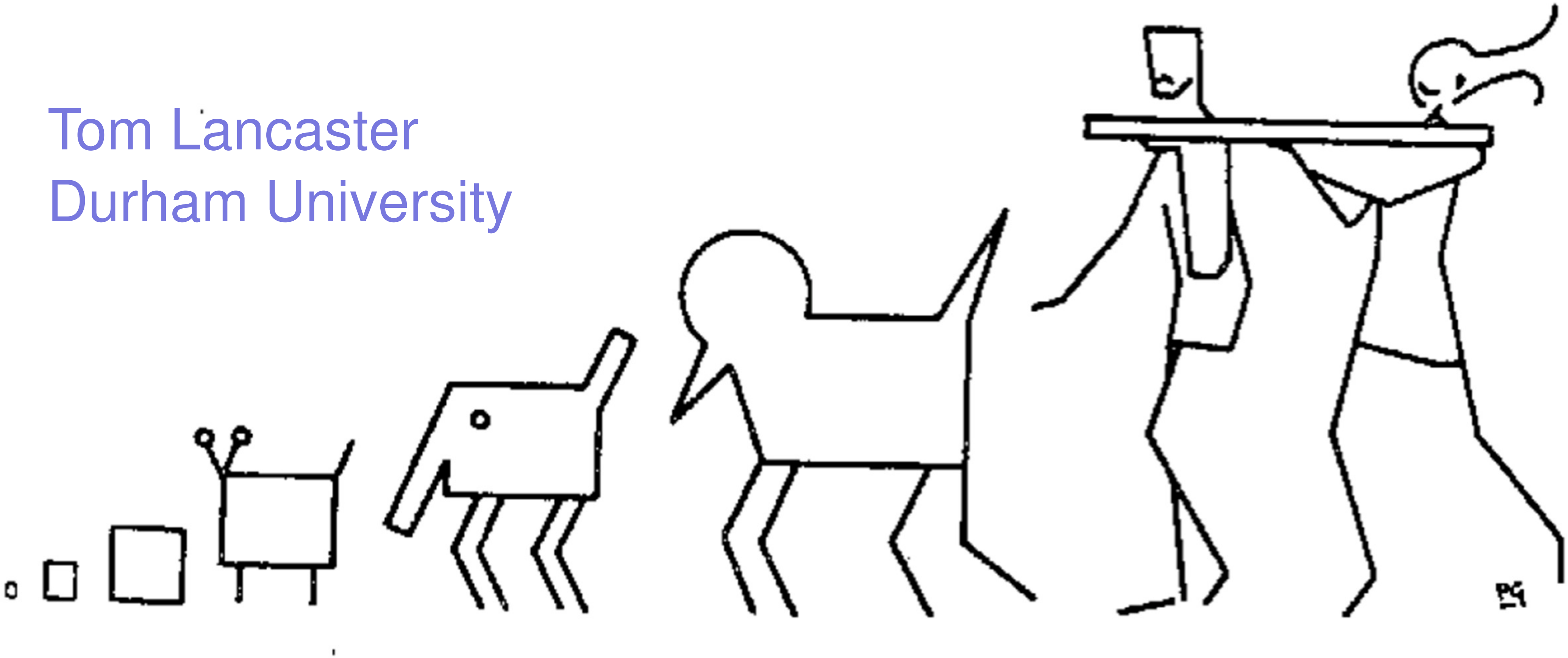
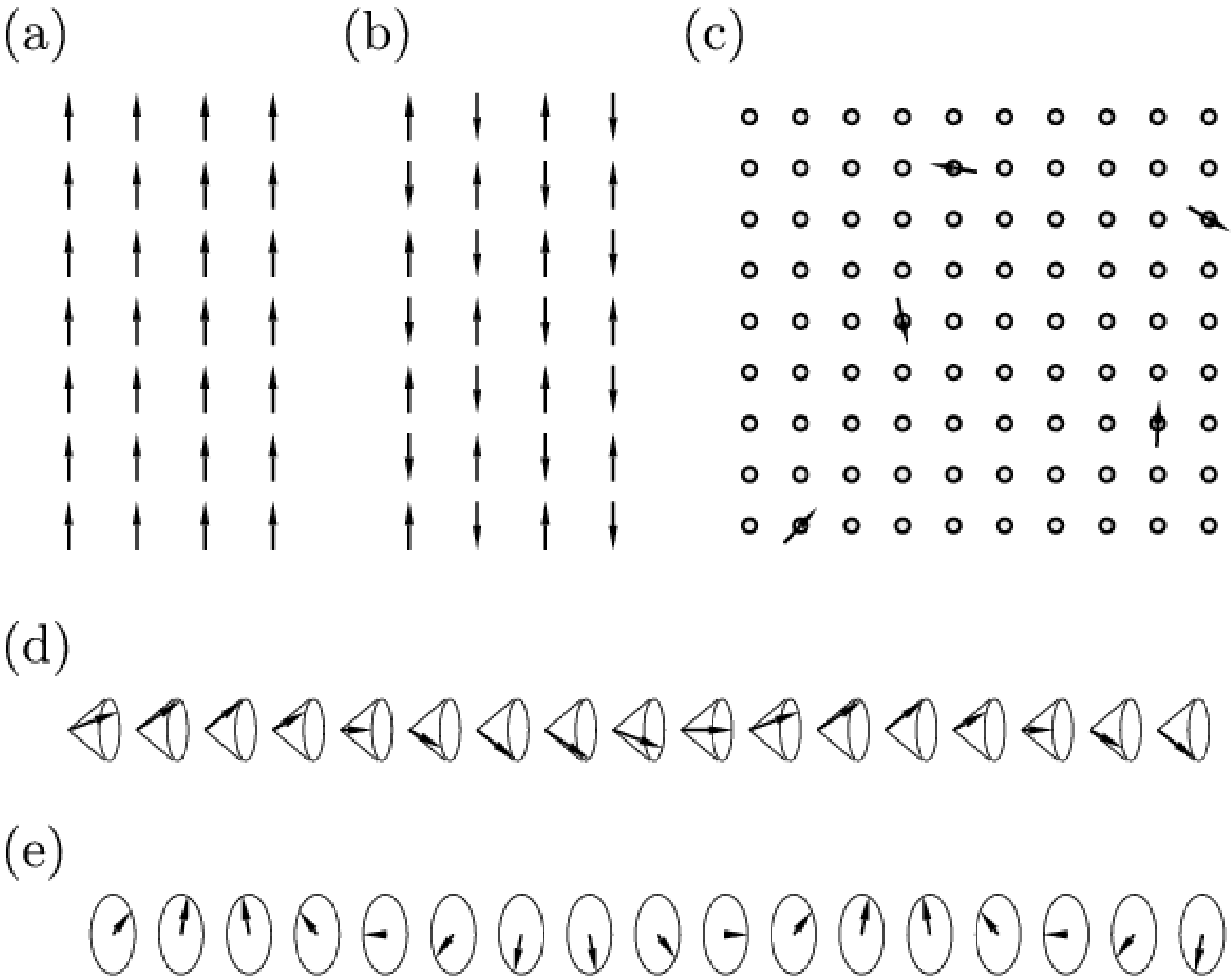
ISIS muon spectroscopy training school 2018: applications to magnetism

Tom Lancaster
Durham University

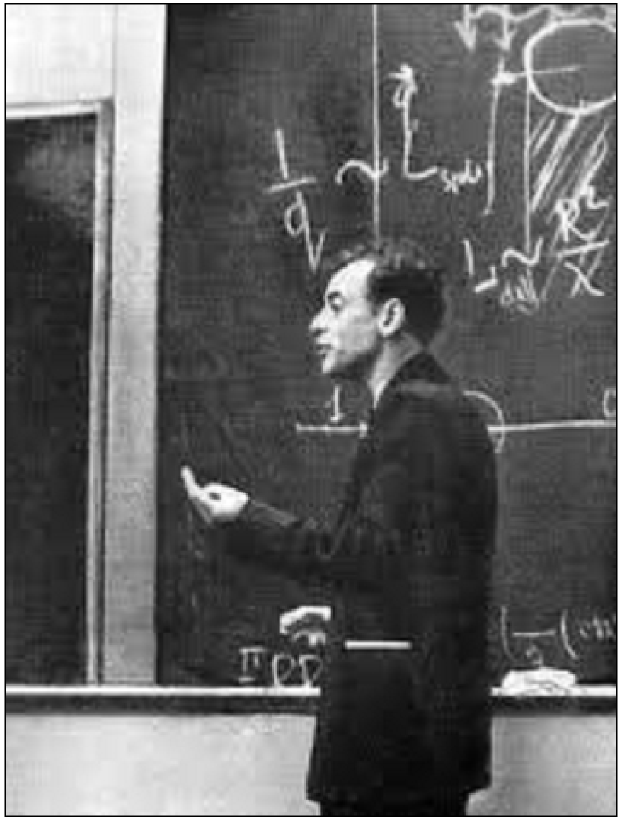


Various animals attempting to follow a scaling law.

The many faces of magnetism



How do we understand the occurrence of magnetic order?



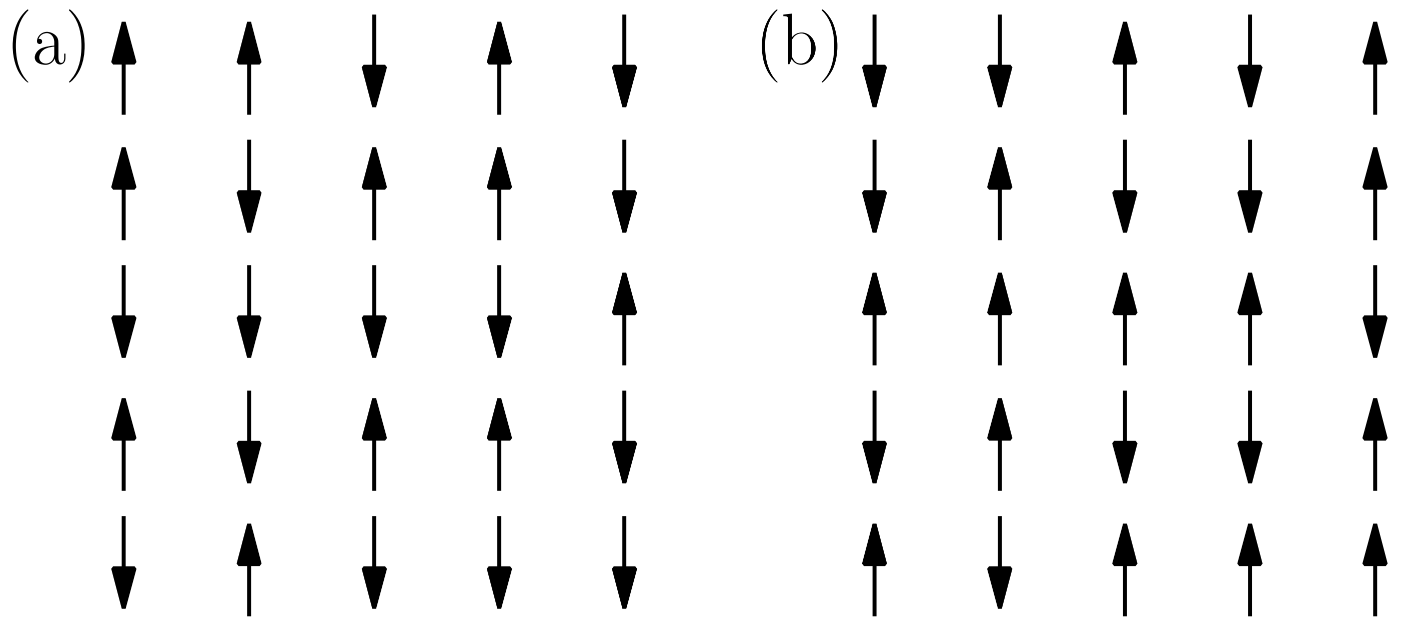
Lev Landau (1908-1968)

Philip Anderson (1923-)

Broken symmetry is a cornerstone of CMP

Consider a magnet

$T > T_c$

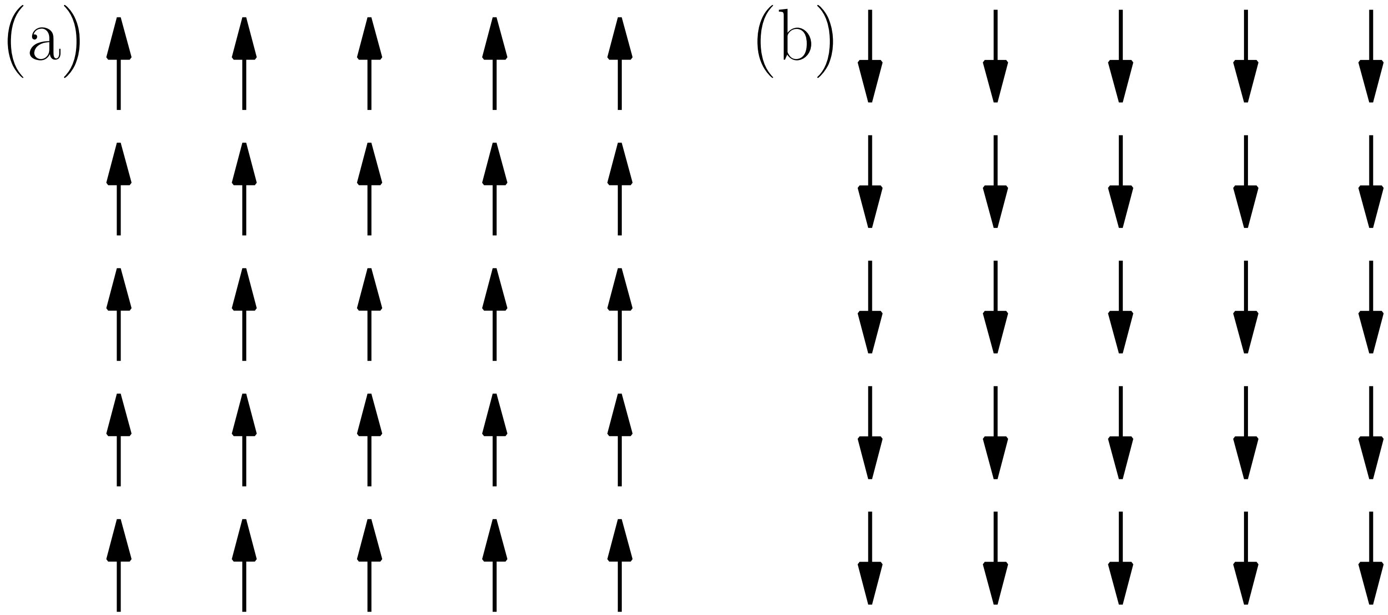


These magnets are the same

Broken symmetry is a cornerstone of CMP

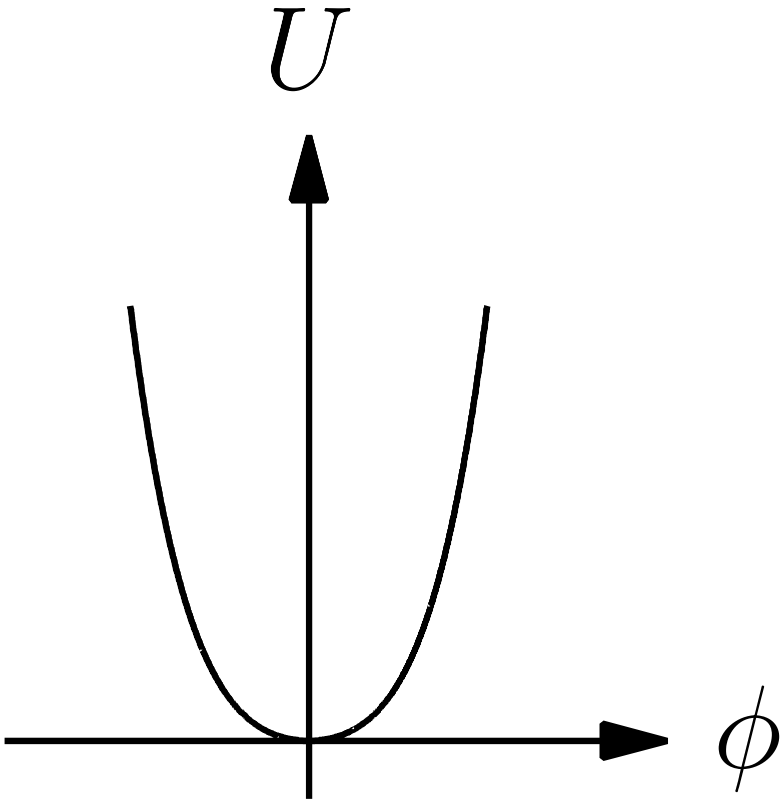
Consider a magnet

$T<T_c$

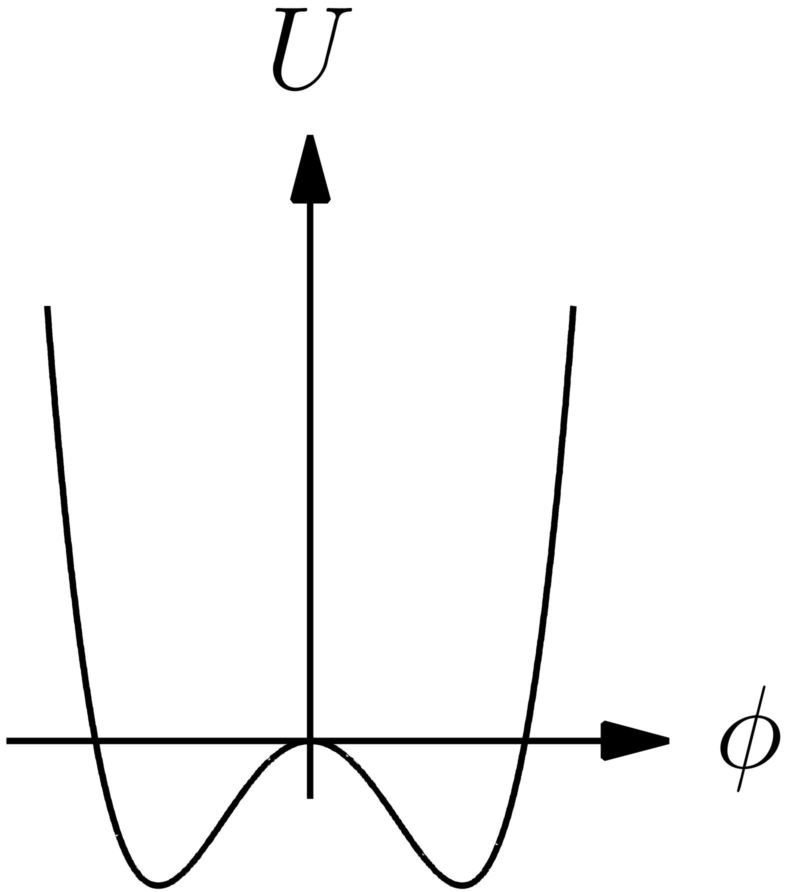


These magnets are different

This has a simple mathematical description



$T > T_c$



$T < T_c$

Mathematical singularity at T_c prevents you following the properties

The 4-fold way of broken symmetry

- Phase transitions

Mathematical singularity at T_c

- Rigidity

order transmits forces

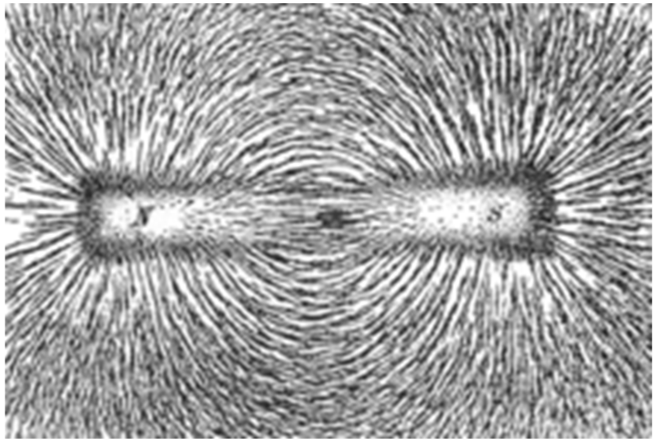
- New excitations

New particle spectrum

- Defects

Walls that separate different order in different places

The magnet

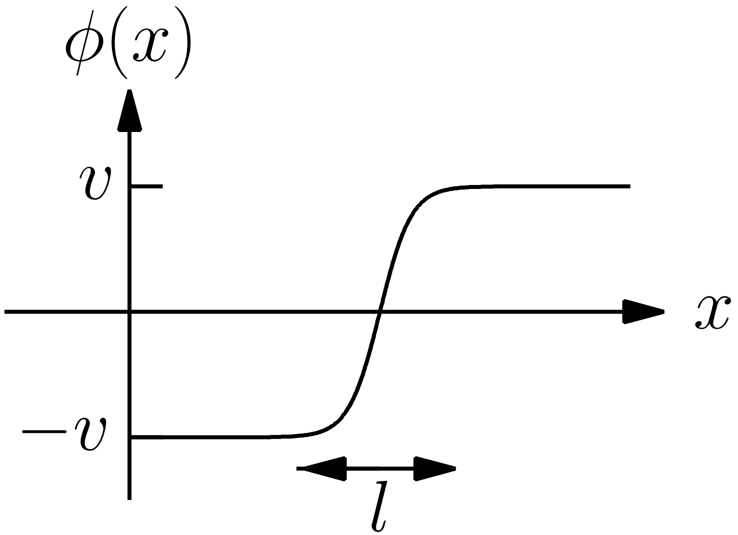


- Order parameter M

- Rigidity: permanent magnetism

- Excitations: magnon particles

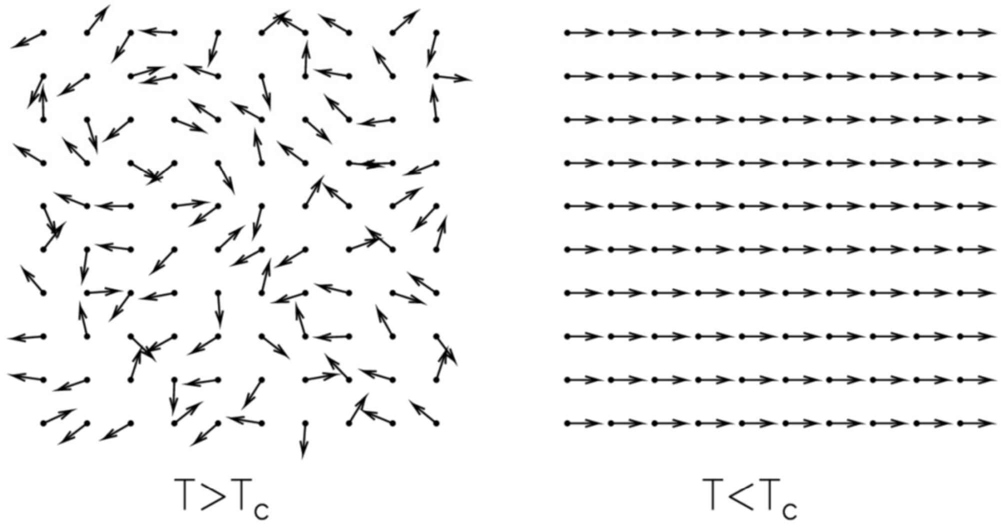
- Defects: domain walls

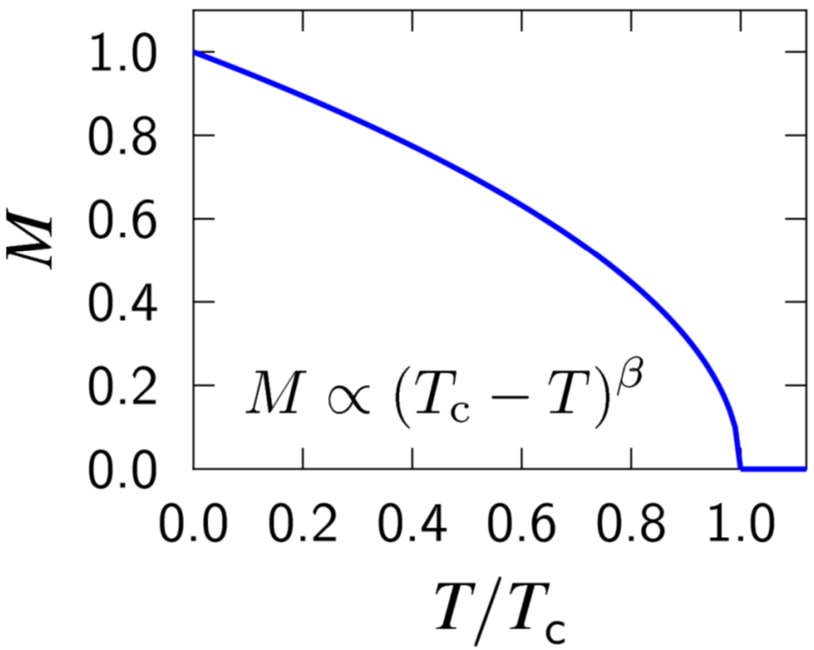


$$\mu$$

The muon

Critical phenomena in magnetism



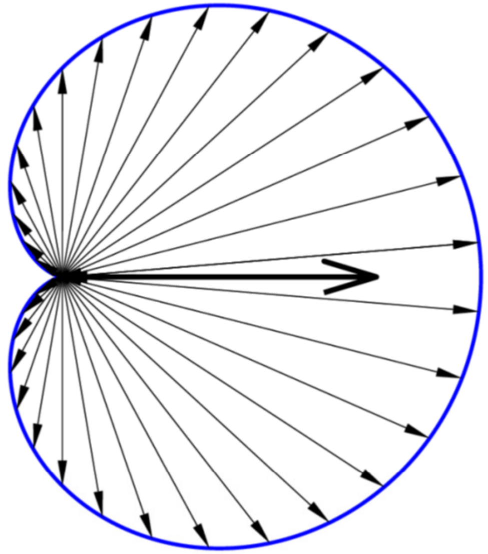


The parameter β is a *critical exponent*

In μ^+SR we measure $\nu(T) \propto M(T)$

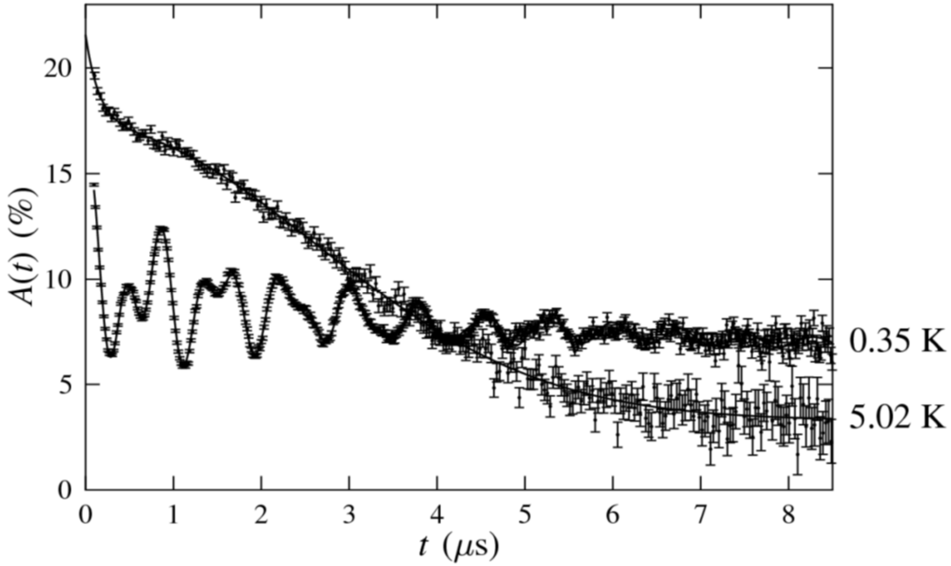
S.J. Blundell *Magnetism in Condensed Matter*

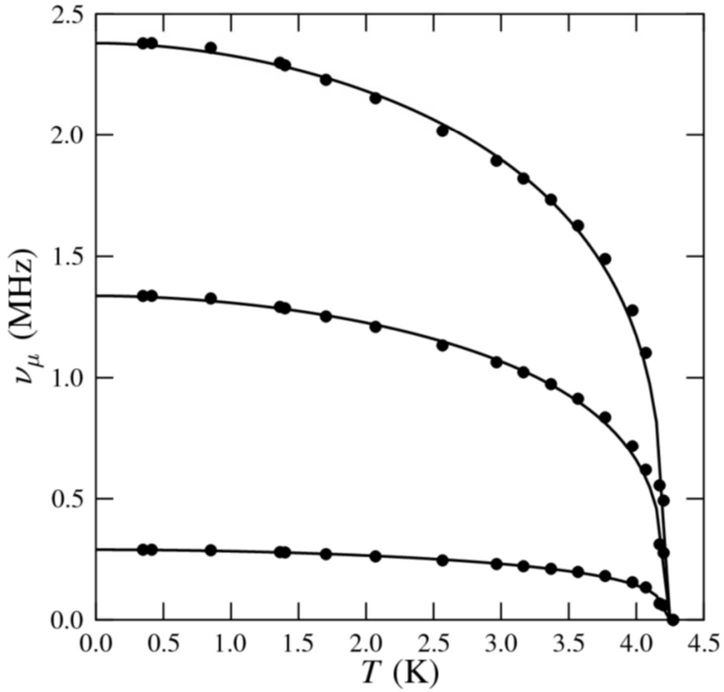
Muons as a probe of magnetism



- Microscopic: sensitive to local effects
- Sensitive to very weak magnetism
- Work well in zero applied field
- One muon at a time $\longrightarrow$ ultra dilute!

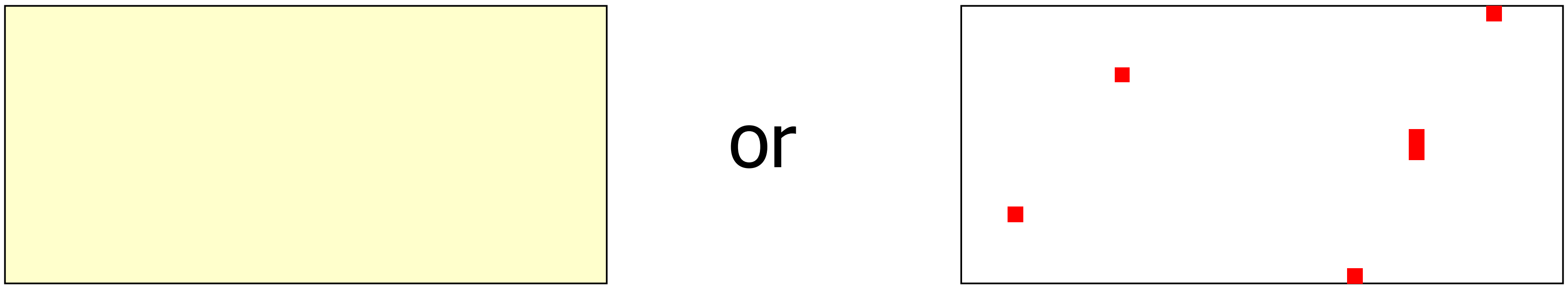
- μ^+SR is great for: small moment magnetism
  random magnetism
  short range effects





Uniformly weakly magnetic

Non-magnetic, with strongly magnetic impurities



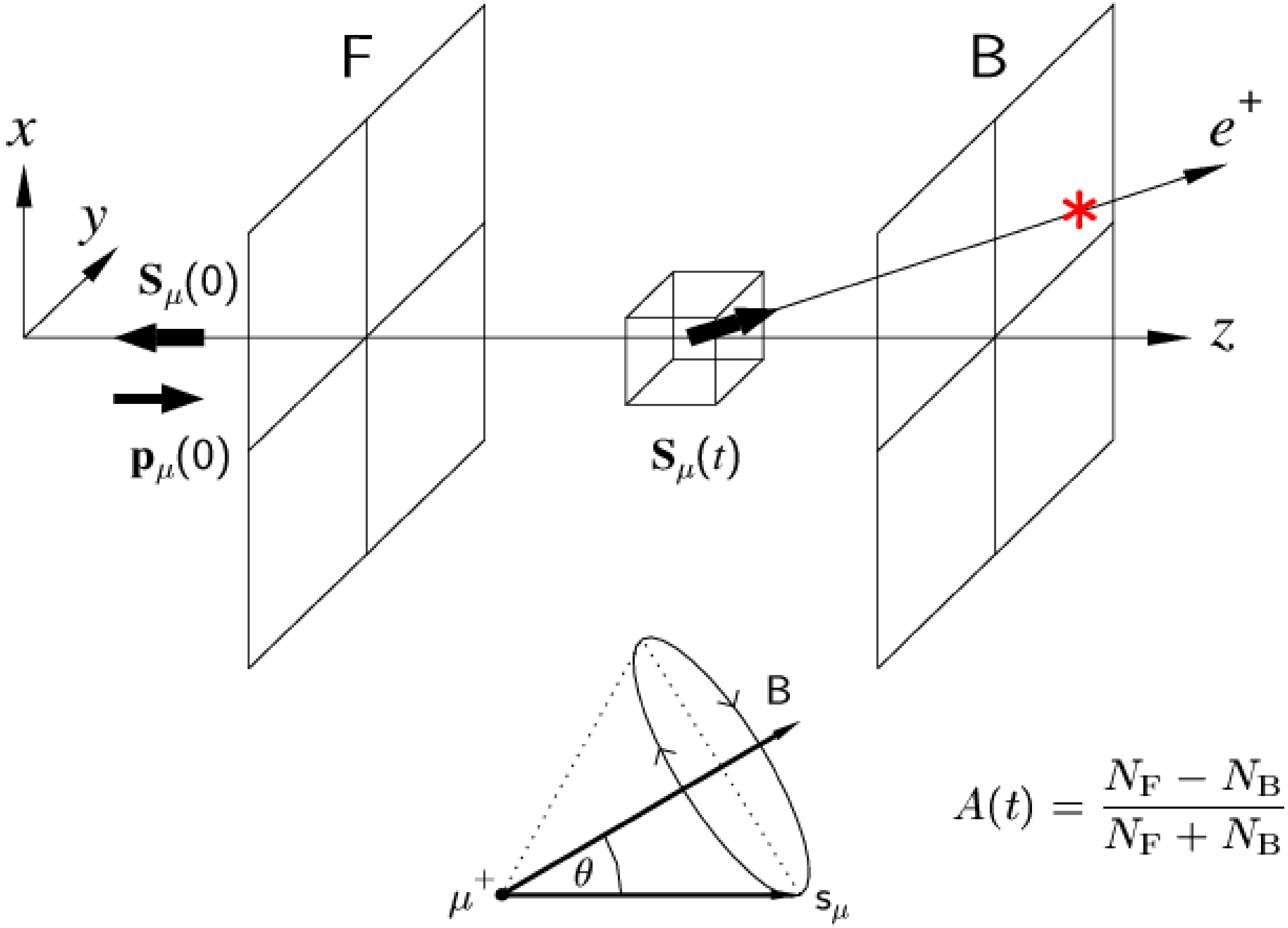
Susceptibility gives **average** information and therefore can give the same response for the situations sketched above

μSR gives **local** information and therefore can distinguish between these two situations.

