

# Magnetic Resonances and Muons



Magnetic resonances allow to probe the properties of matter by following the time evolution of the nuclear/muon/electron magnetization/polarization. Example: for nuclei (NMR and  $\beta$ -NMR) it is driven by the following terms

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

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

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

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

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



Accordingly, the quantities to be measured are similar: the Knight shift, the longitudinal relaxation rate, the transverse relaxation rate, etc...

$$\Delta\tilde{K} = \frac{\sum_k \tilde{A}_k \langle \mathbf{S}_k \rangle}{H_0} \quad \text{Knight shift}$$

$$G'(t) = G'(0) e^{-\langle \Delta\omega^2 \rangle \tau_c^2 [exp(-t/\tau_c) - 1 + (t/\tau_c)]} \quad \text{Polarization decay}$$

$$\frac{1}{T_1} = \frac{\gamma^2}{2} \int_{-\infty}^{+\infty} e^{i\omega_0 t} \langle h_+(t) h_-(0) \rangle dt \quad \text{Spin-lattice relaxation}$$

.....



# Some of the main technical differences

## $\mu$ SR and $\beta$ -NMR:

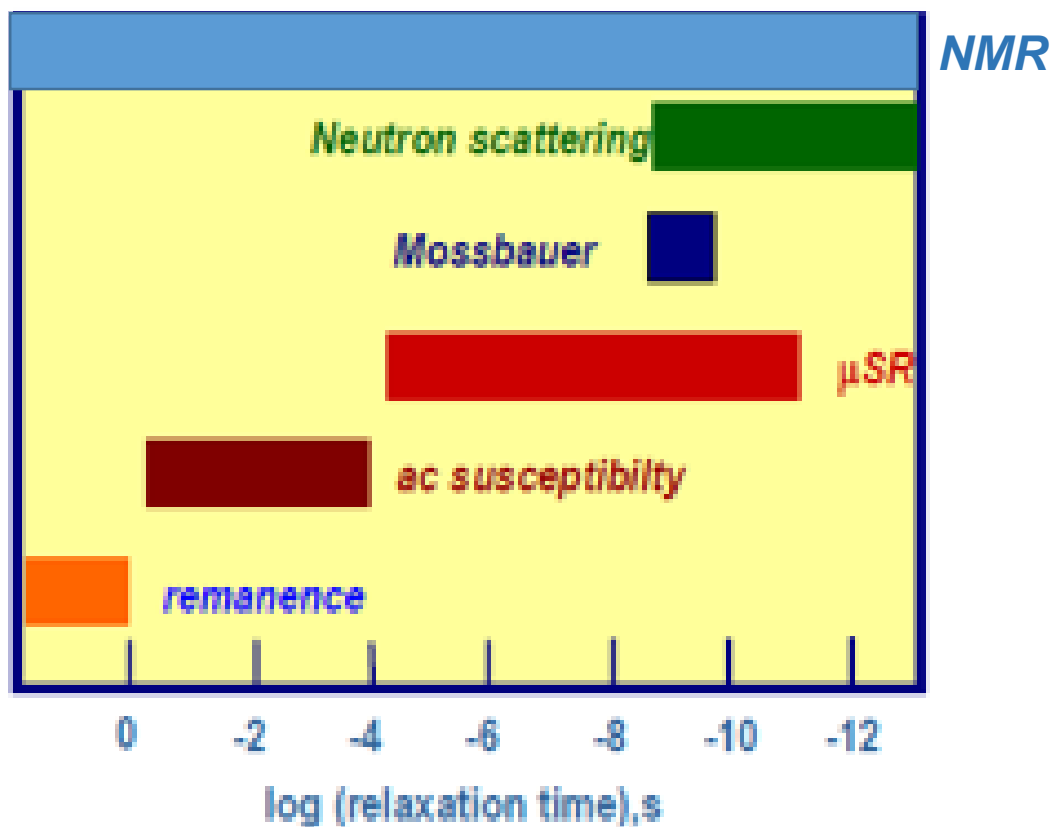
- $e^+$  or  $e^-$  detection.
- Highly spin polarized beam even in ZF.
- Beam penetration depth can be reduced down to a few nm.
- $\beta$ -NMR probe can cause a non-negligible perturbation.
- Expensive.

## Standard NMR and ESR:

- e.m. wave detection: problem in metals and superconductors, particularly for ESR.
- Spin polarization: thermal equilibrium one ( $10^{-5}$  for nuclei at RT). One usually needs an external field to generate it.
- Most experiments are performed on bulk samples.
- Extremely weak perturbation.
- Relatively low cost.
- Many developments and applications...



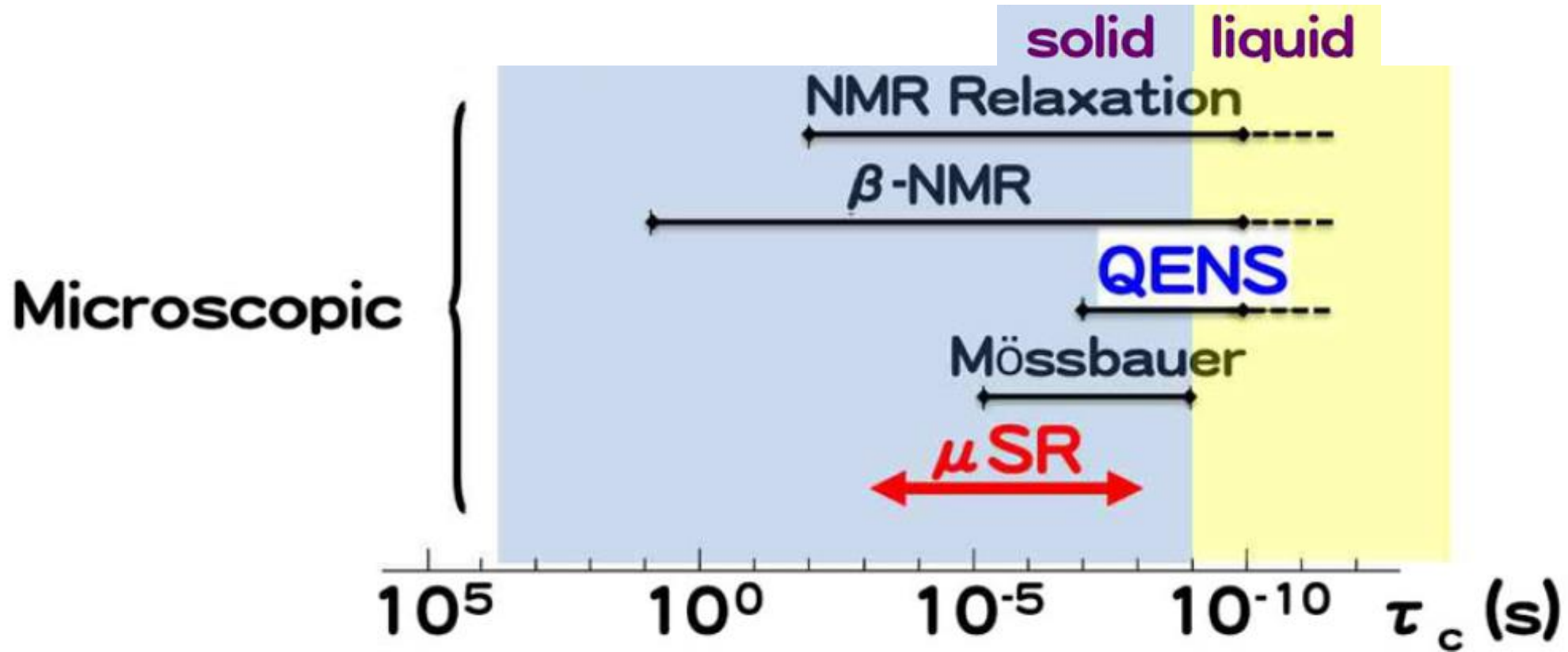
# Very but very indicative time scales accessible by different techniques



<https://muonsources.org/science-with-muons/the-sr-technique.html>



# Typical ionic diffusion time scales accessible by different techniques



J. Sugiyama, Hyperfine Interact 240, 17 (2019)



## $\mu$ SR advantages:

- **A good local probe is missing in the system? Just add it...**
- Fast relaxations (Problems in detecting relaxation times shorter than 10  $\mu$ s in NMR).
- Zero field experiments can be performed. Very important as the magnetic field is often a relevant parameter of the system under investigation. NQR is possible only when a good quadrupole nucleus is present
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Nuclear magnetic moment  $\vec{M} = \gamma \hbar \vec{I}$   
 Common NMR Active Nuclei

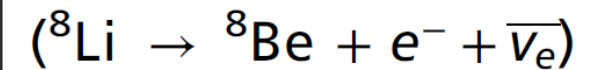
Isotope	Spin $I$	%age abundance	$\gamma$ MHz/T
$^1\text{H}$	1/2	99.985	42.575
$^2\text{H}$	1	0.015	6.53
$^{13}\text{C}$	1/2	1.108	10.71
$^{14}\text{N}$	1	99.63	3.078
$^{15}\text{N}$	1/2	0.37	4.32
$^{17}\text{O}$	5/2	0.037	5.77
$^{19}\text{F}$	1/2	100	40.08
$^{23}\text{Na}$	3/2	100	11.27
$^{31}\text{P}$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





**$\beta$ -NMR** isotopes. Add it but the perturbation is much more dramatic and one needs to consider if one is indeed studying the intrinsic properties.

Isotope	Spin	Quadrupole moment (mb)	$T_{1/2}$ (s)	$\gamma$ (MHz/T)	beta-Decay asymmetry (A)	production rate (s <sup>-1</sup> )
$\mu^+$	1/2		$2.2 \times 10^{-6}$	135.5	0.33	75
$^8\text{Li}$	2	+32	0.842	6.3018	0.33	$10^8$
$^{11}\text{Be}$	1/2		13.8	22	0.33	$10^7$
$^{15}\text{O}$	1/2		122	10.8	.7	$10^8$
$^{17}\text{Ne}$	1/2		0.1		.33	$10^6$

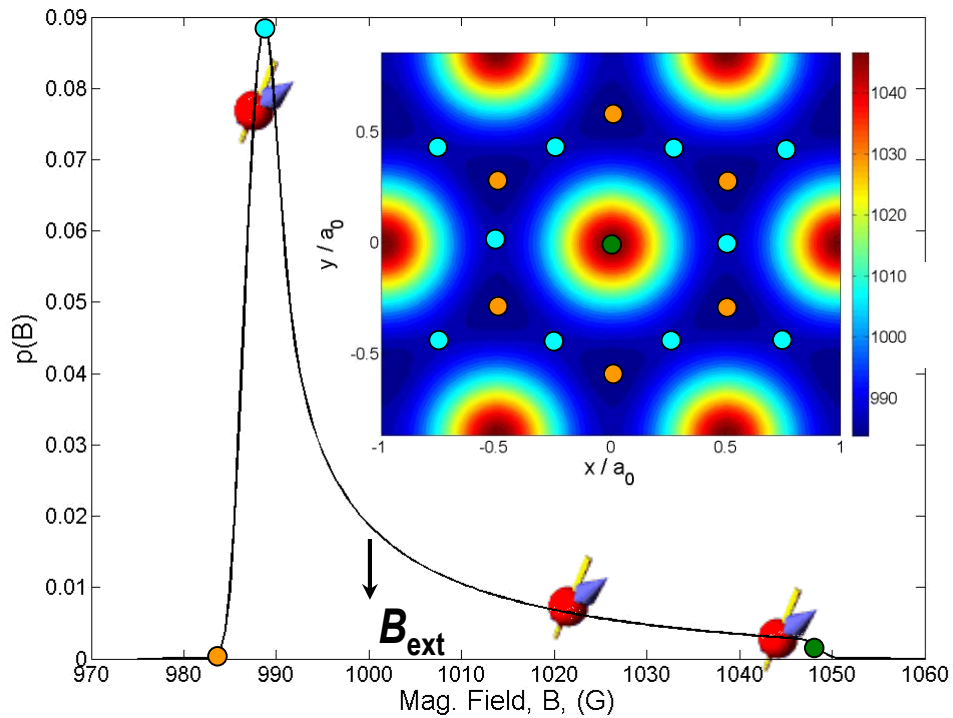


W.A.Mac Farlane, <http://bnmr.triumf.ca/?file=Introduction>

W.A.Mac Farlane, Solid State Nucl. Mag. Reson. 68-69, 1 (2015)



