



# Nuclear magnetic resonance in magnetic systems and metals

**Denis Arčon**

*University of Ljubljana, Faculty of  
mathematics and physics, Slovenia*

*Institute "Jozef Stefan", Ljubljana, Slovenia*



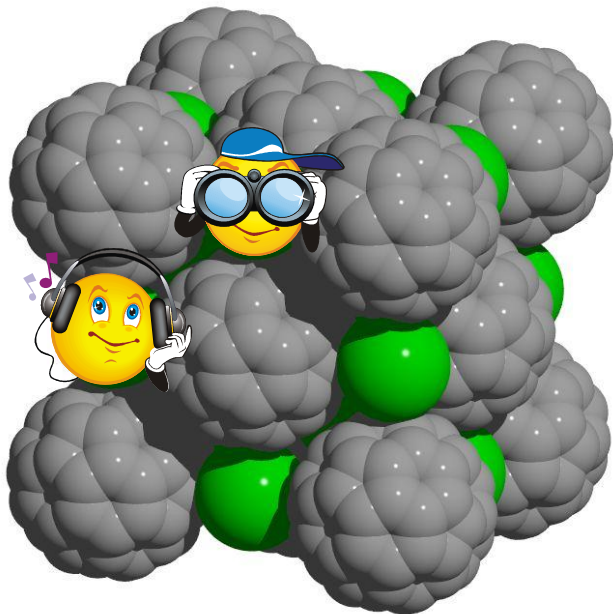
**Durham**  
University



# Motivation

Solid-state physics:

- Crystal structure and lattice dynamics,
- Electronic properties,
- Magnetism, (anti)ferroelectrics, multiferroics
- Superconductors



Experimentalists toys:

Scattering techniques:

- XRD
- Neutron diffraction

Measurements of macroscopic properties:

- Dielectric spectroscopy,
- Magnetization measurements (SQUID, ... )
- Specific heat, thermal conductivity, thermal dilatometry, ...

Vibrational spectroscopies

**Local probes that would be simultaneously sensitive to lattice as well to electrons**





# So, why NMR?

## *Nuclear magnetic resonance (NMR)*

### A TOOL to study condensed matter systems

- Local, microscopic, site-specific probe
- Virtually all elements are NMR active
- study electronic spin structure, lattice structure
  
- Non-invasive – no current, no contacts on the sample
- $\omega_{NMR} \approx 0$  ( $\mu\text{eV}$ ), gives partial  $q$  information (cf. neutron diffraction)
- can be combined with other techniques: transport, magnetization, dielectric, optical, ...
- IJS laboratory: extreme conditions: low temperatures, high pressures, different magnetic fields up to 9.34 T



Elvis is alive and well, working as an NMR spectroscopist in Ljubljana.



# Magnetic resonance - basics

History: **Purcell** (NMR in paraffin), **Bloch** (NMR in H<sub>2</sub>O), **Zavoisky** (EPR)

Magnetic resonance phenomena is found in systems that poses magnetic moments and we are "in tune" with a natural frequency of the magnetic system. **Magnetic resonance technique offers a high resolution experimental probe for the study of static and dynamics properties of local magnetic fields.**

Nuclear magnetic resonance (NMR): typically in the 10-500 MHz range

Electron paramagnetic resonance (EPR): typically in the 1-100 GHz range

NMR is utilized widely not only in physics and/or chemistry but also in medical diagnostics (MRI) and so on.

- Physics

**Condensed matter physics**

- Chemical

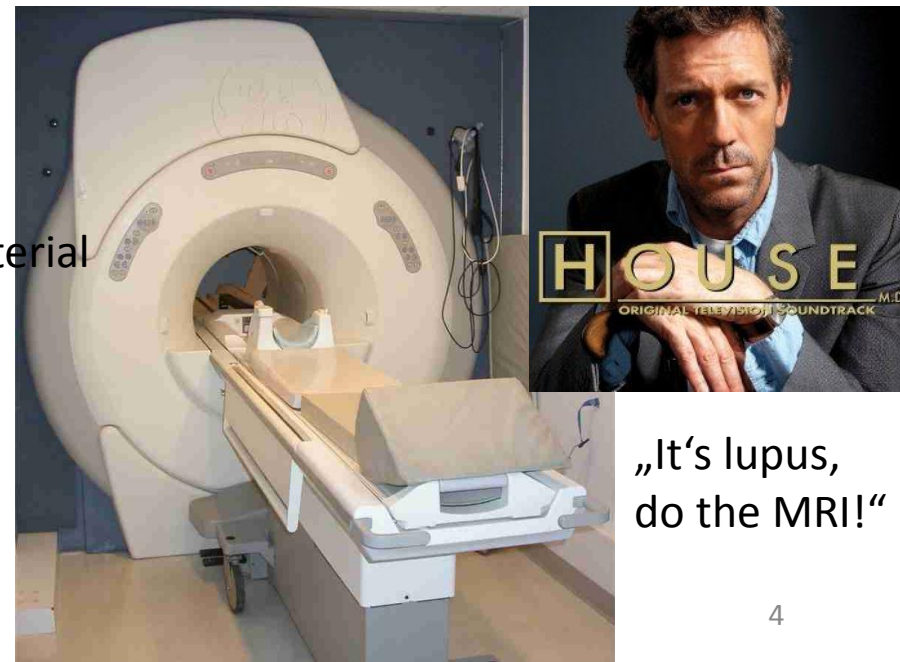
Analysis and/or identification of material

- Biophysics

Analysis of Protein structure

- Medical

MRI (Magnetic Resonance Imaging)





# Outline

Lesson	Subject
1	Introduction to magnetic resonance; Bloch equations, relaxation times, dynamics susceptibility
2	The basic spin Hamiltonian for NMR
3	Hyperfine coupling interaction, Knight shift
4	The Moriya theory of spin-lattice relaxation
5	NMR in the superconducting state (just briefly)
6	NMR in the magnetically ordered state
7	Examples: fullerides, pnictides and quasi-1D magnetoelectric system



# Magnetic resonance - basics

## Nuclear magnetic moments:

A system such as nucleus may consist of many particles coupled together so that for a given state the nucleus possesses a total magnetic moment  $\mu$  related to a total angular momentum  $I$

$$\vec{\mu} = \gamma \vec{I} \quad \text{QM:} \quad \hat{\Gamma} = \hbar \hat{I} \Rightarrow \hat{\mu} = \gamma_N \hbar \hat{I}$$

Here  $\gamma$  is a scalar called gyromagnetic ratio and is typical for nuclei or electrons.

Simple model:

$$\mu = iS = i\pi r^2 ; \Gamma = mvr = m(2\pi/T)r ; i = e/T \rightarrow \gamma = e/2m$$

$\gamma$  thus decreases with increasing particle mass

	$\gamma$ [MHz/T]	$\nu$ [MHz]
proton	$2.675 \times 10^2$	42.58 $B_0$ [T]
electron	$1.759 \times 10^5$	27990 $B_0$ [T]

# Magnetic resonance - basics

Nucleus	$\gamma/2\pi$ (MHz/T)
$^1\text{H}$	42.576
$^2\text{H}$	6.53566
$^3\text{He}$	-32.434
$^7\text{Li}$	16.546
$^{13}\text{C}$	10.705
$^{14}\text{N}$	3.0766
$^{15}\text{N}$	-4.3156
$^{17}\text{O}$	-5.7716
$^{23}\text{Na}$	11.262
$^{63}\text{Cu}$	11.284
$^{65}\text{Cu}$	12.109
$^{51}\text{V}$	11.193
$^{31}\text{P}$	17.235
$^{129}\text{Xe}$	-11.777

Group	I	II	IIIa	IVa	Va	VIa	VIIa	VIIIa	VIIIb	VIIIc	IB	IIB	III	IV	V	VI	VII	VIII										
Period																												
1	1 <a href="#">H</a>																	2 <a href="#">He</a>										
2	3 <a href="#">Li</a>	4 <a href="#">Be</a>											5 <a href="#">B</a>	6 <a href="#">C</a>	7 <a href="#">N</a>	8 <a href="#">O</a>	9 <a href="#">F</a>	10 <a href="#">Ne</a>										
3	11 <a href="#">Na</a>	12 <a href="#">Mg</a>											13 <a href="#">Al</a>	14 <a href="#">Si</a>	15 <a href="#">P</a>	16 <a href="#">S</a>	17 <a href="#">Cl</a>	18 <a href="#">Ar</a>										
4	19 <a href="#">K</a>	20 <a href="#">Ca</a>	21 <a href="#">Sc</a>	22 <a href="#">Ti</a>	23 <a href="#">V</a>	24 <a href="#">Cr</a>	25 <a href="#">Mn</a>	26 <a href="#">Fe</a>	27 <a href="#">Co</a>	28 <a href="#">Ni</a>	29 <a href="#">Cu</a>	30 <a href="#">Zn</a>	31 <a href="#">Ga</a>	32 <a href="#">Ge</a>	33 <a href="#">As</a>	34 <a href="#">Se</a>	35 <a href="#">Br</a>	36 <a href="#">Kr</a>										
5	37 <a href="#">Rb</a>	38 <a href="#">Sr</a>											39 <a href="#">Y</a>	40 <a href="#">Zr</a>	41 <a href="#">Nb</a>	42 <a href="#">Mo</a>	Tc	44 <a href="#">Ru</a>	45 <a href="#">Rh</a>	Pd	47 <a href="#">Ag</a>	48 <a href="#">Cd</a>	49 <a href="#">In</a>	50 <a href="#">Sn</a>	51 <a href="#">Sb</a>	52 <a href="#">Te</a>	53 <a href="#">I</a>	54 <a href="#">Xe</a>
6	55 <a href="#">Cs</a>	56 <a href="#">Ba</a>	* 71 <a href="#">Lu</a>	72 <a href="#">Hf</a>	73 <a href="#">Ta</a>	74 <a href="#">W</a>	75 <a href="#">Re</a>	76 <a href="#">Os</a>	77 <a href="#">Ir</a>	78 <a href="#">Pt</a>	79 <a href="#">Au</a>	80 <a href="#">Hg</a>	81 <a href="#">Tl</a>	82 <a href="#">Pb</a>	83 <a href="#">Bi</a>	84 Po	85 At	86 <a href="#">Rn</a>										
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 <a href="#">La</a>	58 Ce	59 <a href="#">Pr</a>	60 <a href="#">Nd</a>	61 Pm	62 <a href="#">Sm</a>	63 <a href="#">Eu</a>	64 <a href="#">Gd</a>	65 <a href="#">Tb</a>	66 <a href="#">Dy</a>	67 <a href="#">Ho</a>	68 <a href="#">Er</a>	69 <a href="#">Tm</a>	70 <a href="#">Yb</a>												
**Actinides			** 89 Ac	90 Th	91 Pa	92 <a href="#">U</a>	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

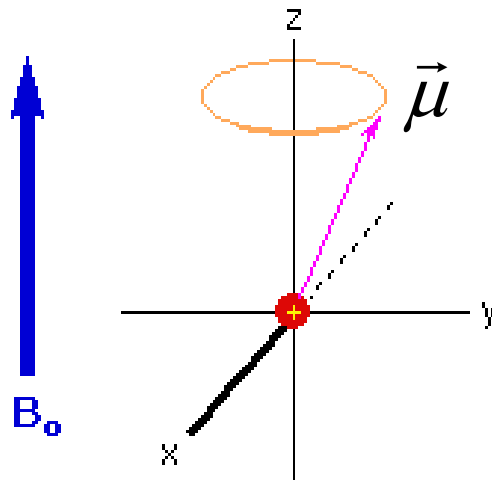
Isotope	Natural Abundance (%)	Nuclear Spin (I)	Magnetogyric ratio ( $10^7 \cdot \text{rad/T} \cdot \text{s}$ )	Quadruple moment ( $10^{28} \cdot \text{Q/m}^2$ )	Resonance frequency (MHz) at 11.744T (500 MHz for $^1\text{H}$ )	Relative sensitivity ( $^1\text{H}=1.00$ )	Absolute sensitivity ( $^1\text{H}=1.00$ )
$^1\text{H}$	99.98	1/2	26.7519	0	500.000	1.00	1.00
$^2\text{H}$	$1.5 \cdot 10^{-2}$	1	4.1066	$2.8 \cdot 10^{-3}$	76.753	$9.65 \cdot 10^{-6}$	$1.45 \cdot 10^{-6}$
$^3\text{H}$	0	1/2	28.535	0	533.317	1.21	0

# Magnetic moment in the external magnetic field

- Torque on the magnetic moment:  $\vec{T} = \vec{\mu} \times \vec{B}$
- Change of the angular momentum

$$\frac{d\vec{L}}{dt} = \vec{\mu} \times \vec{B} \Rightarrow \frac{d\vec{\mu}}{dt} = \gamma \vec{\mu} \times \vec{B}$$

Larmor precession



$$\omega_L = \gamma_N B_0$$

Larmor frequency

Typically in the rf range up  
several hundred MHz



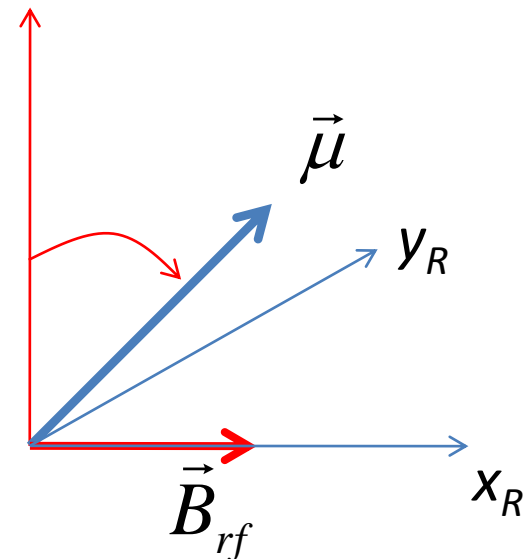
# Effect of rf field

- But, in order to see precession, we first need to shift magnetization away from the z-axis. This is the job of rf pulses.
- In the rotating frame, that rotates with Larmor frequency  $\omega_L$ ,  $\mu$  is static  $\rightarrow B_{eff} = B_0 - \omega_L/\gamma = 0$ .
- rf field  $B_{10} \cos(\Omega t) = B_R + B_L$
- Rotation around the  $x_R$  axis

90° pulse

$$\tau_W \gamma B_{10} = \pi/2$$

$$B_{eff}^R = 0$$



$B_{10}$  of the order of 10 mT

# Magnetic resonance - basics

Quantum mechanics: we have to treat  $\mu$  and  $\Gamma$  as operators.

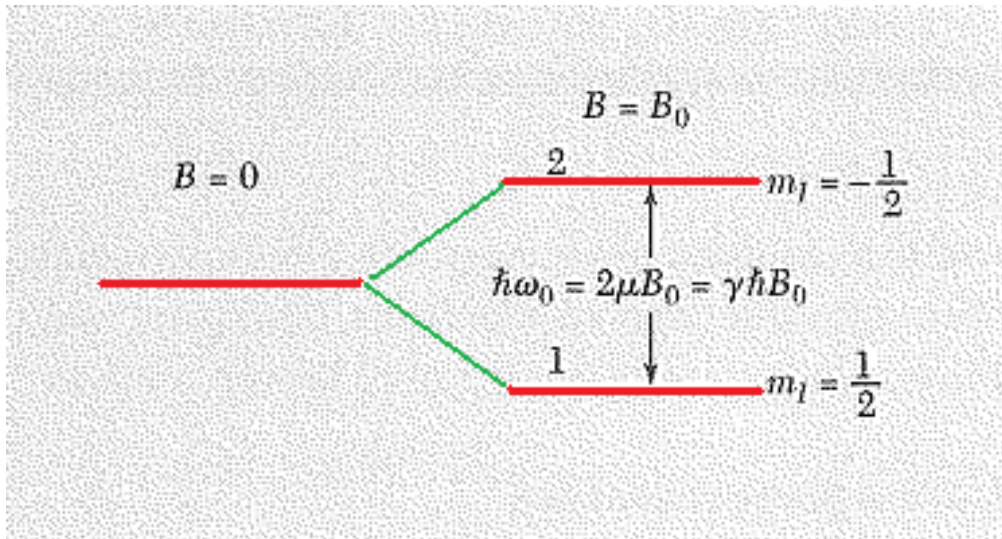
$$\hat{\Gamma} = \hbar \hat{I} \Rightarrow \hat{\mu}_n = \gamma_n \hbar \hat{I}$$

In an applied field,  $\hat{H}_Z = -\hat{\mu} \cdot \vec{B} = -\gamma \hbar B_0 \hat{I}_Z$

$$\mathbf{B}_a = B_0 \hat{z} \rightarrow E_m = -\mu_z \cdot B_0 = -\gamma \hbar B_0 m$$

$$m_l = I, I-1, \dots, -I+1, -I$$

Example:  $I = \frac{1}{2}$  (case of  $^1\text{H}$  or  $^{13}\text{C}$  for instance)



In the MR we attempt to detect the splitting of these energy levels by appropriate perturbation. The interaction must be such, that the angular frequency matches the splitting:

**LARMOR FREQUENCY**

$$\hbar\omega_L = \Delta E = \gamma \hbar B_0$$

Which perturbation will trigger the transitions between these levels? R.f. irradiation perpendicular to  $B_0$  will do the job!

$$H_{rf} = -\gamma \hbar B_{rf} \hat{I}_x \cos \omega_L t$$



## Magnetic resonance - basics

Time dependent Schrödinger equation 
$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}_z \psi$$

has the general solution in the form

$$\psi = \sum_m c_m u_{I,m} e^{-iE_m t / \hbar}$$

We can now calculate the expectation value for  $\mu_z$ , for instance

$$\begin{aligned} \langle \mu_z \rangle &= \int \psi^*(t) \hat{\mu}_z \psi(t) d\tau \\ &= \gamma \hbar \sum_{m,m'} c_{m'}^* c_m e^{-i(E_m - E_{m'})t / \hbar} \langle m' | \hat{I}_z | m \rangle \\ &= \gamma \hbar \sum_m m c_m^* c_m \\ &\xrightarrow{I=1/2} = \frac{1}{2} \gamma \hbar (c_{1/2}^* c_{1/2} - c_{-1/2}^* c_{-1/2}) = \frac{1}{2} \gamma \hbar (a^2 - b^2) \end{aligned}$$

Normalised WF:  $c_{1/2}^* c_{1/2} = a^2 \quad \& \quad c_{-1/2}^* c_{-1/2} = b^2$



## Magnetic resonance - basics

The calculation for the expectation value for  $\mu_x$ , is slightly more complicated, but follows the same steps

$$\begin{aligned}\langle \mu_x \rangle &= \int \psi^*(t) \hat{\mu}_x \psi(t) d\tau \\ &= \gamma \hbar \sum_{m, m'} c_m^* c_m e^{-i(E_m - E_{m'})t/\hbar} \langle m' | \hat{I}_x | m \rangle\end{aligned}$$

By recalling

$$\begin{aligned}\hat{I}_+ |I, m\rangle &= \sqrt{I(I+1) - m(m+1)} |I, m+1\rangle \\ \hat{I}_- |I, m\rangle &= \sqrt{I(I+1) - m(m-1)} |I, m-1\rangle\end{aligned}$$

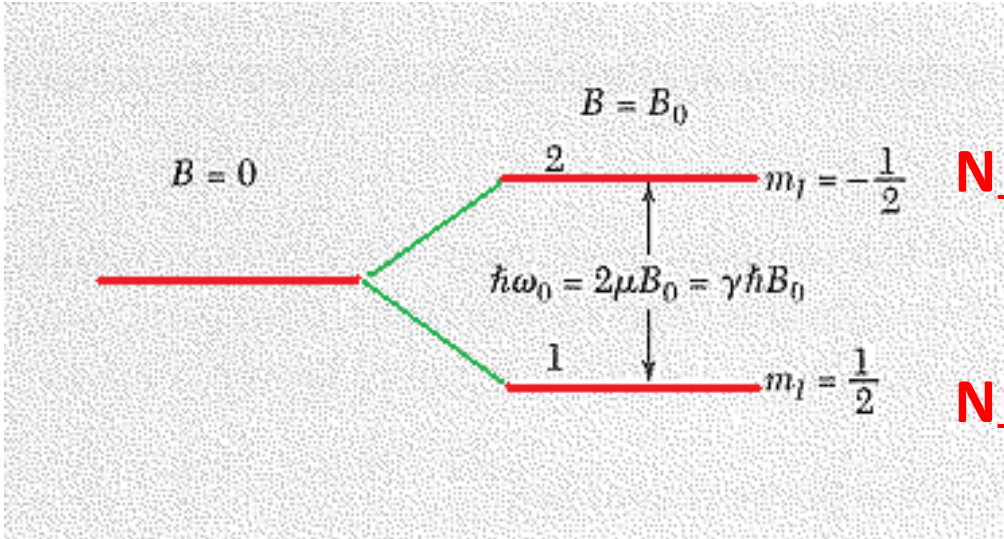
we can derive

$$\langle \mu_x \rangle = \gamma \hbar ab \cos(\omega_0 t + \alpha - \beta)$$

$$\langle \mu_y \rangle = \gamma \hbar ab \sin(\omega_0 t + \alpha - \beta)$$

$$\langle \mu_z \rangle = \frac{1}{2} \gamma \hbar (a^2 - b^2)$$

# Magnetic resonance – basics spin-lattice relaxation



Simple rate equations

$$\frac{dN_+}{dt} = -W_{+-}N_+ + W_{-+}N_-$$

Fermi golden rule:

$$P_{ab} = \frac{2\pi}{\hbar} \left| \langle b | \hat{V} | a \rangle \right|^2 \delta(E_b - E_a - \hbar\omega)$$

$$\left| \langle b | \hat{V} | a \rangle \right|^2 = \left| \langle a | \hat{V} | b \rangle \right|^2 \Rightarrow W_{+-} = W_{-+} \equiv W$$

If we introduce  $n = N_+ - N_-$  and  $N = N_+ + N_-$  then  $N_+ = \frac{1}{2}(N + n)$  and  $N_- = \frac{1}{2}(N - n)$  then we get

$$\frac{dn}{dt} = -2Wn \Rightarrow n(t) = n_0 e^{-2Wt}$$

Initial difference in energy population will exponential decay to zero!



# Magnetic resonance – basics spin-lattice relaxation

Problems:

1. Absorbed power  $dE/dt = N_+ W \hbar \omega_L - N_- W \hbar \omega_L = W \hbar \omega_L n(t)$  will also vanish after some time (not supported by the experiments).
2. What if  $W = 0$  (no perturbation) and we change magnetic field ( $M_z$  should change, what is not predicted by this equation)!

Therefore, there MUST be a process that allows the system to accept (or release) the magnetic energy. It is the coupling to the lattice  $\rightarrow$  spin-lattice relaxation

Thermal equilibrium: difference in the population given by the energy difference

$$\frac{N_-^0}{N_+^0} = e^{-\Delta E/k_B T} = e^{-\gamma \hbar B_0/k_B T}$$

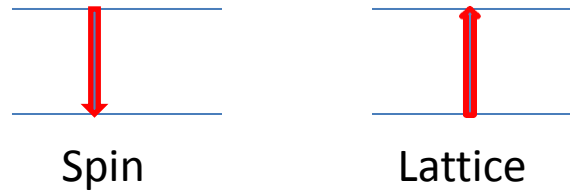
$$\frac{dN_+}{dt} = -W_{\uparrow} N_+ + W_{\downarrow} N_-$$

In thermal equilibrium  $d/dt=0$

$$W_{\uparrow} / W_{\downarrow} = e^{-\gamma \hbar B_0/k_B T}$$

# Magnetic resonance – basics spin-lattice relaxation

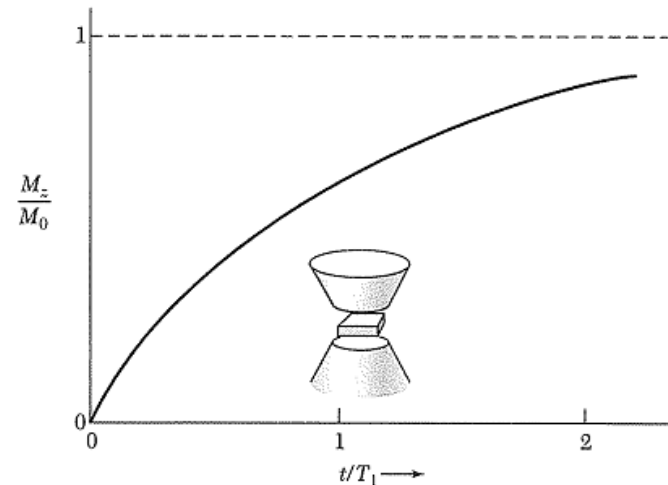
Why now  $W_{\uparrow} \neq W_{\downarrow}$ ?



