Complementary techniques

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Lecture plan

- Magnetization
- Spin precession: NMR and ESR
- Some examples of NMR
- Muon-spin rotation
- Some examples of μSR

Magnetic moment

Magnetic moment:

$$\boldsymbol{\mu} = \gamma \mathbf{L}$$

Energy:

$$E = -\boldsymbol{\mu} \cdot \mathbf{B}$$

Torque:

$$\mathbf{G} = \boldsymbol{\mu} \times \mathbf{B}$$

$$\frac{\mathrm{d}\boldsymbol{\mu}}{\mathrm{d}t} = \gamma \boldsymbol{\mu} \times \mathbf{B}$$

Magnetic moment

Magnetic moment comes from thermodynamics, via the partition function *Z*

$$F = -k_{\mathrm{B}} T \ln Z$$

$$\mu = -\left(\frac{\partial F}{\partial B}\right)_T$$

Magnetization

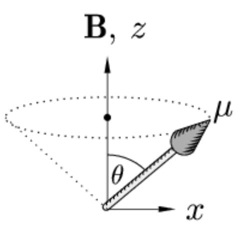
Magnetization is the magnetic moment per unit volume

$$M = \frac{\text{magnetic moment}}{\text{volume}}$$

Susceptibility is a bulk measurement
measures "volume-averaged" magnetic properties.

$$\chi = \lim_{\delta H \to 0} \frac{\delta M_{\mathrm{av}}}{\delta H} \qquad M_{\mathrm{av}} = \frac{1}{V}\int_V M \,\mathrm{d}V$$

Spin precession



$$\hat{\mathcal{H}} = g\mu_{\mathrm{B}} \mathbf{B} \cdot \hat{\mathbf{S}} = g\mu_{\mathrm{B}} B \hat{S}_z.$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \hat{\mathbf{S}} \rangle = \frac{1}{\mathrm{i}\hbar}\langle [\hat{\mathbf{S}}, \hat{\mathcal{H}}] \rangle = -\frac{g\mu_{\mathrm{B}}}{\hbar}\langle \hat{\mathbf{S}} \rangle \times \mathbf{B},$$

$$\gamma = -\frac{g\mu_{\mathrm{B}}}{\hbar} = -\frac{ge}{2m_{\mathrm{e}}}.$$

Consider the case in which $\mathbf{B}$ is along the z-direction and $\boldsymbol{\mu}$ is initially at an angle of θ to $\mathbf{B}$ and in the xz plane. Then

$$\begin{aligned} \dot{\mu}_x &= \gamma B \mu_y \\ \dot{\mu}_y &= -\gamma B \mu_x \\ \dot{\mu}_z &= 0, \end{aligned}$$

so that μ_z is constant with time and μ_x and μ_y both oscillate. Solving these differential equations leads to

$$\begin{aligned} \mu_x(t) &= |\boldsymbol{\mu}| \sin\theta \cos(\omega_{\mathrm{L}} t) \\ \mu_y(t) &= |\boldsymbol{\mu}| \sin\theta \sin(\omega_{\mathrm{L}} t) \\ \mu_z(t) &= |\boldsymbol{\mu}| \cos\theta, \end{aligned}$$

where

$$\omega_{\mathrm{L}} = \gamma B$$

is called the **Larmor precession frequency**.

Relaxation to equilibrium

Both the quantum mechanical and classical treatments of spin precession have left out thermodynamics!

The spin system will eventually come to equilibrium, which means no net magnetization (in the case of zero field) or very small magnetization (in the case of non-zero applied field).

Relaxation to equilibrium

Two relaxation times:

T_1 = **spin-lattice relaxation time**
= longitudinal relaxation time

(involves a change of energy)

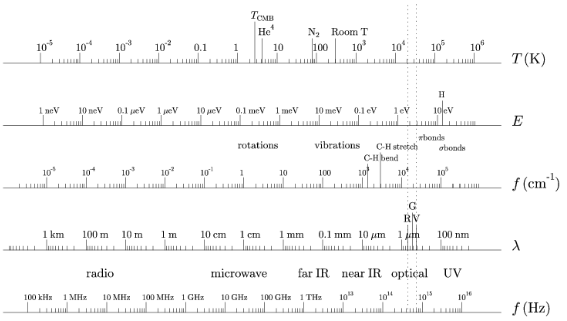
T_2 = **spin-spin relaxation time**
= transverse relaxation time

