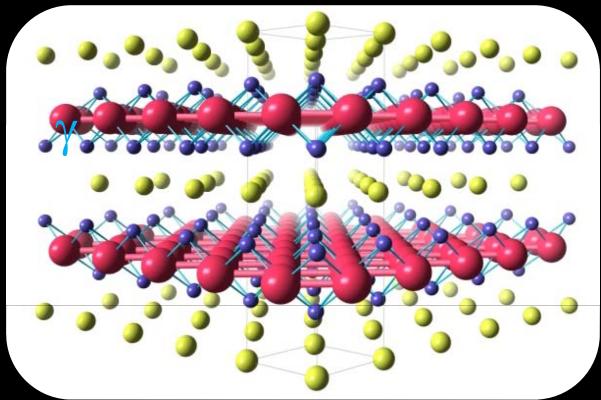
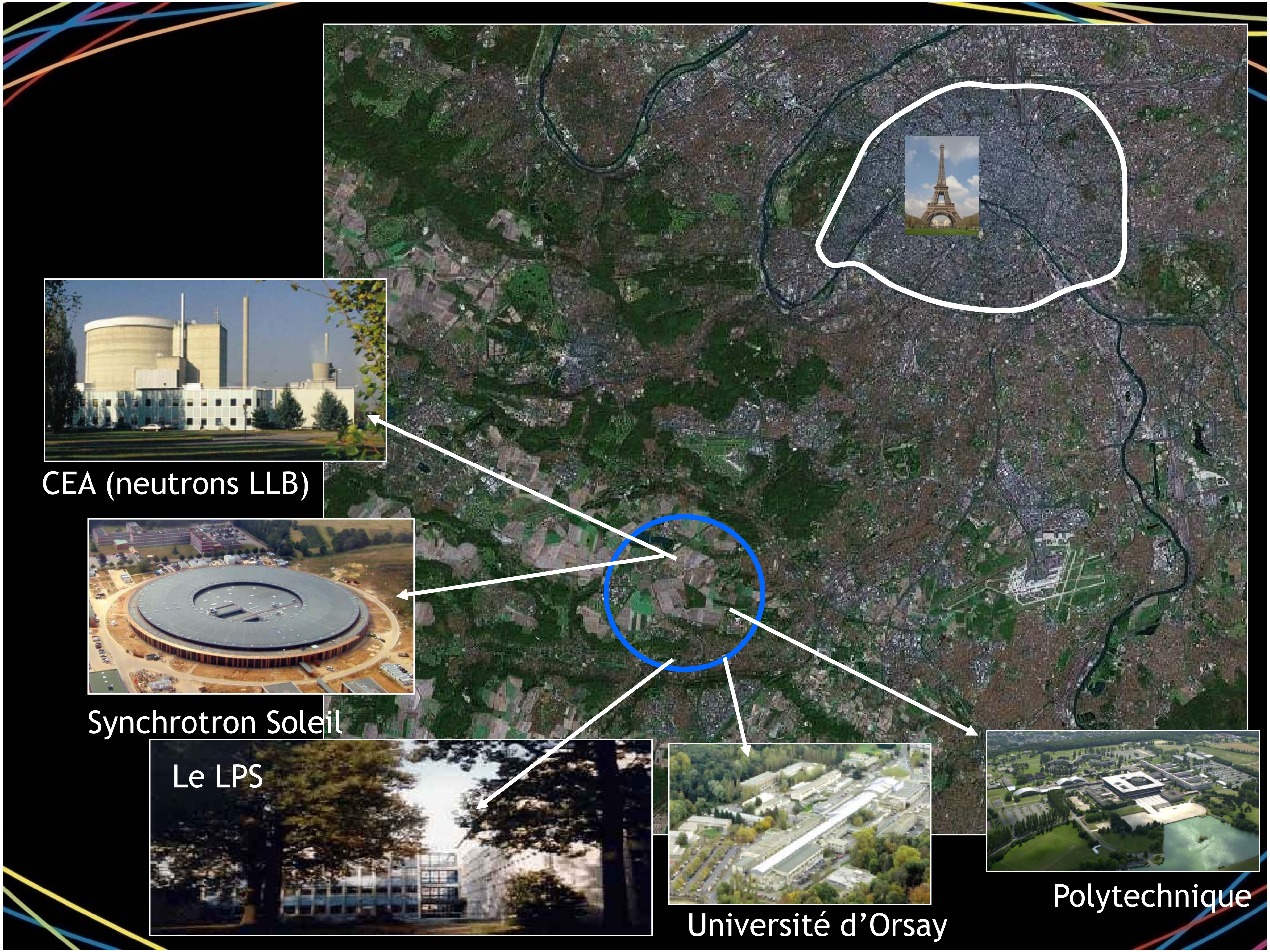
1. NMR

2. Pnictides

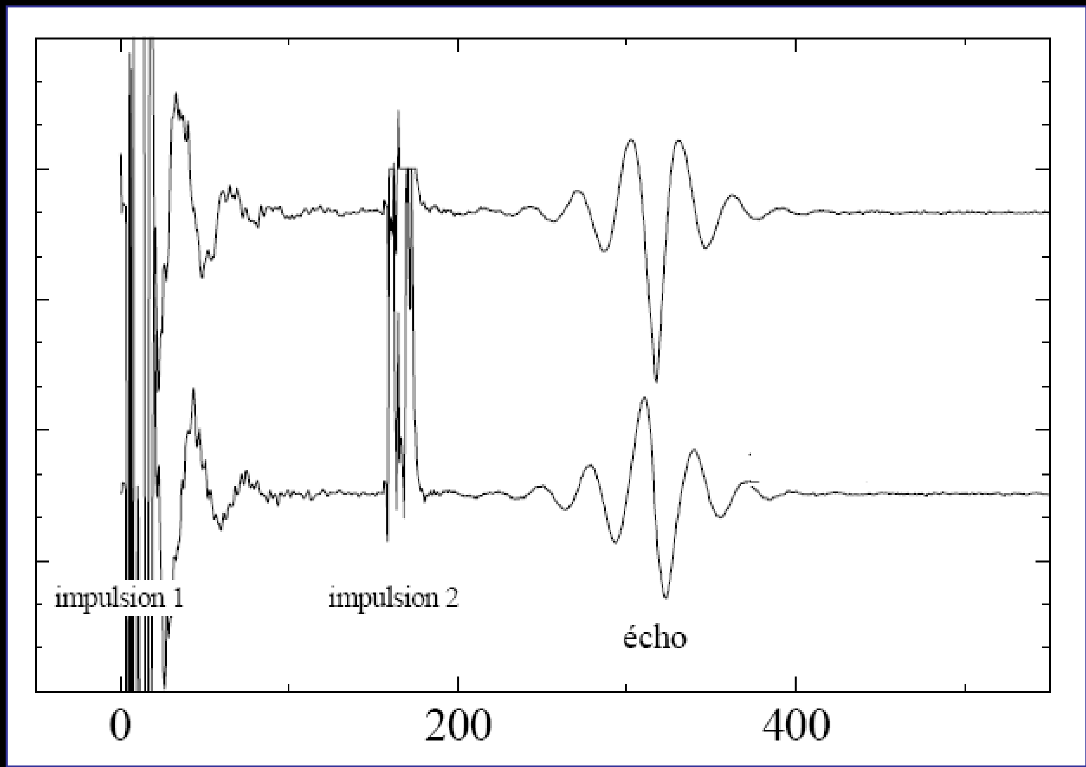


J. Bobroff
Laboratoire de Physique des Solides, Orsay, France

TRIANGLE DE LA PHYSIQUE
UNIVERSITÉ PARIS-SUD 11
CNRS
LPS ORSAY


CEA (neutrons LLB)
Synchrotron Soleil
Le LPS
Université d’Orsay
Polytechnique

Nuclear Magnetic Resonance

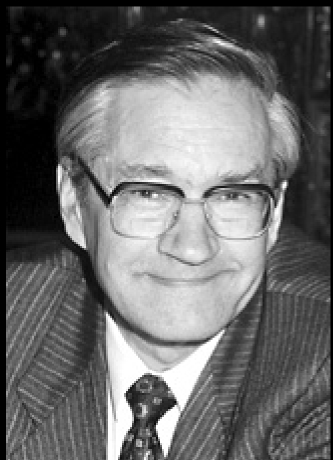


NMR Nobel Prices

Zeeman,
Nobel Physique 1902

Rabi,
Nobel Physique 1944

Bloch & Purcell,
Nobel Physique 1952



Ernst,
Nobel Chimie 1991

Wuthrich,
Nobel Chimie 2002

Lauterbur & Mansfeld,
Nobel Medecine 2003

First NMR signal in a solid and a liquid

Nuclear Induction

F. Bloch, W. W. Hansen, and Martin Packard
Stanford University, Stanford University, California
January 29, 1946

THE nuclear magnetic moments of a substance in a constant magnetic field would be expected to give rise to a small paramagnetic polarization, provided thermal equilibrium be established, or at least approached. By superposing on the constant field (z direction) an oscillating magnetic field in the x direction, the polarization, originally parallel to the constant field, will be forced to precess about that field with a latitude which decreases as the frequency of the oscillating field approaches the Larmor frequency. For frequencies near this magnetic resonance frequency one can, therefore, expect an oscillating induced voltage in a pick-up coil with axis parallel to the y direction. Simple calculation shows that with reasonable apparatus dimensions the signal power from the pick-up coil will be substantially larger than the thermal noise power in a practicable frequency band.

We have established this new effect using water at room temperature and observing the signal induced in a coil by the rotation of the proton moments. In some of the experiments paramagnetic catalysts were used to accelerate the establishment of thermal equilibrium.

By use of conventional radio techniques the induced voltage was observed to produce the expected pattern on an oscillograph screen. Measurements at two frequencies ν showed the effect to occur at values H of the z field such that the ratio H/ν had the same value. Within our experimental error this ratio agreed with the g value for protons, as determined by Kellogg, Rabi, Ramsey, and Zacharias.[1]

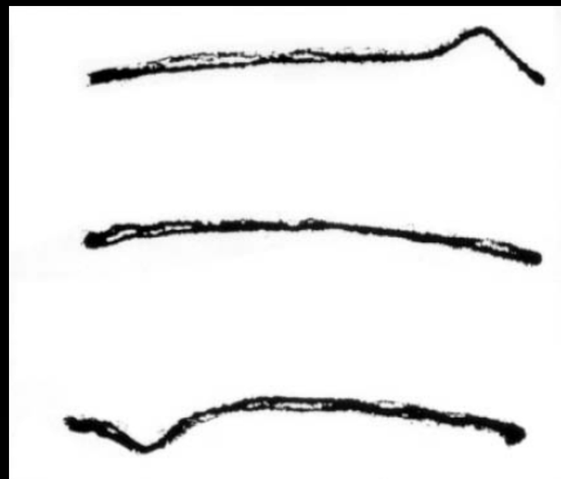
We have thought of various investigations in which this effect can be used fruitfully. A detailed account will be published in the near future.

[1] J. M. B. Kellogg, I. I. Rabi, N. F. Ramsey, and J. R. Zacharias, Phys. Rev. 56, 738 (1939).

Resonance Absorption by Nuclear Magnetic Moments in a Solid

E. M. Purcell, H. C. Torrey, and R. V. Pound*
Radiation Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts
December 24, 1945

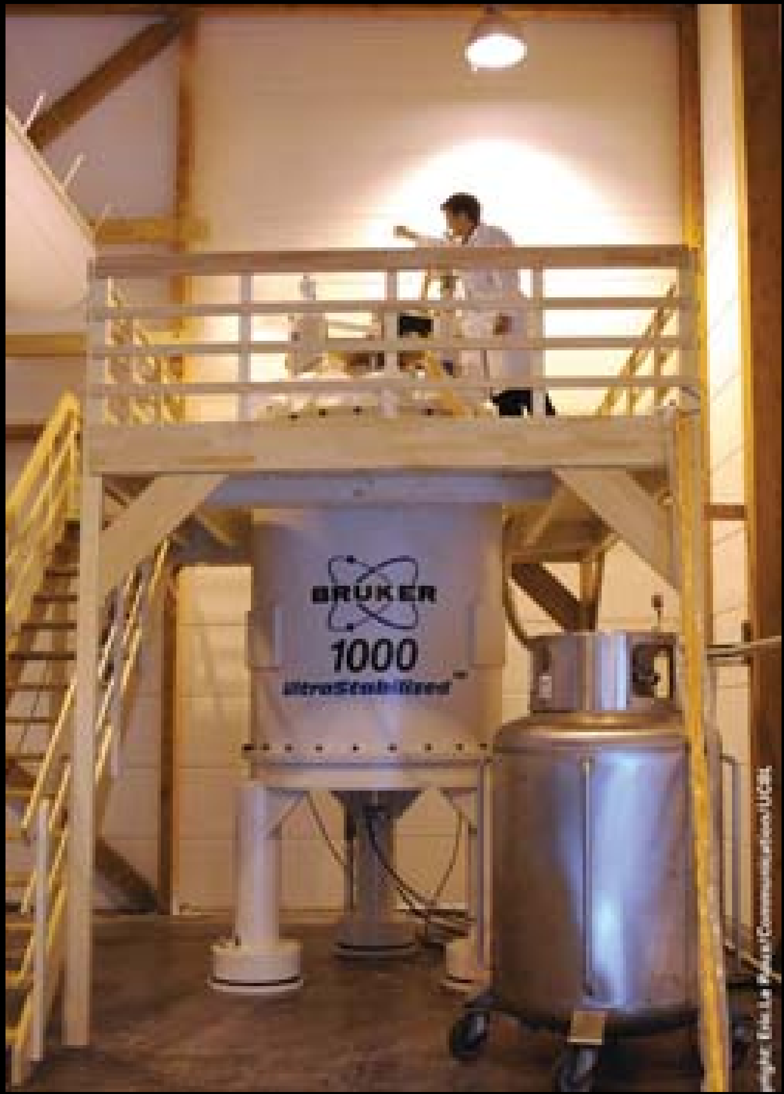
IN the well-known magnetic resonance method for the determination of nuclear magnetic moments by molecular beams,[1] transitions are induced between energy levels which correspond to different orientations of the nuclear spin in a strong, constant, applied magnetic field. We have observed the absorption of radiofrequency energy, due to such transitions, in a *solid* material (paraffin) containing protons. In this case there are two levels, the



MRI

Chemistry NMR

14 Tesla

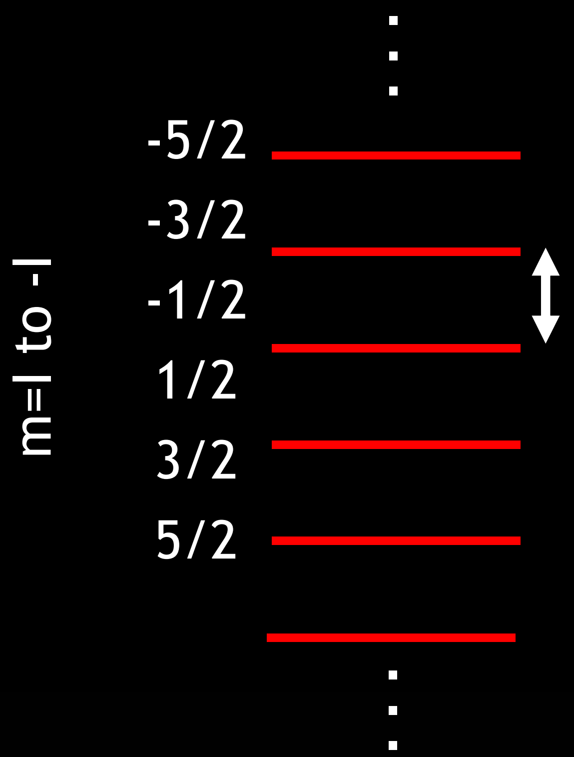


23 Tesla

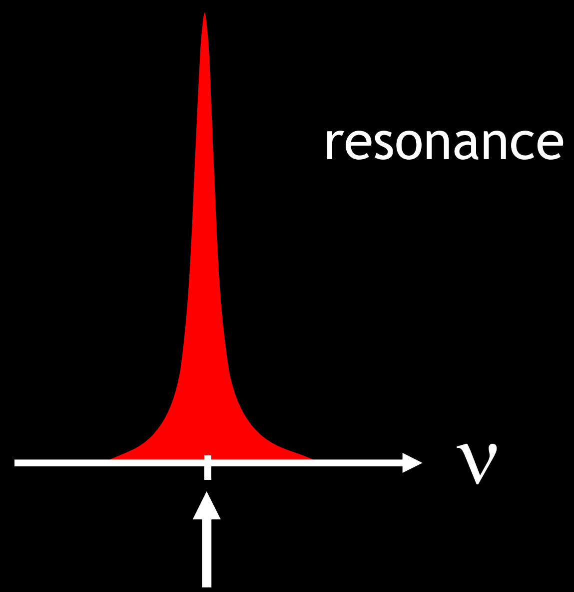
A nuclear spin I in a magnetic field H_0

Zeeman Effect

$$H_{hf} = -\overrightarrow{M}_{noyau}.\overrightarrow{H_0} = -\gamma\hbar H_0 I_z$$



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



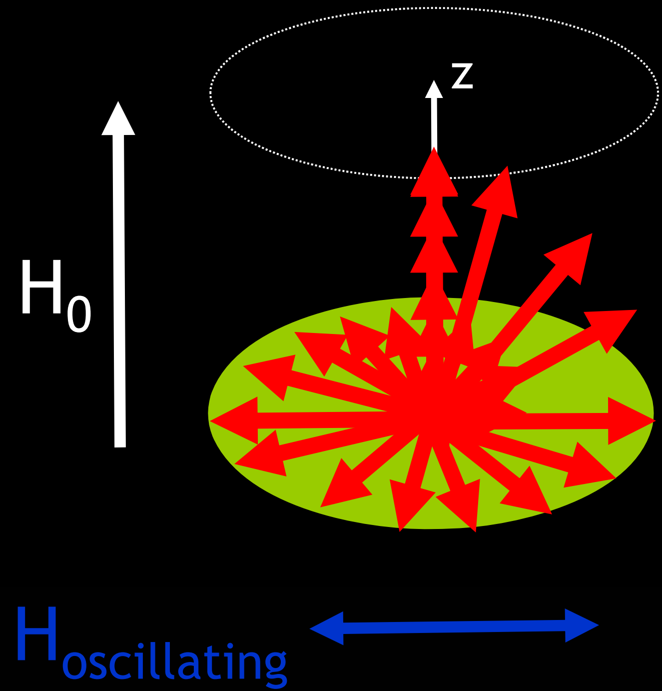
$$\nu = \gamma/2\pi\, H_0$$

How do we measure the resonance ?

1. put the nuclear spin in a static field

2. put a transverse oscillating field : at the resonance, it will rotate the spin

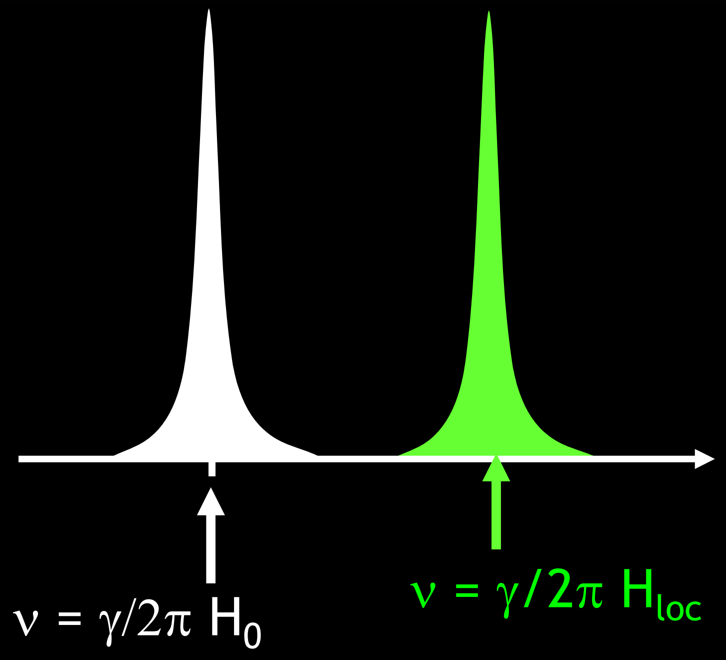
3. stop the transverse field and measure



Why doing NMR ?

Zeeman : $\nu = \gamma/2\pi \, H_0$

in matter : $\nu = \gamma/2\pi \, H_{local}$

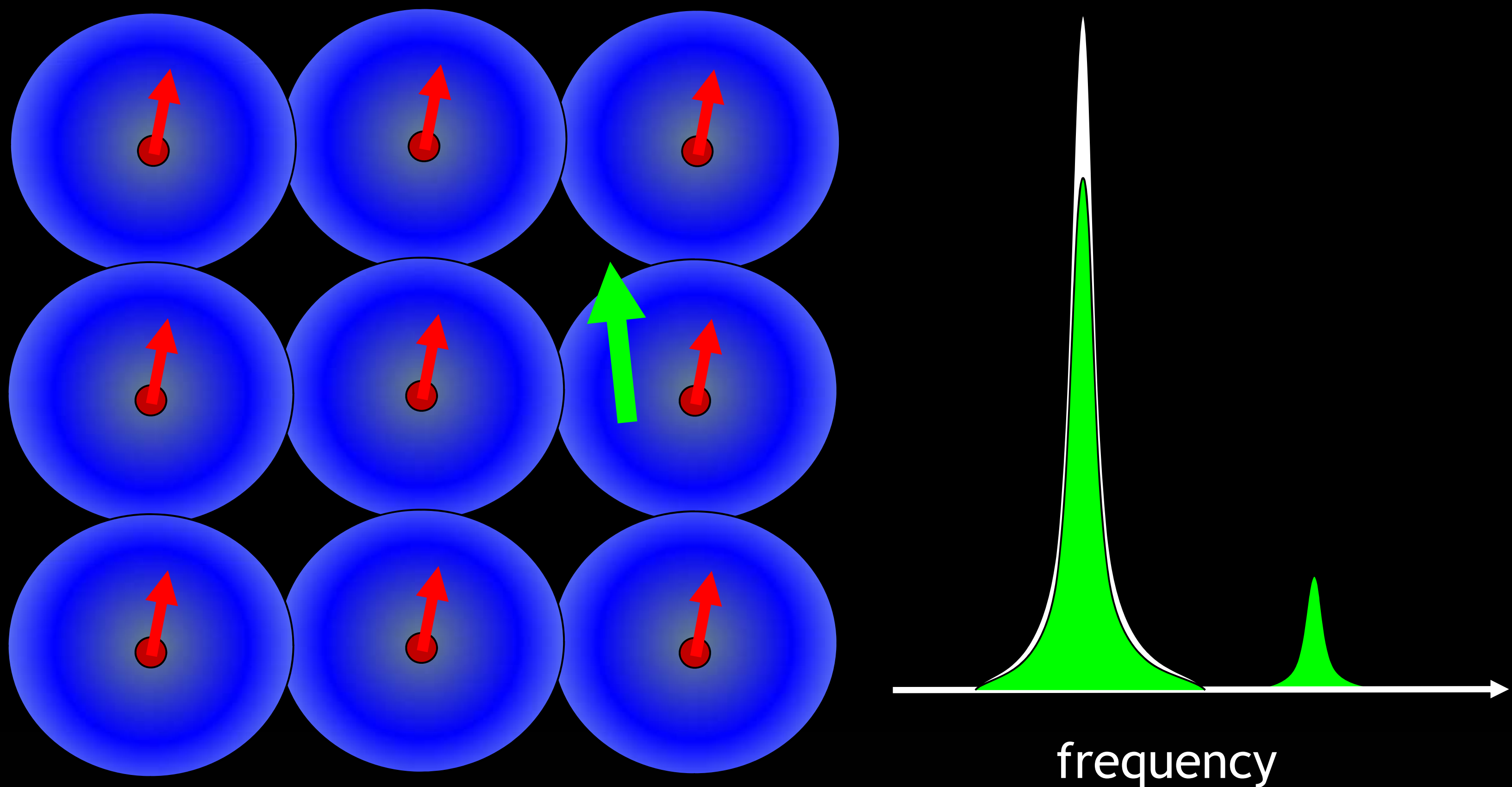


Difference between H_{local} and H_0 :

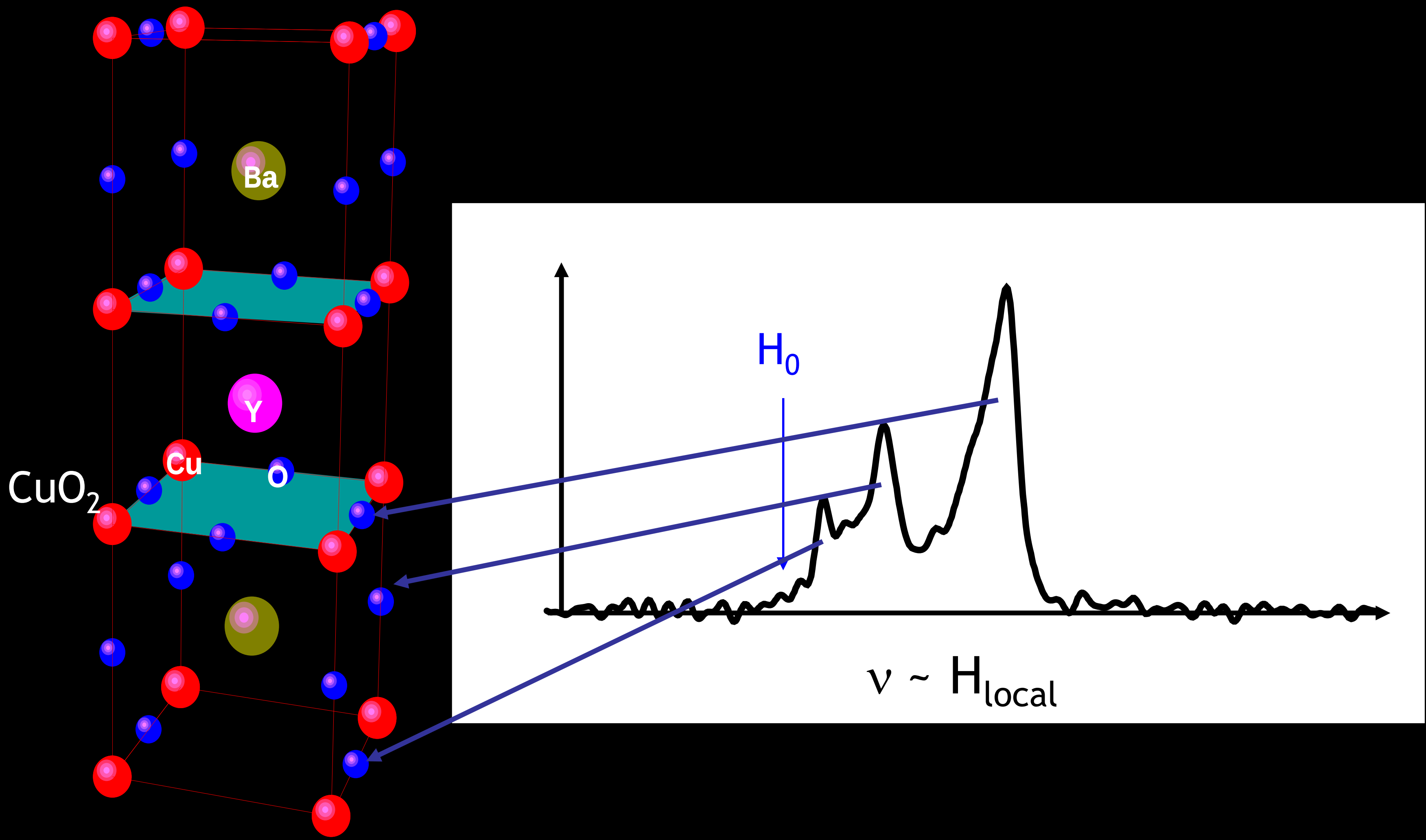
information about the viscinity of the nucleus

NMR is a local probe

because coupling between nuclear spin I
and its neighboring is very short range



NMR of oxygen in a cuprate



$YBa_2Cu_3O_7$

What can you measure ?

