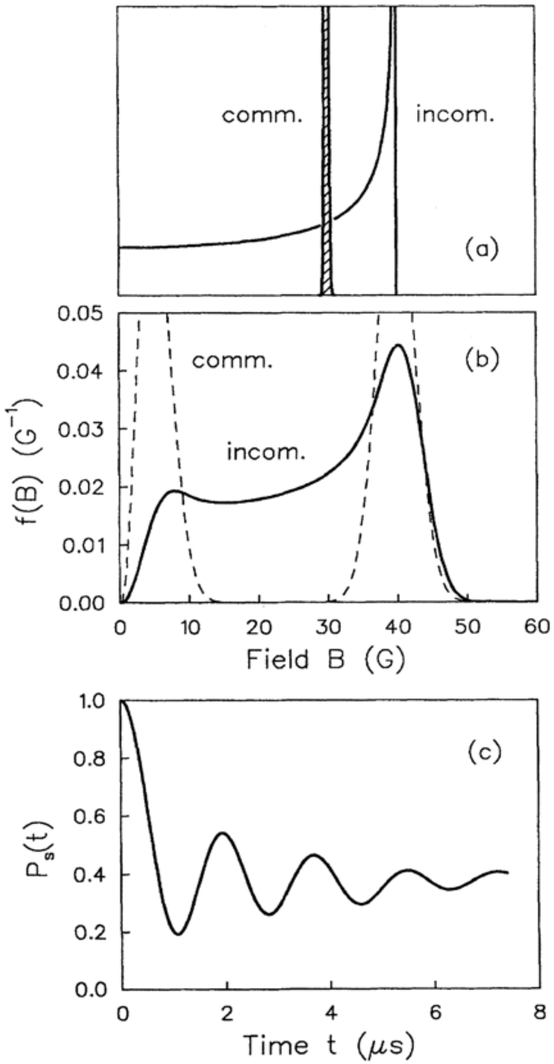


μSR: direct comparison, easiness to track transitions, ZF

Detection of small frozen moments



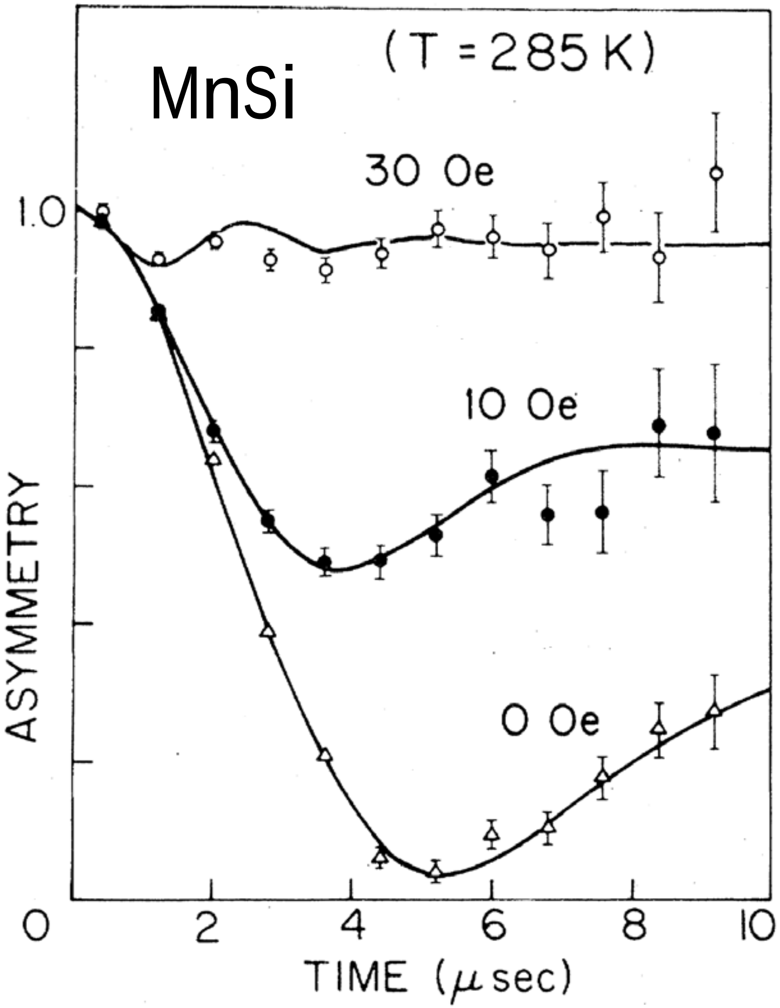
P. Mendels et al, PRL 98, 077204 (2007)

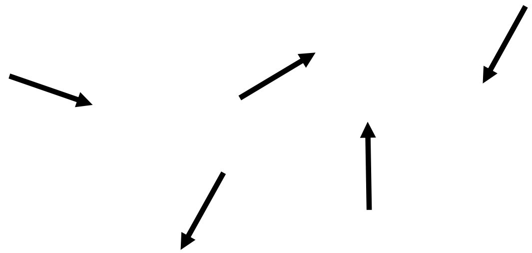


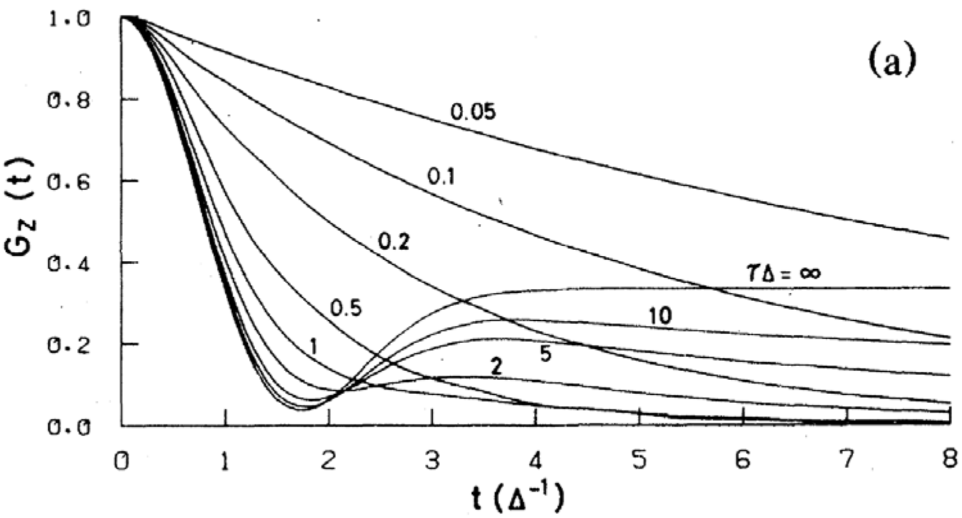
L.P. Le et al, PRB 48, 7284 (1993)