Particle properties

	charge	spin	mass	moment	$\gamma\ /\ 2\pi$ (kHz G^{-1})	lifetime (μs)
e	$\pm e$	$1/2$	m_e $= 0.51$ MeV	$657\ \mu_p$	2800	∞
μ	$\pm e$	$1/2$	$207\ m_e$ $= 105.7$ MeV	$3.18\ \mu_p$	13.5	2.19
p	$\pm e$	$1/2$	$1836\ m_e$ $= 938$ MeV	μ_p	4.26	∞

Muon spin relaxation

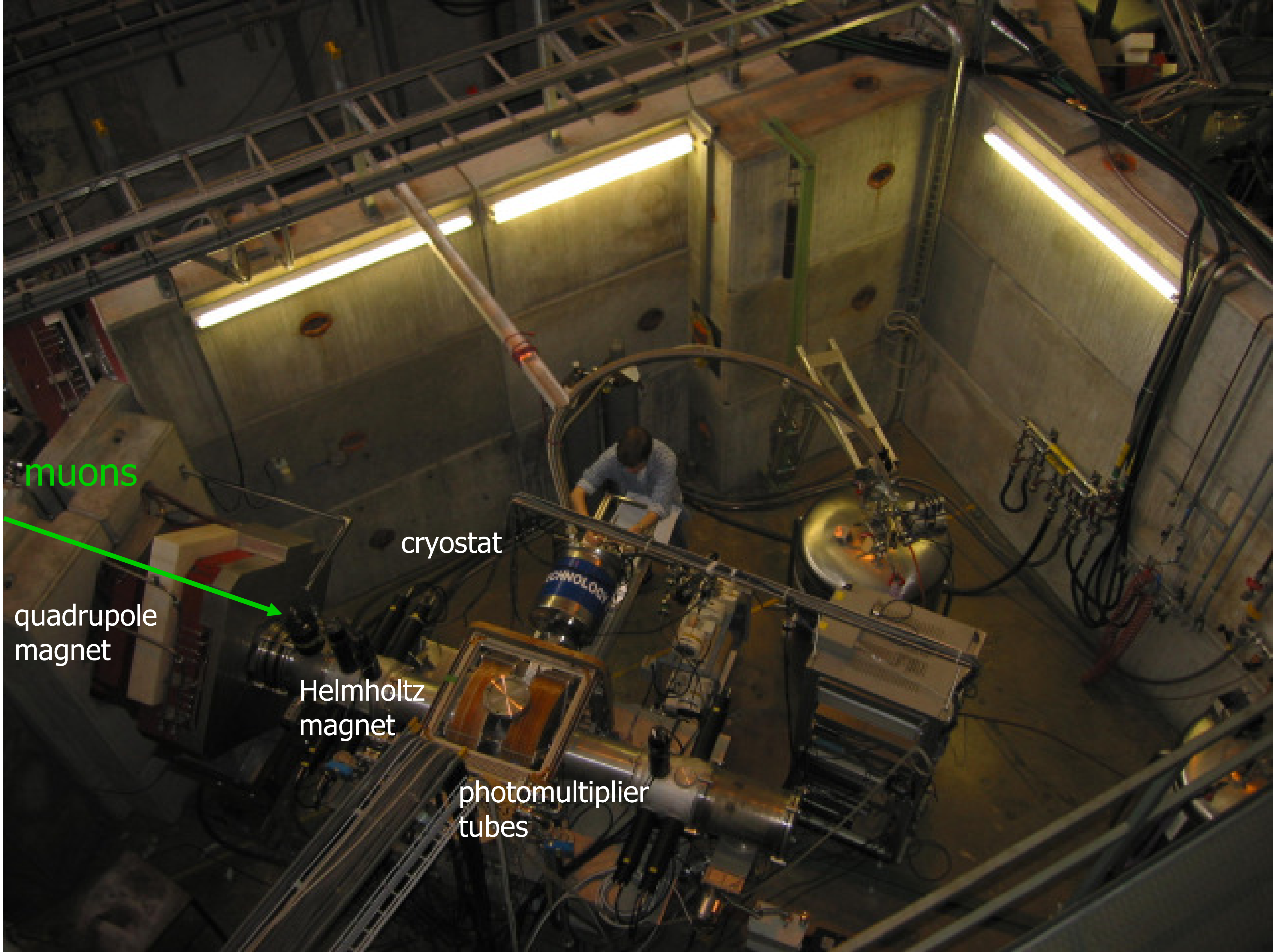


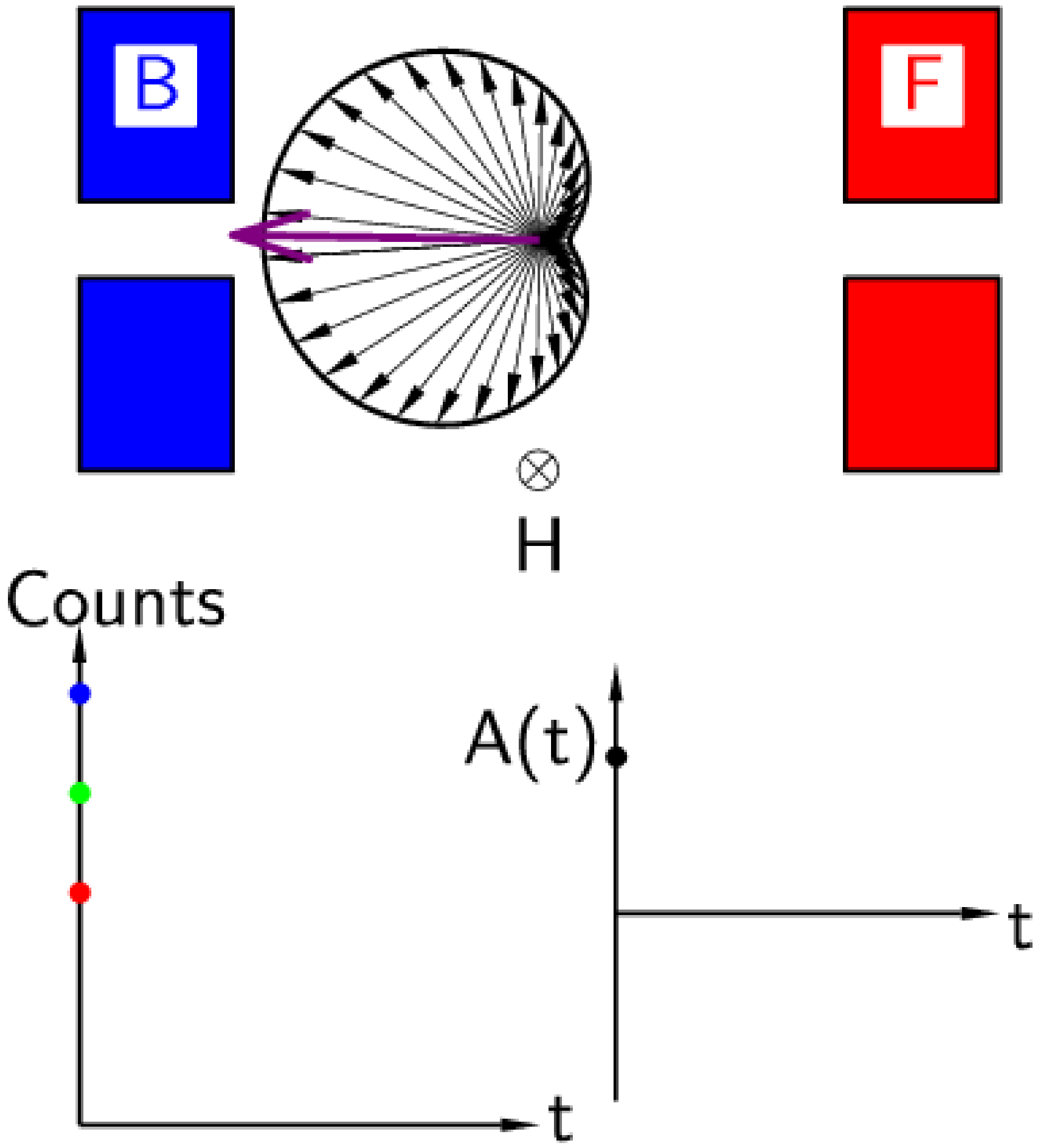
$$A(t) = \frac{N_\mathrm{F} - N_\mathrm{B}}{N_\mathrm{F} + N_\mathrm{B}}$$