(does not involve a change of energy)

Bloch equations

$$\begin{aligned} \frac{\mathrm{d}M_x}{\mathrm{d}t} &= \gamma(\mathbf{M}\times\mathbf{B})_x - \frac{M_x}{T_2}, \\ \frac{\mathrm{d}M_y}{\mathrm{d}t} &= \gamma(\mathbf{M}\times\mathbf{B})_y - \frac{M_y}{T_2}, \\ \frac{\mathrm{d}M_z}{\mathrm{d}t} &= \gamma(\mathbf{M}\times\mathbf{B})_z + \frac{M_0 - M_z}{T_1} \end{aligned}$$

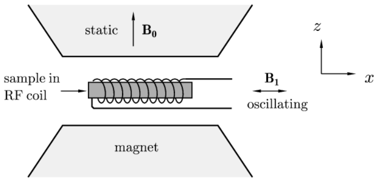
Couple to EM radiation



Nuclear magnetic resonance

Nucleus	Z	N	I	μ/μ_{N}	g_I	ν (in MHz for $B = 1$ T)
n	0	1	$\frac{1}{2}$	-1.913	-3.826	29.17
p=^{1}H	1	0	$\frac{1}{2}$	2.793	5.586	42.58
d=^{2}H	1	1	1	0.857	0.857	6.536
t=^{3}H	1	2	$\frac{1}{2}$	-2.128	4.255	32.43
^{12}C	6	6	0	0	0	0
^{13}C	6	7	$\frac{1}{2}$	0.702	1.404	10.71
^{14}N	7	7	1	0.404	0.404	3.076
^{16}O	8	8	0	0	0	0
^{17}O	8	9	$\frac{5}{2}$	-1.893	-0.757	5.772
^{19}F	9	10	$\frac{1}{2}$	2.628	5.257	40.05
^{31}P	15	16	$\frac{1}{2}$	1.132	2.263	17.24
^{33}S	16	17	$\frac{3}{2}$	0.643	0.429	3.266

Nuclear magnetic resonance

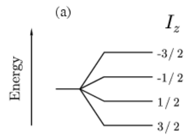


Nuclear magnetic resonance

I=3/2 nucleus

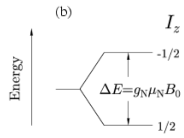
e.g. Na or Cu

selection rule $\Delta m_I = \pm 1$



I=1/2 nucleus

e.g. for a proton, I=1/2, for B~1 T, the energy splitting is ~ 10^{-7} eV ~ 1 mK



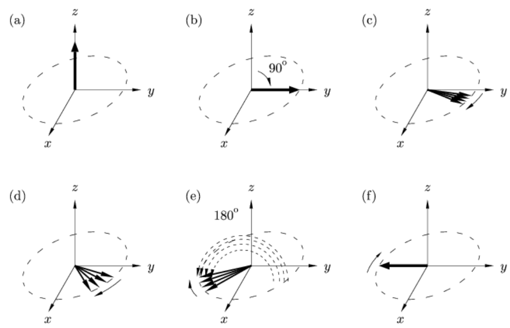
Nuclear magnetic resonance

Measurement of T_2 using a free induction decay

Use short 90° pulse to flip the nuclear spins, then watch them precess in the magnetic field

Resulting interference pattern results from inequivalent sites in system (e.g. chemical shifts)

Spin echo

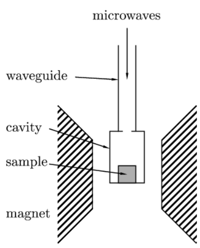


Electron spin resonance

Sample sits in resonant cavity (with high *Q* factor)

Microwave radiation enters via a waveguide

The microwave absorption is studied as a function of the magnetic field *B*



Electron spin resonance

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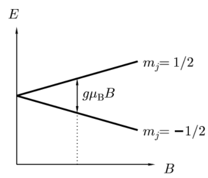
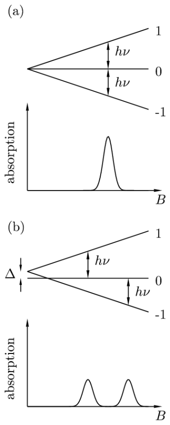
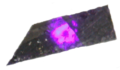