Rate equations are solved by introducing  $n$  and  $N$  and we get

$$\frac{dn}{dt} = N(W_{\downarrow} - W_{\uparrow}) - n(W_{\downarrow} + W_{\uparrow}) = \frac{n_0 - n}{T_1}$$

$$\frac{1}{T_1} \equiv (W_{\downarrow} + W_{\uparrow}) \quad n_0 = N \frac{(W_{\downarrow} - W_{\uparrow})}{(W_{\downarrow} + W_{\uparrow})}$$



In terms of magnetization, this actually reads as

$$\frac{dM_z}{dt} = -\frac{M_z - M_0}{T_1}$$



# Magnetic resonance – basics spin-lattice relaxation

Spin-lattice relaxation also solves the problem of absorption of r.f. energy. Namely, if we take into account external perturbation (described by  $W$ ) and spin-lattice relaxation together, then we derive

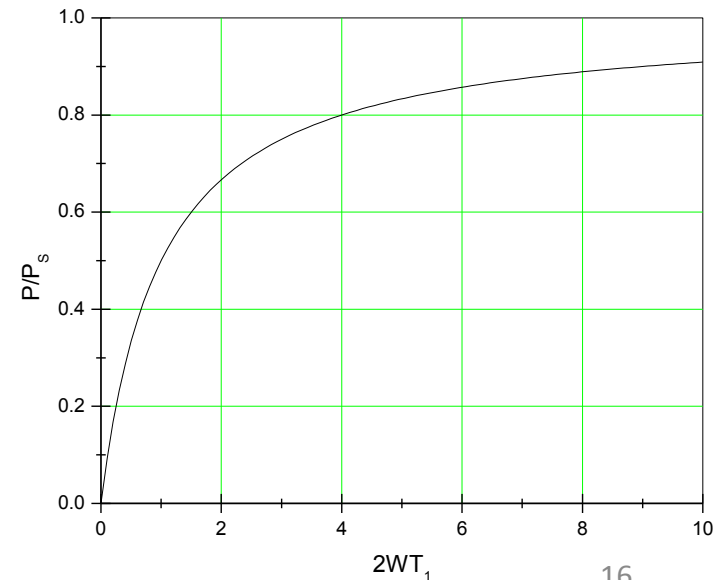
$$\frac{dn}{dt} = -2Wn + \frac{n_0 - n}{T_1}$$

In the steady state

$$n = n_0 \frac{1}{1 + 2WT_1}$$

And the absorbed power will be

$$\frac{dE}{dt} = nW\hbar\omega = n_0W \frac{\hbar\omega}{1 + 2WT_1}$$







# Magnetic resonance – basics

## Bloch equations

Classical description of the motion of magnetic moments in external magnetic field

Torque due to the action of  $B_0$   $\vec{\mu} \times \vec{B}_0$

This torque will change the angular momentum

$$\frac{d\vec{\Gamma}}{dt} = \vec{\mu} \times \vec{B}_0 \Rightarrow \frac{d\vec{\mu}}{dt} = \gamma \vec{\mu} \times \vec{B}_0 \Rightarrow \frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{B}_0$$

In addition we have also relaxation phenomena to return back to equilibrium. We define two relaxation times  $T_1$  – spin-lattice relaxation time and  $T_2$  – spin-spin relaxation time to allow longitudinal and transverse magnetizations to come back

$$\frac{dM_x}{dt} = \gamma B_0 M_y - \frac{M_x}{T_2}$$

$$\frac{dM_y}{dt} = -\gamma B_0 M_x - \frac{M_y}{T_2}$$

$$\frac{dM_z}{dt} = -\frac{M_z - M_0}{T_1}$$

Please note that changes in  $M_x$  and  $M_y$  do not change the magnetic energy



# Magnetic resonance – basics

## Bloch equations

Bloch equations in compact form

$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{B}_0 - \underline{\underline{R}}(\vec{M} - \vec{M}_0) \quad \underline{\underline{R}} = \begin{pmatrix} 1/T_2 & 0 & 0 \\ 0 & 1/T_2 & 0 \\ 0 & 0 & 1/T_1 \end{pmatrix}$$

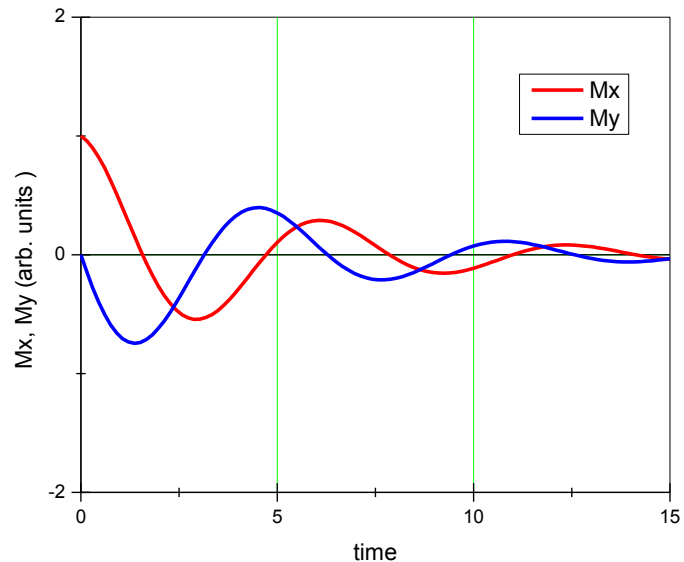
With initial conditions  $M_x(0) = m$ ,  $M_y(0) = 0$ ,  $M_z(\infty) = M_0$

we have solutions in the form

$$M_x(t) = m e^{-t/T_2} \cos \omega_0 t$$

$$M_y(t) = -m e^{-t/T_2} \sin \omega_0 t$$

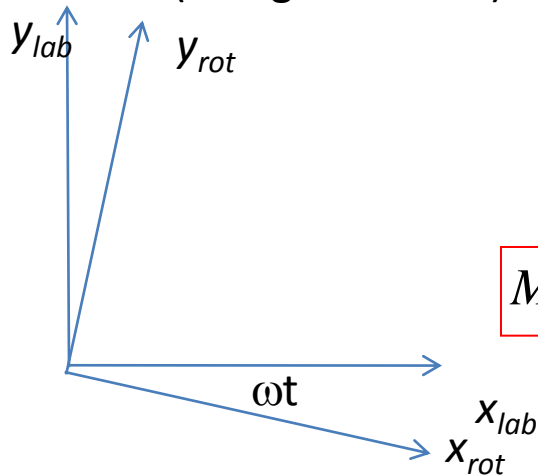
$$M_z(t) = M_0 (1 - e^{-t/T_1})$$



# Magnetic resonance – basics

## Bloch equations

The application of rf field perpendicular to the static magnetic field will thus lead to an extra transverse magnetization. In a typical experiment, the rf field will be linearly polarized (along the x-axis)



Rotating frame with field

The result of previous calculations is that, we can write  $M_x$  component of the magnetization in the laboratory frame as

$$M_x(t) = M_x^{rot} \cos \omega t + M_y^{rot} \sin \omega t = (\chi' \cos \omega t + \chi'' \sin \omega t) B_1$$

We thus defined a complex r.f. susceptibility

$$\chi = \chi' + i\chi''$$

with components

$$M_x = \frac{(\omega - \omega_L) T_2^2}{1 + (\omega - \omega_L)^2 T_2^2 + \gamma^2 B_{rf}^2 T_1 T_2} \gamma B_{rf} M_0$$

$$M_y = \frac{T_2}{1 + (\omega - \omega_L)^2 T_2^2 + \gamma^2 B_{rf}^2 T_1 T_2} \gamma B_{rf} M_0$$

$$M_z = \frac{1 + (\omega - \omega_L)^2 T_2^2}{1 + (\omega - \omega_L)^2 T_2^2 + \gamma^2 B_{rf}^2 T_1 T_2} M_0$$



$$\chi' = \frac{\chi_0}{2} \omega_0 T_2 \frac{(\omega_0 - \omega) T_2}{1 + (\omega_0 - \omega)^2 T_2^2}$$

$$\chi'' = \frac{\chi_0}{2} \omega_0 T_2 \frac{1}{1 + (\omega_0 - \omega)^2 T_2^2}$$



# Magnetic resonance – basics

## Bloch equations

When the detection coil is filled with measured material, its inductance changes by

$$L=L_0(1+\chi)$$

The complex impedance of the coil thus also changes as

$$Z=R+i\omega L=R-\omega L_0\chi''+i\omega L_0\chi'$$

The real part of  $Z$  changes by  $\Delta R/R=\omega L_0\chi''/R=Q\chi''$

In unperturbed coil, the relation between the magnetic energy and the current producing that magnetic field is  $\frac{1}{2}L_0i_0^2=\frac{1}{2}B_1^2V/\mu_0$

Because of change in the impedance, the average dissipated power is

$$P = \frac{1}{2} \Delta R i_0^2 = \frac{1}{2\mu_0} B_1^2 V \omega \chi''$$

In MR experiments we are thus measuring  $\chi''$ . But  $\chi'$  is related to  $\chi''$  through Kramers-Kronig relations, so we in principle know both of them.

Also, please note that  $P$  is proportional to  $\chi_0$  so it can provide a quantitative information about the static magnetic susceptibility of the samples!



# Magnetic resonance – basics

## Method of moments

The experimentalists thus measure the absorption  $\chi''(\omega)$ . The theorists tend to be more familiar with the Green functions or time-correlation functions of spin operators. In a linear response theory, developed for MR by Kubo and Tomita,  $\chi''(\omega)$  is expressed as

$$\chi''(\omega) = \frac{\omega V}{2k_B T} \int_{-\infty}^{\infty} \langle \hat{M}_x(t) \hat{M}_x(0) \rangle e^{-i\omega t} dt$$

A time evolution of  $M_x$  operator is calculated in the interaction representation

$$\hat{M}_x(t) = e^{i\hat{H}t/\hbar} \hat{M}_x e^{-i\hat{H}t/\hbar}$$

Lets define the spectral lineshape as

$$f(\omega) = \frac{\chi''(\omega)}{\omega} = \frac{V}{2k_B T} \int_{-\infty}^{\infty} \langle \hat{M}_x(t) \hat{M}_x(0) \rangle e^{-i\omega t} dt$$

If we perform inverse FT of the above expression, we can derive

$$\frac{V}{2k_B T} \langle \hat{M}_x(t) \hat{M}_x(0) \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(\omega) e^{i\omega t} d\omega$$



# Magnetic resonance – basics

## Method of moments

If we look at the above expression at time  $t=0$ , then we notice the following

$$\frac{V}{2k_B T} \langle \hat{M}_x(0) \hat{M}_x(0) \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(\omega) d\omega \quad \leftarrow \quad \begin{aligned} \hat{\mu}_x &= \sum_i \hat{\mu}_{i,x} \\ \langle \hat{\mu}_{i,x}^2 \rangle &= \langle \hat{\mu}_{i,y}^2 \rangle = \langle \hat{\mu}_{i,z}^2 \rangle = \frac{1}{3} \langle \hat{\mu}_i^2 \rangle = \frac{\gamma^2 \hbar^2 I(I+1)}{3} \end{aligned}$$

Therefore  $\langle M_x^2 \rangle$  is a measure for the area under the resonance curve.

But, if we take the time derivative and then take its value at  $t=0$ , we can make even a step further

$$\frac{V}{2k_B T} \frac{d}{dt} \langle \hat{M}_x(t) \hat{M}_x(0) \rangle \Big|_{t=0} = \frac{1}{2\pi} \int_{-\infty}^{\infty} i\omega f(\omega) d\omega$$

The  $n$ -th time derivative will be thus

$$\frac{V}{2k_B T} \frac{d^n}{dt^n} \langle \hat{M}_x(t) \hat{M}_x(0) \rangle \Big|_{t=0} = \frac{(i)^n}{2\pi} \int_{-\infty}^{\infty} \omega^n f(\omega) d\omega$$



# Magnetic resonance – basics

## Method of moments

We can thus define n-th moment of the resonance as

$$\langle \omega^n \rangle = \frac{\int_{-\infty}^{\infty} \omega^n f(\omega) d\omega}{\int_{-\infty}^{\infty} f(\omega) d\omega} = (-i)^n \frac{\frac{d^n}{dt^n} \langle \hat{M}_x(t) \hat{M}_x(0) \rangle |_{t=0}}{\langle \hat{M}_x^2 \rangle}$$

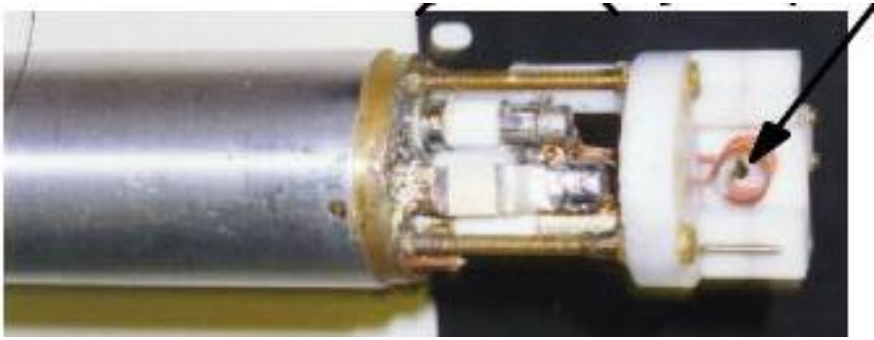
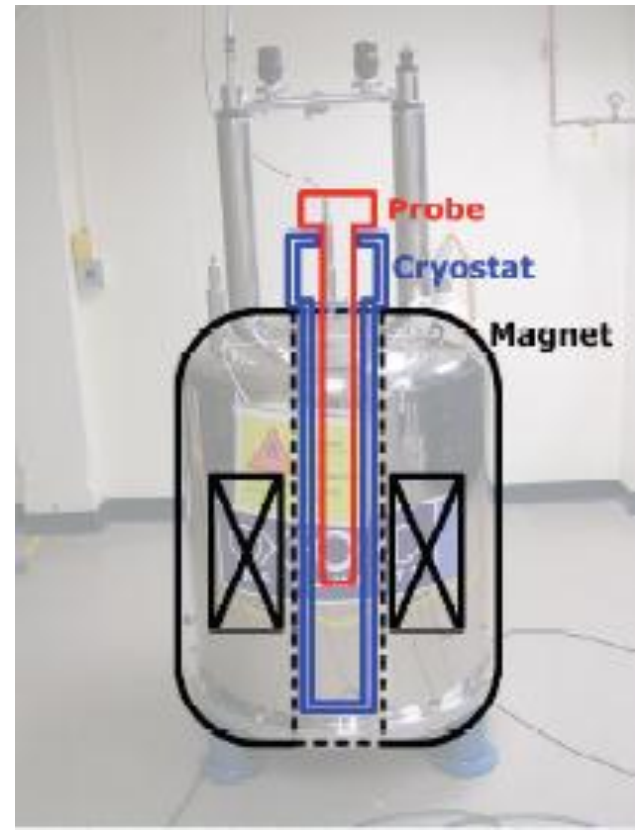
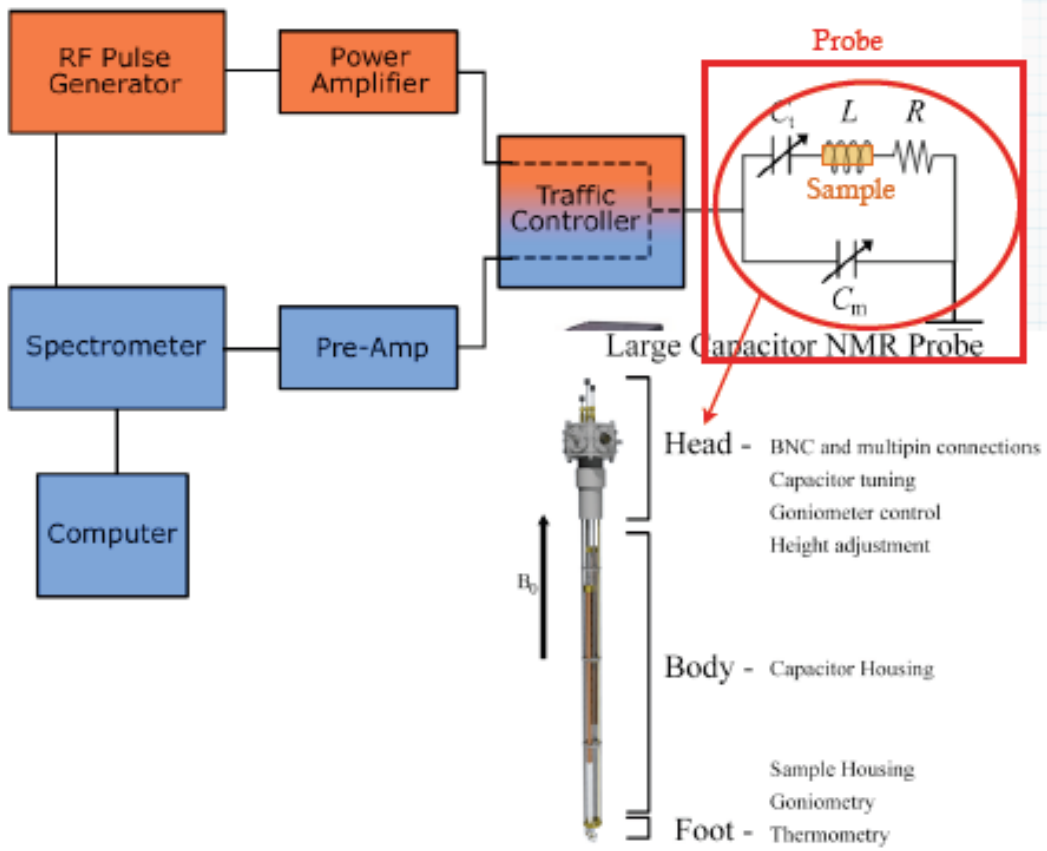
Let us calculate the second moment of the the line

$$\begin{aligned} \frac{d^2}{dt^2} \langle e^{i\hat{H}t/\hbar} \hat{M}_x(0) e^{-i\hat{H}t/\hbar} \hat{M}_x(0) \rangle &= \frac{i}{\hbar} \frac{d}{dt} \langle e^{i\hat{H}t/\hbar} (H\hat{M}_x - \hat{M}_x H) e^{-i\hat{H}t/\hbar} \hat{M}_x(0) \rangle \\ &= -\frac{1}{\hbar^2} \langle e^{i\hat{H}t/\hbar} [H, [H, \hat{M}_x]] e^{-i\hat{H}t/\hbar} \hat{M}_x(0) \rangle \end{aligned}$$

Taking the above expression at t=0 and slightly rearranging terms, we finally derive

$$\langle \omega^2 \rangle = \frac{\int_{-\infty}^{\infty} \omega^2 f(\omega) d\omega}{\int_{-\infty}^{\infty} f(\omega) d\omega} = -\frac{1}{\hbar^2} \frac{\langle [H, \hat{M}_x]^2 \rangle}{\langle \hat{M}_x^2 \rangle}$$

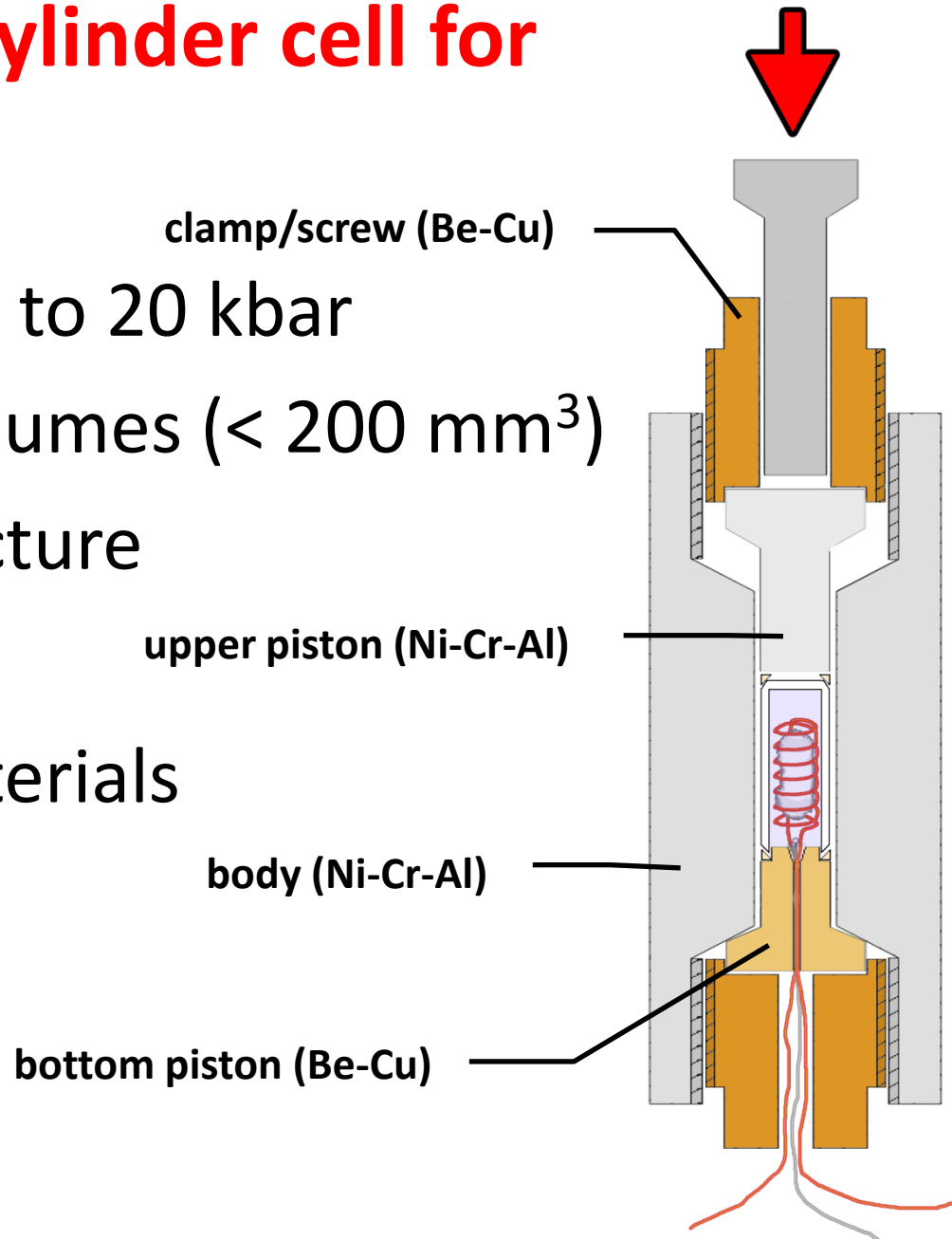
# How do we do it then?