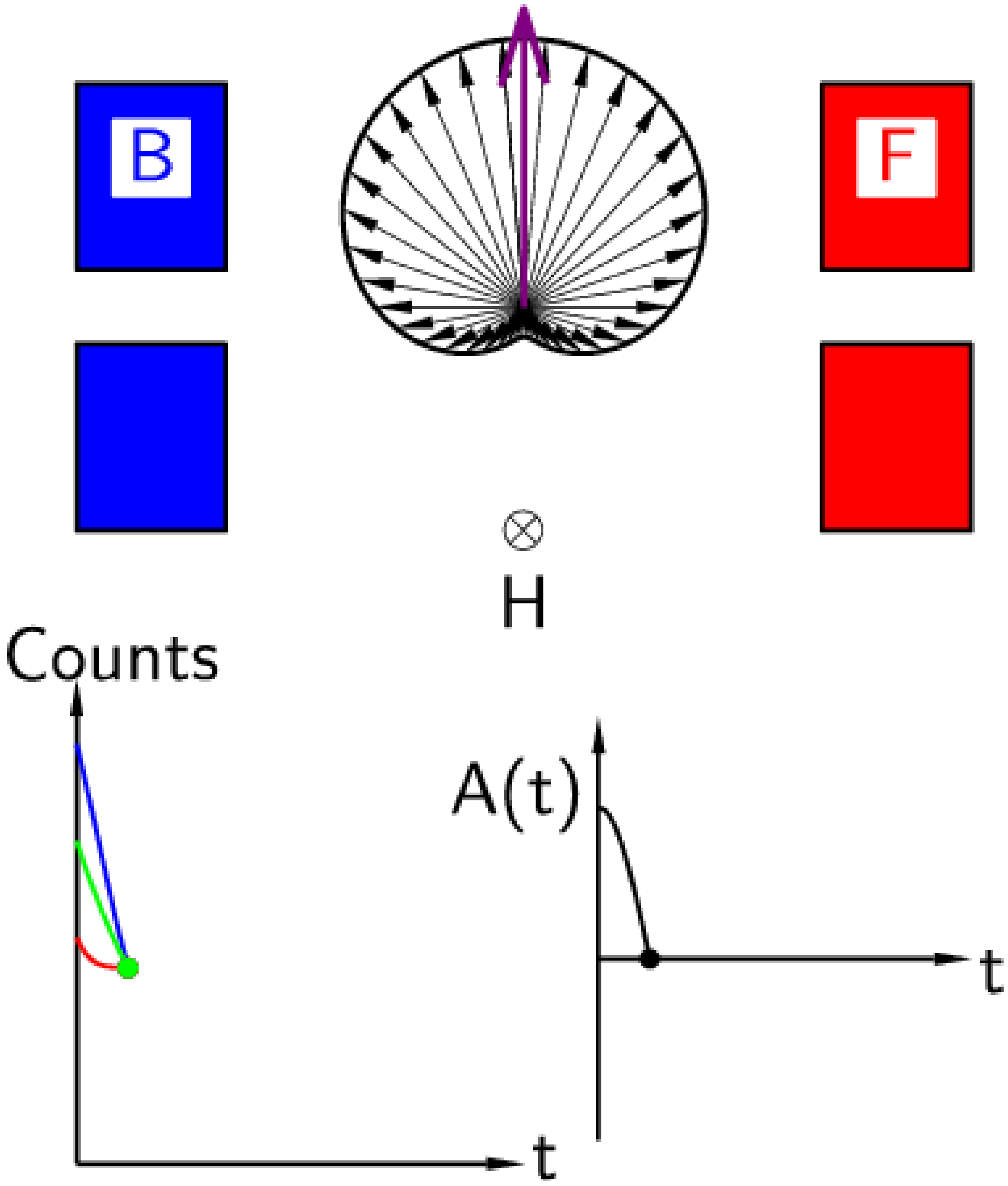
spin antiparallel to momentum

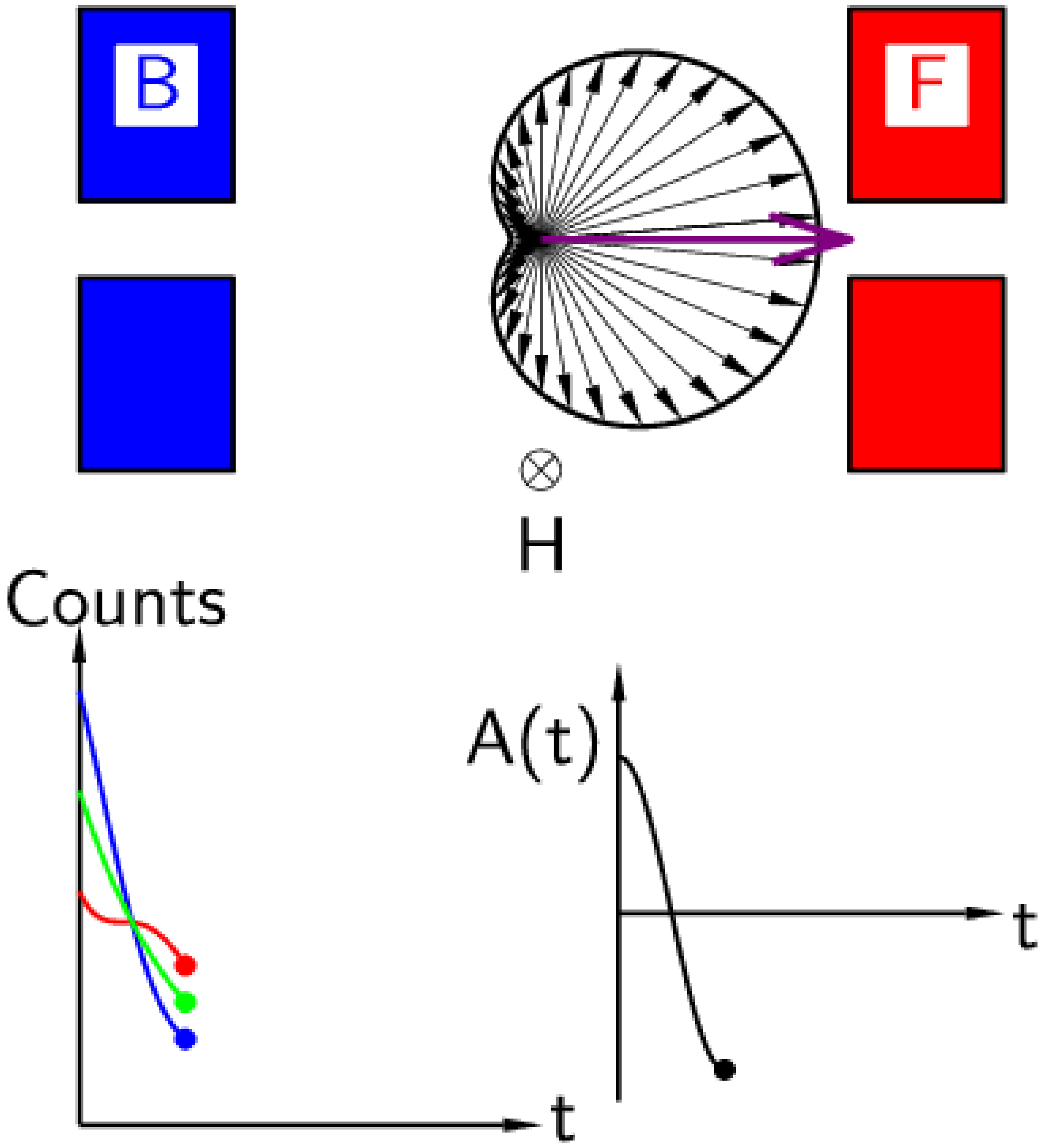
μ^+ decays at rest

$A(t) \propto$ Polarization

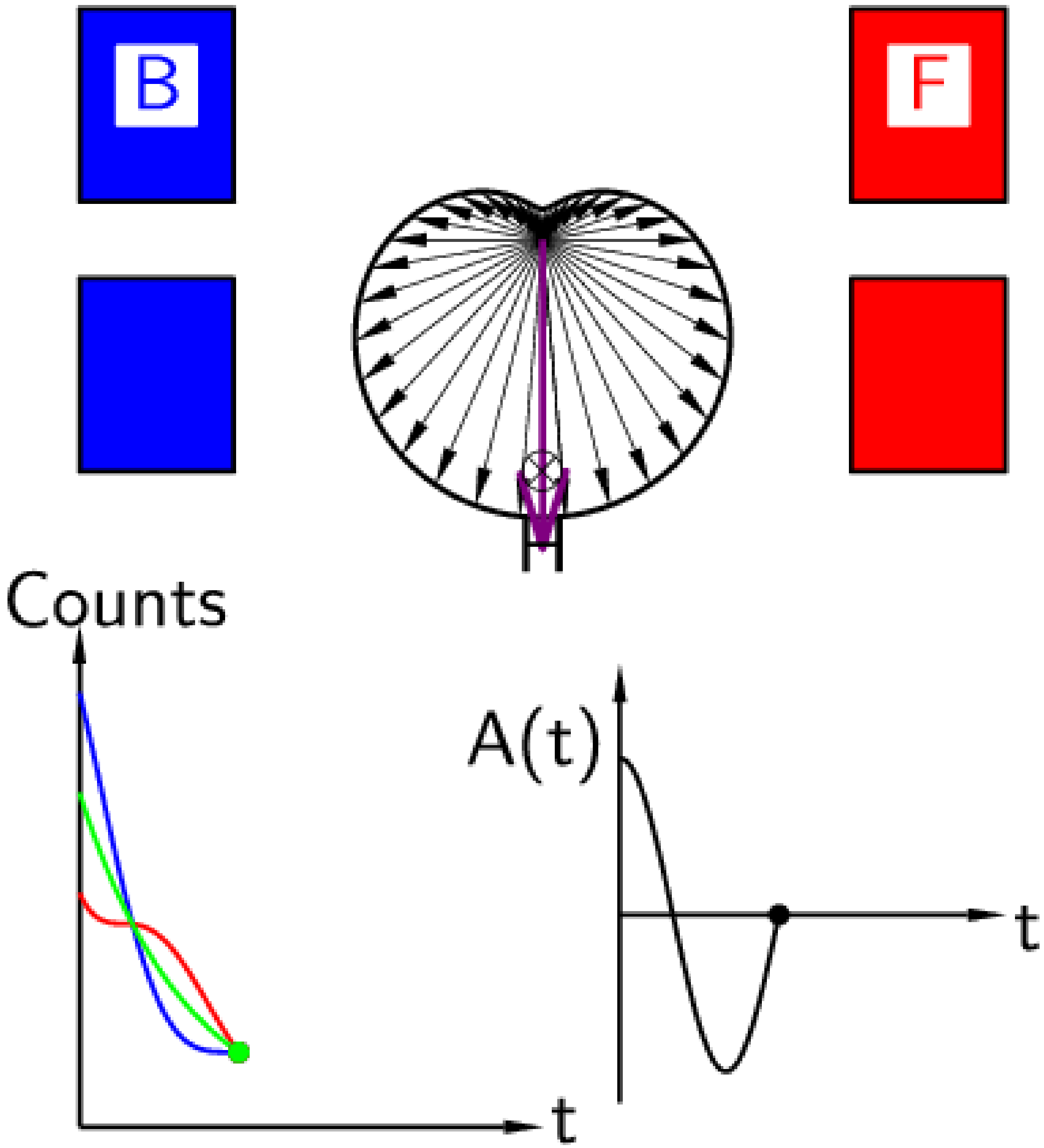

muons
cryostat
quadrupole
magnet
Helmholtz
magnet
photomultiplier
tubes

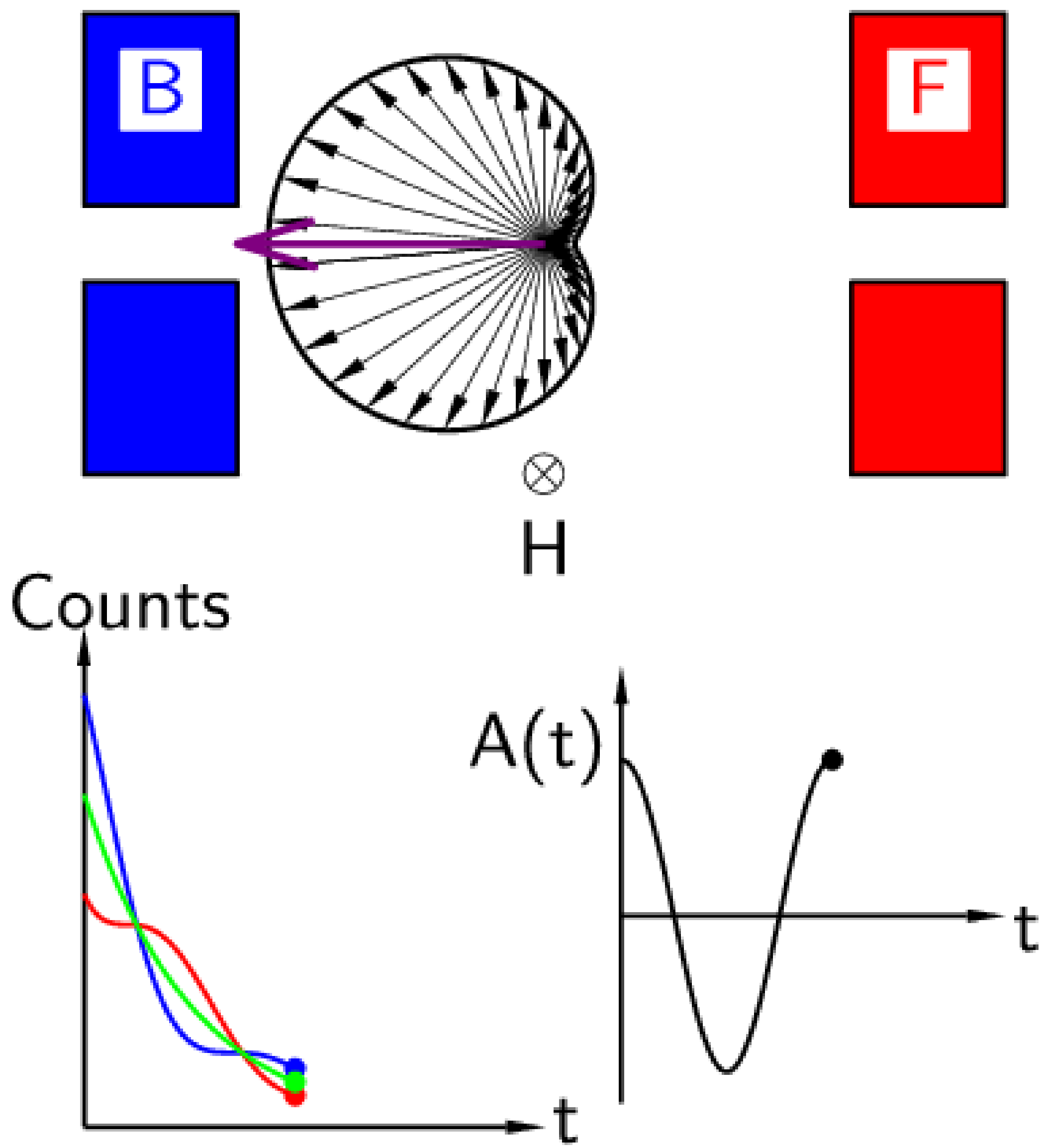

B
F
H
Counts
t
A(t)
t

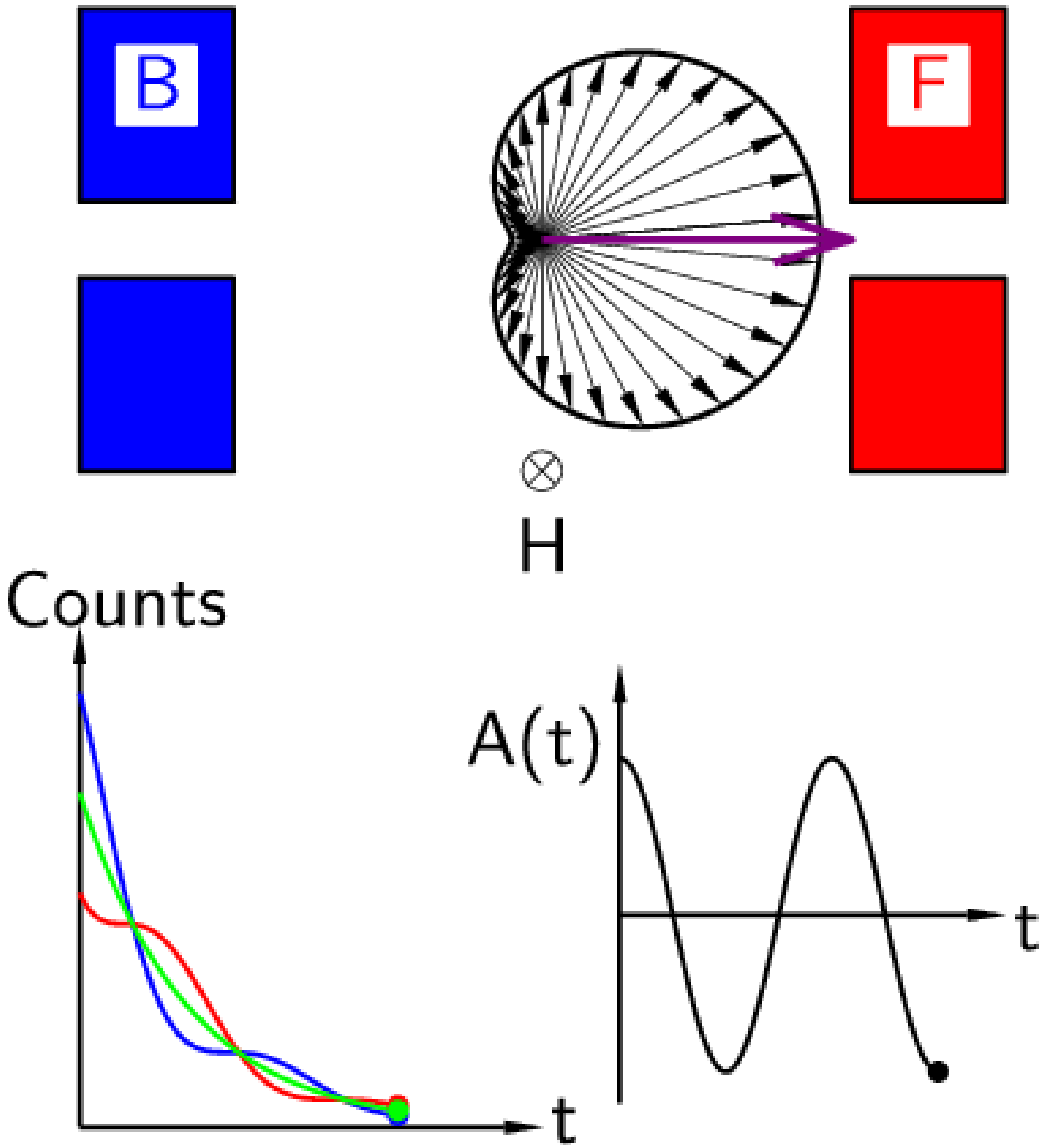

B
F
H
Counts
t
A(t)
t

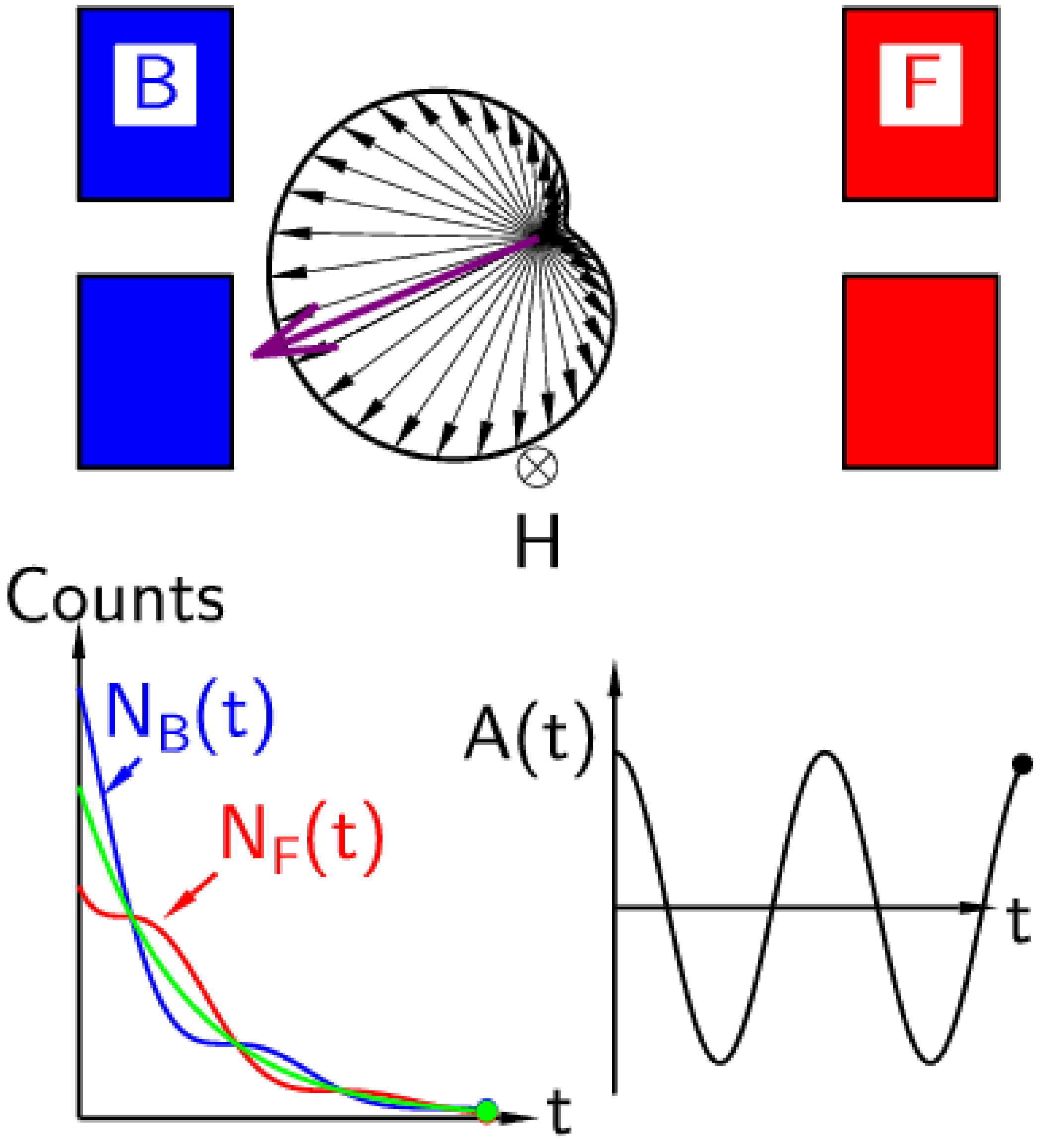


B
F
H
Counts
t
A(t)
t


B
F
Counts
t
A(t)
t


B
F
H
Counts
t
A(t)
t

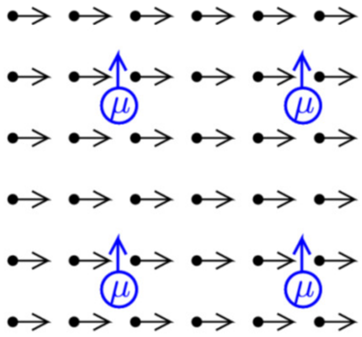

B
F
H
Counts
t
A(t)
t

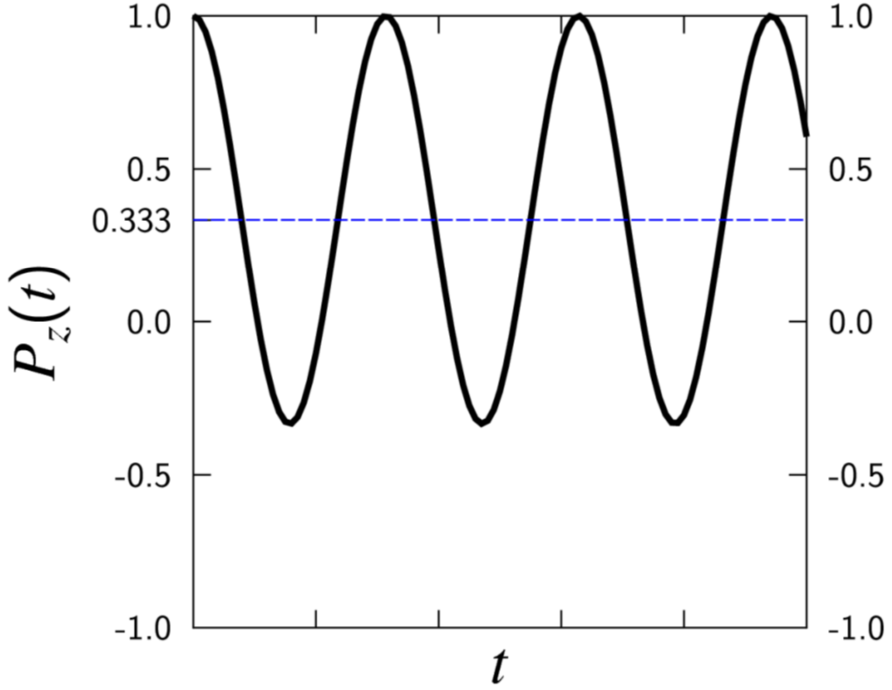


B
F
H
Counts
$N_B(t)$
$N_F(t)$
t
A(t)
t

Typical spectra for polycrystalline samples

Case I:
static order



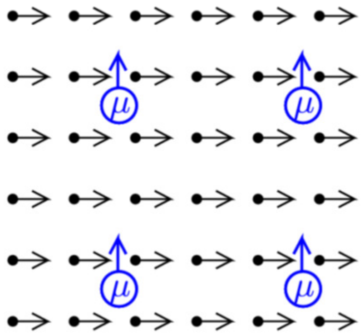


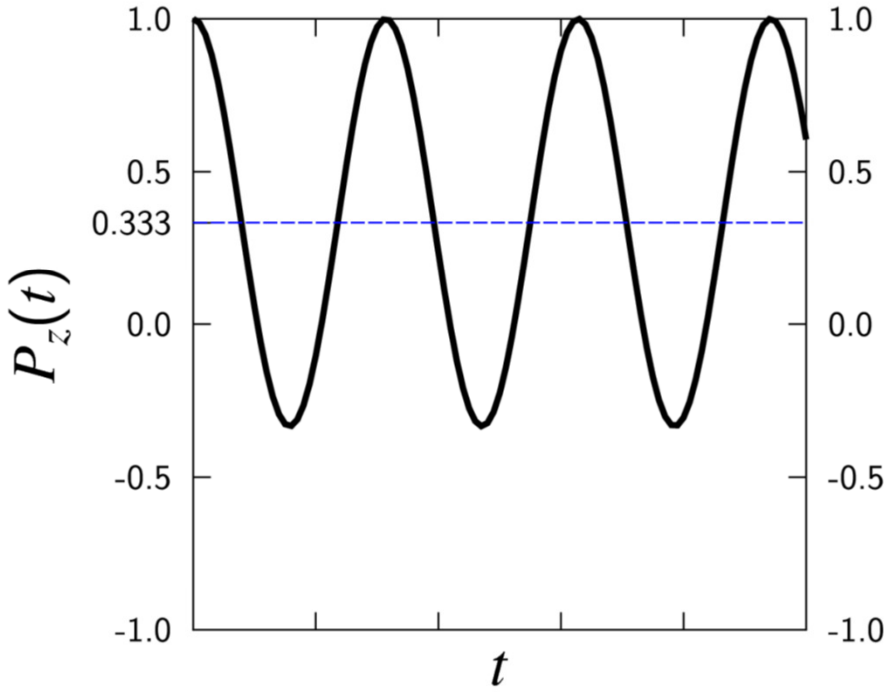
$$P_z(t) = \frac{1}{3} + \frac{2}{3}\cos(\gamma B_\mu t)$$

Typical spectra for polycrystalline samples

Case I:

static order

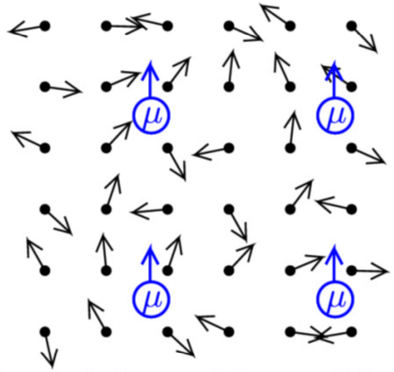


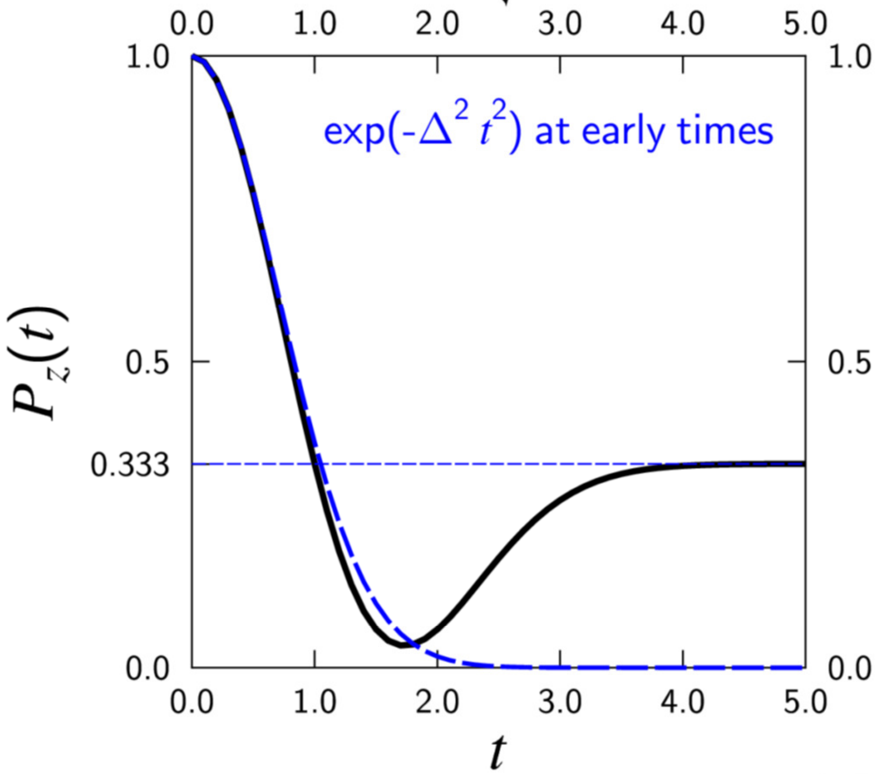


$$P_z(t) = \frac{1}{3} + \frac{2}{3}\cos(\gamma B_\mu t)$$

Case II:

static disorder





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

More on relaxation functions

$$A(t) \sim \sum_{i} A_i \cos(\gamma_\mu |B_i| t)$$

muon sites

field at site

In general $$A(t) \sim \int p(B) \cos(\gamma_\mu B t) \mathrm{d}B$$

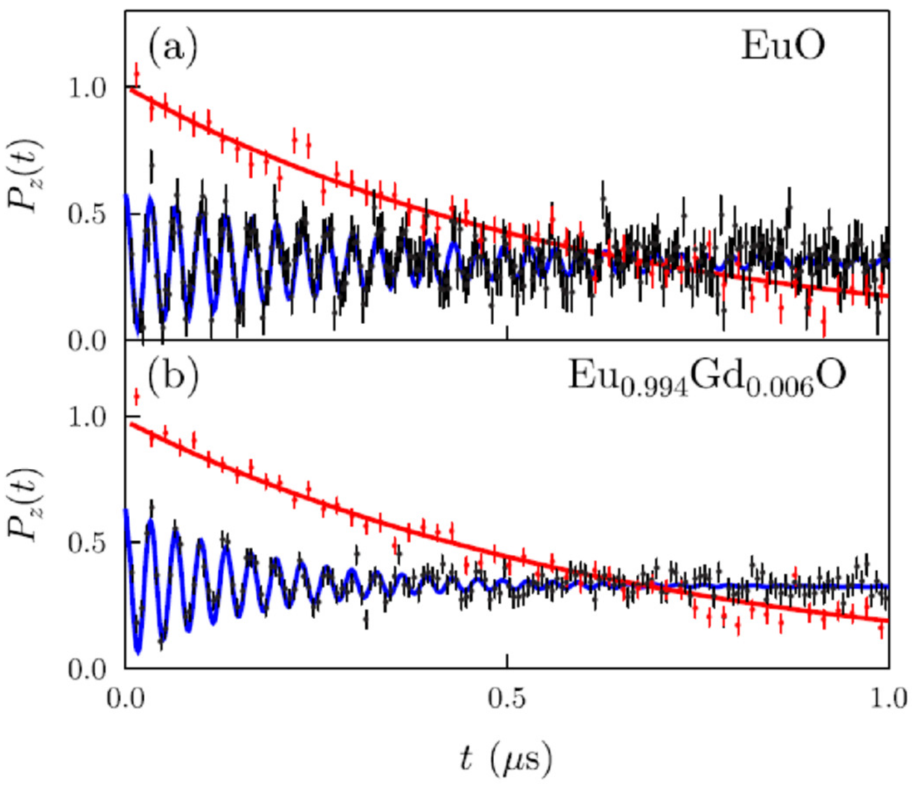
Usually we only have one or two muon sites but we need to take account of broadening/dynamics

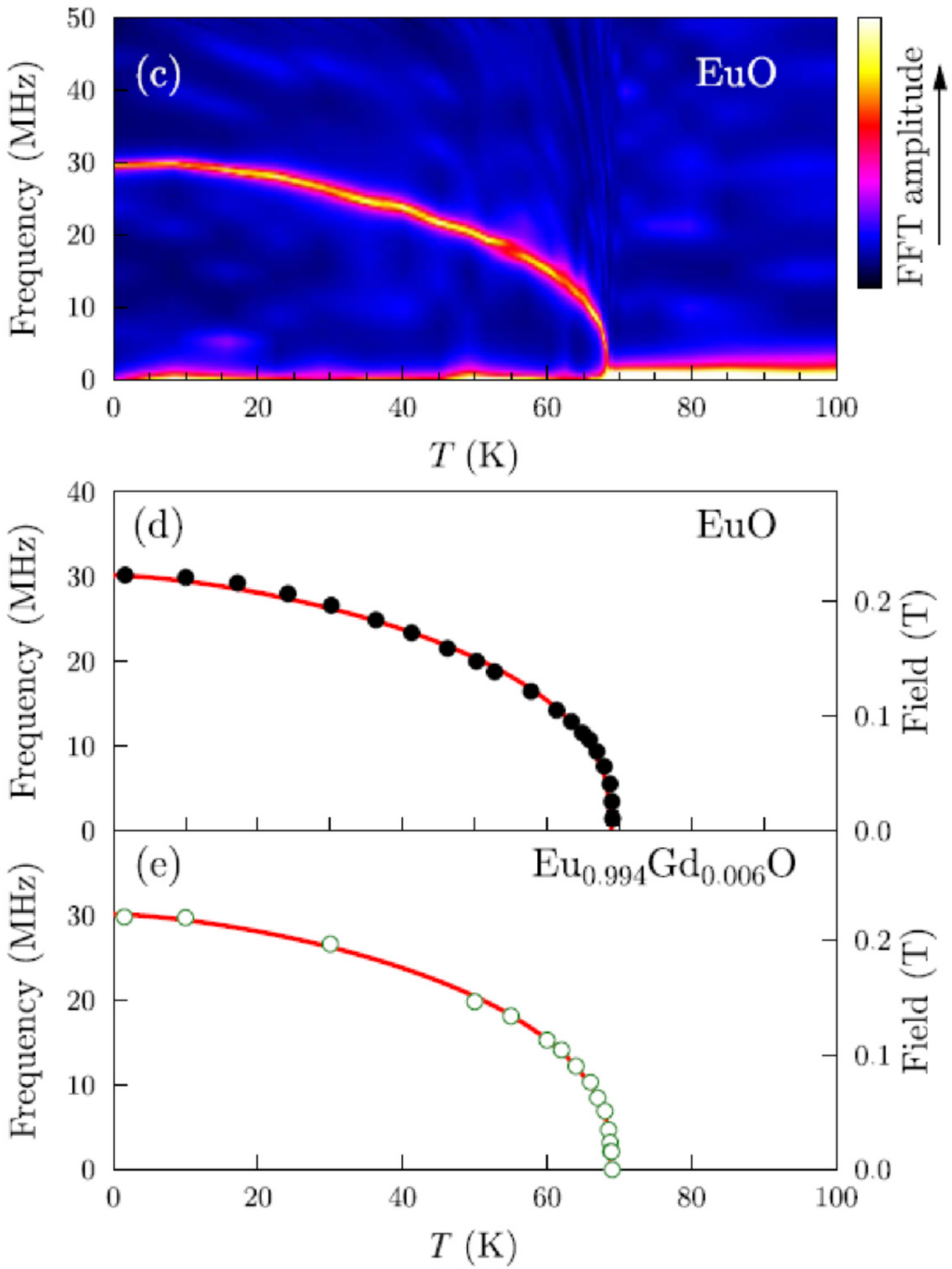
$$A(t) = \frac{1}{3} \exp(-\lambda_\parallel t) + \frac{2}{3} \exp(-\lambda_\perp t) \cos(\gamma_\mu B t)$$

$1/T_1$

$1/T_2$

EuO is THE localized ferromagnet





$$\nu(T) = \nu(0)\left[1 - (T/T_{\rm c})^{\alpha}\right]^{\beta}$$

$T_{\rm c}$=69.01(1) K

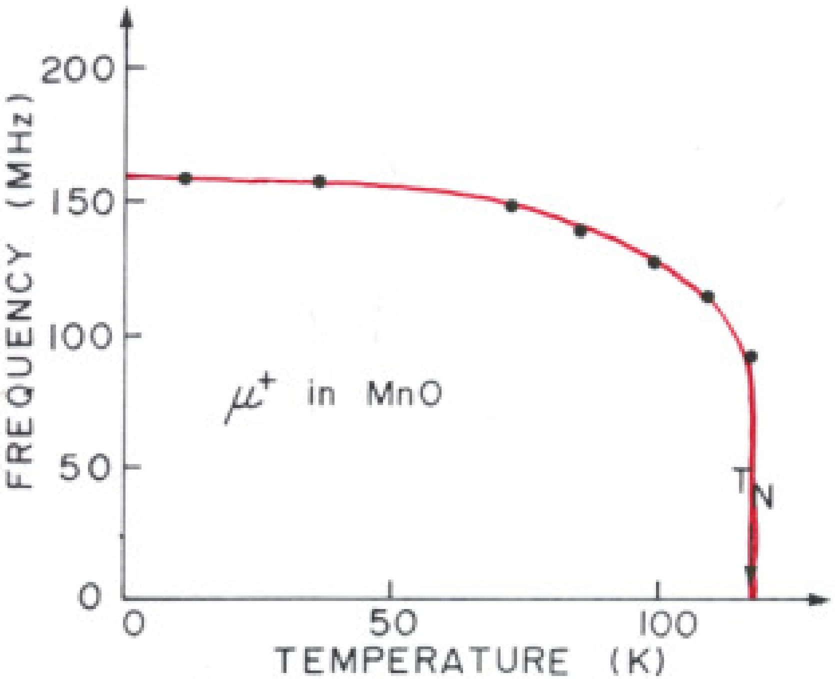
β= 0.32(1)

S.J. Blundell *et al.* PRB **81**, 092407 (2010)

Antiferromagnets.

μSR works just as well with AFMs ∵ probes LOCAL fields

Example: MnO

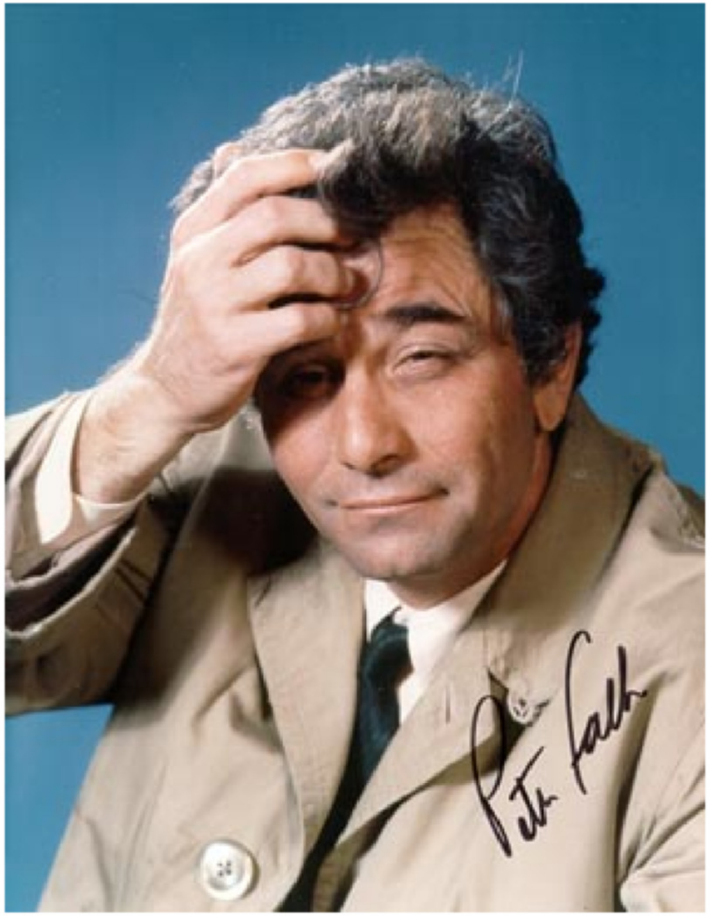


good spin precession signal (corresponds to 1.14 T at 0 K, in ~ agreement with $S = 5/2$ dipolar field and hyperfine field).

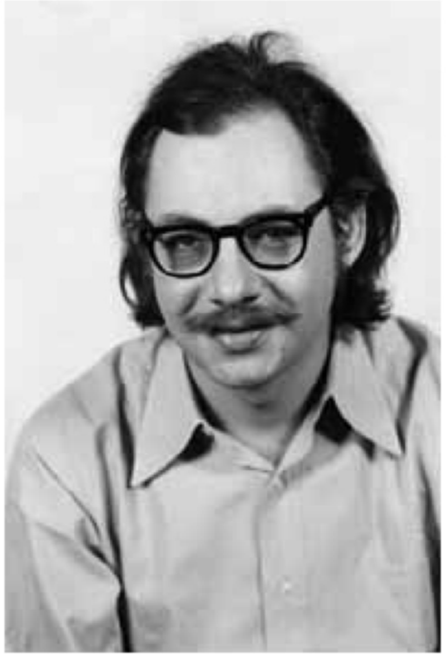
Uemura et al Hyp. Int. 17, 339 (1984)

Case study

One dimensional molecular magnets



Models of low dimensional magnetism



	$D=1$, Ising	$D=2$, XY	$D=3$, Heisenberg
$d=1$	no order	no order	no order
$d=2$	order	no order	no order
$d=3$	order	order	order

D= Dimension of the spins

d=dimension of the lattice

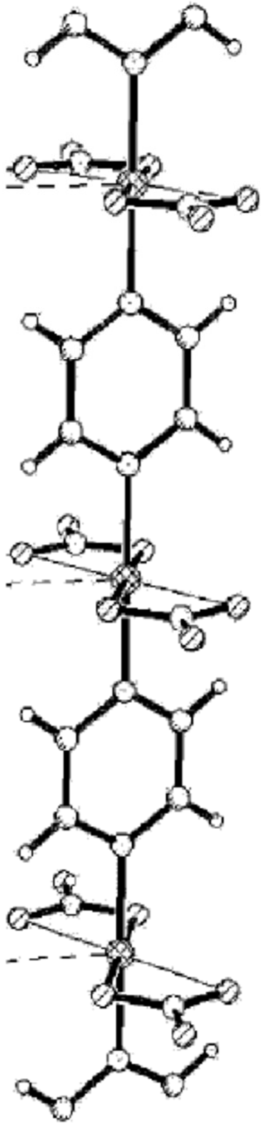
Coleman-Mermin-Wagner theorem forbids breaking a continuous symmetry for d=1 and 2 for $T > 0$

We can describe the physics with a deceptively simple looking equation

$$H = \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

Anderson *Basic notions in Condensed Matter Physics*

$Cu(NO_3)_2(pyz)$ Magnetism in 1 dimension



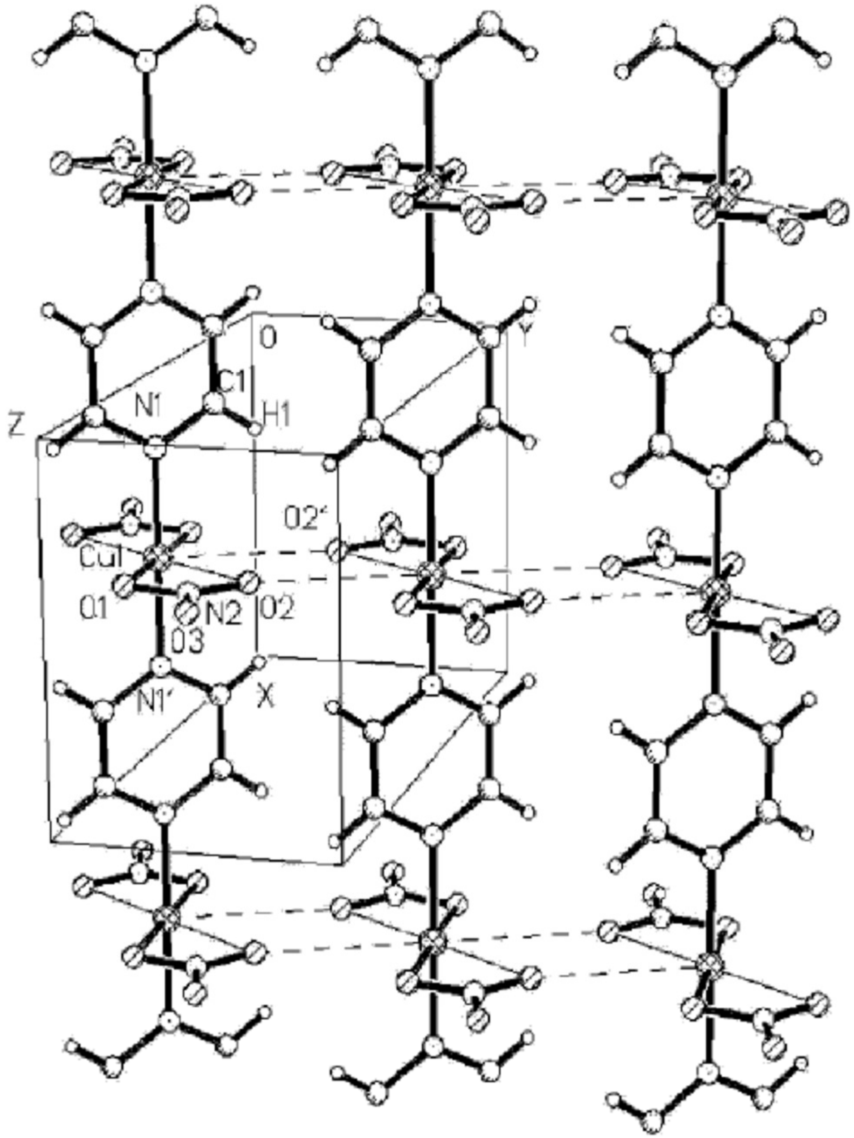
$S=1/2$ Cu^{2+} ions linked by pyz

1D Cu-(pyz)-Cu chains along a

A Santoro *et al.*, Acta. Cryst., **95** 5780 (1973)
P R Hammar *et al.*, Phys. Rev. B, **59** 1008 (1999)

$Cu(NO_3)_2(pyz)$

Magnetism in 1 dimension



S=1/2 Cu^{2+} ions linked by pyz

1D Cu-(pyz)-Cu chains along a

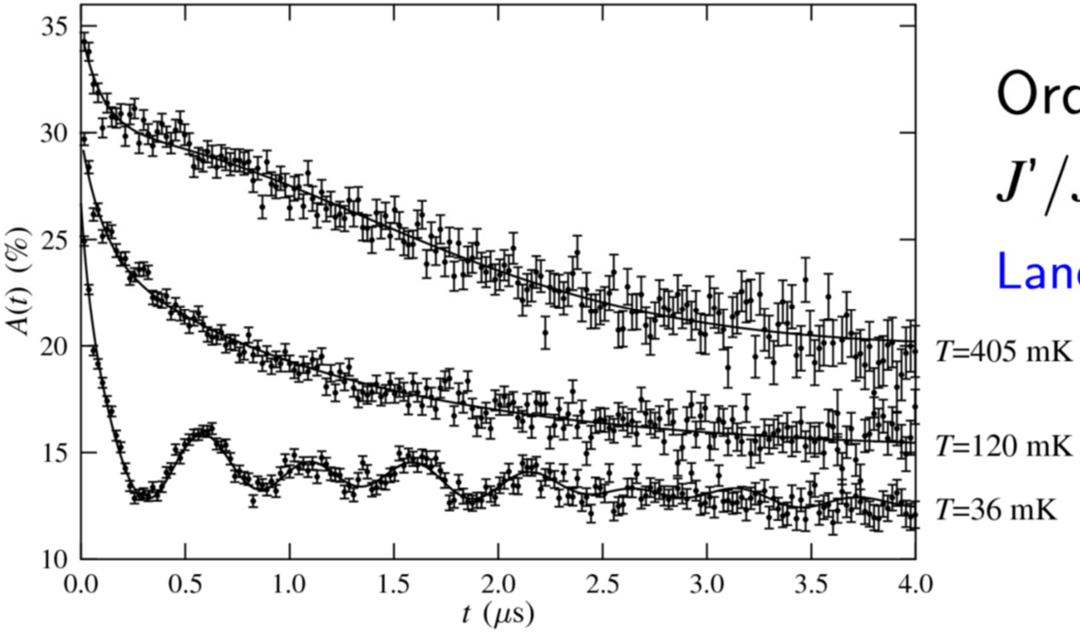
High field magnetization and specific heat give $|J|/k_B$=10.3 K

No evidence of magnetic order down to 70 mK

A Santoro *et al.*, Acta. Cryst., **95** 5780 (1973)
P R Hammar *et al.*, Phys. Rev. B, **59** 1008 (1999)

Molecular magnets: muons are unique!