Example: in  $\text{CeRu}_2$  there is no «good» nuclear isotope.  
 How can one study the flux lines lattice in the superconducting phase?  $\mu\text{SR}$



A. Yamashita et al., Phys. Rev. Lett. **79**, 3771 (1997)

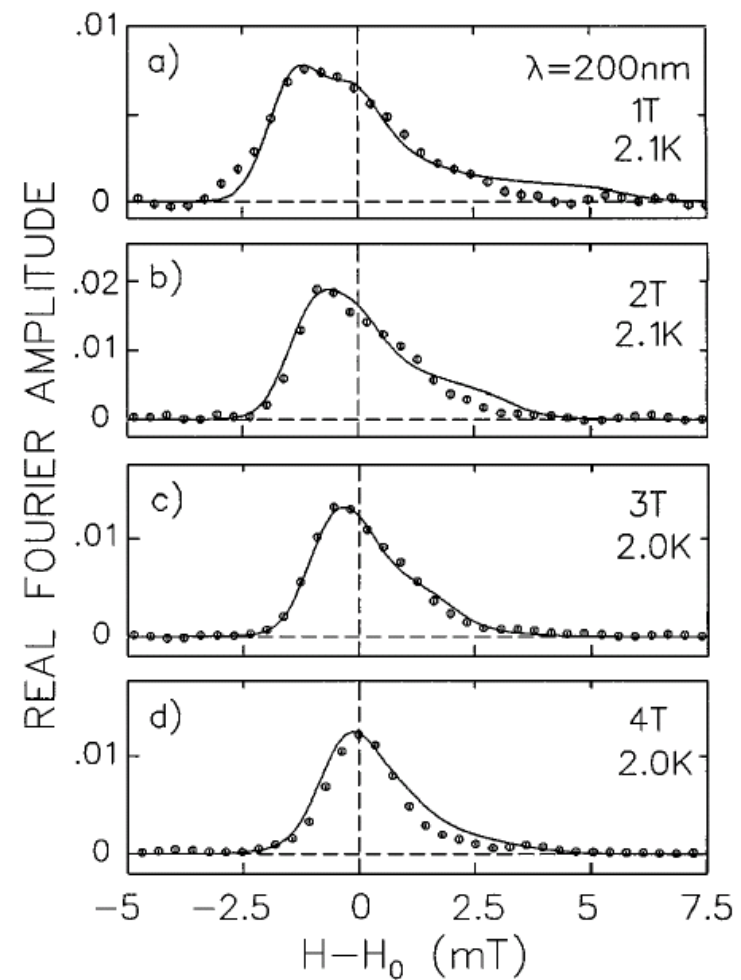


FIG. 2. Fourier-transformed TF- $\mu\text{SR}$  time spectra at (a) 0.985 T, (b) 1.96 T, (c) 2.93 T, and (d) 3.90 T in  $\text{CeRu}_2$  at  $\sim 2$  K (with a strong apodization described in Ref. [9]). The solid curves are calculated by a model with a fixed penetration depth ( $\lambda = 2000 \text{ \AA}$ ) and a background yield ( $=13.5\%$ ) common for (a)–(d).



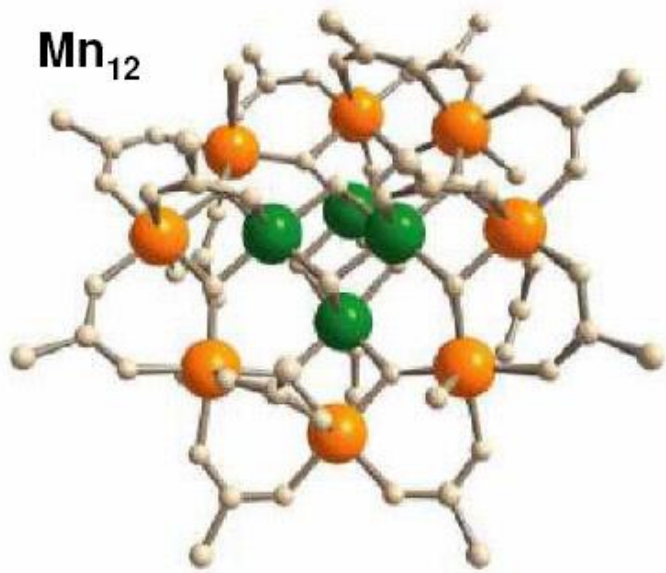
# $\mu$ SR advantages:

- A good local probe is missing in the system? Just add it...
- **Fast relaxations (Problems in detecting relaxation times shorter than 10  $\mu$ s in NMR). Notice that if one can detect the ESR signal one can access even faster relaxation times.**
- Zero field experiments can be performed. Very important as the magnetic field is often a relevant parameter of the system under investigation. NQR is possible only when a good quadrupole nucleus is present
- In metals and moreover in superconductors one can probe the whole system and not just over a length of the order of the skin depth or of the London penetration depth..
- Information on the spin density at interstitial positions
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Example: in Mn12 molecular magnet proton relaxation becomes too fast at low T and one cannot detect the NMR signal. One can study the local spin dynamics with  $\mu$ SR.

Mn12  $S = 10$



A. Lascialfari et al., Phys. Rev. Lett. **81**, 3773 (1998)

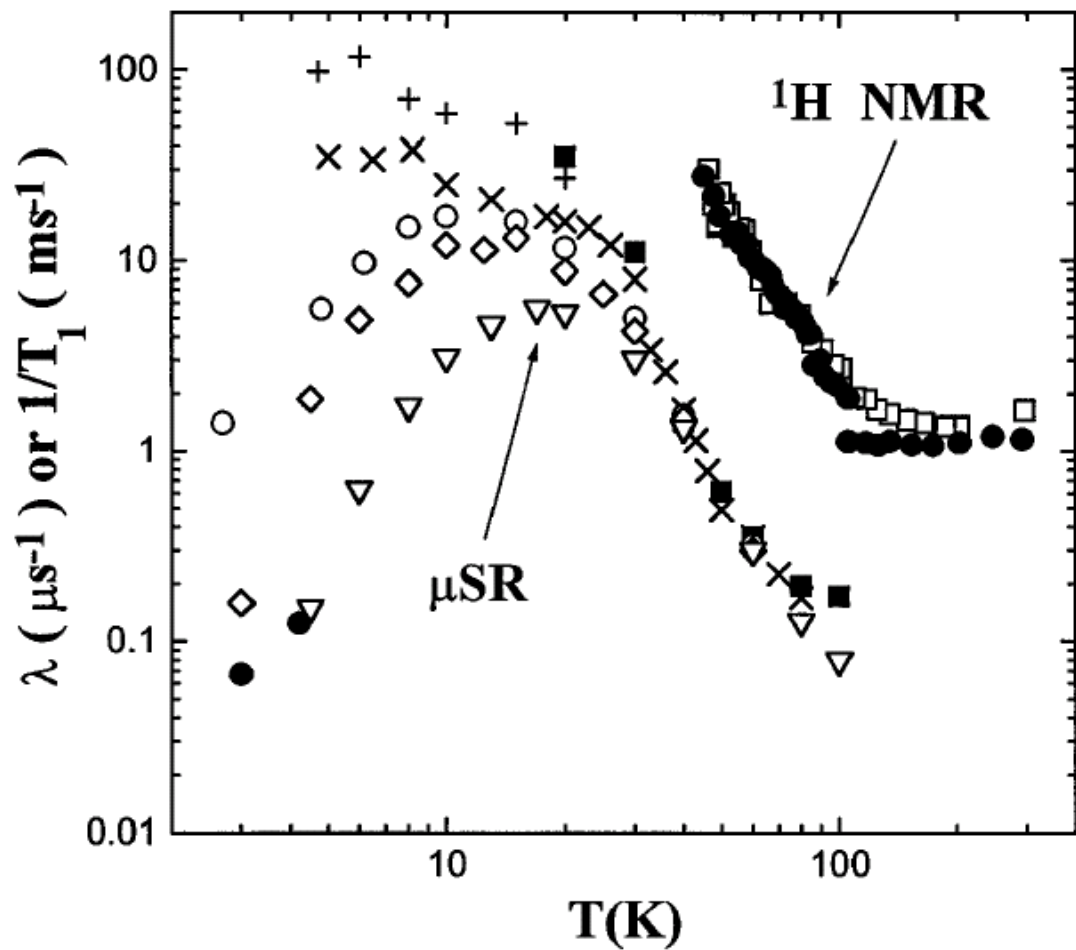
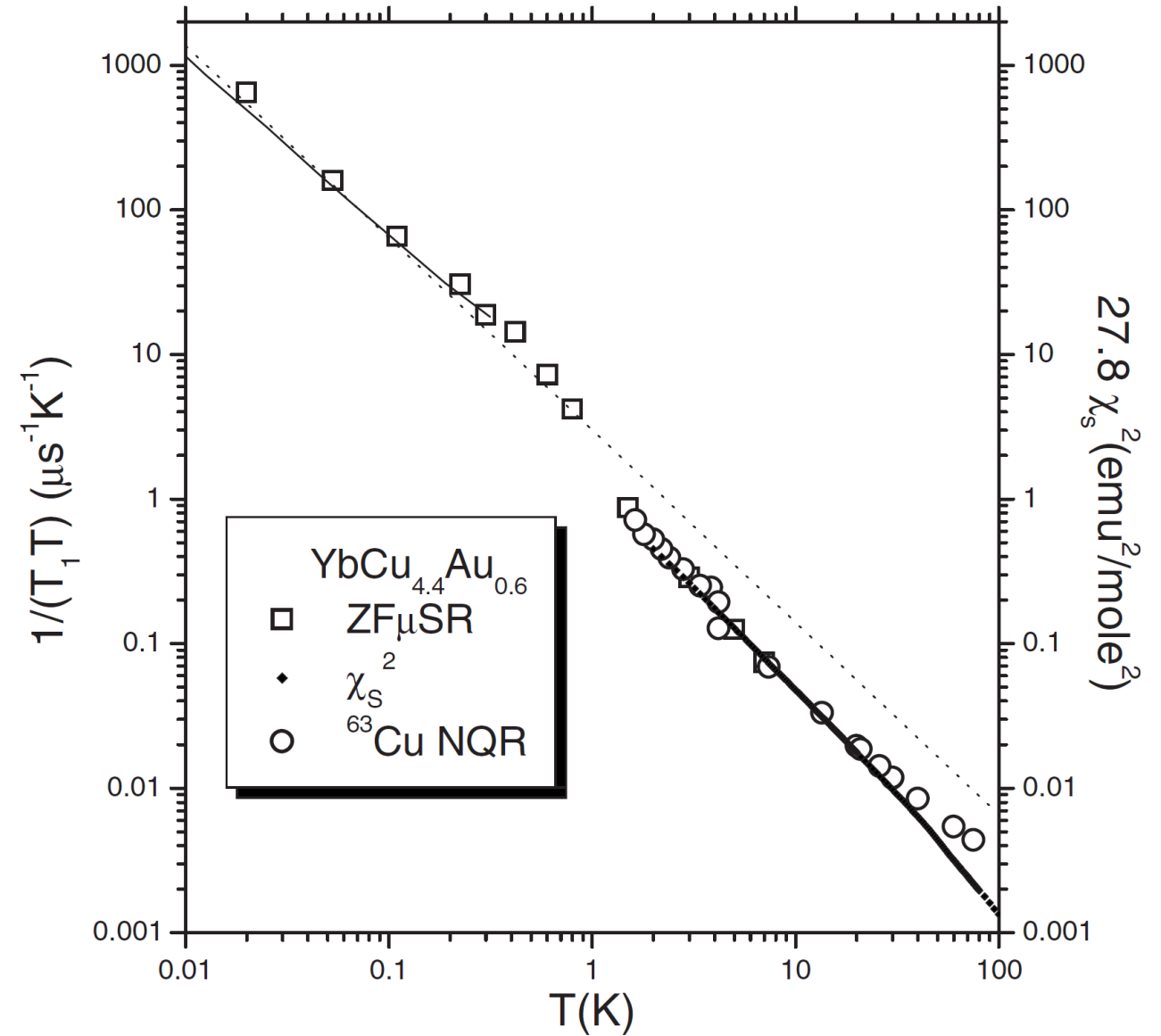


FIG. 2. Longitudinal spin-lattice relaxation rate for protons ( $T_1^{-1}$ ) and muons ( $\lambda$ ) plotted versus temperature for different applied magnetic fields. NMR: ( $\square$ ) 0.33 T ( $\bullet$ ) 0.73 T;  $\mu$ SR: ( $\blacksquare$ ) zero field, (+) 0.025 T, ( $\times$ ) 0.1 T, ( $\circ$ ) 0.15 T, ( $\diamond$ ) 0.2 T, ( $\nabla$ ) 0.37 T.