μ^+: small nuclear fields (~G) in the paramagnetic state

Spin glasses (1): statics

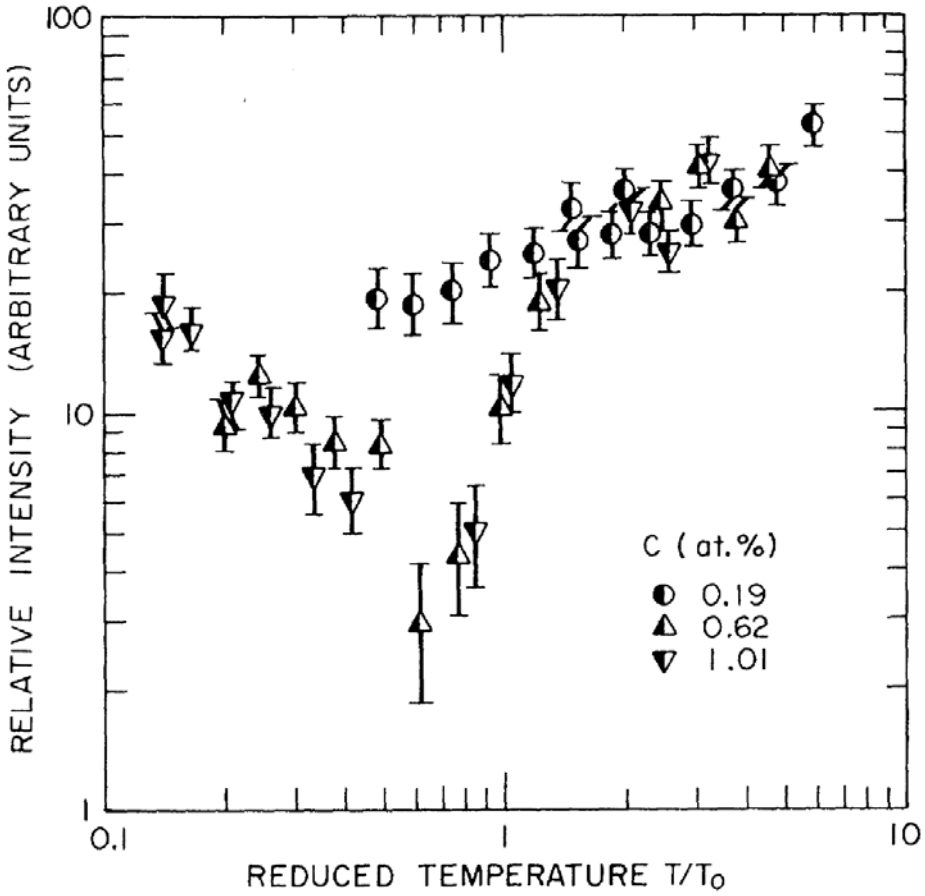




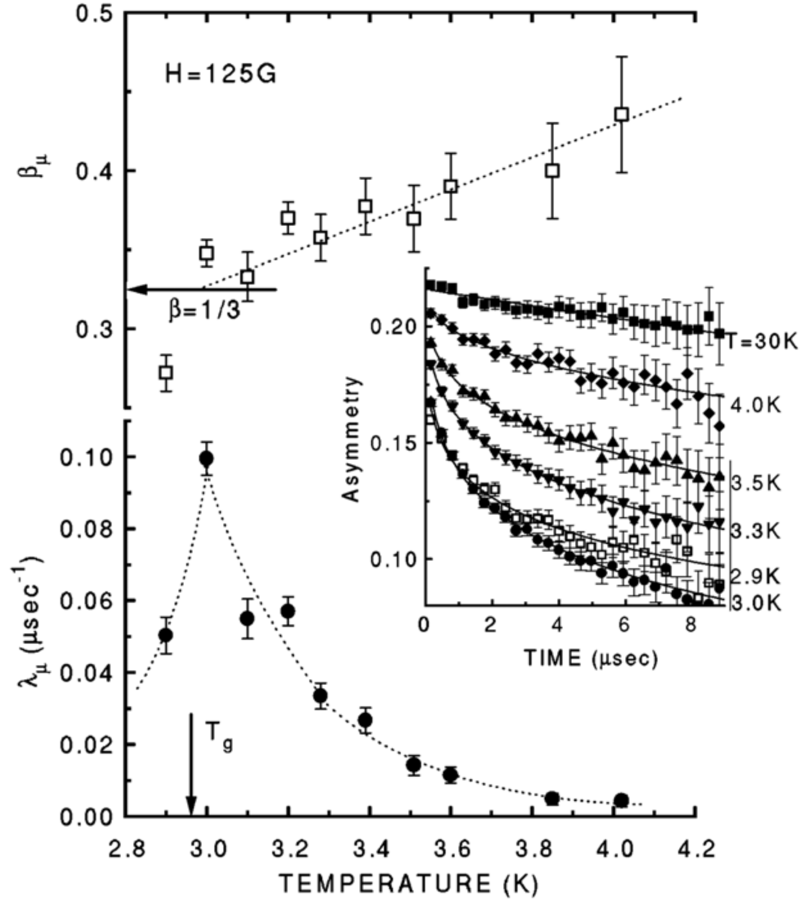


μ⁺: smaller couplings, shorter times ⟷ broad lines

Spin glasses (2): dynamics



D.E.MacLaughlin and H. Alloul, PRL 1976

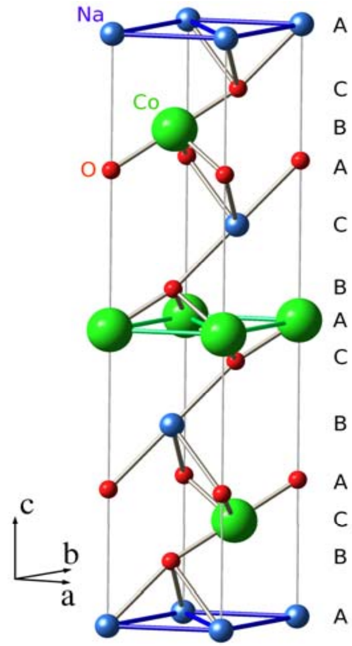


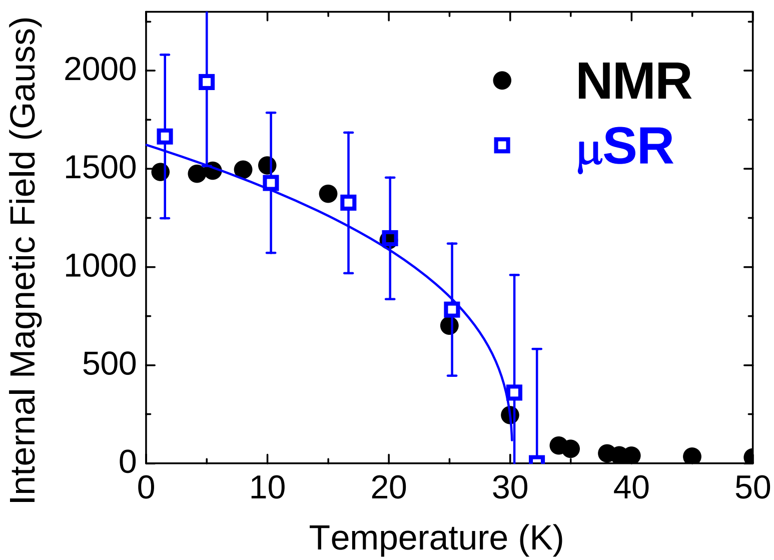
A. Keren, P. Mendels et al., PRL 1996

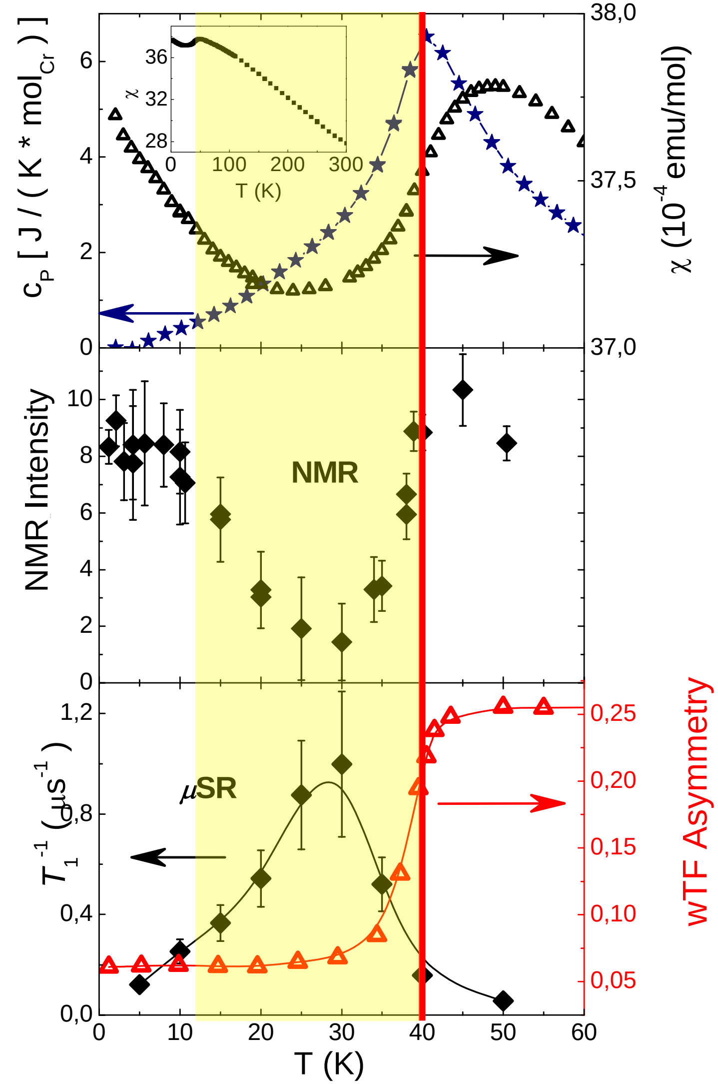