Observation of magnetic order - invisible to other techniques

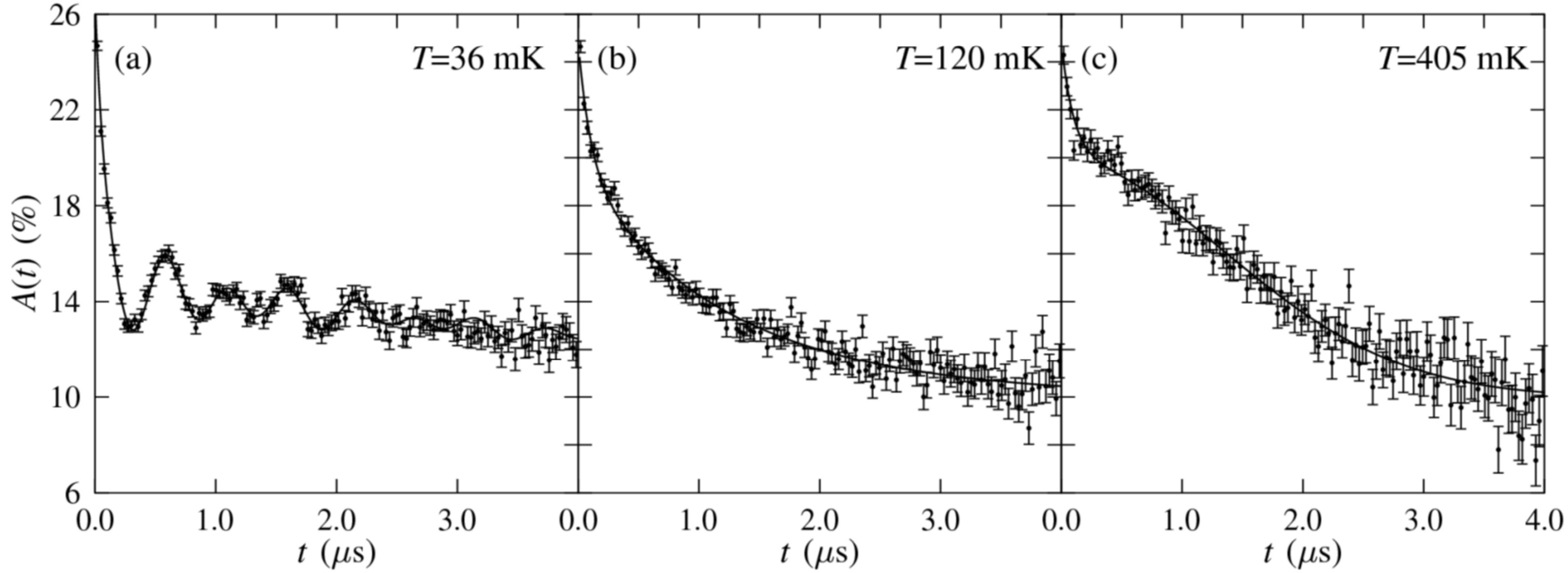


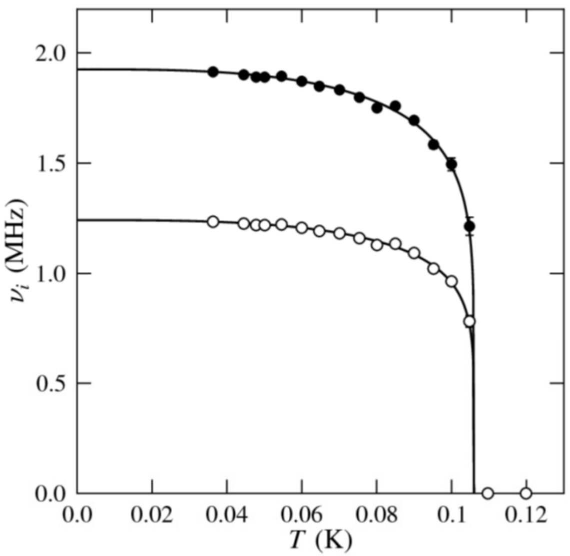
Order observed in CuPzN with T_{N}=107 mK

J'/J=4.4 $\times 10^{-3}$

Lancaster *et al*. Phys. Rev. B, **73** 020410(R) (2006)

$Cu(NO_3)_2(pyz)$ μ^+SR results



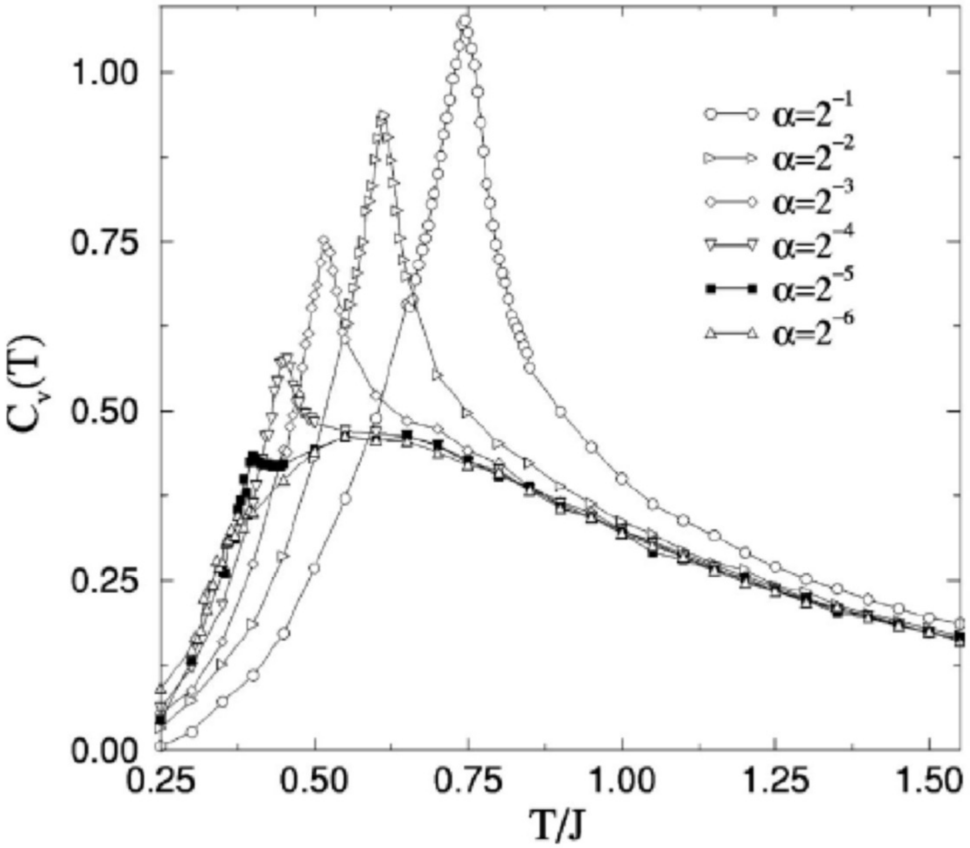


We detect magnetic order with μ^+SR

T_N=107 mK

T Lancaster *et al.* Phys. Rev. B, **73** 020410 (2006)

The problem with finding T_{N} in low-d systems



Stochastic series QMC simulations say

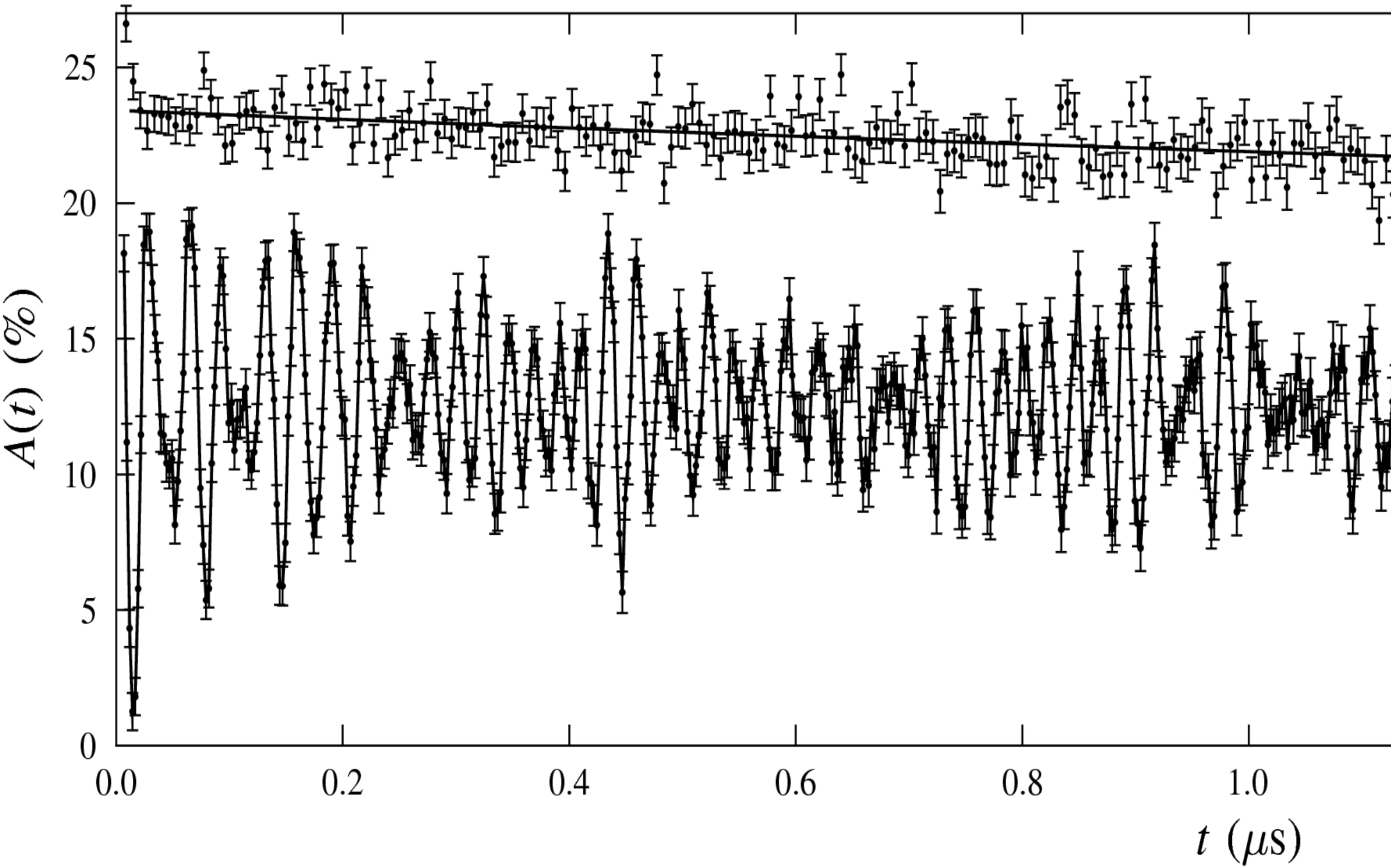
The anomaly in C_v decreases with decreasing α

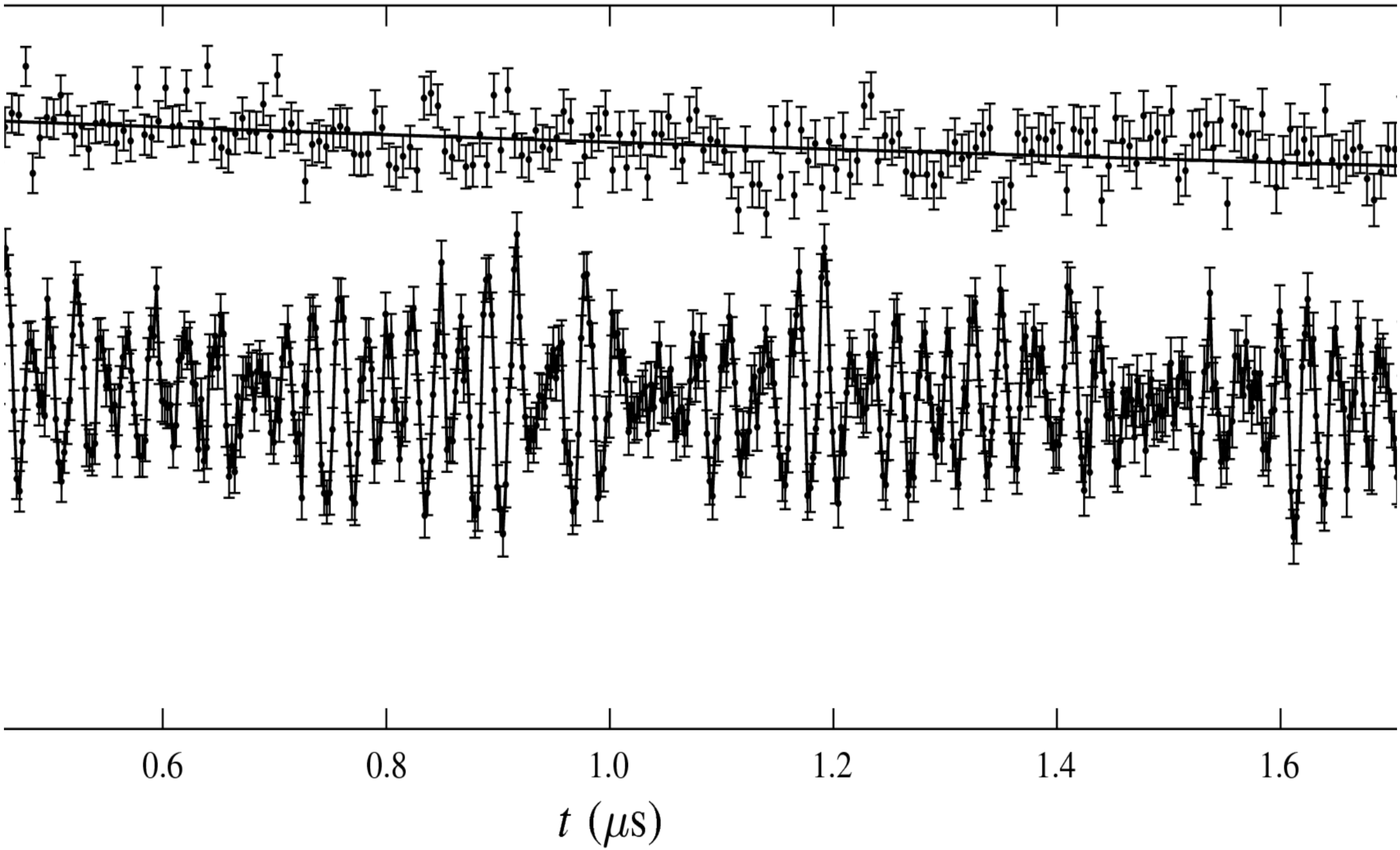
This is due to correlations above T_{N} (ΔS at T_{N} is therefore reduced)

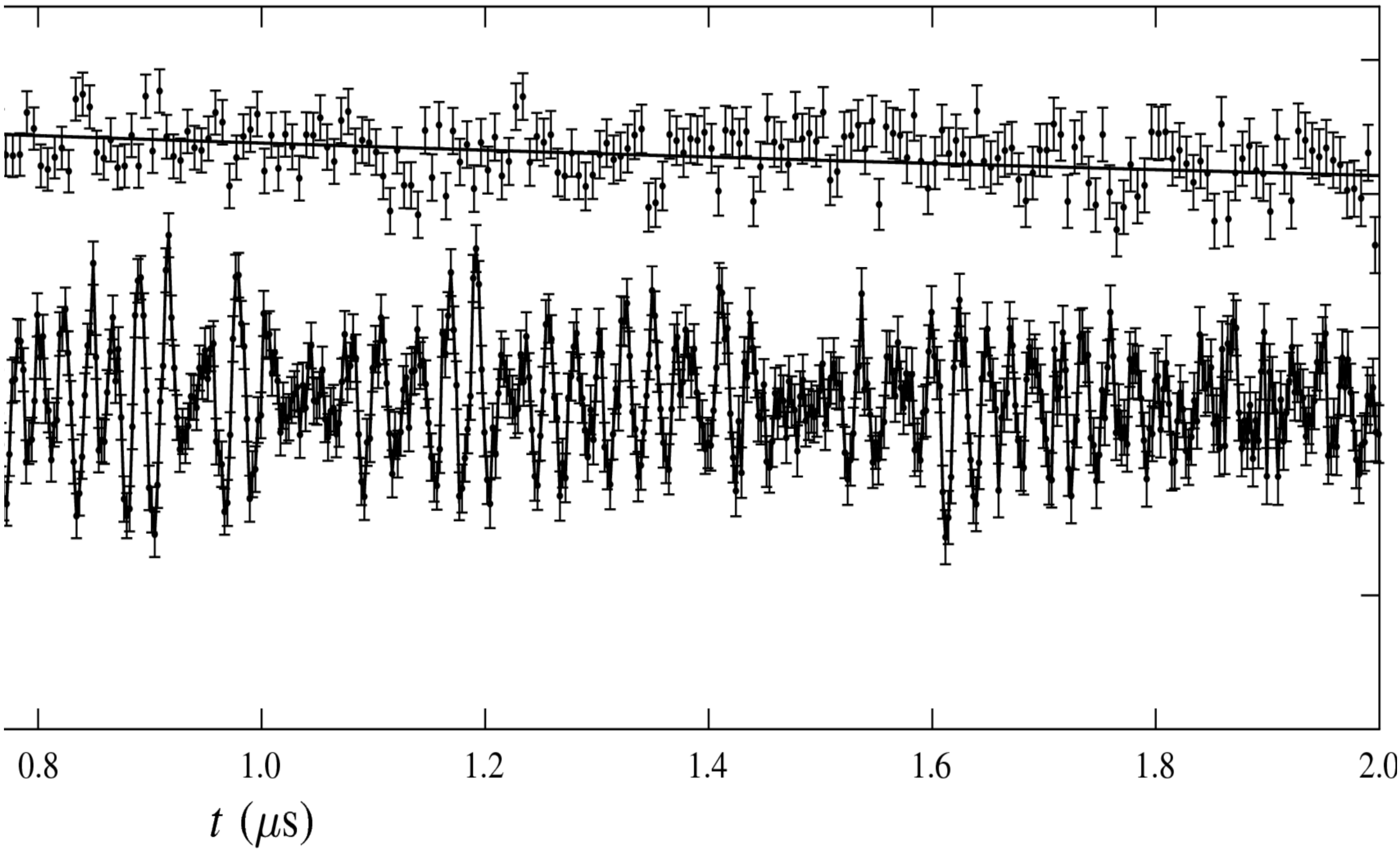
Other measurements made difficult by the small magnetic moment in anisotropic systems

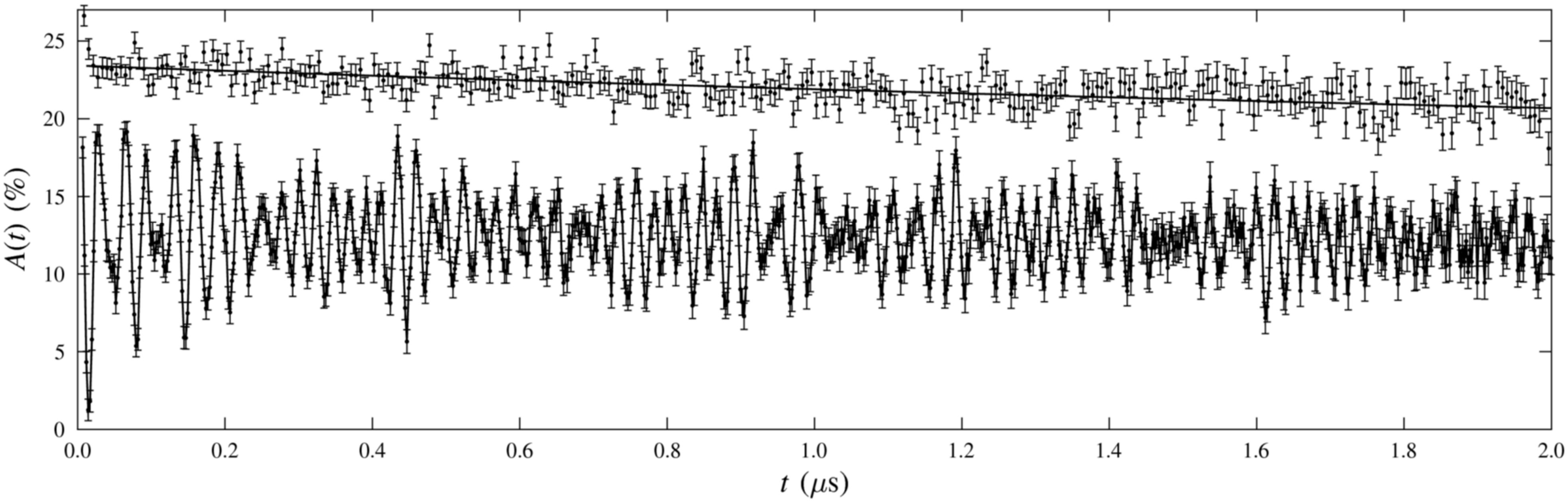
P Sengupta *et al.* Phys Rev B **68** 94423 (2003)

The most beautiful magnetic spectrum ever recorded?

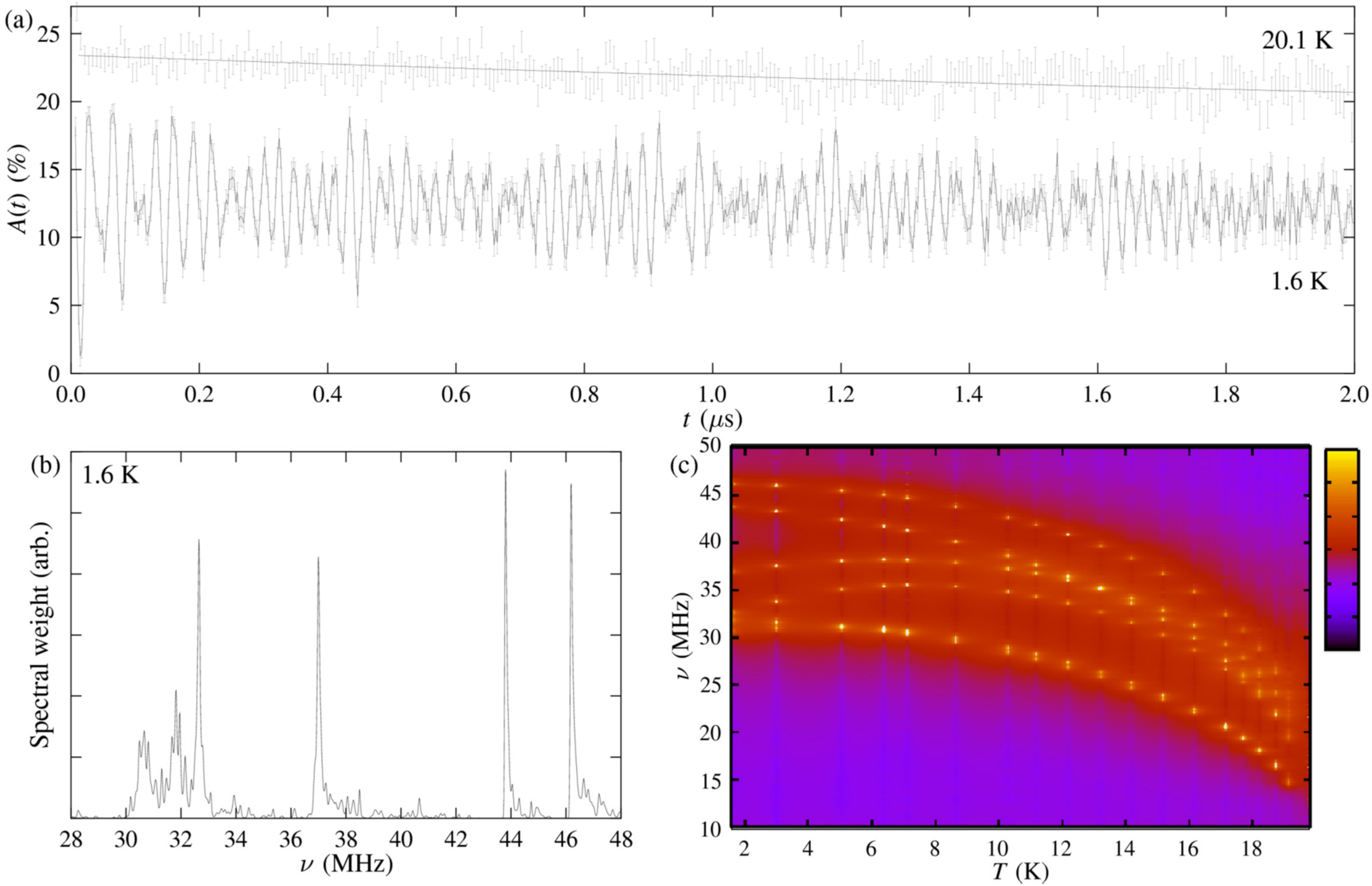



0.6
0.8
1.0
1.2
1.4
1.6
t (μs)

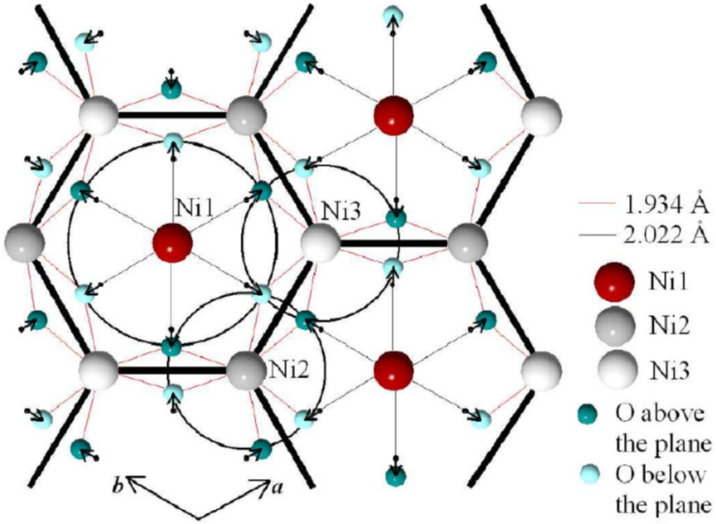

0.8
1.0
1.2
1.4
1.6
1.8
2.0
t (μs)

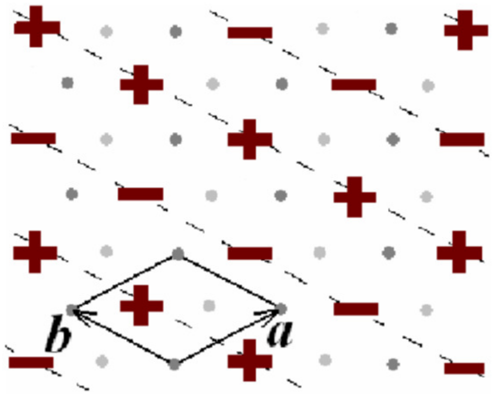


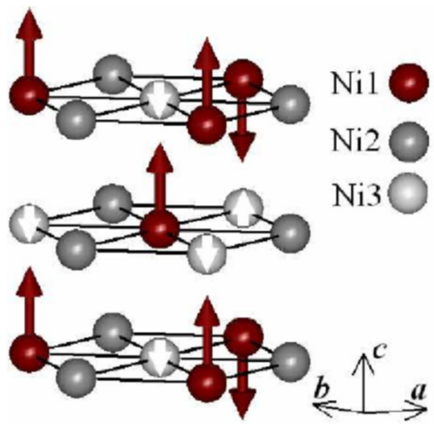
A(t) (%)
t (μs)
0
5
10
15
20
25
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0

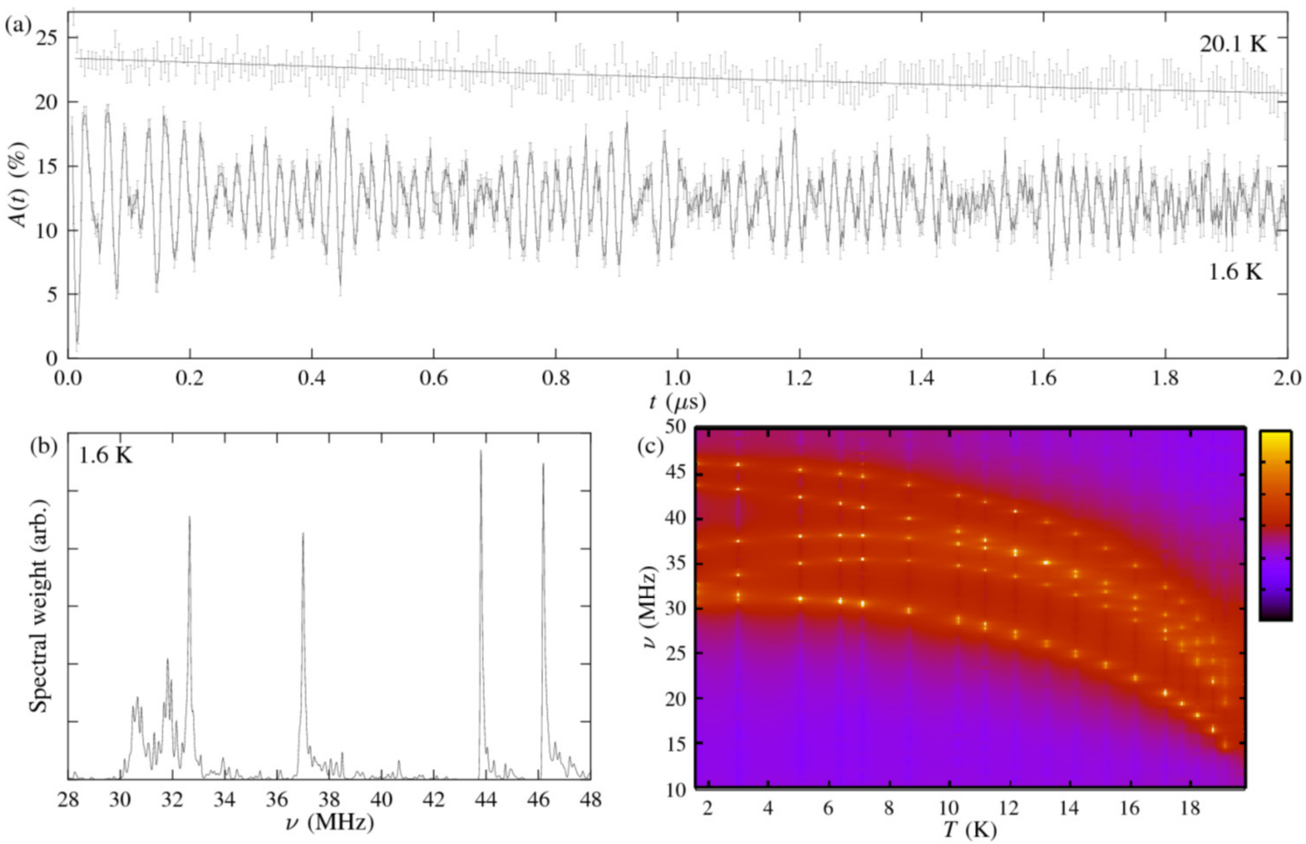

(a)
20.1 K
1.6 K
A(t) (%)
t (μs)
(b)
1.6 K
Spectral weight (arb.)
ν (MHz)
(c)
ν (MHz)
T (K)

$AgNiO_2$: a new charge ordered state of matter?









Orbital degeneracy lifted via a charge ordering mechanism

This gives rise to a well defined magnetic structure

Muons see this, but show an anomalous T dependence

Lancaster *et al.*, PRL **100** 017206 (2008)

What on earth are we measuring?

Local magnetic field at the muon site

* $B_L = \frac{\mu_0 M}{3}$ — **LORENTZ FIELD**

  site independent
  zero for antiferromagnets

* $B_{dip}(\underline{r}_\mu)$ — **DIPOLAR FIELD**

  depends on muon site
  depends on direction of $\underline{M}$

* $B_{hf}(\underline{r}_\mu)$ — **HYPERFINE FIELD**

  due to electron spin density at muon site

* B_{demag} — **DEMAGNETIZATION FIELD**

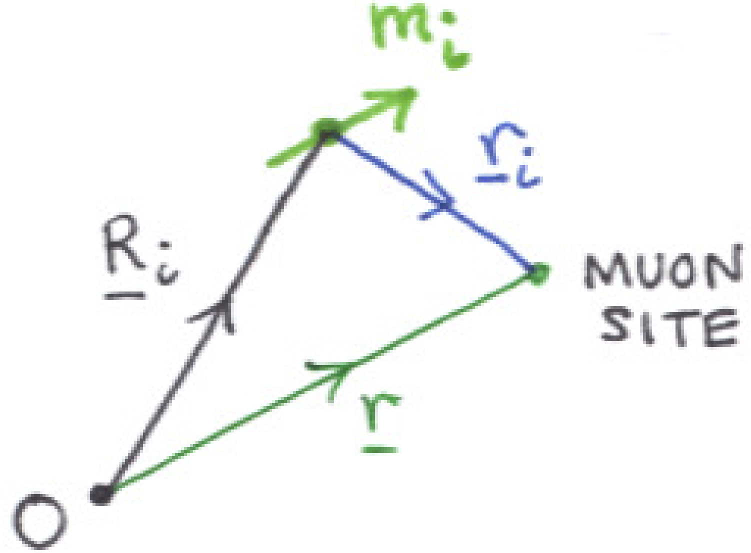
  depends on sample shape or domain structure

Dipole-dipole field

$$\underline{B}_{dip}(\underline{r}) = \frac{\mu_0}{4\pi} \sum_i \frac{1}{r_i^3} \left[\frac{3(\underline{m}_i \cdot \underline{r}_i)\,\underline{r}_i}{r_i^2} - \underline{m}_i \right]$$

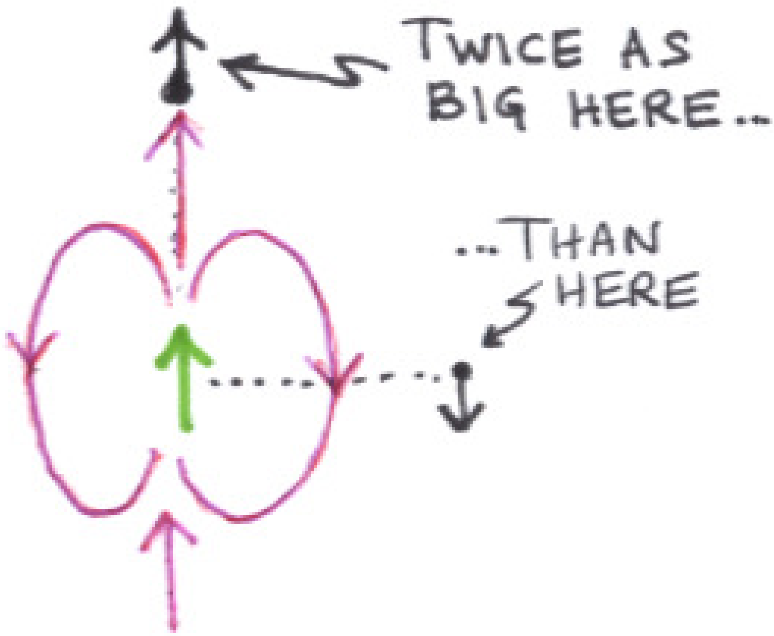
Dipole-dipole field

$$\underline{B}_{dip}(\underline{r}) = \frac{\mu_0}{4\pi} \sum_i \frac{1}{r_i^3} \left[\frac{3(\underline{m}_i \cdot \underline{r}_i)\underline{r}_i}{r_i^2} - \underline{m}_i \right]$$



Dipole-dipole field

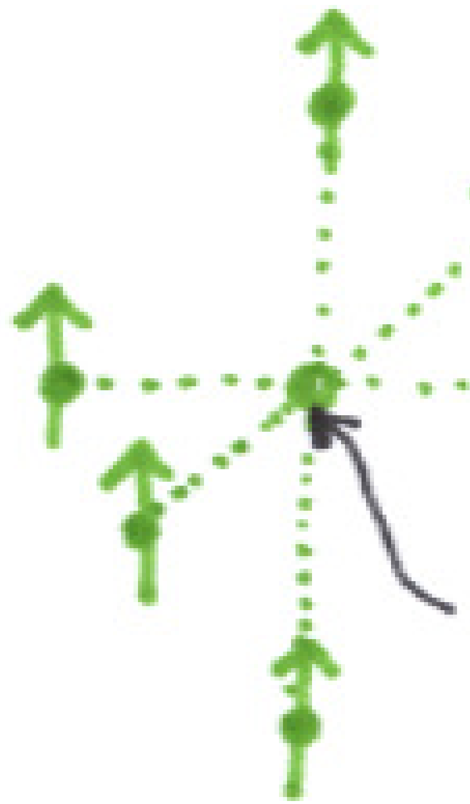
$$\underline{B}_{dip}(\underline{r}) = \frac{\mu_0}{4\pi} \sum_i \frac{1}{r_i^3} \left[\frac{3(\underline{m}_i \cdot \underline{r}_i)\underline{r}_i}{r_i^2} - \underline{m}_i \right]$$