Example: Critical dynamics in heavy fermion compounds at the Quantum Critical Point. Combining ZF $\mu$ SR and NQR.

P.Carretta et al., Phys. Rev. B **79**, 020401(R) (2009)



## $\mu$ SR advantages:

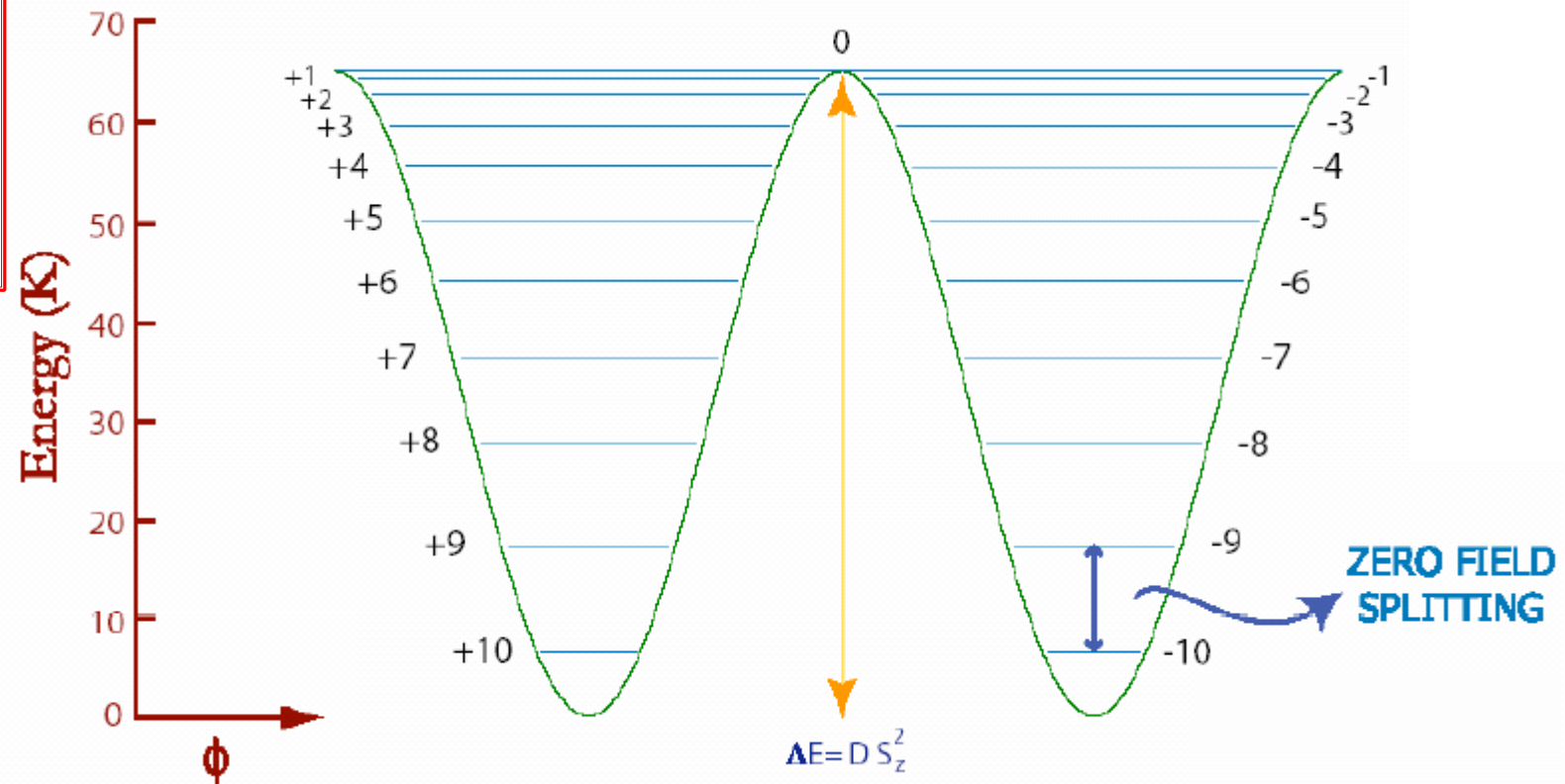
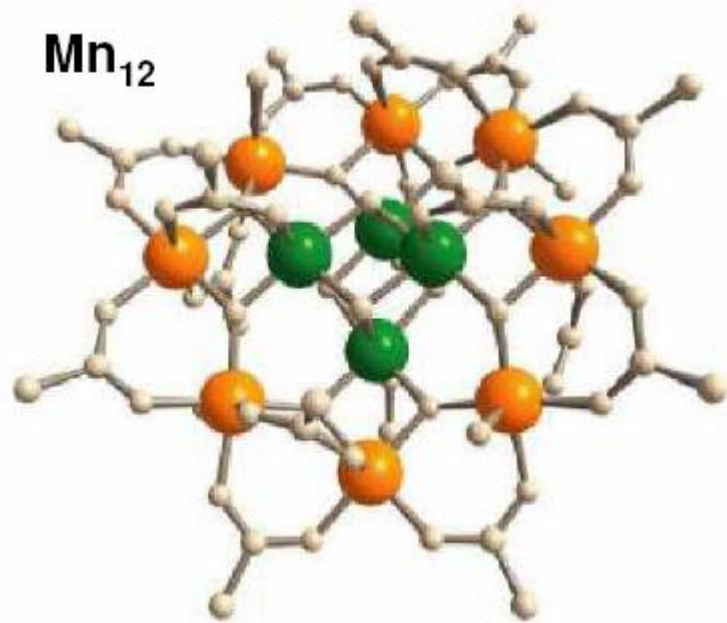
- A good local probe is missing in the system? Just add it...
- Fast relaxations (Problems in detecting relaxation times shorter than 10  $\mu$ s in NMR).
- **Zero field experiments can be performed. Very important as the magnetic field is often a relevant parameter of the system under investigation. NQR is possible only when a good quadrupolar nucleus is present**
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Example: in molecular magnets the magnetic field affects the energy level splitting and then the spin dynamics.

Mn12  $S = 10$



$$E(M_s) = DM_s^2 + 2\mu_B M_s H$$

Example: in  $(\text{TMTSF})_2\text{-X}$  Field induced Spin Density Wave phases are present. It is important to study their properties from zero up to high fields.

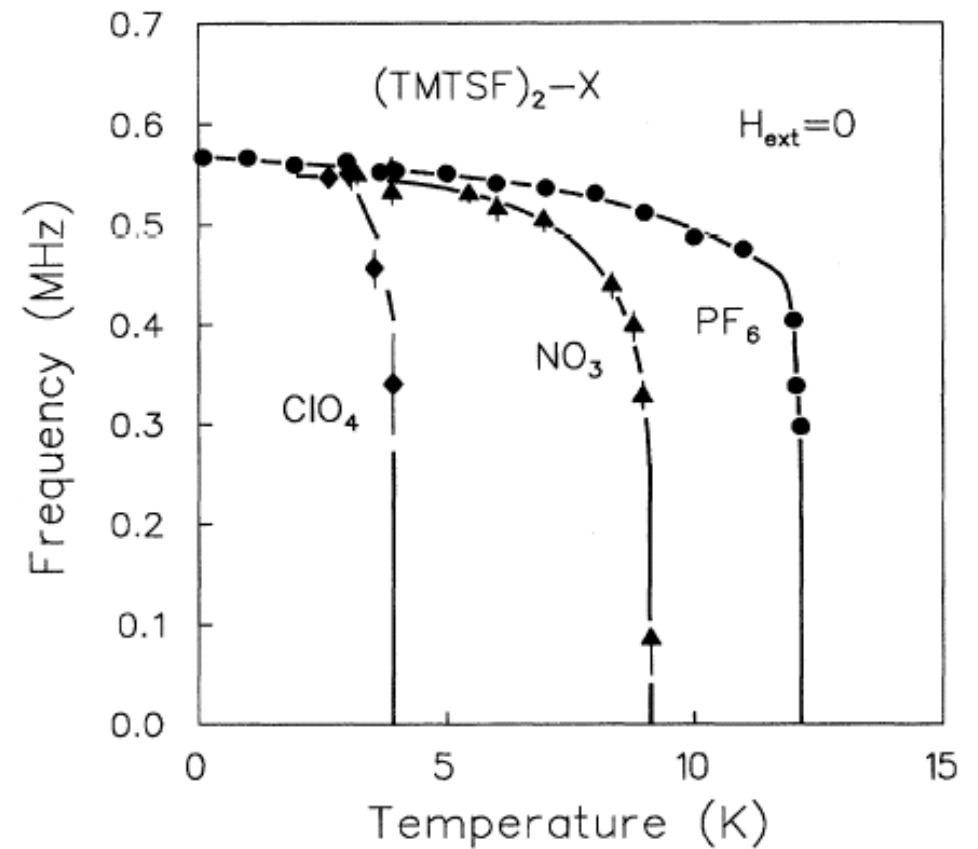
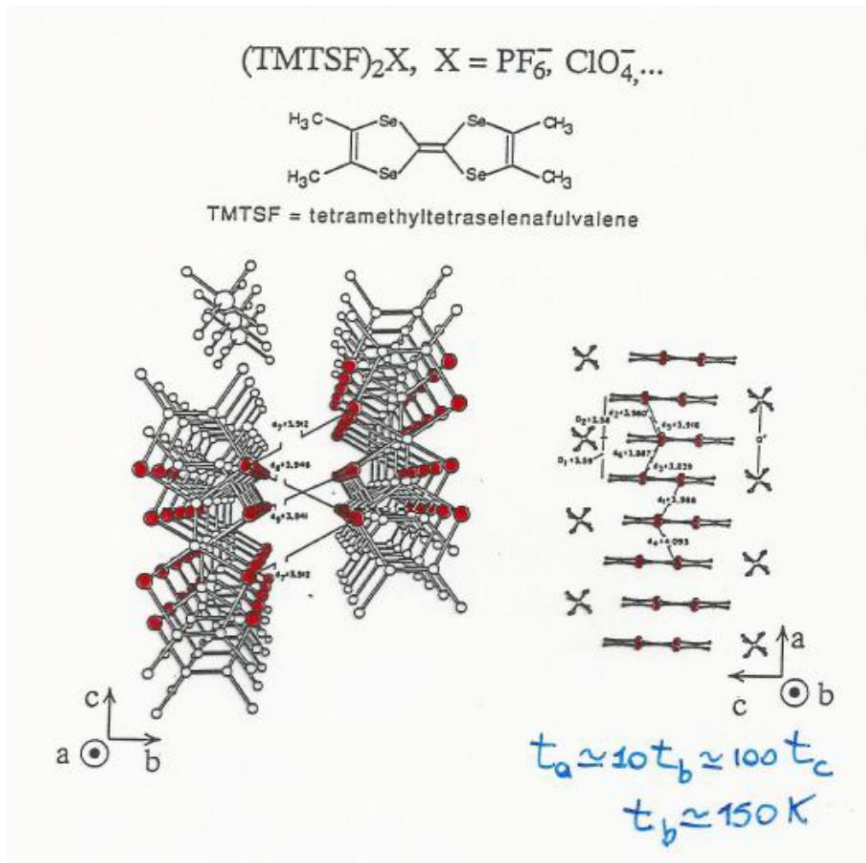


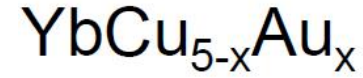
FIG. 7. Temperature dependence of the muon-spin precession frequency in zero field observed in  $(\text{TMTSF})_2\text{-X}$ . The  $\text{PF}_6$ ,  $\text{NO}_3$ , and  $\text{ClO}_4$  compounds show roughly the same precession frequency at zero temperature.