The electron :

- Orbitals
- Magnetic susceptibility in different positions
- Inhomogeneities

Dynamics of electrons:

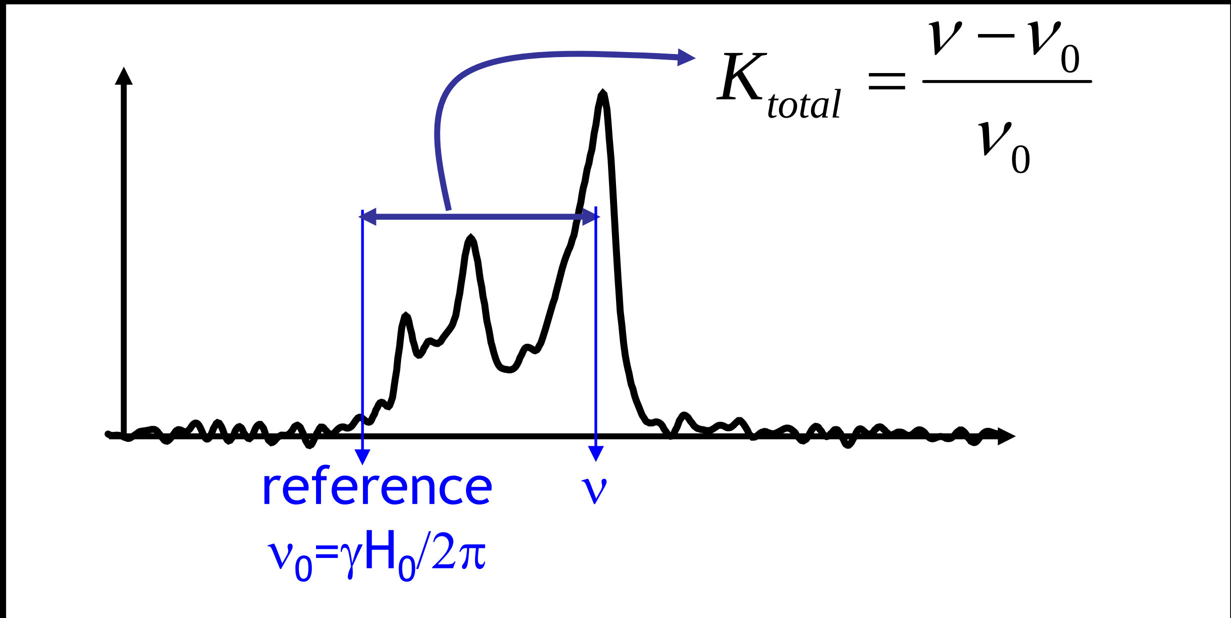
- correlations
- Gap and symetries in superconductors
- Magnetic transitions

Local fields :

- magnetic orders
- charge orders
- vortex
- spin liquids

…

The NMR shifts



$$\nu^{i=x,y,z} = \frac{\gamma}{2\pi}(1 + K^i_{orb} + K^i_{spin})$$

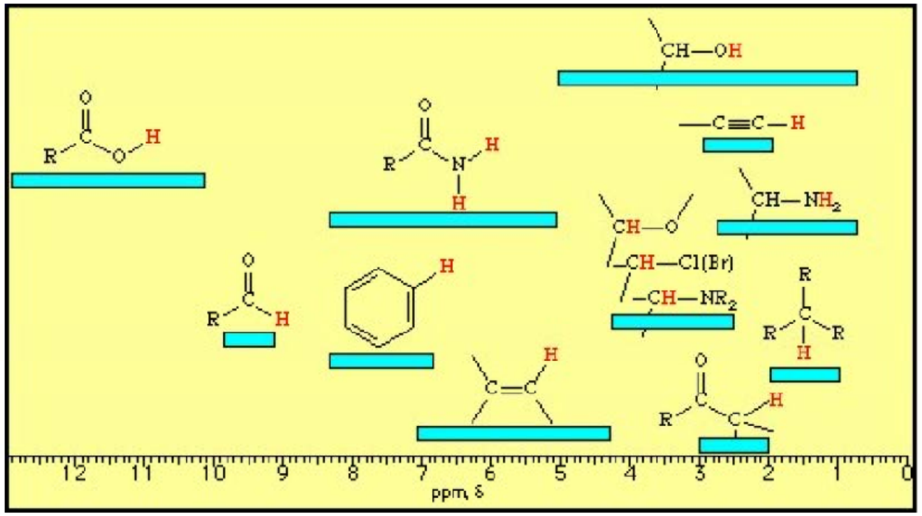
gyromagnetic ratio depends on the nucleus

orbital or chemical shift

spin shift

Orbital Shift

used in chemistry to characterize orbitals



Shift orbital

gasoline

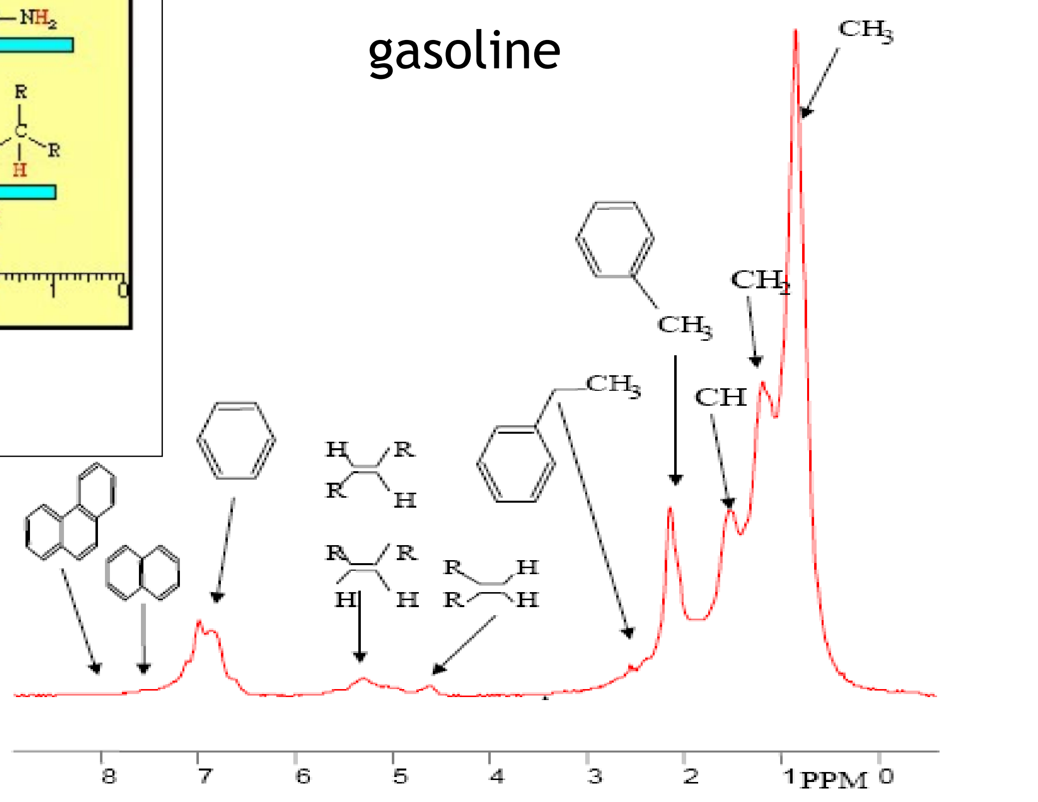
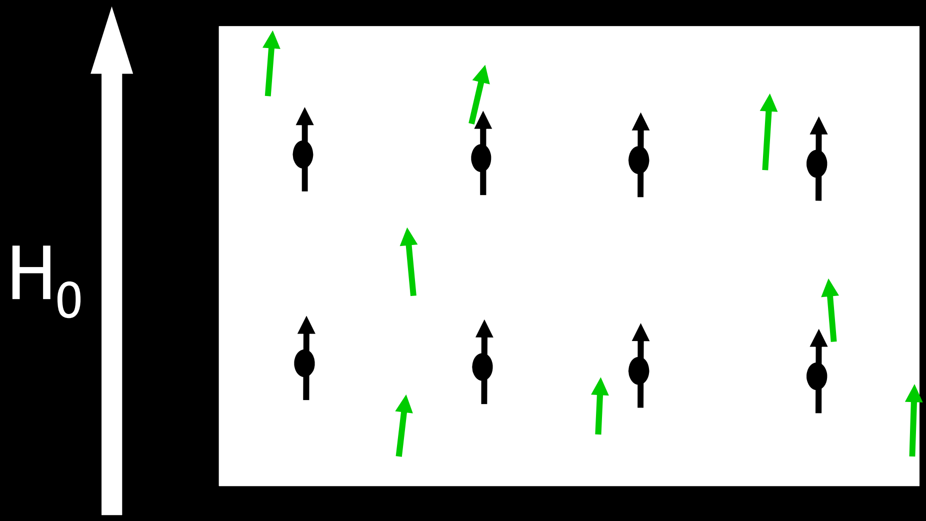


Figure 3: H-Types Observed in a Gasoline 1 H NMR Spectrum

Spin Shift K_{spin}



$$H_{loc}=H_0+a\chi H_0$$

measures uniform magnetic susceptibility
close to the nucleus

$$K_{spin} = A_{hf} \frac{1}{\hbar^2 \gamma_n \gamma_e} \chi_{electron}$$

hyperfine coupling

K_{spin} measures χ

High Tc superconductor Cuprate $YBa_2Cu_3O_{6+x}$

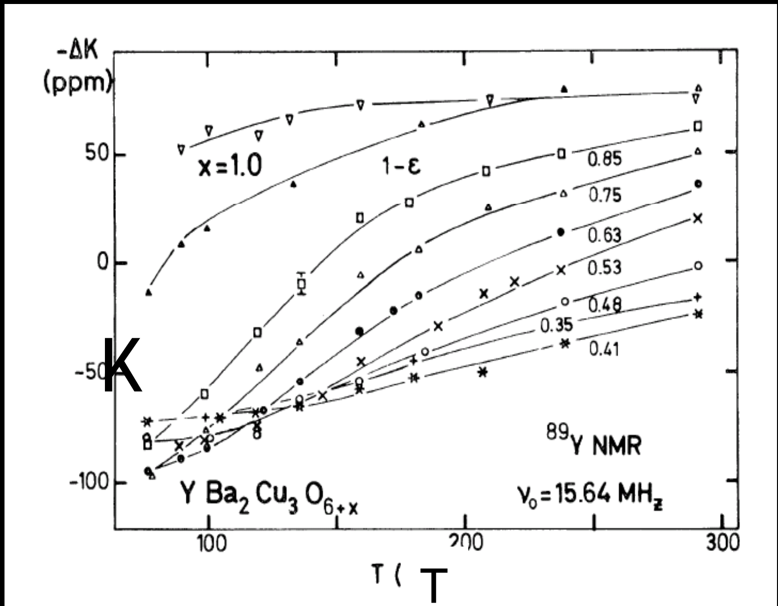
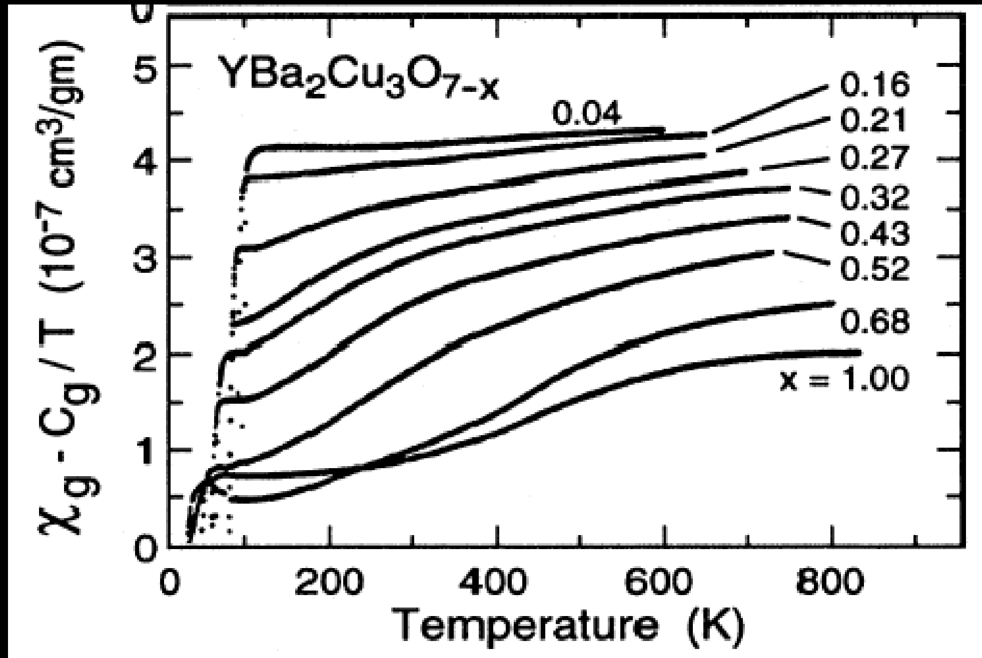


FIG. 1. The shift ΔK of the ⁸⁹Y line, referenced to YCl_3 plotted vs T, from 77 to 300 K. The lines are guides to the eye.

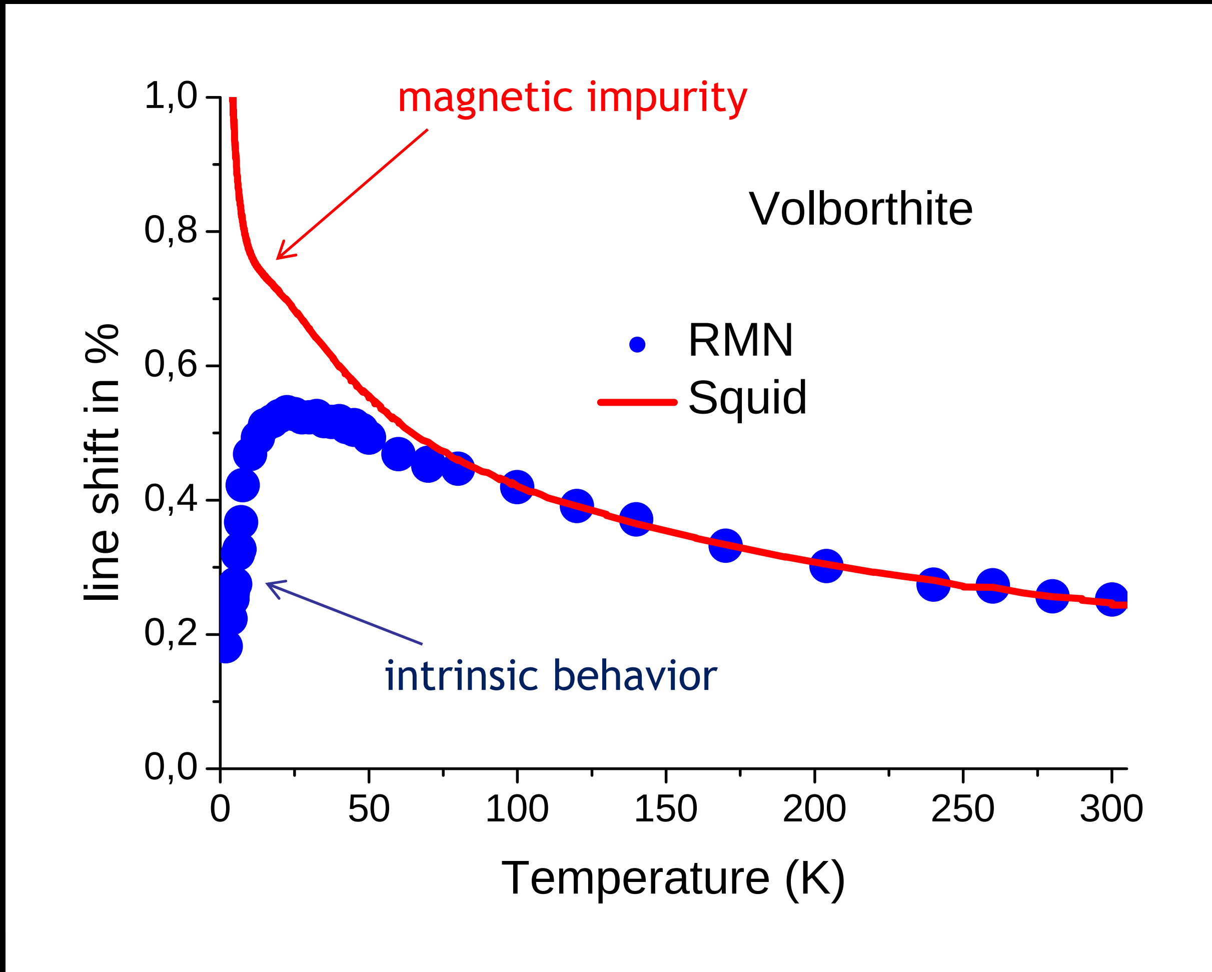


Alloul et al., PRL (1989)

Why not measure
macroscopic susceptibility instead ?

K_{spin} measures intrinsic χ not affected by impurity

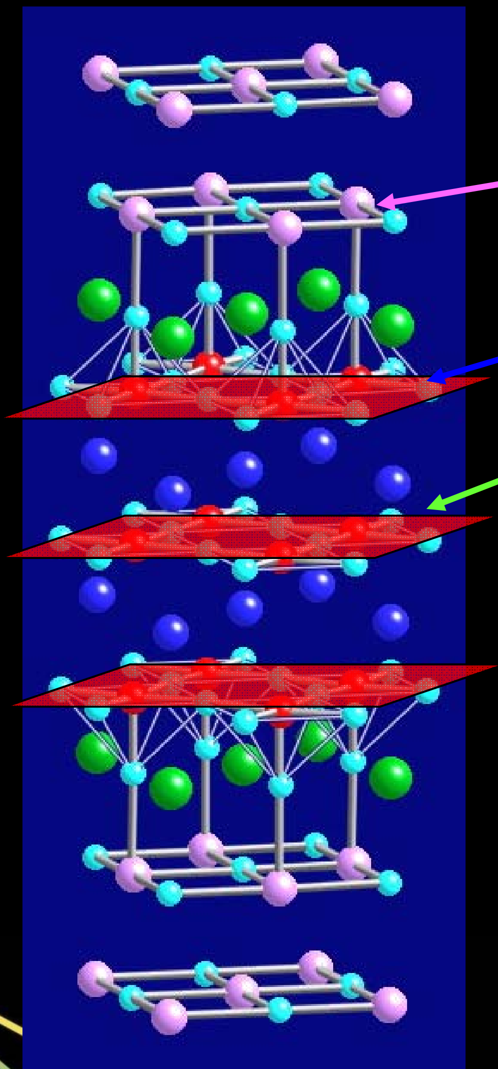
Volborthite
spin liquid

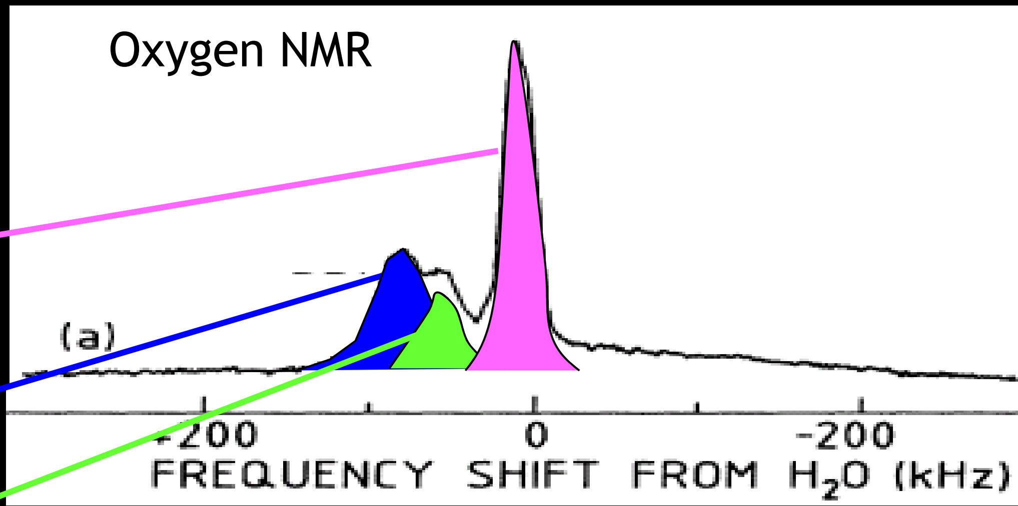


Mendels et al., PRL (2000)