Dipole-dipole field

$$\mathbf{B}_{dip}(\mathbf{r}) = \frac{\mu_0}{4\pi} \sum_i \frac{1}{r_i^3} \left[\frac{3(\mathbf{m}_i \cdot \mathbf{r}_i)\mathbf{r}_i}{r_i^2} - \mathbf{m}_i \right]$$

Problem:



FIELD HERE $= 0$

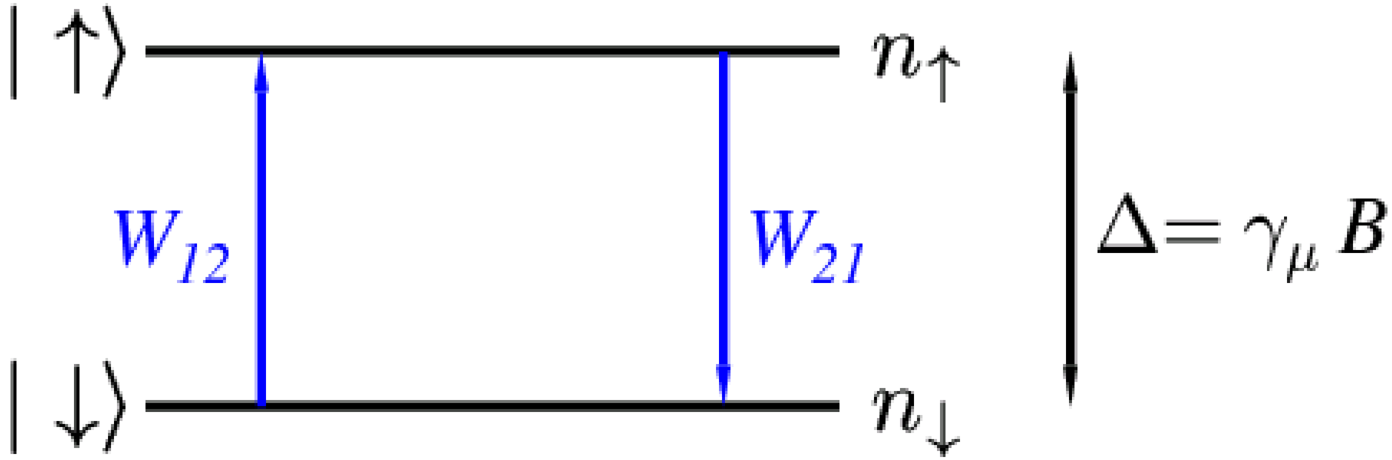
Dynamics in magnetic systems

- Random fluctuations
- Elementary excitations
- Diffusive modes
- Hydrodynamics

We measure *correlations* in the local magnetic fields

$$\langle B(t)B(0)\rangle$$

The muon as a probe of dynamics



$$\dot{n}_\uparrow = -W_{21} n_\uparrow + W_{12} n_\downarrow$$

$$\dot{n}_\downarrow = W_{21} n_\uparrow - W_{12} n_\downarrow$$

$$\delta P(t) \propto \exp(-(W_{21} + W_{12})t) = \exp(-\lambda t)$$

Muon-spin relaxation

$$P_z(t) = P_z(0)\, e^{-\Gamma t}$$

Muon polarization

Relaxation rate

$$\Gamma = \int_0^\infty \gamma_\mu^2 \underbrace{\langle B_\perp(t)\, B_\perp(0) \rangle}_{\text{Field-field correlation function}} \cos \omega_L t \; dt$$

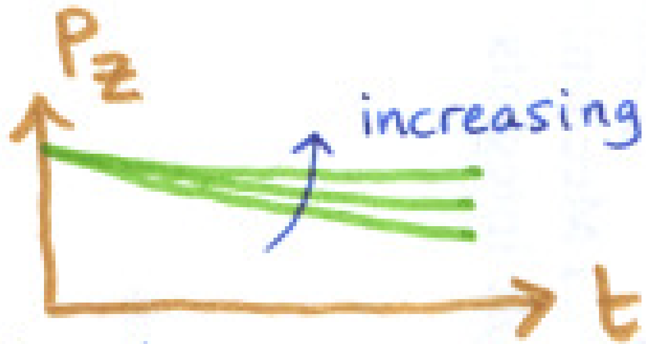
$\gamma_\mu B_L$

longitudinal field

If $$\langle B_\perp(t)\,B_\perp(0)\rangle = \overbrace{\langle B_\perp^2\rangle}^{2(\Delta/\gamma_\mu)^2}\, e^{-\nu t}$$

field-field correlation rate

$$\Rightarrow \quad \Gamma = \frac{2\Delta^2\nu}{\nu^2+\omega_L^2}$$

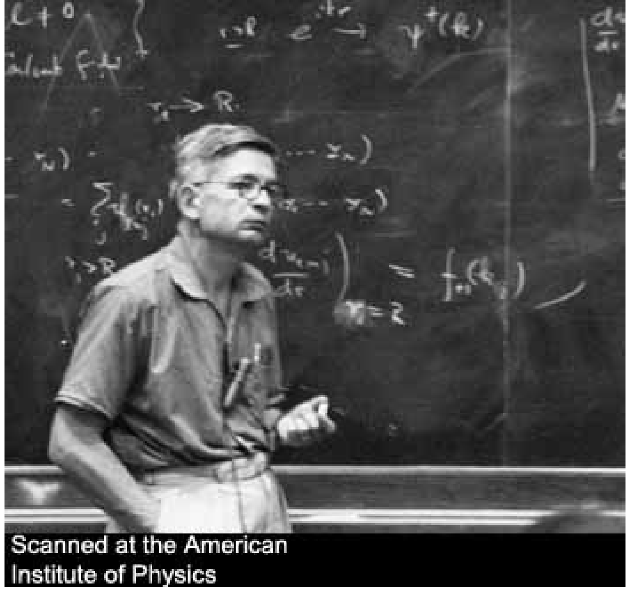


"motional narrowing"

- $\omega_L = 0 \qquad \Gamma = 2\Delta^2/\nu$

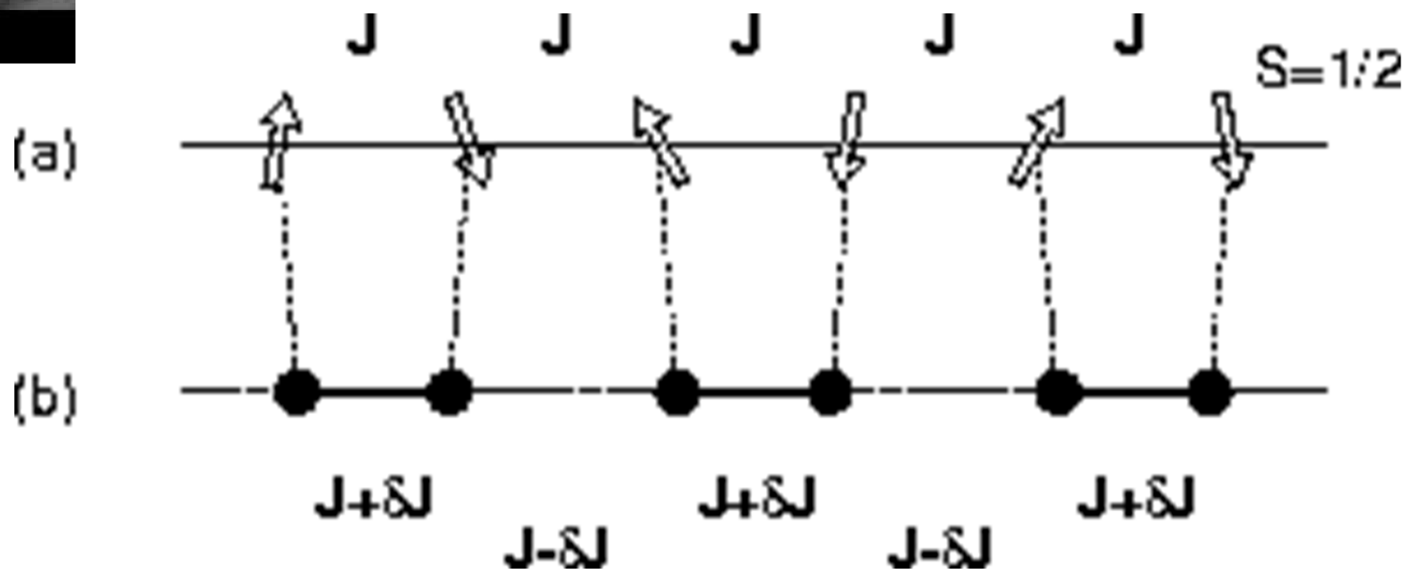
- $\omega_L \neq 0 \qquad \Gamma \to 0 \quad \text{as} \quad \dfrac{\omega_L}{\nu} \to \infty$

Systems with energy gaps



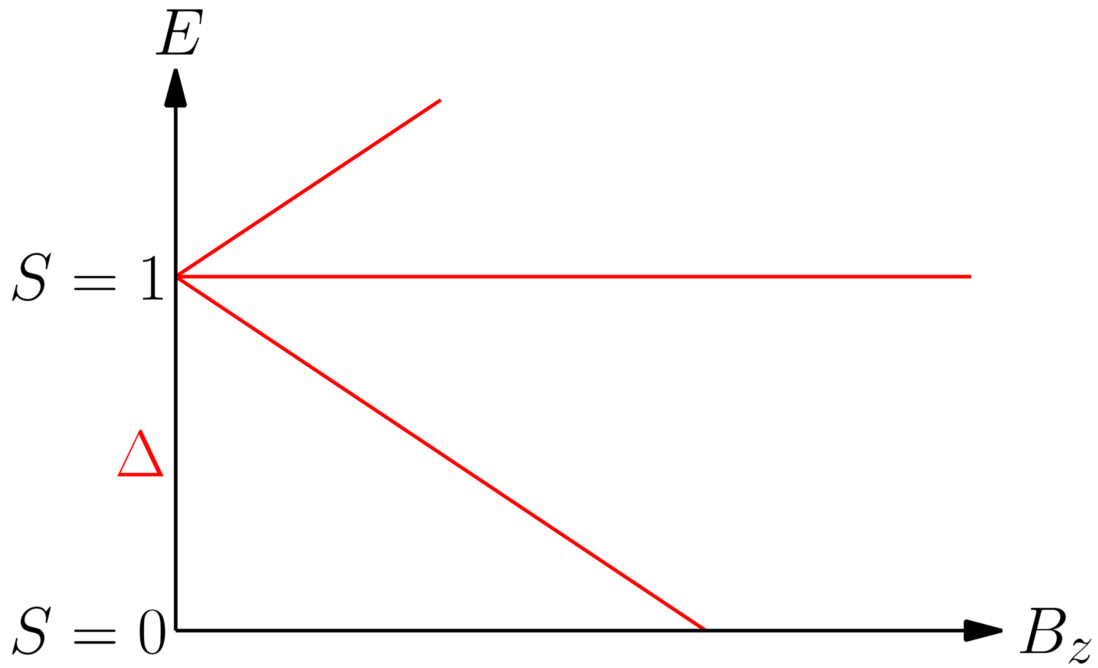
Spin Peierls: another fate for 1D spin systems

Uniform spin system



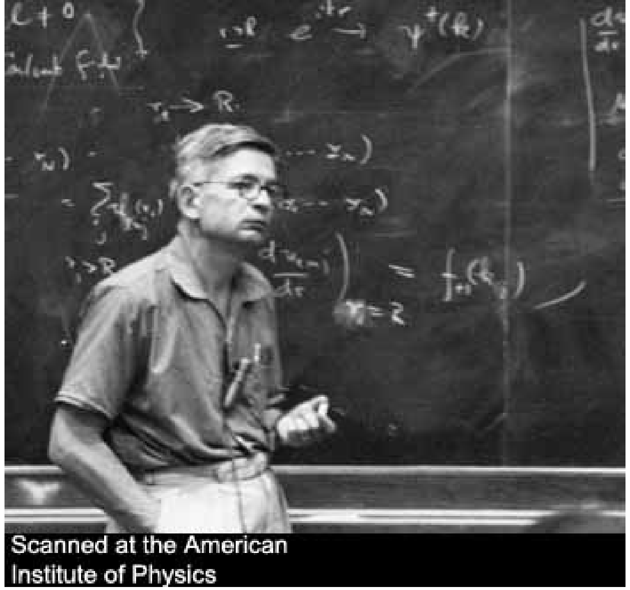
Dimerized spin system below T_{sp}

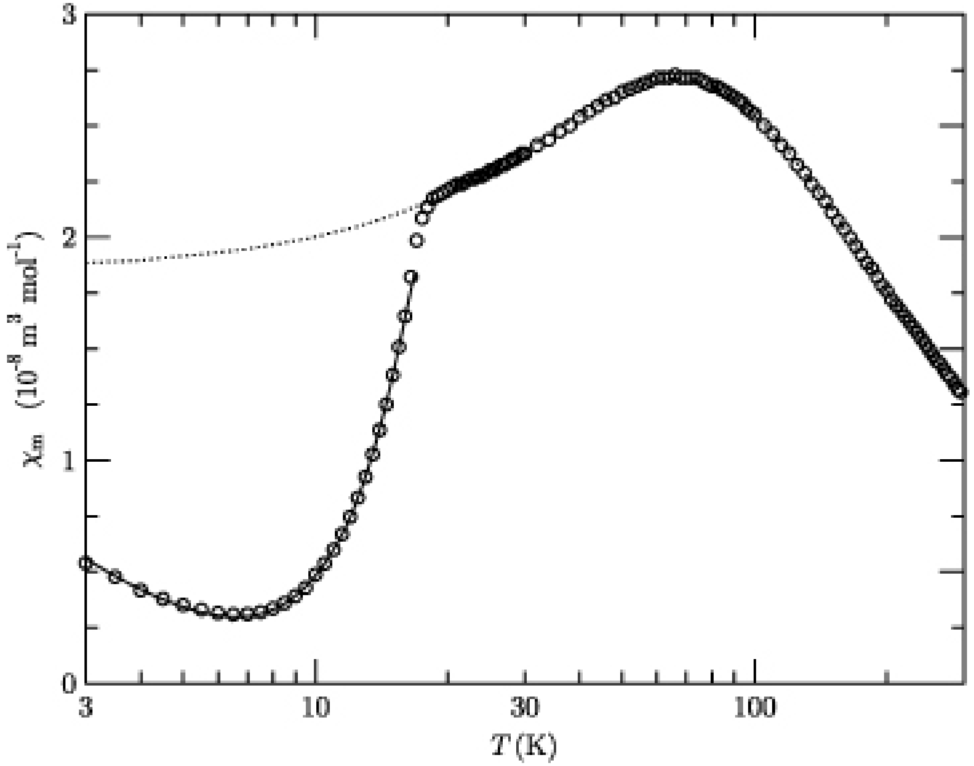
Isolated dimers



Dimers have an S=0 ground state (no magnetization) and a gap to the first excited magnetic state.

Spin Peierls: another fate for 1D spin systems



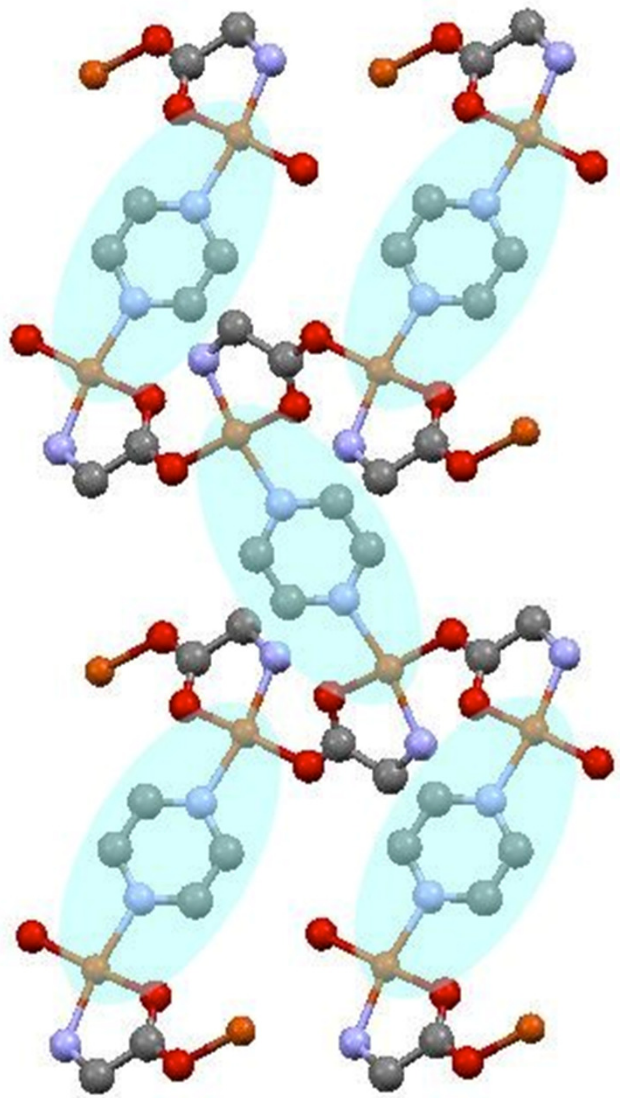


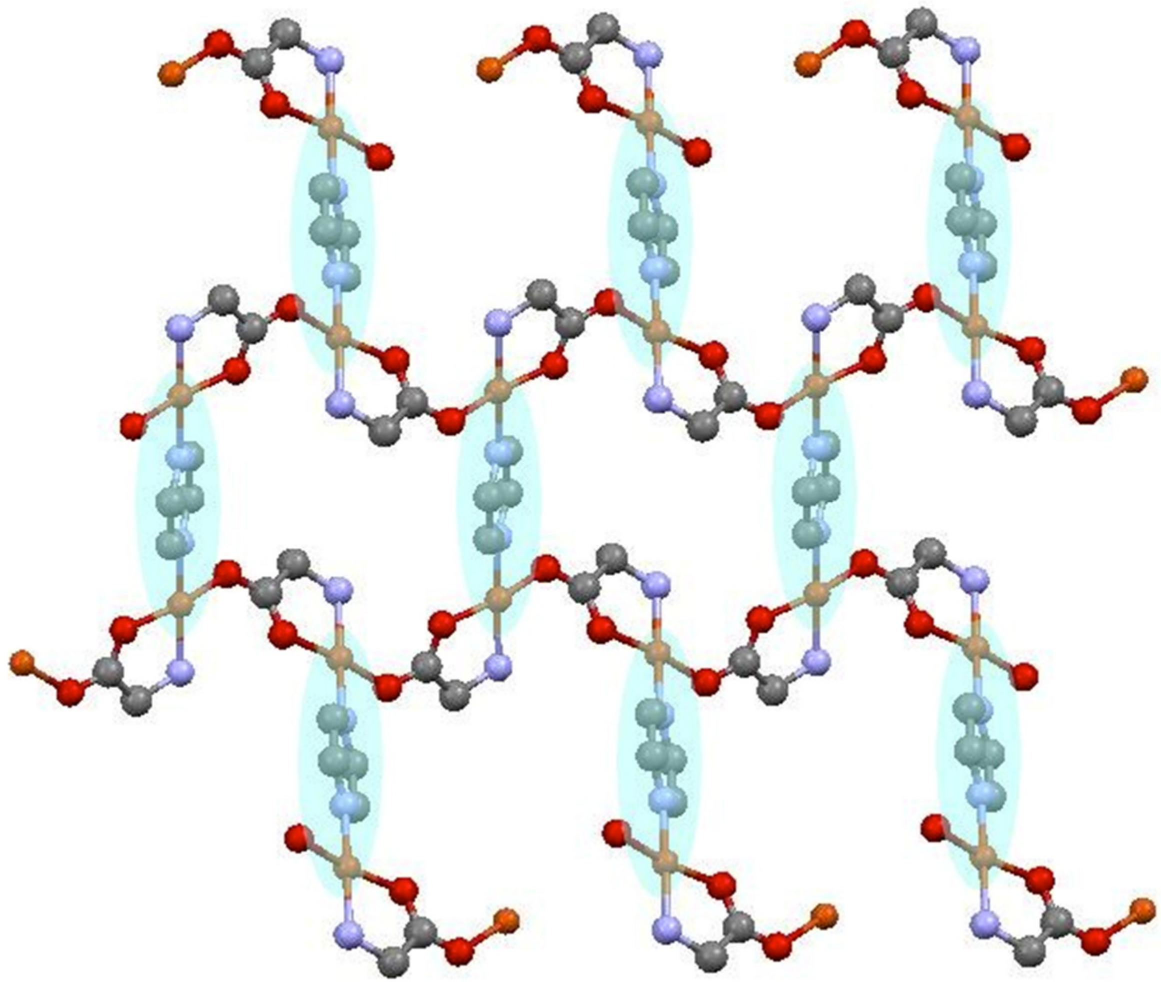
MEM(TCNQ)$_2$

S.J. Blundell et al., JPCM 9 L119 (1997)

Quantum magnetism and dimers

$[Cu(gly)(pyz)](ClO_4)$

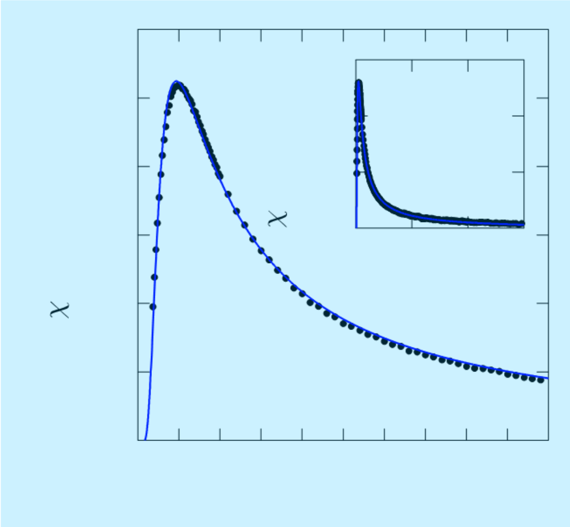


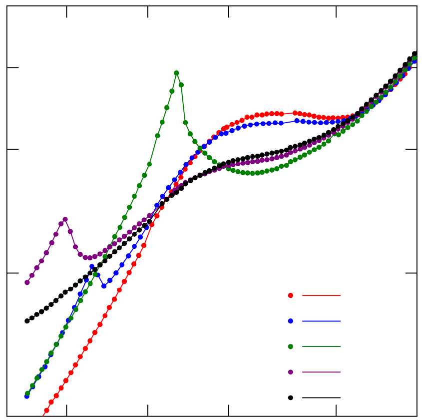


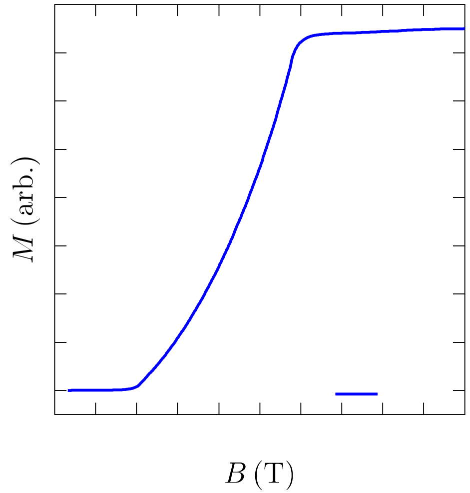
arXiv:1311.7614

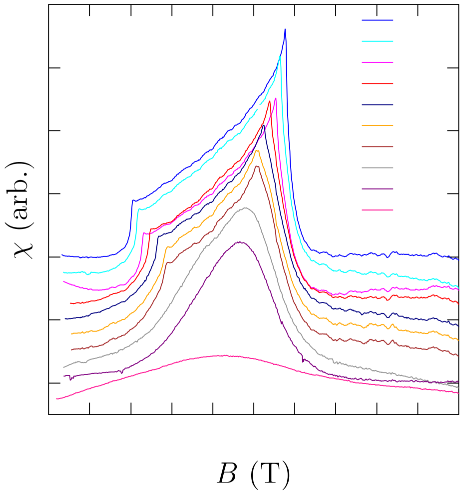
[Cu(gly)(pyz)](ClO_4)

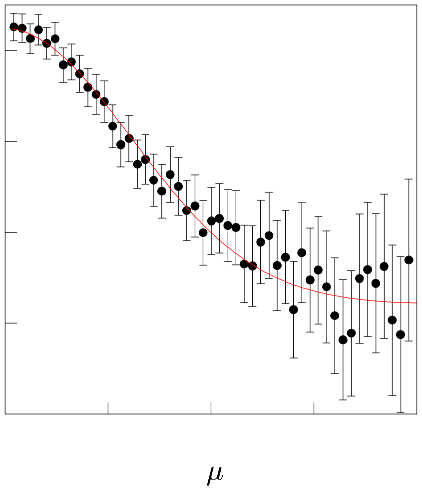
Bleaney-Bowers
Susceptibility: J=7.5 K

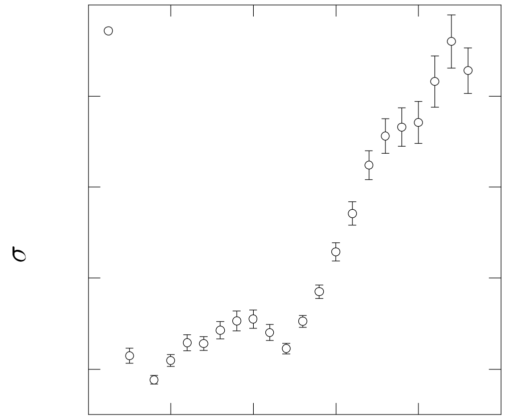






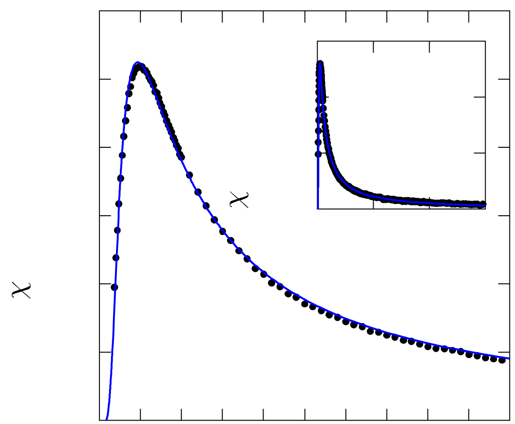


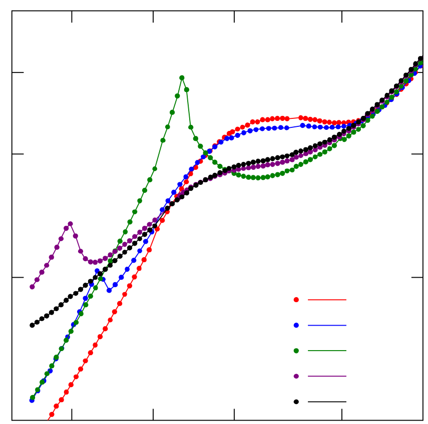


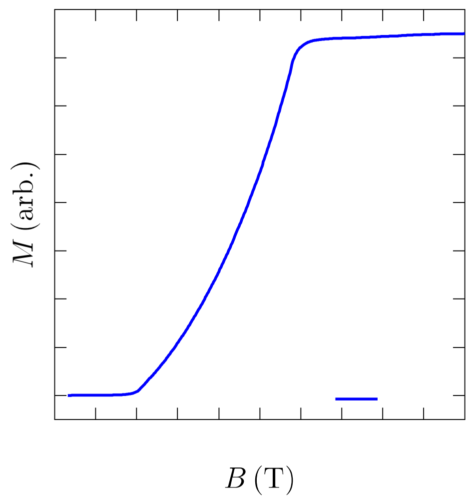


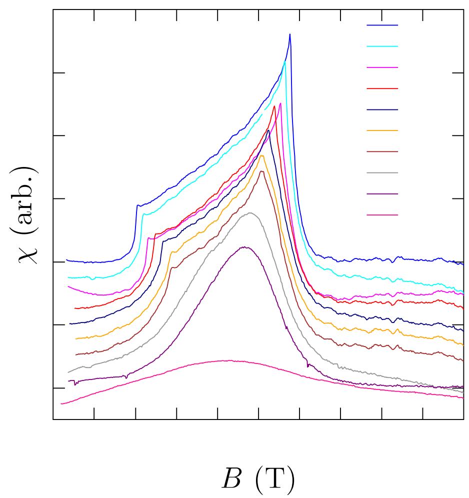
[Cu(gly)(pyz)](ClO_4)