L. P. Le et al., Phys. Rev. B **48**, 7284 (1993)

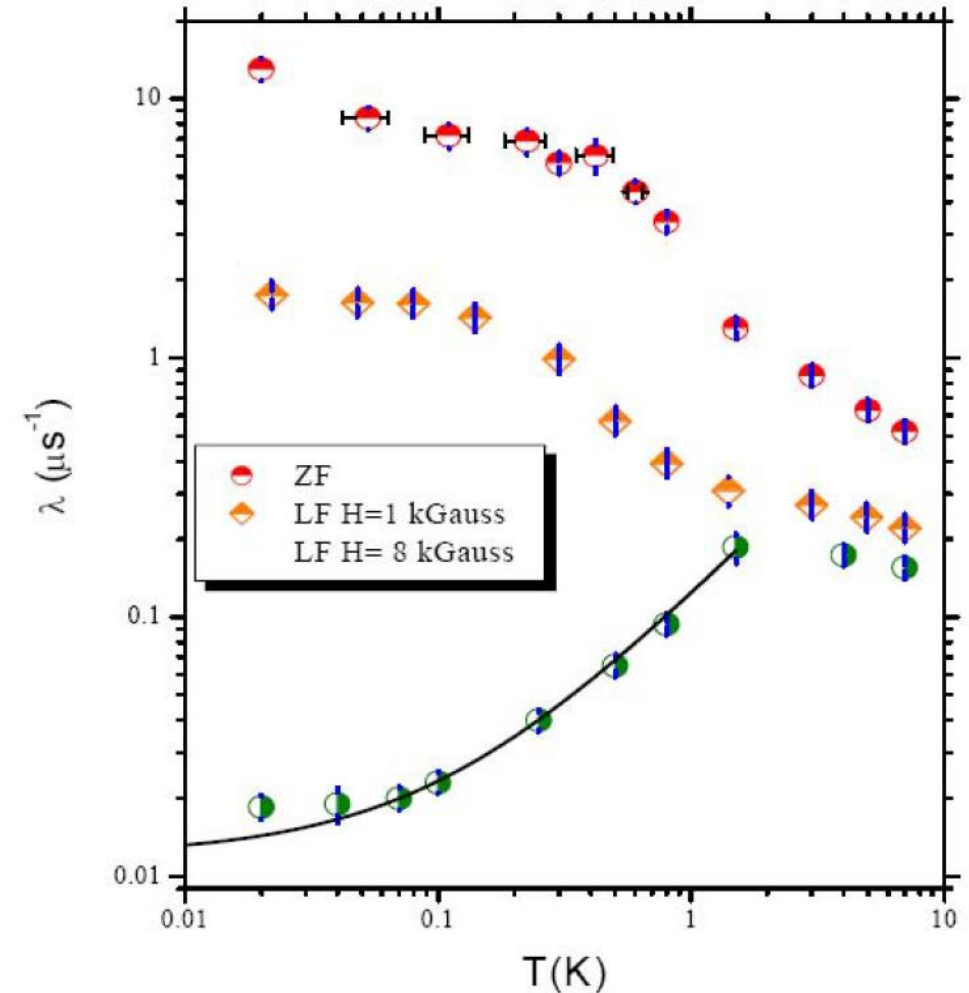




Example: Field induced Non-Fermi liquid to Fermi liquid crossover in heavy fermion compounds close to a QCP.



P.Carretta et al., Phys. Rev. B **79**, 020401(R) (2009)



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- **In metals and moreover in superconductors one can probe the whole system and not just over a length of the order of the skin depth or of the London penetration depth. Problem for NMR and even more for ESR.**
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# Example: High $T_c$ superconductors, Uemura plot

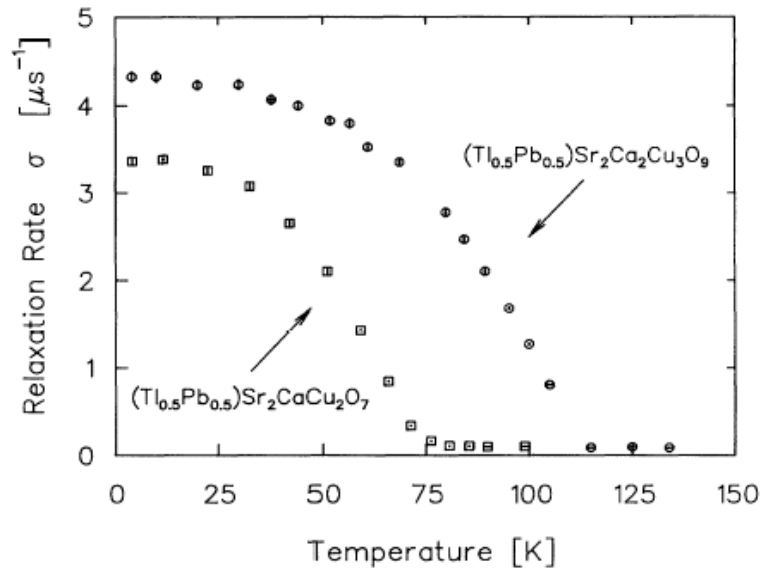
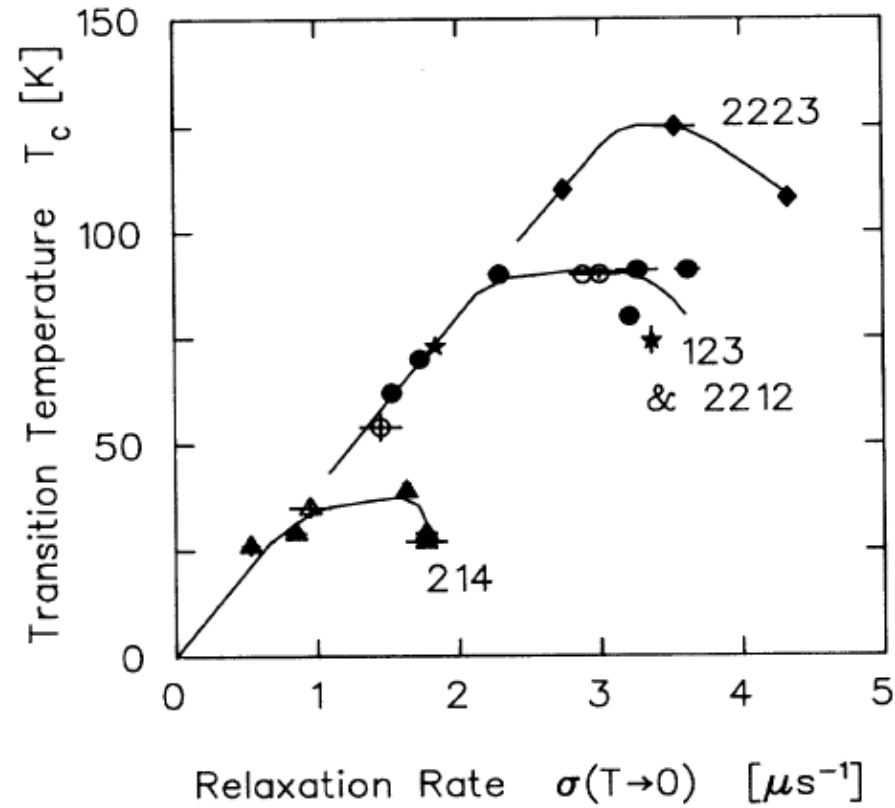


FIG. 1. The temperature dependence of the muon-spin-relaxation rate  $\sigma$  observed in  $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{CaCu}_2\text{O}_7$  (open squares) and in  $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_9$  (open circles). The former material has the double CuO planes while the latter has the triple (see Ref. 5 for resistivity and crystal structures).



$$\sigma_{\text{SC}}(T) \propto 1/\lambda^2(T)$$

Y.J.Uemura et al., Phys. Rev. Lett. **62**, 2317 (1989)

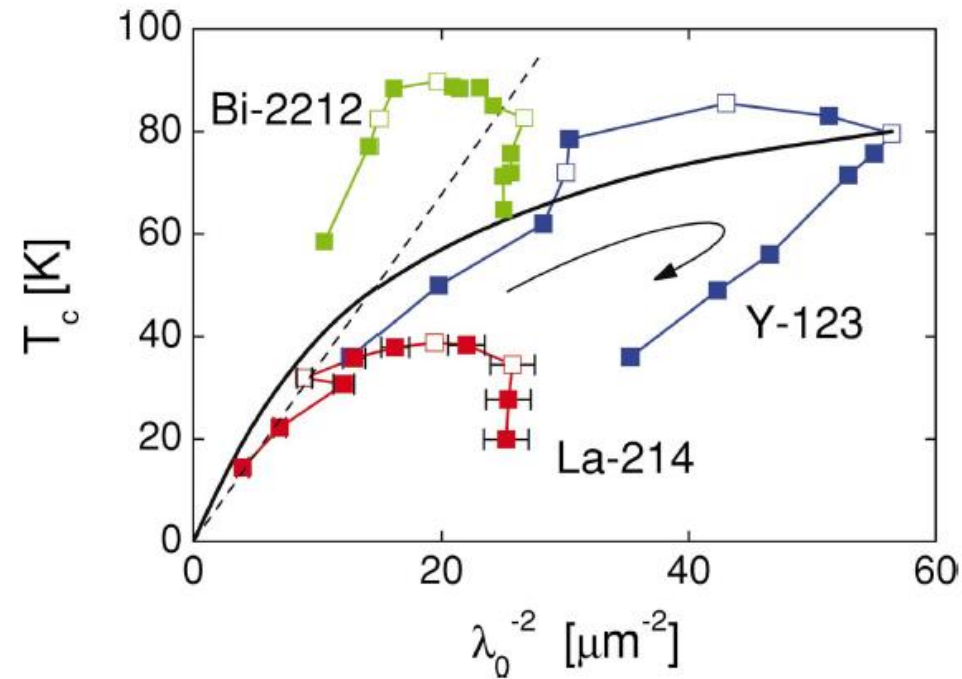


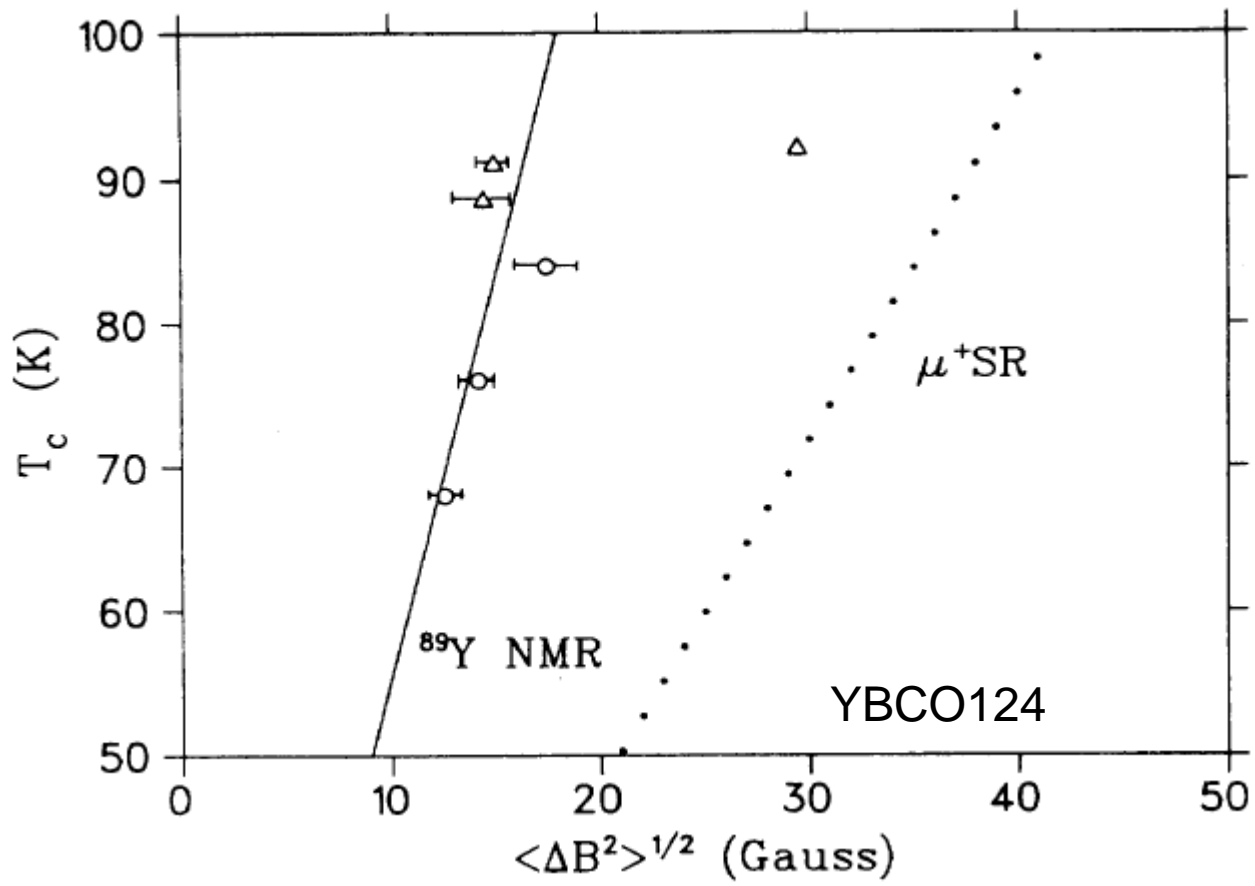
# Example: Uemura plot

PHYSICAL REVIEW B **68**, 180501(R) (2003)