Ni^{2+} with no crystal field (leads to a single ESR line)

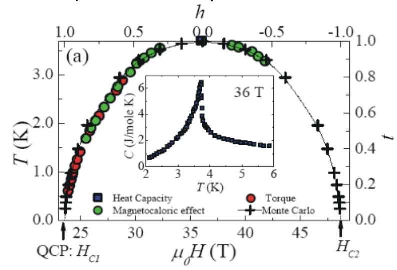
Ni^{2+} in an octahedral environment which leads to a crystal field splitting (leads to 2 ESR lines)



$BaCuSi_2O_6$



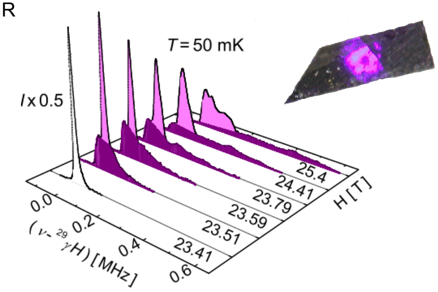
Cu-dimer system exhibiting a Bose-Einstein condensation quantum critical point



M. Jaime et al. PRL 93, 087203 (2004); S. E. Sebastian et al. PRB 74, 180401 (2006)

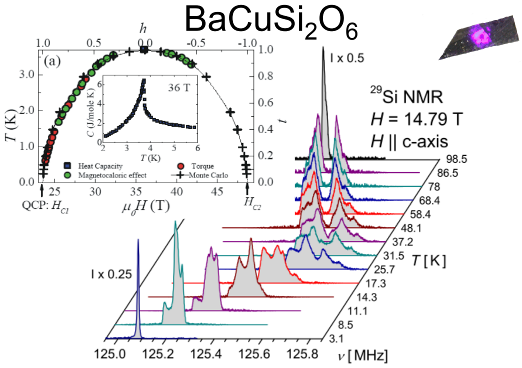
$BaCuSi_2O_6$

^{29}Si NMR



S. Krämer et al. PRB 76, 100406(R) (2007)

$BaCuSi_2O_6$

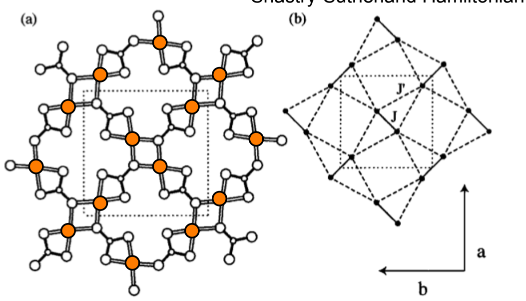


S. Kramer et al. PRB 76, 100406(R) (2007)

$SrCu_2(BO_3)_2$

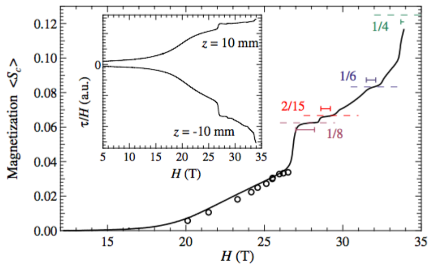
Cu: S=1/2 spins

Shastry-Sutherland Hamiltonian



$SrCu_2(BO_3)_2$

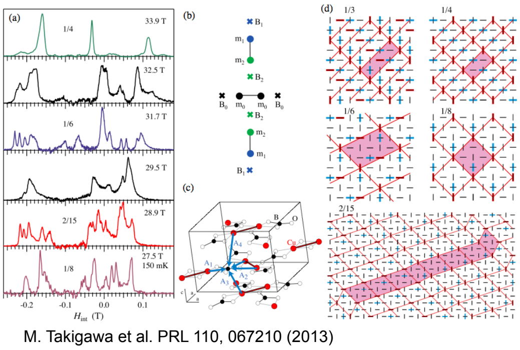
Magnetization plateaux



M. Takigawa et al. PRL 110, 067210 (2013)

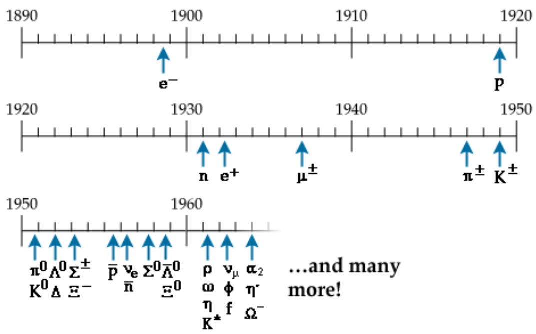
$SrCu_2(BO_3)_2$

^{11}B-NMR



M. Takigawa et al. PRL 110, 067210 (2013)

A timeline of particle physics



Electron

mass m_e, charge –e, spin 1/2

moment –1.001μ_B, γ_e=28024.2 MHz/T

lifetime > 4x10^{23} years

Muon

mass 206.8m_e, charge +e, spin 1/2

moment 0.00484μ_B, γ_μ=135.53 MHz/T

lifetime = 2.19903x10^{-6} s

Muon spin rotation (μSR)

Susceptibility is a bulk measurement