Bleaney-Bowers
Susceptibility: J=7.5 K

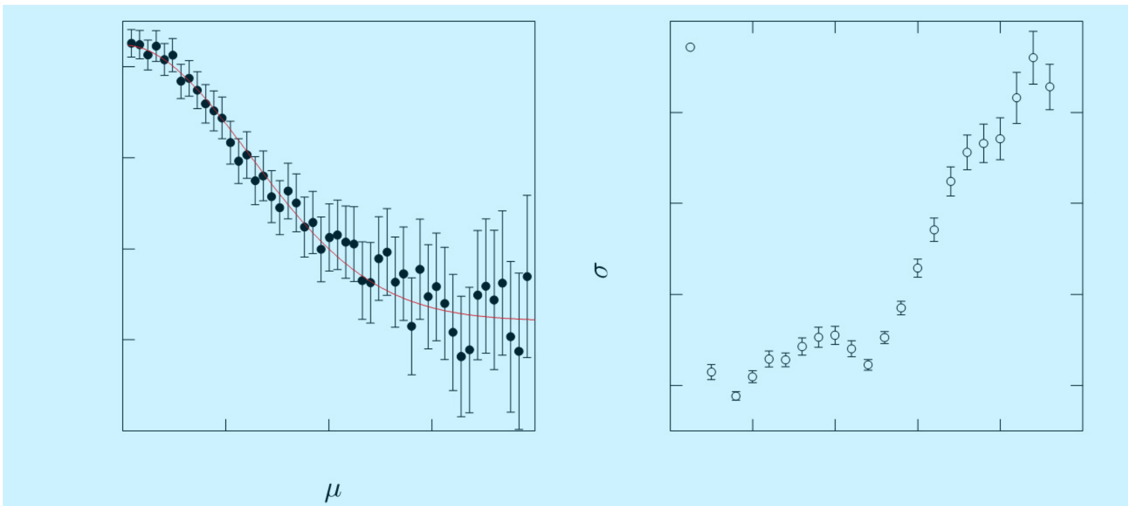




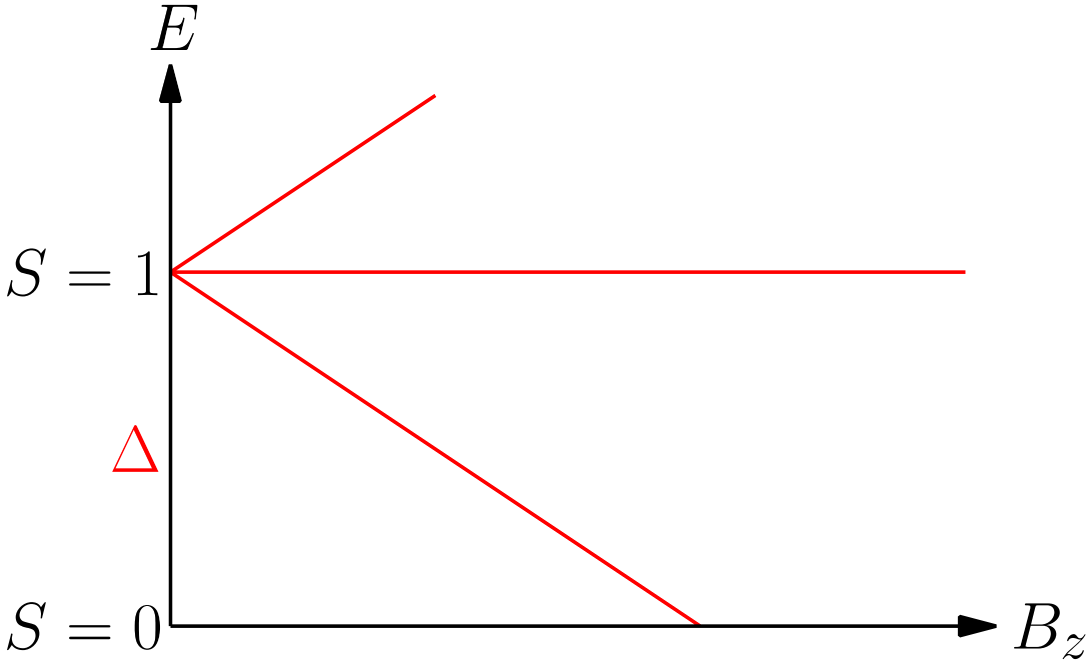




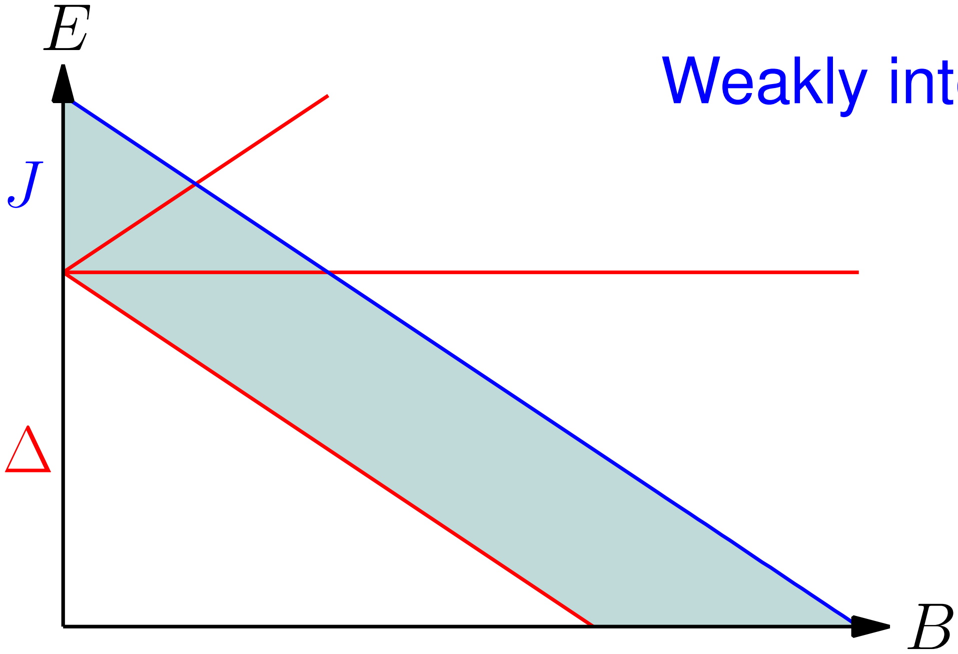
No order in ZF
down to 30 mK



Isolated dimers

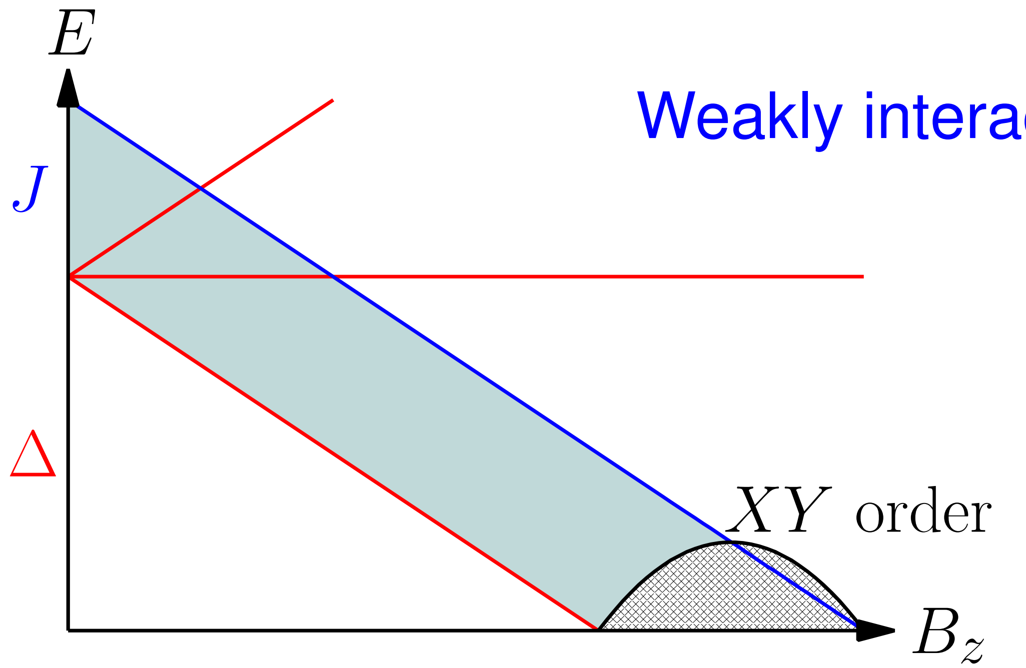


Weakly coupled dimers



In an idealized case we expect a quantum phase transition to *XY* magnetic order

Weakly coupled dimers

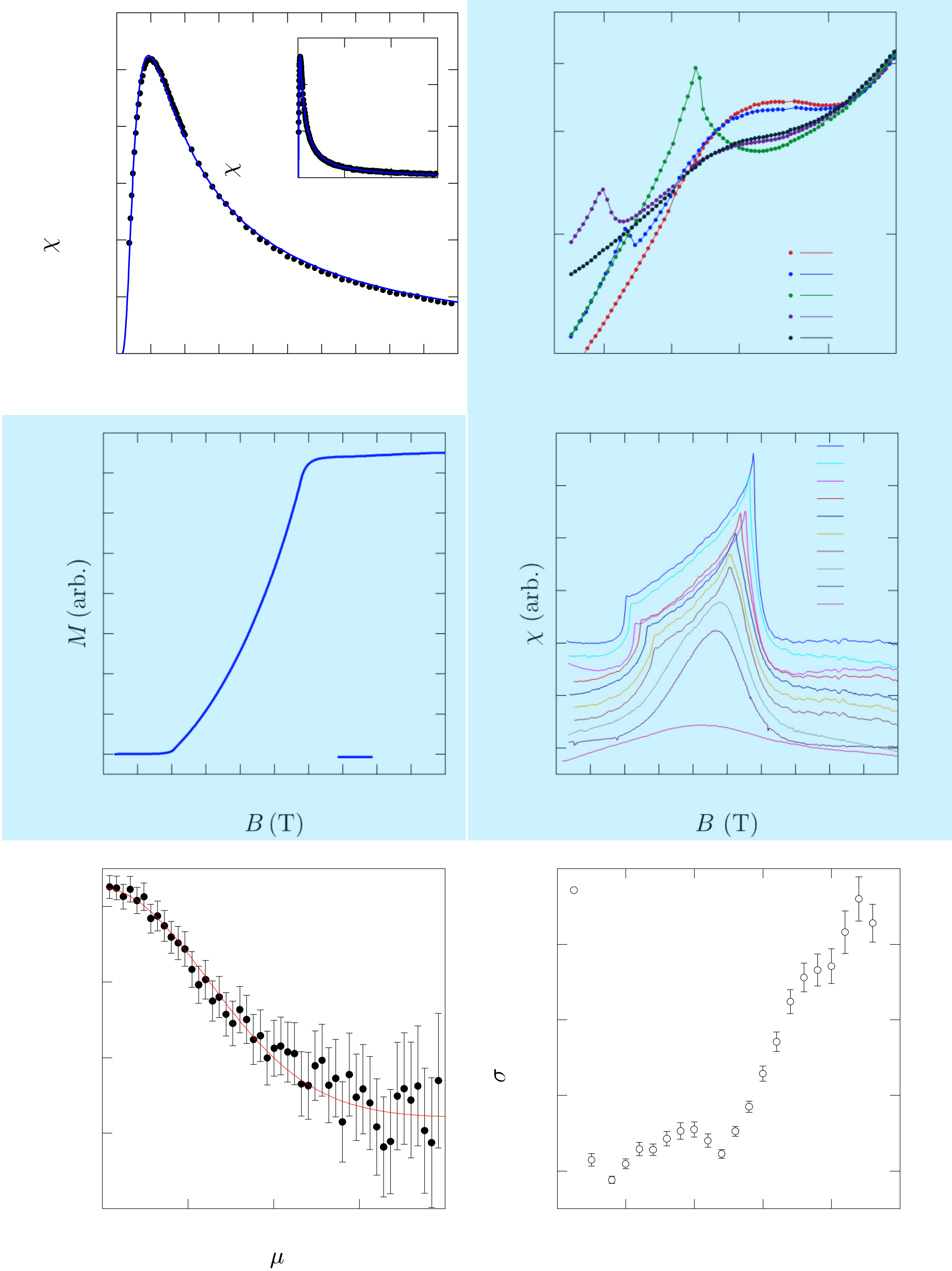


In an idealized case we expect a quantum phase transition to *XY* magnetic order

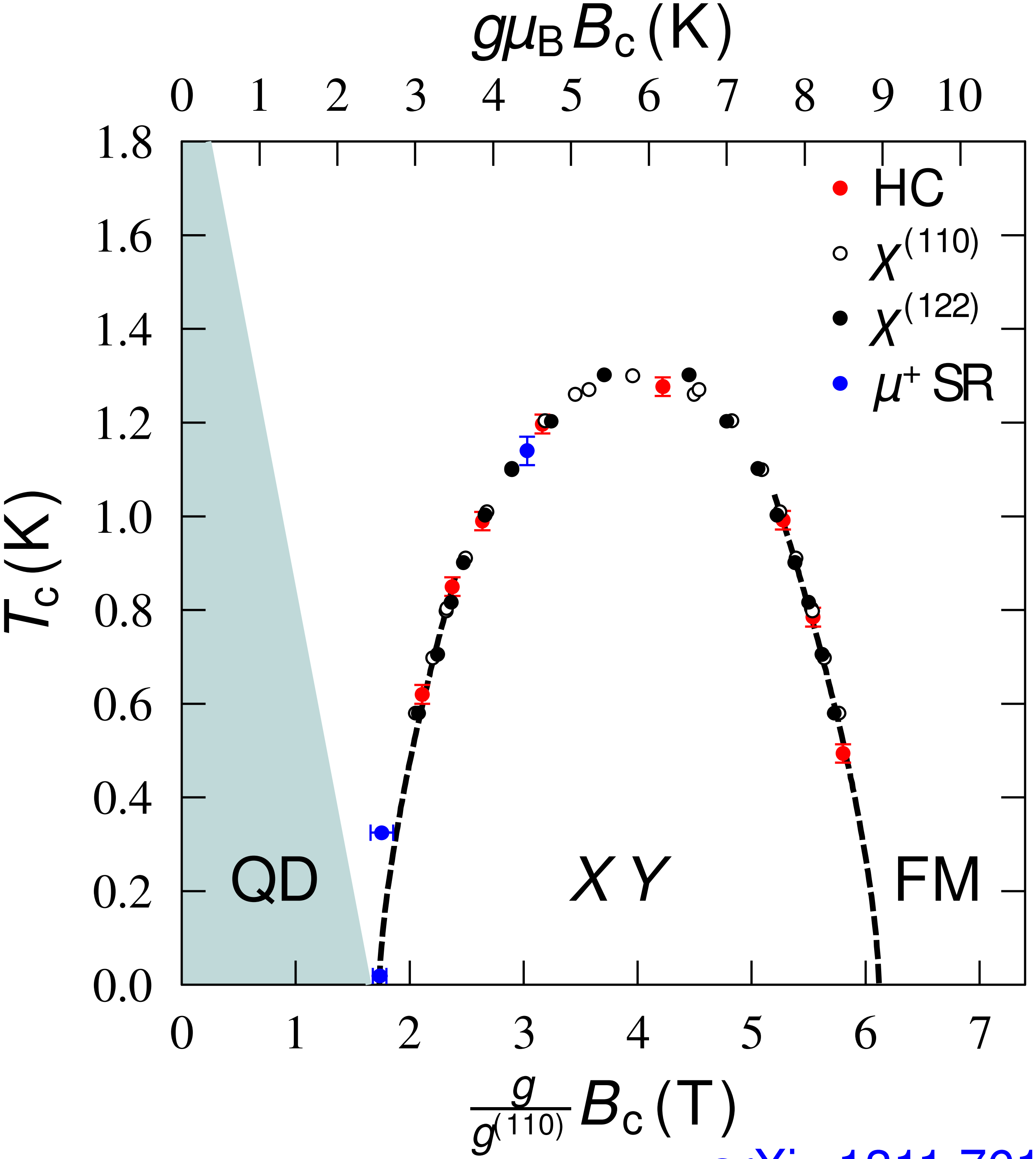
$[Cu(gly)(pyz)](ClO_4)$

Bleaney-Bowers
Susceptibility: J=7.5 K

Two set of transitions
in applied field



$[Cu(gly)(pyz)](ClO_4)$

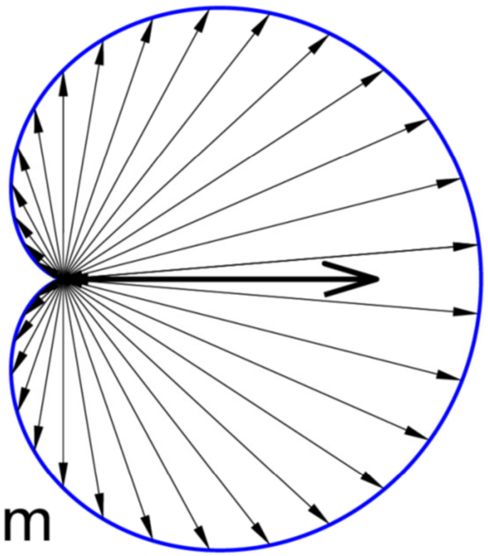


Consistent with a FM
Coupled dimers

Suggests $J = 7.3$ K
and $J' = 3.3$ K

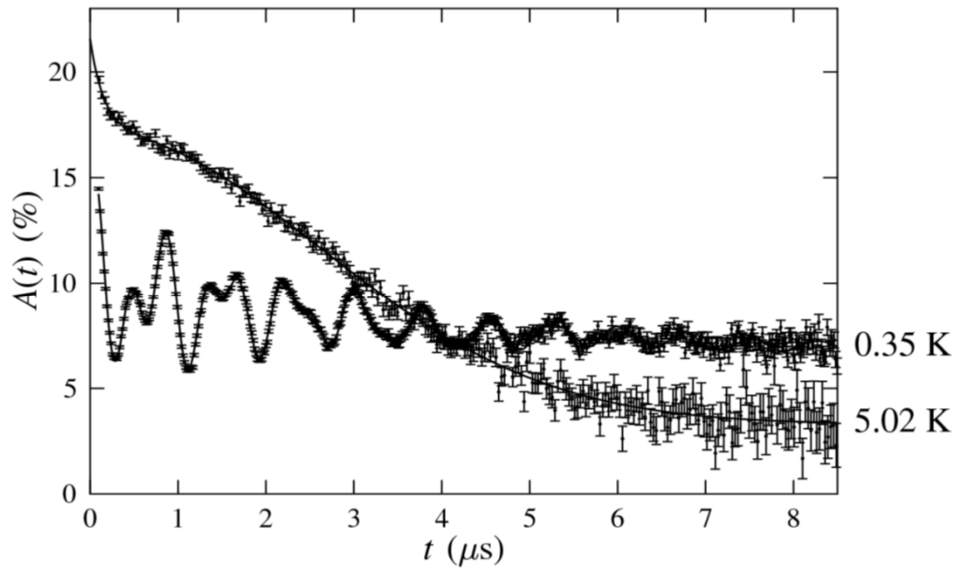
arXiv:1311.761

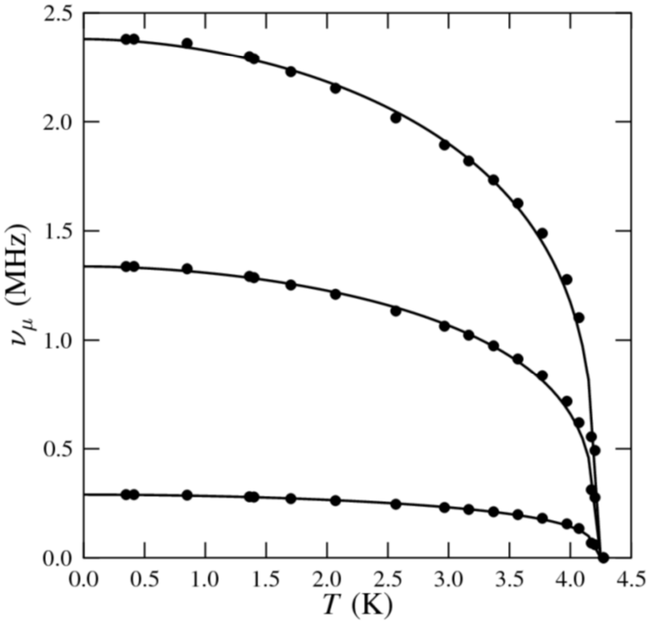
Conclusions



- Muons are a sensitive probe of magnetism
- Useful for static and dynamic effects
- Work well at low temperatures

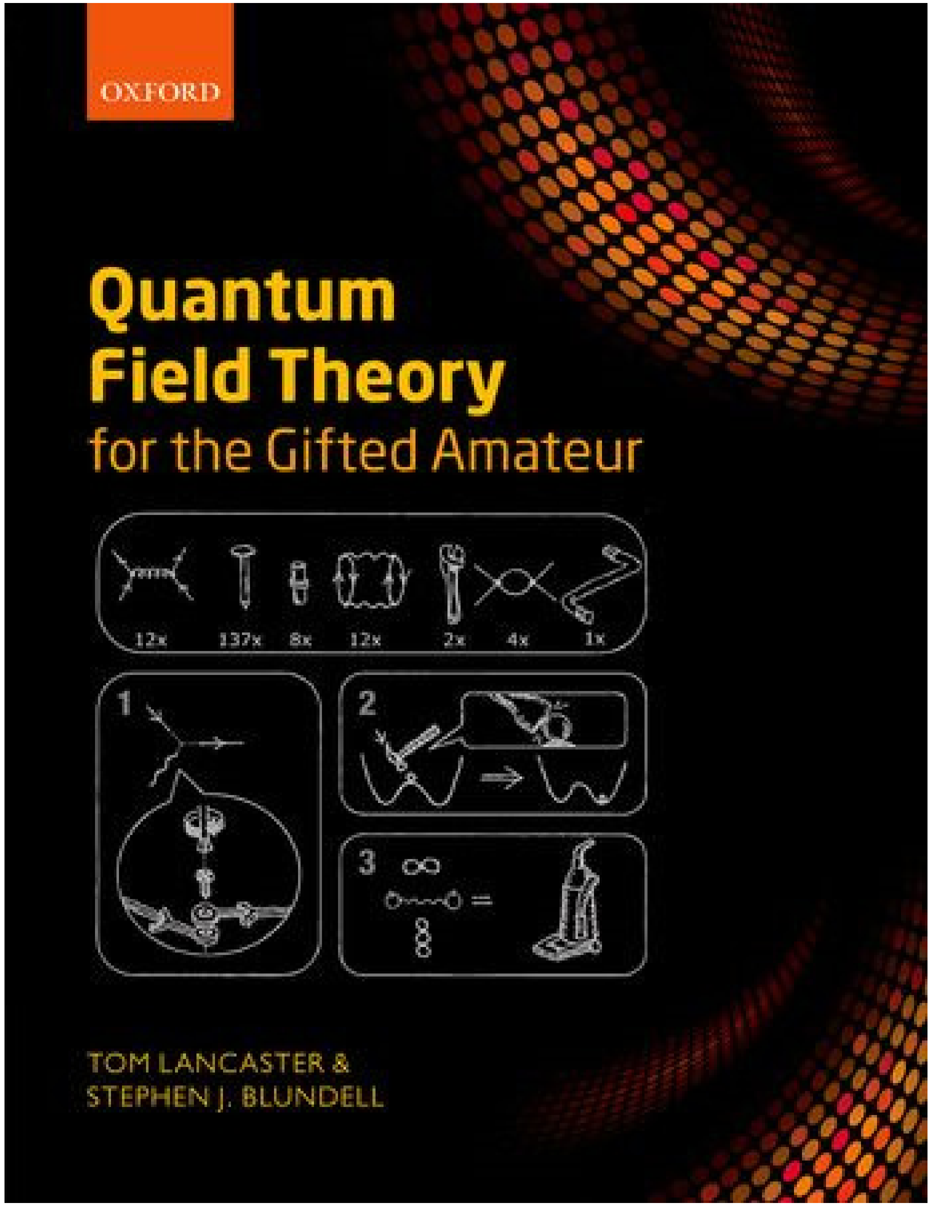
- Examples include: low-dimensional magnetism
  incommensurate structures
  dynamics



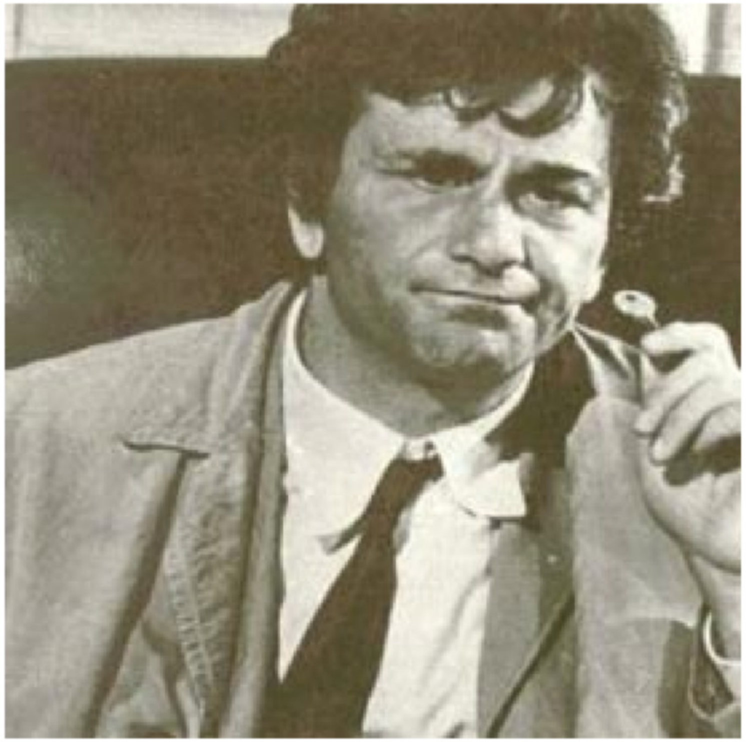


You can find out more about magnetism in many books

Including:



... just one more thing:

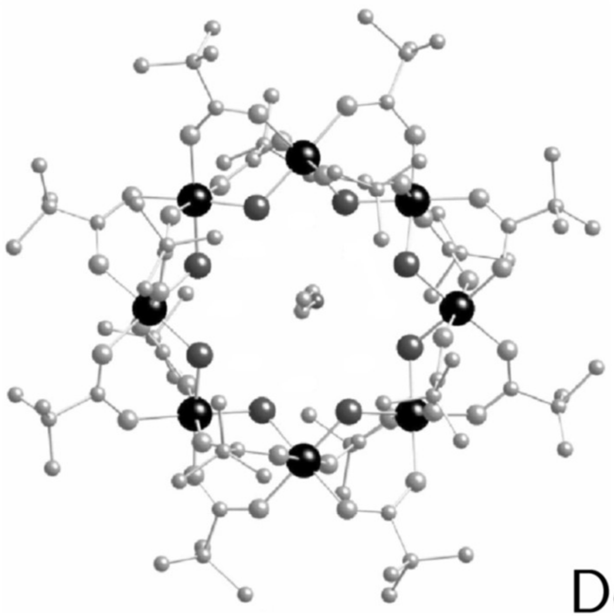


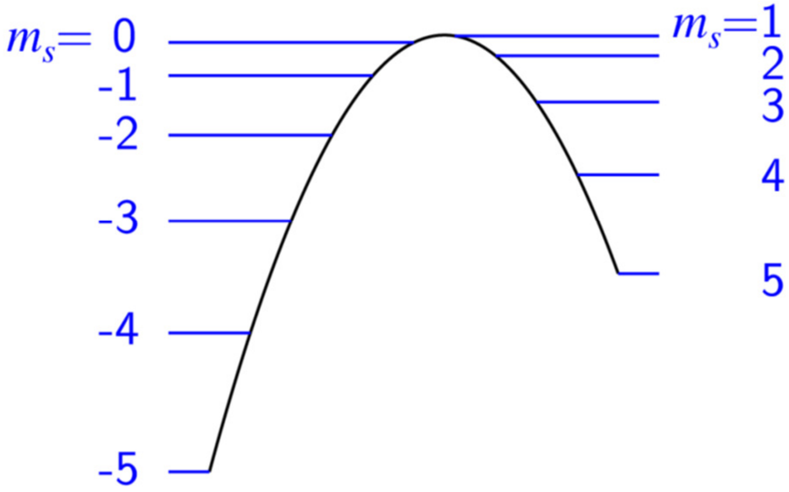
Case study:
Dynamics in molecular nanomagnets

Single molecule magnets

Magnetic ion clusters which couple to give large S with negative anisotropy

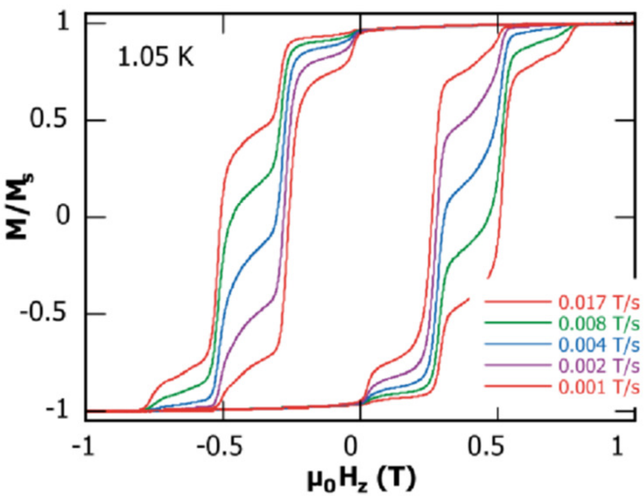
$$\hat{H}_e = -D\hat{S}_z^2 + g\mu_\mathrm{B}\hat{\mathbf{S}}\cdot\mathbf{B}$$





Double well of spin states $\longrightarrow$ quantum tunneling

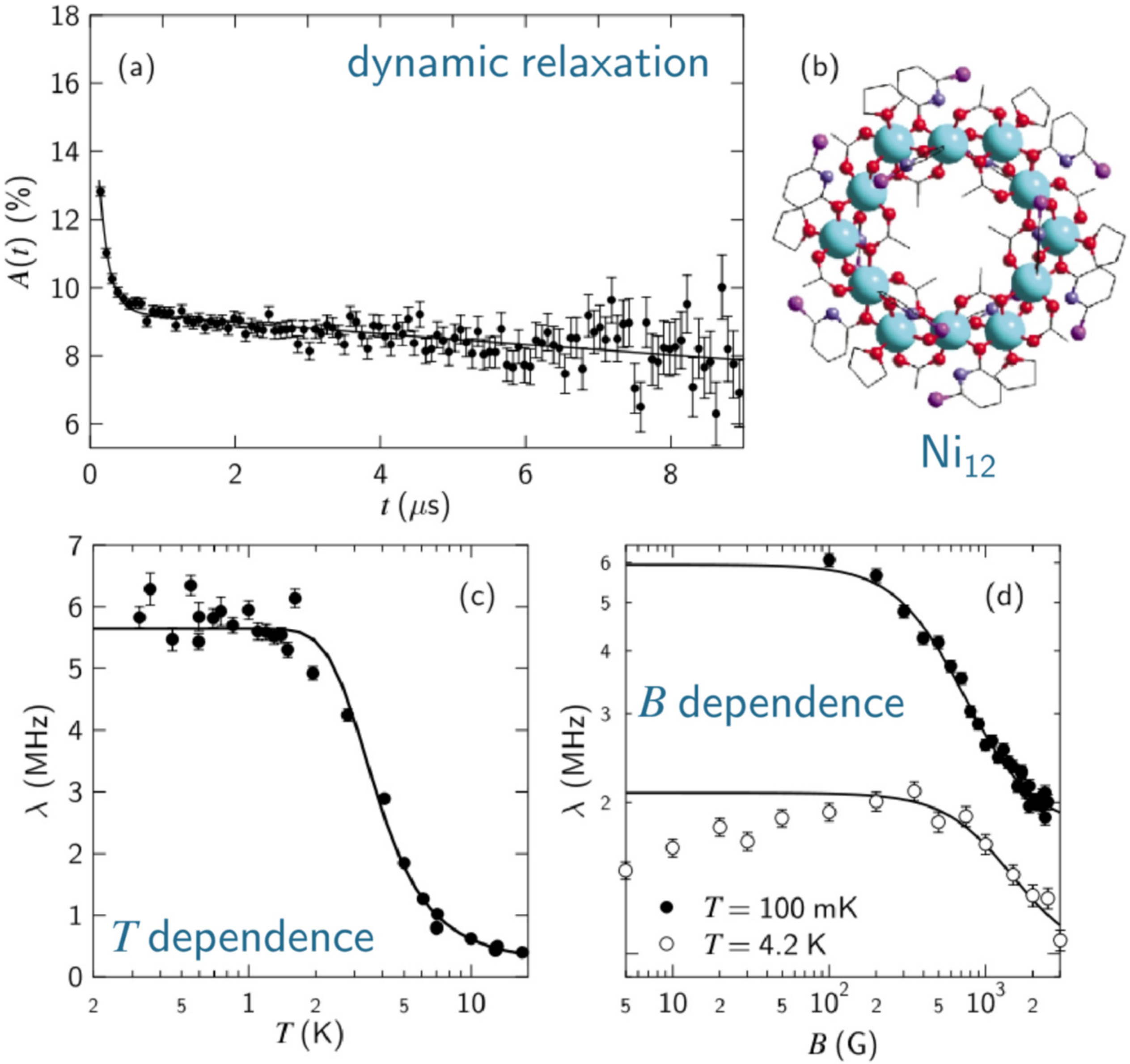
$$B = \frac{(l-n)D}{g\mu_\mathrm{B}}$$



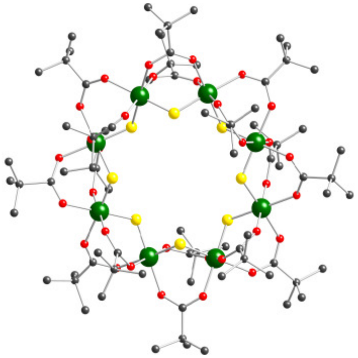
μ^+SR results have been ambiguous...

...but similar results seen in all cases

What does it all mean?