## Superfluid density in cuprate high- $T_c$ superconductors: A new paradigm

J. L. Tallon,<sup>1</sup> J. W. Loram,<sup>2</sup> J. R. Cooper,<sup>2</sup> C. Panagopoulos,<sup>2</sup> and C. Bernhard<sup>3</sup>

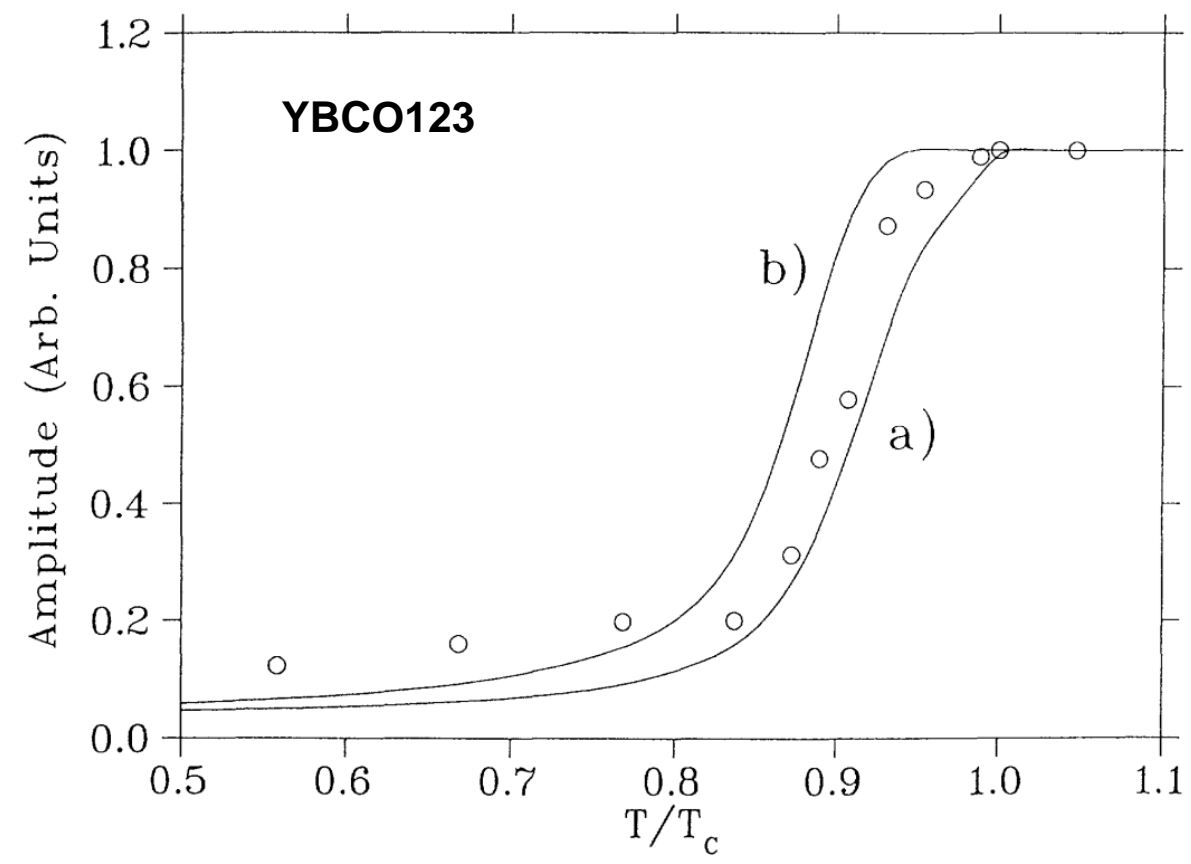
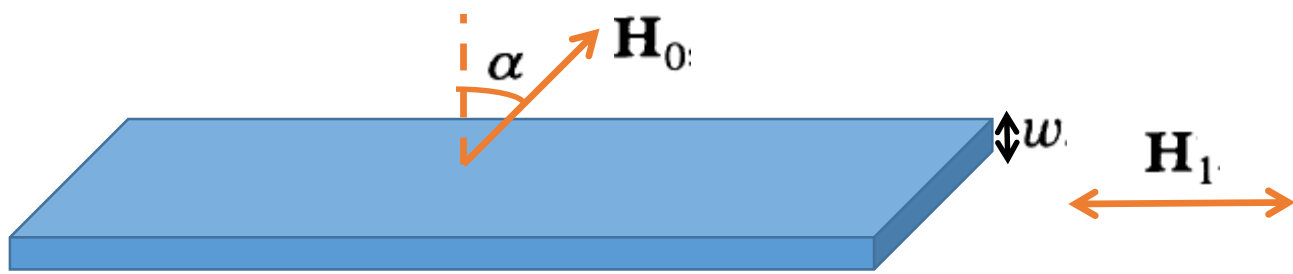




- NMR Problems:
- RF penetration
  - Effect of RF pulses on FL motions

P.Carretta, PRB 45, 5760 (1992)

Reduction of the NMR signal in YBCO high  $T_c$  superconductors due to RF screening.



P.Carretta, PRB 48, 528 (1993)

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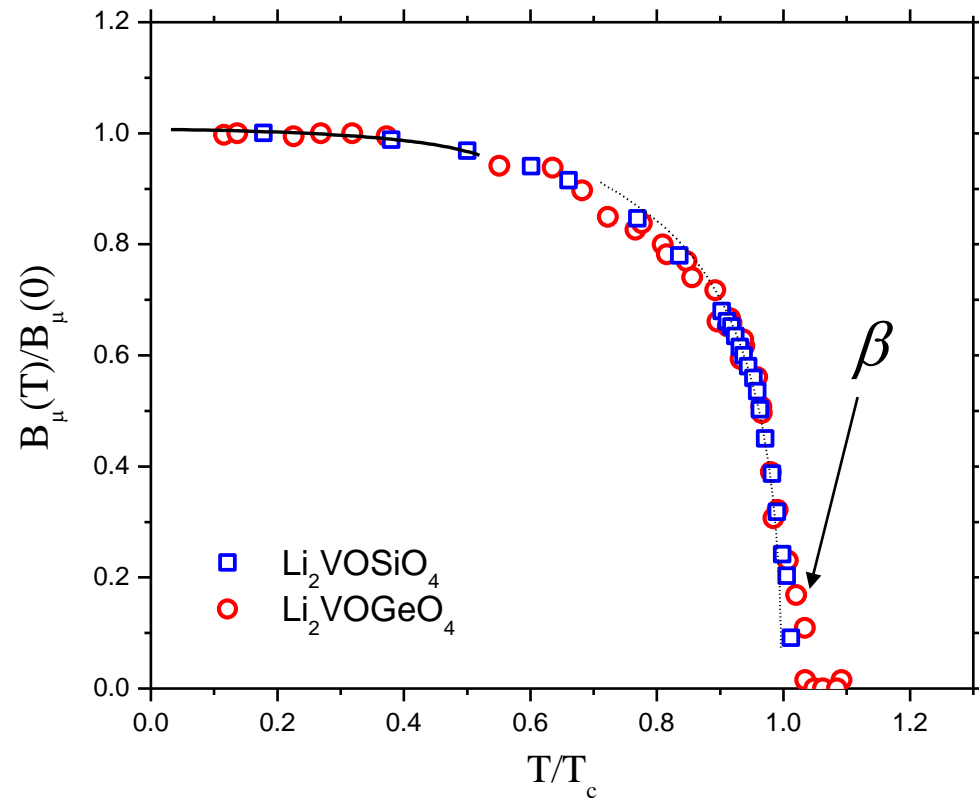
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Magnetic order parameter from ZF $\mu$ SR



$$\mathbf{B}_\mu \propto \sum_i A_i \langle \mathbf{S}_i \rangle$$

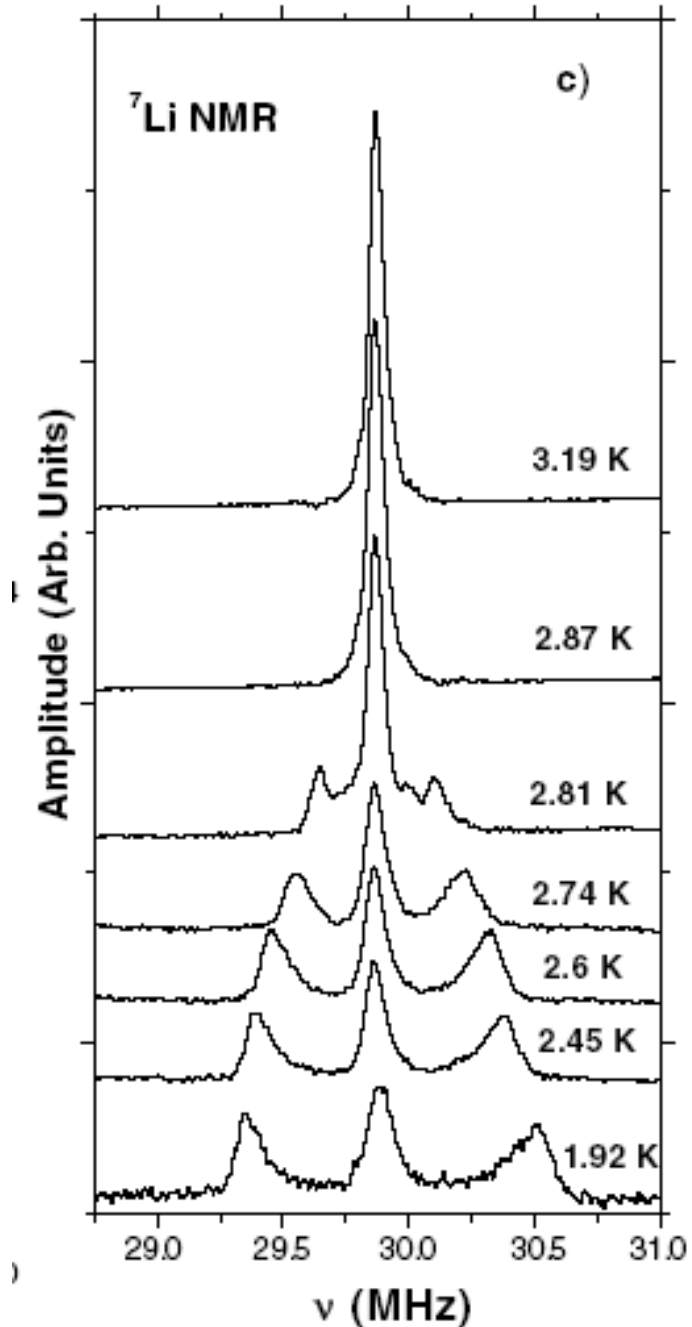
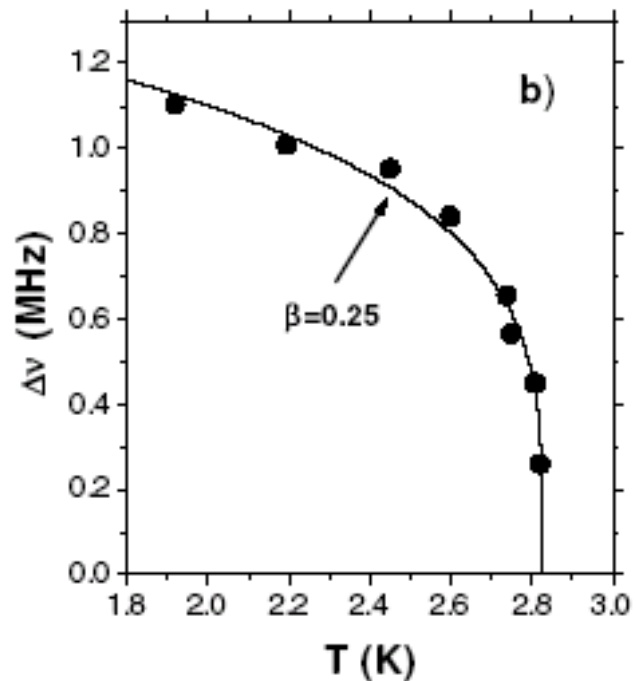
$$B_\mu(T) = B_\mu(0)(1 - T/T_c)^\beta$$

$$\beta \approx 0.236 \Rightarrow \text{2D XY}$$

P.Carretta et al., Phys. Rev. Lett. **88**, 047601 (2002)