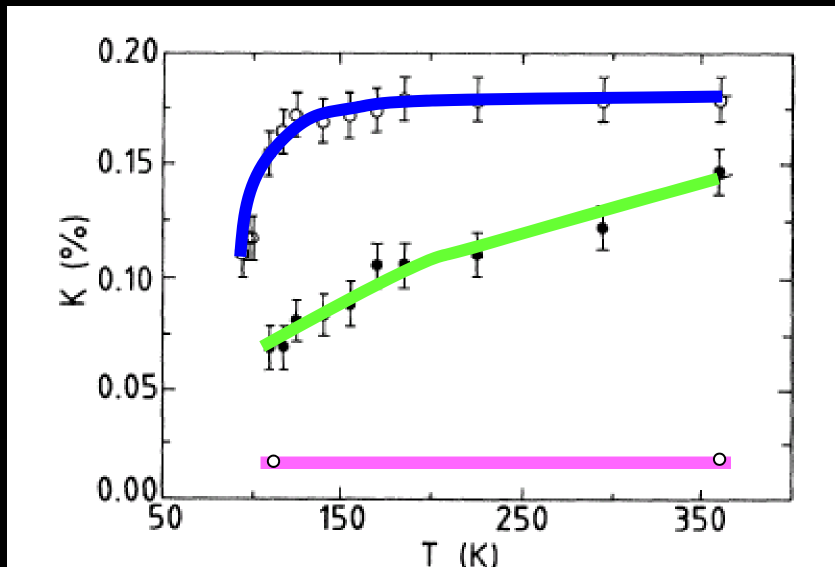
K_{spin} measures χ at different locations of the cell

Bi2212





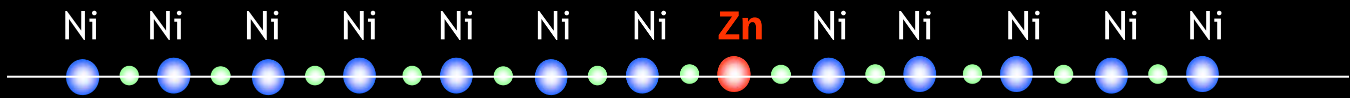
Trokiner et al., PRB (1991)

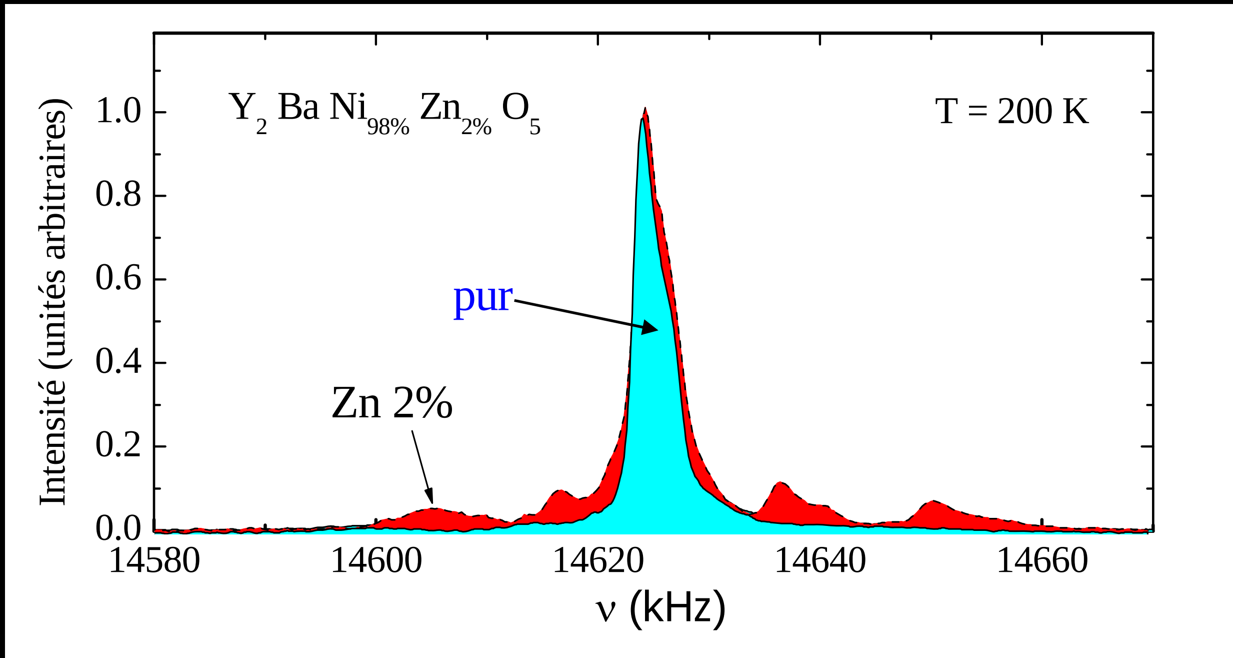


→ different susceptibilities so different dopings for each plane

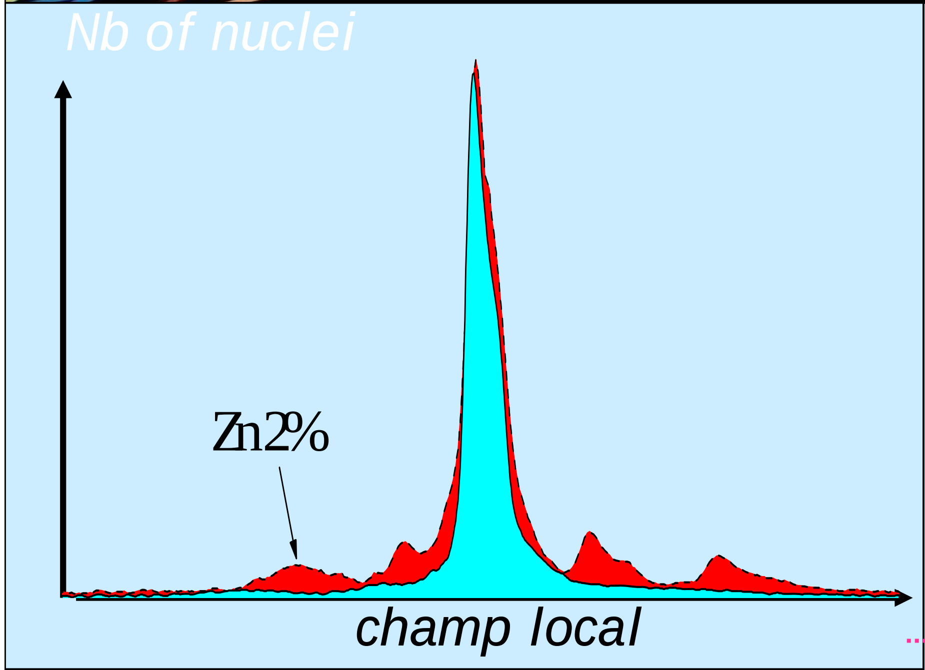
K_{spin} measures a histogram of χ , not a sum: access to local variations

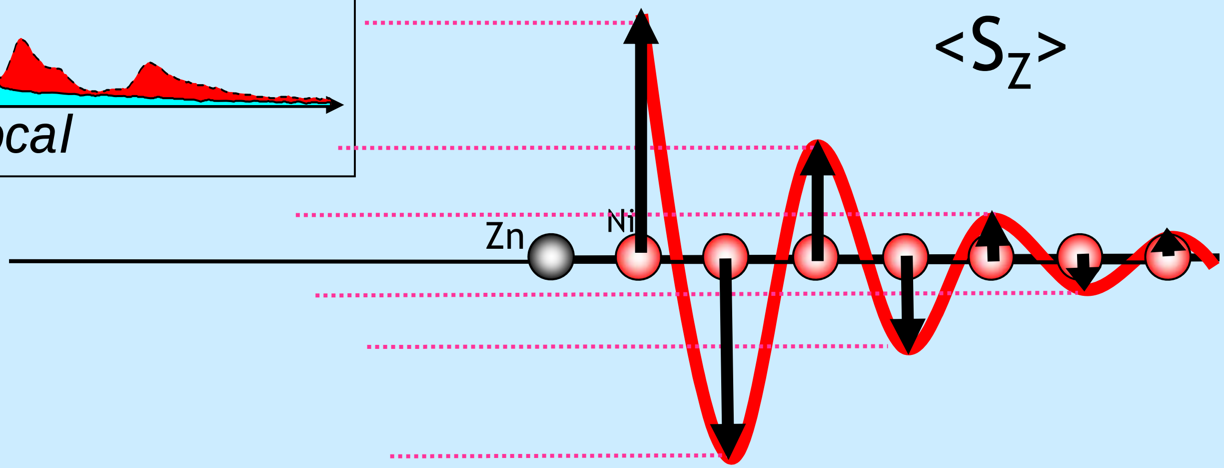
spin chain with non magnetic impurities





Tedoldi *et al.*, PRL 99; Das *et al.*PRB 04

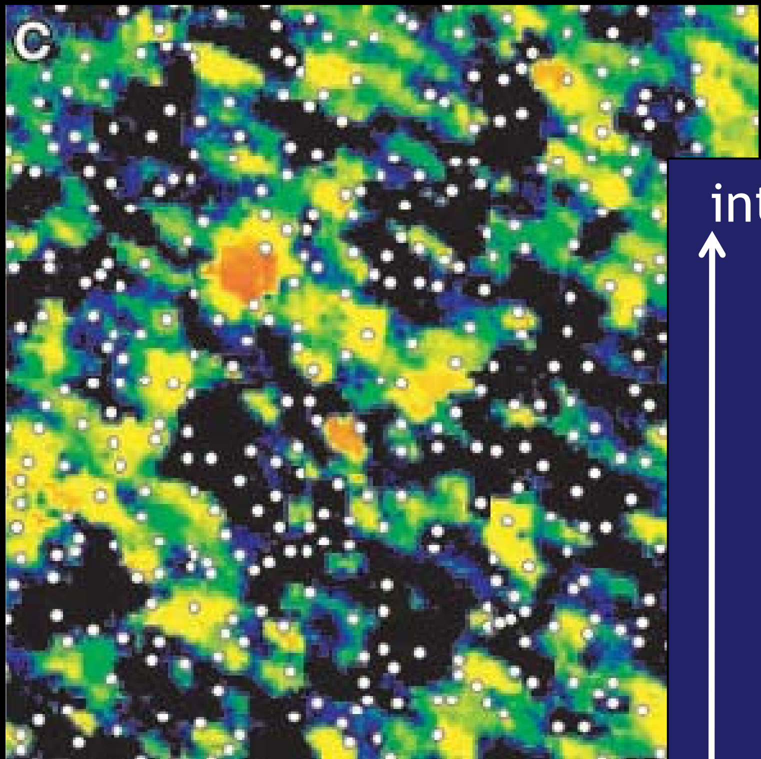




Alloul, Bobroff, Gabay, Hirschfeld, RMP 2009

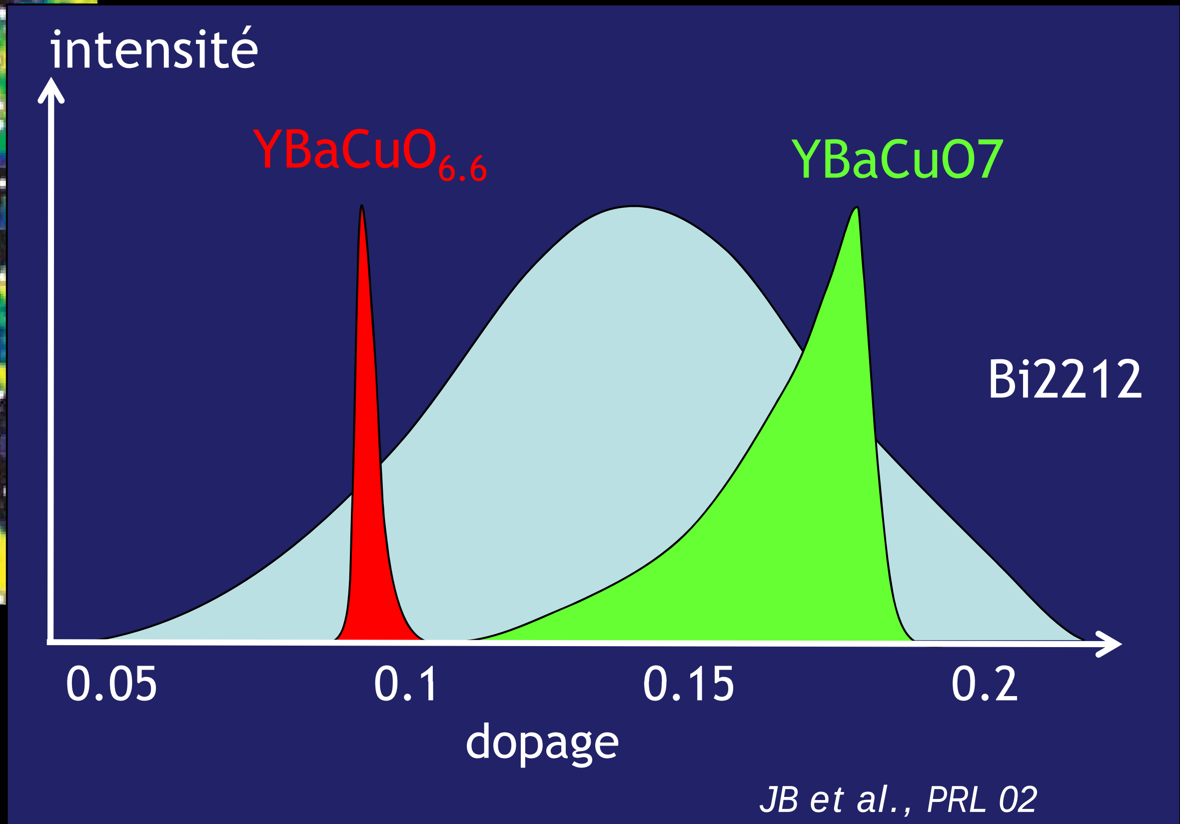
K_{spin} measures inhomogeneities

STM



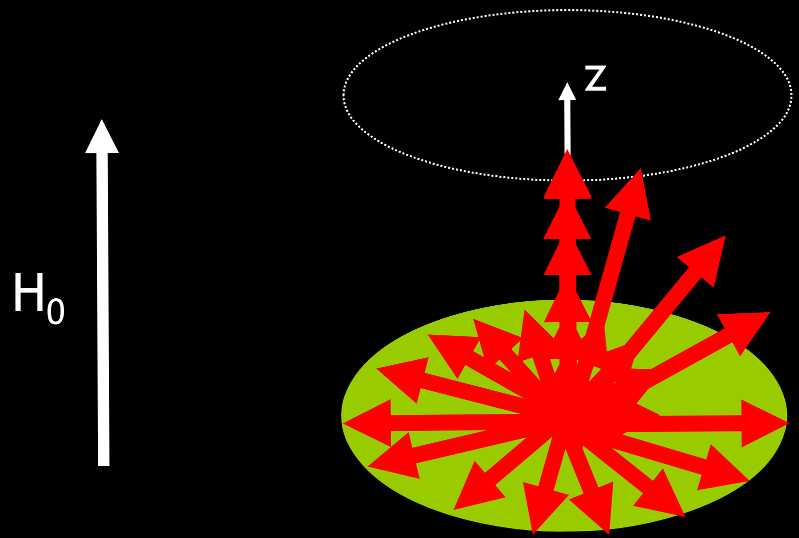
Cren et al., PRL 2000
Pan et al., Nature 2001
McElroy et al. Science 2005

RMN



dynamics

Relaxation times in NMR



T_1

T_2

transverse relaxation T_2
energy is conserved

$$\frac{dM_{X,Y}}{dt} = \frac{-M_{X,Y}}{T_2} + \gamma\left(\overrightarrow{M} \times \overrightarrow{H}\right)_{X,Y}$$

longitudinal relaxation T_1
exchange with the network

$$\frac{dM_Z}{dt} = \frac{M_{equilibrium} - M_Z}{T_1} + \gamma\left(\overrightarrow{M} \times \overrightarrow{H}\right)_Z$$

longitudinal relaxation T1

due to fluctuations of local magnetic field at ω_{RMN}

$$\frac{1}{T_1} \sim \int_{-\infty}^{\infty} < B_L^+(t) B_L^-(0) > \exp\left(-i\omega_{RMN}\, t\right) dt$$

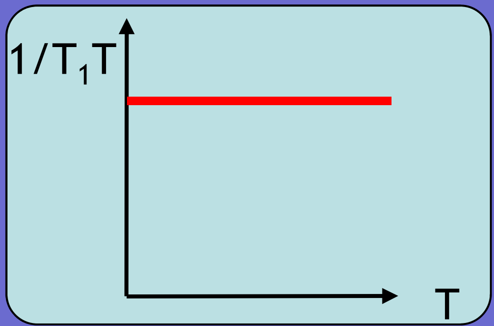
$$\frac{1}{T_1 T} = \frac{1}{\hbar^2} \frac{k_B}{(g\mu_B)^2} \sum_q \left|A(q)\right|^2 \frac{\chi_t''(q,\omega_n)}{\omega_n}$$

examples of T_1

metal

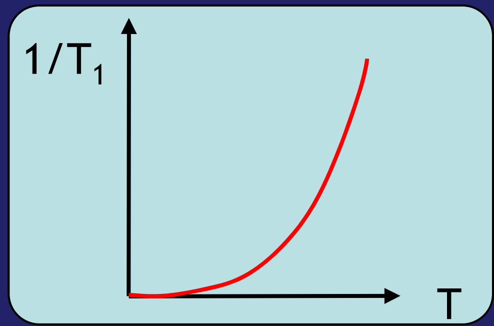
Korringa Law

$$\frac{1}{T_1 T K^2} = \frac{4\pi k_B}{\hbar}\left(\frac{\gamma_n}{\gamma_e}\right)^2$$

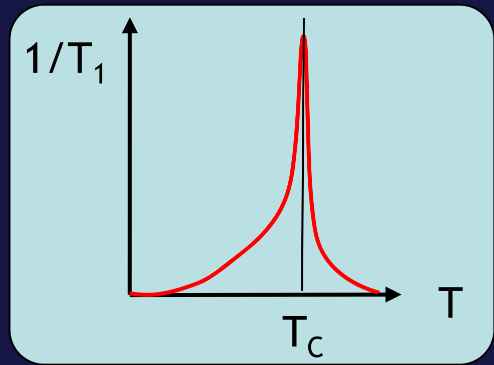


spin-gap system

$$\frac{1}{T_1} = Ae^{-\frac{\Delta}{T}}$$

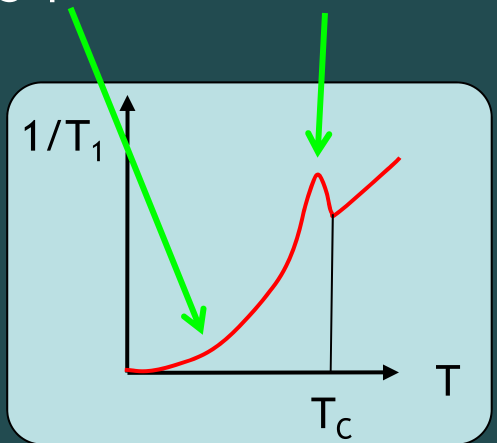


Magnetic Order



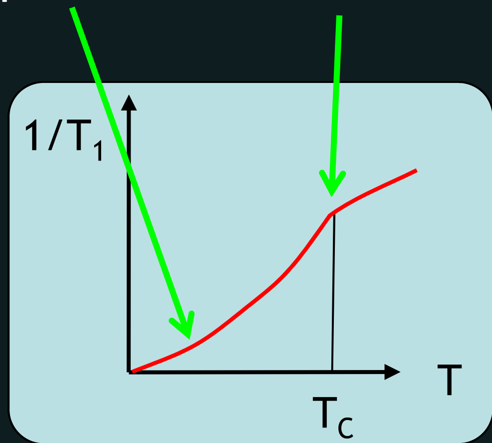
BCS superconductor

gap + Hebel-Slichter Peak



unconventional superconductor

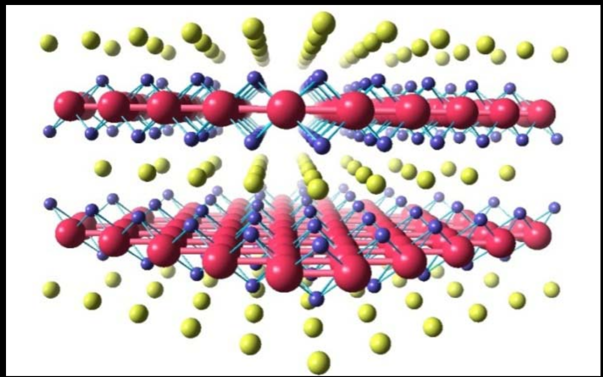
power law + no Peak

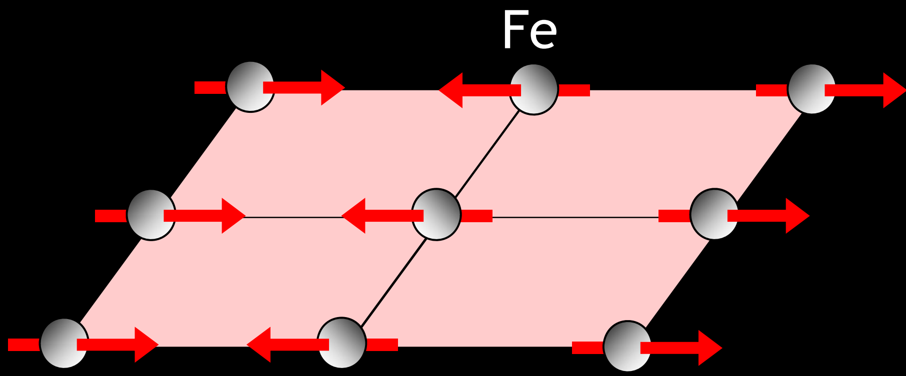


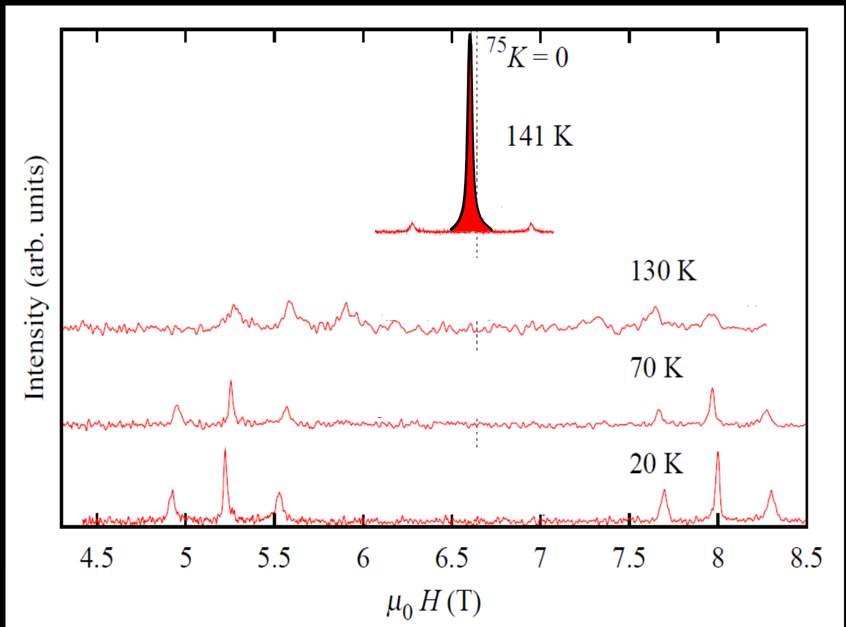
Local fields in NMR

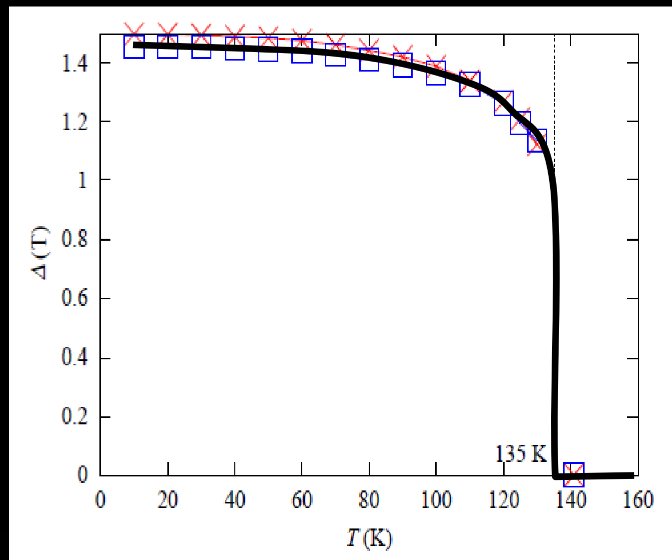
magnetic orders,
charge orders,
vortex…

Example : AF order in pnictides







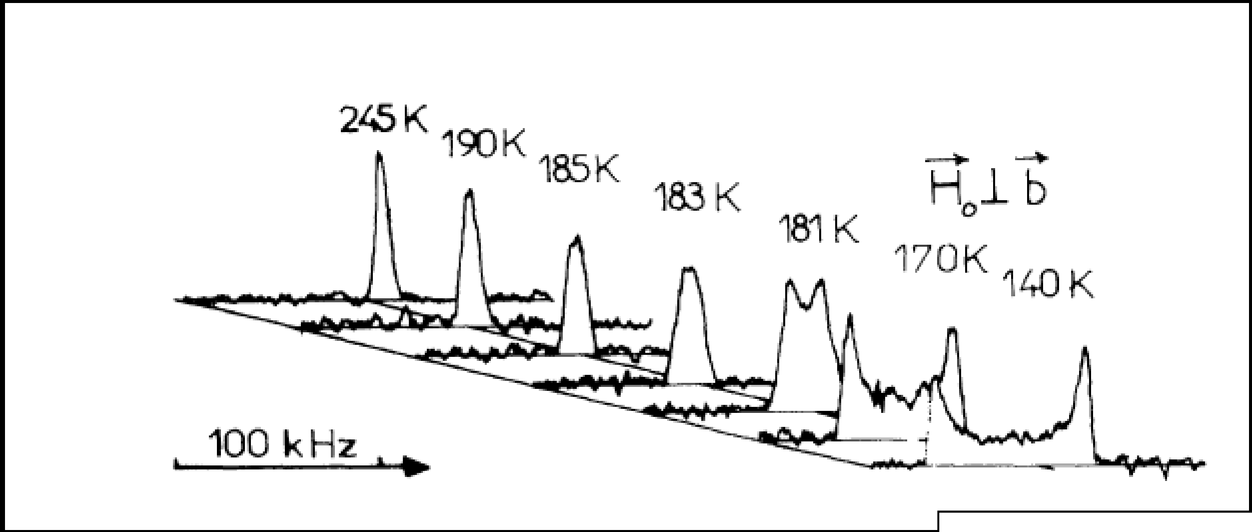


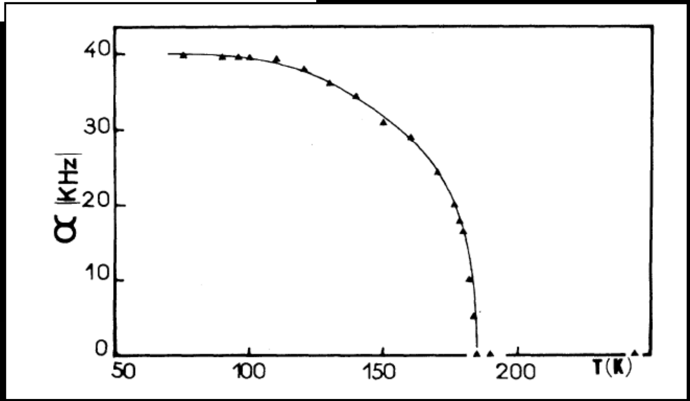
Kitagawa, JPSJ 08

Effect of a charge order

sensitivity to charge through electric field gradiants (NQR)