Lancaster *et al.* JPCM **16**, S4563 (2004)

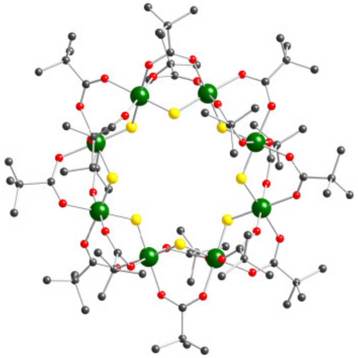


Amit Keren's suggestion

large electron spins $\qquad\qquad$ μ^+ spins

$\tau_e \xrightarrow{\text{relax}} \lambda$

Keren *et al.* PRL **98** 257204 (2007)



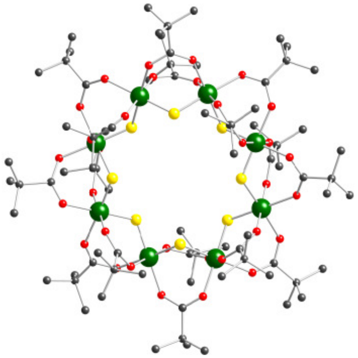
Amit Keren's suggestion

Proton fluctuations determine the muon response

Stochastic fluctuations of proton spins $\xrightarrow{\text{relax}}$ large electron spins $\xrightarrow{\text{relax}}$ μ^+ spins

τ_{n} $\qquad$ τ_{e} $\qquad$ λ

Keren *et al.* PRL **98** 257204 (2007)



Amit Keren's suggestion

Proton fluctuations determine the muon response

Stochastic fluctuations of proton spins τ_n → relax → large electron spins τ_e → relax → μ^+ spins λ

For muons

$$\lambda \;\square\; \frac{\langle B_\mu^2 \rangle \tau_e}{1 + (\gamma_\mu B_{app} \tau_e)^2}$$

$$\square\; \langle B_\mu^2 \rangle \tau_e$$

but electron spins are being relaxed

$$\frac{1}{\tau_e} \;\square\; \langle B_n^2 \rangle \tau_n$$

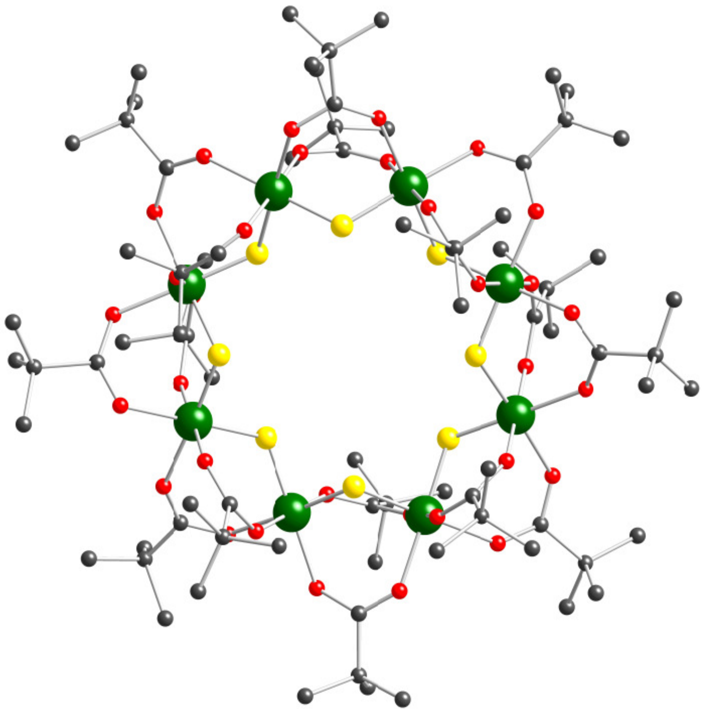
Conclusion

$$\lambda \;\square\; \frac{\langle B_\mu^2 \rangle}{\langle B_n^2 \rangle} \frac{1}{\tau_n}$$

Keren *et al.* PRL **98** 257204 (2007)

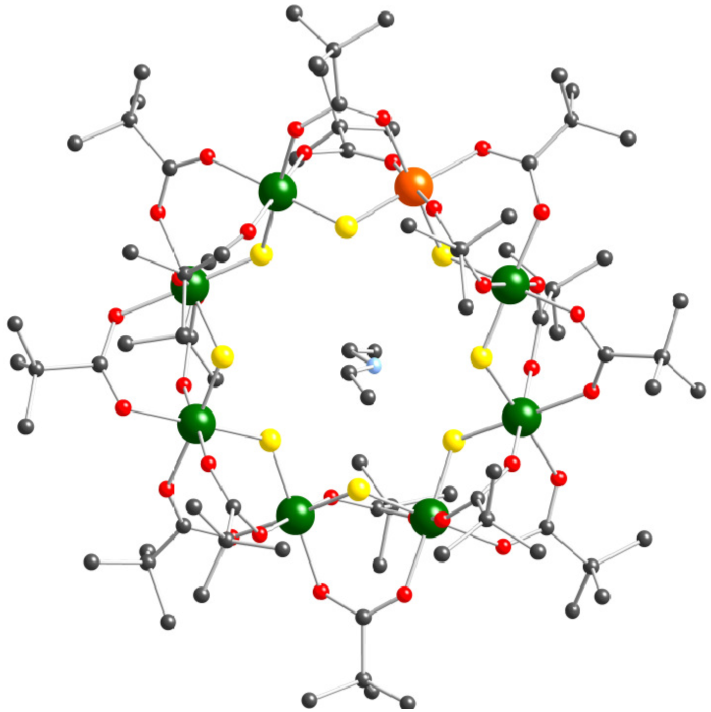
Step 1: show that electronic spins relax the muon spins

Make measurements on $S=0$ and $S=1$ materials



$[Cr_8F_8(O_2CC(CH_3)_3)_{16}]$

Cr$_8$ $S=0$

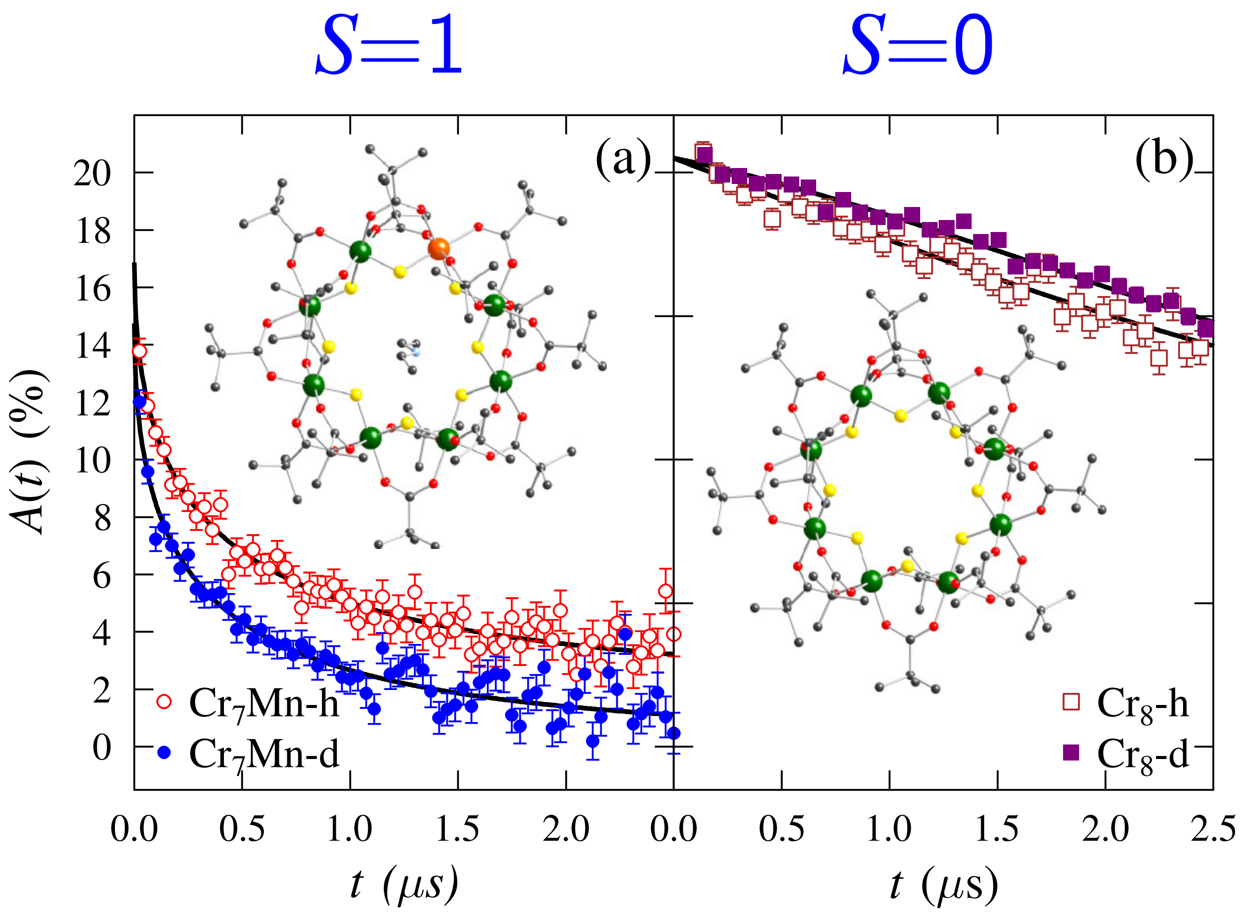


Cr$_7$Mn $S=1$

Prediction: significantly more relaxation from $S=1$ material

Lancaster *et al.*, PRB **81**, 140409(R)

The effect of electronic moments

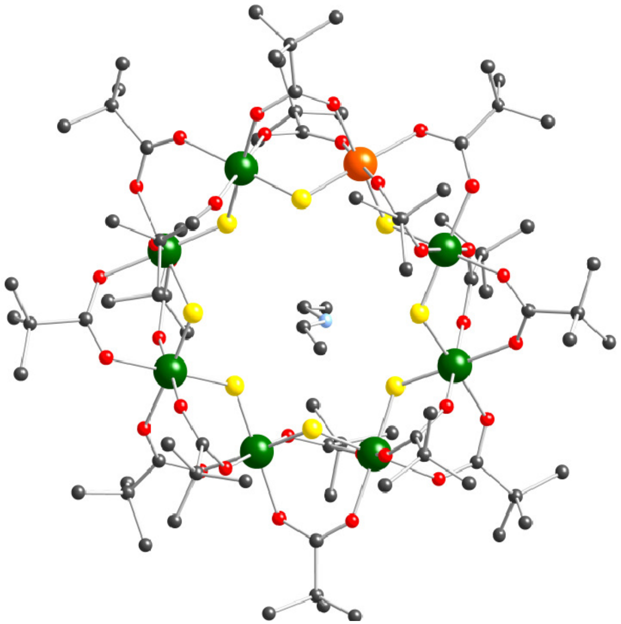


Conclusion: electronic moments on the MNMs relax the muon spins

Lancaster *et al.* PRB **81**, 140409(R) (2010)

Step 2: show that nuclear spins relax the electronic spins

Make measurements on protonated and deuterated materials



Cr_7Mn $S=1$

Prediction

$$\lambda \,\square\, \frac{\langle B_\mu^2 \rangle}{\langle B_n^2 \rangle} \frac{1}{\tau_n}$$

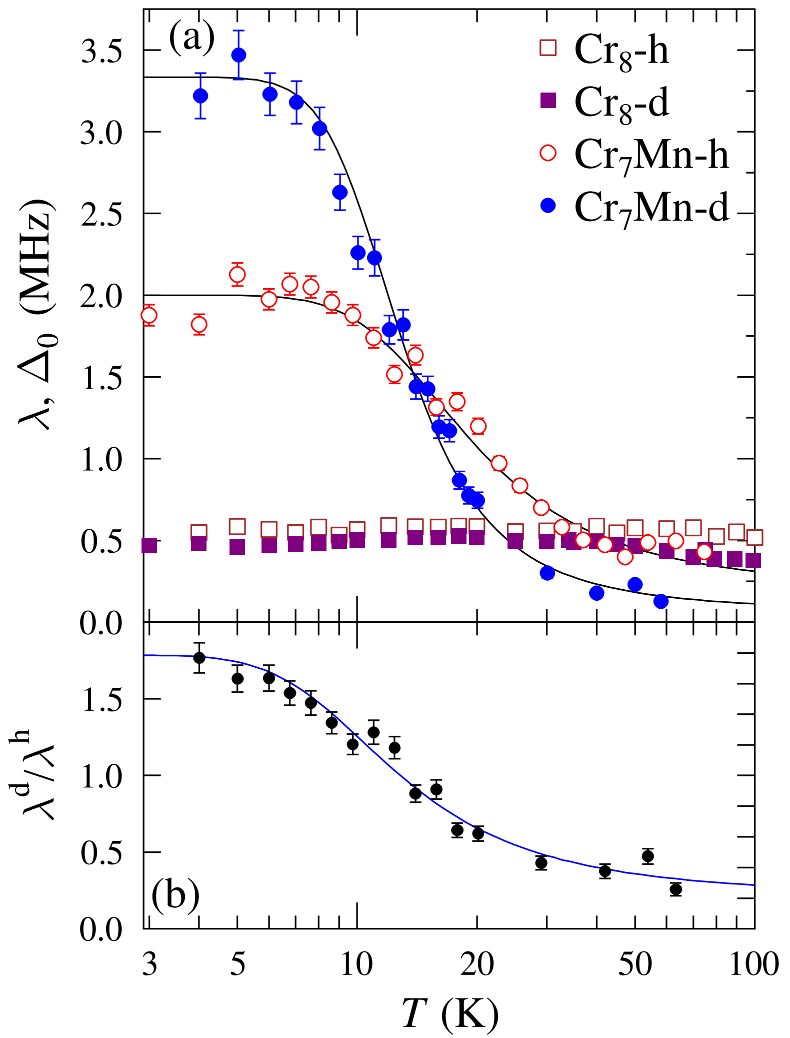
proton has $\mu = 2.8\ \mu_N$

deuteron has $\mu = 0.857\ \mu_N$

Prediction: more relaxation from deuterated material

Lancaster *et al.*, PRB **81**, 140409(R)

The effect of nuclear moments



If we have

$$\langle B_n^2 \rangle \quad \square \quad \gamma_\mu^2 I_n(I_n + 1)$$

$$\tau_n \quad \square \quad 1/\left[\gamma_\mu \sqrt{I_n(I_n+1)}\right]$$

then expect a factor of ~ 4

Larger relaxation observed for deuterated materials

Conclusion: nuclear moments on the MNMs relax the electronic spins

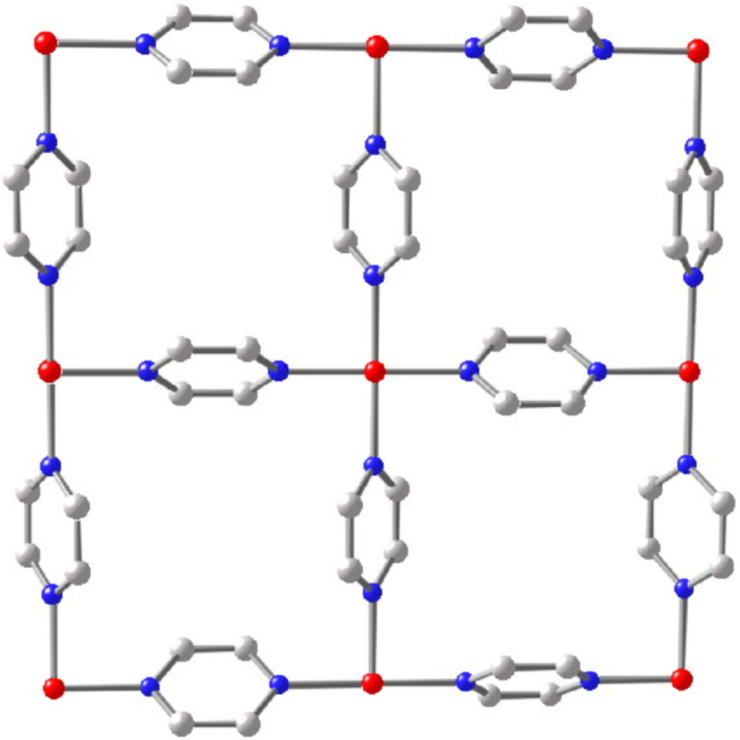
Lancaster *et al.* PRB **81**, 140409(R) (2010)

$[Cu(pyz)_2HF_2]X_2$ (X=BF_4, ClO_4, PF_6, AsF_6, SbF_6)

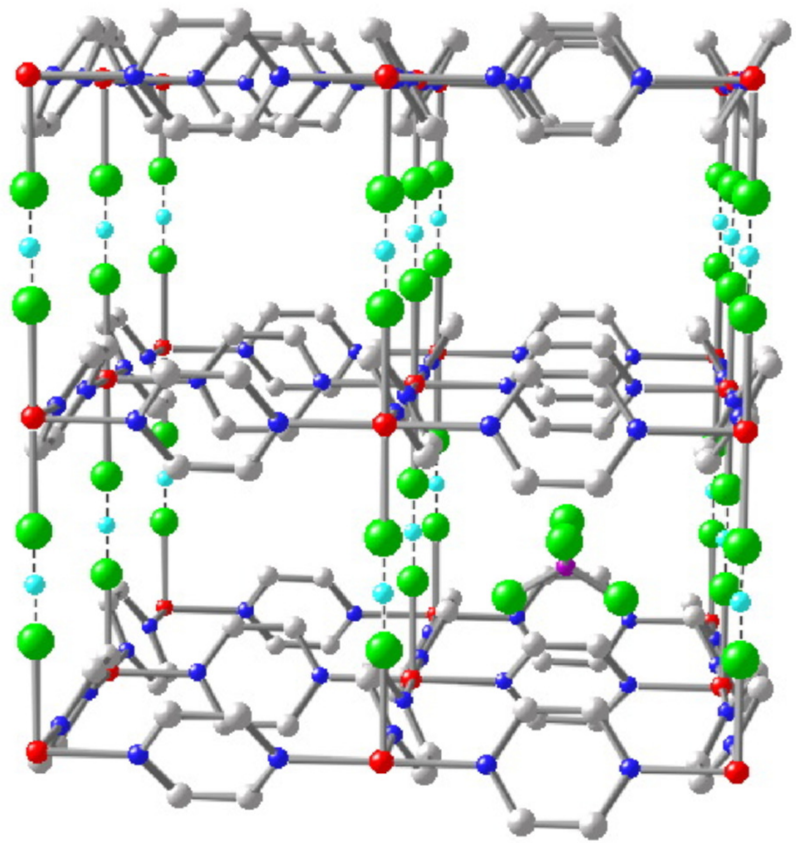
Highly tunable, self-assembled nanostructures with 2D character

First coordination polymer containing the HF_2^- ion

(strongest known hydrogen bond!)



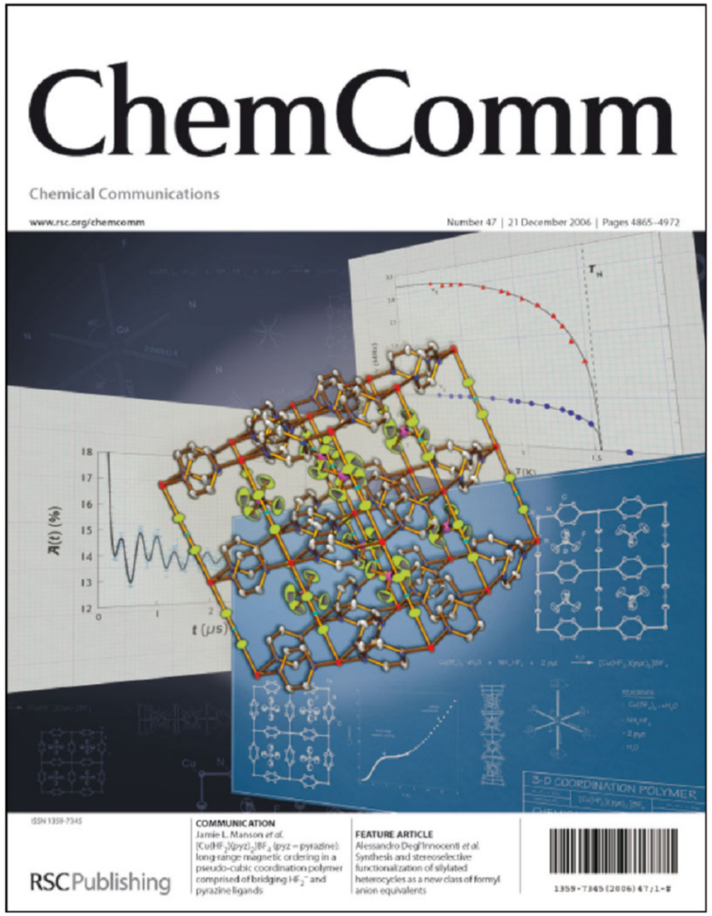
2D square lattice of Cu^{2+} $S=1/2$ spins

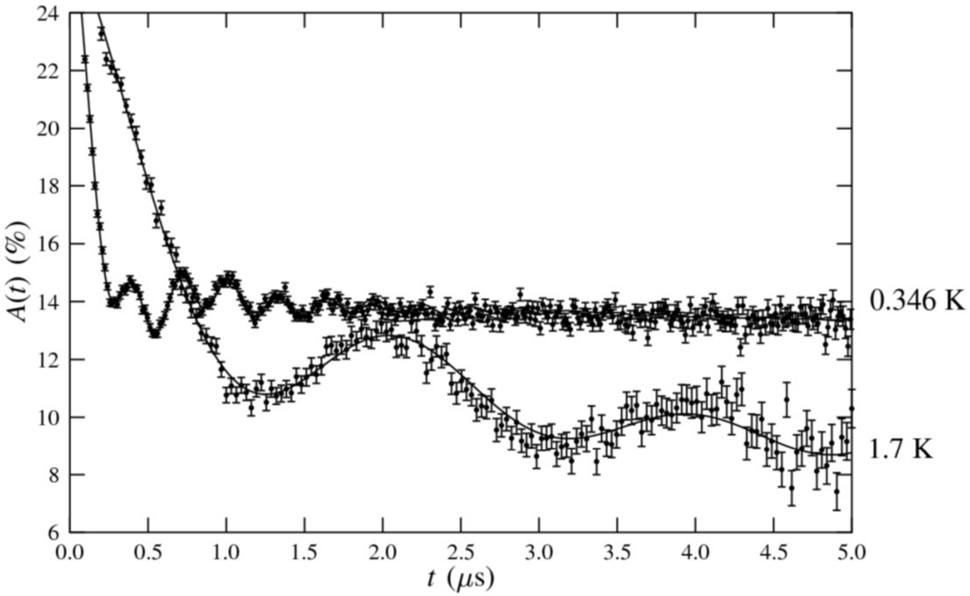


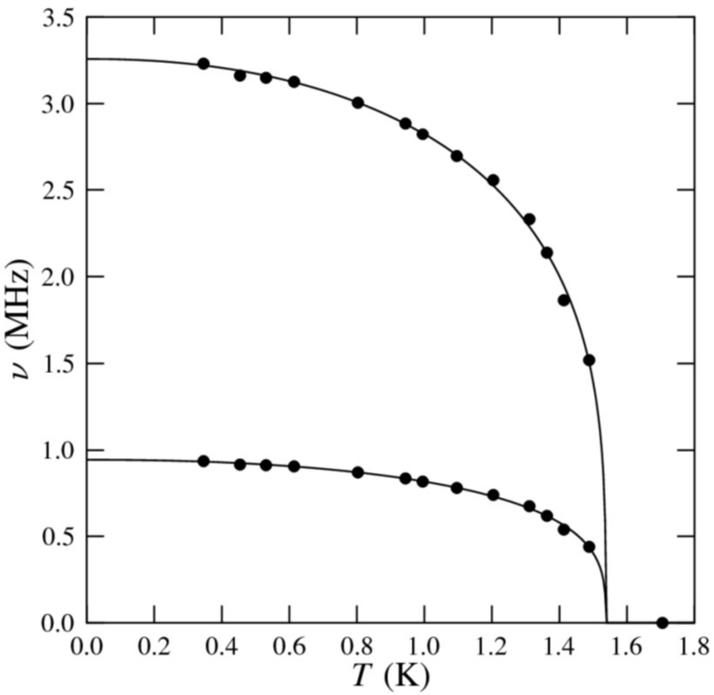
Linked by HF_2^- to form 3D structure

(with X anions in the cubes)

$[Cu(pyz)_2HF_2]BF_4$







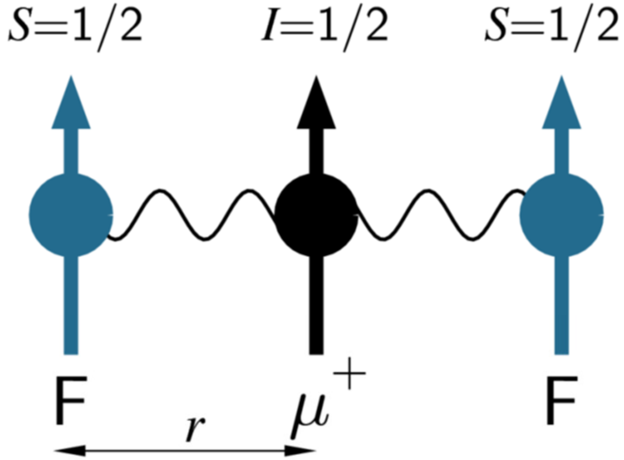
Magnetic order below T_N=1.54 K

Slow oscillations above 1.54 K
aren't due to magnetic order...

Chem. Comm. 4894 (2006)

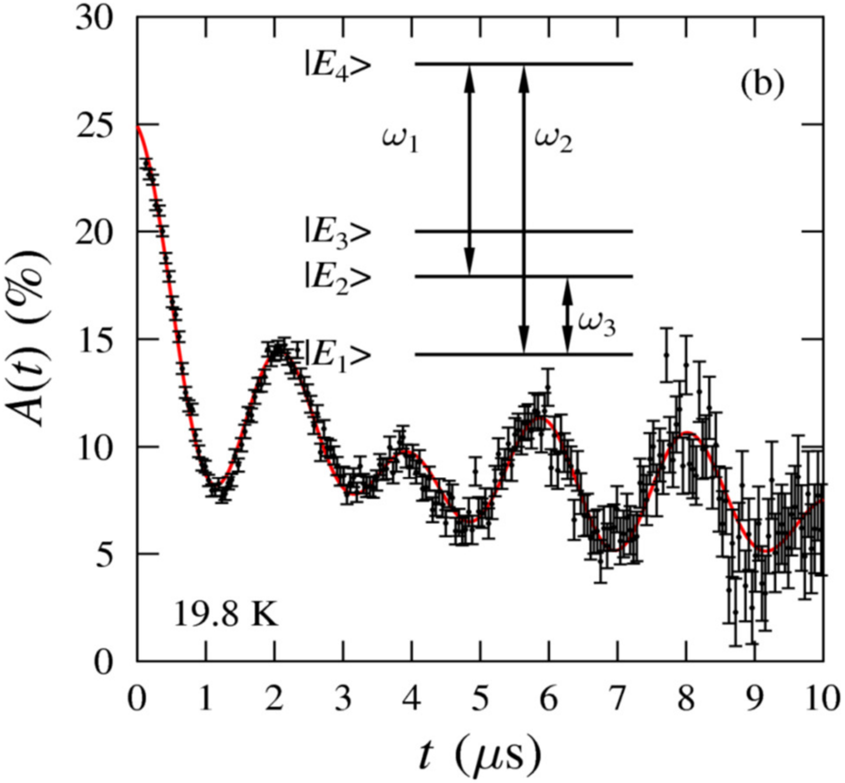
Quantum entanglement: F-μ^+ dipole-dipole interaction

The muon forms a bond with electronegative fluorine



$$H_0 = \sum_i \frac{\mu_0}{4\pi r_i^3}\left(\hat{\mathbf{S}}\cdot\hat{\mathbf{I}} - \frac{3(\hat{\mathbf{S}}\cdot\mathbf{r})(\hat{\mathbf{I}}\cdot\mathbf{r})}{r_i^2}\right)$$

$$P_z(t) = \mathrm{Tr}(\rho e^{\mathrm{i}H_0 t}\sigma_z e^{-\mathrm{i}H_0 t})$$



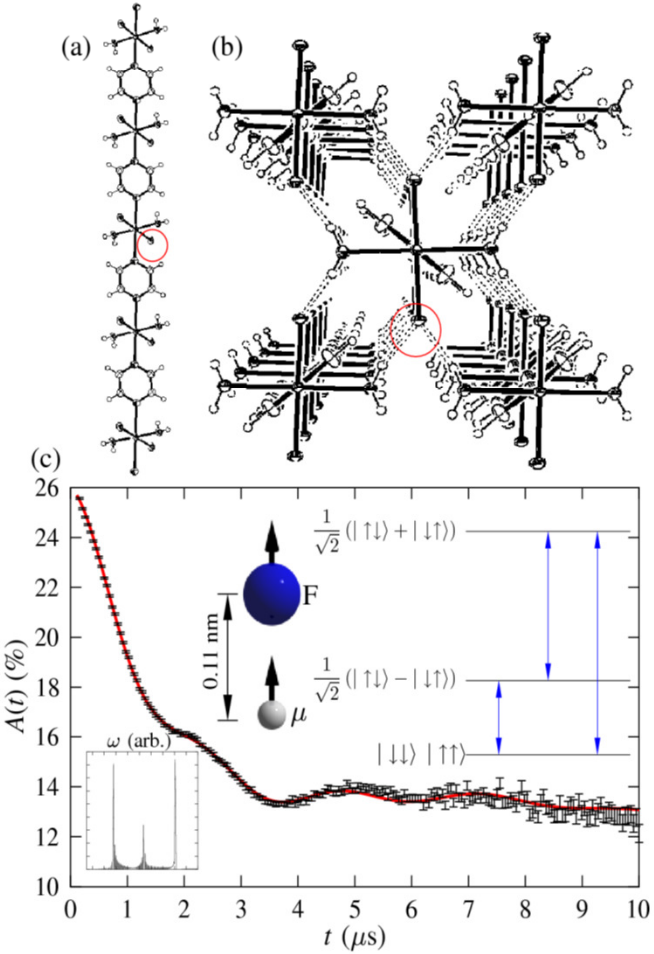
e.g. linear F-mu-F states exist in Cs_2AgF_4
T Lancaster *et al.* PRB (2007)

Typically r=0.11 nm for the linear bond

In general, can we locate the muon and assess the degree of distortion?