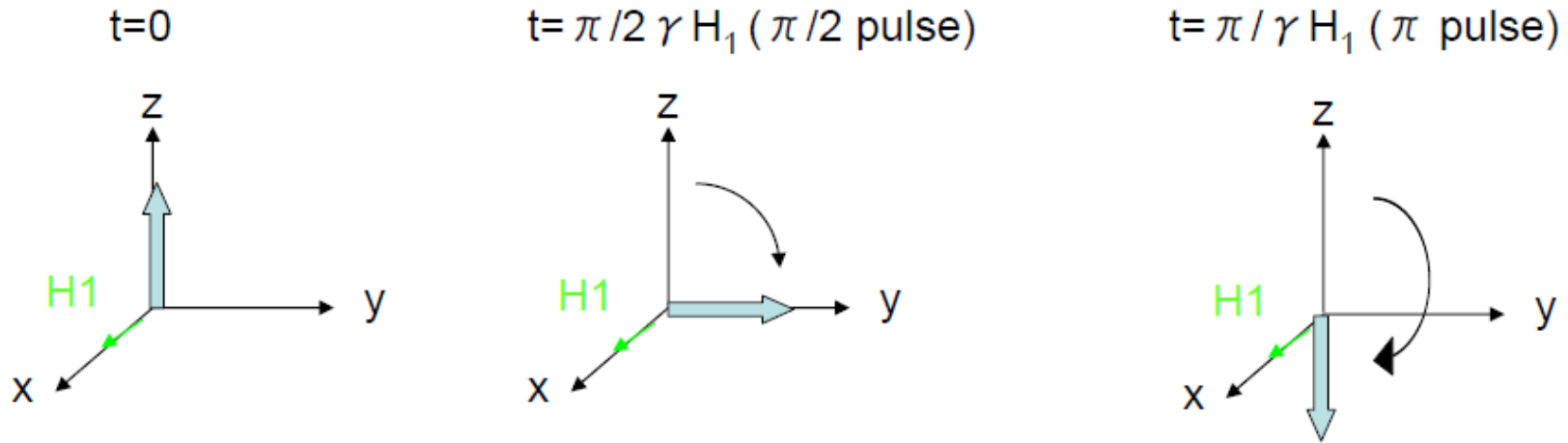
# Current Piston-cylinder cell for NMR

- for pressures up to 20 kbar
- large sample volumes ( $< 200 \text{ mm}^3$ )
- easy to manufacture
- inexpensive materials
- dangerous

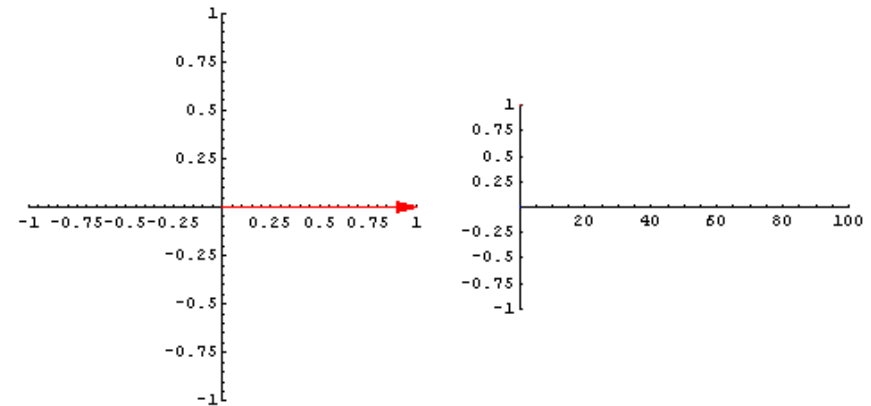
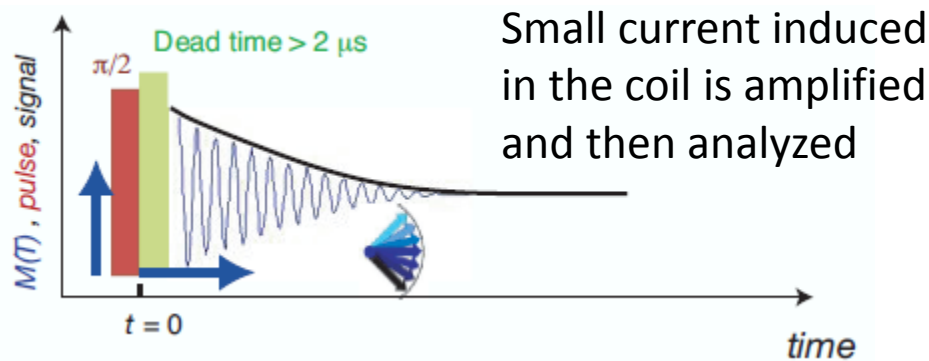


# Magnetic resonance – basics pulses

If we can neglect the effect of relaxation times (typically this is justified when the duration of rf fields is short compared to  $T_1$  and  $T_2$ ), then one can also show that the effect of rf field will be to rotate the magnetization



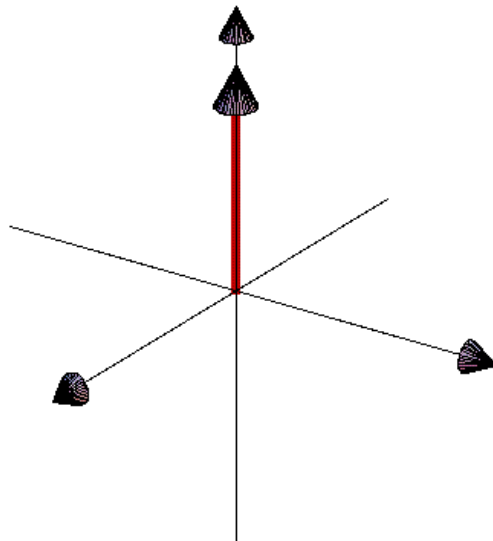
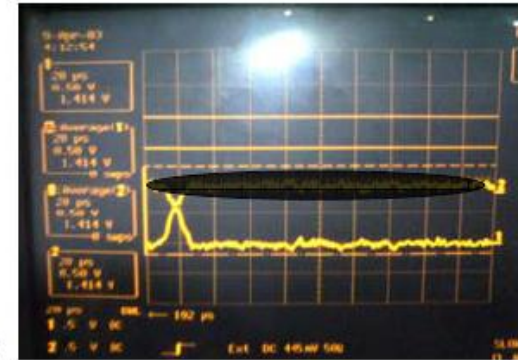
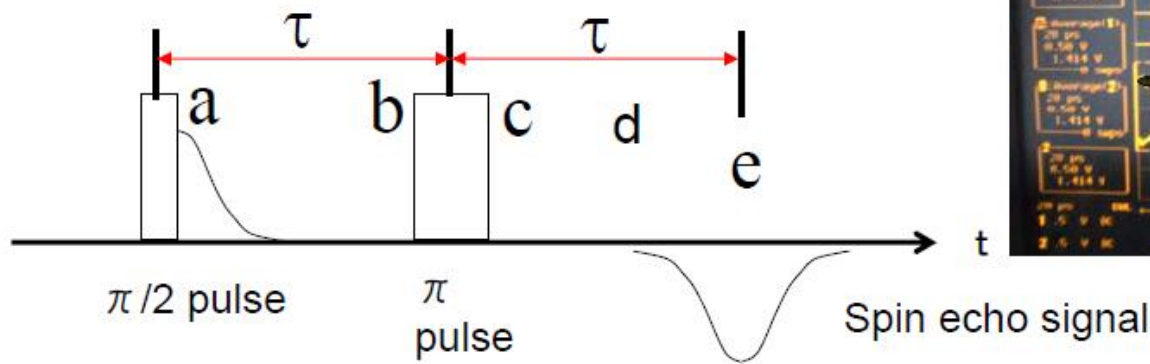
After  $\pi/2$  pulse we observe FID



# Magnetic resonance – spin echo

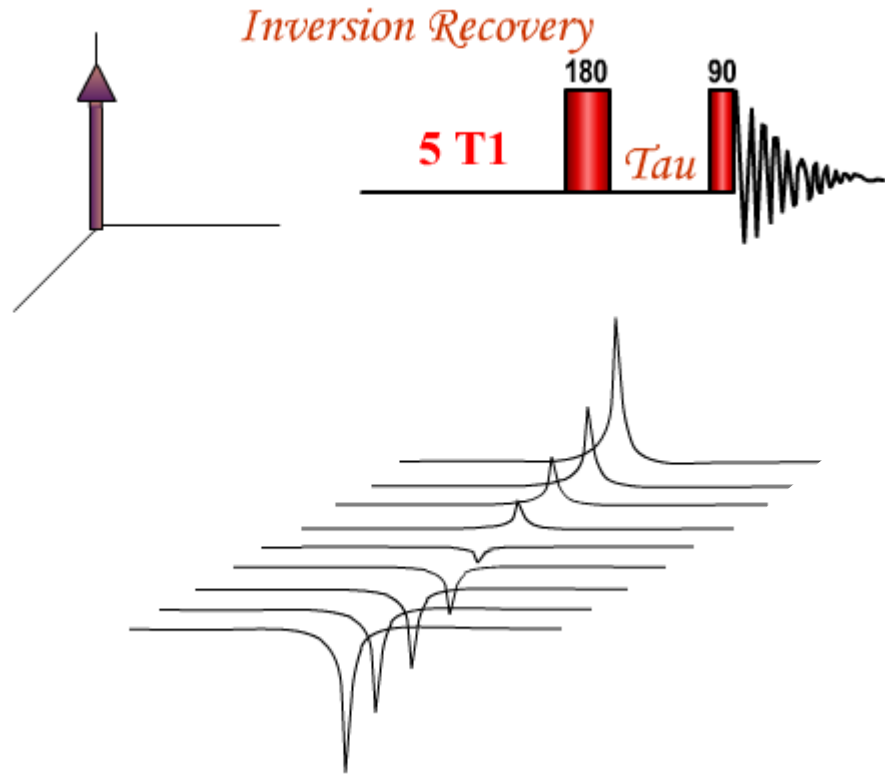
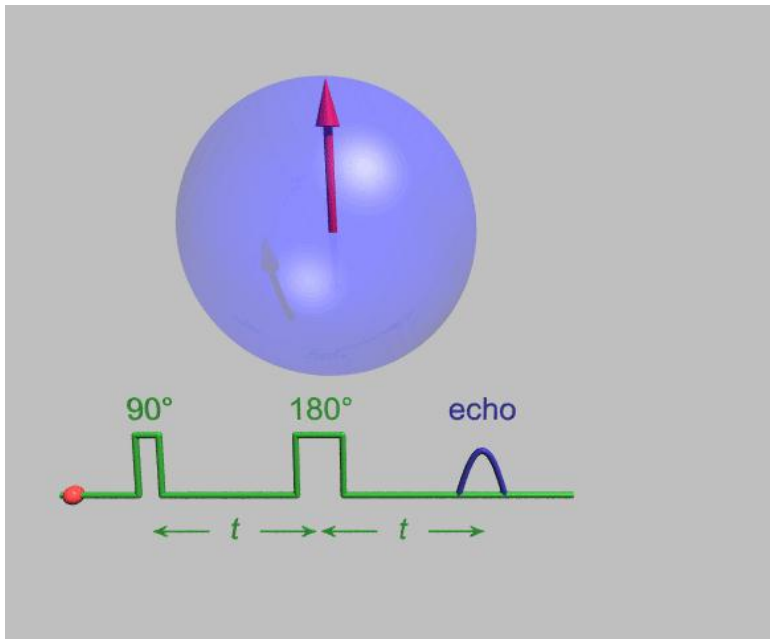
When FID is too short to be observed then we may want to try with spin echo

### Two pulse sequence



Spin Echo (Hahn, *Phys. Rev.* **80**, 5801 (1950))

# Measurements of relaxation times

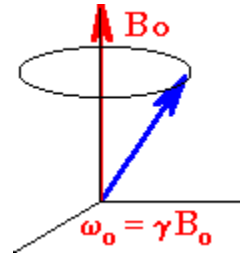
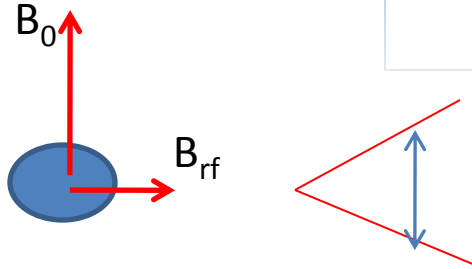




# Magnetic resonance – what we have learnt so far?

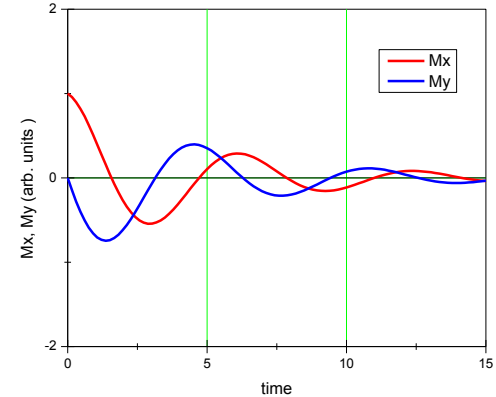
1. **Classical Bloch equations** (torque +  $T_1 + T_2$ )
2.  $T_1$  processes must result in a transfer of energy since it involves magnetic dipoles reorienting in a magnetic field. Quantum mechanically, it is a change of populations between spin-down states to spin-up states which are nondegenerate in a magnetic field. Since the energy is typically gained by the lattice,  $T_1$  is termed as **the lattice or longitudinal spin relaxation time**.
3. QM treatment in the Schrödinger and Heisenberg picture
4. In magnetic resonance we are measuring the imaginary part of the **r.f. spin susceptibility**  $\chi''(\omega)$ .
5. **Method of moments:**
  1. 0-th moment  $M_0 = \int f(\omega) d\omega$  is proportional to the static spin susceptibility
  2. Higher moments are in fact given by the commutators  $[H', I_x]$ . In particular we emphasized the first moment  $M_1 = \int \omega f(\omega) d\omega / M_0$ , which is just the center of the resonance and the second moment  $M_2 = \int (\omega - M_1)^2 f(\omega) d\omega / M_0$  which is a measure for the linewidth.

# Magnetic resonance – a brief summary after first lectures



Bloch equations in compact form

$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{B}_0 - \underline{\underline{R}}(\vec{M} - \vec{M}_0) \quad \underline{\underline{R}} = \begin{pmatrix} 1/T_2 & 0 & 0 \\ 0 & 1/T_2 & 0 \\ 0 & 0 & 1/T_1 \end{pmatrix}$$



Magnetic resonance measures

Method of moments

$$\chi''(\omega) = \frac{\omega V}{2k_B T} \int_{-\infty}^{\infty} \langle \hat{M}_x(t) \hat{M}_x(0) \rangle e^{-i\omega t} dt$$

$$\langle \omega - \omega_0 \rangle = \frac{\int_{-\infty}^{\infty} (\omega - \omega_0) f(\omega) d\omega}{\int_{-\infty}^{\infty} f(\omega) d\omega} = \frac{1}{\hbar} \frac{\langle [H', \hat{M}_x] \hat{M}_x \rangle}{\langle \hat{M}_x^2 \rangle}$$

$$\langle (\omega - \omega_0)^2 \rangle = \frac{\int_{-\infty}^{\infty} (\omega - \omega_0)^2 f(\omega) d\omega}{\int_{-\infty}^{\infty} f(\omega) d\omega} = \frac{1}{\hbar} \frac{\langle [H', \hat{M}_x]^2 \rangle}{\langle \hat{M}_x^2 \rangle}$$



**NMR = local, real-space probe where the behaviour of nuclear spins can be monitored on a site-to-site basis.**

**Types of NMR observables:**

1. **NMR spectrum** is fundamental and major element of sample characterization
  - Width & distribution
    - Sample quality
    - Crystallographic inequivalent sites
    - Local site disorder
  - NMR shifts, which are measured as a frequency shift proportional to the applied field is a fundamental measure of the various terms in spin Hamiltonian. In magnetic systems is a measure of local spin susceptibilities. Various sources:
    - s-contact shift (in metals = Knight shift)
    - Core-polarization shift
    - Dipolar shift
    - Chemical shift
2. **NMR dynamics** as represented by the **spin-lattice relaxation time  $T_1$** .  $T_1$  is linked to  $\chi''(\mathbf{q}, \omega)$  via the fluctuation-dissipation theorem.

$$\delta = \frac{\nu_{res}}{\gamma B_0} - 1 = \frac{\nu_{res}}{\nu_0} - 1$$



Nuclear magnetic moments in solids constitute nearly perfect example of an ensemble that is weakly coupled to its neighborhood. In NMR we attempt to explore this weak coupling to measure sample's static and dynamic properties.

General spin Hamiltonian

$$H = H_Z + H_{dip} + H_Q + H_{e-n}$$

1. Zeeman term

$$H_Z = -\gamma\hbar B_0 \hat{I}_Z$$

NMR: detect the transitions between these levels. It is usually the strongest term and in most experiments it will range between 10-500 MHz.





## 2. Dipolar term

$$H_{dip} = \frac{\gamma^2 \hbar^2}{2} \sum_{i,j} \left( \frac{\hat{I}_i \cdot \hat{I}_j}{r_{ij}^3} - \frac{3(\hat{I}_i \cdot \vec{r}_{ij})(\hat{I}_j \cdot \vec{r}_{ij})}{r_{ij}^5} \right)$$

It is much weaker than Zeeman term as it is at most in the several 10 kHz range. It will give rise to a Gaussian type of broadening of resonances with a second moment

$$\langle \Delta\omega^2 \rangle = \frac{3}{4} \gamma^4 \hbar^2 I(I+1) \frac{1}{N} \sum_{i,j} \left( \frac{(3 \cos^2 \vartheta_{ij} - 1)^2}{r_{ij}^6} \right)$$

Calculated from the definition of the second moment

$$\langle \Delta\omega^2 \rangle = \frac{\int_{-\infty}^{\infty} (\omega - \omega_0)^2 f(\omega) d\omega}{\int_{-\infty}^{\infty} f(\omega) d\omega} = \frac{1}{\hbar^2} \frac{\langle [H_{dip}, \hat{M}_x]^2 \rangle}{\langle \hat{M}_x^2 \rangle}$$

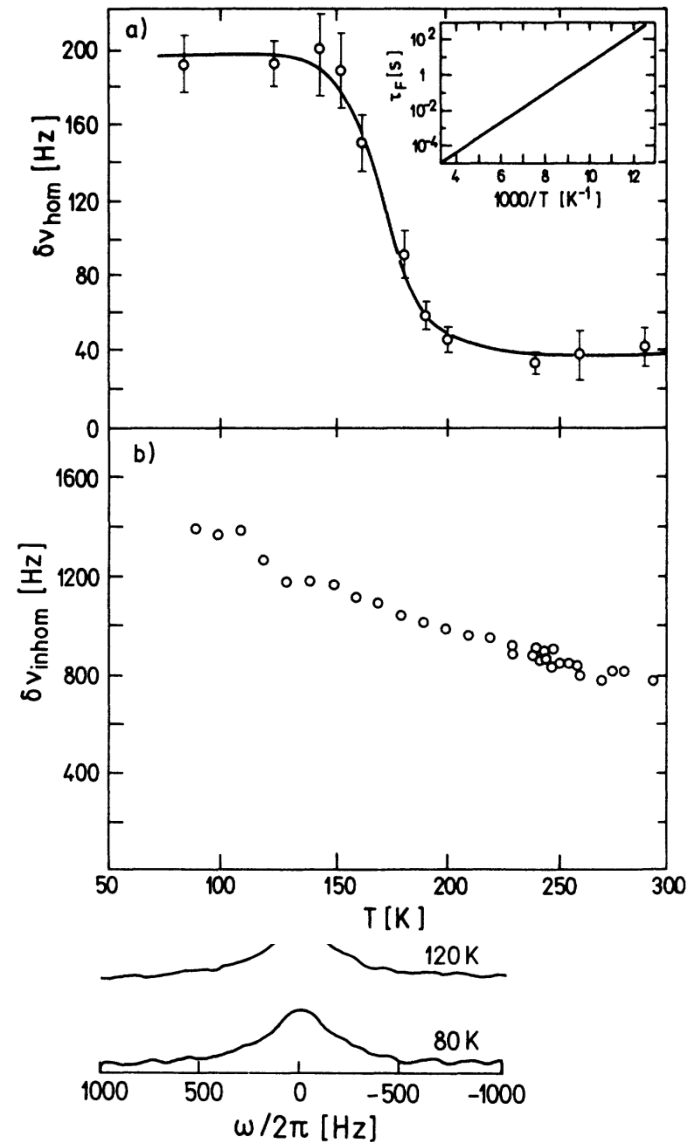
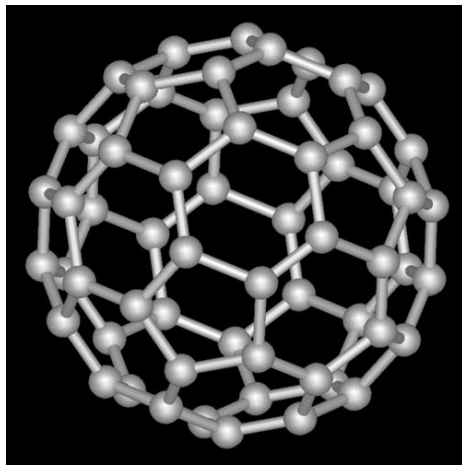
# NMR – dipolar interaction; example

## 2. Dipolar term

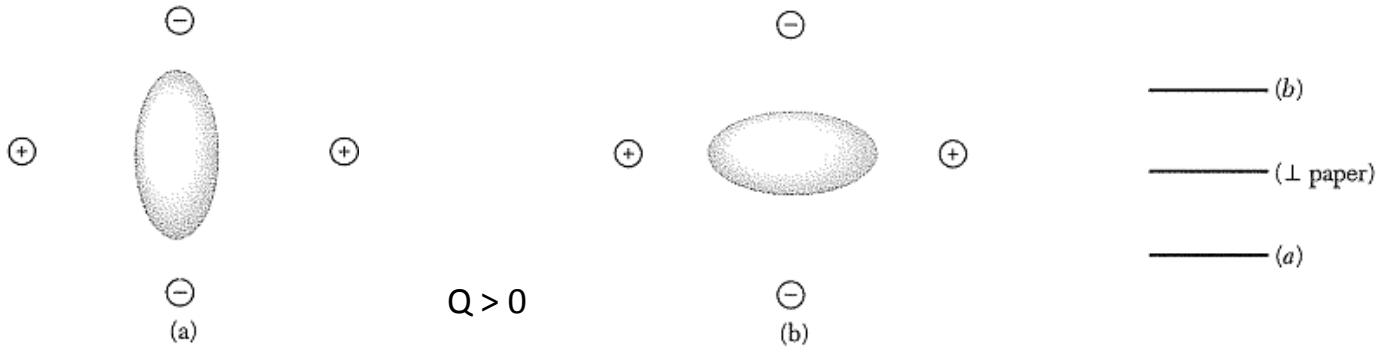
Effect of molecular motions: we need to  
 Take a time average over the dipolar term

$$\overline{(3 \cos^2 \vartheta_{ij} - 1)}$$

$$\langle \Delta\omega^2 \rangle = \frac{3}{4} \gamma^4 \hbar^2 I(I+1) \frac{1}{N} \sum_{i,j} \left( \frac{\overline{(3 \cos^2 \vartheta_{ij} - 1)^2}}{r_{ij}^6} \right)$$



# Quadrupole Interaction



Q in field gradient

Nuclei of spin  $I \geq 1$  have electric quadrupole moment.

Ref: C.P.Slichter, "Principles of Magnetic Resonance", 2<sup>nd</sup> ed., Chap 9.

$Q > 0$  for convex (egg shaped) charge distribution.

$$H_Q = \frac{1}{3!} \sum_{\alpha, \beta} V_{\alpha\beta} Q_{\alpha\beta} \quad V_{\alpha\beta} = \left. \frac{\partial^2 V}{\partial x_\alpha \partial x_\beta} \right|_{\mathbf{r}=0} \quad Q_{\alpha\beta} = e \sum_{k \in \text{protons}} (3x_{\alpha k} x_{\beta k} - \delta_{\alpha\beta} r_k^2)$$

Wigner –Eckart Theorem: 
$$H_Q = \frac{eQ}{6I(2I-1)} \sum_{\alpha, \beta} V_{\alpha\beta} \left[ \frac{3}{2} (I_\alpha I_\beta + I_\beta I_\alpha) - \delta_{\alpha\beta} I^2 \right]$$

Quadrupole term: 
$$H_Q = \frac{e^2 q Q}{4I(2I-1)} \left[ 3\hat{I}_z^2 - I(I+1) + \frac{\eta}{2} (I_+^2 + I_-^2) \right]$$

$eq = V_{zz}$   
 $eQ = \langle I I | Q_{zz} | I I \rangle$

Axial symmetry: 
$$E_Q = \frac{e^2 q Q}{4I(2I-1)} [3m^2 - I(I+1)]$$

$\eta = (V_{xx} - V_{yy}) / V_{zz}$



Some comments about the Quadrupole term:

1. It is frequently the leading (perturbation) term in NMR when  $I \neq 1/2$ . It is not unusual to find it in the several 10 MHz range. In fact in some experiments we deliberately switch off magnetic field and observe only the transitions between the quadrupole split levels (Nuclear Quadrupole Resonance).
2. For  $I=1/2$  the nuclear quadrupole moment  $Q$  vanishes identically according to the Wigner-Eckart theorem.
3. The choice made in the above equation is such that the principal axes for the EFG tensor are chosen in such a way that  $|V_{xx}| < |V_{yy}| < |V_{zz}|$ . That is,  $|V_{zz}|$  is the largest principal value.
4. The symmetry plays an important role. For instance in cubic symmetries because of  $\Delta V=0$  we see that  $V_{xx}=V_{yy}=V_{zz}=0$ . In other words, in this case  $H_Q=0$ ! However, even in cubic structures, strains can play a role as they effectively give rise to some distribution of  $v_Q$ . Then due to the first order broadening only the central transition  $-1/2 \leftrightarrow 1/2$  will be resolved.
5. In tetragonal or trigonal symmetries we find that  $V_{xx}=V_{yy}$  or  $\eta=0$ ! We have an axially symmetric EFG.