Also study of critical exponents at magnetic transitions

μ^+: smaller couplings, shorter times. NMR wipe-out

$NaCrO_2$: original dynamics







Measurement of local susceptibility (1)

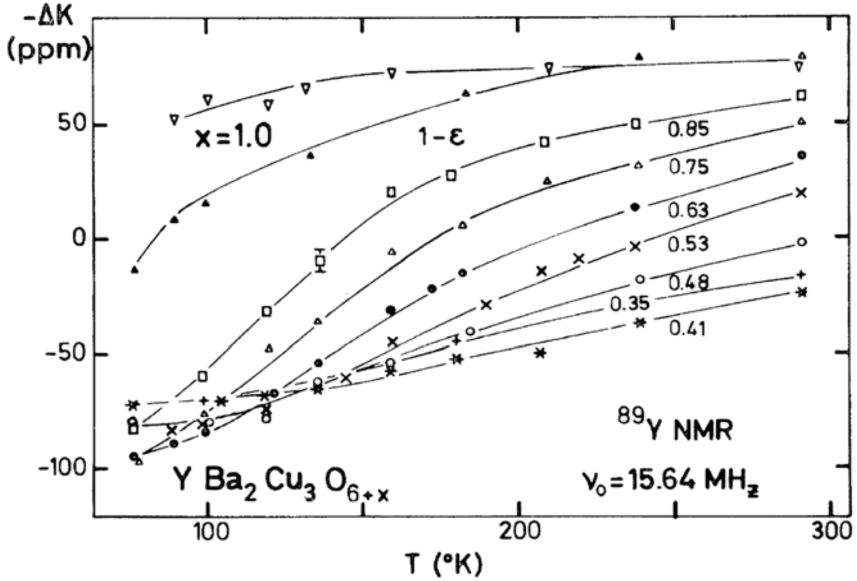
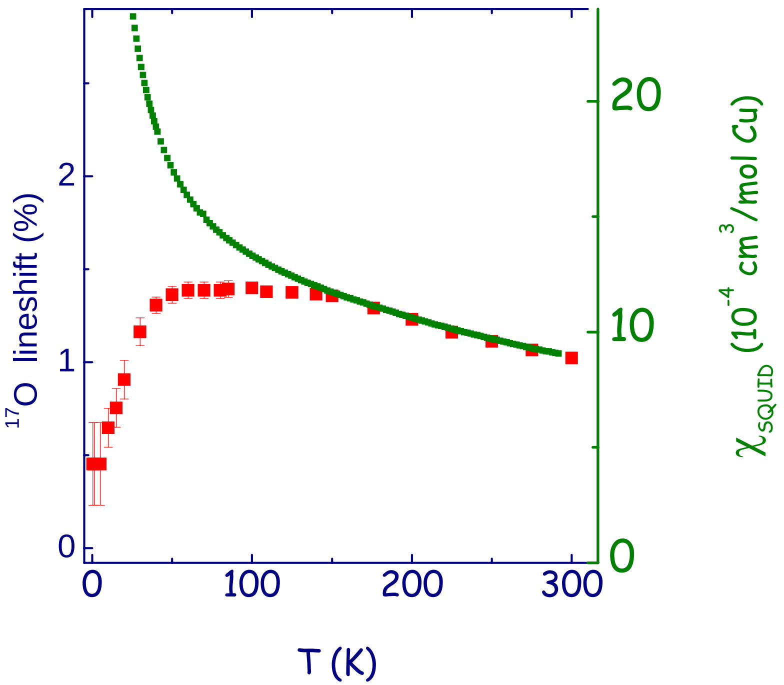
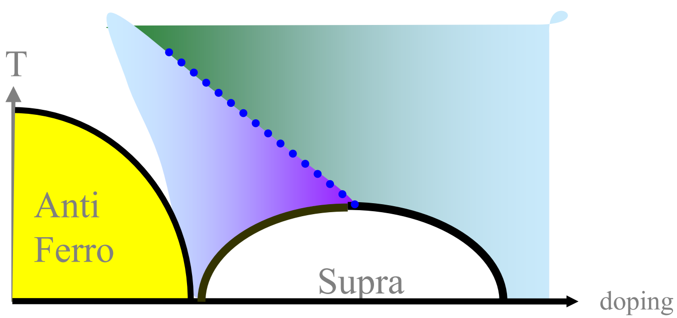
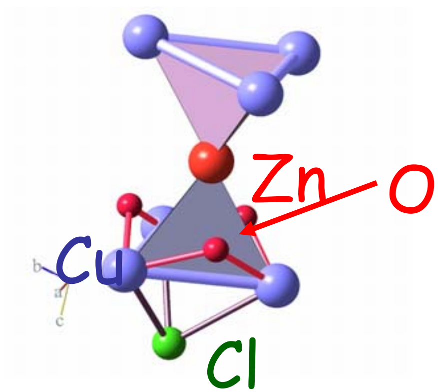


FIG. 1. The shift ΔK of the ^{89}Y line, referenced to YCl_3 plotted vs T, from 77 to 300 K. The lines are guides to the eye.