# Magnetic order parameter from $^7\text{Li}$ NMR



R.Melzi et al., Phys. Rev. Lett. **85**, 1318 (2000)

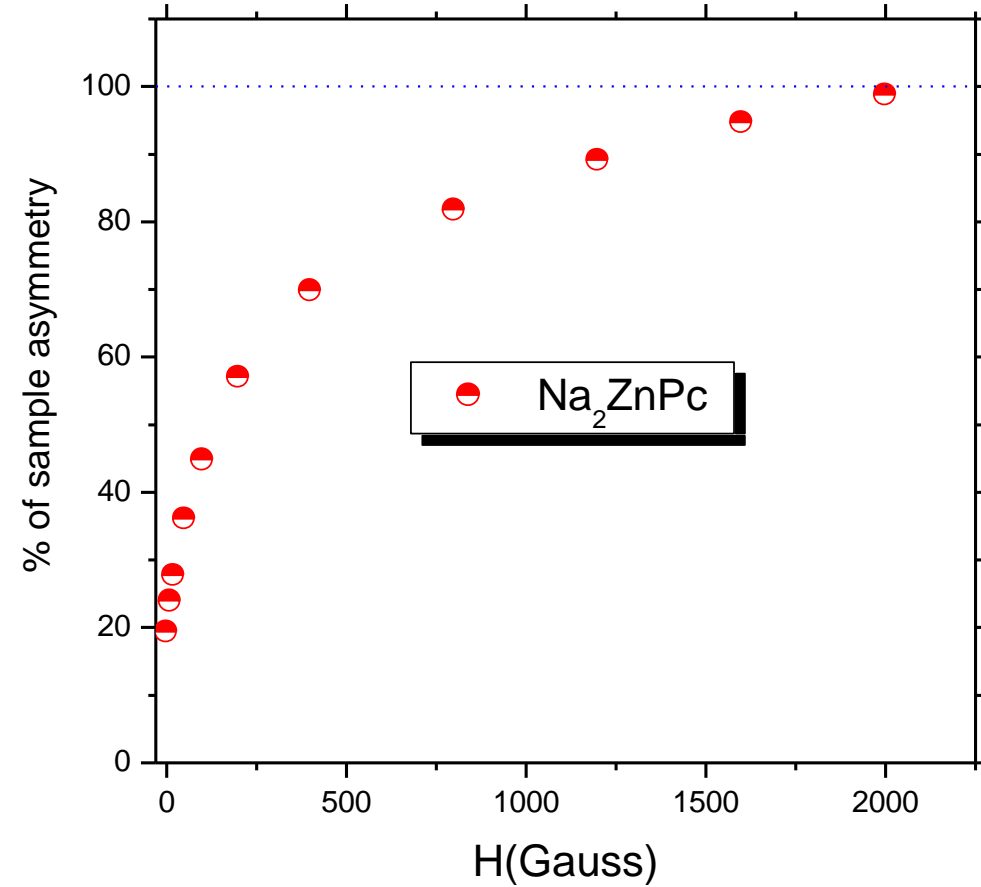
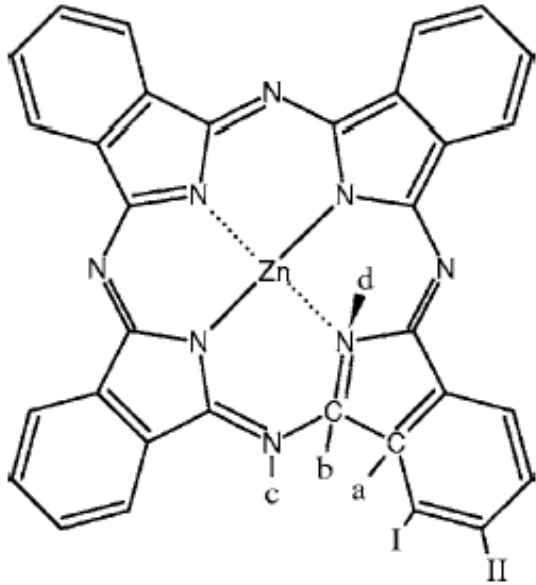


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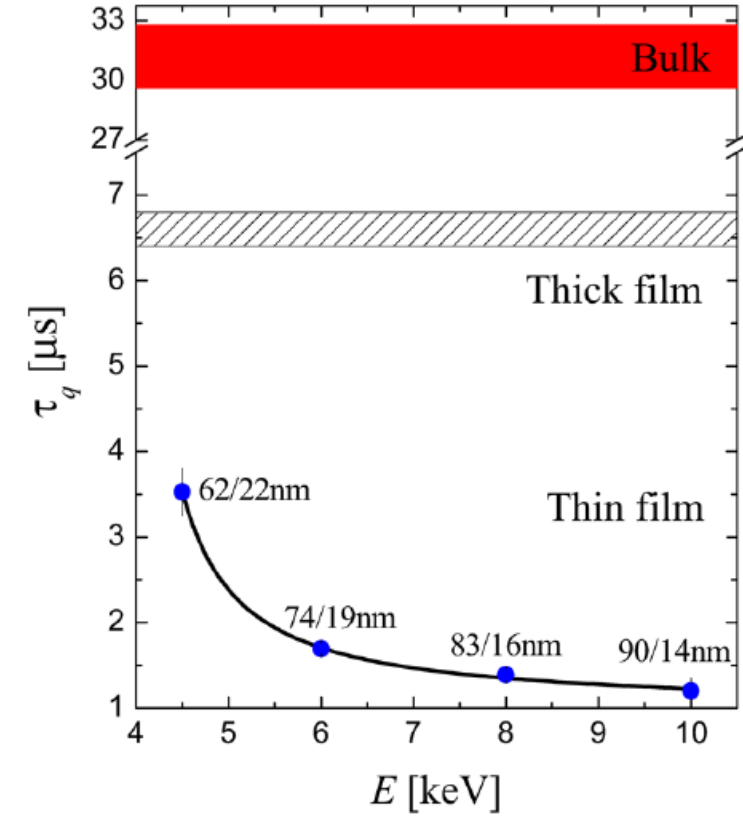
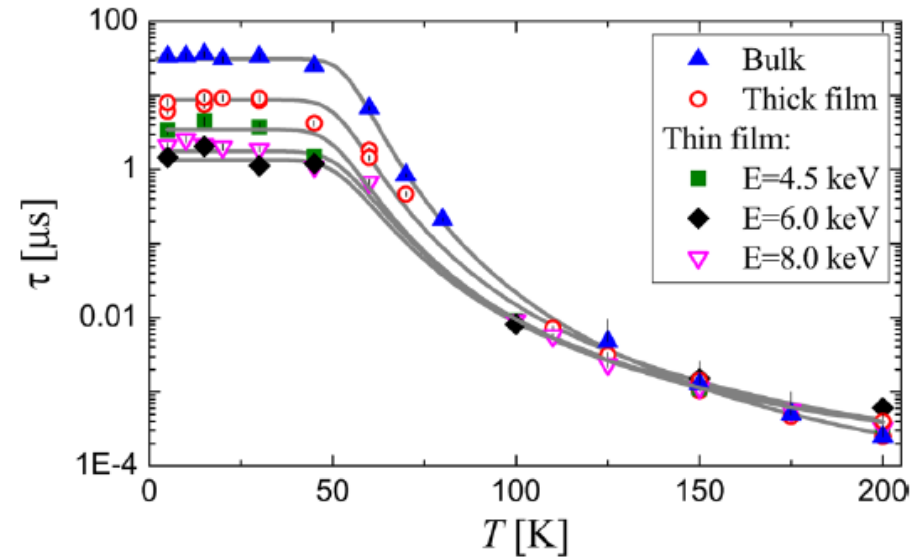
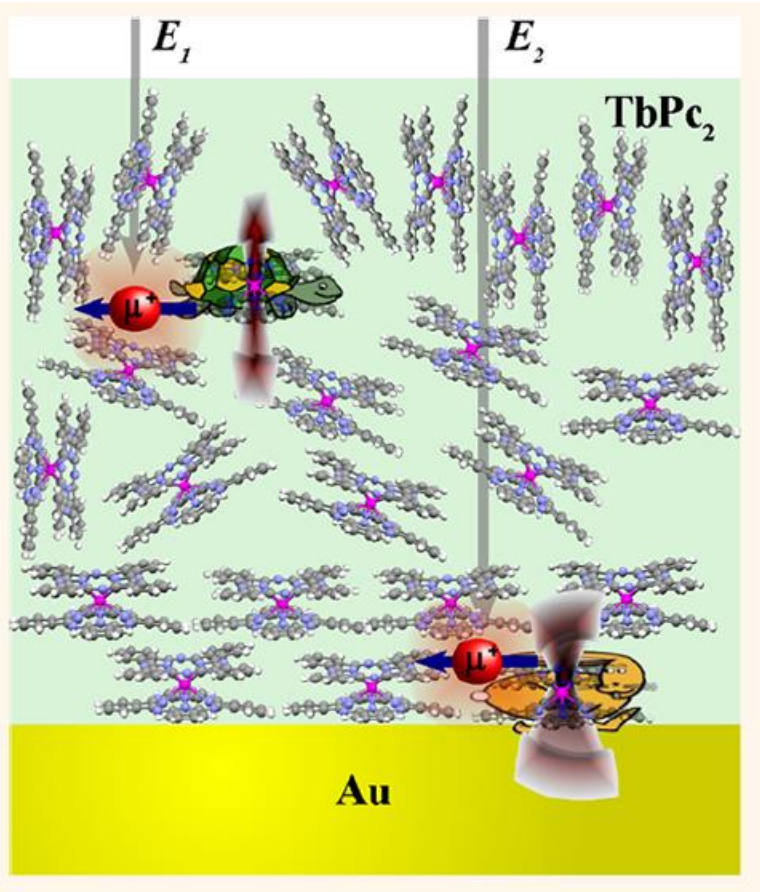
By studying the amount of muonium formed in  $\text{Na}_x\text{ZnPc}$  one can learn where Na binds.