measures “volume-averaged” magnetic properties.

$$\chi = \lim_{\delta H \to 0} \frac{\delta M_{av}}{\delta H} \qquad M_{av} = \frac{1}{V}\int_V M \, dV$$

Muon-spin rotation is a local measurement
measures magnetic properties at a local level

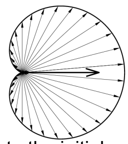
$$\omega_\mu = \frac{B_\mu}{\gamma_\mu} \qquad B_\mu \propto M \qquad p(M) \Longrightarrow p(B_\mu)$$

What the technique is not!
(mistakes to avoid)

- “~~Mu[illegible]ng~~” – no, the muons stop in the sample and they do not scatter!
- “~~Mu[illegible]ce~~” - no, unlike NMR and ESR you do not need to use resonant techniques (though you can).

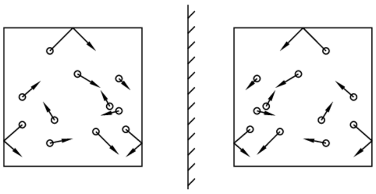
Muon spin rotation (μSR)

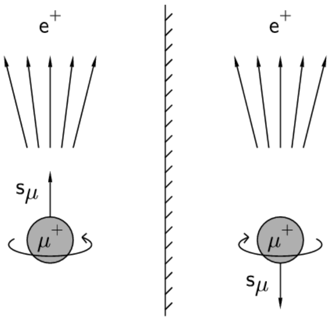
- Muons produced via pion decay:
  $$\pi^+ \to \mu^+ + \nu_\mu$$
  PION MUON NEUTRINO
- Muons 100% spin polarized, speed~c/4, K.E.~4 MeV.
- Muon decays into a positron:
  $$\mu^+ \to e^+ + \nu_e + \bar{\nu}_\mu$$
  MUON POSITRON NEUTRINOS



- Positron decay is asymmetric with respect to the initial muon-spin polarization because of parity violation (weak interaction)

(see S.J. Blundell, Contemp. Phys. **40**, 175 (1999))

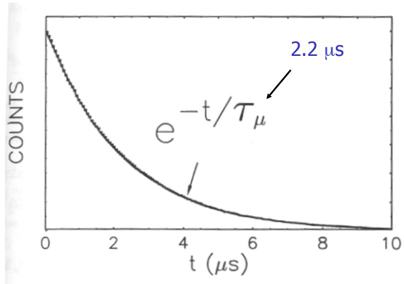




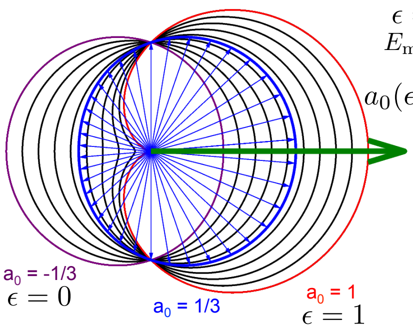
"I cannot believe God is a weak left-hander"

Wolfgang Pauli
(1900-1958)