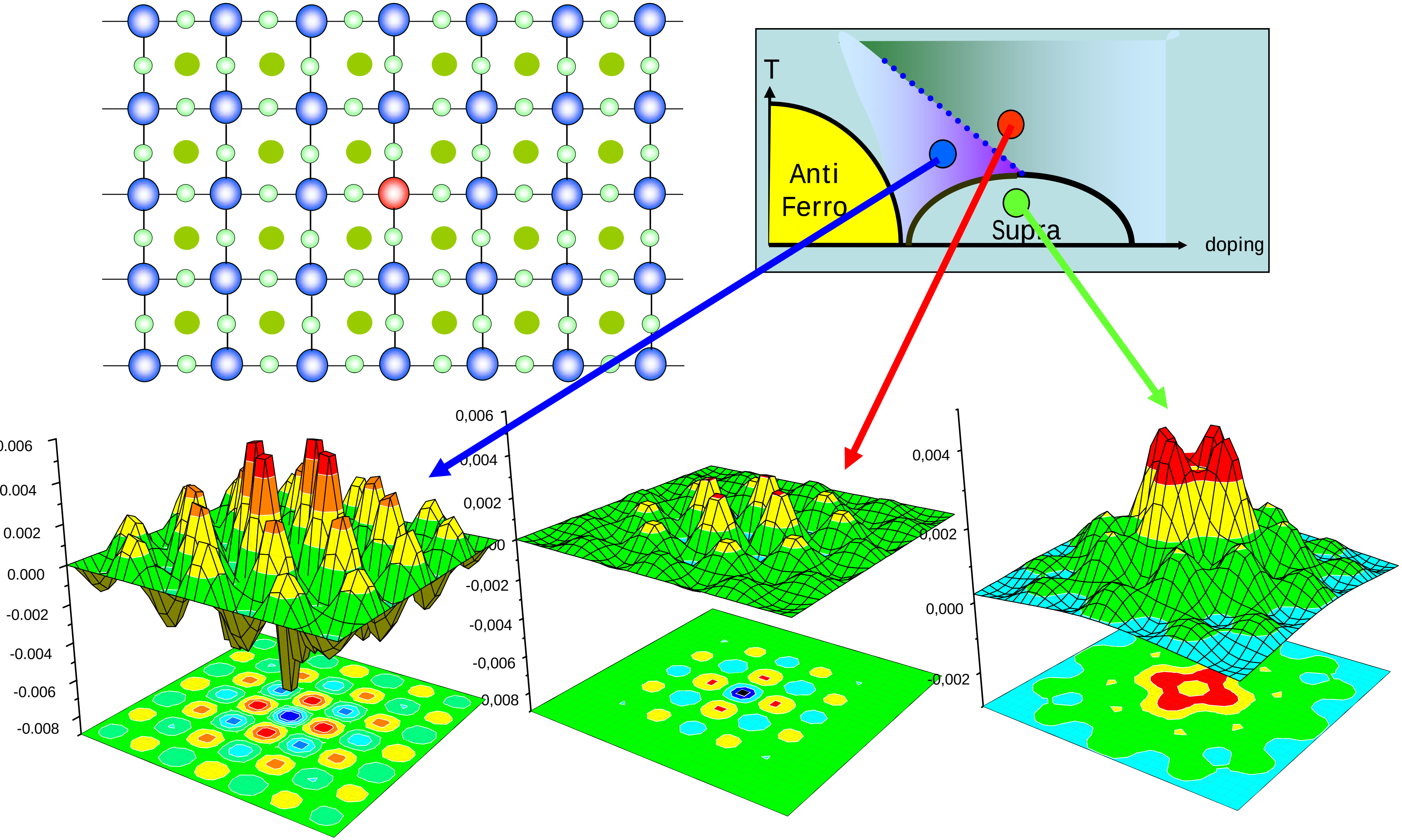






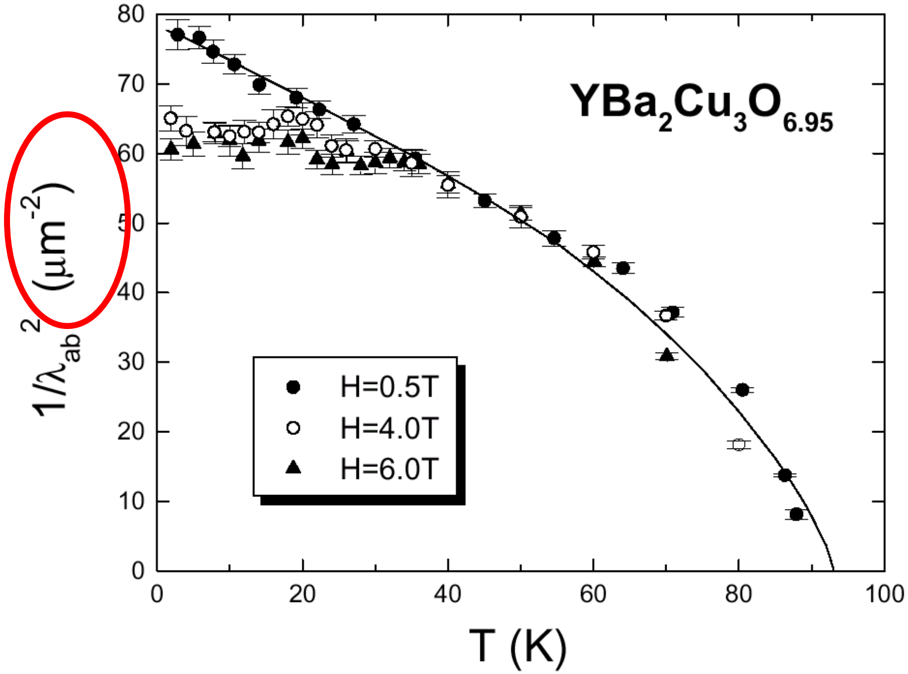
μ^+: smaller coupling, located differently…but where?