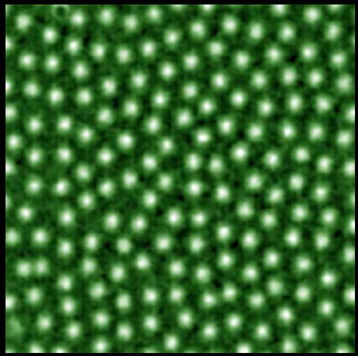
Charge Density Wave in $Rb_{0.30}MoO_3$

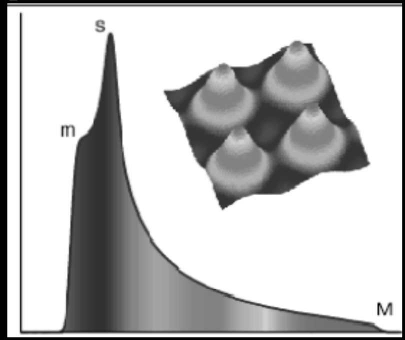




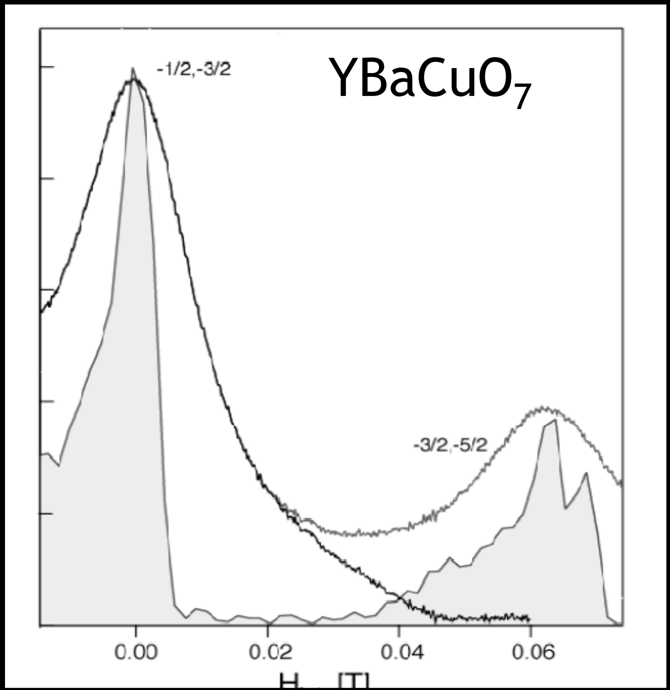
Butaud et al., PRL 1985

vortex in superconductor

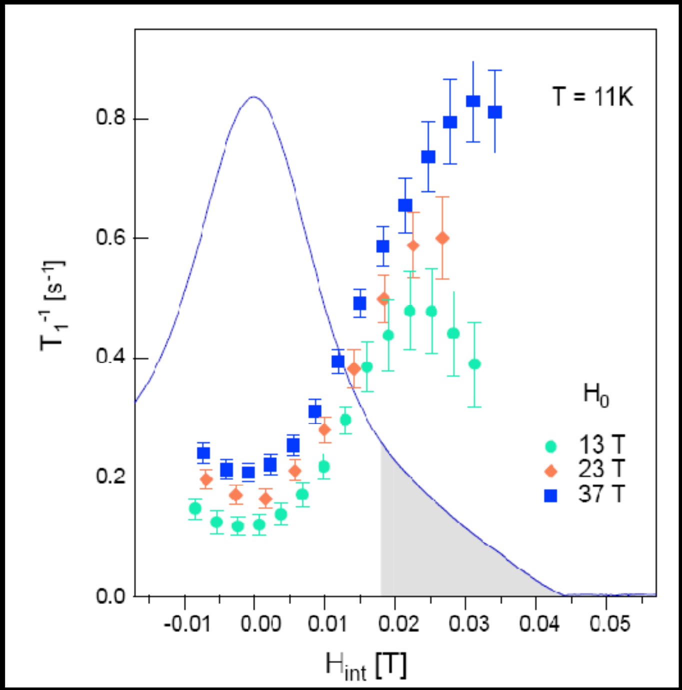




champ local



La RMN donne la carte de champs associée aux vortex



Le T1 varie selon la position par rapport au vortex

Mitrovic et al., Nature (2001)

Summary

NMR allows to measure…

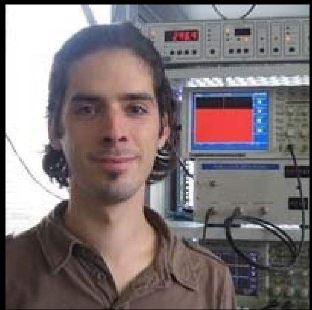
Using the spectrum position and shape:

- type of orbitals (K_{orb})
- spin susceptibility at various positions (K_{spin})
- magnetic orderings or freezings, order parameters…
- charge orders, vortex…
- inhomogeneities

Using dynamics:

- dynamical susceptibilities $\chi''(q,\omega)$
- correlations, spin fluctuations
- gaps, magnetic excitations
- superconducting symetries and gaps

NMR study of superconductivity and magnetism in pnictides

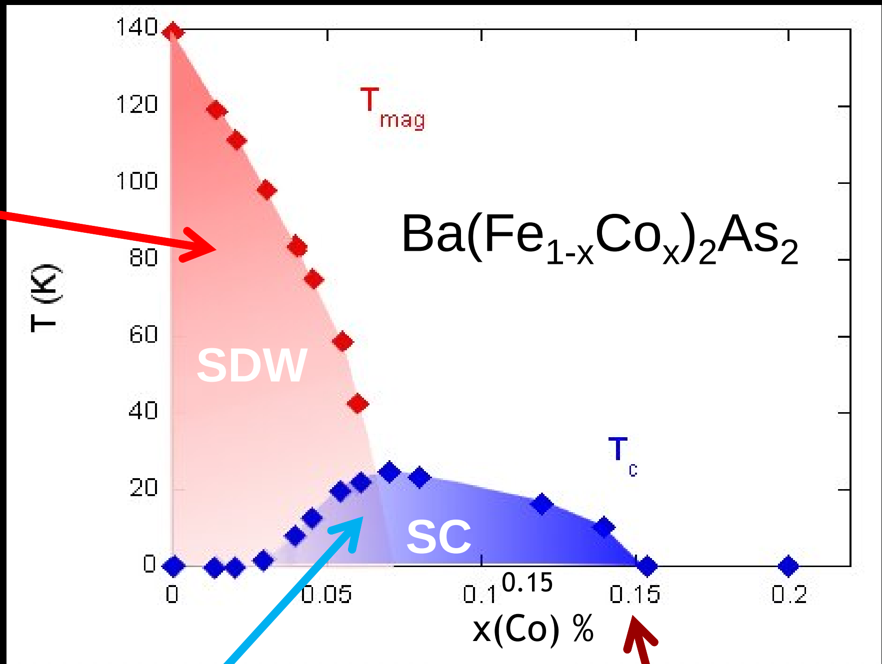


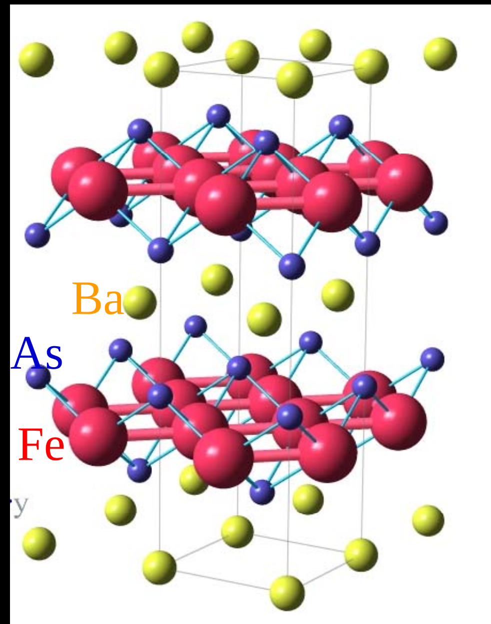
Y. Laplace, J. Bobroff
Laboratoire de Physique des Solides, Orsay

D. Colson, F. Rullier-Albenque, A. Forget
SPEC, CEA Gif Sur Yvette

TRIANGLE DE LA PHYSIQUE UNIVERSITÉ PARIS-SUD 11 cnrs LPS ORSAY

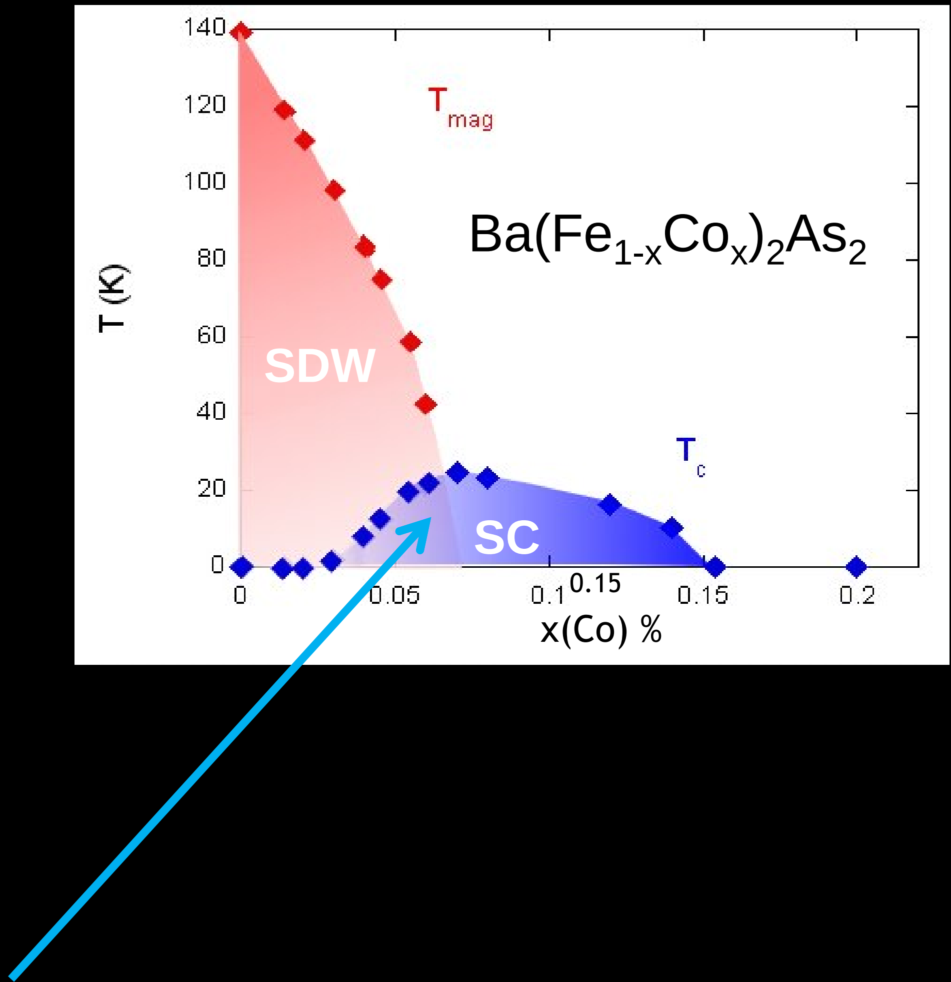
Nature of magnetism ?





Coexistence ?

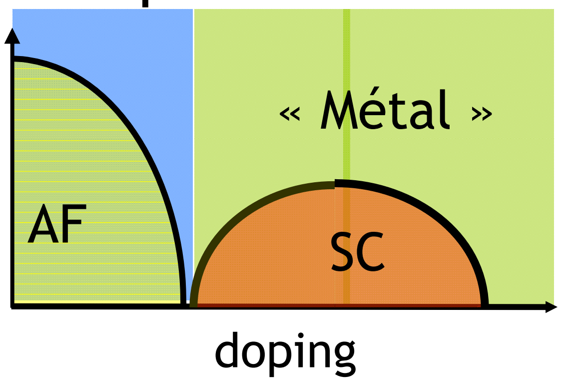
what is doping really doing ?



Coexistence ?

An old question...

Cuprates High Tc superconductors

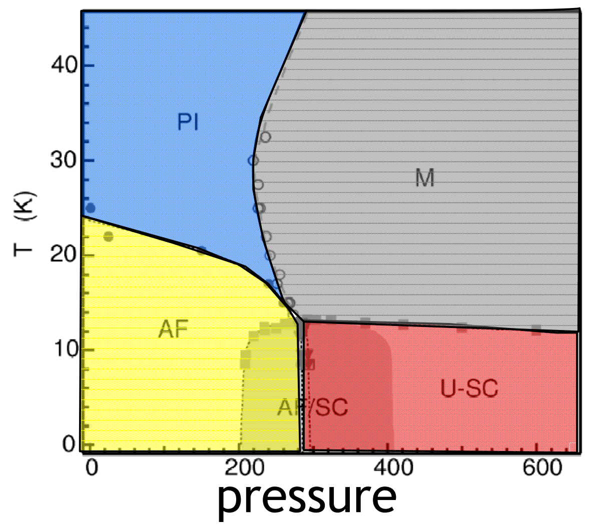


↓

Depends on families rather nano-segregated (stripes)

Miller, PRB 2009
Sanna, PRL 2004

Organic SC



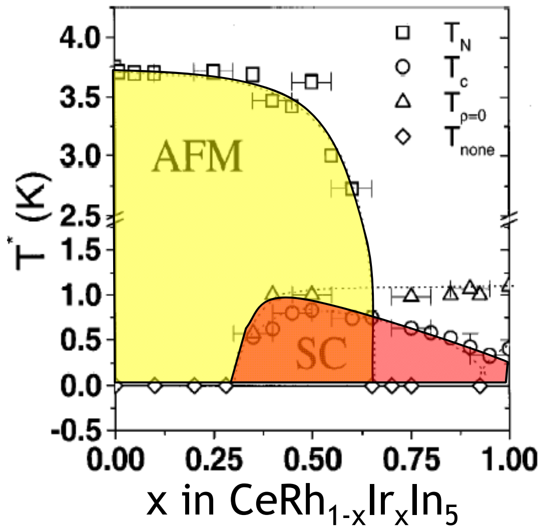
Lefebvre 2000

↓

Not yet settled, rather segregated

Lee, PRL 2005

Heavy fermions



Pagliuso 2001

↓

Yes


VOLUME 90, NUMBER 7 PHYSICAL REVIEW LETTERS week ending 21 FEBRUARY 2003

Coexistence of Antiferromagnetism and Superconductivity near the Quantum Criticality of the Heavy-Fermion Compound $CeRhIn_5$

T. Mito,[1,*] S. Kawasaki,[1] Y. Kawasaki,[1] G.-q. Zheng,[1] Y. Kitaoka,[1] D. Aoki,[2,†] Y. Haga,[3] and Y. Ōnuki[2]

Mito et al., PRL 2003

A key question for the determination of the superconducting gap symmetry

Interplay between magnetism and superconductivity in Fe-pnictides

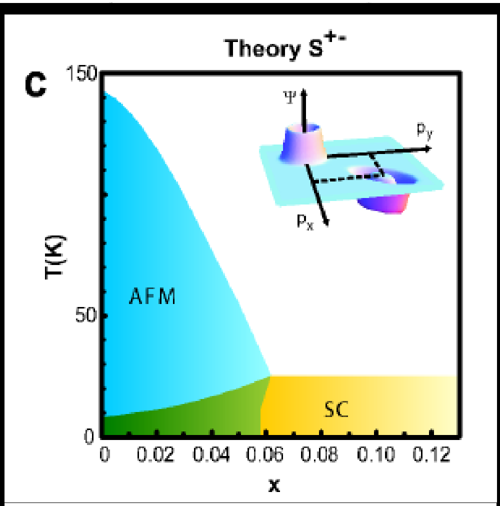
A. B. Vorontsov, M. G. Vavilov, and A. V. Chubukov — PRB 2009

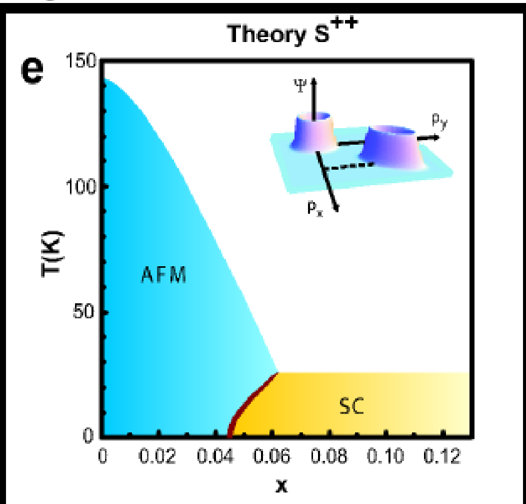
Coexistence of superconductivity and a spin-density wave in pnictide superconductors: Gap symmetry and nodal lines

D. Parker,[1] M. G. Vavilov,[2] A. V. Chubukov,[2] and I. I. Mazin[1] — PRB 2009

Unconventional pairing in the iron arsenide superconductors — PRB 2010

Rafael M. Fernandes,* Daniel K. Pratt, Wei Tian, Jerel Zarestky, Andreas Kreyssig, Shibabrata Nandi, Min Gyu Kim, Alex Thaler, Ni Ni, Paul C. Canfield, Robert J. McQueeney, Jörg Schmalian, and Alan I. Goldman

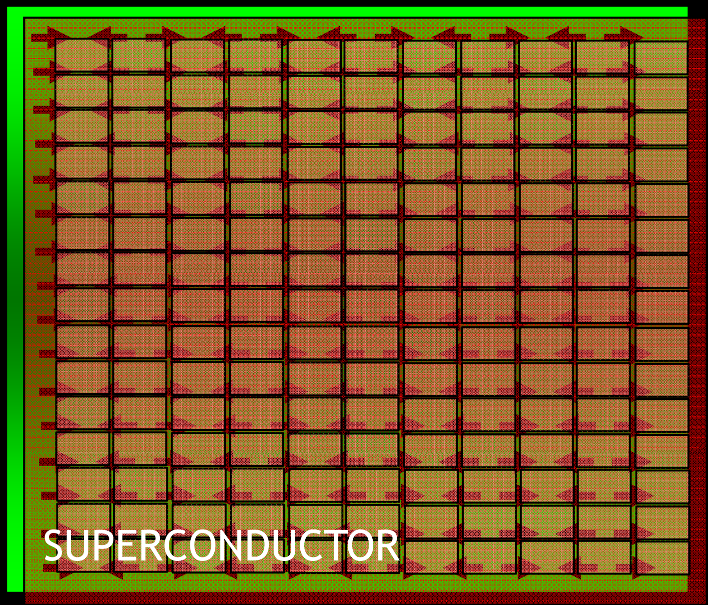




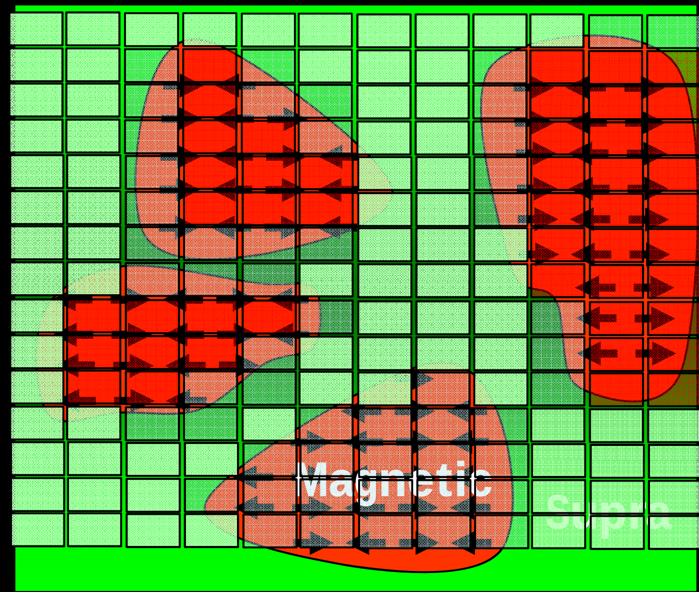
A true atomic coexistence is only compatible with a s+- gap symmetry

Two possible situations

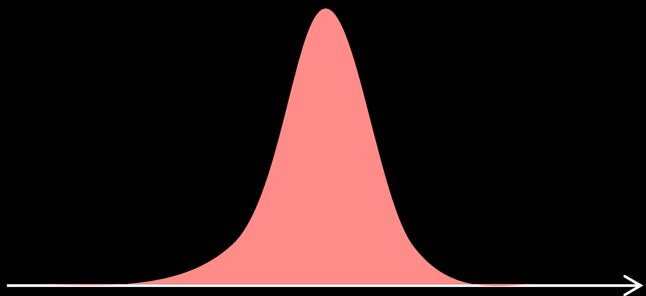
True local coexistence

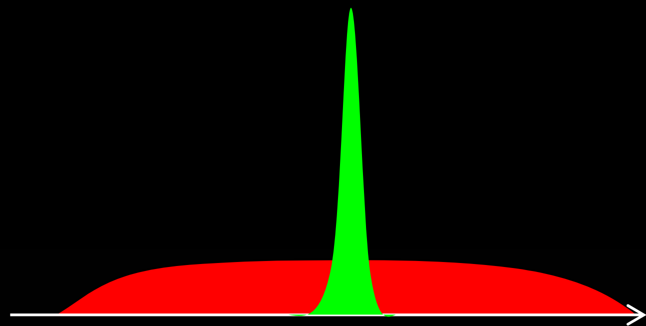


Segregation



Need a local probe :RMN, μSR, Mossbauer...