Every single μSR experiment….
…looks like this



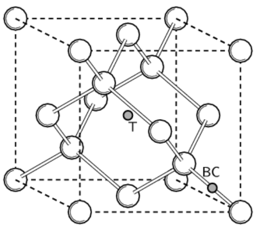
$$\epsilon = E/E_{\max}$$
$$E_{\max} = 52\,\mathrm{MeV}$$
$$a_0(\epsilon) = \frac{2\epsilon - 1}{3 - 2\epsilon}$$

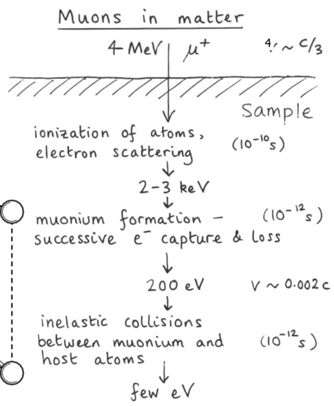


$$p(\theta) \propto 1 + a_0(\epsilon)\cos\theta$$

μSR worldwide

Muons STOP in a sample, they do not diffract, or reflect

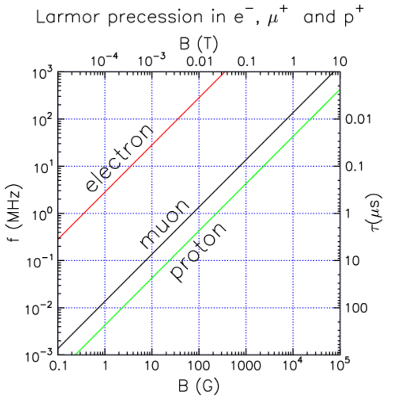




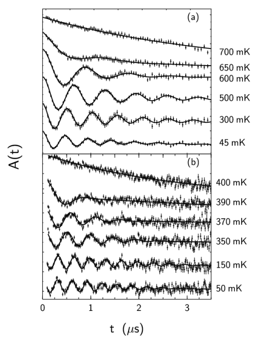
$\omega_e = \gamma_e B_e$

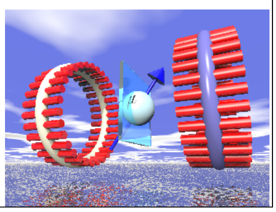
$\omega_\mu = \gamma_\mu B_\mu$

$\omega_p = \gamma_p B_p$

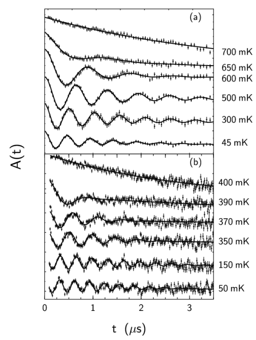


μSR of ordered magnets





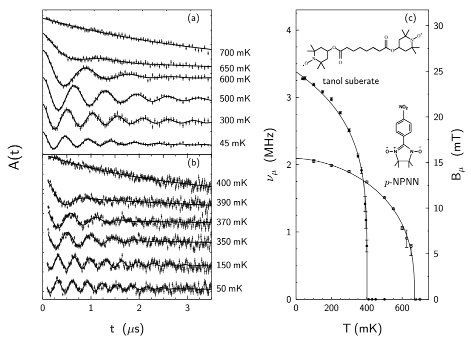
μSR of ordered magnets



Ferromagnet

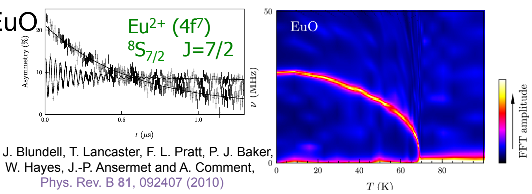
Antiferromagnet

μSR of ordered magnets



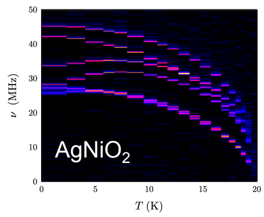
Zero-field data

EuO



S. J. Blundell, T. Lancaster, F. L. Pratt, P. J. Baker, W. Hayes, J.-P. Ansermet and A. Comment, Phys. Rev. B **81**, 092407 (2010)

$AgNiO_2$

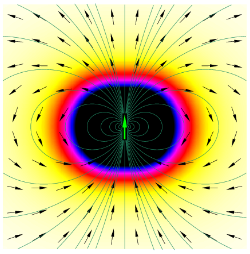


T. Lancaster, S. J. Blundell, P. J. Baker, M. L. Brooks, W. Hayes, F. L. Pratt, R. Coldea, T. Soergel and M. Jansen, Phys. Rev. Lett. **100**, 017206 (2008)