M.Filibian, Ph.D. thesis University of Pavia (2008)



# Low-energy muons: a powerful probe to study thin films



A. Hoffman et al., ACS Nano 6, (2012)



# $\beta$ -NMR: a powerful probe to study thin films

## Nanoscale $\beta$ -nuclear magnetic resonance depth imaging of topological insulators

Dimitrios Koumoulis<sup>a</sup>, Gerald D. Morris<sup>b</sup>, Liang He<sup>c</sup>, Xufeng Kou<sup>c</sup>, Danny King<sup>a</sup>, Dong Wang<sup>d</sup>, Masrur D. Hossain<sup>b,d</sup>, Kang L. Wang<sup>c</sup>, Gregory A. Fiete<sup>e</sup>, Mercuri G. Kanatzidis<sup>f</sup>, and Louis-S. Bouchard<sup>a,g,1</sup>

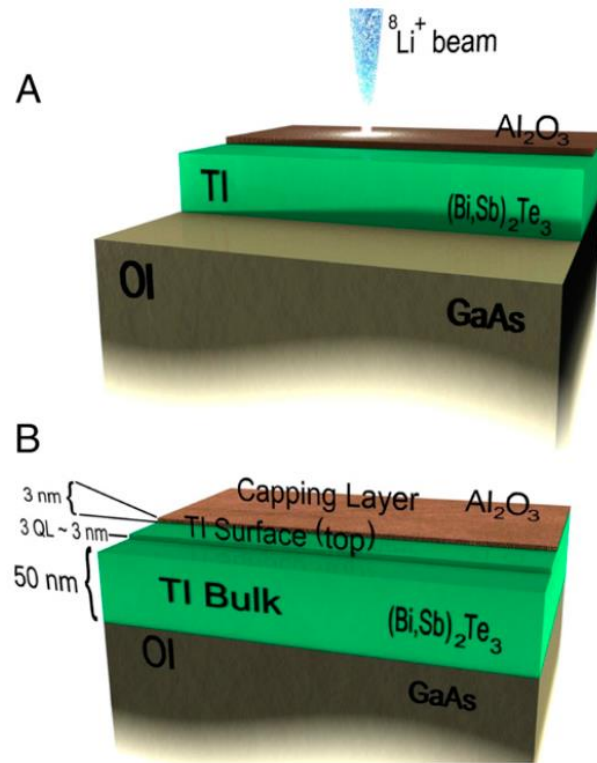
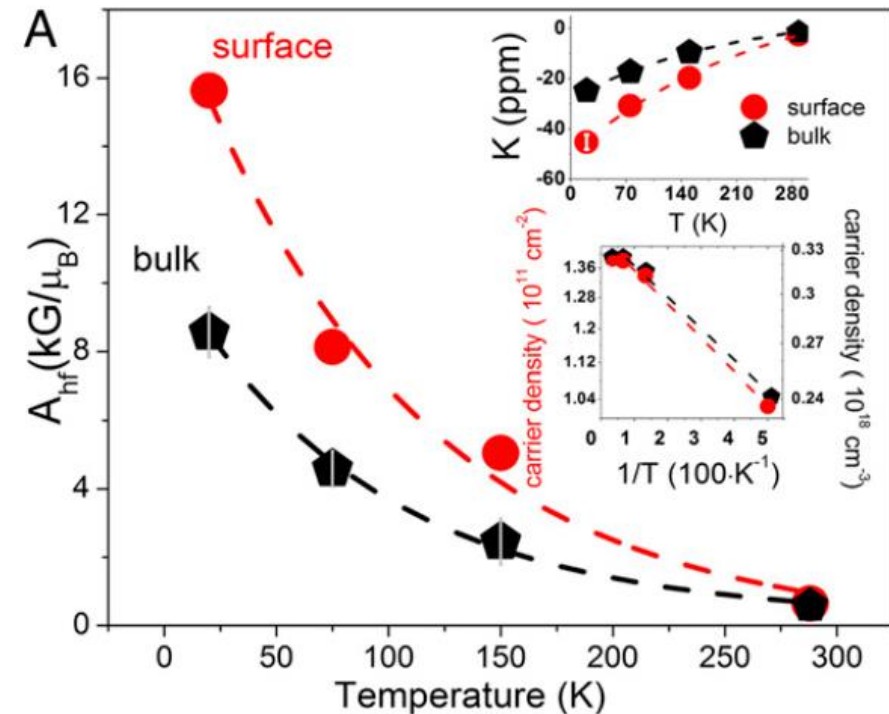


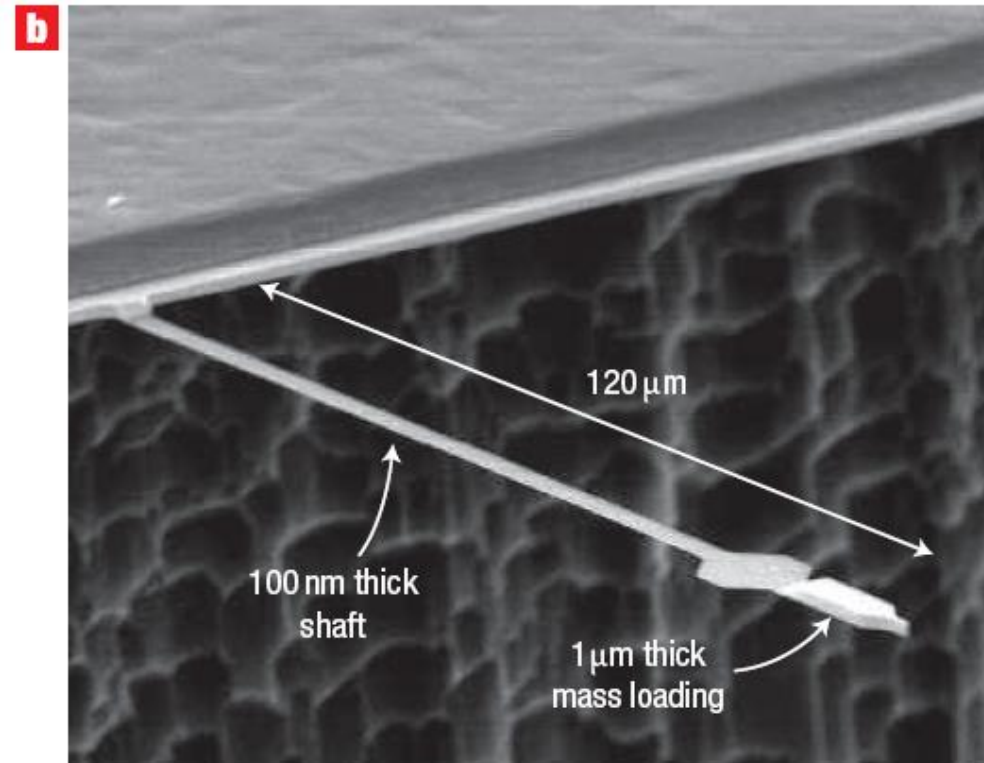
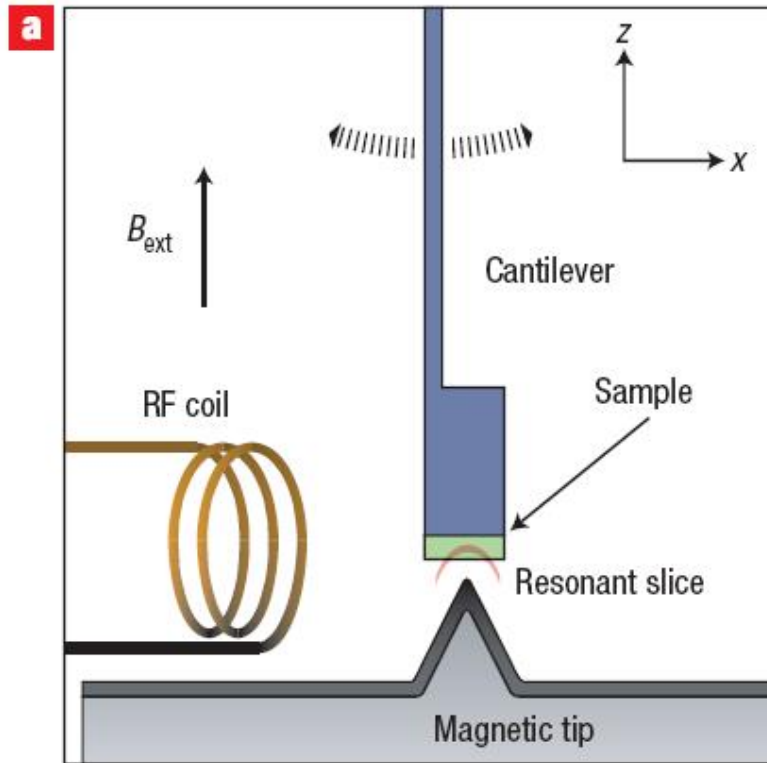
Fig. 1. Schematic diagram of the  $\beta$ -NMR experimental setup. The direction of the  $^8\text{Li}^+$  ion beam and the different epitaxial layers are shown in A. Structure of the TI-OI multilayered  $(\text{Bi,Sb})_2\text{Te}_3$  sample [capping layer ( $<3\text{nm Al}_2\text{O}_3$ ), TI [50-nm  $(\text{Bi,Sb})_2\text{Te}_3$ ], and OI (350- $\mu\text{m GaAs}$ )] as a function of depth (nm) (B).

D.Koumoulis et al., PNAS 112, E3645 (2015)





# Nuclear Magnetic Resonance Force Microscopy

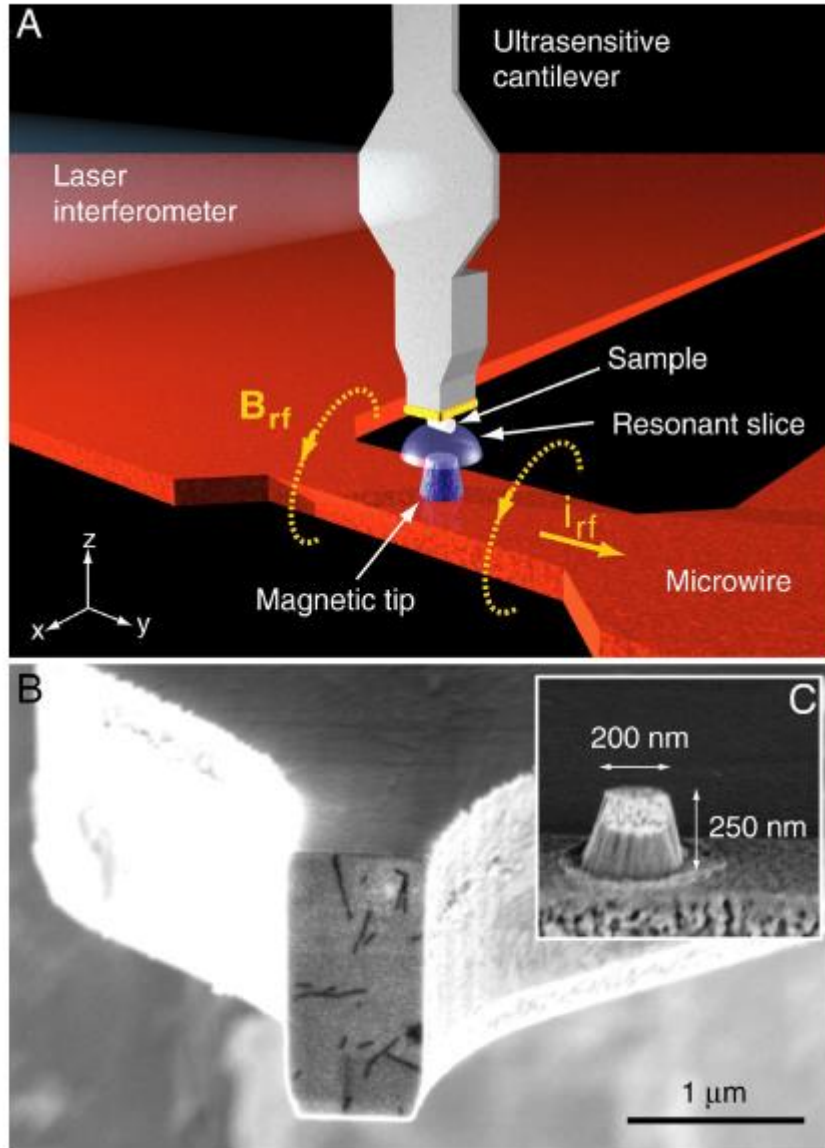


H.J.Mamin et al., Nature Nanotech.2, 301 (2007)