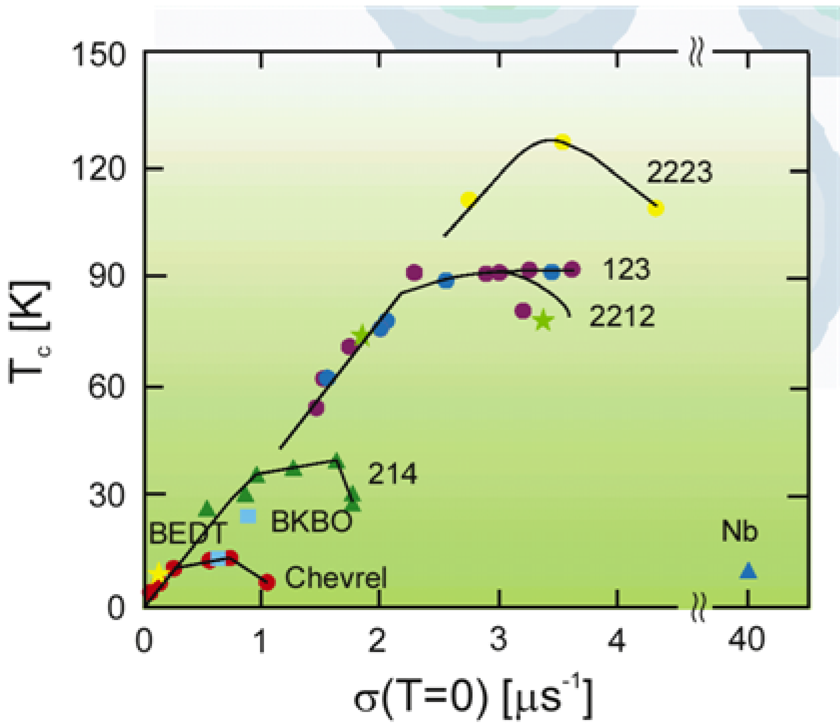
Measurement of local susceptibility (2)



Perturb to reveal: selectivity of the coupling in NMR

Superconductivity: penetration depth





J. Sonier et al., PRL 1994, 1999
Review of Modern Physics,(2000)

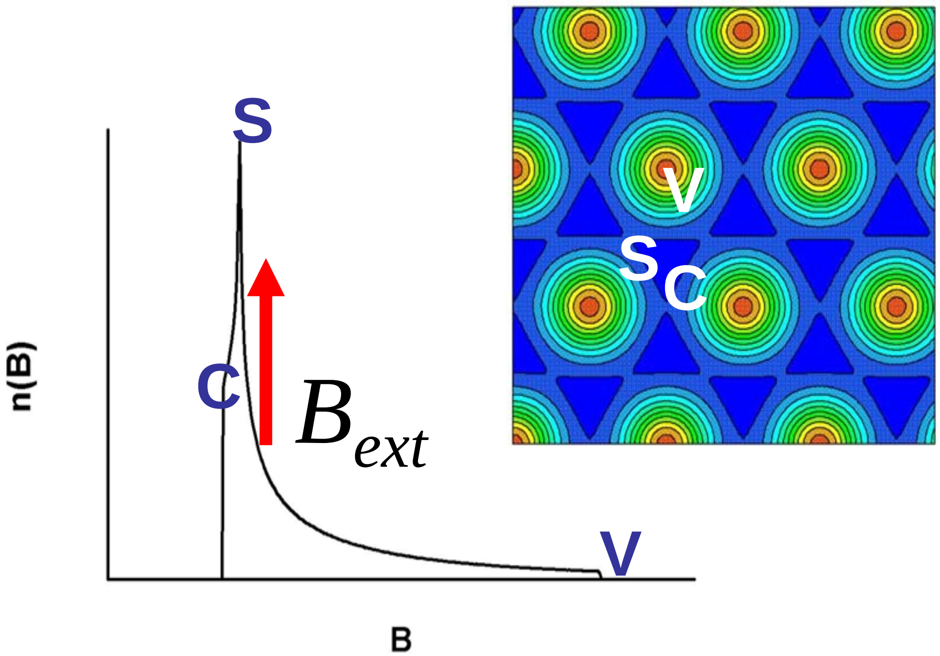
Y.J. Uemura et al., PRL1991

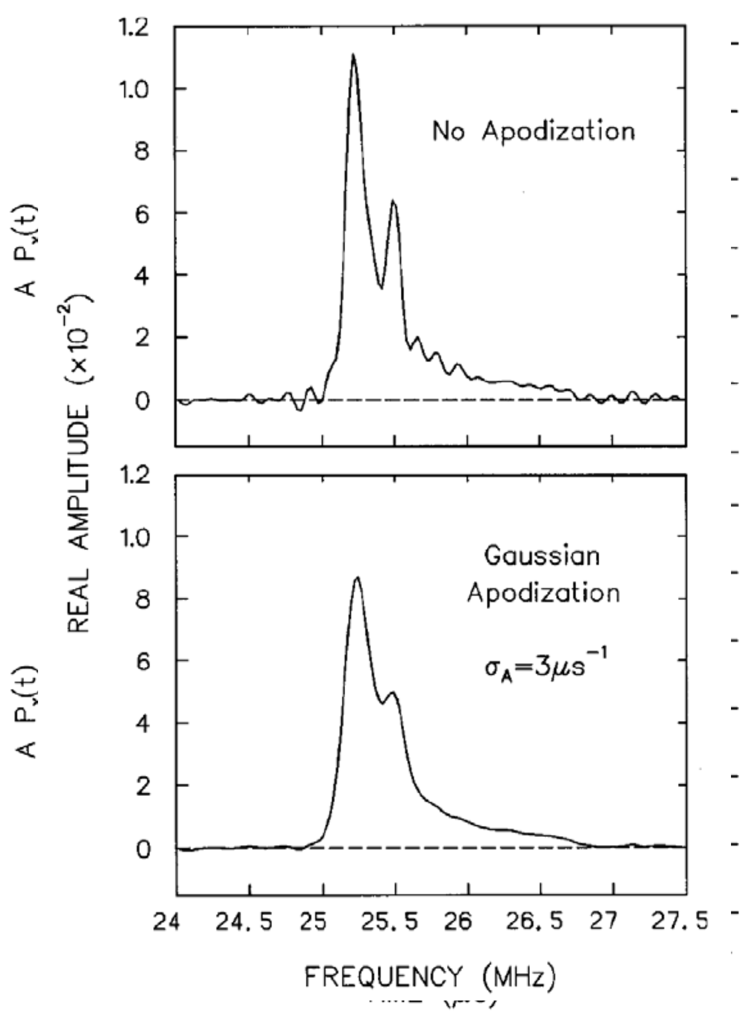
μ^+: absolute value of λ but hard to probe vortex cores;