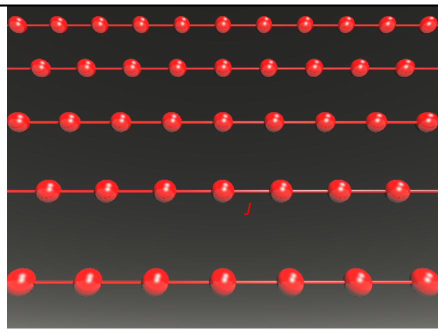
Dipole fields

$$B^{\alpha}(\mathbf{r}_{\mu}) = \sum_{i} D_{i}^{\alpha\beta}(\mathbf{r}_{\mu})\, m_{i}^{\beta}$$

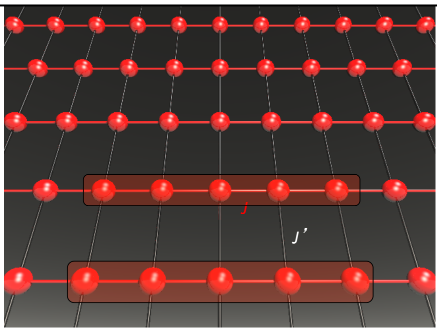
Dipole field at muon-site i^{th} moment



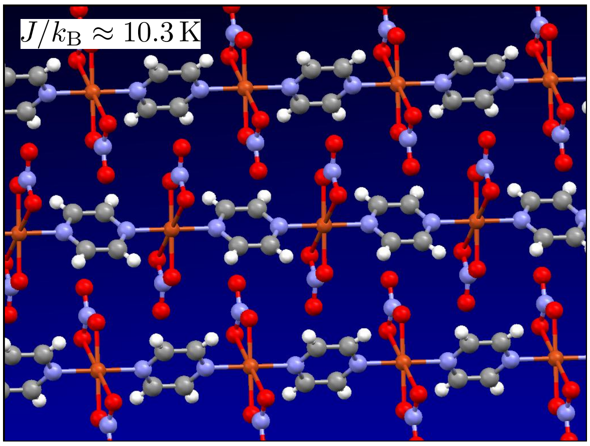
|B|



A purely one-dimensional system will not undergo a transition to long range order (LRO) because fluctuations (entropy) win when *T*>0. Nevertheless, as you cool down, spins begin to correlate and the size of correlated region increases

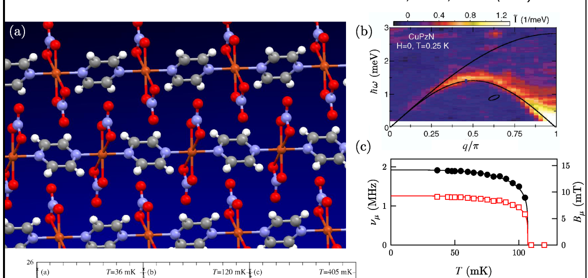


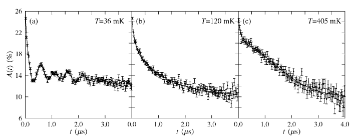
The *interchain exchange J'* can have an effect in driving the system into LRO below a *non-zero* T_c.



$J/k_{\mathrm{B}} \approx 10.3\,\mathrm{K}$

M.B. Stone et al, PRL 91, 037205 (2003)



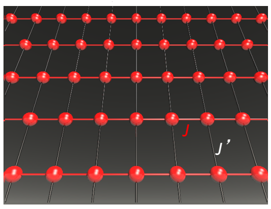


T. Lancaster et al.
Phys Rev B **73**, R020410 (2006)

$T_{\mathrm{N}} = 107\ \mathrm{mK}$

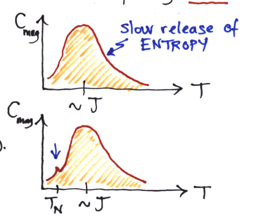
$k_{\mathrm{B}}T_{\mathrm{N}}/J \approx 0.01$