# Quadrupole interaction

Case of  $\eta=0$

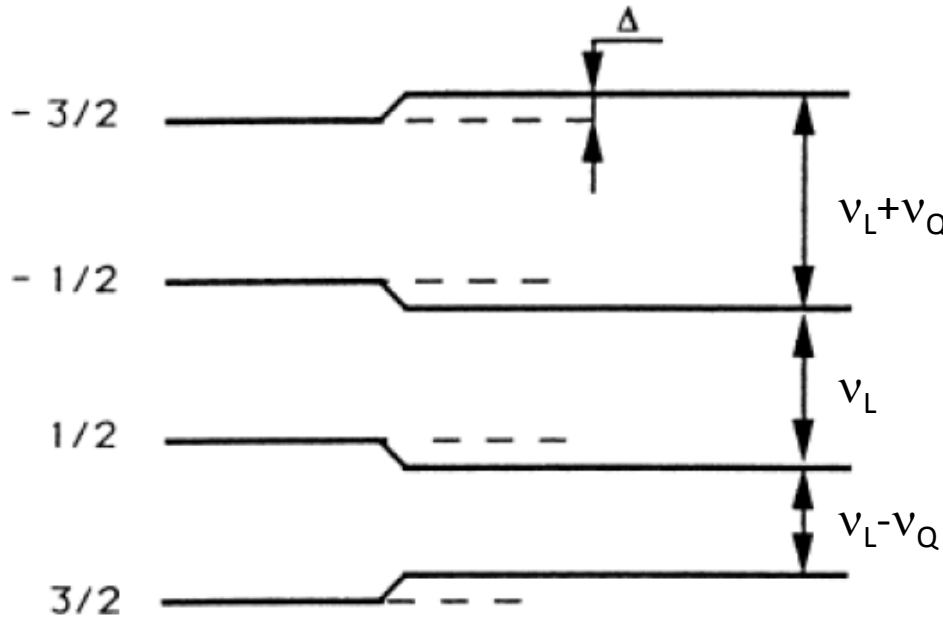
$$E_m = -\gamma\hbar B_0 m + \frac{1}{2} h\nu_Q \left( m^2 - \frac{1}{3} I(I+1) \right)$$

$$\nu_Q = \frac{3e^2 qQ}{2hI(2I-1)}$$

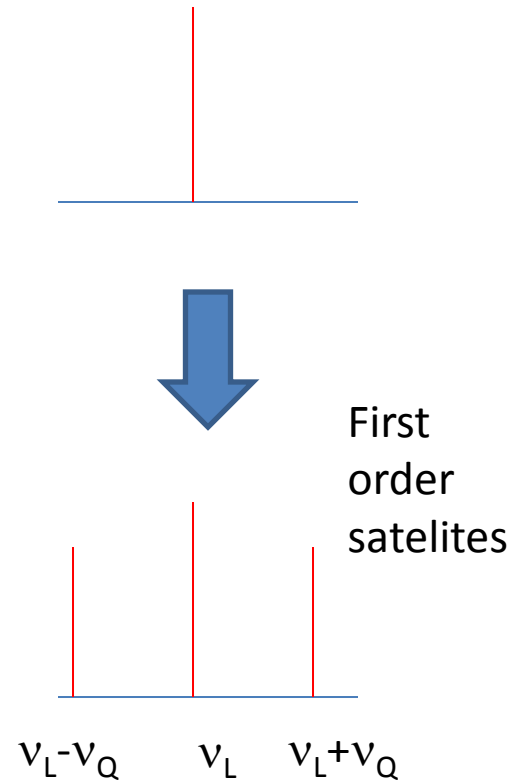
For  $\theta \neq 0$ :

$$\nu = \nu_L \pm \frac{1}{2} n \nu_Q (3 \cos^2 \theta - 1)$$

$$I = 3/2$$



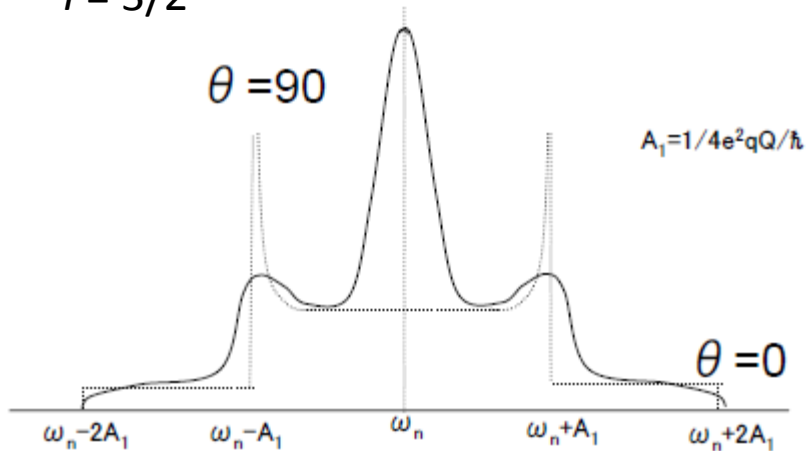
Quadrupole frequency



# Quadrupole interaction – powder lineshape

In case of powder samples with uniform distribution of  $q$  over the unit sphere, the first order transitions give rise to an intensity distribution between  $\nu_L + n\nu_Q$  and  $\nu_L - \frac{1}{2}n\nu_Q$  with a square root singularity at  $\nu_L - \frac{1}{2}n\nu_Q$

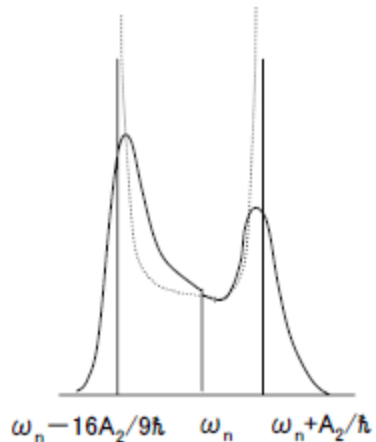
$I = 3/2$



$$\nu = \nu_L \pm \frac{1}{2} n \nu_Q (3 \cos^2 \vartheta - 1)$$

$m$  is no longer strictly a good quantum number so there are a second order frequency shifts. Interestingly they cancel out for the satellite transition, but they give a second order shift

$$\nu_{\pm \frac{1}{2}}^{(2)} = \nu_L - \frac{\nu_Q^2}{16\nu_L} \left( I(I+1) - \frac{3}{4} \right) \sin^2 \vartheta (9 \cos^2 \vartheta - 1)$$



# Quadrupole interaction - example

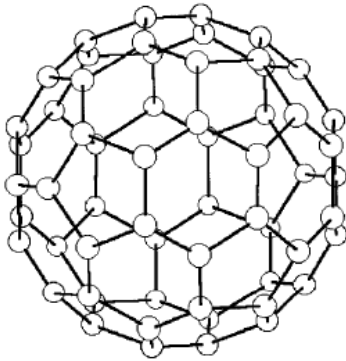
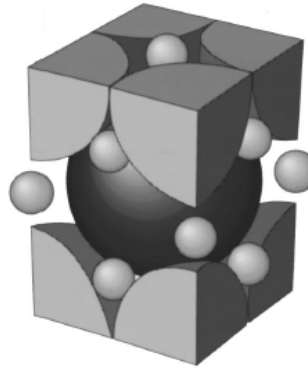


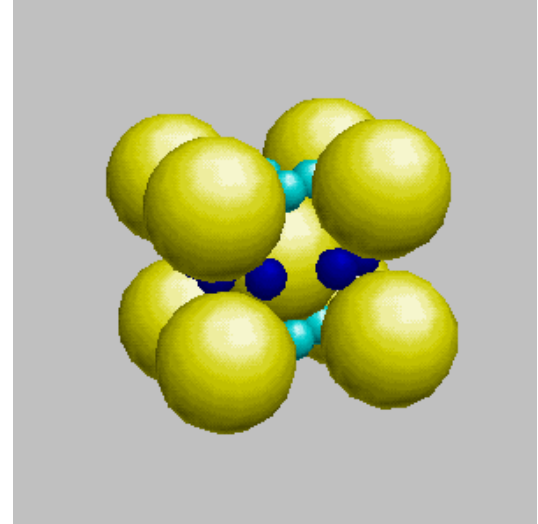
FIG. 1. The fullerene C<sub>60</sub>.

This is followed by a summary and concluding remarks in Sec. VII.



A<sub>3</sub>C<sub>60</sub>

FIG. 2. Unit cell of A<sub>3</sub>C<sub>60</sub> (Murphy *et al.*, 1992). The small spheres represent alkali ions and the large spheres are the C<sub>60</sub> molecules. In a given unit cell there are two ions with tetrahedral coordination and one ion with octahedral coordination.

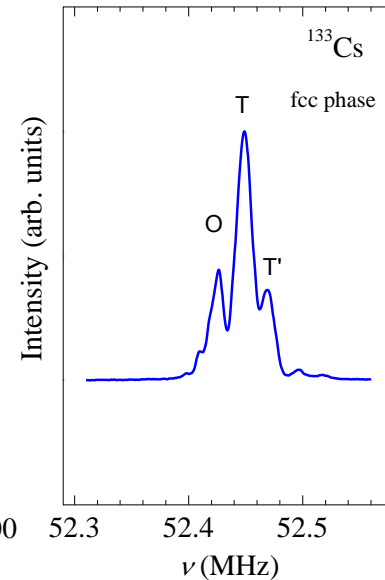
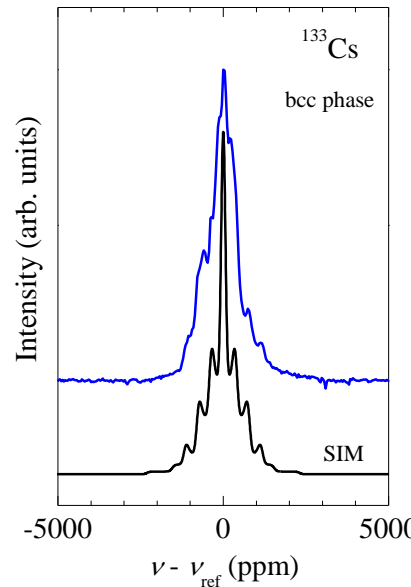


fcc lattice: Octahedral (O)  
and tetrahedral (T) sites

bcc lattice: only a  
single intercalation site

fcc: site symmetries for the two Cs sites are 23 and *m*-3 => EFG=0

bcc: site symmetry (-4*m*.2) => η=0



<sup>133</sup>Cs I=7/2

7/2 ↔ 5/2, 5/2 ↔ 3/2, ..., -5/2 ↔ -7/2



The coupling between the nuclear and electron moments can be divided into three contributions

$$H_{e-n} = H_l + H_{e-n}^{dip} + H_{hf}$$

Chemical shift:

$$H_l = \gamma \hbar g \mu_B \vec{I} \cdot \vec{l} / r^3$$

Shift:

$$\sigma = \frac{\nu - \nu_0}{\nu_0}$$

Dimensionless second-rank tensor

... is the interaction to the electron orbital moment and is usually contained in the so-called chemical shift in materials where the angular momentum is quenched. If this is the case, then the extra magnetic field at the nuclear site, which is a result of the orbital moment of the electrons, is expressed as

$$H_{CS} = -\gamma \hbar \vec{I} \cdot \underline{\underline{\sigma}} \cdot \vec{B}_0$$

$$\sigma = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix}$$



The range of  $\sigma$  component is somewhere in the ppm range, so it's really a small perturbation to the Zeeman hamiltonian. For this reason we will need only  $\sigma_{zz}$  component of the tensor.

Chemical shift is widely explored in chemistry for recognising chemical groups and thus for the reconstruction of the chemical components. The calculation of  $\sigma$  is however very tedious job and we shall leave it to quantum chemists. For us it will be a parameter, which is determined directly from the experiments.

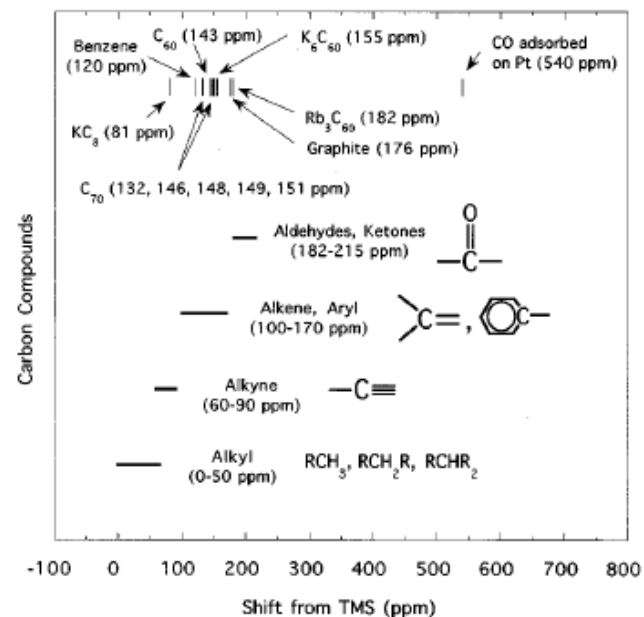


FIG. 10.  $^{13}\text{C}$  NMR shifts at room temperature for a range of carbon compounds. The shifts are measured in parts per million (ppm) from tetramethylsilane (TMS). Graphite and alkali-intercalated graphite  $\text{C}_8\text{K}$  resonate at 176 and 81 ppm, respectively (Mizutani *et al.*, 1981). Solid  $\text{C}_{60}$  is at 143 ppm, in the range of aromatic compounds, and the superconducting alkali-fulleride compound  $\text{Rb}_3\text{C}_{60}$  is at 182 ppm. The inequivalent carbon sites of  $\text{C}_{70}$  in a mixed  $\text{C}_{60}/\text{C}_{70}$  powder (resolved by magic-angle spinning methods) are at 132, 146, 148, 149, and 151 ppm (Tycko, Dabaghi, Fleming, *et al.*, 1991), also in the aromatic range. Insulating  $\text{K}_6\text{C}_{60}$  is at 155 ppm (Tycko, Haddon, *et al.*, 1991). Finally, the  $^{13}\text{C}$  resonance of carbon monoxide adsorbed on a platinum surface is at 540 ppm (Shore, 1986), a "world record" shift for  $^{13}\text{C}$ . Also shown for comparison are ranges of shifts for  $^{13}\text{C}$  nuclei in various types of organic compound (Solomons, 1990).

Zeeman + Chemical shift Hamiltonians

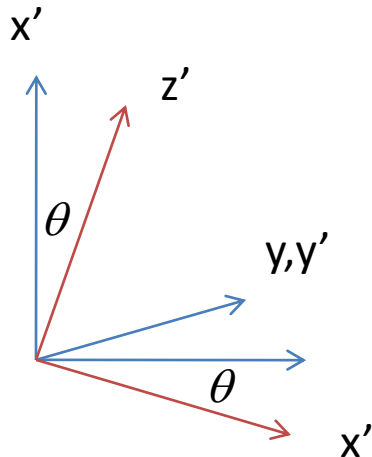
$$H = -\gamma \hbar \vec{I} \cdot (1 + \underline{\underline{\sigma}}) \cdot \vec{B}_0$$

$\sigma_{ij} \ll 1$

$$\nu = \gamma B_0 (1 + \sigma_{zz}) = \nu_L (1 + \sigma_{zz})$$

Principal axes system

$$\sigma' = \begin{bmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{bmatrix}$$



Axial symmetry

$$\sigma_{xx} = \sigma_{yy}$$

$$\underline{\underline{\sigma}} = R_y(\vartheta) \underline{\underline{\sigma'}} R_y^{-1}(\vartheta)$$

# Chemical Shift – powder spectrum

The  $\sigma_{zz}$  component, which we are looking for is

$$\sigma_{zz} = \sigma_{\perp} + (\sigma_{\parallel} - \sigma_{\perp}) \cos^2 \vartheta$$

The resonance frequency this reads

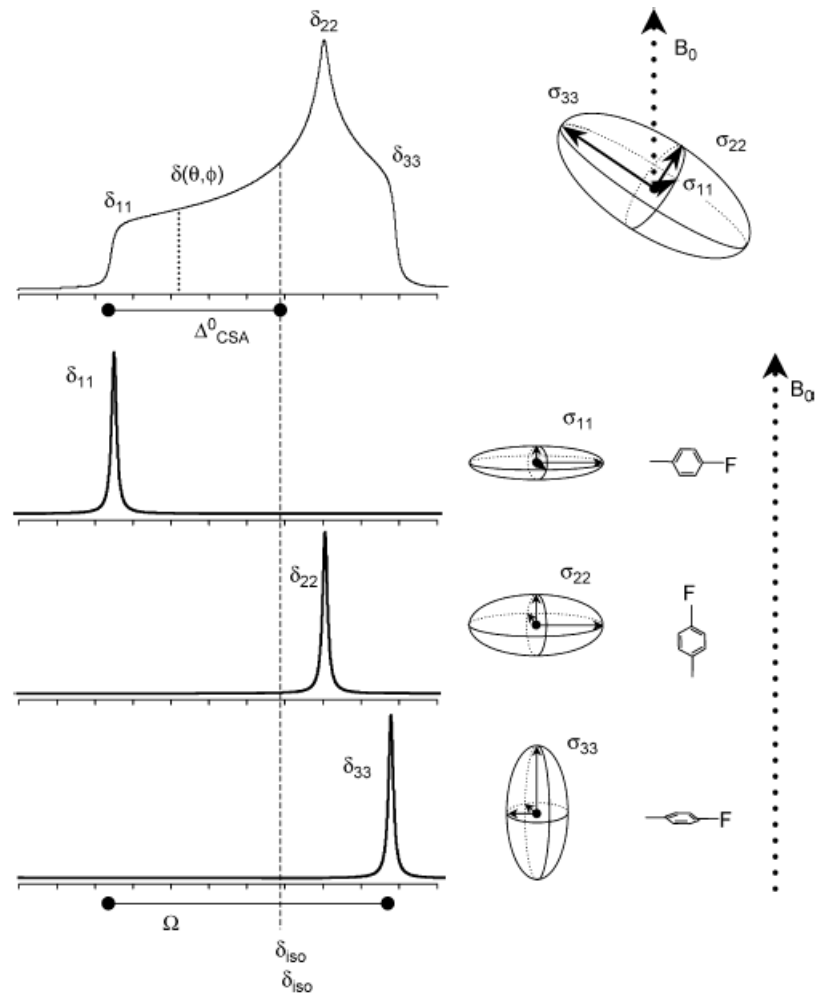
$$\nu = \nu_L (1 + \sigma_{\perp} + (\sigma_{\parallel} - \sigma_{\perp}) \cos^2 \vartheta)$$

To calculate the spectrum

$$f(\nu) d\nu = g(\Omega) d\Omega = \text{const.} d \cos \vartheta$$

$$f(\nu) = \frac{\text{const.}}{d\nu} = \frac{\text{const.}}{\nu_L 2(\sigma_{\parallel} - \sigma_{\perp}) \cos \vartheta}$$

$$f(\nu) = \frac{\text{const.}}{2\nu_L \sqrt{(\sigma_{\parallel} - \sigma_{\perp})(\nu - \nu_L(1 + \sigma_{\perp}))}}$$



$$\nu \in [\nu_L(1 + \sigma_{\perp}), \nu_L(1 + \sigma_{\parallel})]$$

Presence of motions: can average the CS anisotropy even in powders

Example: pristine  $C_{60}$

Molecular rotations at high temperatures

$T > T_s = 260$  K: rapid isotropic rotational diffusion

That means that the angle between the external magnetic field and the principal  $z'$  axis randomly changes  $\Rightarrow$  need to average over theta  $\langle \cos^2 \theta(t) \rangle = 1/3$

$$\begin{aligned} \nu &= \nu_L (1 + \sigma_{\perp} + (\sigma_{\parallel} - \sigma_{\perp}) \langle \cos^2 \theta(t) \rangle) \\ &= \nu_L (1 + \sigma_{\perp} + (\sigma_{\parallel} - \sigma_{\perp}) \frac{1}{3}) \\ &= \nu_L (1 + (\sigma_{\parallel} + 2\sigma_{\perp}) \frac{1}{3}) \\ &= \nu_L (1 + \frac{1}{3} Tr\{\underline{\underline{\sigma}}\}) \end{aligned}$$

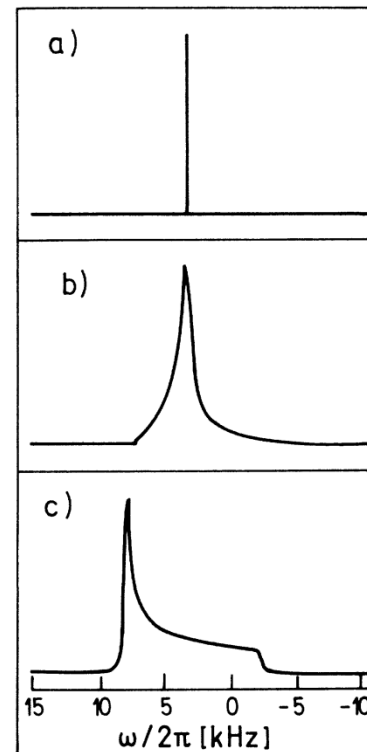


FIG. 5. Simulated inhomogeneous  $^{13}\text{C}$  NMR line shape of powdered  $C_{60}$  for (a) fast isotropic reorientation, (b) fast uniaxial rotation, and (c) a static powder spectrum. In all three cases, the  $^{13}\text{C}$  chemical-shift tensor was assumed to be axially symmetric.

Example: pristine  $C_{60}$

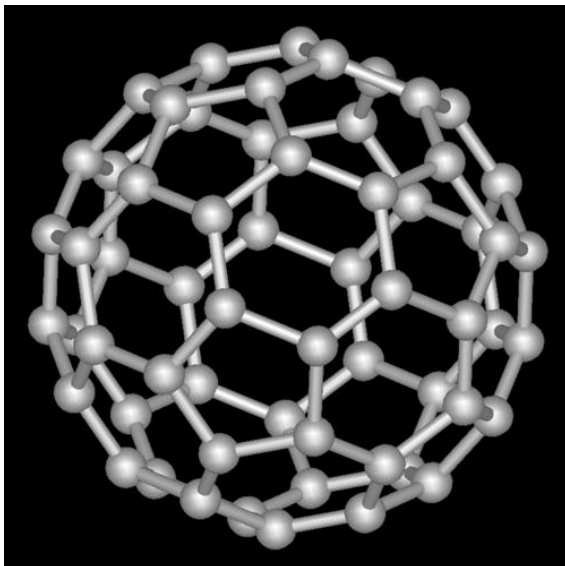
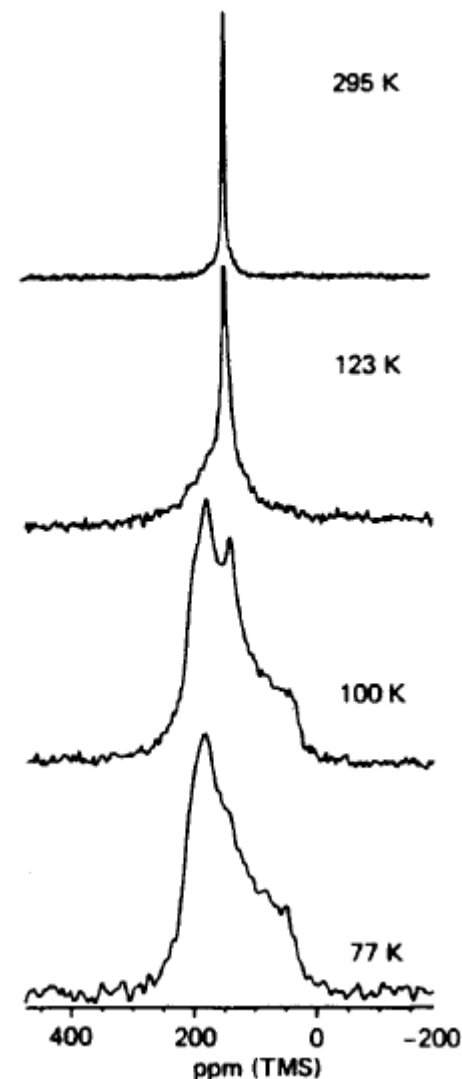


FIG. 20.  $^{13}\text{C}$  NMR spectra of solid  $C_{60}$  obtained at ambient temperatures of 123, 100, and 77 K (Yannoni, Bernier, *et al.*, 1991). The  $^{13}\text{C}$  NMR spectrum of  $C_{60}$  is expected to be a broad "powder pattern" resonance (width greater than  $\approx 200$  ppm) reflecting the chemical-shift anisotropy of the  $^{13}\text{C}$  nuclei averaged over the crystallite orientations. The "motionally narrowed" NMR line at 295 K (143 ppm from tetramethyl silane) proves that  $C_{60}$  molecules are rotating rapidly with respect to the NMR time scale, which is defined by the inverse of the spectral spread ( $\approx 10^{-4}$  s). As the temperature is reduced, the powder pattern is recovered as the molecular motion decreases. At 77 K there is little evidence of the narrow line at 143 ppm, and a fit to this line shape yields an asymmetric chemical-shift tensor with components of 220, 186, and 25 ppm.





## Electron-nuclear interactions cont.

We mentioned that the angular momentum interaction will give rise to a temperature independent chemical shift. However, in paramagnetic solids we need to take into account also the interaction between the electron and nuclear spins. When they are separated in space, then we can always count on the el-nuclear dipolar interactions

$$H_{dip}^{e-n} = \gamma \hbar^2 g \mu_B \sum_{i,j} \left( \frac{3(\hat{S}_i \cdot \vec{r}_{ij})(\hat{I}_j \cdot \vec{r}_{ij})}{r_{ij}^5} - \frac{\hat{S}_i \cdot \hat{I}_j}{r_{ij}^3} \right)$$

This will hold well also for p- and d-state electrons. For them we can in fact rewrite the above equation in terms of a coupling traceless tensor  $T$

$$H_{dip}^{e-n} = \gamma \hbar^2 g \mu_B \hat{I} \cdot \underline{T} \cdot \vec{B}_0$$

For p-electrons the spatial averaging gives the components

$$T_{\parallel} = \frac{4}{5} \left\langle \frac{1}{r^3} \right\rangle \chi_S \quad T_{\perp} = -\frac{2}{5} \left\langle \frac{1}{r^3} \right\rangle \chi_S$$



## Electron-nuclear interactions cont.

The difficulties arise for the s-state electrons. There the dipolar approximation breaks down since we have a non-zero spin density at the nuclear site. We will treat this case within a simple first-order approximation that is reasonably accurate at high magnetic fields. A more rigorous treatment utilises the Dirac equation (see for instance C.P. Slichter, Principles of Magnetic resonance)

S-orbitals have spherical symmetry and non-zero spin density at the nuclear site.

Therefore hf interactions involving s-orbitals are large and isotropic!

The simple model for this interaction is a current loop representing the magnetic moment of the nucleus.