So easy that early materials are an issue with respect to quality

Superconductivity: vortex lattice

Need of a sizeable transverse field, $H_{c1} < H < H_{c2}$



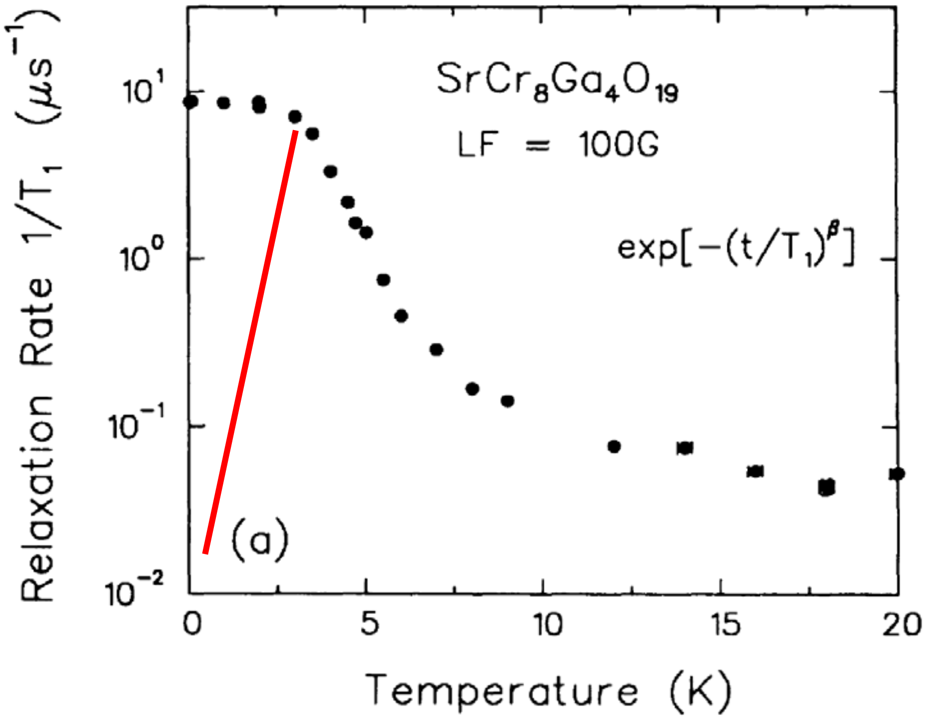


NMR: relaxation from vortex cores

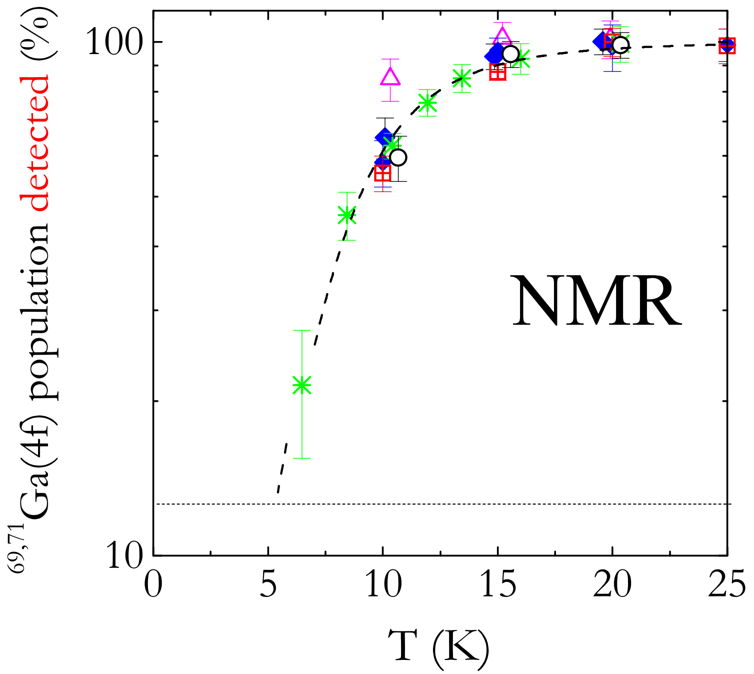
Frustrated magnets: spin liquid like states

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!

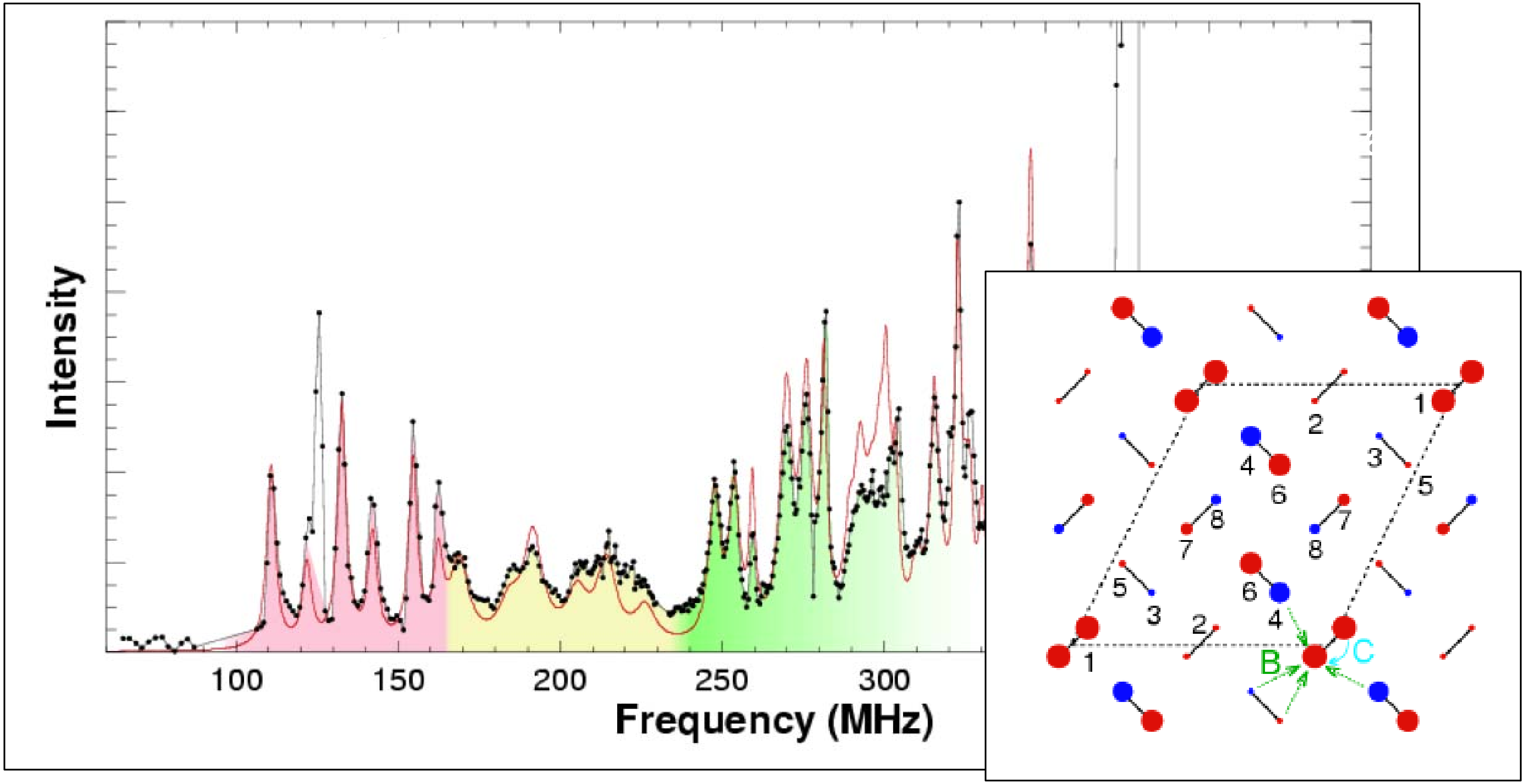


Wipe-out!