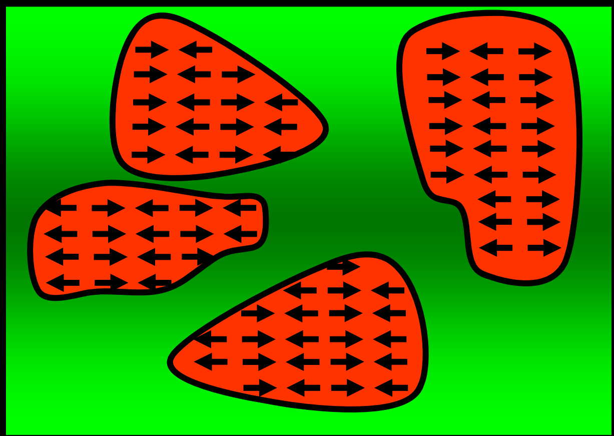


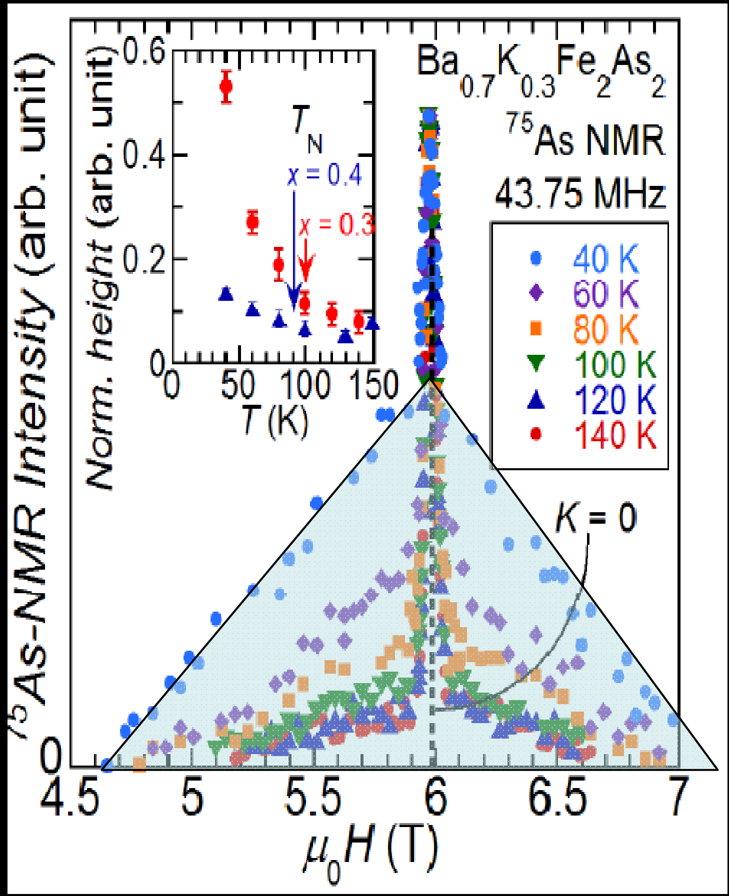
- SmOFeAs : segregation

  Drew et al, Nat. Mat. 08

- $Ba_{1-x}K_xFe_2As_2$: segregation

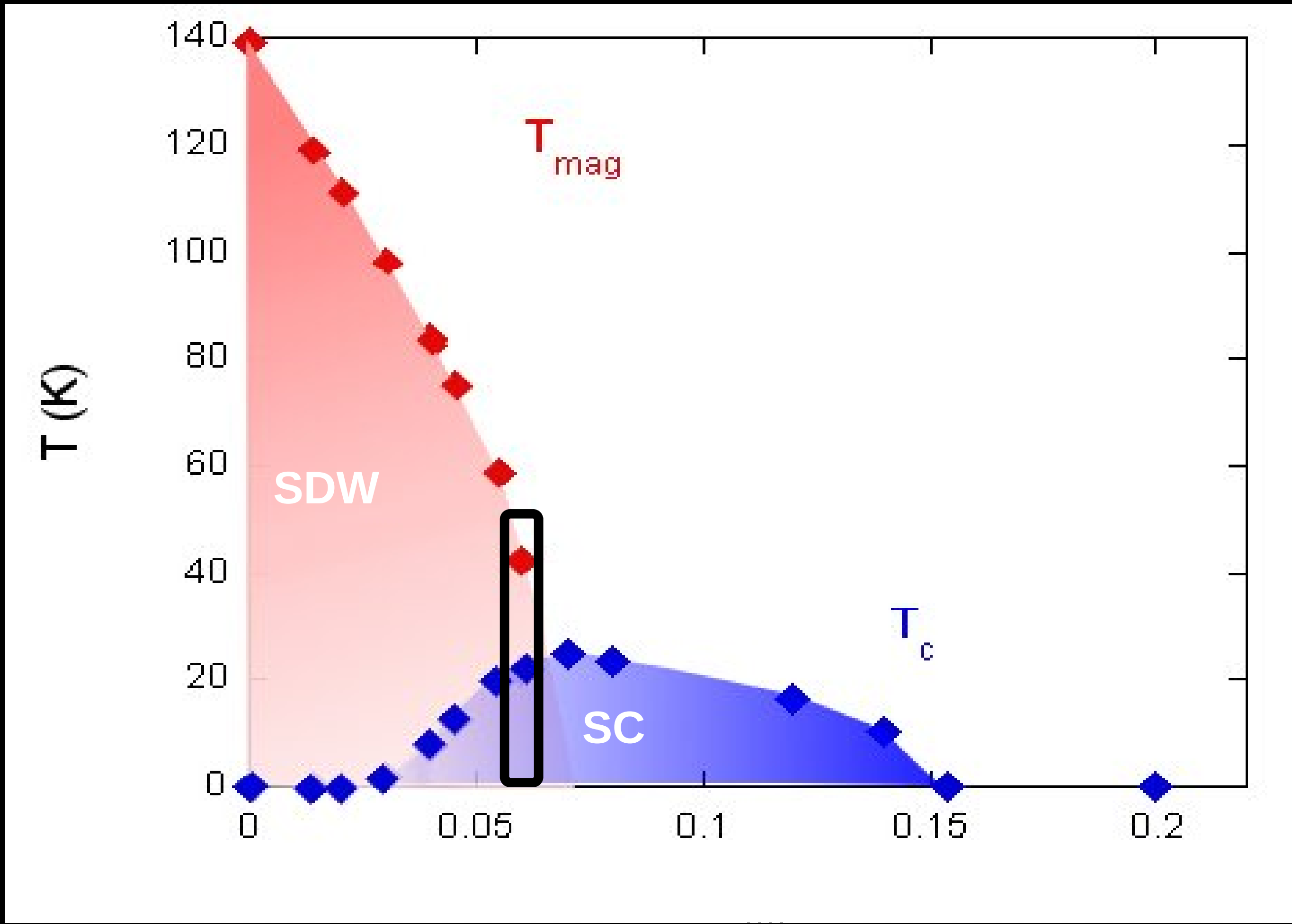
  Takeshita et al. JPSJ;
  Aczel et al. PRB 08;
  Goko PRL 08;
  Fukazawa et al.,JPSJ 09;
  Julien et al. EuroPhys.Lett.09



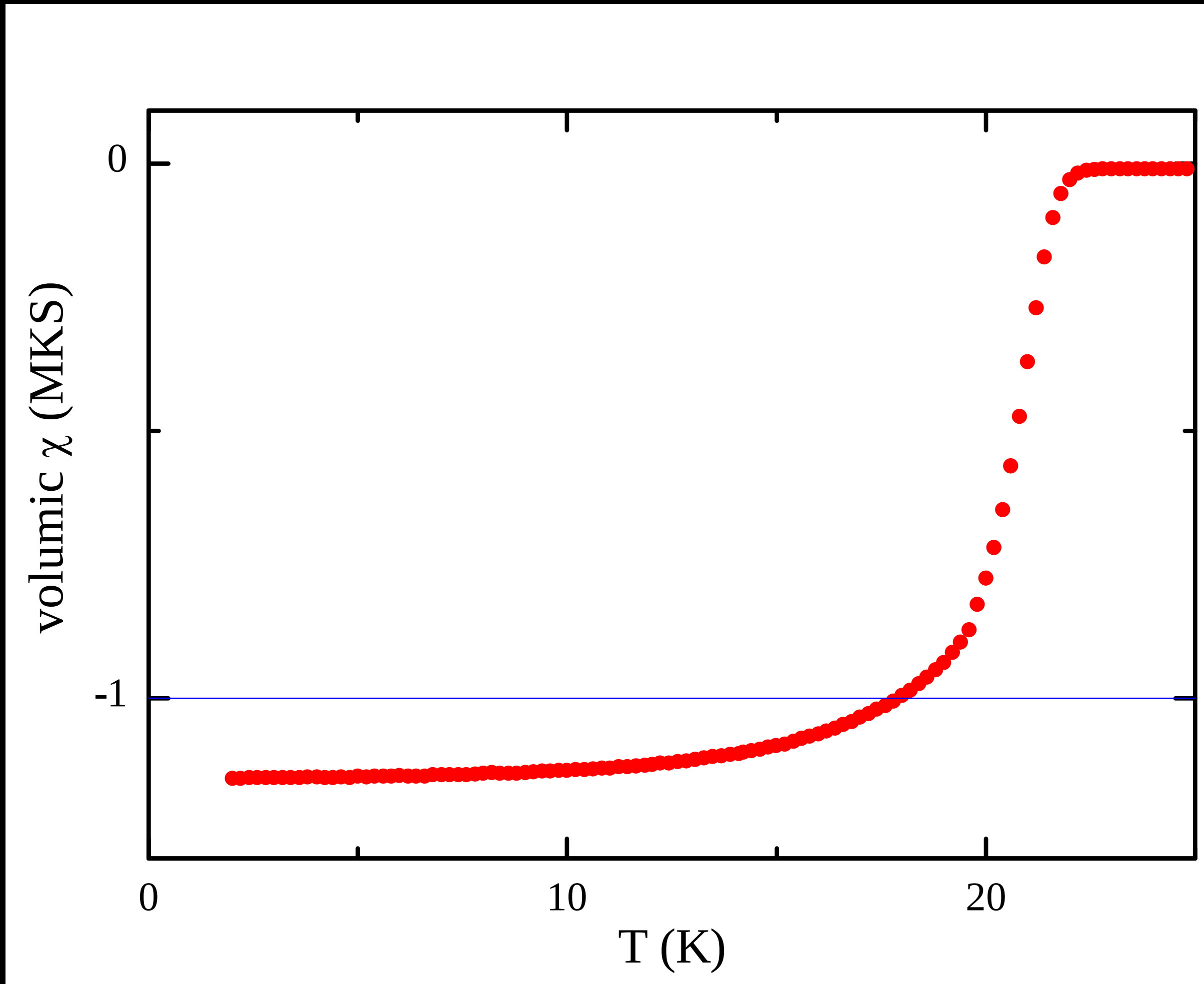


Fukazawa JPSJ 09

$Ba(Fe_{1-x}Co_x)_2As_2$

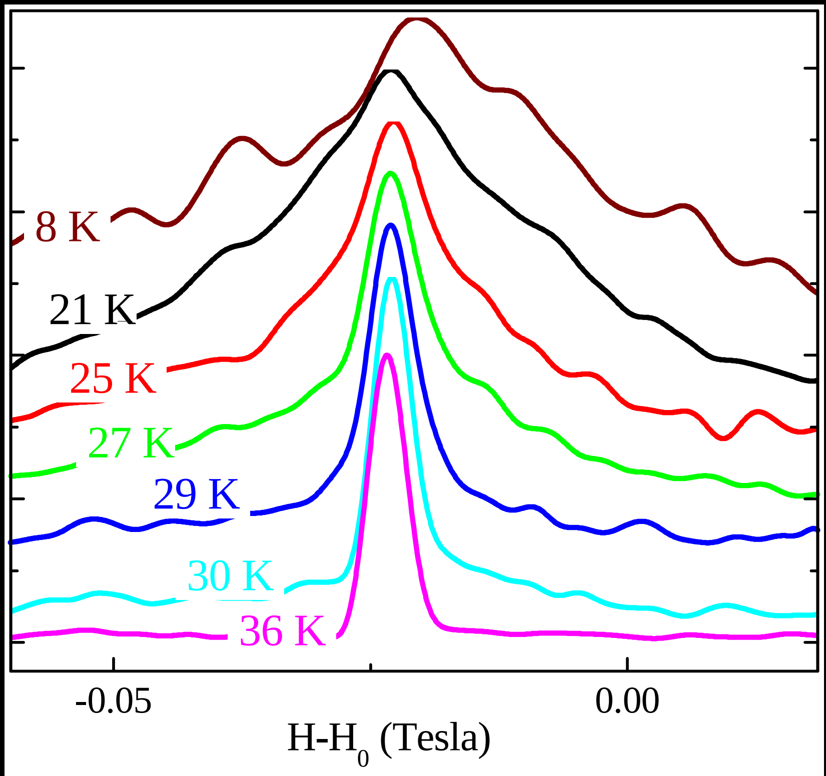


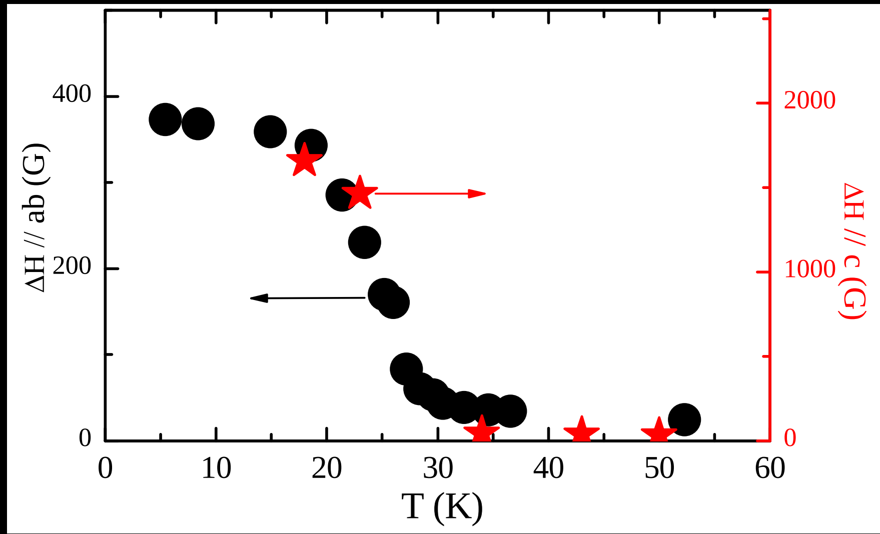
$Ba(Fe_{0.94}Co_{0.06})_2As_2$



Superconducting fraction : 90 - 100%

^{75}As RMN x=6% : spectrums

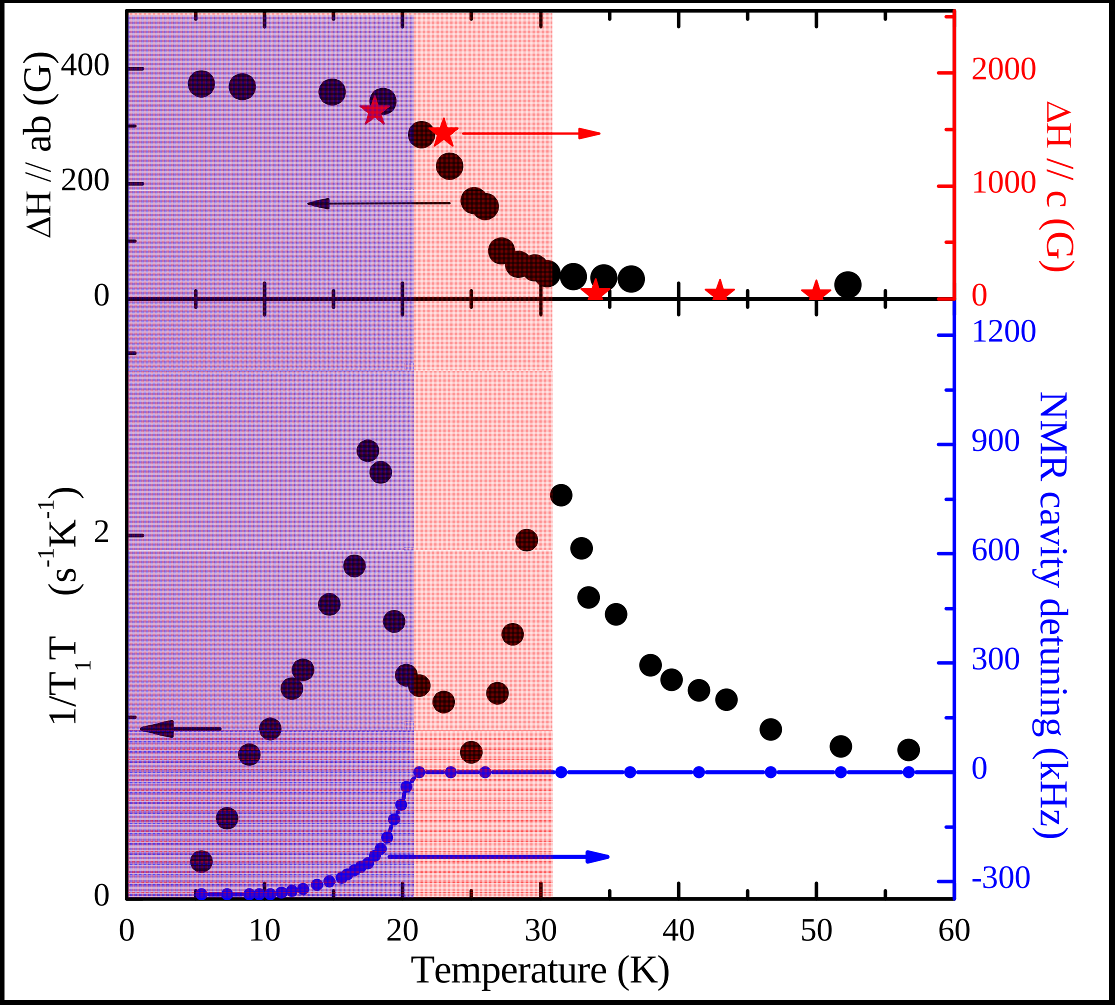




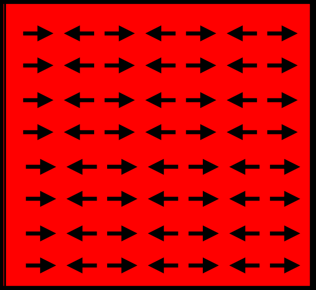
Homogeneous magnetic broadening :

100% magnetic fraction below 31K

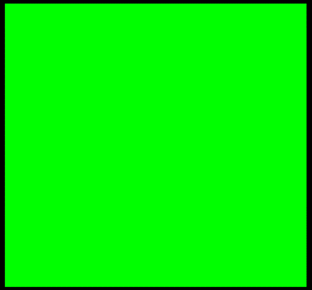
Coexistence in $Ba(Fe_{0.94}Co_{0.06})_2As_2$



100% magnetic below 31K



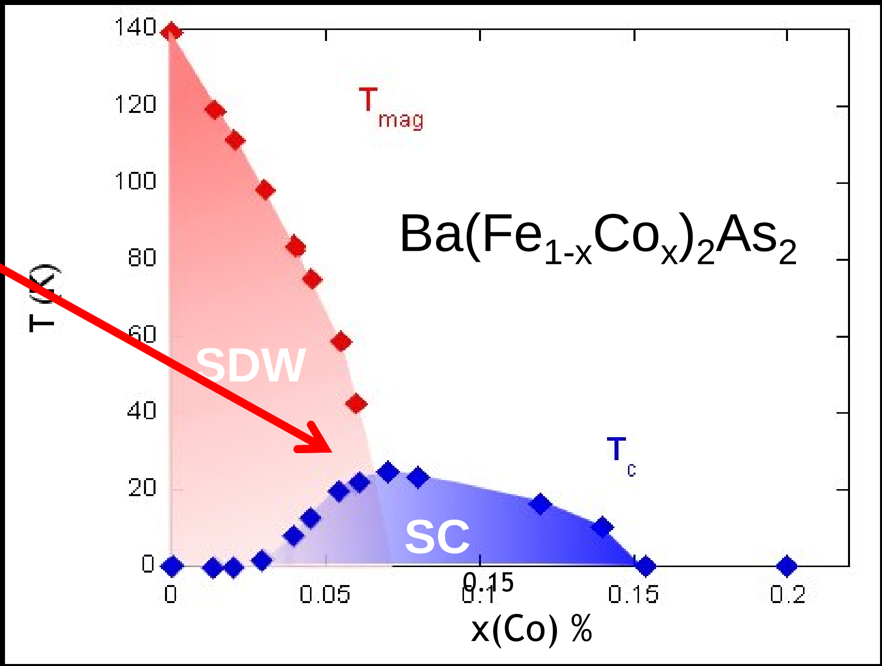
100% superconduct. below 21K



Dynamically, the same Fe atoms display magnetism and superconductivity

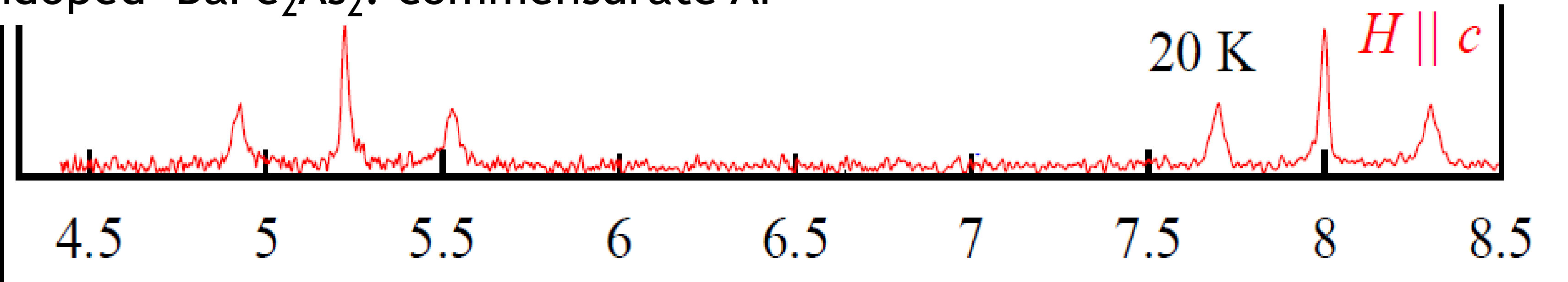
→ True atomic coexistence

Nature of magnetism ?