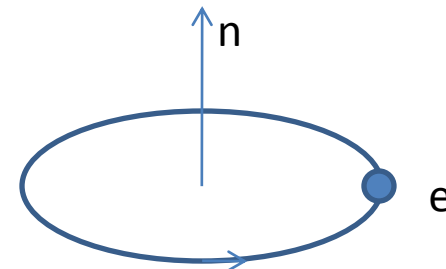
$$\vec{\mu}_N = Si\hat{n} \Rightarrow i = \mu_N / \pi r^2$$

Biot-Savart law: MF at the center of the loop is

$$\vec{B}_N = \frac{\mu_0}{4\pi} \int i \frac{d\vec{l} \times \vec{r}}{r^3} = \frac{\mu_0}{2\pi r^3} \vec{\mu}_N$$

The average field inside a sphere of radius r is

$$\begin{aligned} B_{av} &= B_N (\text{probability density})(\text{volume}) = \\ &= B_N |\psi_e(0)|^2 \frac{4}{3} \pi r^3 = \frac{2}{3} \mu_0 \mu_N |\psi_e(0)|^2 \end{aligned}$$





The energy of the electron magnetic moment in this field will be

$$E = -\vec{\mu}_e \cdot \vec{B}_{av} = \frac{2}{3} \mu_0 g \mu_B \gamma \hbar |\psi_e(0)|^2 \vec{I} \cdot \vec{S} = a \vec{I} \cdot \vec{S}$$

Lets take 1s WF

$$\psi_e(\vec{r}) = \sqrt{\frac{1}{\pi r_B^3}} e^{-r/r_B} \quad r_B = 5.29 \cdot 10^{-11} \text{ m}$$

to get

$$a_{1s} / g \mu_B = \frac{2}{3} \mu_0 \gamma \hbar |\psi_e(0)|^2 = 0.5076 \text{ T}$$

The more general treatment would actually give the famous Fermi contact interaction

More formalistic calucaltion: see J.D. Jackson, Classical Electrodynamics, Ch. 5

$$\mathbf{A} = \frac{\mu_0}{4\pi} \mathbf{m}_N \times \frac{\hat{\mathbf{r}}}{r^2} = \frac{\mu_0}{4\pi} \mathbf{m}_N \times \frac{\mathbf{r}}{r^3}.$$

$$\mathbf{B} = \nabla \times \mathbf{A} :$$

$$H_{hf} = \frac{8\pi}{3} g \mu_B \gamma \hbar^2 \vec{I} \cdot \vec{S} \cdot \delta^3(\vec{r})$$



# Core-polarization hf coupling

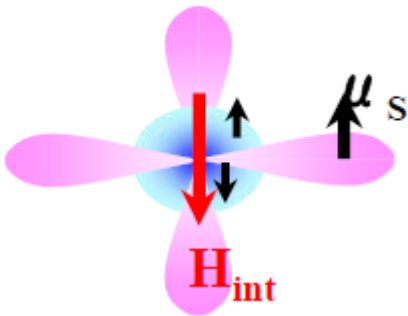
*d*-electrons: Do we expect Fermi contact hf interaction (zero spin density)?

They will frequently lead to the anisotropic hf interactions, which can be generally written as

$$H = \sum_{i=x,y,z} a_i I_i S_i \Rightarrow \sum_{i=x,y,z} a_i \frac{\chi}{g\mu_B \hbar} I_i B_i$$

We may thus define the Knight-shift tensor with component

$$K_{ii} = \frac{a_i}{g\mu_B \gamma \hbar^2} \chi_i$$



The result may be at first sight surprising since *d*-WF vanishes at the nuclear site. However, *d*-electrons can interact indirectly by polarizing core electrons. The Coulomb repulsion drives core *s*-states (fully occupied) closer to the nucleus. However, because of the Pauli principle “down-spin” *s*-orbitals will shrink more than “up-spin” *s*-orbitals. This will create a total negative hf field at the nuclear site. The associated fields can be in fact quite substantial sometimes. For  $\text{Mn}^{2+}$  in  $\text{MnF}_2$  it can be as large as  $-127 \text{ kOe}/\mu_B$ . 49

# Hyperfine interaction

What will Fermi contact interaction do in magnetic systems?

$$H_{hf} = \frac{8\pi}{3} g\mu_B \gamma \hbar^2 \vec{I} \cdot \vec{S} \cdot \delta^3(\vec{r}) \quad \rightarrow \quad \omega_n = \gamma_n B_{loc} = \gamma_n \left( B_0 + \langle B_{hf} \rangle \right)$$

Since we expect that the electron spin dynamics will be fast on the time-scale of NMR experiments (over 10  $\mu$ s) we can take average of  $e^-$  spin operator  $||B_0$

$$\langle \mathbf{B}_{hf} \rangle = \sum_i \mathbf{A}_i \cdot \langle \mathbf{S}_i \rangle$$

Hyperfine tensor:

- on-site: Fermi contact, A= very strong and  $\sim$ known
- Transferred: A can be anything
- Dipole: A can be calculated, usually very weak; it vanished in sites having cubic symmetry

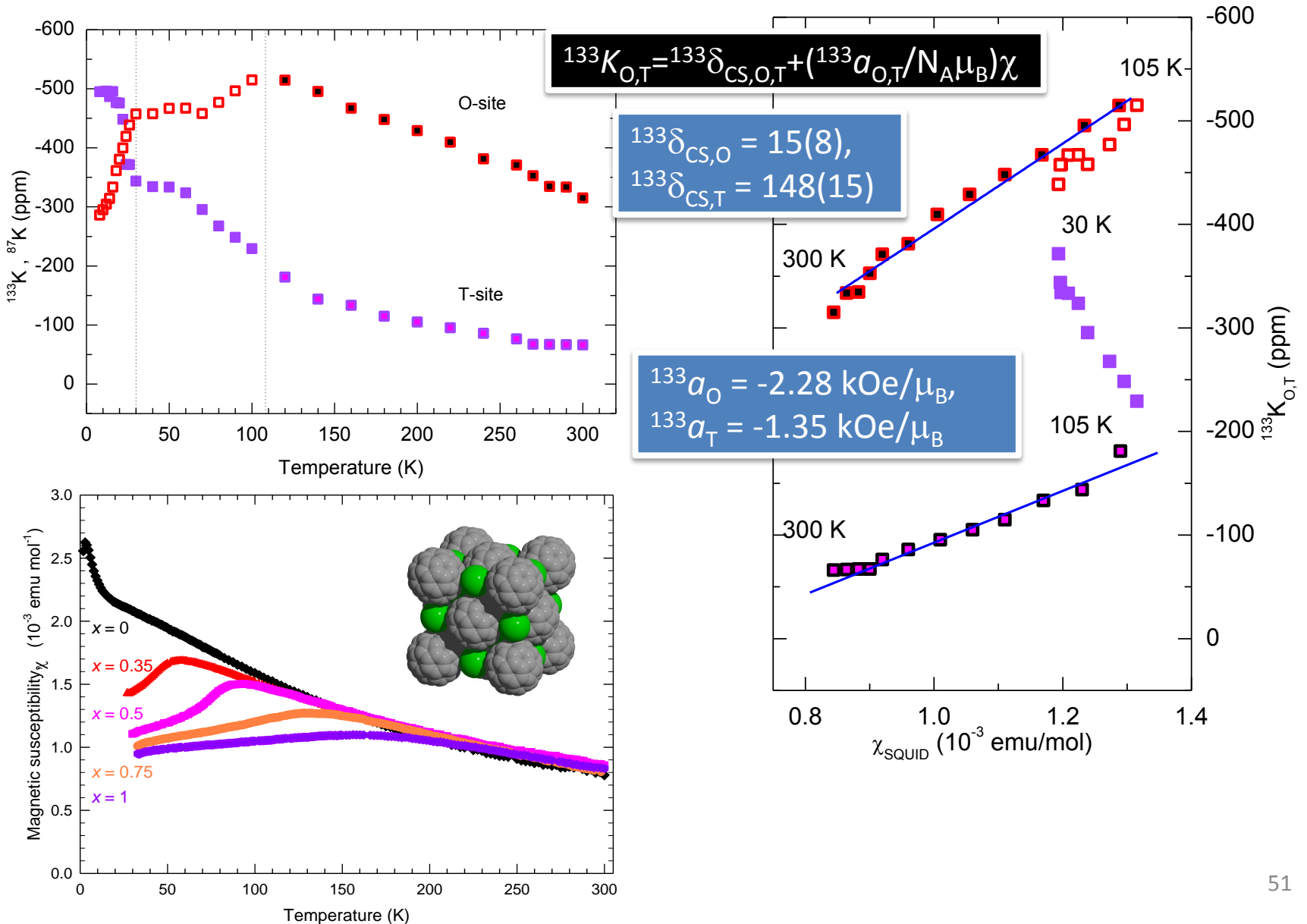
$$A \vec{I} \cdot \vec{S} \rightarrow A I_Z \langle S_Z \rangle = A I_Z \frac{\mu_Z}{g\mu_B \hbar} = \gamma_n I_Z \frac{A \chi_S}{\gamma_n N_A g\mu_B \hbar} B_0 \quad \rightarrow \quad K = \frac{A}{\gamma_n N_A g\mu_B \hbar} \chi_S$$

Units of A found in the literature:

- $A/\hbar$  [ $s^{-1}$ ]
- $10^{-3} A/\gamma_n \hbar$  [kG/spin]
- $10^{-3} A/\gamma_n g \hbar$  [kG/ $\mu_B$ ]
- $A/1.602 \times 10^{-12}$  [eV]

# Hyperfine interaction

## How do we extract hyperfine tensor?

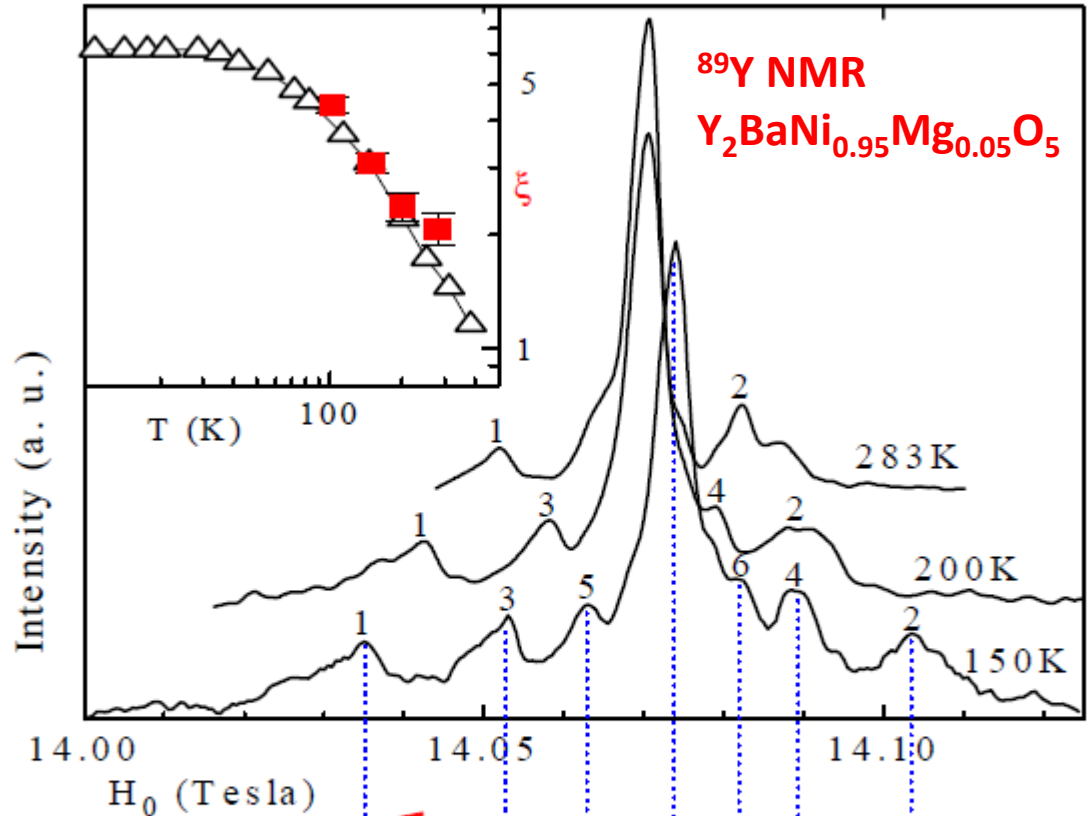


# Hyperfine interaction

**But, be carefull! NMR is still a local real-space probe!**  
**Example, doping of Haldane chain system**

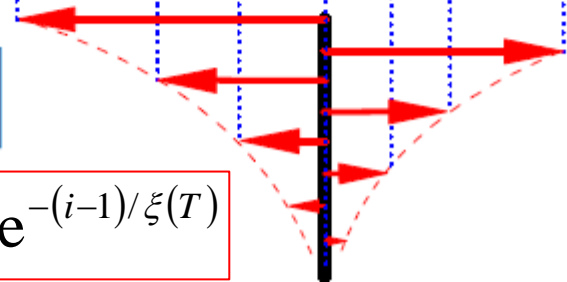
F. Tedoldi et al., PRL 1999

- valence bond solid with a single valence bond connecting every neighboring pair of sites
- the ends of the chain behave like spin  $S=1/2$  moments even though the system consists of  $S=1$  only



$$\nu_{\text{RF}} = \frac{\gamma}{2\pi} (H_0 + h_j^z) = \frac{\gamma}{2\pi} \left[ H_0 + \left( \sum_{l,k} \hat{A}_{lkj} \langle \vec{S}_{lk} \rangle \right)^z \right]$$

$$\Delta H_i(T) = (-1)^{i-1} \Delta H_1(T) e^{-(i-1)/\xi(T)}$$





# Knight shift

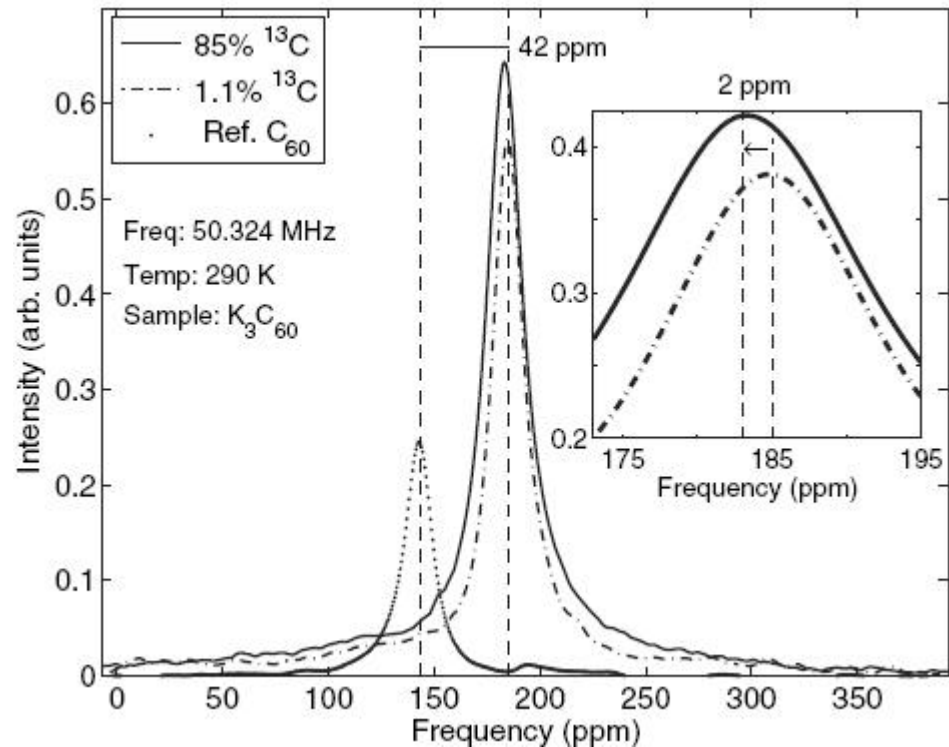
## In metals:

- The shift is always (almost) positive
- The shift is very nearly temperature independent
- The shift in principle increases with the nuclear charge  $Z$ .

The fact that metals have a weak spin-paramagnetism suggest that the shift may simply represent the pulling of the magnetic flux into the metal. However, the susceptibilities are too small to account for such effect.

Knight postulated that the shift arises because of the **interaction of nuclear spins with the conduction electrons through the s-state hf interaction.**

## $C_{60}$ versus $K_3C_{60}$





# Knight shift

What will Fermi contact interaction do in metals?

$$H_{hf} = \frac{8\pi}{3} g\mu_B \gamma \hbar^2 \vec{I} \cdot \vec{S} \cdot \delta^3(\vec{r})$$

Since we expect that the electron spin dynamics will be fast on the time-scale of NMR experiments we can

$$\vec{I} \cdot \vec{S} \rightarrow I_Z \langle S_Z \rangle = I_Z \frac{\mu_Z}{g\mu_B \hbar} = I_Z \frac{\chi_{mol}}{g\mu_B \hbar} B_0$$

In order to calculate the spin density at the nuclear site, we start with the Bloch WF

$$\psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \quad \Rightarrow \quad \rho_e = |\psi_{\vec{k}}(\vec{r})|^2$$

We need to consider only states at the Fermi level

Putting everything together we derive

$$H_{hf} = \frac{8\pi}{3} \gamma \hbar \chi |u_k(0)|_{E_F}^2 I_Z B_0 \equiv \gamma \hbar K I_Z B_0$$

With a **Knight shift**

$$K = \frac{8\pi}{3} |u_k(0)|_{E_F}^2 \chi$$

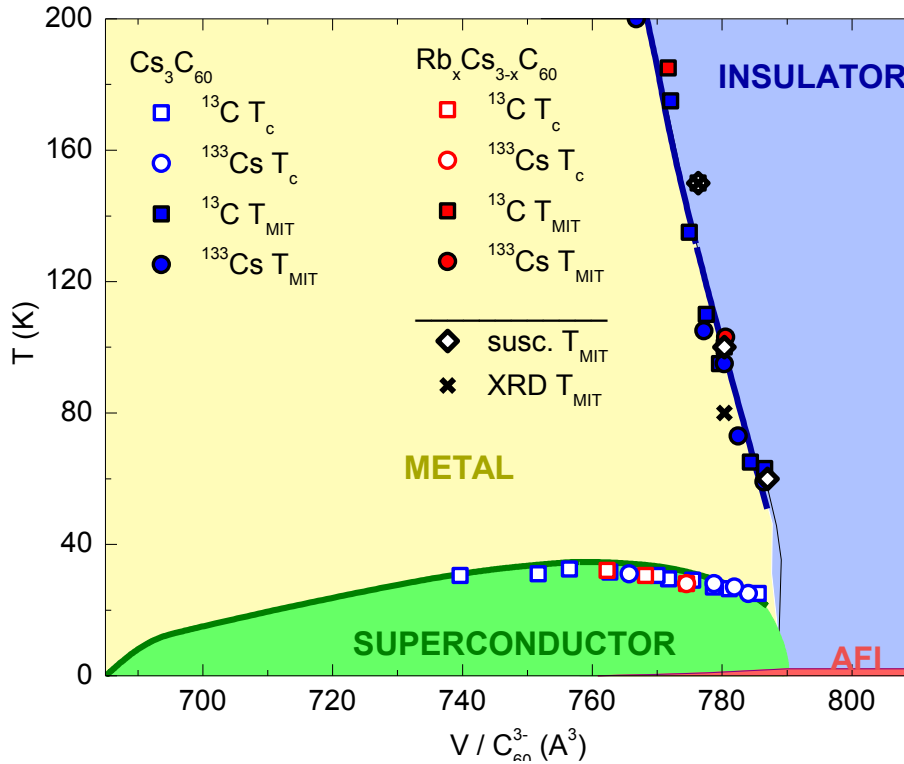


Measurement of spin-only susceptibility  $\rightarrow N(E_F)$

# METALLIC/SC STATE

## $T_{MIT}$ , $T_{SC}$ dependence pressure/doping

MIT line is not vertical



Thinking about CC explanation

$$dp/dT = \Delta S / \Delta V$$

If the magnetic entropy (calculated per  $C_{60}$ ) is

$$\Delta S = k_B \ln [S(S+1)] = k_B \ln 2.$$

Structural study:

$$\Delta V = 4 \text{ \AA}^3 \text{ per } C_{60}$$

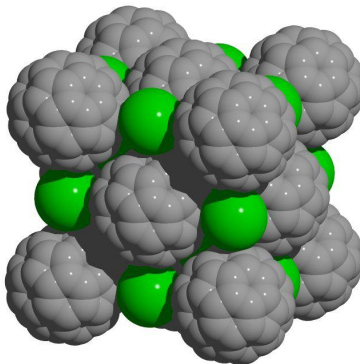
We thus estimate

$$dp/dT = k_B \ln 2 / \Delta V$$

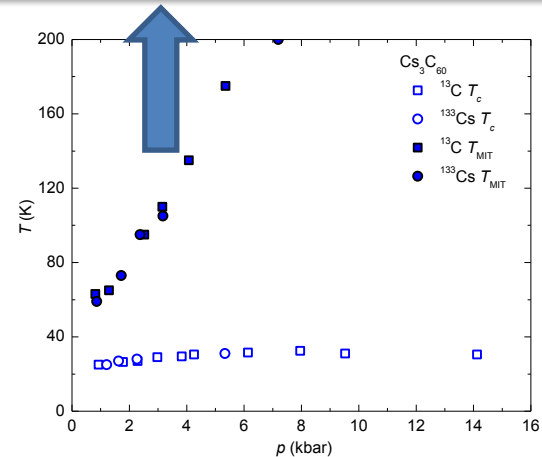
$$= 1.4 \cdot 10^6 \text{ Pa/K}$$

Experimental value:

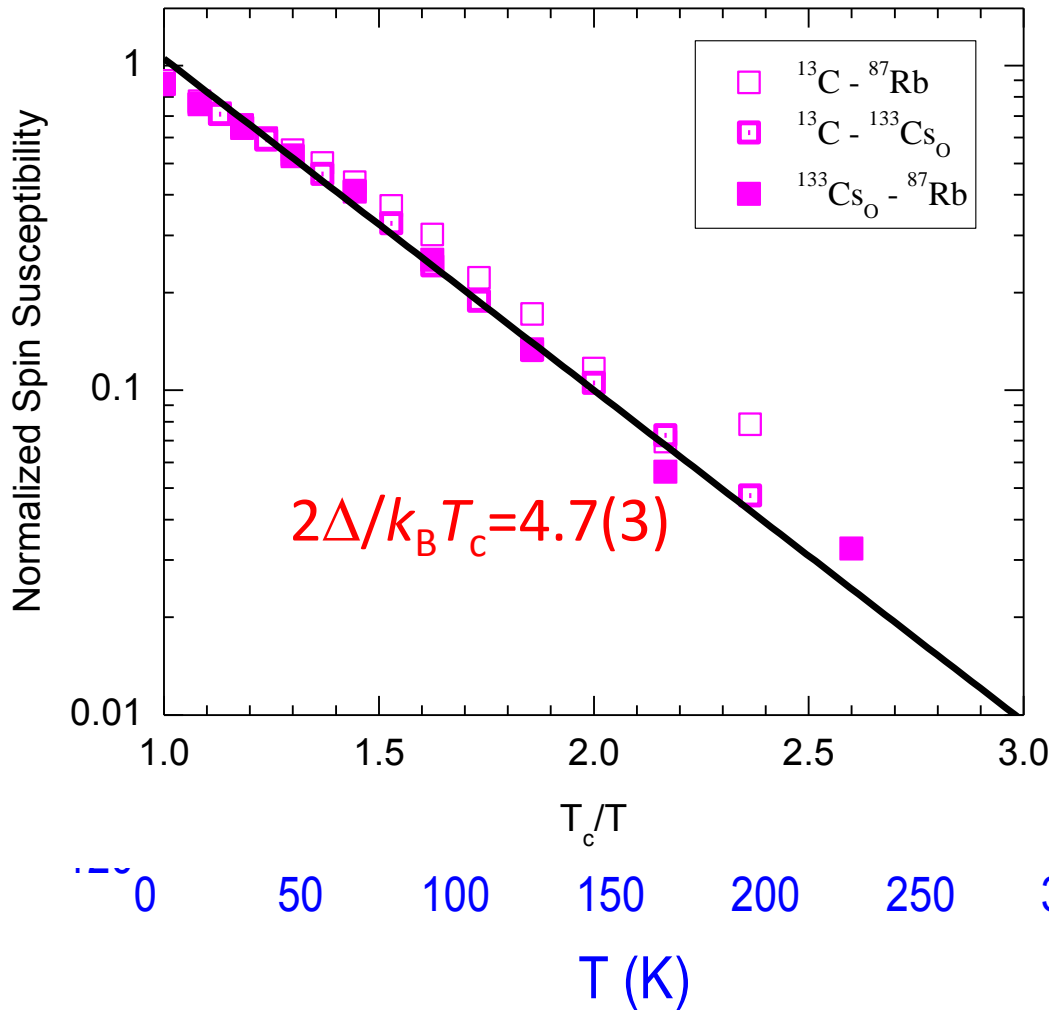
$$dp/dT = 0.6 \text{ GPa/150 K} = 4 \cdot 10^6 \text{ Pa/K.}$$



NMR  
 $T_{MIT}$  vs  $p$  diagram



# Superconducting state



## Superconducting state

$$\eta \delta = \eta \delta_{\text{CS}} + \frac{\eta a}{N_A \mu_B} \chi_S + \frac{\Delta B}{B_0}$$

$$Y(T) = \int_{-\infty}^{\infty} dE \left( -\frac{\partial f}{\partial E} \right) \text{Re} \left[ \frac{E}{(E^2 - \Delta^2)^{1/2}} \right],$$

demagnetization due to the Meissner screening currents and is in general not known

After subtraction of two shifts

$$\eta \delta - \eta' \delta = \Delta_{\text{CS}} + A \chi_S$$

$$\Delta_{\text{CS}} = \eta \delta_{\text{CS}} - \eta' \delta_{\text{CS}}$$

$$A = (\eta a - \eta' a) / N_A \mu_B$$





## Summary of interactions

$$H = H_Z + H_{dip} + H_Q + H_{e-n}$$

$$H_Z = -\gamma\hbar B_0 \hat{I}_Z$$

$$H_{dip} = \frac{\gamma^2 \hbar^2}{2} \sum_{i,j} \left( \frac{\hat{I}_i \cdot \hat{I}_j}{r_{ij}^3} - \frac{3(\hat{I}_i \cdot \vec{r}_{ij})(\hat{I}_j \cdot \vec{r}_{ij})}{r_{ij}^5} \right)$$

$$H_Q = \frac{e^2 q Q}{4I(2I-1)} \left[ 3\hat{I}_Z^2 - I(I+1) + \frac{\eta}{2} (I_+^2 + I_-^2) \right]$$