Low-dimensional magnets



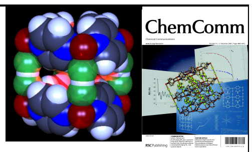
- if $J' \to 0$, no LRO but ξ grows on cooling (roughly $\xi \propto T^{-1}$)

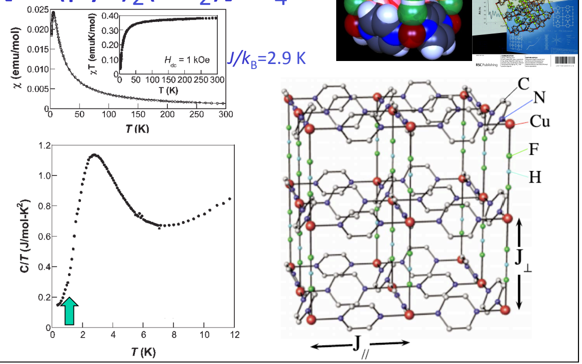
∴ heat capacity broad



- when $J' \neq 0$, get 3D LRO at $T_N \ll J$, but only see SMALL BLIP in heat capacity. This is EASY TO MISS!

A two-dimensional magnet
$[Cu(pyz)_2(HF_2)]BF_4$





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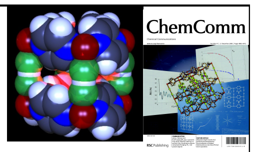
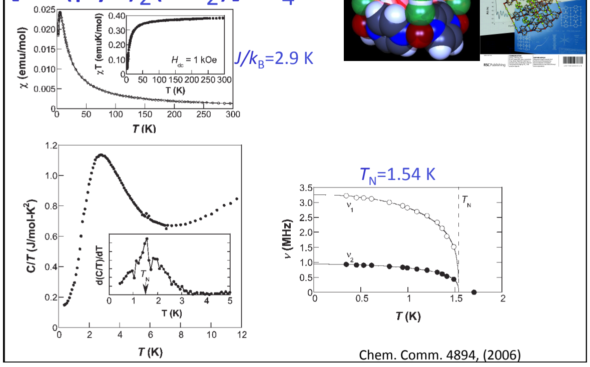
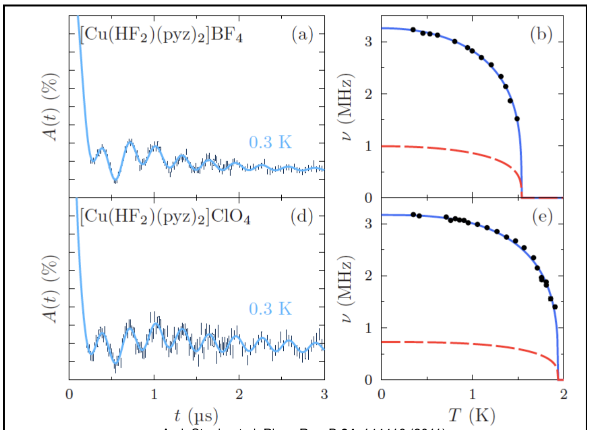
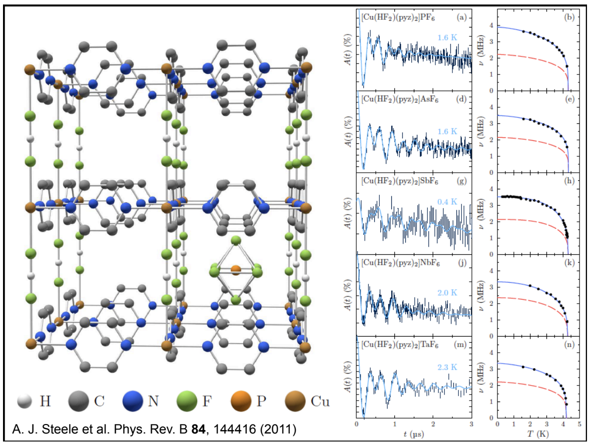




Chem. Comm. 4894, (2006)