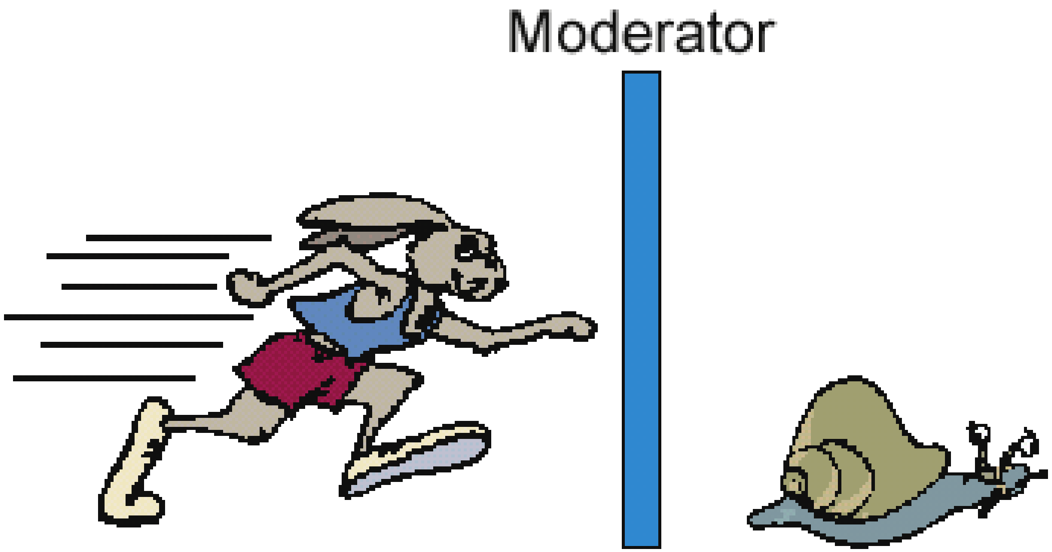
NMR: wipe-out when slowing down of fluctuations

NMR in High Magnetic Fields

Kodama, Science 2002



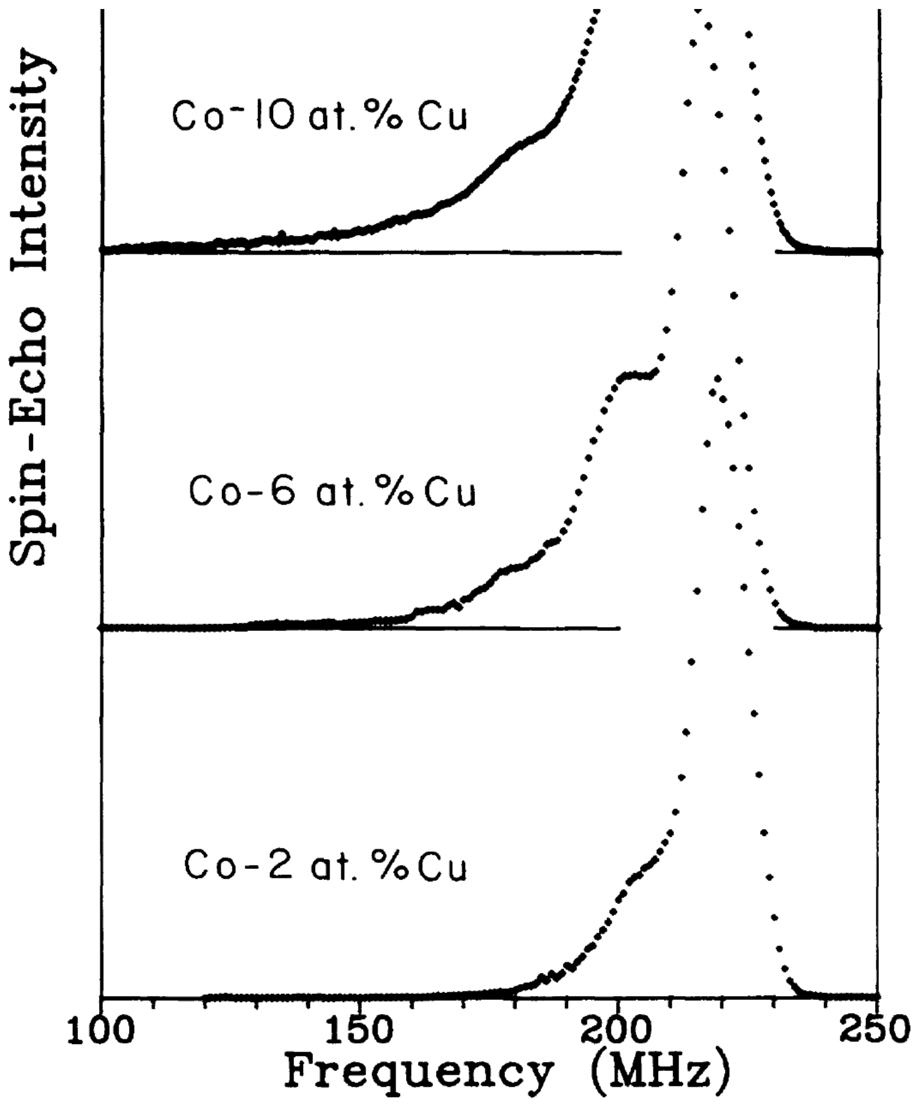
Large scale facilities … users friendly?


Moderator

NMR in ferromagnetic multilayers

TABLE I. Characteristics of the measured multilayers.

Sample	Co thickness (Å)	Cu thickness (Å)	Buffer
(15-Å Co)/(15-Å Cu)	15	15	Fe
(15-Å Co)/(20-Å Cu)	15	20	Fe
(60-Å Co)/(20-Å Cu)	60	20	Cu
(60-Å Co)/(60-Å Cu)	60	60	Cu
(60-Å Co)/(90-Å Cu)	60	90	Cu



Work from Panissod
Co/Cu mutilayers (1992)

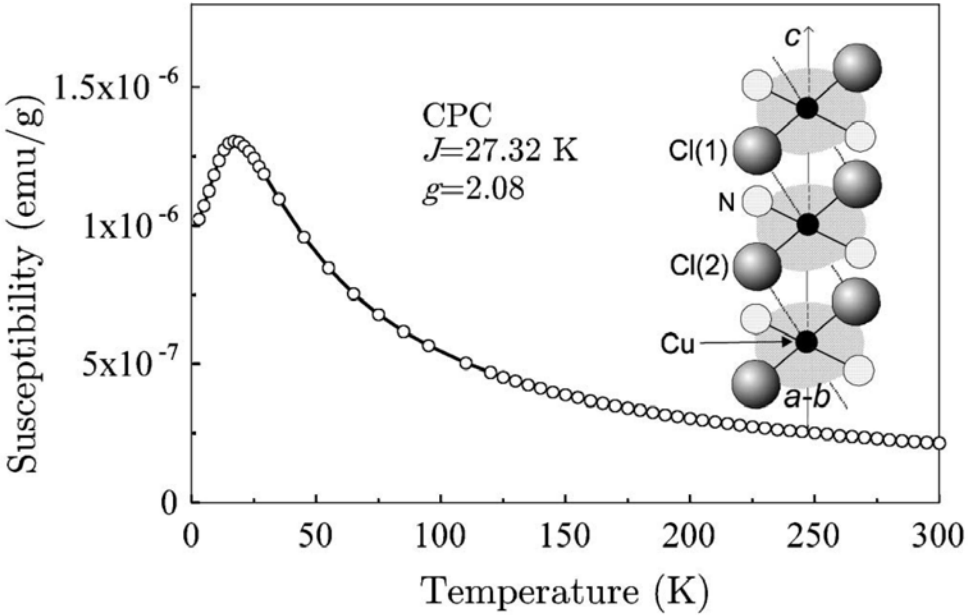
Marginal as compared to the world of thin films

Do μ^+ impact the physics?