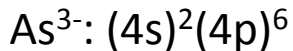
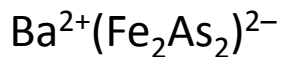
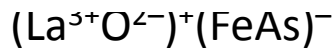
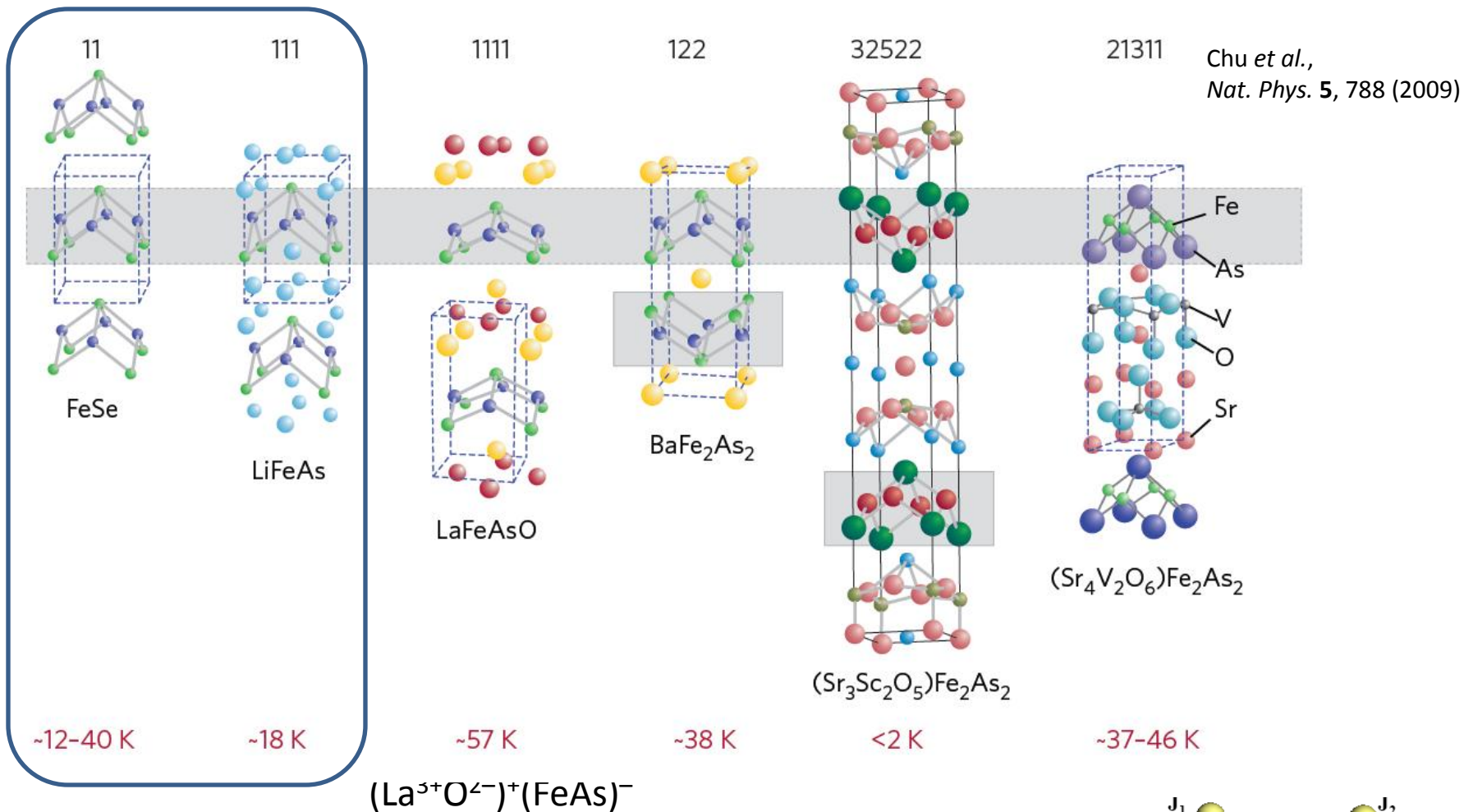
$$H_{CS} = -\gamma\hbar \vec{I} \cdot \underline{\underline{\sigma}} \cdot \vec{B}_0$$

$$H_{dip}^{e-n} = \gamma\hbar^2 g\mu_B \hat{I} \cdot \underline{\underline{T}} \cdot \vec{B}_0$$

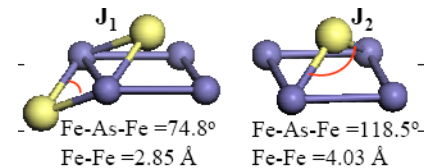
$$H_{hf} = \frac{8\pi}{3} g\mu_B \gamma\hbar^2 \vec{I} \cdot \vec{S} \cdot \delta^3(\vec{r})$$

$$K_{ii} = \frac{a_i}{g\mu_B \gamma\hbar^2} \chi_i$$

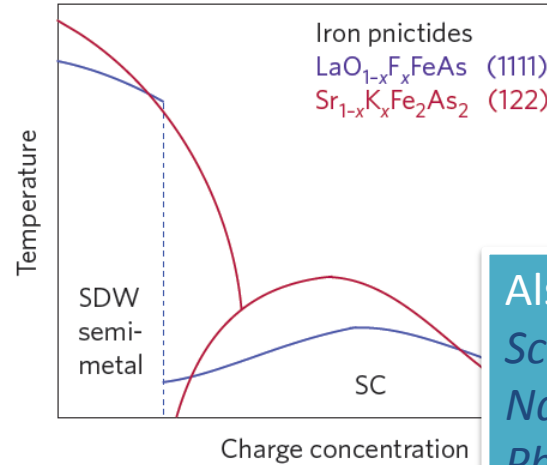
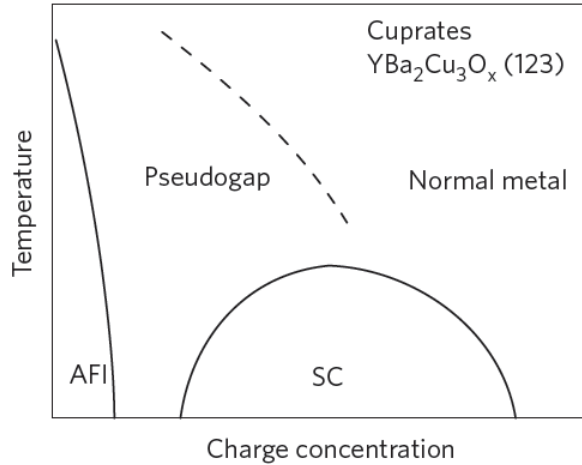
# Example - Pnictides



Se atom has one extra electron compared to an As atom,  
 $\text{Se}^{2+}: (4s)^2(4p)^6$



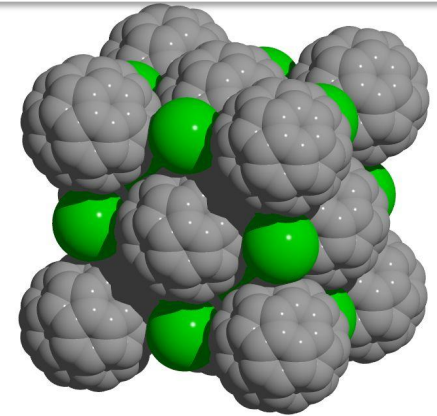
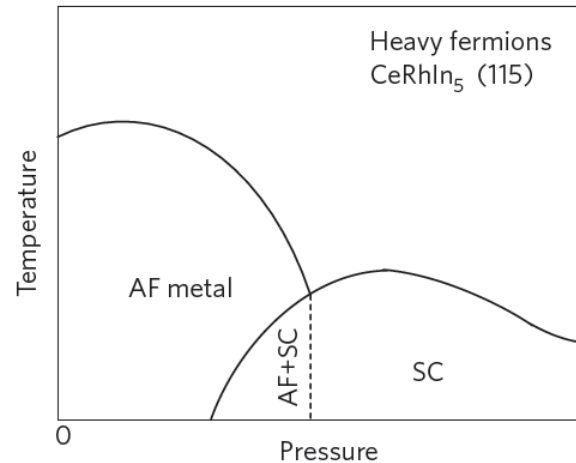
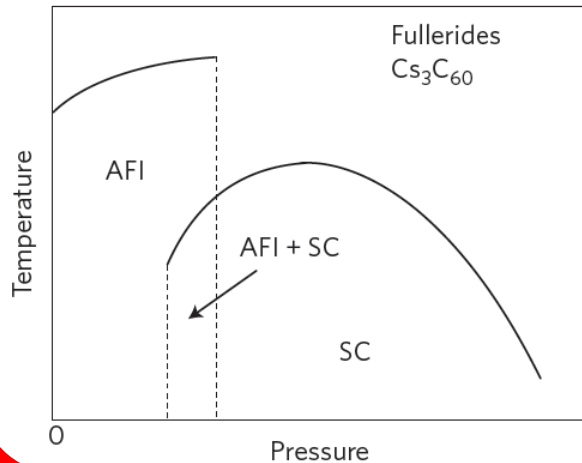
# Phase diagrams



Chu *et al.*,  
*Nat. Phys.* **5**, 787 (2009)

SC: superconducting  
 AFI: AFM insulating

Also see our papers  
*Science* **323**, 1585 (2009)  
*Nature* **466**, 221-225 (2010)  
*Phys. Rev. B* **80**, 195424 (2009)

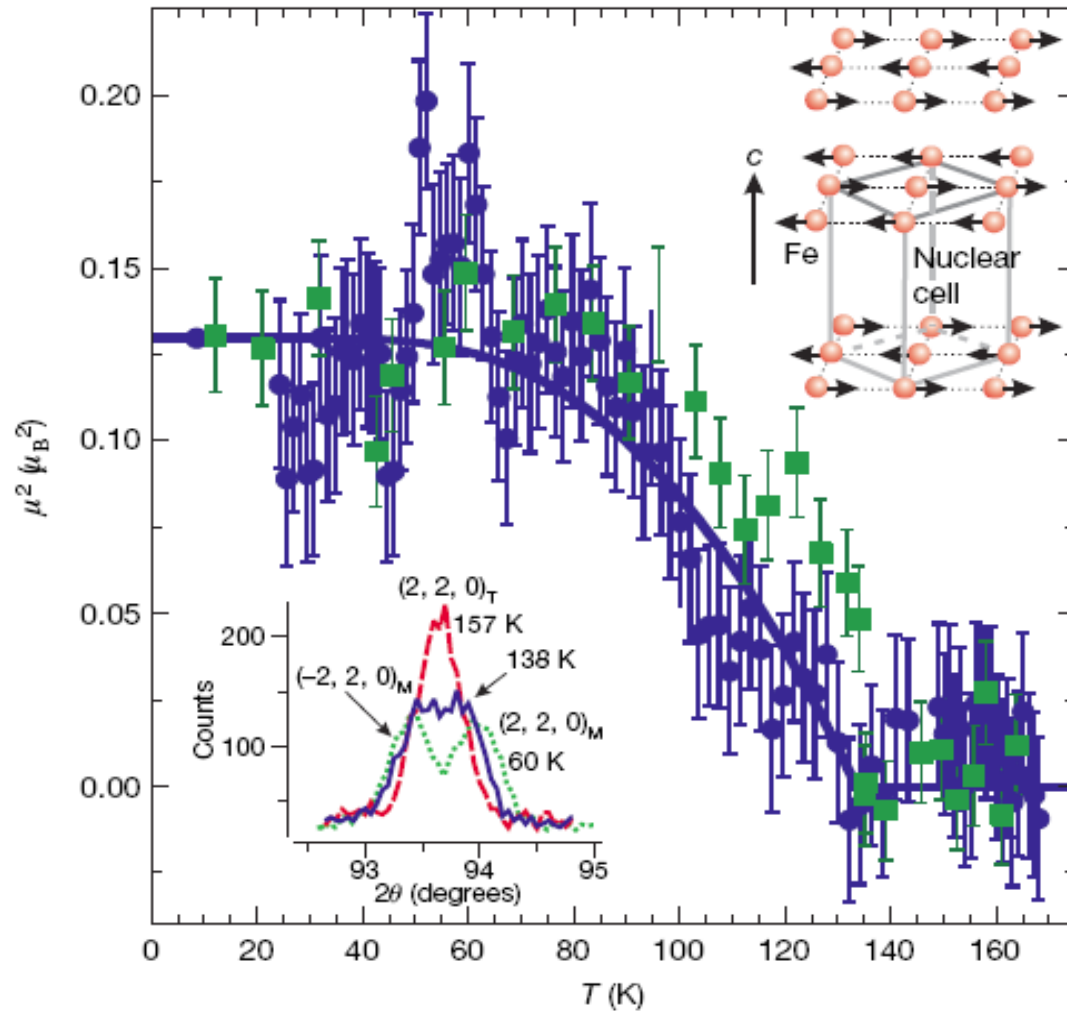


1. AFI phase next to SC is a hallmark of electron correlations. Correlations are strong and onsite.
2. No symmetry change through MIT!
3. Charge versus pressure controle of SC!

4. No disorder caused by the doping (off stoichiometries ...)
5. 3D vs 2D!
6. Importance of cubic symmetry!

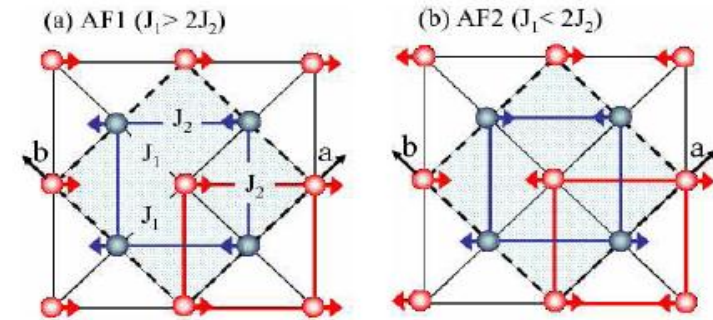
# Example: NMR in magnetically ordered state

## SDW in pnictides (1111 phase)



Cruz et al., *Nature* **453**, 899 (2008)

Yildirim, arXiv:0804.2252



Fully frustrated

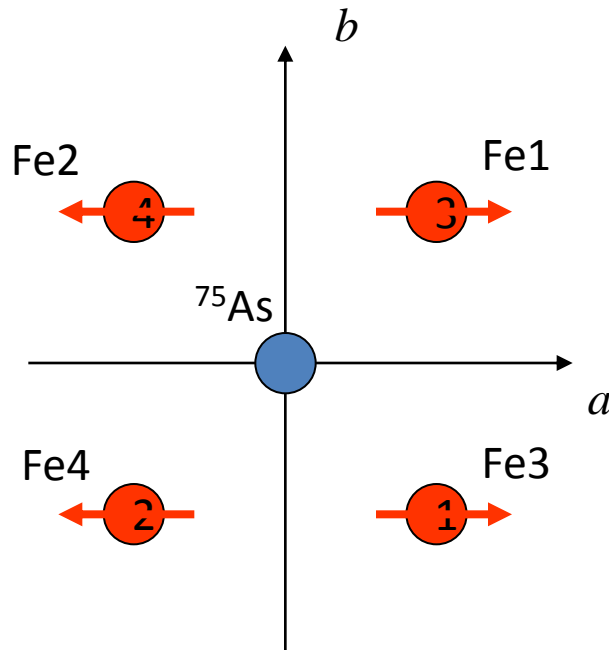
The frustration is lifted by a structural distortion

- SDW order with  $Q=(\pi,\pi)$  for  $\sqrt{2}a \times \sqrt{2}a$  due to the interband nesting between the hole  $\alpha$ - and electron  $\beta$ -bands
- magnetic moments  $\sim 0.3 \mu_B$

# Example: NMR in magnetically ordered state

## **SDW in pnictides (1111 phase)**

$^{75}\text{As}$  coupling to Fe moments



$$\vec{B}_{As} = \sum_{i=1}^4 \mathbf{A}_i \cdot \vec{\mu}_i$$

Symmetry considerations: mirror reflection with respect to bc plane

$$\mathbf{A}_1 = \begin{pmatrix} a_{xx} & a_{xy} & a_{xz} \\ a_{xy} & a_{yy} & a_{yz} \\ a_{xz} & a_{yz} & a_{zz} \end{pmatrix}; \quad \mathbf{A}_2 = \begin{pmatrix} a_{xx} & -a_{xy} & -a_{xz} \\ -a_{xy} & a_{yy} & a_{yz} \\ -a_{xz} & a_{yz} & a_{zz} \end{pmatrix}$$

$$\mathbf{A}_3 = \begin{pmatrix} a_{xx} & -a_{xy} & a_{xz} \\ -a_{xy} & a_{yy} & -a_{yz} \\ a_{xz} & -a_{yz} & a_{zz} \end{pmatrix}; \quad \mathbf{A}_4 = \begin{pmatrix} a_{xx} & a_{xy} & -a_{xz} \\ a_{xy} & a_{yy} & -a_{yz} \\ -a_{xz} & -a_{yz} & a_{zz} \end{pmatrix}$$

**PM phase:**  $\vec{M} = \chi \vec{H}_0$

$$\delta\nu = 4a_{xx}\chi B_0$$

ONLY ISOTROPIC PART!!!!

**AF phase** – taken from LaOFeAs data

$$\mathbf{Q} = (1, 0, 1)$$

Fe magnetic moments are aligned along the  $a$ -axis

$$\mu_{Fe} \sim 0.3\mu_B$$

$$\vec{B}_{As} = 4a_{xz}\mu_{Fe} \cdot \hat{e}_c \longrightarrow B_{eff} = B_0 \sqrt{1 + (B_{int}/B_0)^2} + (B_{int}/B_0) \cos \mathcal{G}$$

ONLY OFF-DIAGONAL TERMS!!!!

# Example: NMR in magnetically ordered state

PHYSICAL REVIEW B **79**, 094515 2009

**NdOFeAs**

T phase: As reside on the 2c (1/4, 1/4, z) position, which is axially symmetric.

$$\eta = (V_{xx} - V_{yy}) / V_{zz} = 0$$

$$\nu_Q = 3 e V_{zz} Q / 2I(2I-1) = 11.8 \text{ MHz}$$

**NdFeAsO<sub>0.85</sub>F<sub>0.15</sub>**

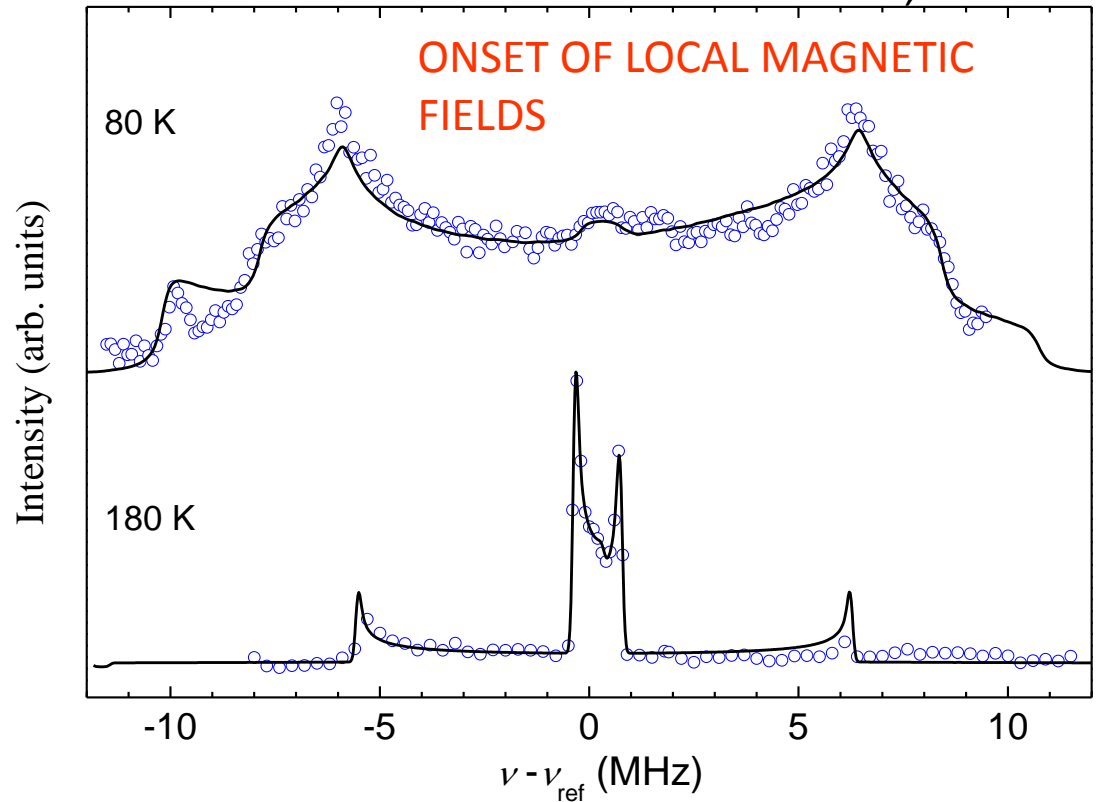
$$\nu_Q = 12.8 \text{ MHz}$$

Low-T orthorhombic phase: As is on 4g (0, 1/4, z) position,  $\eta=0.102$

EFG mainly originates from As 4p Electrons with a prolate p electron distribution in agreement with the negative  $V_{zz}$ .

comparison

(LaO<sub>0.9</sub>F<sub>0.1</sub>FeAs:  $\nu_Q = 11 \text{ MHz}$ )



$$\nu_{m \rightarrow m-1} = \gamma_{As} B_{eff} + \Delta \nu_Q^{(1)}(\mathcal{J}, \varphi) + \Delta \nu_Q^{(2)}(\mathcal{J}, \varphi)$$

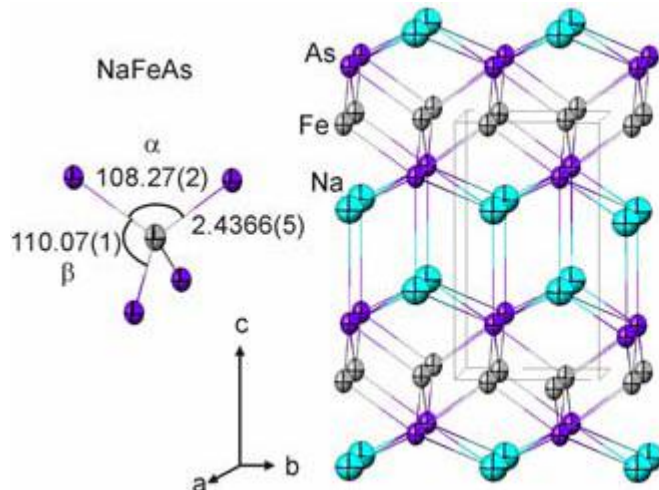


$$A_{xz} = 10.5 \text{ kOe}/\mu_B$$

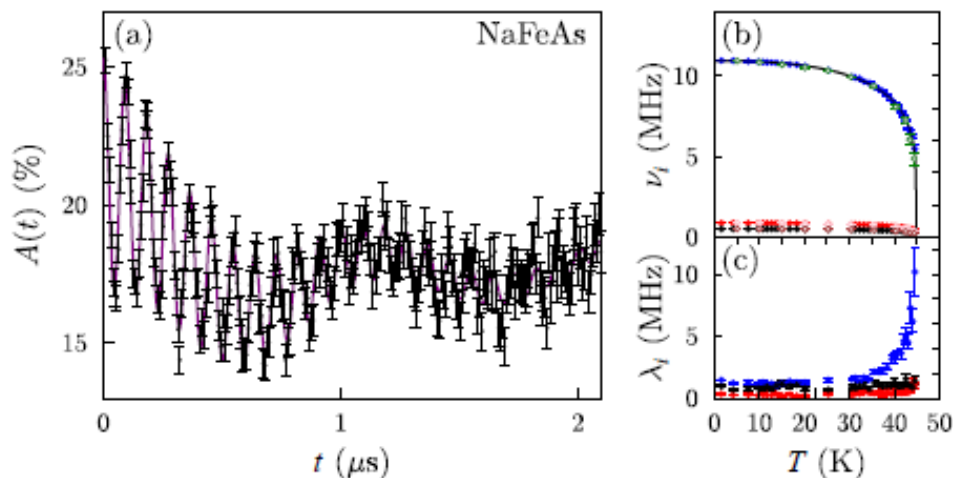
large anisotropic hyperfine fields  $\rightarrow$  experimental evidence for the Fe 3d and As 4p hybridizations

# '111' family

## NaFeAs

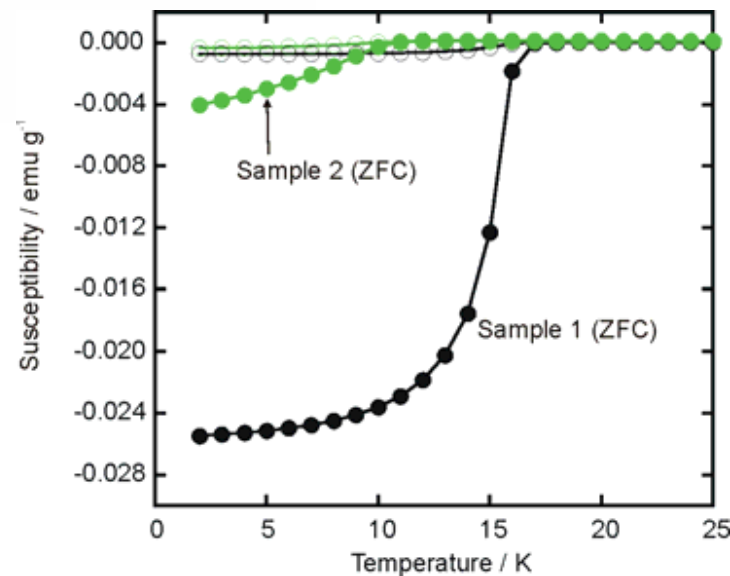
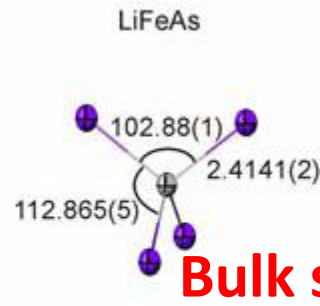


SDW below  $T_{SDW} = 45$  K



D.R. Parker et al.,  
PRL 104, 057007 (2010).