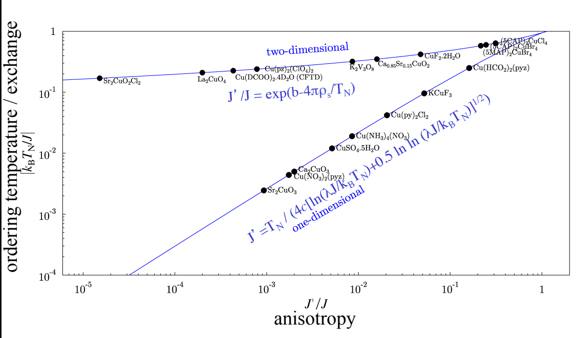


A. J. Steele et al. Phys. Rev. B **84**, 144416 (2011)



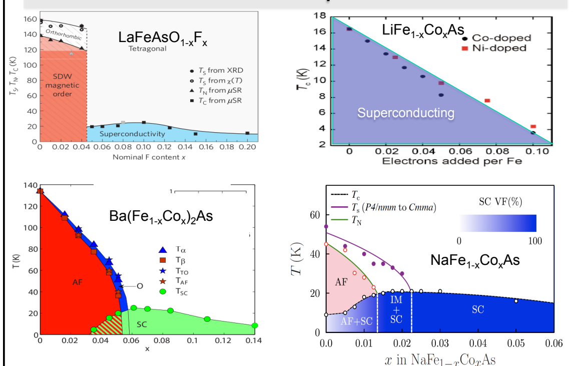
A. J. Steele et al. Phys. Rev. B **84**, 144416 (2011)

Low-dimensional magnets



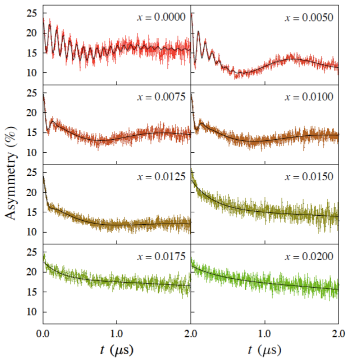
SJB et al., J. Phys. Chem. Solids **68**, 2039 (2007)

New iron-based superconductors



Nature Mat. **8**, 305 (2009); 8, 310 (2009); PRB **80,** 052503 (2009); **79,** 144523 (2009); JPSJ **79**, 113702 (2010)
J. Am. Chem. Soc. **132,** 10467 (2010); PRL **104**, 057007 (2010); PRB **85** 054503 (2012),

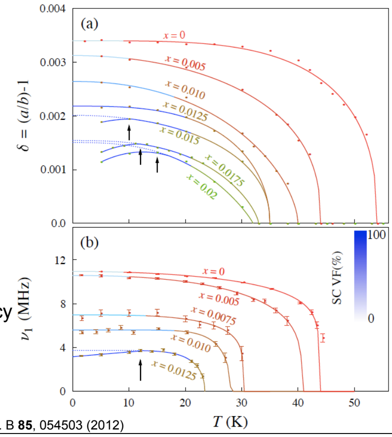
$NaFe_{1-x}Co_xAs$



D. R. Parker et al. Phys. Rev. Lett. **104**, 057007 (2010)
J. D. Wright et al. Phys. Rev. B **85**, 054503 (2012)

structural distortion

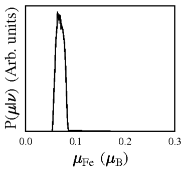
precession frequency

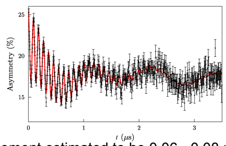


J. D. Wright et al. Phys. Rev. B **85**, 054503 (2012)

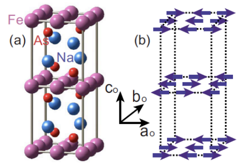
Magnetic moment determination

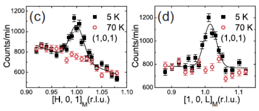
- a Bayesian approach





Moment estimated to be 0.06 - 0.08 μ_B from our muon results





Moment estimated to be 0.09(4) μ_B from neutron diffraction

J. D. Wright et al. Phys. Rev. B **85**, 054503 (2012)
S. Li et al. Phys. Rev. B **80**, 020504 (2009)

Comparison with neutrons

- No problem with Ir, B, etc
- Samples not deuterated
- High throughput of samples
- Sensitive to very weak moments
- Good for problems involving phase separation
- Complementary information on superconductivity
- Local probes have a role to play

BUT

- Lack the direct mapping of S(Q,ω)
- Neutrons best for magnetic structure determination