μ^+ is an added moment

...

Or an added charge which changes J



A marginal case, then physically interesting!

Do μ⁺ impact the physics?

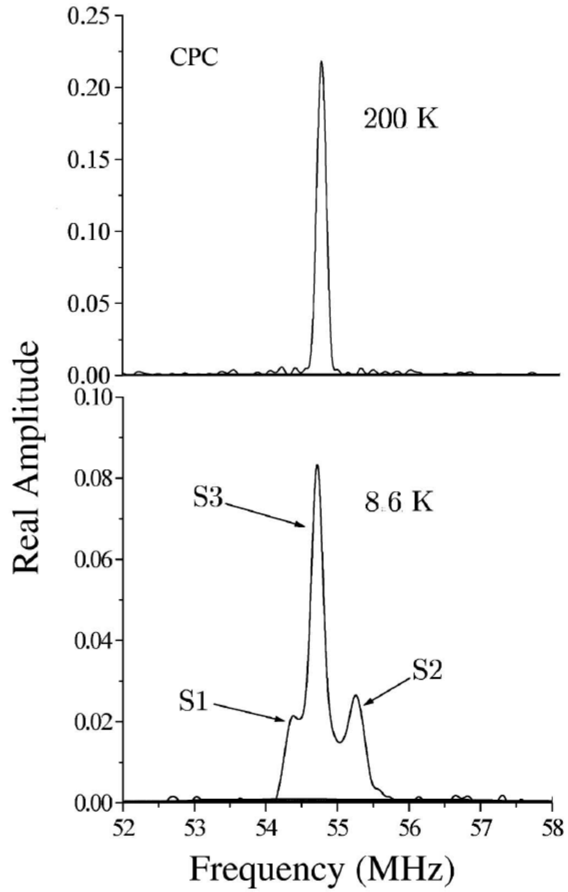
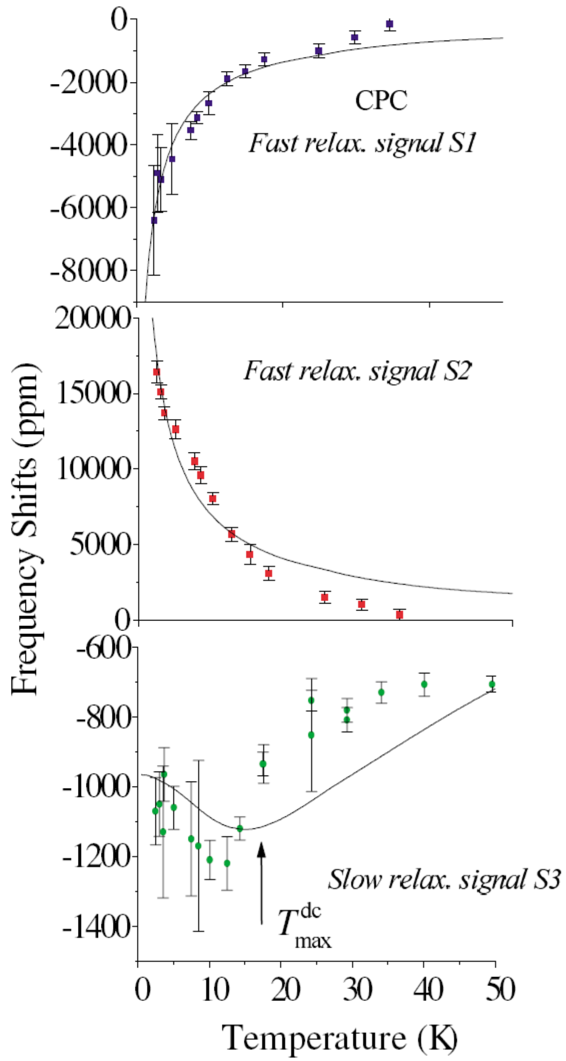


FIG. 2. The evolution of the FFT transforms with temperature in CPC.

and sample (22 ppm), we obtain the frequency shifts for the three sites shown in Fig. 3.



Chakhalian, PRL 2003

A marginal case, then physically interesting!

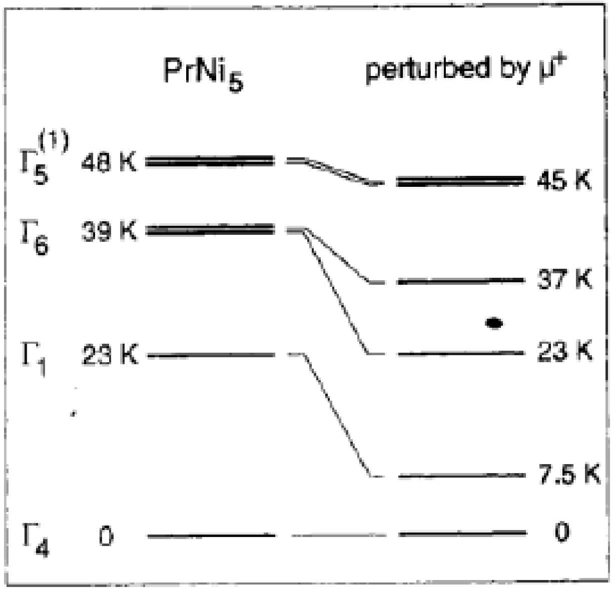
Do μ^+ impact the physics?

More with High Tc's vs orbital currents
(Varma)

A marginal case, then physically interesting!

Do μ^+ impact the physics?

μ^+ is an added charge!



Feyerherm, 1995

Crystal field levels in rare earth compound PrNi5

With RE elements, depending on CEF, $\chi_{\mu SR}$ is modified!

References

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- Slichter C.P., Principles of Magnetic Resonance, Springer Verlag, 1978
- A.Narath: Hyperfine Interactions, ed. A. J. Freeman and R. B. Frankel (Academic Press, New York, 1967) Chap. 7
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- **More specialized** :
- R. Walstedt, The NMR probe of high Tc materials, Springer Tracts in Modern Physics
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- Berthier C., Julien M.H., Horvatic M., Berthier Y., J. Phys. I France 6, 2205 (1996)
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- Nuclear magnetic resonance of C60 and fulleride superconductors, Charles H. Pennington and Victor A. Stenger, Rev. Mod. Phys. 68, 855 (1996)
- **On the web** *:*
- « the basics of NMR » http://www.cis.rit.edu/htbooks/nmr/inside.htm
- Spectroscopy site : http://www.spectroscopynow.com/coi/cda/home.cda?chId=0
- See also the very complementary examples from P. Carretta at the previous school

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