Muon-fluorine entangled states in molecular magnets

Above T_N entanglement allows us to locate the muon site



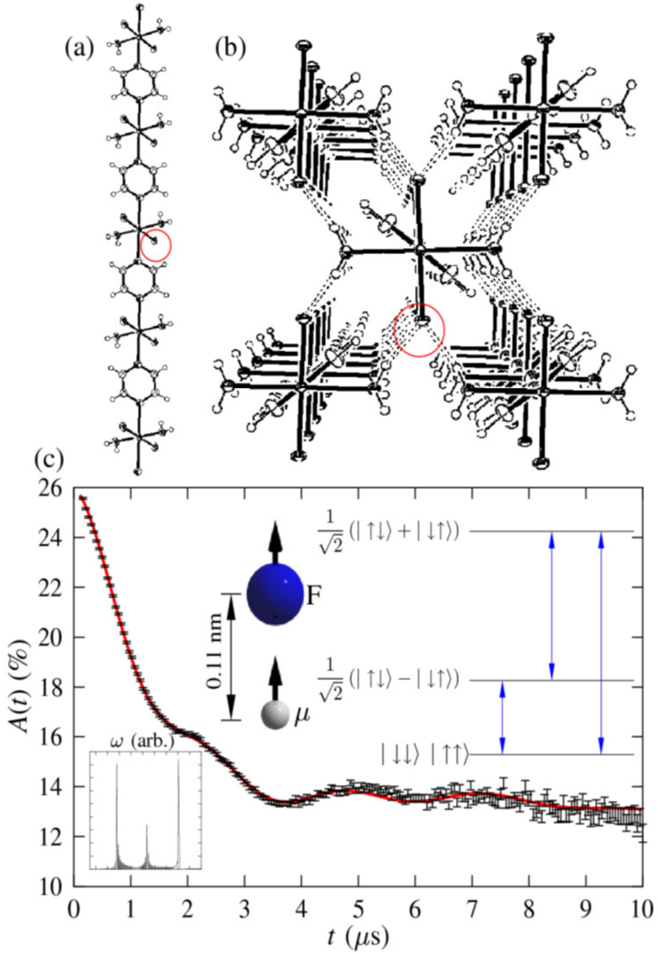
$CuF_2(H_2O)_2(pyz)$

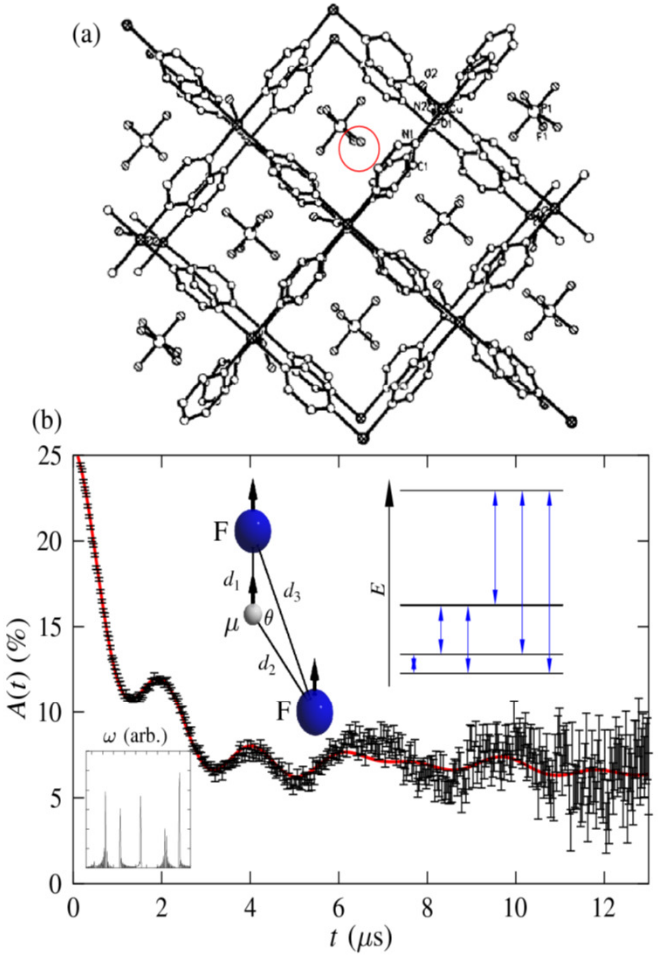
Single fluorine

T Lancaster *et al.* PRL **99** 267601 (2007)

Muon-fluorine entangled states in molecular magnets

Above T_N entanglement allows us to locate the muon site





$CuF_2(H_2O)_2(pyz)$

Single fluorine

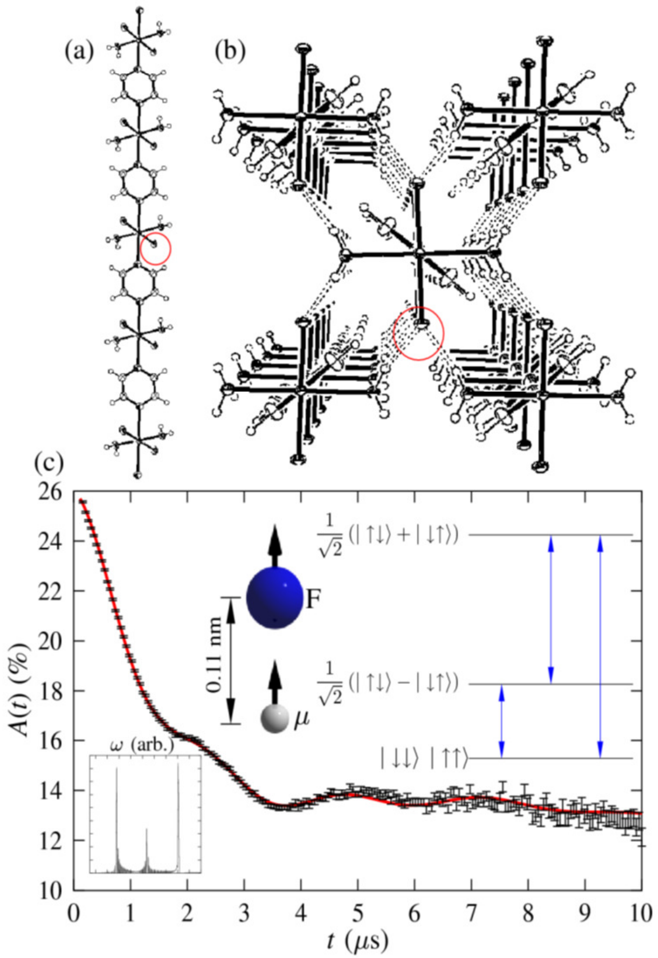
$[Cu(pyz)_2(NO_3)](PF_6)$

Octahedral PF_6^-

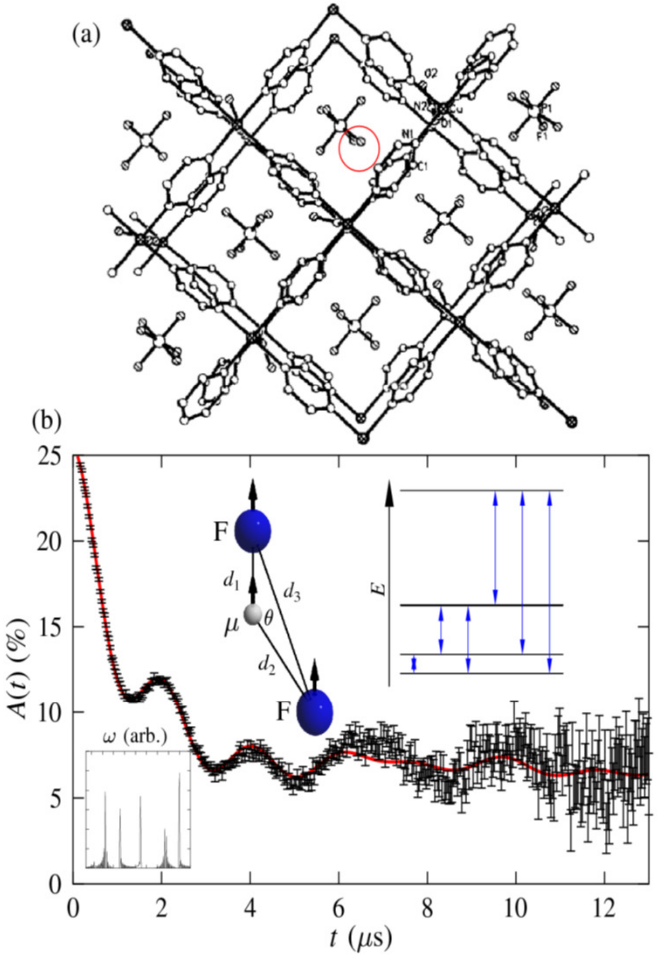
T Lancaster *et al.* PRL **99** 267601 (2007)

Muon-fluorine entangled states in molecular magnets

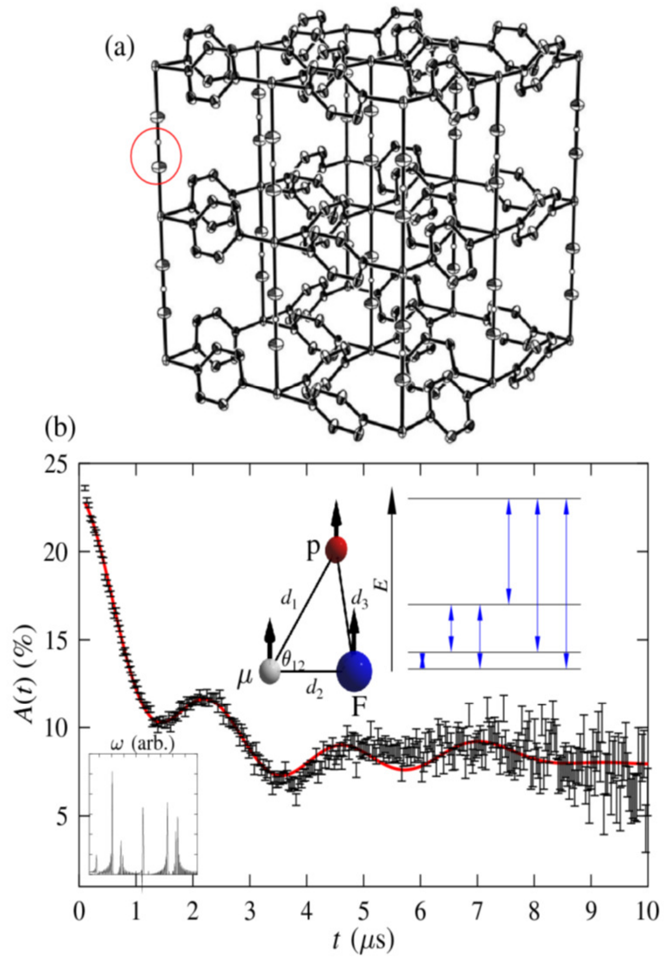
Above T_N entanglement allows us to locate the muon site



CuF$_2$(H$_2$O)$_2$(pyz)
Single fluorine



[Cu(pyz)$_2$(NO$_3$)](PF$_6$)
Octahedral PF$_6^-$

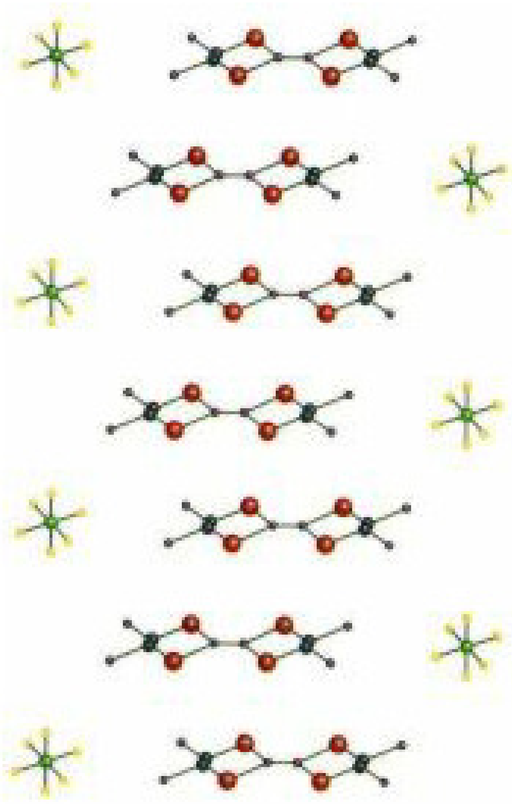


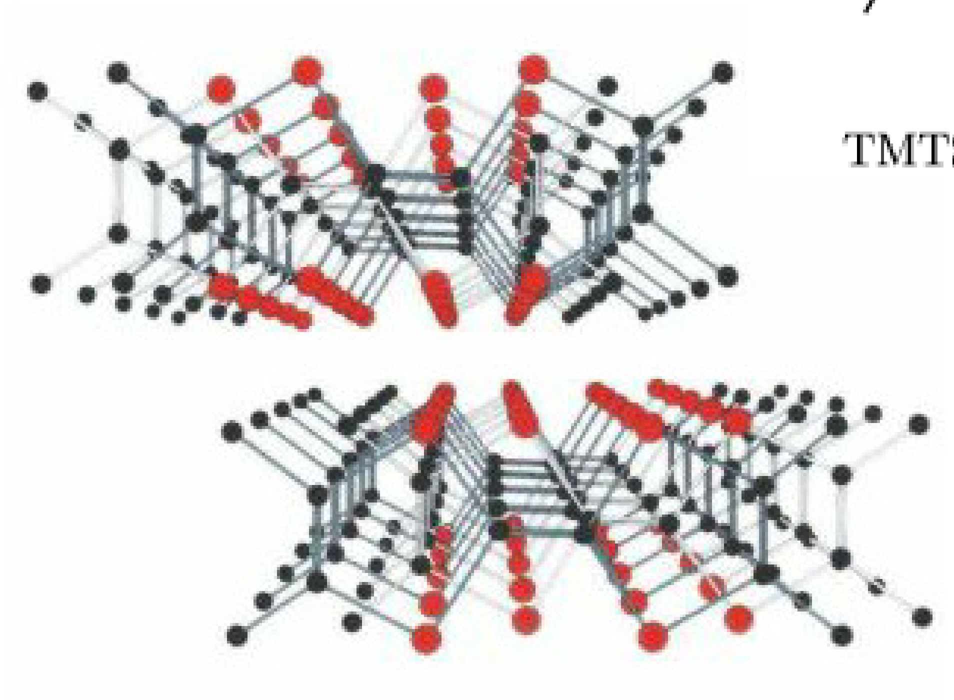
[Cu(HF$_2$)(pyz)$_2$]ClO$_4$
HF$_2^-$ ion

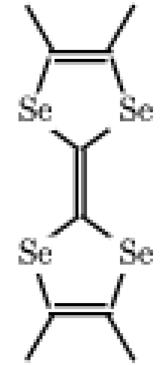
T Lancaster *et al.* PRL **99** 267601 (2007)


That's all Folks!

TMTSF salts





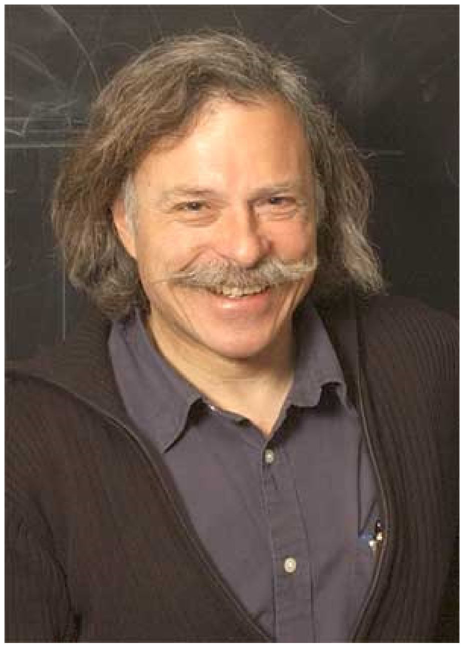


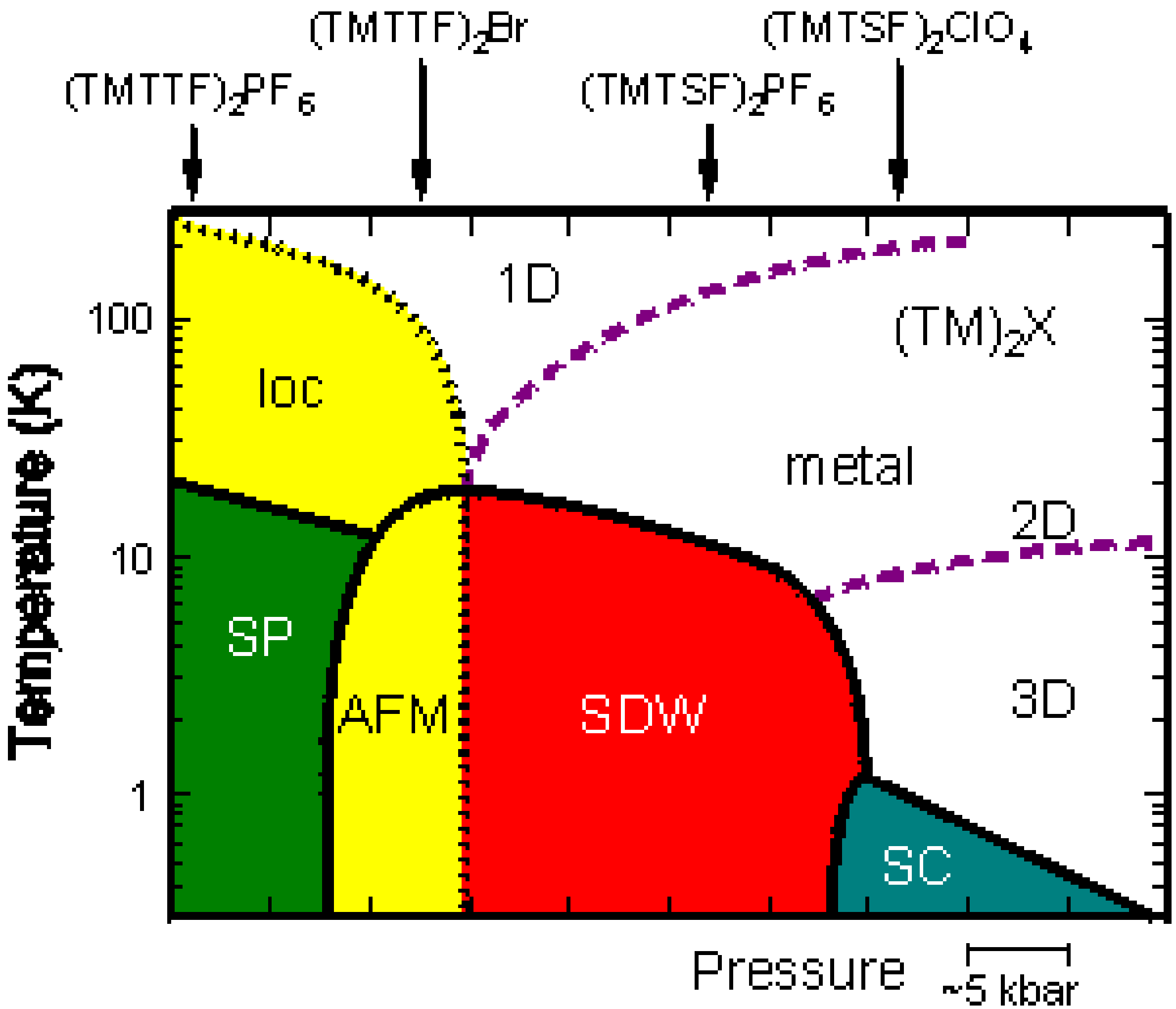
TMTSF

Stacks of TMTSF molecules $\Rightarrow$ 1D chains

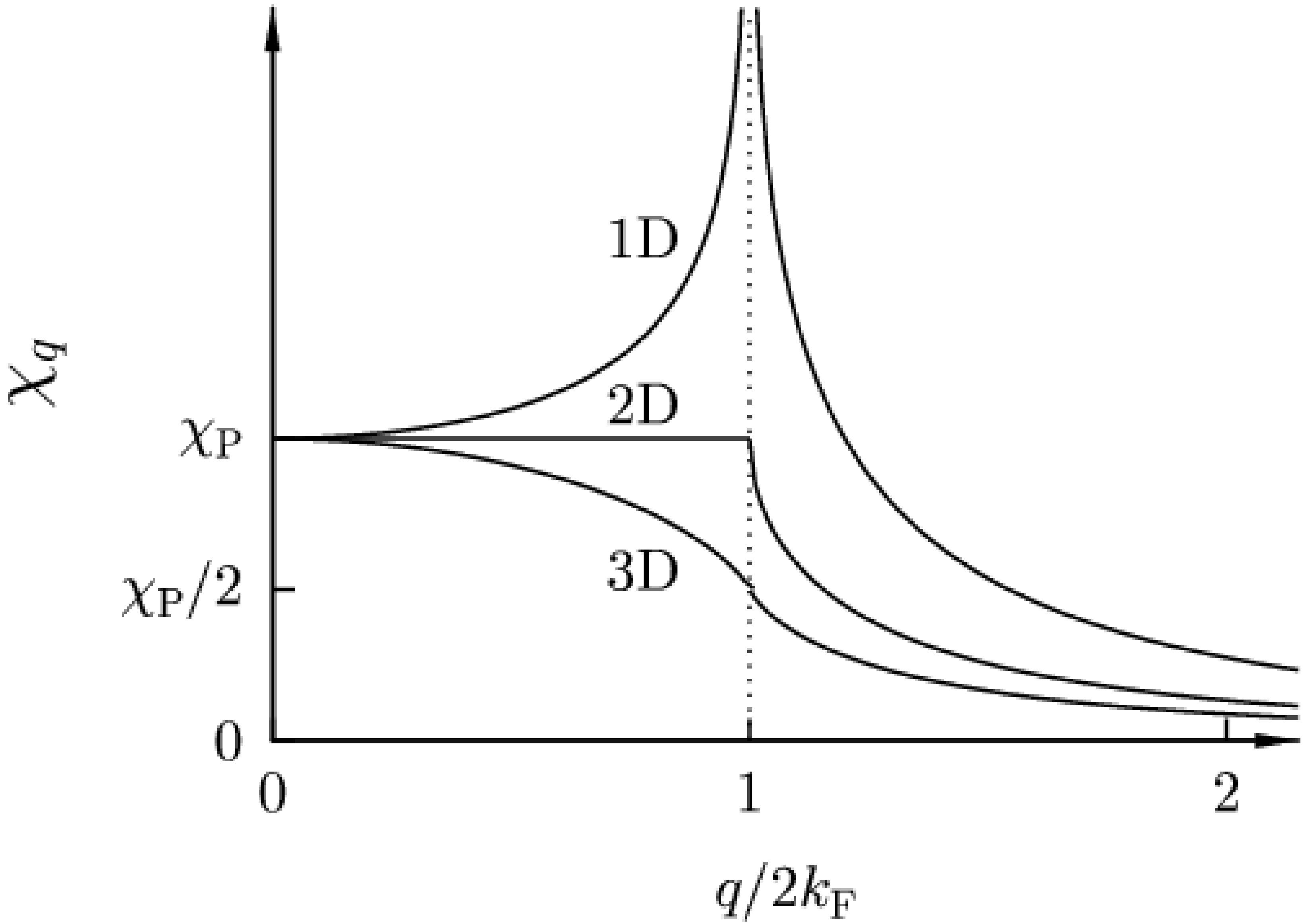
TMTSF salts

Very rich
phase diagram

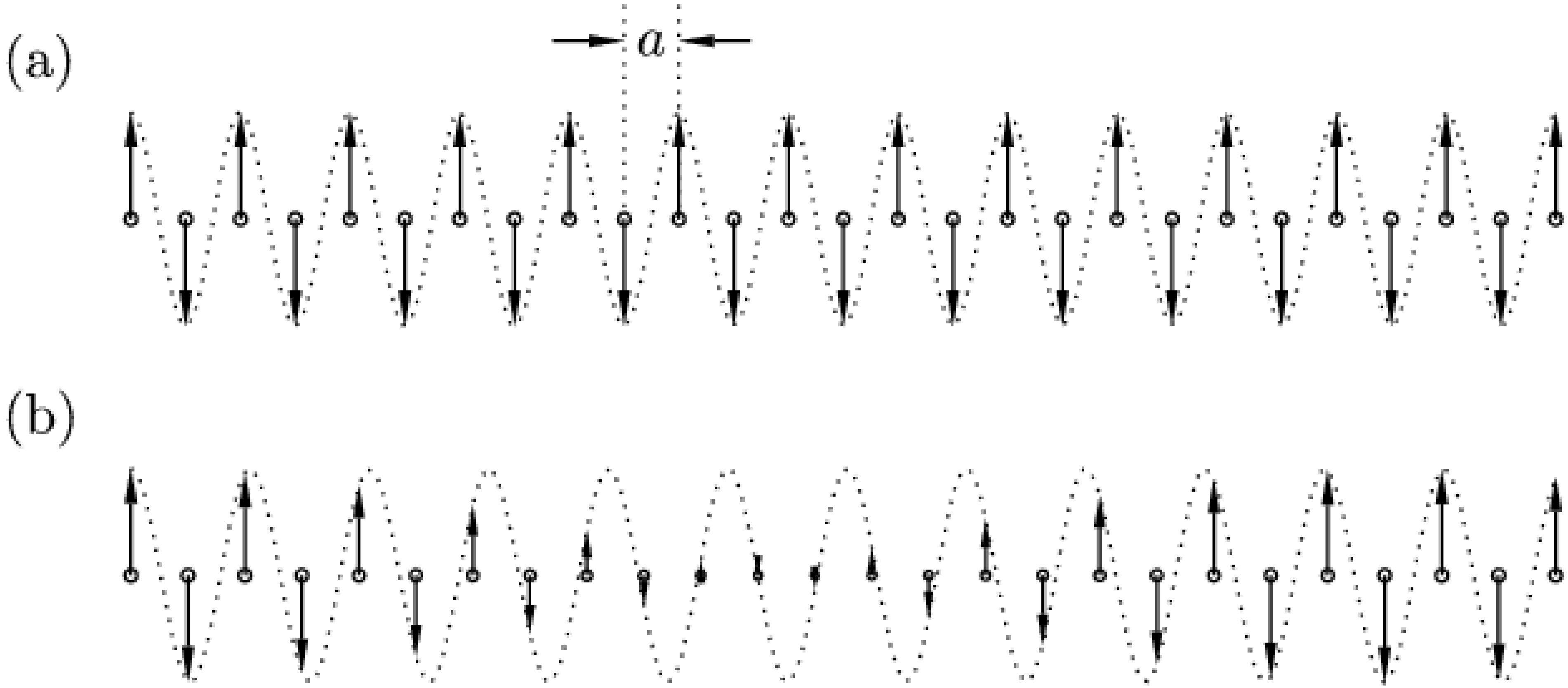




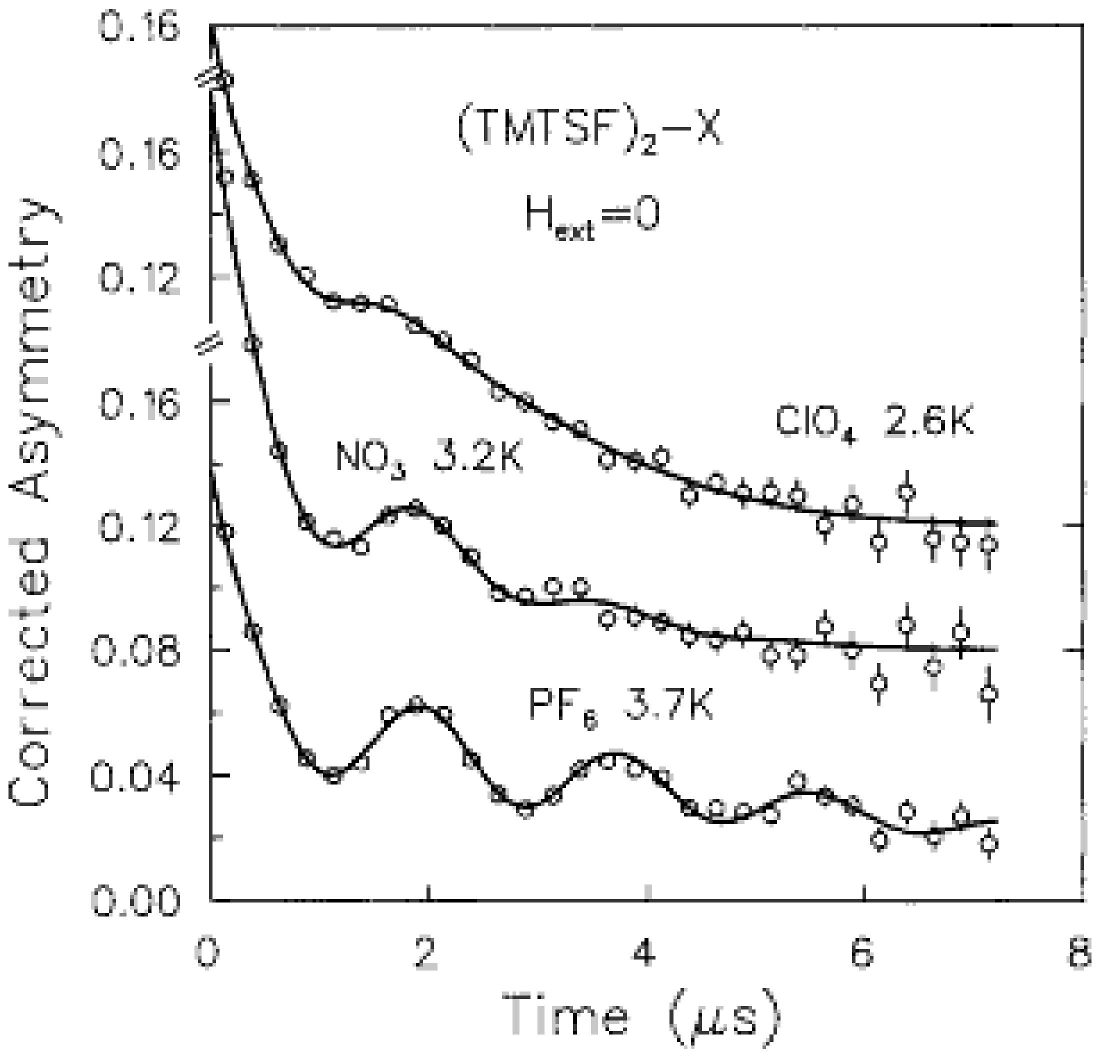
1D electron gas unstable to SDW formation



Spin-density wave

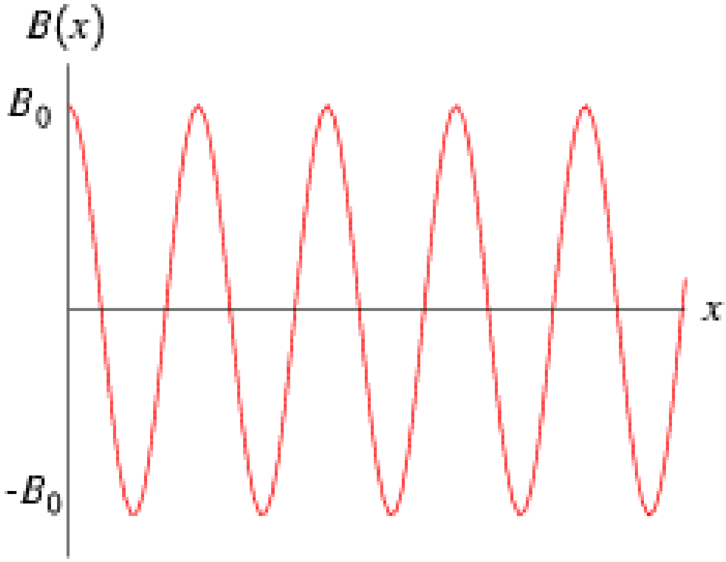


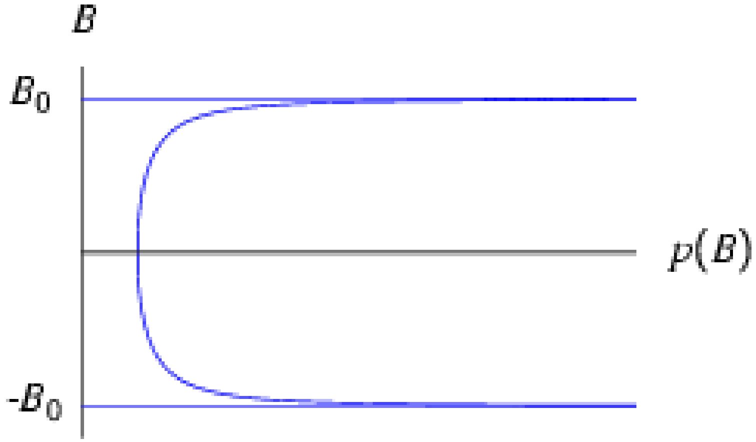
Raw muon data on $TMTSF_2X$



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

Spin density wave system: μ^+SR response





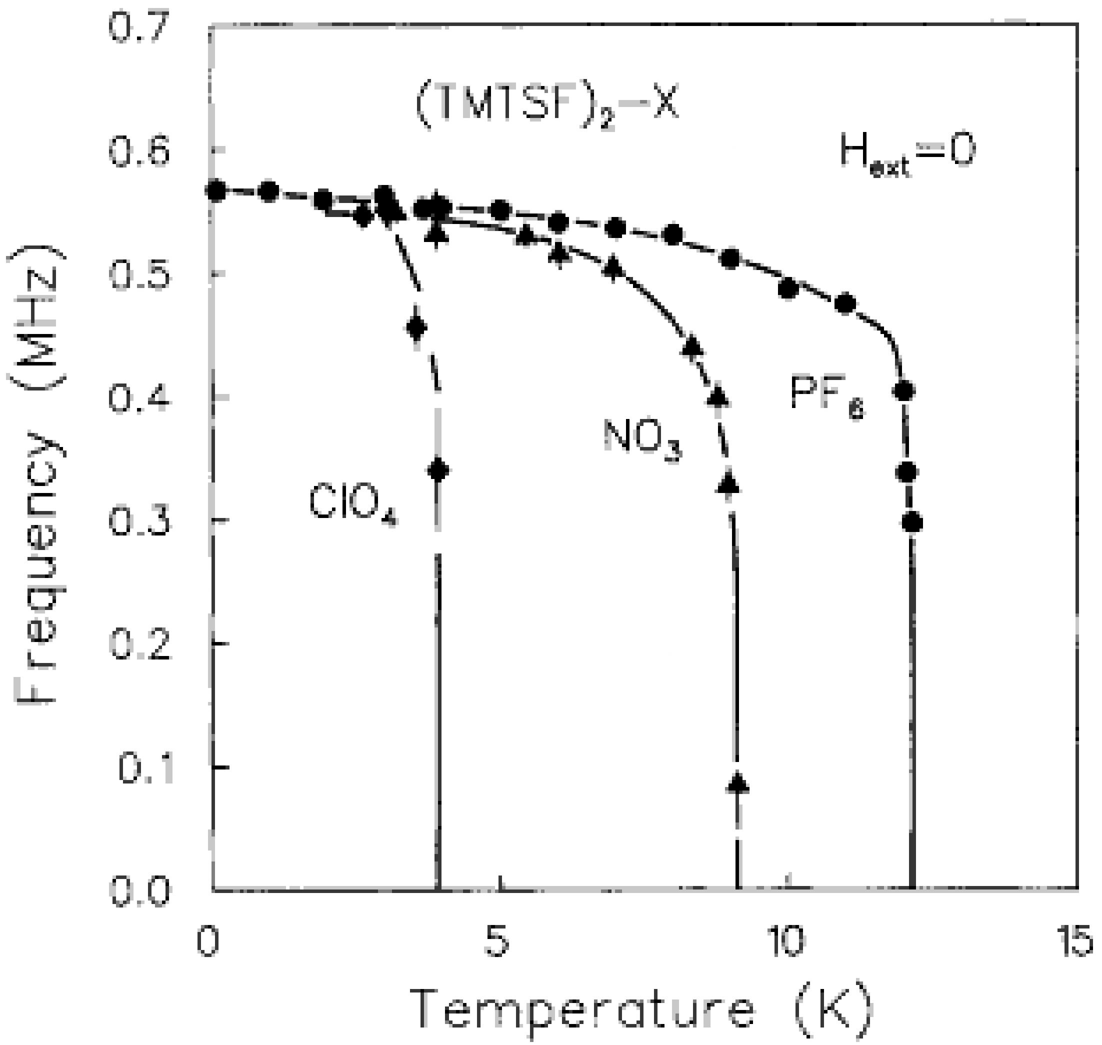
$$B(x) = B_0 \cos(x)$$

$$p(B) = \frac{2}{\pi} \frac{1}{(B^2 - B_0^2)^{-\frac{1}{2}}}$$

$$A(t) = \int_{-B_0}^{B_0} p(B) \cos(\gamma_\mu B t) \mathrm{d}B = J_0(\gamma_\mu B t)$$

Note also that as $\eta >> 1$ $\quad J_0(\eta) \sim (\frac{2}{\pi\eta})^{\frac{1}{2}} \cos(\eta - \pi/4)$

SDW phase in $(TMTSF)_2X$



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