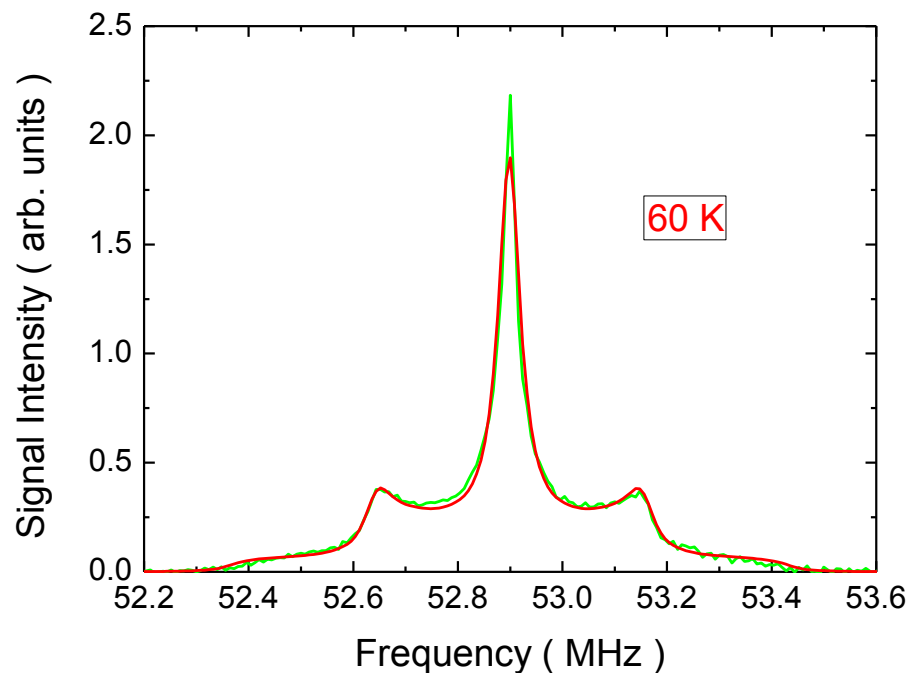
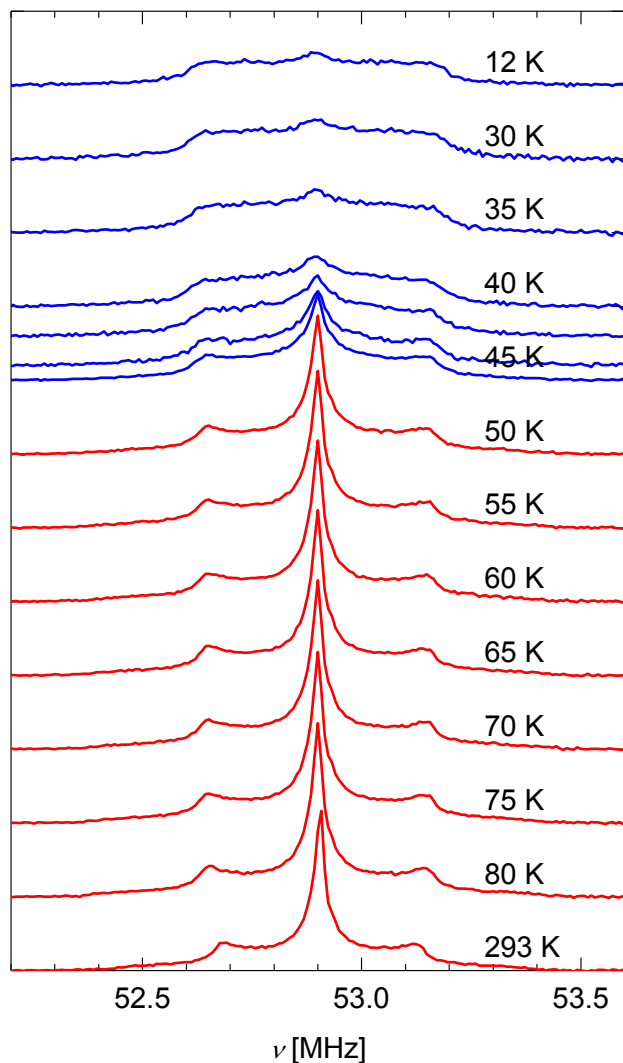
## LiFeAs



M.J. Pitcher et al.,  
Chemical Communications 5918 - 5920 (2008).

# $^{23}\text{Na}$ ( $I = 3/2$ ) NMR in NaFeAs

## $^{23}\text{Na}$ NMR, $\text{Na}_1\text{FeAs}$



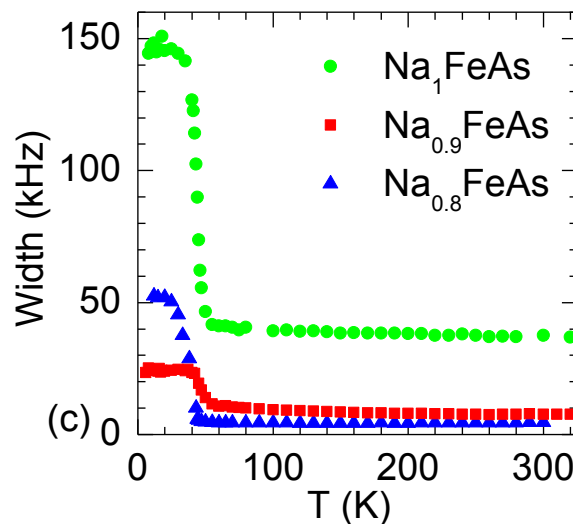
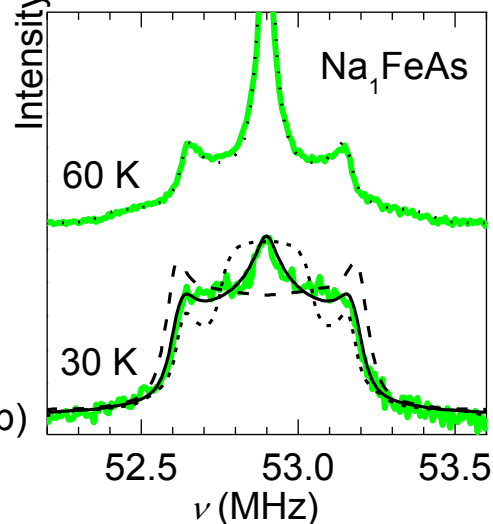
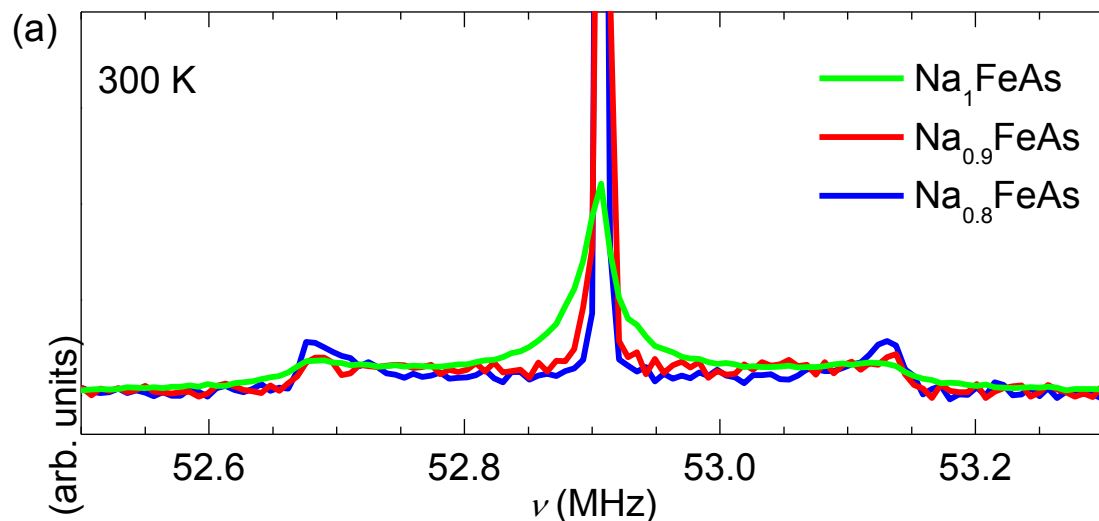
$\nu_Q = 530$  kHz and the electric field gradient (EFG) asymmetry parameter  $\eta = 0$ , in agreement with the high-temperature Na site symmetry.



**No structural phase transition between RT and 60 K**



# $^{23}\text{Na}$ ( $I = 3/2$ ) NMR in $\text{Na}_x\text{FeAs}$



They are isostructural!

Na vacancies in Na-deficient samples are expected to result in the local disorder and thus broadened NMR lines, which is in contrast to the measured  $^{23}\text{Na}$  central transition linewidth in the temperature range 50 – 300K  
→  $\text{Na}^+$  migration??

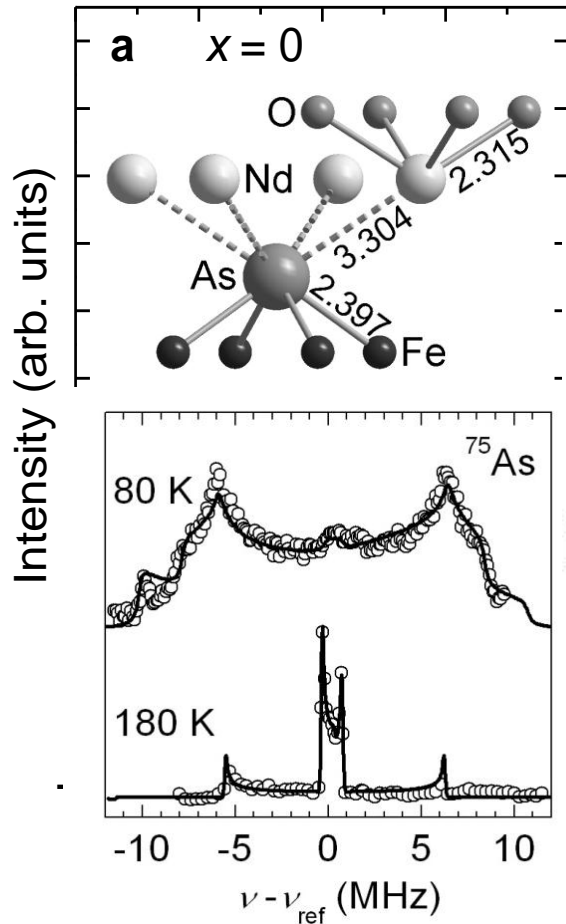
Lineshape broadening is a clear indication of SDW transition.

Variation of SDW order parameter with  $x$ .

Still single line so NO phase segregation in this case.

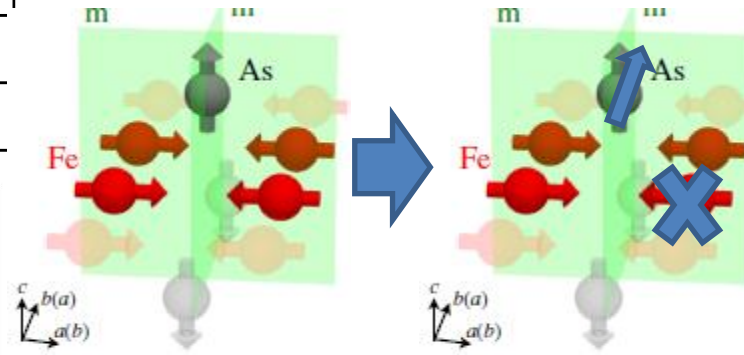
# Incommensurate SDW vs. other solutions

## Commensurate SDW



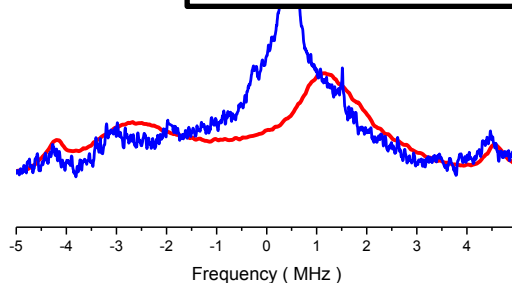
NdOFeAs; P. Jeglič, PRB 2009

Commensurate SDW order with large local amplitude variations in the vicinity of the dopant Curro et al (2010).



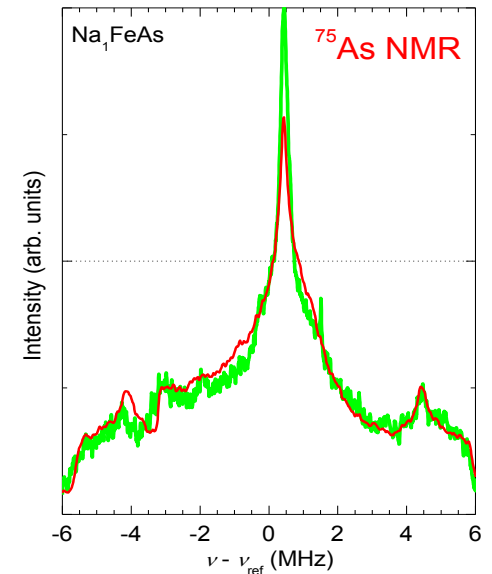
IC SDW amplitude of

$x=1$	$0.28\mu_B$
$x=0.9$	$0.04\mu_B$
$x=0.8$	$0.13\mu_B$

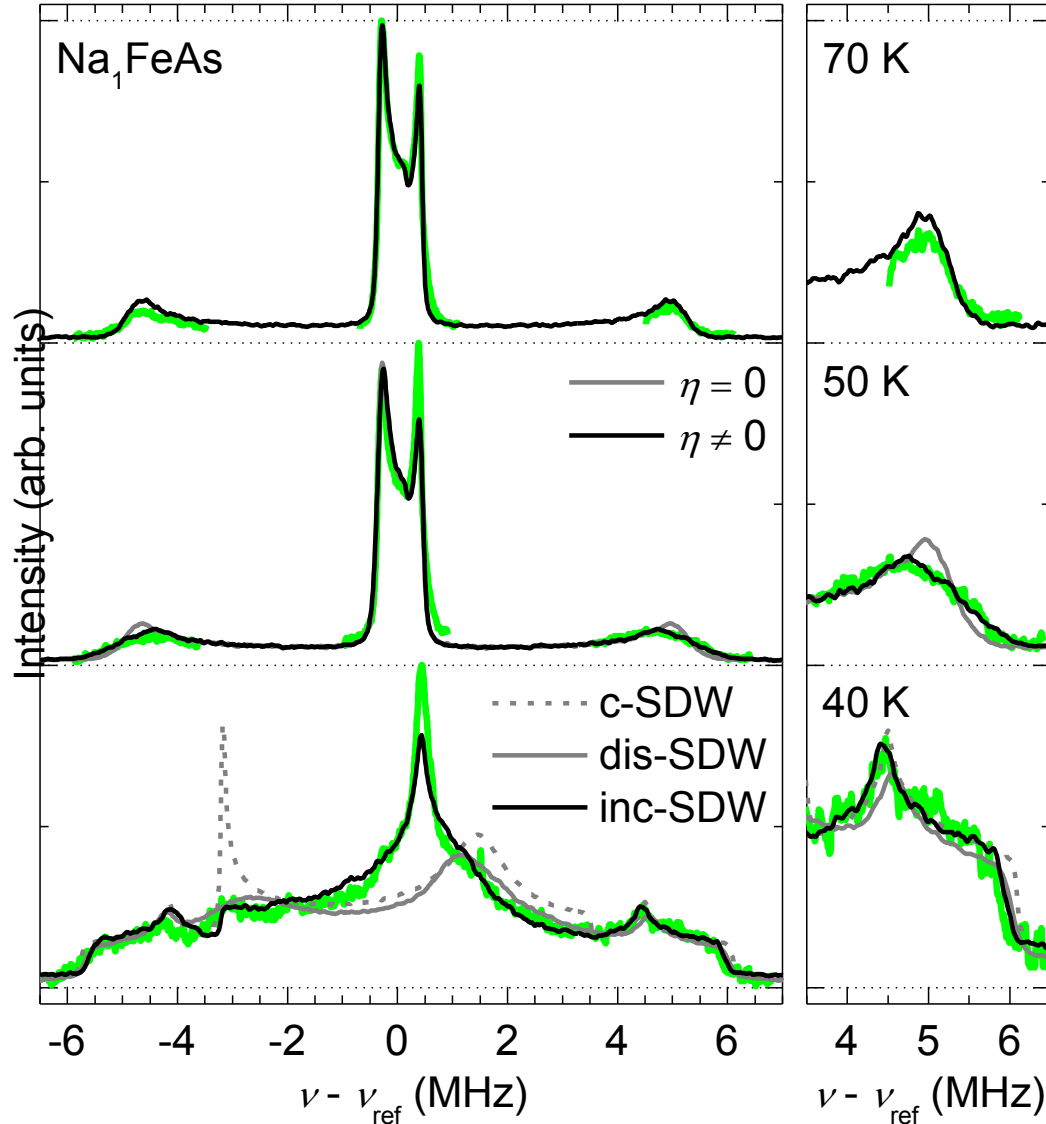


## INCOMMENSURATE SDW

$B_{\text{int}} = B_0 \sin \alpha$   
 with  $\alpha \in [0, 2\pi]$  and  $B_0 = 0.45 \text{ T}$   
 ordering vector  $(1/2 - \epsilon, 0, 1/2)$  for  $\epsilon \rightarrow 0$



# $^{75}\text{As}$ ( $I = 3/2$ ) NMR in $\text{Na}_x\text{FeAs}$ for $T < T_{SDW}$ : Nature of the order?

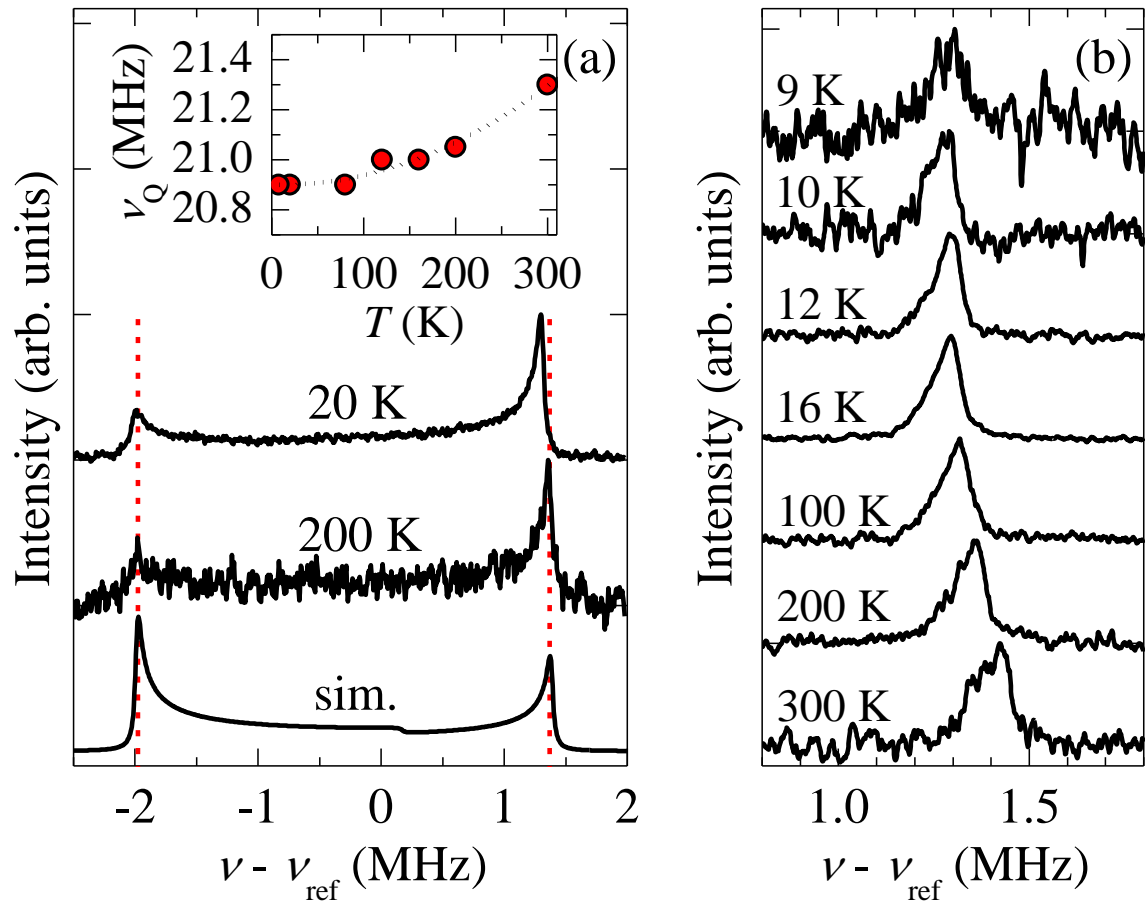


Still no structural phase transition, but some distribution due to local inhomogeneities

Structural phase with low-temperature tetragonal phase between 60 K and  $T_{SDW}$

**THE MAGNETIC ORDER IS INCOMMENSURATE!!!**

# LiFeAs – $^{75}\text{As}$ NMR

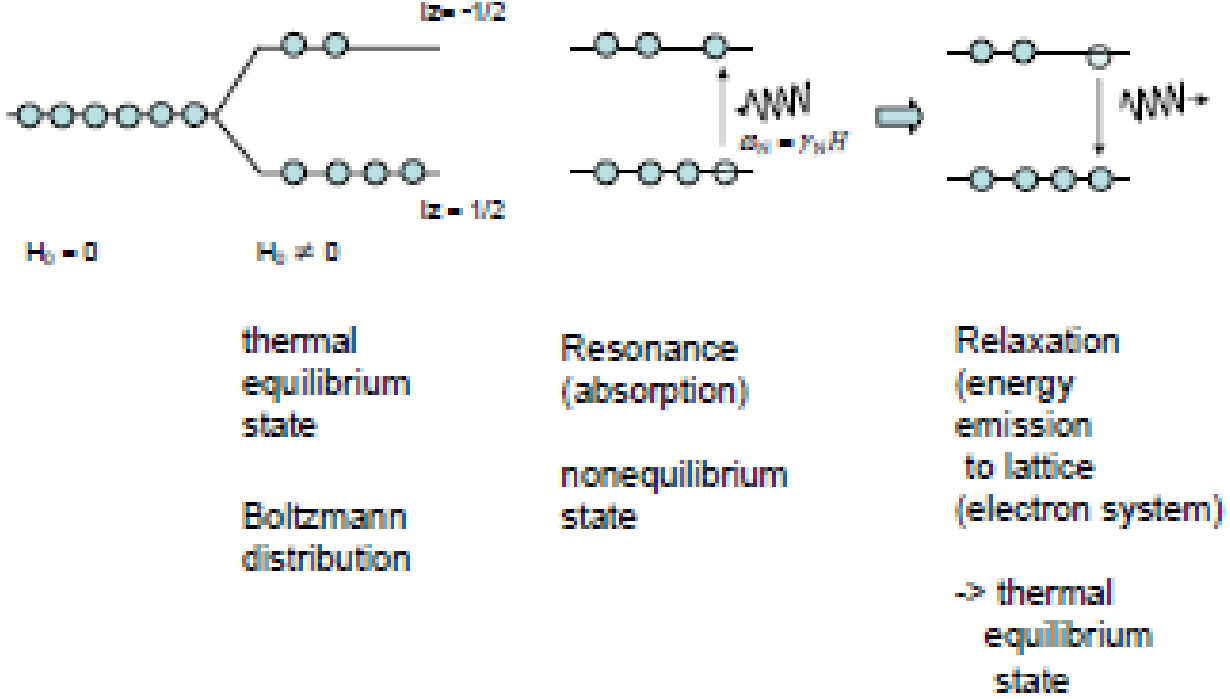


Jeglič et al.,  
PHYSICAL REVIEW B **81**,  
140511R (2010)

- Axially symmetric tensor in agreement with the  $^{75}\text{As}$  site symmetry
- Weakly temperature dependent  $\nu_Q$
- **No anomalies that would indicate SDW transition**
- Below  $T_c \approx 16$  K (9 T) – wipeout effect  $\Rightarrow$  onset of SC

# Spin-lattice relaxation time

Lets recall that



In order to calculate spin-lattice relaxation, we should look at the terms in the spin Hamiltonian that produce transitions between energy levels => we need transverse time-dependent magnetic field

$$H' = -\gamma_n \hbar \vec{I} \cdot \delta \vec{B}_\perp(t) = -\frac{\gamma_n \hbar}{2} (I_+ \delta B_-(t) + I_- \delta B_+(t))$$



# Spin-lattice relaxation time

Fermi golden rule 
$$P_{ab} = \frac{2\pi}{\hbar} \left| \langle b | H' | a \rangle \right|^2 \delta(E_a - E_b)$$

$$P_{m \rightarrow m+1} = \frac{2\pi}{\hbar} \left( \frac{\gamma_n \hbar}{2} \right)^2 \left| \langle m+1 | I_+ | m \rangle \langle \nu' | \delta B_-(t) | \nu \rangle \right|^2 \delta(E_{\nu'} - E_\nu - \hbar\omega)$$