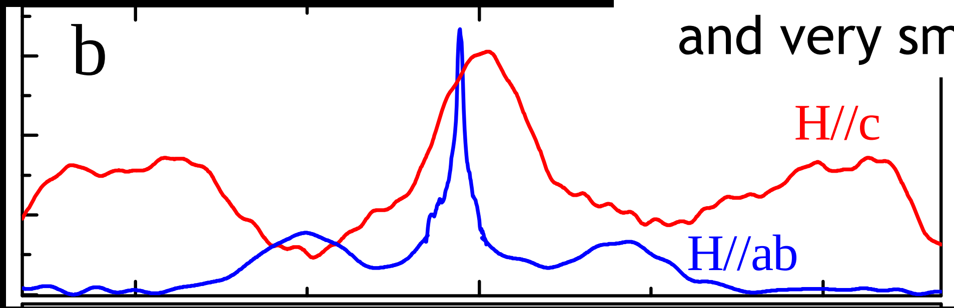
Nature of the magnetism

undoped $BaFe_2As_2$: commensurate AF

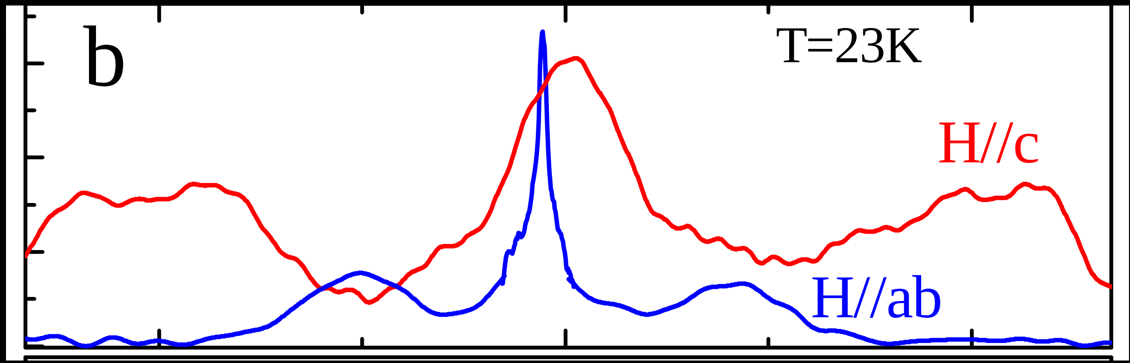


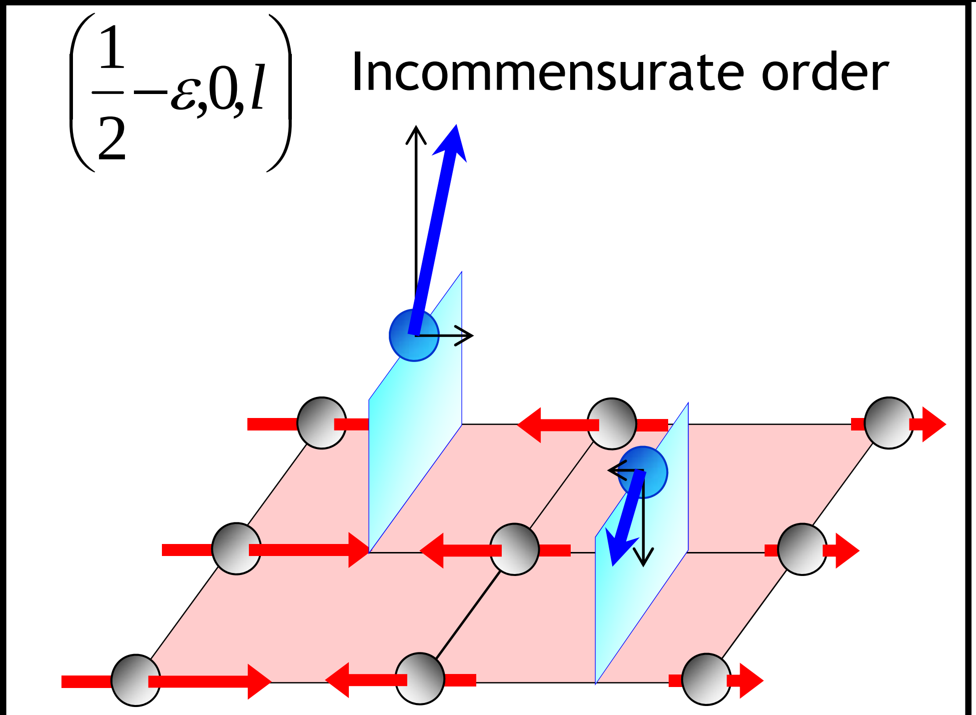
Kitagawa, JPSJ 08

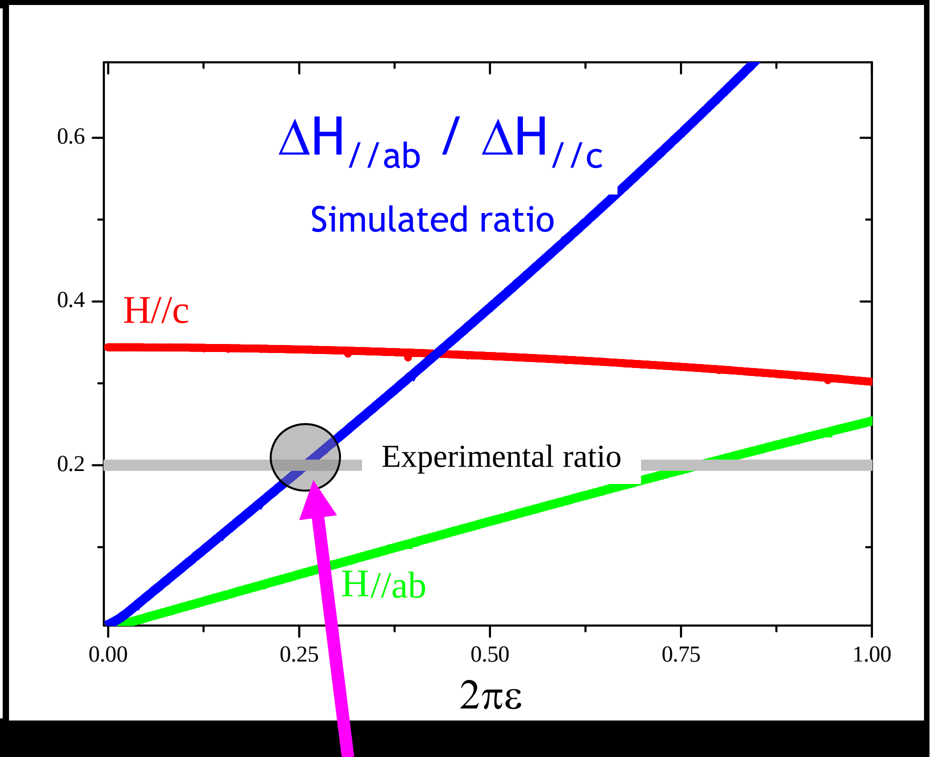
Co6% : incommensurate AF
and very small moment



Incommensurability







$\varepsilon \sim 0.04$

Non doped x=0%

doped x=6%

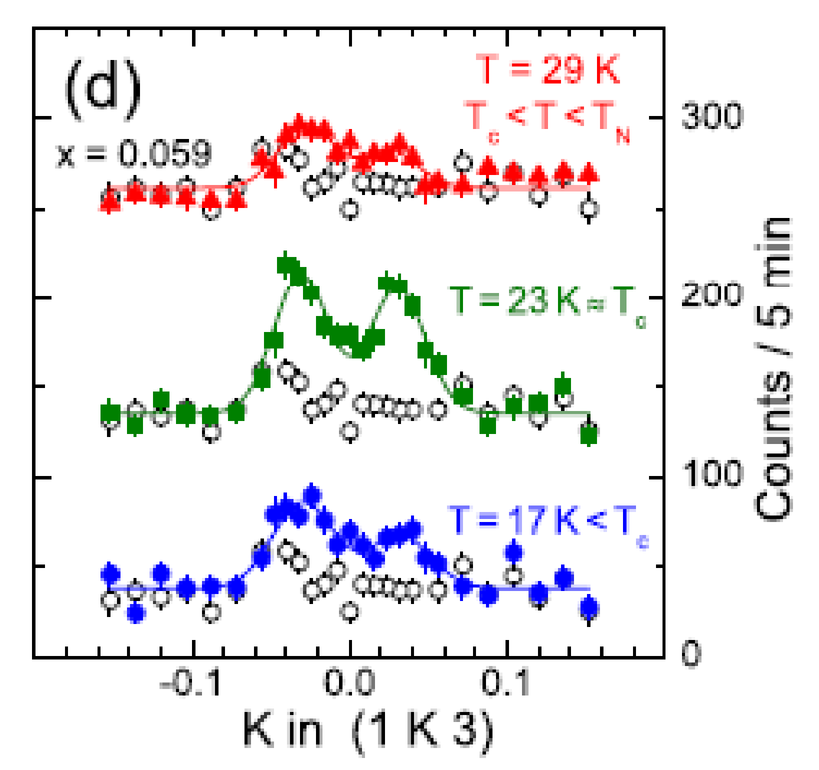
T_N=135K → T_N=31K

moment ~ 0.9 μ_B → moment < 0.1 μ_B

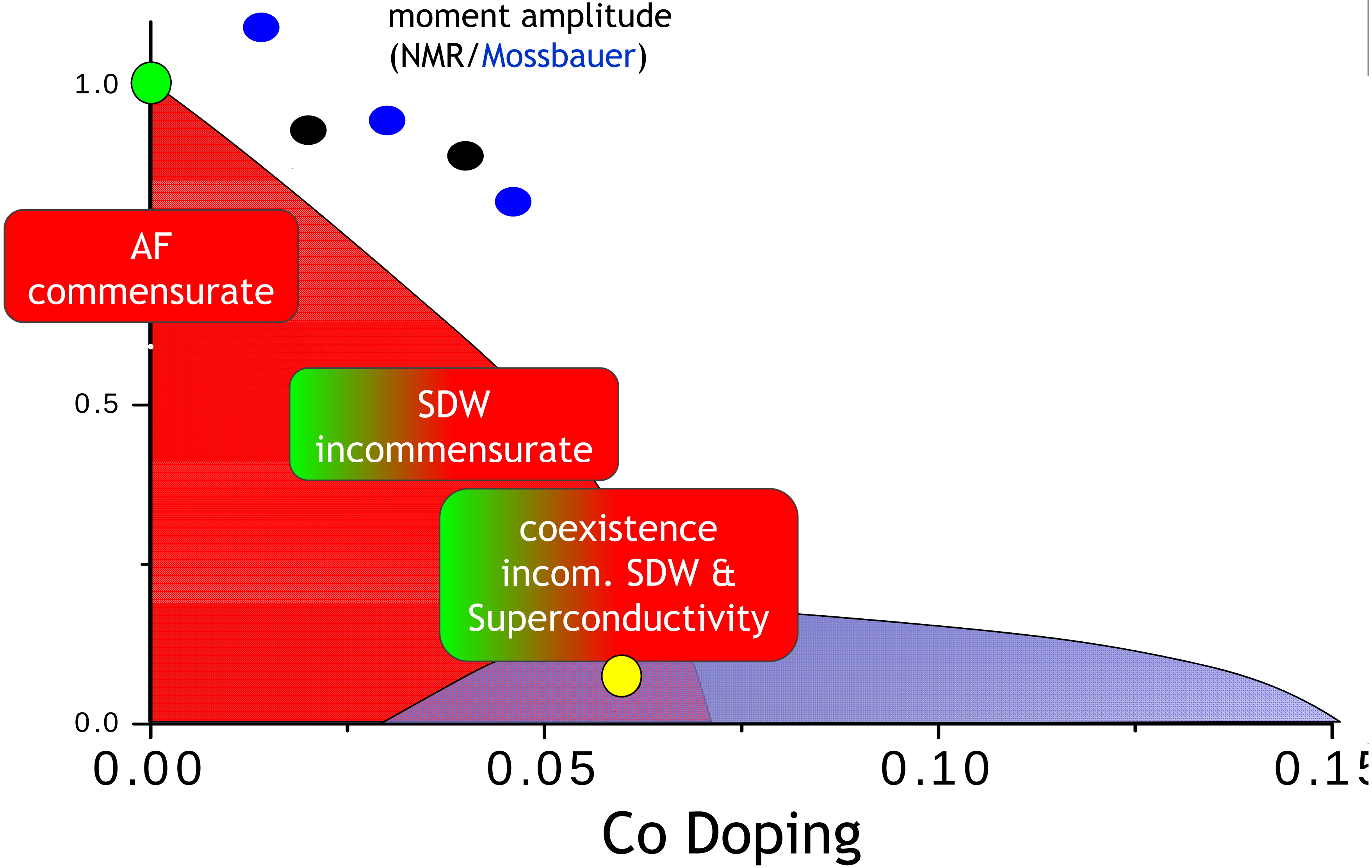
commensurate AF order → incommensurate SDW

Incommensurability recently confirmed by neutrons

Pratt et al. Phys. Rev. Lett. 106, 257001 (2011)



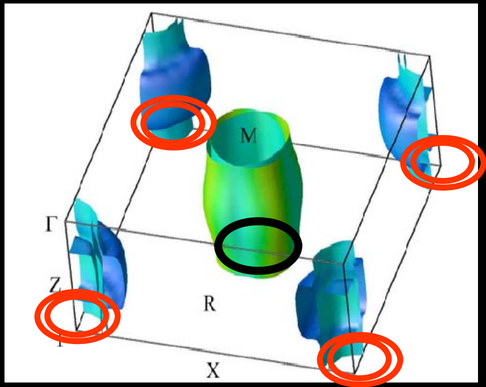
Phase diagram from NMR/Mossbauer



How can magnetism and superconductivity coexist together ?

• A consequence of the multi(5)-band character of the Fermi Surface ?

M could originate from a nesting driven instability
SC could gap different Fermi sheets

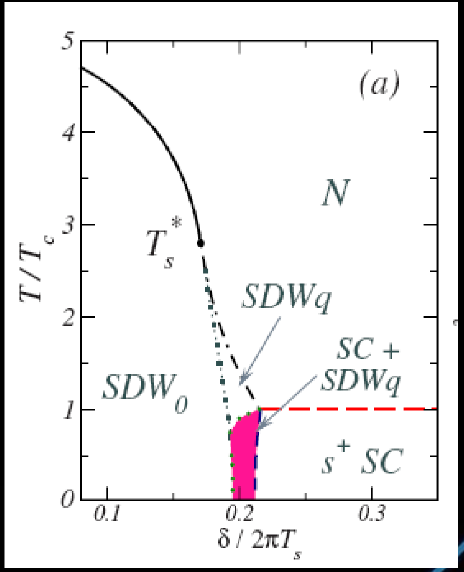


Singh & al., PRL 08

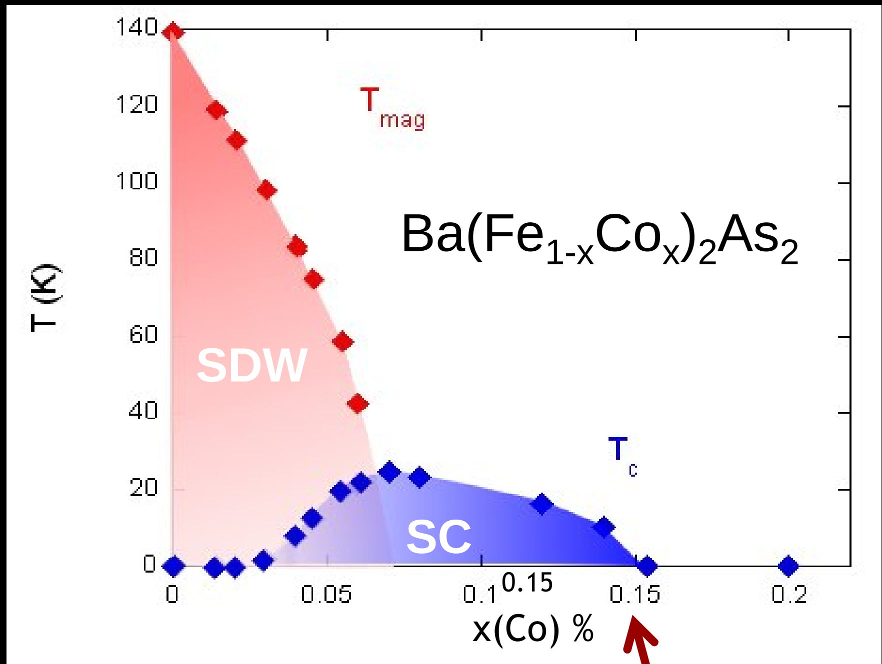
•Competition/Coexistence over different parts of the Fermi Surface seems possible even in a two band model

In this model, coexistence is possible only if the magnetic state is incommensurate.

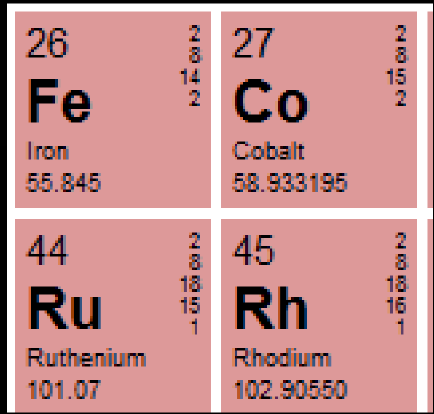
--> COMPATIBLE WITH OUR MEASUREMENTS

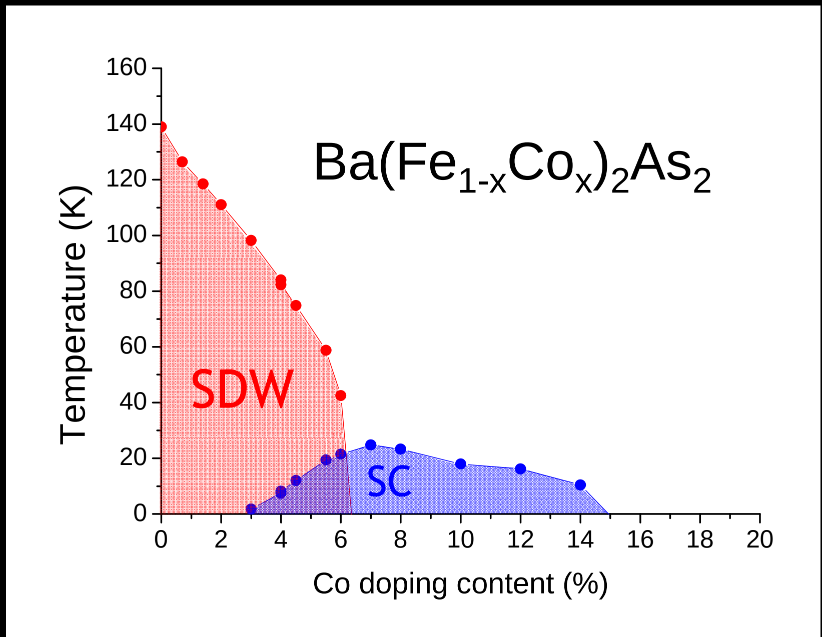


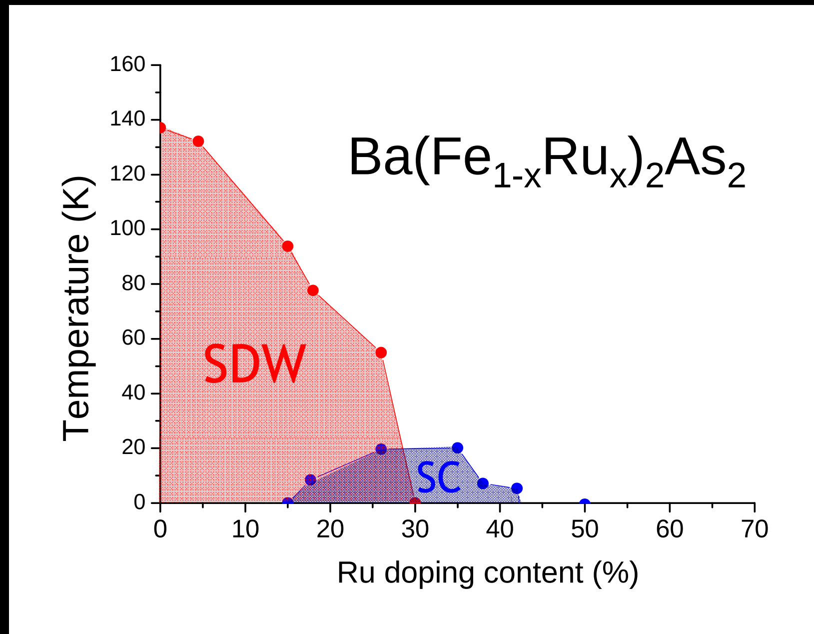
Vorontsov & al., PRB 09



what is doping really doing ?







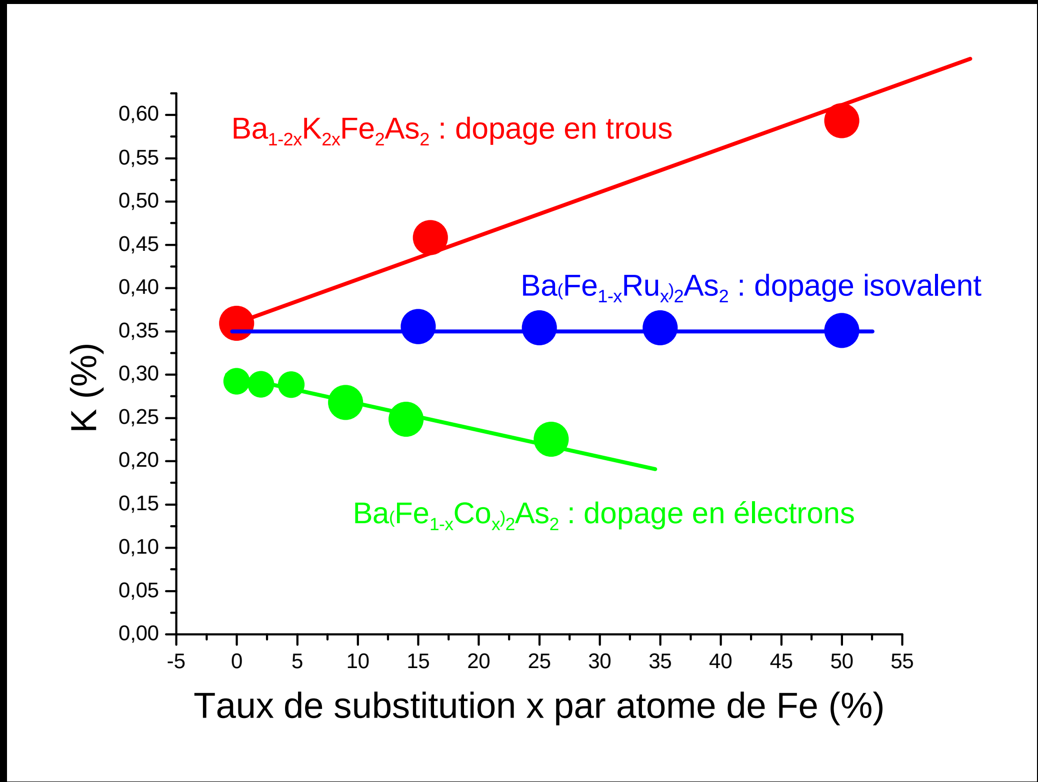
simple rigid band filling
electron doping

Increase both the number of holes & electrons , V_{Fermi} increases, correlatio decrease by a factor 3

Brouet et al., 2011

Co vs Ru doping

NMR shift vs substitution in the normal state :

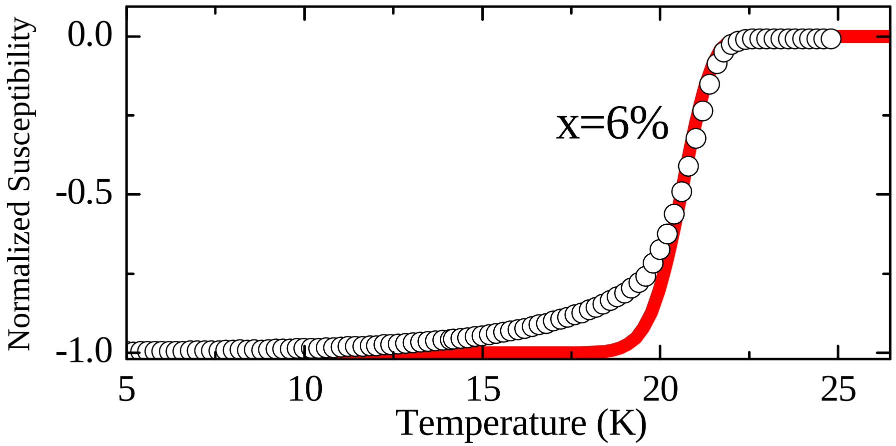


Co = electron doping

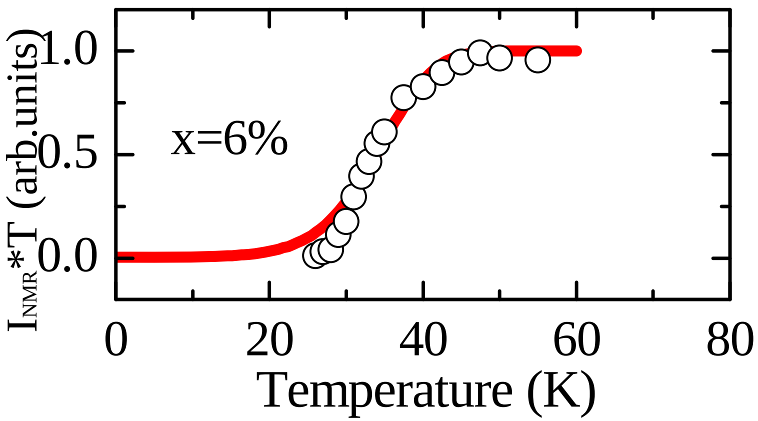
Ru = chemical pressure (isovalent doping)

