Diffuse scattering

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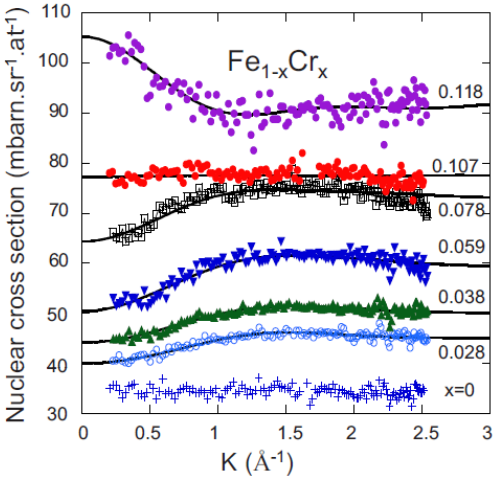
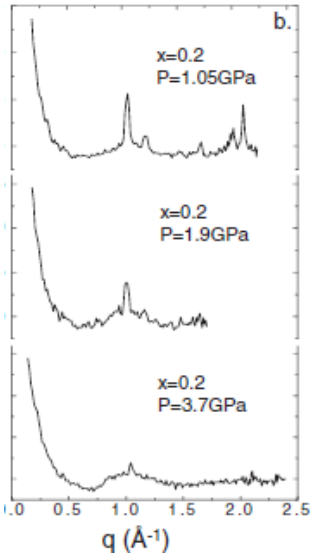
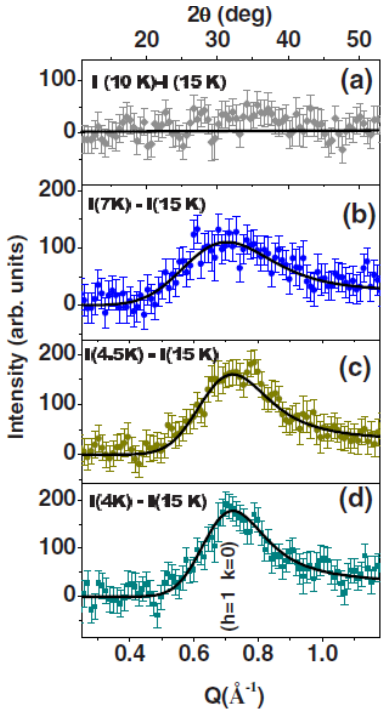
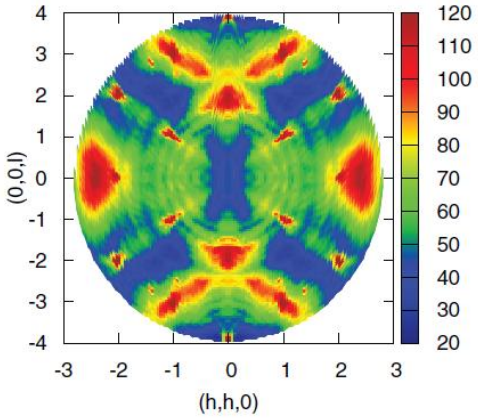
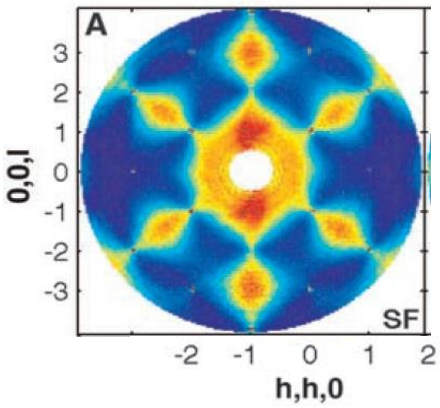
through a few examples











Outline

- General features

- Nuclear diffuse scattering:

local chemical order and/or static displacements

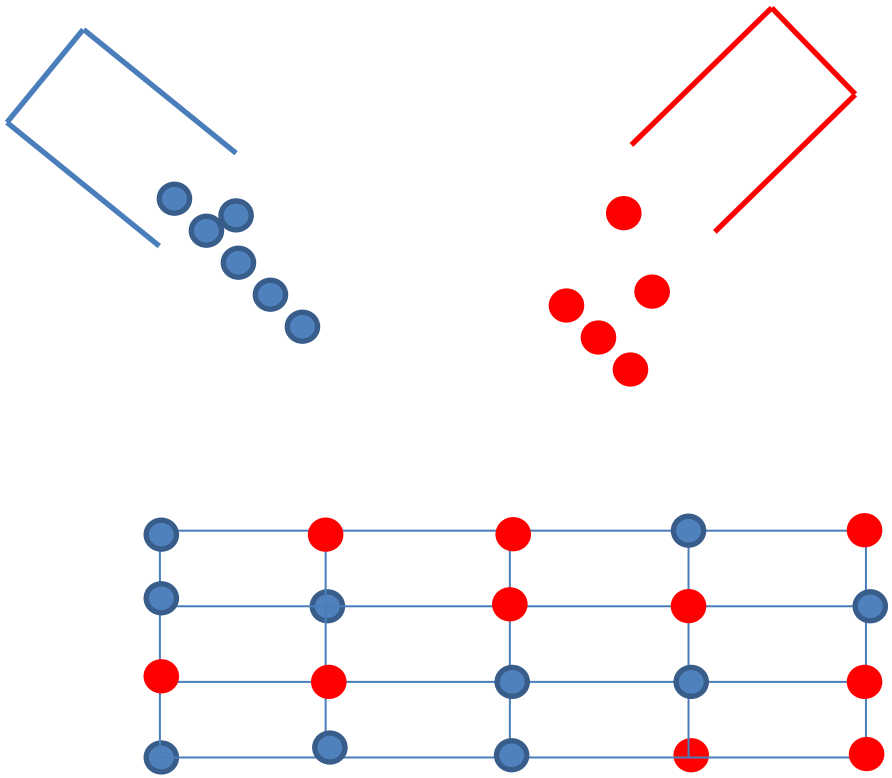
- Magnetic diffuse scattering:

local magnetic order

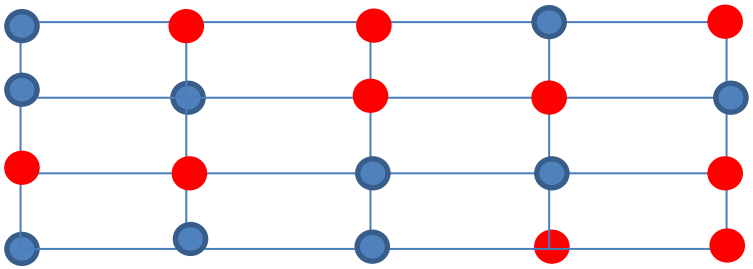
General features

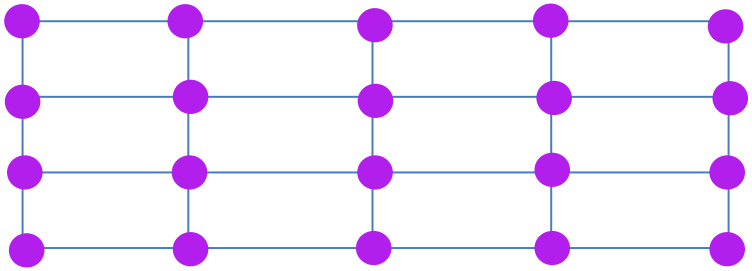
- A simple example
- How to describe the diffuse scattering?
- Several lengthscales
- NO time scale: what does the spectrometer measure**?**