We next use the definition of Dirac's delta function

$$\delta(E_{\nu'} - E_\nu - \hbar\omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{i(E_{\nu'} - E_\nu - \hbar\omega)t/\hbar} dt$$

And plug it into the above expression

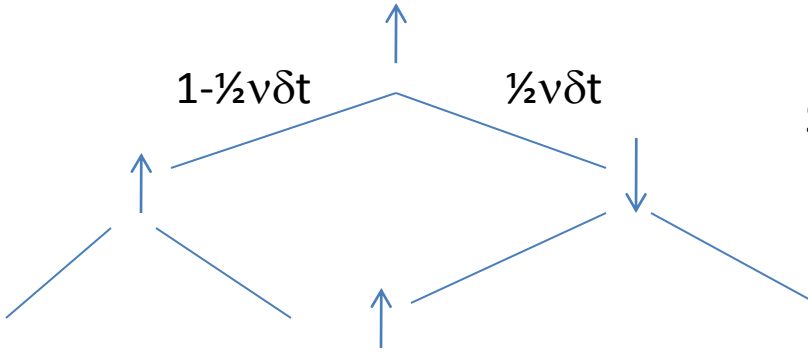
$$\begin{aligned} P_{m \rightarrow m+1} &= \frac{\gamma_n^2}{2} \left| \langle m+1 | I_+ | m \rangle \right|^2 \underbrace{\int_{-\infty}^{\infty} \langle \nu' | e^{iE_{\nu'}t/\hbar} \delta B_+(0) e^{-iE_{\nu'}t/\hbar} \delta B_-(0) | \nu \rangle e^{-i\omega t} dt}_{e^{iH_{\nu'}t/\hbar} \delta B_+(0) e^{-iH_{\nu'}t/\hbar} \equiv \delta B_+(t)} = \\ &= \frac{\gamma_n^2}{2} (I - m)(I + m + 1) \int_{-\infty}^{\infty} \langle \delta B_+(t) \delta B_-(0) \rangle e^{-i\omega t} dt \end{aligned}$$

Spin-lattice relaxation time is then given by

$$\frac{1}{T_1} = \frac{P_{m \rightarrow m+1} + P_{m+1 \rightarrow m}}{(I - m)(I + m + 1)}$$

# Spin-lattice relaxation time – some simple considerations

Lets assume that the local magnetic field jumps between two sites with a typical correlation time  $\tau$ . Therefore, the probability for  $\delta B$  to change is given by  $\frac{1}{2}v\delta t$  with  $v=1/\tau$ .



$$S(\delta t)S(0) = (1 - \frac{1}{2}v\delta t) S^2 + \frac{1}{2}v\delta t (-S^2) = S^2(1 - v\delta t)$$

$$S(N\delta t)S(0) = S^2(1 - v\delta t)^N$$



$$\langle S(t)S(0) \rangle = S^2 e^{-vt} = S^2 e^{-t/\tau}$$



FT

$$S^2 \int_{-\infty}^{\infty} e^{-t/\tau} \cos(\omega t) dt = S^2 \sqrt{\frac{2}{\pi}} \frac{\tau}{1 + \omega^2 \tau^2}$$



$$\frac{1}{T_1} = \frac{a^2}{2\hbar^2} \int_{-\infty}^{\infty} \langle [S_+(t), S_-(0)] \rangle \cos \omega t dt$$

$1/T_1$  maximum when  $\omega\tau=1$   
 BPP dependence



## Spin-lattice relaxation time

Lets now assume, that the fluctuation field comes from the electronic field through the hyperfine coupling intercation

$$H' = \vec{I} \cdot a_i \cdot \vec{S}_i(t) = -\gamma_n \hbar \vec{I} \cdot \delta \vec{B}_\perp$$

Expressing  $\delta B$  we finally get for  $T_1$

$$\frac{1}{T_1} = \frac{a^2}{2\hbar^2} \int_{-\infty}^{\infty} \langle [S_+(t), S_-(0)] \rangle \cos \omega t dt$$

$$[A, B] = (AB - BA) / 2$$

After Fourier transformation

$$S_{\vec{q}} = \sum_i S_i e^{-\vec{q} \cdot \vec{r}_i} \quad \frac{1}{T_1} = \frac{1}{2} \sum_{\vec{q}} A_{\vec{q}} A_{-\vec{q}} \int_{-\infty}^{\infty} \langle [S_{\vec{q}}^+(t), S_{-\vec{q}}^-(0)] \rangle \cos \omega t dt$$

Finally we fluctuation-dissipation theorem, which states

$$\frac{1}{2} \int_{-\infty}^{\infty} \langle [S_{\vec{q}}^+(t), S_{-\vec{q}}^-(0)] \rangle \cos \omega t dt = \frac{2\hbar \chi''_{\perp}(\vec{q}, \omega)}{(\gamma_e \hbar)^2 (1 - e^{-\hbar\omega/kT})}$$

To get  $T_1$  in the high-T expansion

$$\frac{1}{T_1} = \frac{2\gamma_n^2 kT}{(\gamma_e \hbar)^2} \sum_{\vec{q}} A_{\vec{q}} A_{-\vec{q}} \frac{\chi''_{\perp}(\vec{q}, \omega)}{\omega}$$





## Spin-lattice relaxation in metals

The perturbing interaction is the s-contact interaction

$$H_{hf} = \frac{8\pi}{3} g\mu_B \gamma \hbar^2 \vec{I} \cdot \vec{S} \cdot \delta^3(\vec{r})$$

Transitions from state  $|k \uparrow m\rangle$  to  $|k \downarrow m+1\rangle$  where  $m$  is the initial nuclear quantum number

$$P_{k' \downarrow m+1 \rightarrow k \uparrow m} = \frac{2\pi}{\hbar} \left| \langle k' \uparrow m+1 | H_{hf} | k \downarrow m \rangle \right|^2 \delta(E_{k'} - E_k)$$

We take Bloch WFs and calculate the corresponding matrix elements

$$\left| \langle k' \uparrow m+1 | H_{hf} | k \downarrow m \rangle \right|^2 = \left[ \frac{4\pi}{3} \gamma_n \gamma_e \hbar^2 |u_k(0) u_{k'}(0)| \right]^2 (I-m)(I+m+1)$$

We make an approximation that all states in the vicinity of Fermi surface have approximately the same probability density at the nucleus. Next we need to sum over all  $k$  and  $k'$  states then we can finally write

$$\frac{1}{T_1} = \frac{4\pi}{\hbar} \left[ \frac{4\pi}{3} \gamma_n \gamma_e \hbar^2 \langle |u_k(0)|^2 \rangle \right]^2 \sum_{k,k'} \delta(E_k - E_{k'})$$

# Spin-lattice relaxation in metals

It is important to bear in mind, that the sum over  $k, k'$  is restricted to states fully occupied at  $k$  and empty at  $k'$ . The sum over  $k$  can be replaced by the integration over energy with introducing the density of states  $n(E)$ , i.e.  $\int n(E) dE$ . The occupation restriction is enforced with the Fermi occupation function  $f(E) = [\exp((E-E_F)/kT) + 1]^{-1}$ . The summation then becomes

$$\int dE \int dE' n(E)n(E') f(E)(1-f(E'))\delta(E-E')$$

$$f(E)(1-f(E')) = k_B T \frac{\partial f}{\partial E} = k_B T \delta(E-E_F)$$



Remember Knight shift:

$$K = \frac{8\pi}{3} |u_k(0)|_{E_F}^2 \chi$$

$$\frac{1}{T_1} = \frac{4\pi k_B T}{\hbar} \left[ \frac{4\pi}{3} \gamma_n \gamma_e \hbar^2 \langle |u_k(0)|^2 \rangle \right]^2 n(E_F)^2$$

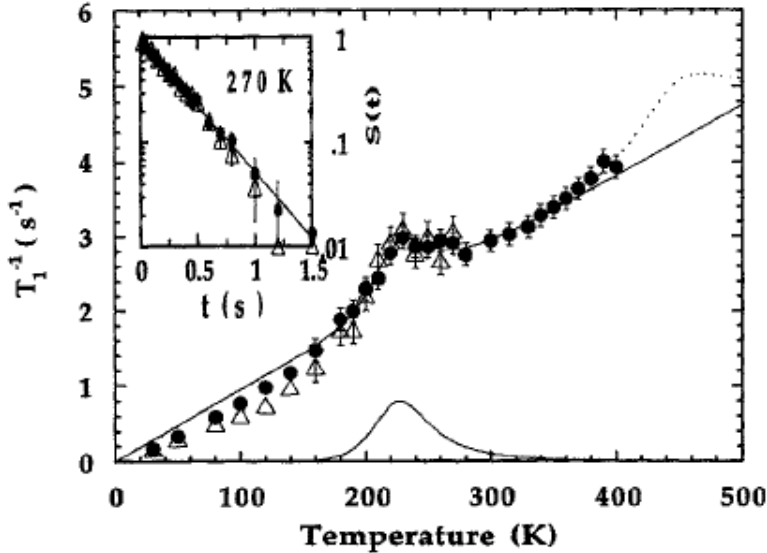
$$\frac{1}{T_1 T K^2} = \frac{4\pi k_B}{\hbar \gamma_e^2}$$

Famous Korringa relation

The final result depends only on elementary constants and not on materials; this holds only for simple metals, where correlations can be neglected

# Korringa relation - examples

$^{13}\text{C}$  NMR in  $\text{K}_3\text{C}_{60}$   
Yoshinari et al. (1993)



$$\frac{1}{T_1 T K^2} = \frac{4\pi k_B}{\hbar \gamma_e^2}$$

In practice, simple Korringa relation is not satisfied. Let's check some simple alkali metals

metal	$K_s(\%)$	$T_1 T$ (exp)	$T_1 T$ (calc)	ratio
$^7\text{Li}$	0.0263	45 Ks	26 Ks	0.58
$^{23}\text{Na}$	0.112	4.8 Ks	3.1 Ks	0.65
$^{63}\text{Cu}$	0.232	0.7 Ks	0.7 Ks	0.78

Various corrections can be made to Korringa relation. In principle electron-electron interaction potential can enhance the spin susceptibility thus correcting K.R. in the right way.

However, exchange fluctuations would also enhance spin-lattice relaxation. We will come to this point later, but for now we just introduce Korringa factor  $\beta$ , which should be  $\beta < 1$  (AFM) fluctuations,  $\beta > 1$  (FM) fluctuations

$$\frac{1}{T_1 T K^2} = \frac{4\pi k_B}{\hbar \gamma_e^2} \beta$$



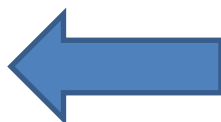
## Korringa relation - corrections

Various corrections can be made to Korringa relation. In principle electron-electron interaction potential can enhance the spin susceptibility thus correcting K.R. in the right way.

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$$\frac{1}{T_1 T K^2} = \frac{4\pi k_B}{\hbar \gamma_e^2} \beta$$

$$\beta = \langle (1 - \alpha_q)^2 / (1 - \alpha_0)^2 \rangle_{E_F}$$



Stoner enhancement factor

$$\chi = \frac{\chi_0}{1 - \alpha_0}$$

RPA (random phase approximation)

$$\chi(q, \omega) = \frac{\chi_0(q, \omega)}{1 - \alpha_0 [\chi_0(q, \omega) / \chi_0(0, 0)]}$$

$$K \sim \chi \sim \frac{1}{(1 - \alpha_0)}$$

$$\frac{1}{T_1 T} \sim \{N(\epsilon_F)(1 - \alpha_q)\}^2$$



## Spin-lattice relaxation time – some simple considerations

To a reasonable approximation we may try to write

$$\chi''_{\perp}(\vec{q}, \omega) = \chi(\vec{q}, 0) \frac{\omega_e \omega_n}{\omega_e^2 + \omega_n^2} \approx \chi(\vec{q}, 0) \frac{\omega_n}{\omega_e}$$

Then

$$\frac{1}{T_1} = \frac{2\gamma_n^2 kT}{(\gamma_e \hbar)^2} \sum_{\vec{q}} A_{\vec{q}} A_{-\vec{q}} \frac{\chi(\vec{q}, 0)}{\omega_e}$$

Where  $\omega_{ex} = [2zk_B^2 J^2 S(S+1)/3\hbar^2]^{1/2}$

# Example: $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$

Moriya expression

$$\frac{1}{T_1 T} \propto \sum_{\mathbf{q}} |A(\mathbf{q})|^2 \frac{\chi''(\mathbf{q}, \omega_n)}{\omega_n}$$

$$A(\mathbf{q}) = \sum_j C_j \exp(i\mathbf{q} \cdot \mathbf{r}_j)$$

Millis, Monien and Pines assumed that the spin dynamics is described by

$$\lim_{\omega \rightarrow 0} \chi''(\mathbf{q}, \omega) = \frac{\pi \chi_0 \hbar \omega}{\Gamma} \left[ 1 + \beta \frac{\xi^4}{\left[ 1 + (\mathbf{q} - \mathbf{q}_{AFM})^2 \xi^2 \right]^2} \right]$$

$${}^{63}K = (A + 4B)\chi_s$$

$${}^{17}K = 2C\chi_s$$

$$|{}^{63}A(\mathbf{q})|^2 = \left( A + 2B [\cos q_x a + \cos q_y a] \right)^2$$

$$|{}^{17}A(\mathbf{q})|^2 = 4C^2 \cos^2 \frac{q_x a}{2}$$

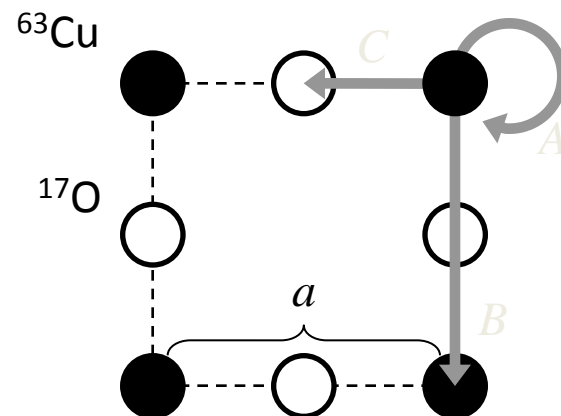
$$\mathbf{q}_{AFM} = \left( \frac{\pi}{a}, \frac{\pi}{a} \right)$$

$$\Rightarrow |{}^{63}A(\mathbf{q}_{AFM})|^2 = (A - 4B)^2$$

$$|{}^{17}A(\mathbf{q}_{AFM})|^2 = 0$$

Millis, Monien & Pines  
*PRB* **42**, 167 (1990)

$\text{CuO}_2$  layer with  $\text{Cu}^{2+}$   
localized moments

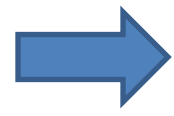
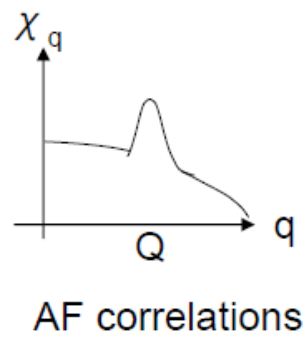
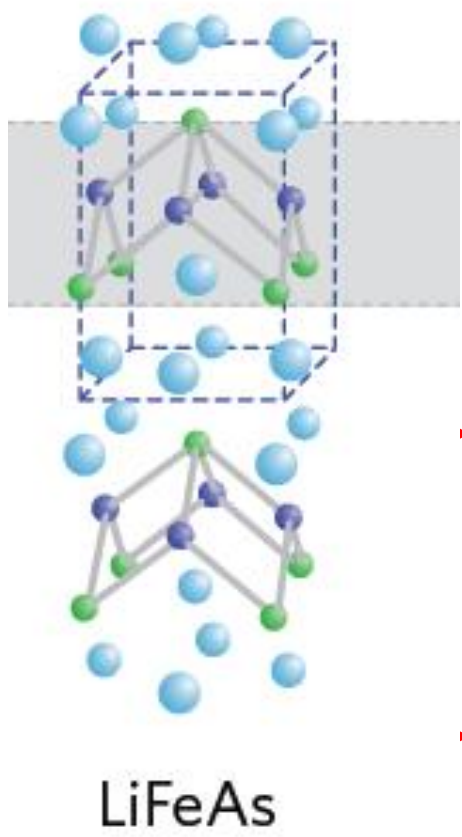


$A$ : on-site coupling  
 $B, C$ : transferred couplings

Mila & Rice,  
*Physica C* **157**, 561 (1990)

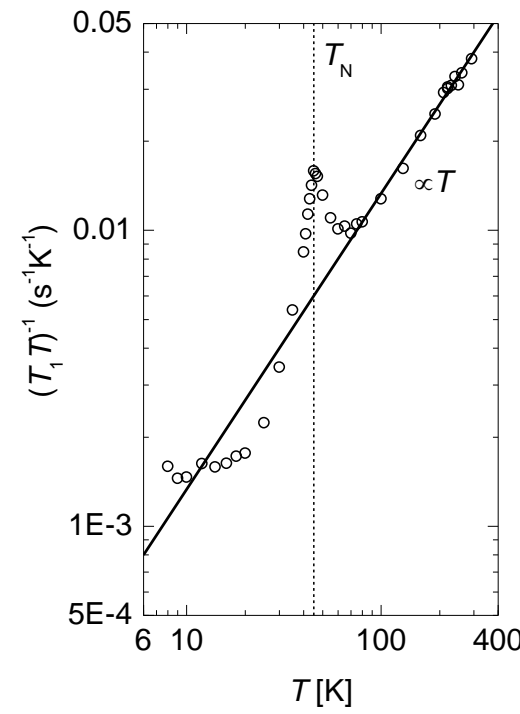
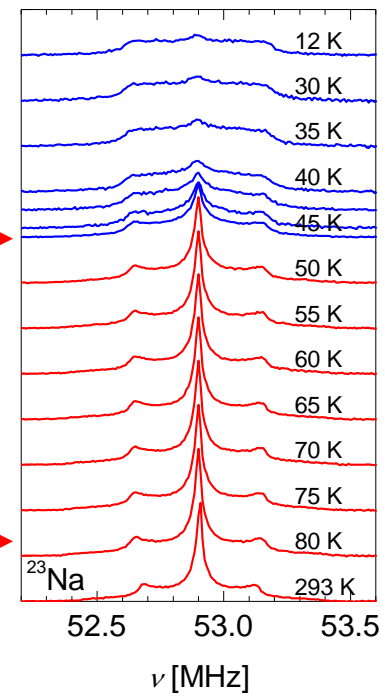
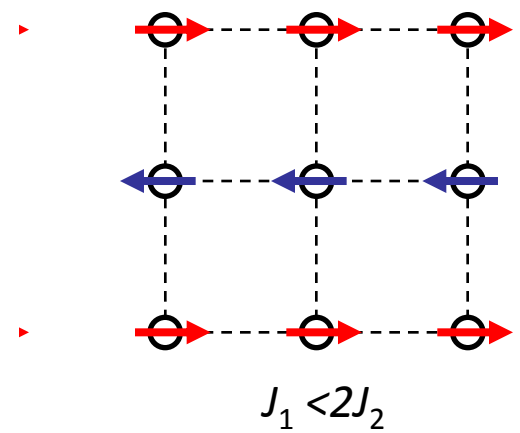
# Spin-lattice relaxation time – critical fluctuations

111



$$\frac{1}{T_1} = \frac{2\gamma_n^2 kT}{(\gamma_e \hbar)^2} \sum_{\vec{q}} A_{\vec{q}} A_{-\vec{q}} \frac{\chi(\vec{q}, 0)}{\omega_e}$$

Enhancement of  $1/T_1$  close to  $T_N$



11, 057010 (2008)

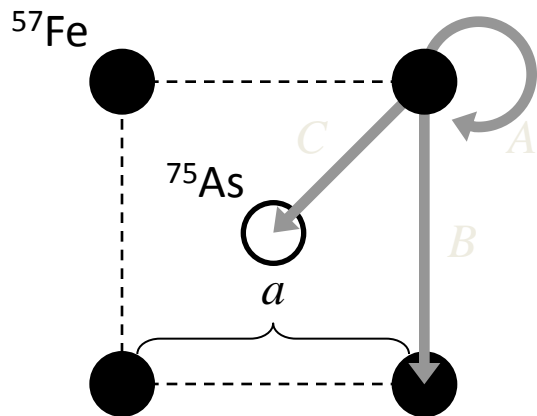
# Example: LiFeAs

## A

Localized Fe<sup>2+</sup> spins

$${}^{75}K = 4C\chi_s$$

$$|{}^{75}A(\mathbf{q})|^2 = 16C^2 \cos^2 \frac{q_x a}{2} \cos^2 \frac{q_y a}{2}$$



## B

Itinerant Fe 3d electrons

$${}^{75}K = c\chi_s$$

$$|{}^{75}A(\mathbf{q})|^2 = c^2$$

Supported by density-functional calculations:

- Katrin Koch & Helge Rosner, MPI-CPFS
- Calculated electric-field gradients correctly reproduce the experimental values for both <sup>75</sup>As and <sup>7</sup>Li sites.

Jeglič *et al.*, ArXiv: 0912.0692

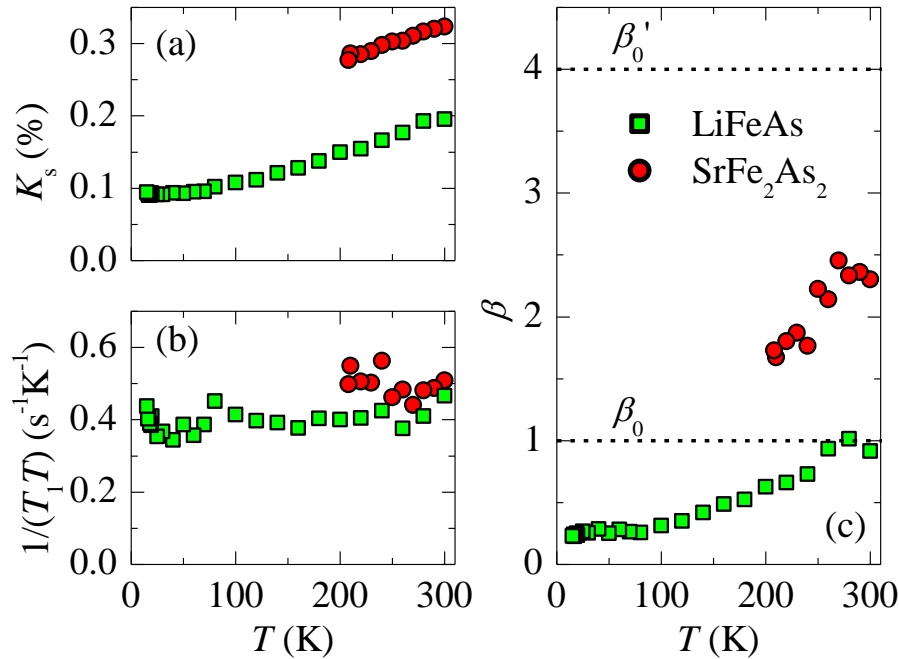
$$\frac{1}{T_1 T} \propto \sum_{\mathbf{q}} |A(\mathbf{q})|^2 \frac{\chi''(\mathbf{q}, \omega_n)}{\omega_n}$$

For noninteracting spins  $\chi''(\mathbf{q}, \omega_n)$  can be taken out of the summation. In this limit we can calculate  $\beta_0$  and  $\beta_0'$  for the localized spins and itinerant scenario. If  $c = 4C \Rightarrow$

$$\begin{aligned} \frac{\beta_0'}{\beta_0} &= \frac{\sum_{\mathbf{q}} c^2}{\sum_{\mathbf{q}} |A(\mathbf{q})|^2} = \\ &= \frac{16C^2 \iint dq_x dq_y}{16C^2 \iint dq_x dq_y \cos^2 \frac{q_x a}{2} \cos^2 \frac{q_y a}{2}} = 4 \end{aligned}$$



# Example: AFM fluctuations in LiFeAs



Korrington factor  $\beta$ , measured for LiFeAs (green circles) and SrFe<sub>2</sub>As<sub>2</sub> (red circles). Horizontal dashed lines indicate expected  $\beta$  values for noninteracting electrons.

**If the transferred coupling is active,  $1/T_1 T$  is enhanced for a factor of  $15 \pm 5$ !**

Jeglič *et al.*,  
ArXiv: 0912.0692

## How strong are AFM fluctuations in LiFeAs?

1. We cannot unambiguously discriminate between the on-site Fermi contact (itinerant) and the transferred coupling mechanism (localized moment at the Fe sites).
2. Cross-terms between different bands in the LiFeAs multiband structure can modify Korringa relation.



# Summary

**NMR = local, real-space probe where the behaviour of nuclear spins can be monitored on a site-to-site basis.**

**Observables:**

- **NMR spectrum**
- **Relaxation rates**

**Hyperfine interaction (Fermi contact, transferred hf, dipolar interaction)**

**Knight shift, shift in the superconducting state**

**Spin-lattice relaxation rate, Korringa relation**

$$\frac{1}{T_1} = \frac{2\gamma_n^2 kT}{(\gamma_e \hbar)^2} \sum_{\vec{q}} A_{\vec{q}} A_{-\vec{q}} \frac{\chi''_{\perp}(\vec{q}, \omega)}{\omega}$$

# Acknowledgements

**Ljubljana:**

**Peter Jeglič, Martin Klanjšek, Andrej Zorko, Anton Potočnik, Kristjan Anderle  
and Andraž Kranjc**

[www.lemsuper.eu](http://www.lemsuper.eu)