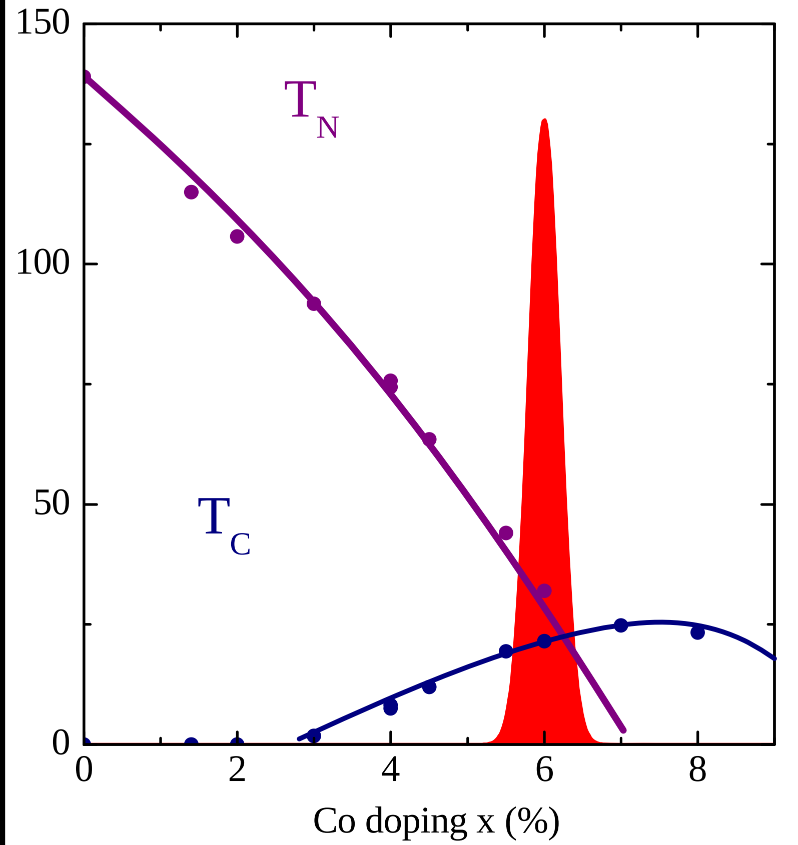
Co doping homogeneous both from macroscopic and local probes

superconducting transition



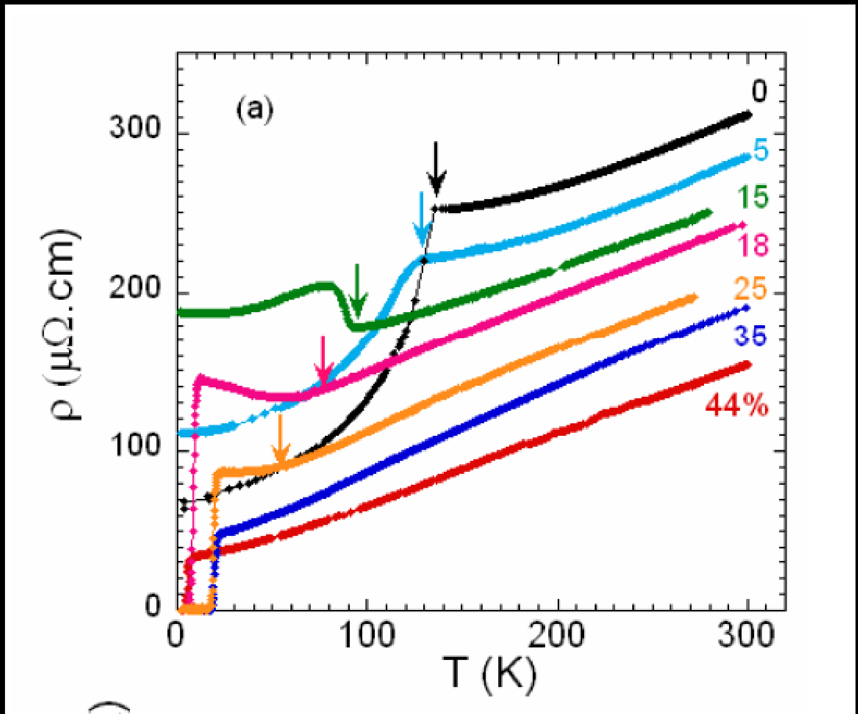
magnetic transition



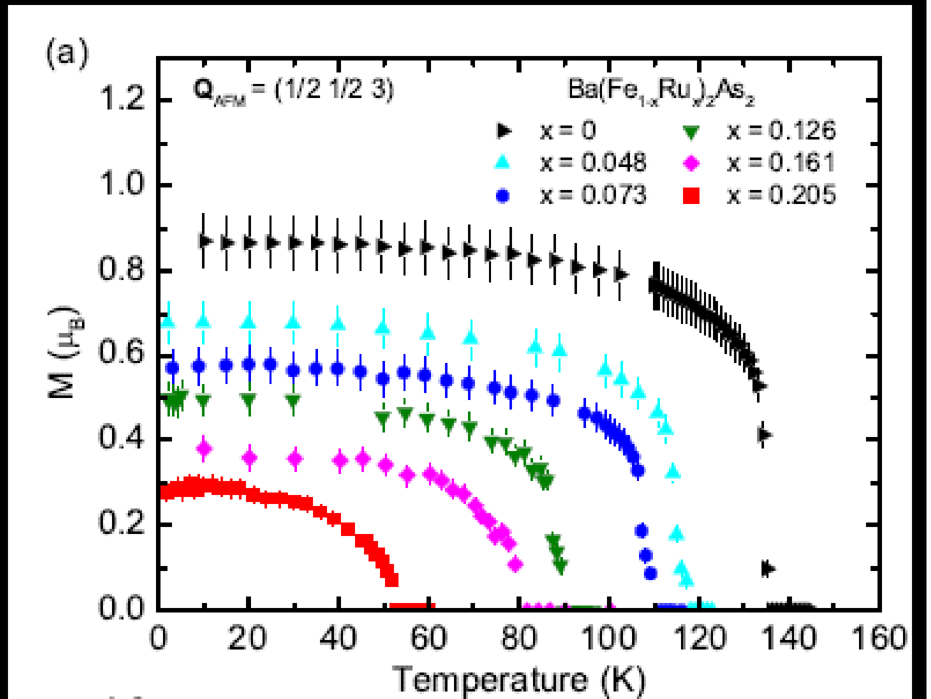


Ru doping homogeneous from macroscopic probes

transport & neutrons

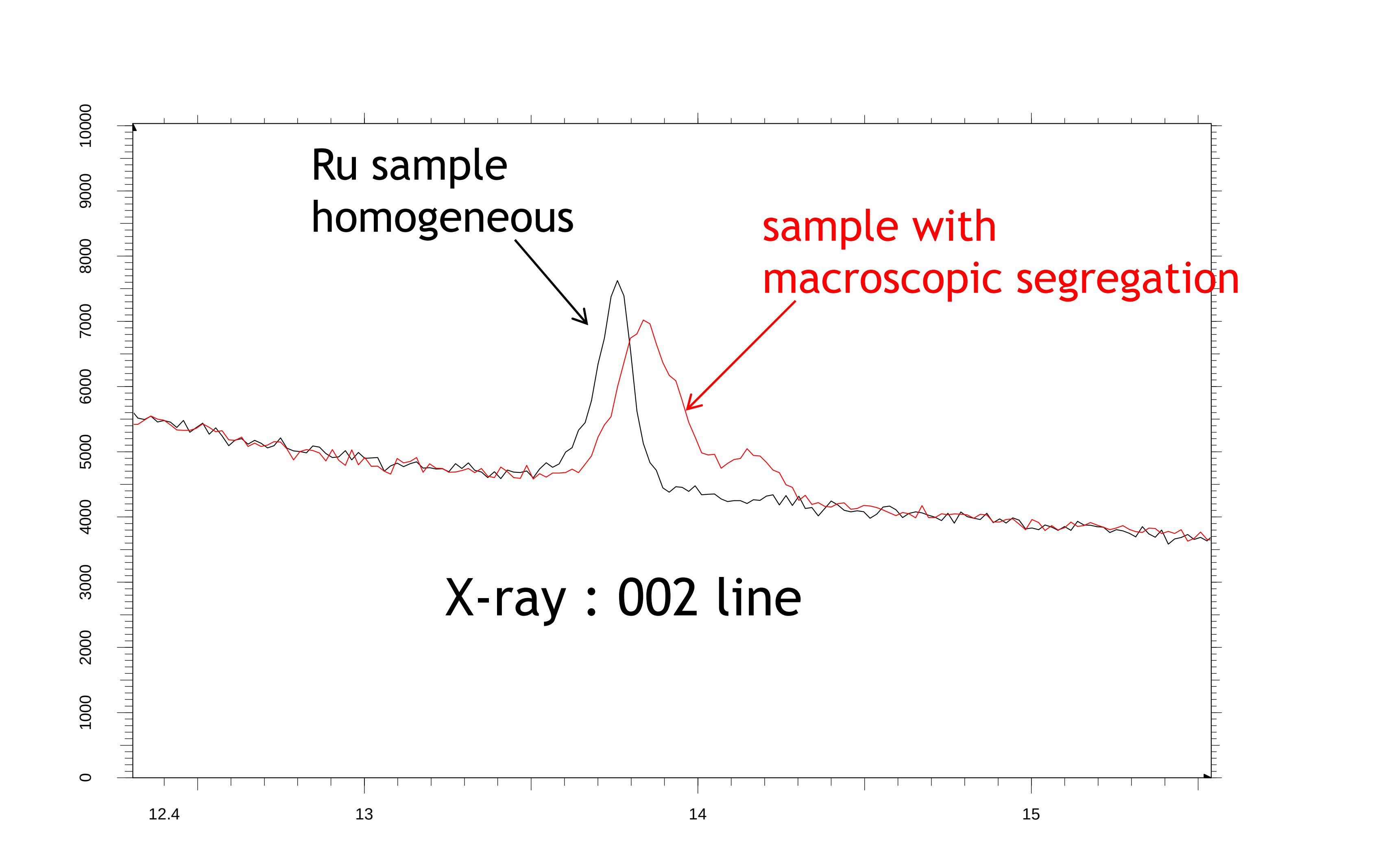


Rullier-Albenque et al., PRB 2010

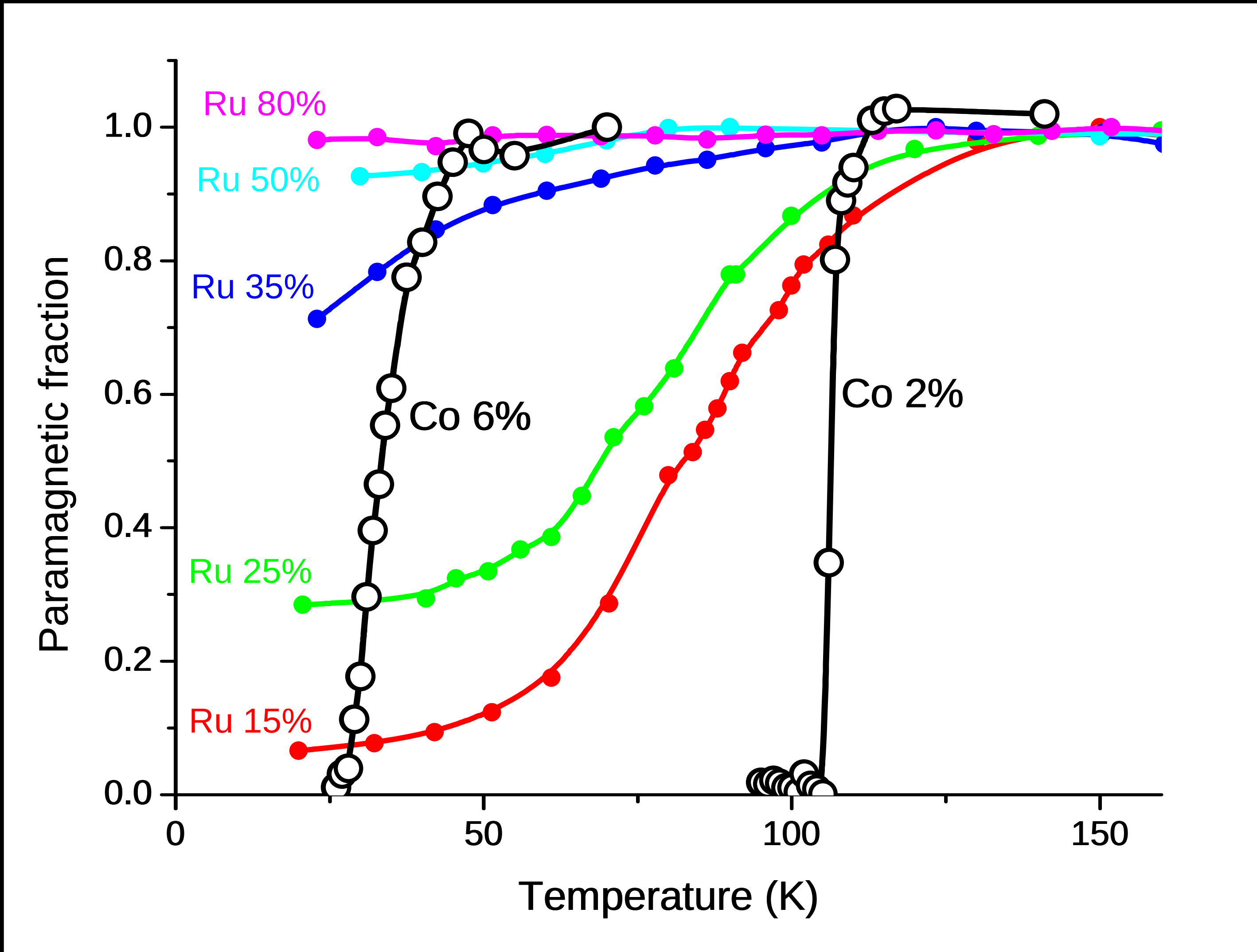


Kim et al. PRB 2011

Ru doping homogeneous from X-ray

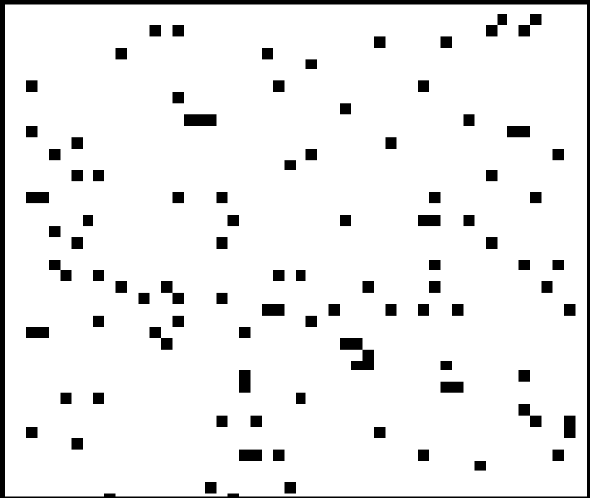


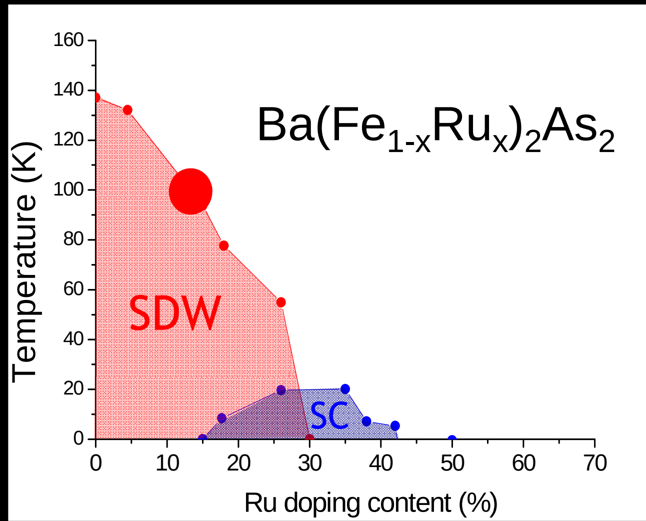
But... Ru doping not homogeneous from NMR

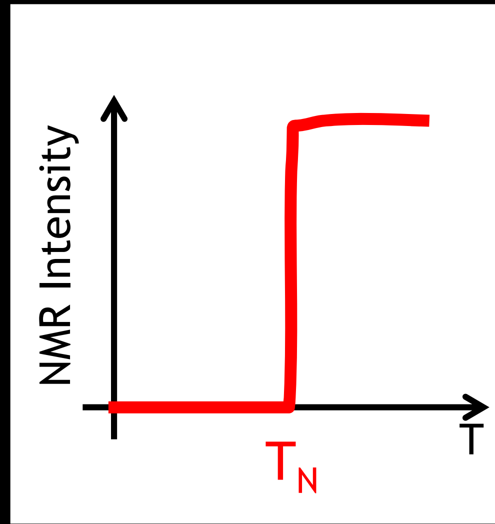


How to reconcile
NMR inhomogeneity &
macroscopic homogeneity ?

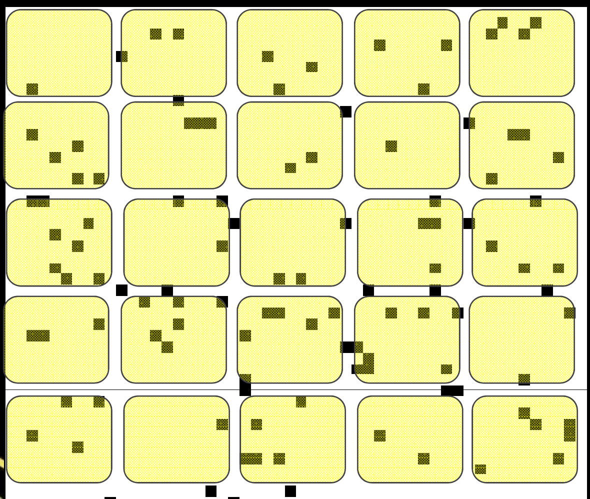
if Ru effect effect is homogeneous

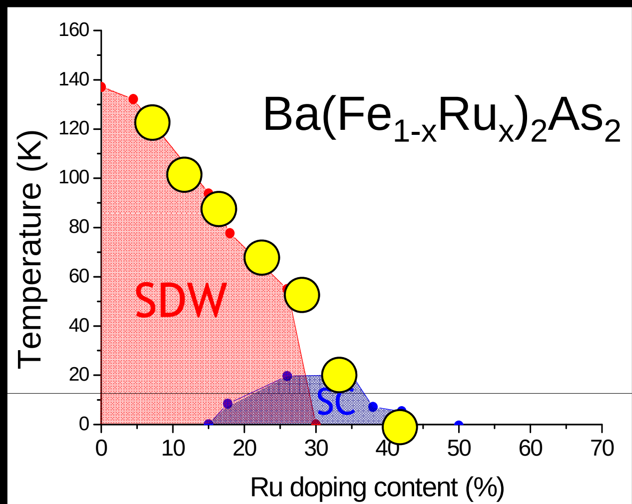


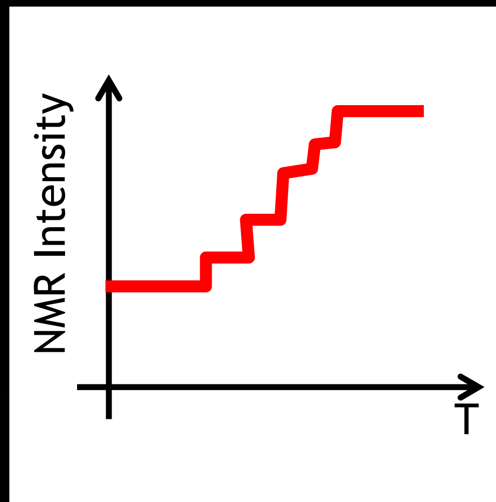




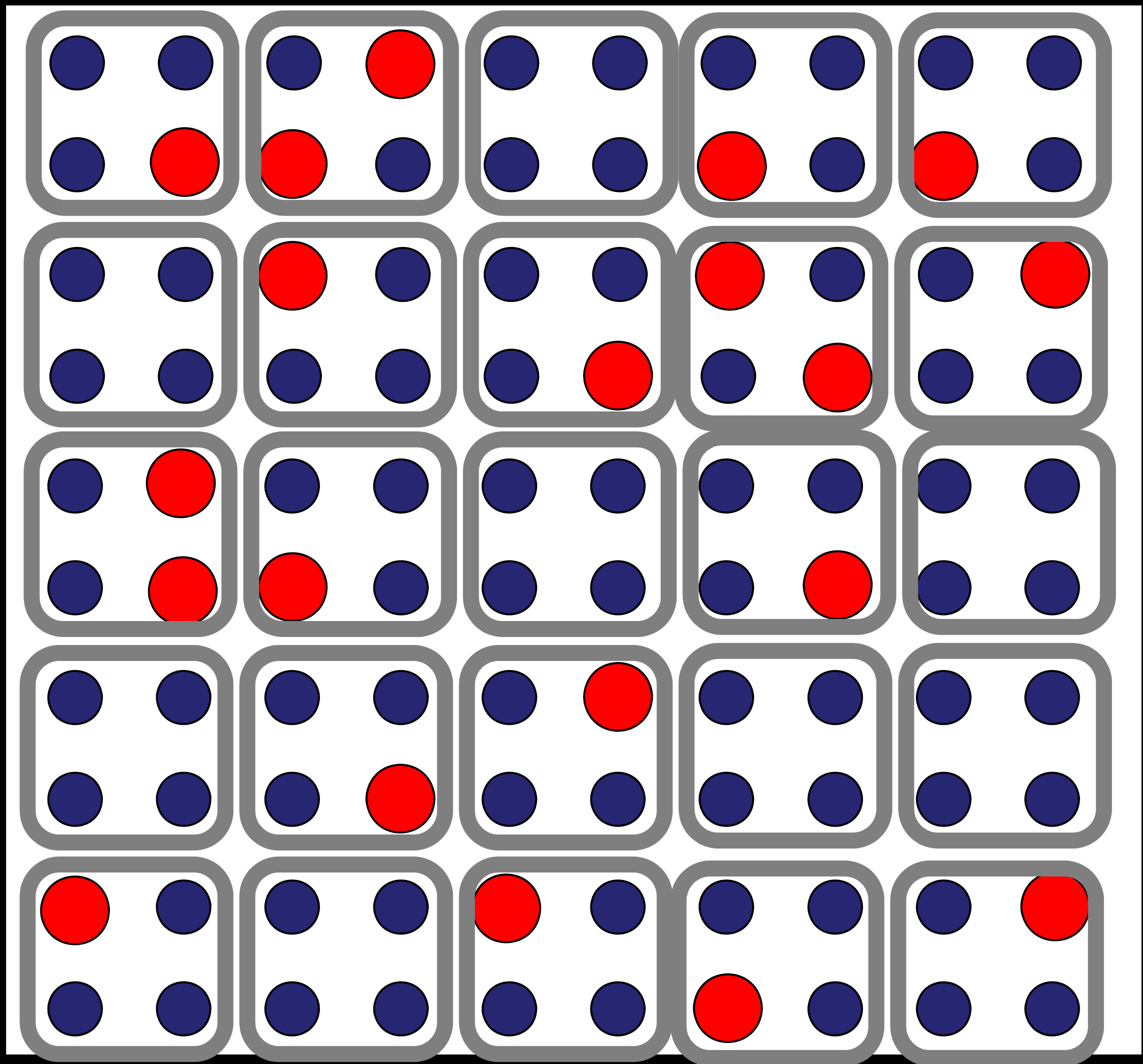
if Ru effect is averaged but on a nanoscale