A simple example



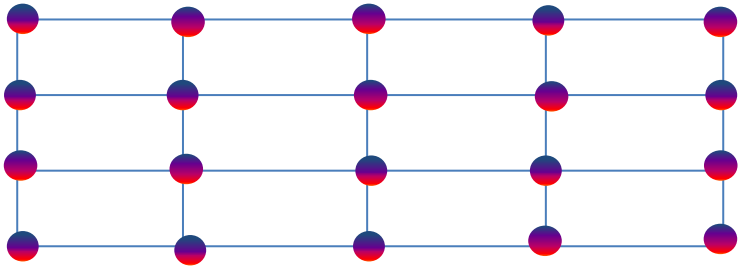
A simple example





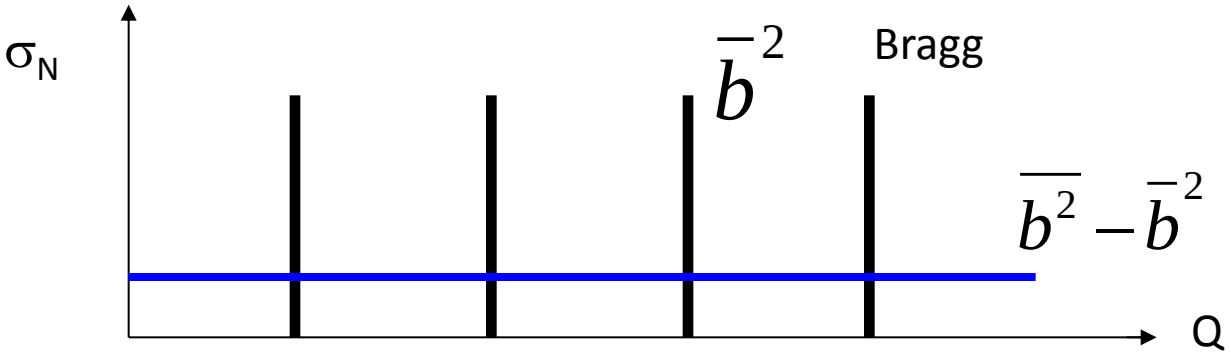
$\overline{b}^2$

Bragg



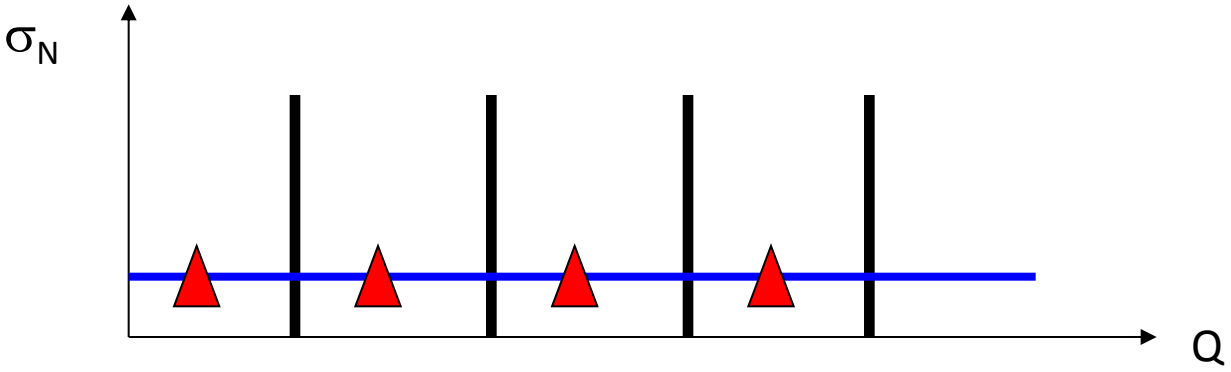
$\overline{b^2} - \overline{b}^2$

Diffuse scattering

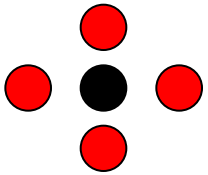


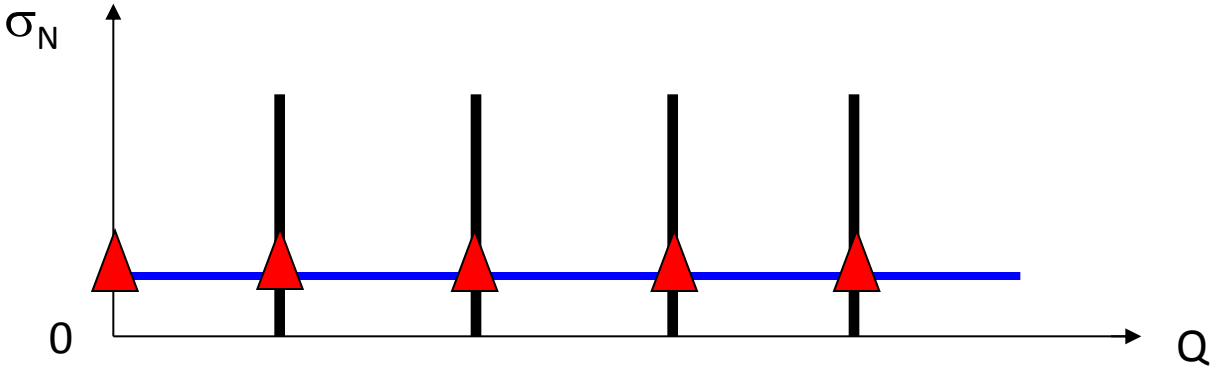
Laue background

A, B random

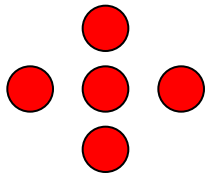


Towards ordering





Towards clustering



How to describe the diffuse scattering ?

in real space:

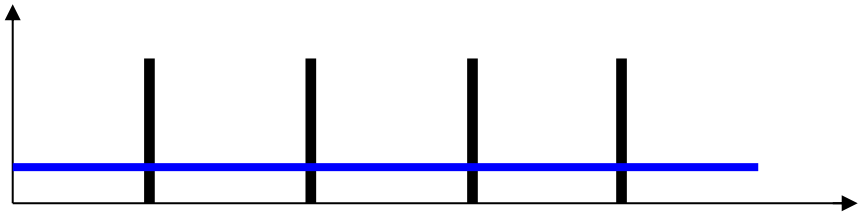
a deviation from the random/ordered state