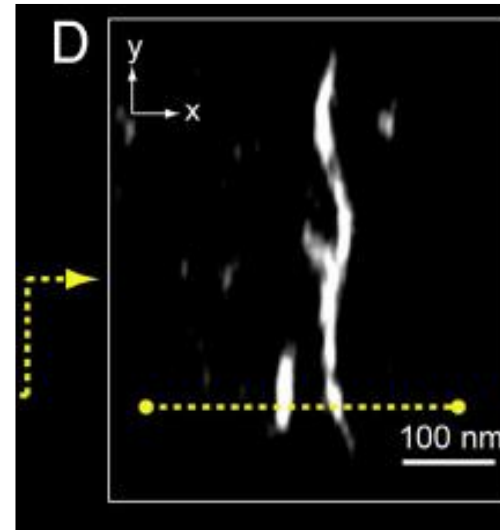
**Martino Poggio group** <http://poggiolab.unibas.ch/>



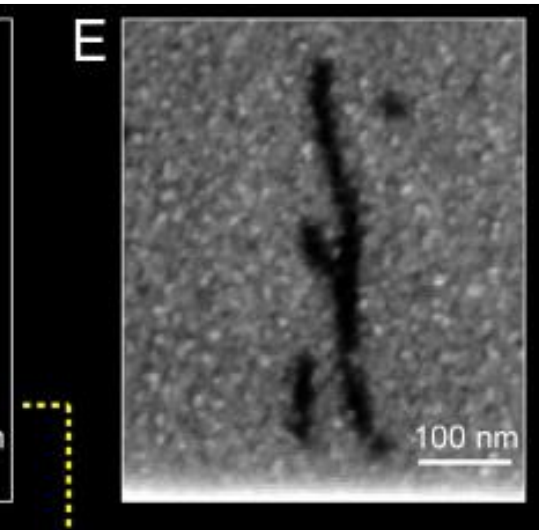
# Nuclear Magnetic Resonance Force Microscopy



Nuclear MRFM



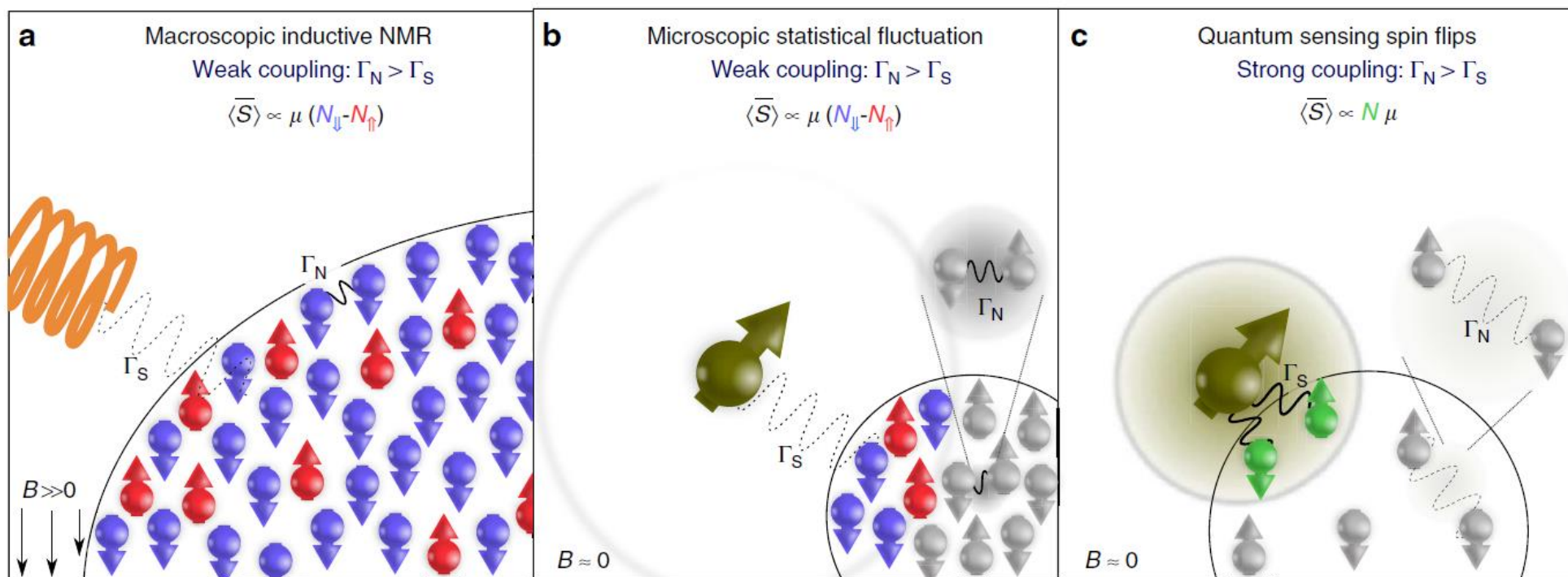
SEM





# Nuclear magnetic resonance spectroscopy with single spin sensitivity

C. Müller<sup>1,2,\*</sup>, X. Kong<sup>1,3,4,\*</sup>, J.-M. Cai<sup>2,5</sup>, K. Melentijević<sup>1,2</sup>, A. Stacey<sup>6</sup>, M. Markham<sup>6</sup>, D. Twitchen<sup>6</sup>, J. Isoya<sup>7</sup>, S. Pezzagna<sup>8</sup>, J. Meijer<sup>8</sup>, J.F. Du<sup>3,4</sup>, M.B. Plenio<sup>2,5</sup>, B. Naydenov<sup>1,2</sup>, L.P. McGuinness<sup>1,2</sup> & F. Jelezko<sup>1,2</sup>



# Playing with nuclei and muons: NUClear DEcoupled $\mu$ SR ... and Level-crossing resonance

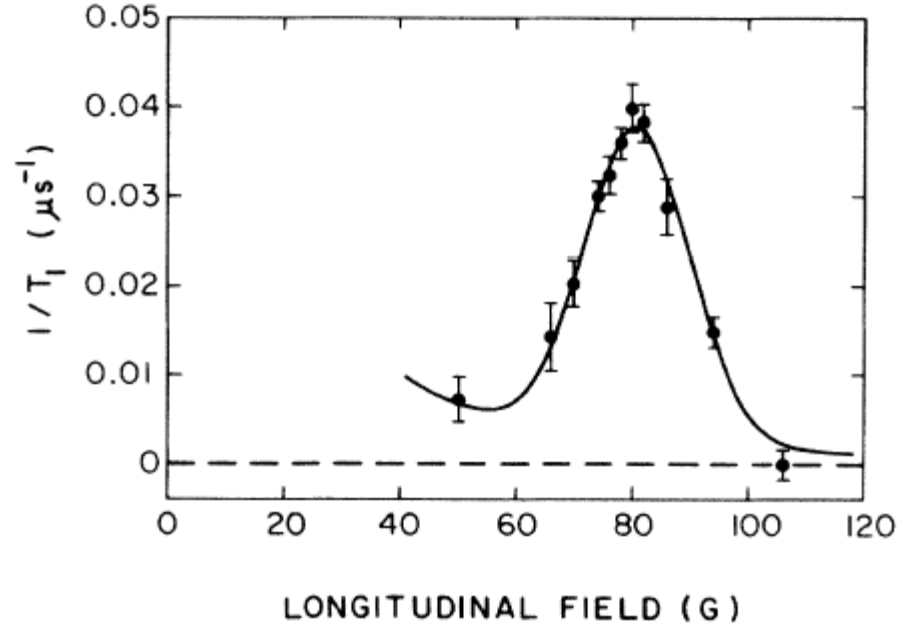
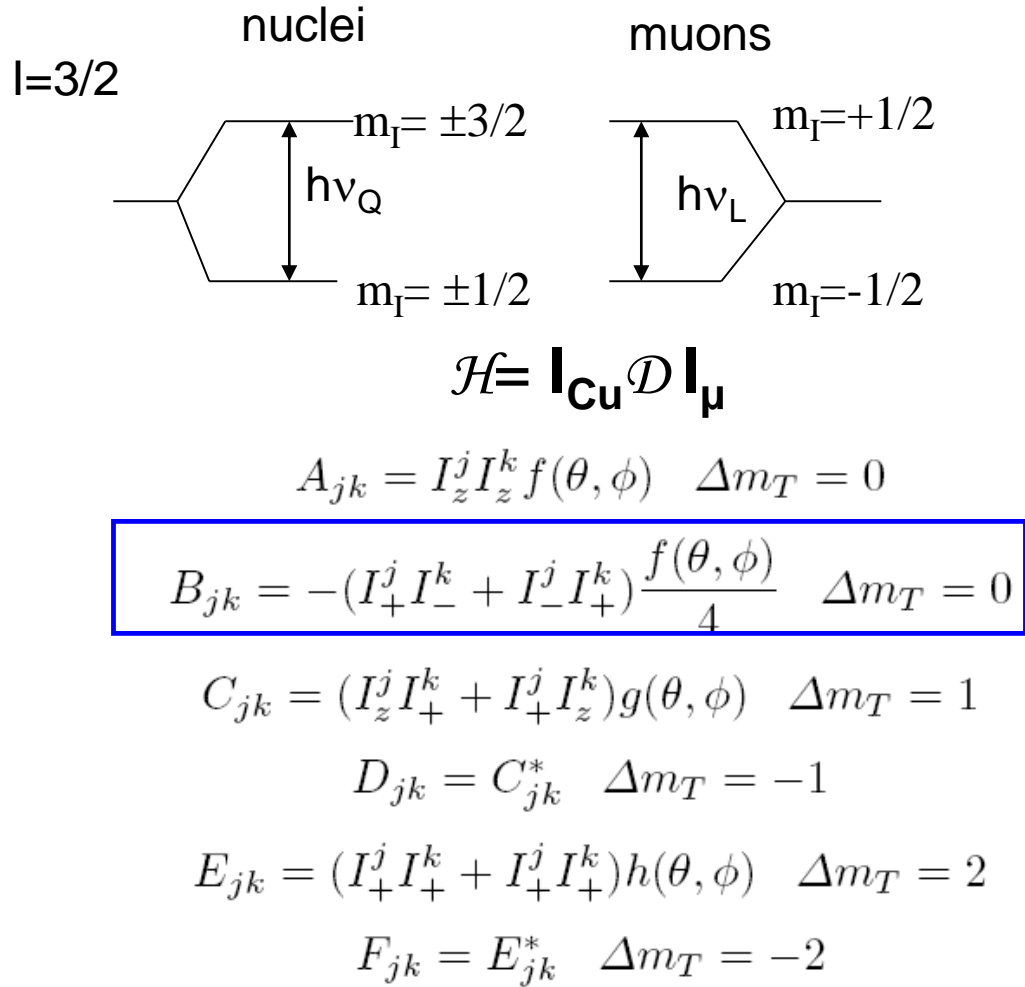


FIG. 2. Longitudinal-field muon-spin-relaxation level-crossing resonance in a Cu crystal at 20 K with [111] axis parallel to the external magnetic field  $\mathbf{B}$ . The line through the points is a fit with a Gaussian lineshape on top of a background decreasing as  $B^{-2}$  (see text).

S.R. Kreitzman et al., Phys. Rev. Lett. 56, 181 (1986)

## NMR advantages:

- Many...NMR is known since almost 80 years and is by now applied in many different areas.
- Low cost.
- Sensitive to small hyperfine couplings and hence very useful to reconstruct organic molecular structures and to evidence their presence. In other terms one can measure very long relaxation times which cannot be measured with  $\mu$ SR.
- Since one can work at high fields very accurate shift measurements can be performed.
- One can use different RF pulse sequence to separate T1 from T2 relaxation mechanisms, while in  $\mu$ SR. it is not always simple to separate them.
- One does not have to perturb the system with an additional charge.
- One can work with extremely small samples.



## **ESR advantages:**

- Allows to probe directly the local spin susceptibility
- Allows to measure the Landé g-factor and correlate it with the local ionic configuration and the crystal field
- Measure directly the hyperfine coupling with the surrounding nuclei.
- Measure directly the electronic decoherence time in potential qubits.
- Measure directly electron-phonon coupling.
- Single electron spin detection.

## **ESR drawbacks:**

- One needs a good ion as a probe. In particular it is better if it is weakly coupled and carries no orbital angular momentum otherwise phonons cause a fast relaxation.
- Strong electronic correlations give rise to a significant line broadening and to a suppression of the ESR signal.
- Microwave penetration in metals and superconductors is poor and ESR signal refers just to the surface.



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# Engineering coherent interactions in molecular nanomagnet dimers

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