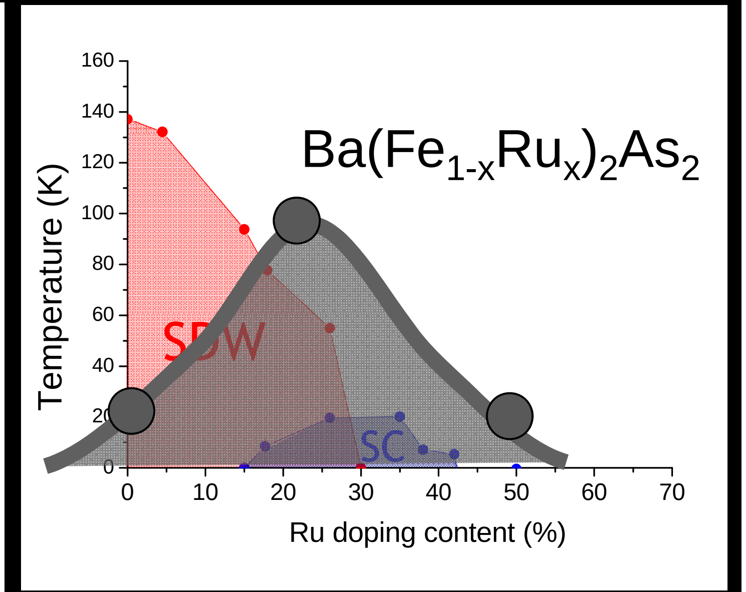




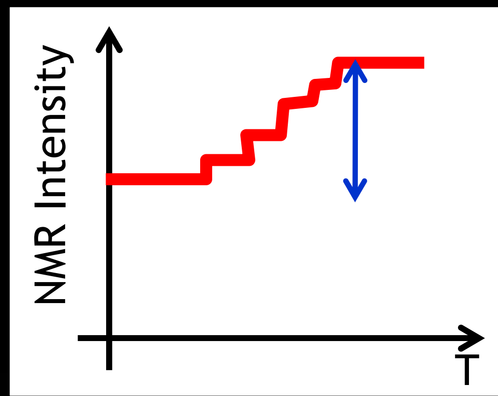


Ru 20%



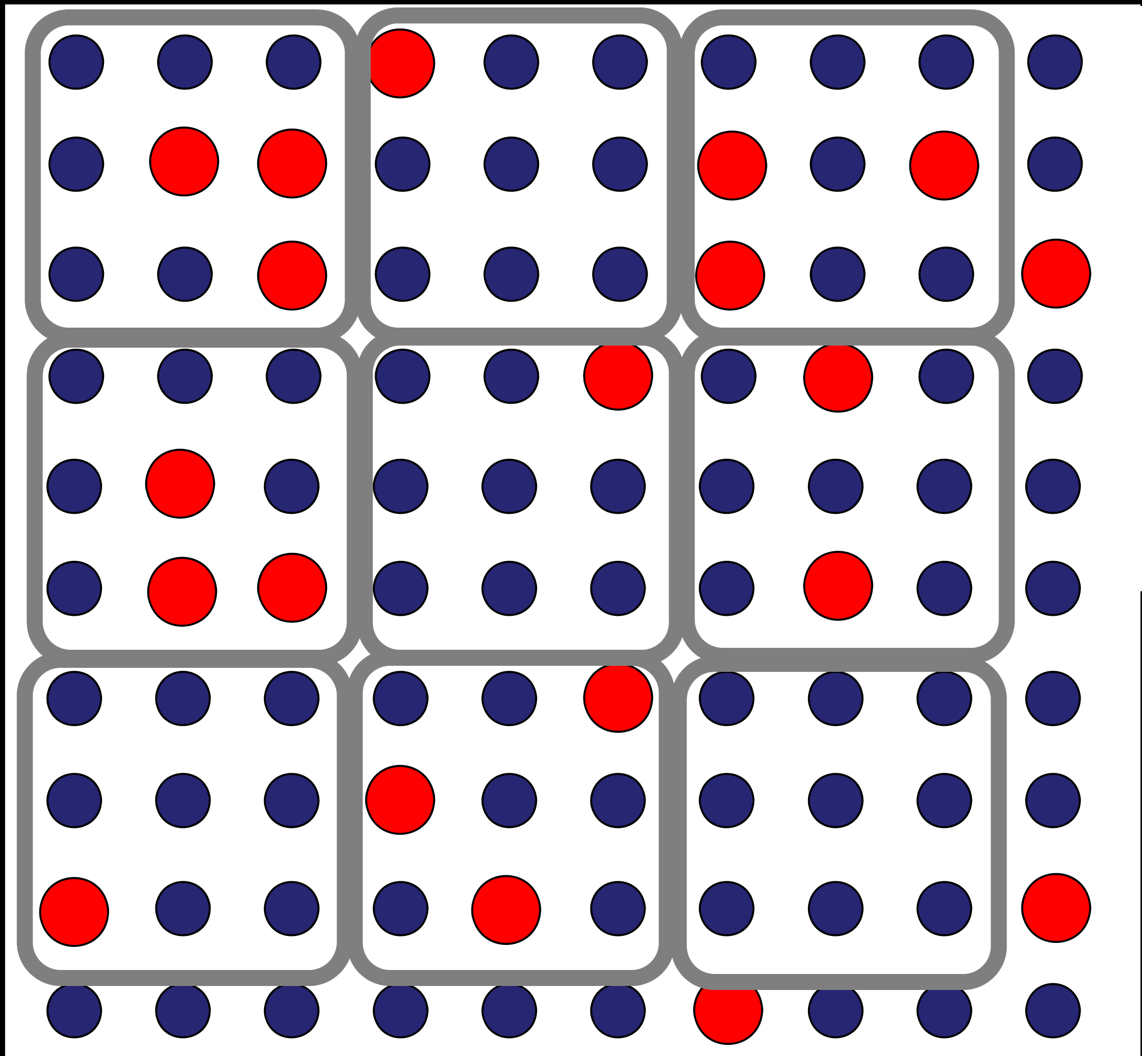


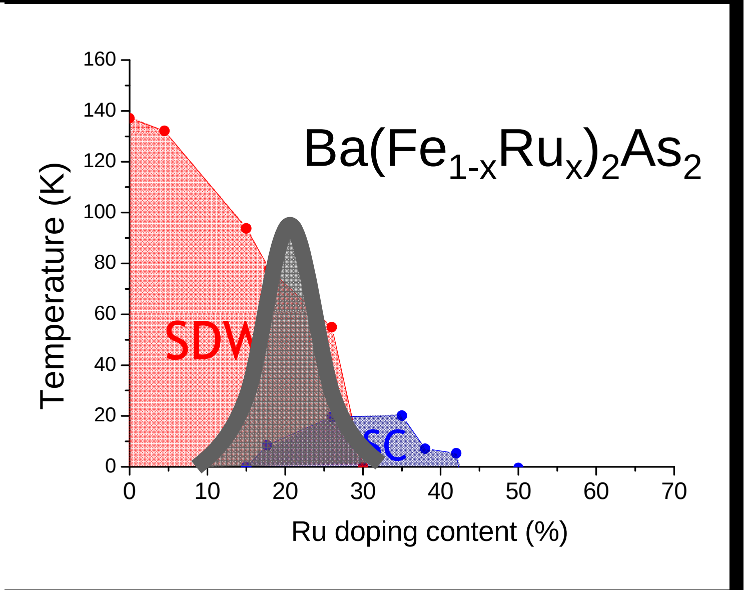
$Ba(Fe_{1-x}Ru_x)_2As_2$
Temperature (K)
Ru doping content (%)
SDW
SC
0
10
20
30
40
50
60
70
0
20
40
60
80
100
120
140
160

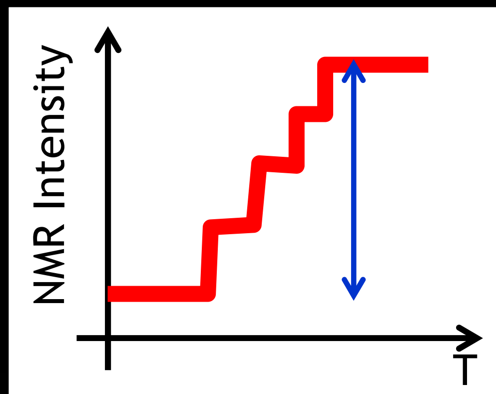


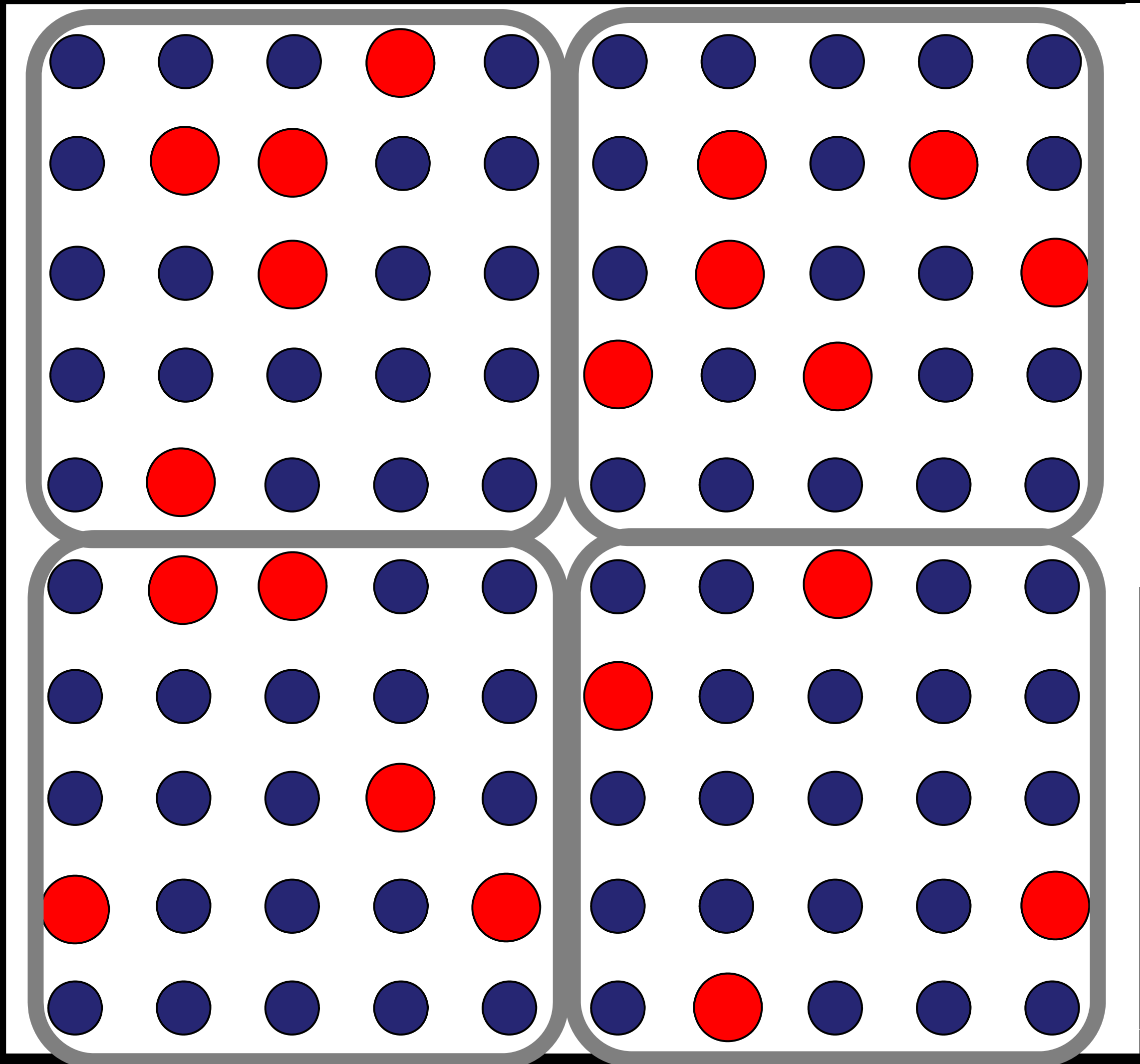
NMR Intensity
T

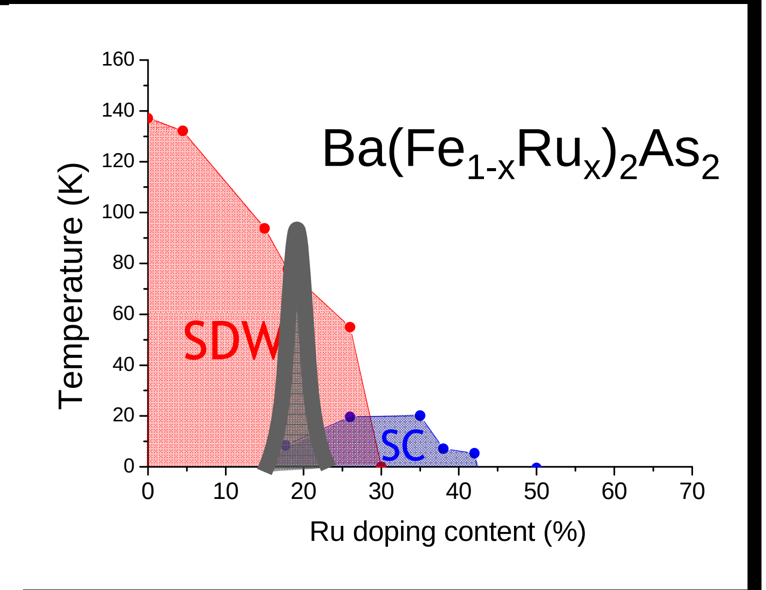
Ru 20%

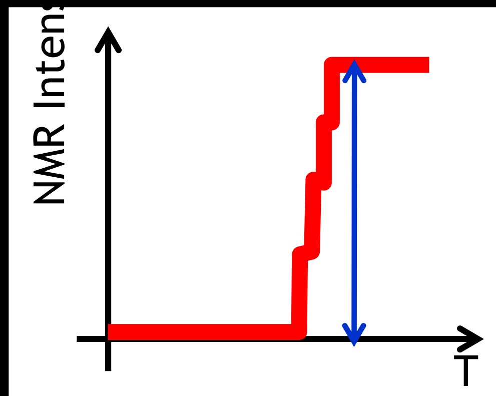


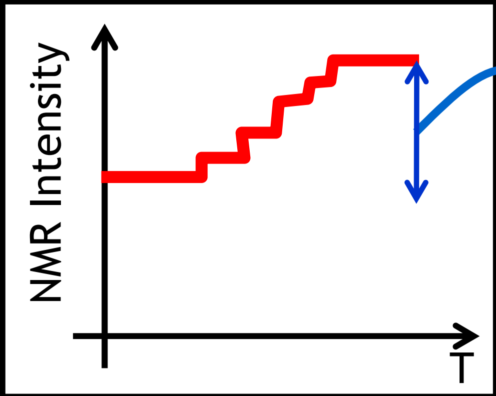

Ba(Fe1-xRux)2As2
Temperature (K)
160
140
120
100
80
60
40
20
0
SDW
SC
0
10
20
30
40
50
60
70
Ru doping content (%)

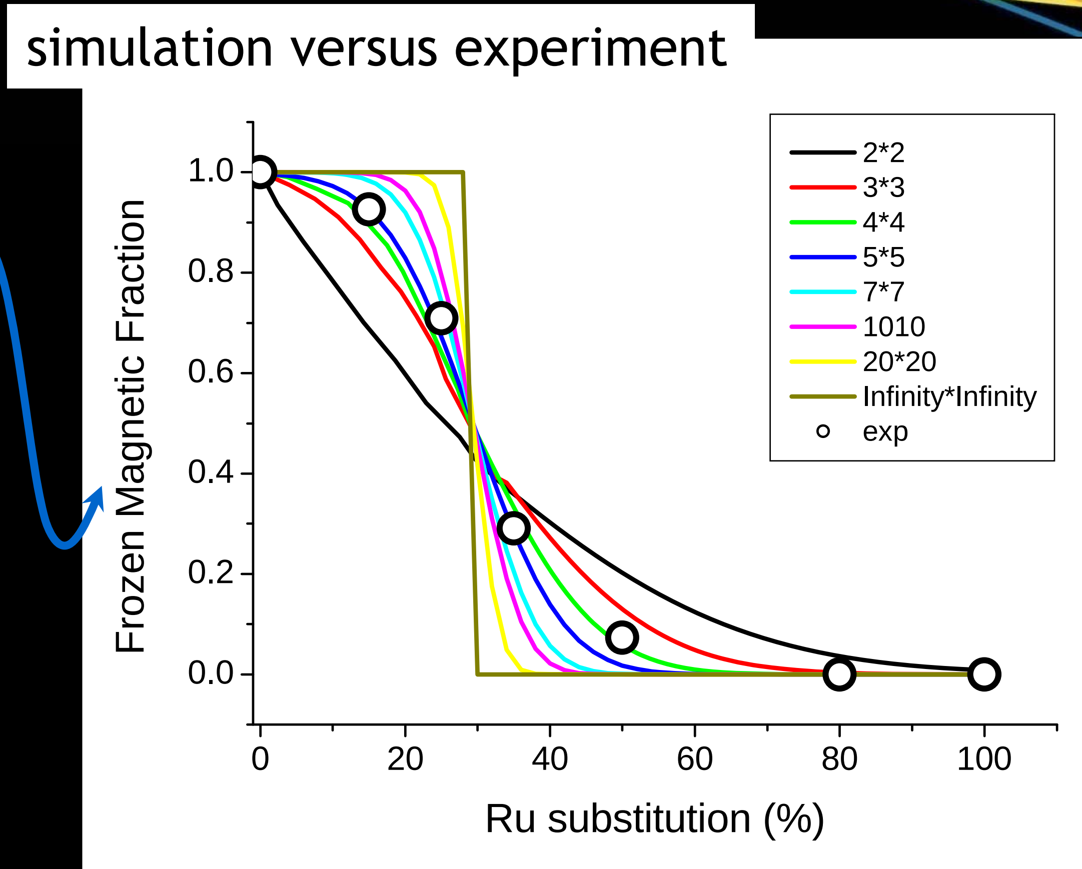

NMR Intensity
T



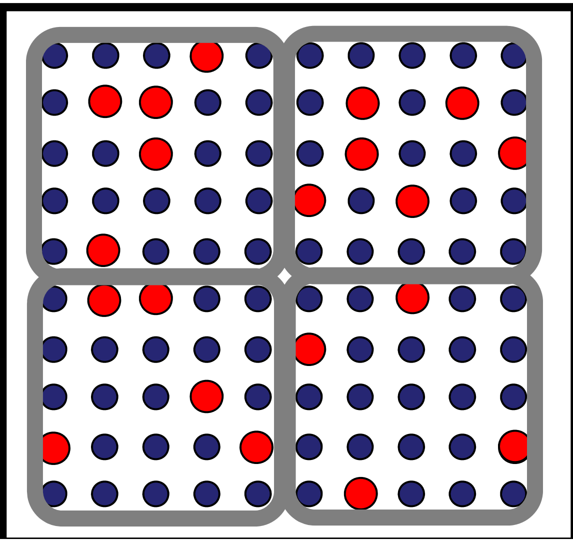

Ba(Fe1-xRux)2As2
Temperature (K)
Ru doping content (%)
SDW
SC
0
20
40
60
80
100
120
140
160
0
10
20
30
40
50
60
70


NMR Intens
T

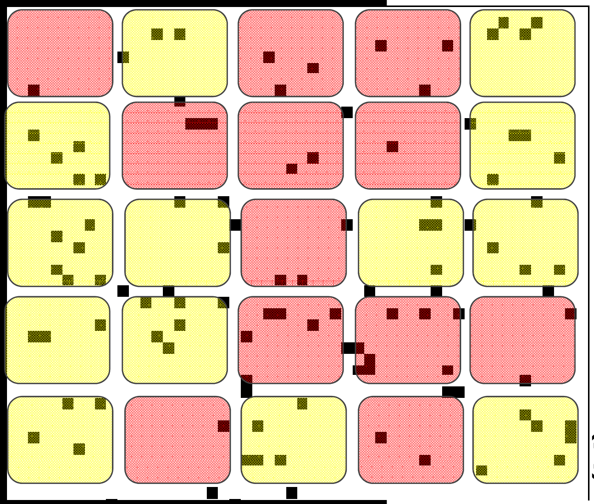


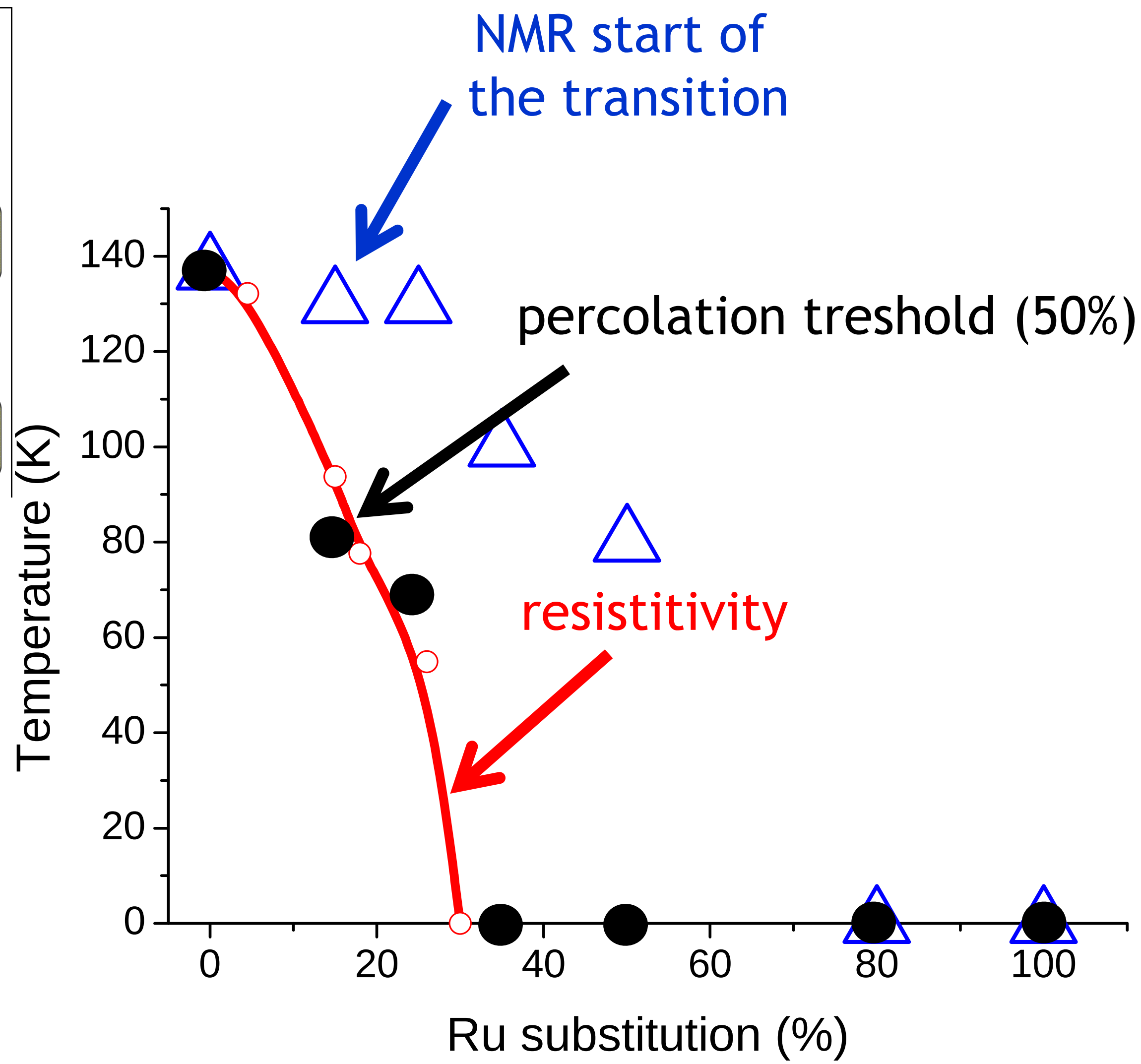


Local averaging of Ru effect
over 5*5 cell units



Reconcile macro and local

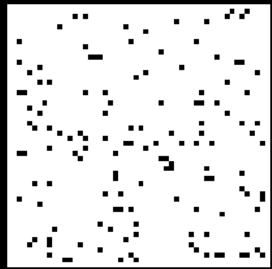




summary

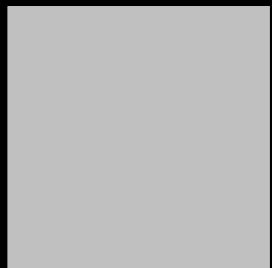
Co doping

Random
Co distribution :

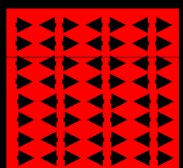


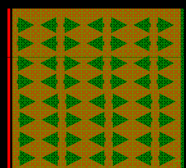
Electron delocalization

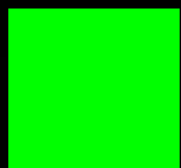
Homogeneous
electronic state



Homogeneous
low temperature
phases

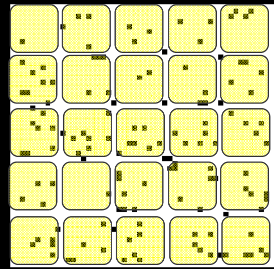






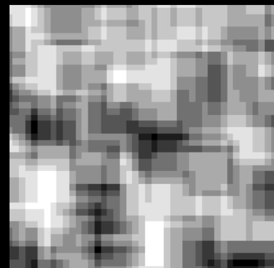
Ru doping

Random
Ru distribution :



Local chemical pressure
averaged over 1 nm

Inhomogeneous
electronic state



Inhomogeneous
low temperature
phases on 1 nm scale