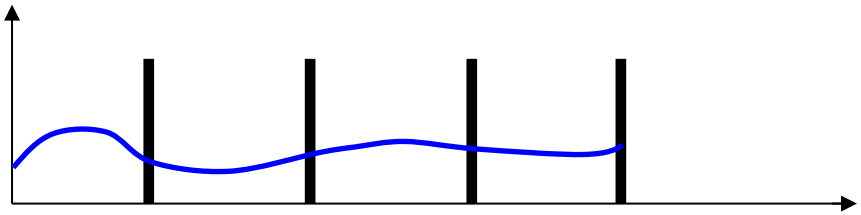
in reciprocal space

a modulation between the Bragg peaks

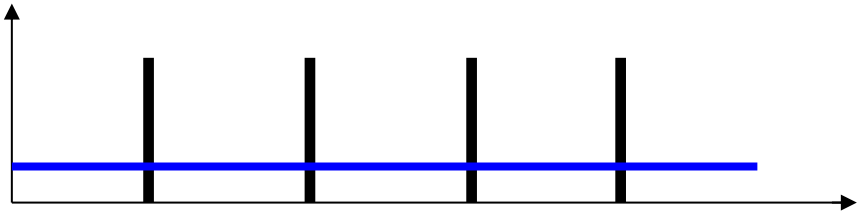
2 options (+1)

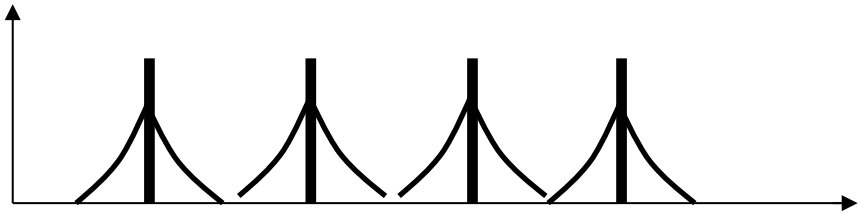
- from the random state





- from the ordered state





How to describe the diffuse scattering ?

- ***from the disordered state***

Short range order parameters

- Deviation from random distribution
- Local lattice distortions
- Pair distribution function (pdf)
- Local magnetic perturbations

- ***from the ordered state***

- Correlation lengths
- Critical behaviours

From local constraints

- entropy
- Mapping and gauge fields

No obvious « a priori » description!

choice of the model depends on the context

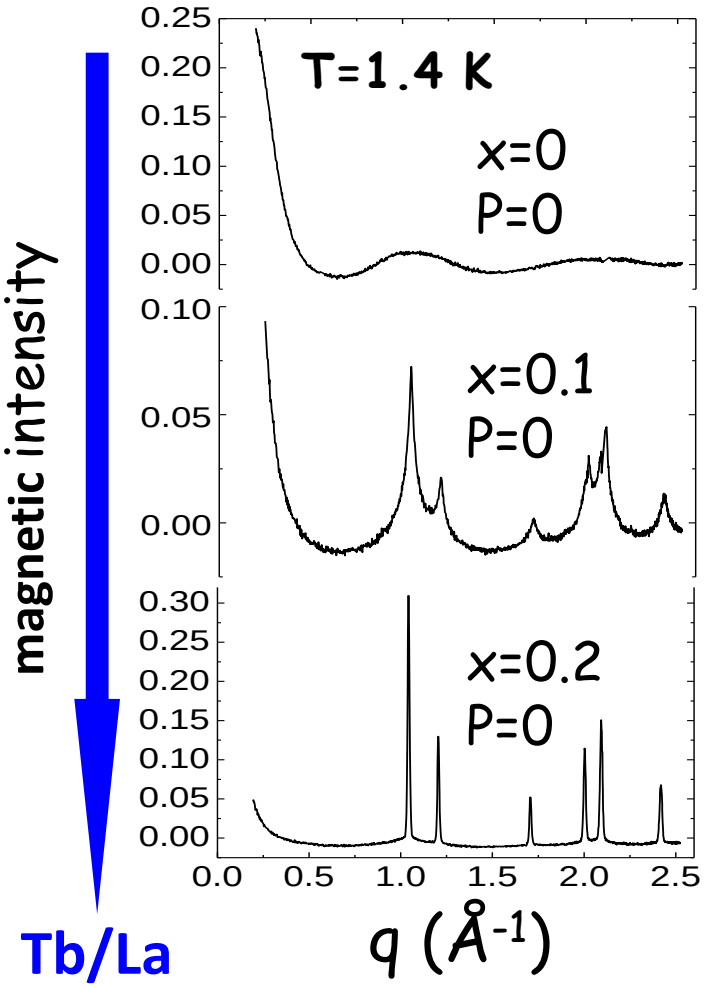
Measure in absolute scale

To decide if the model is realistic or not

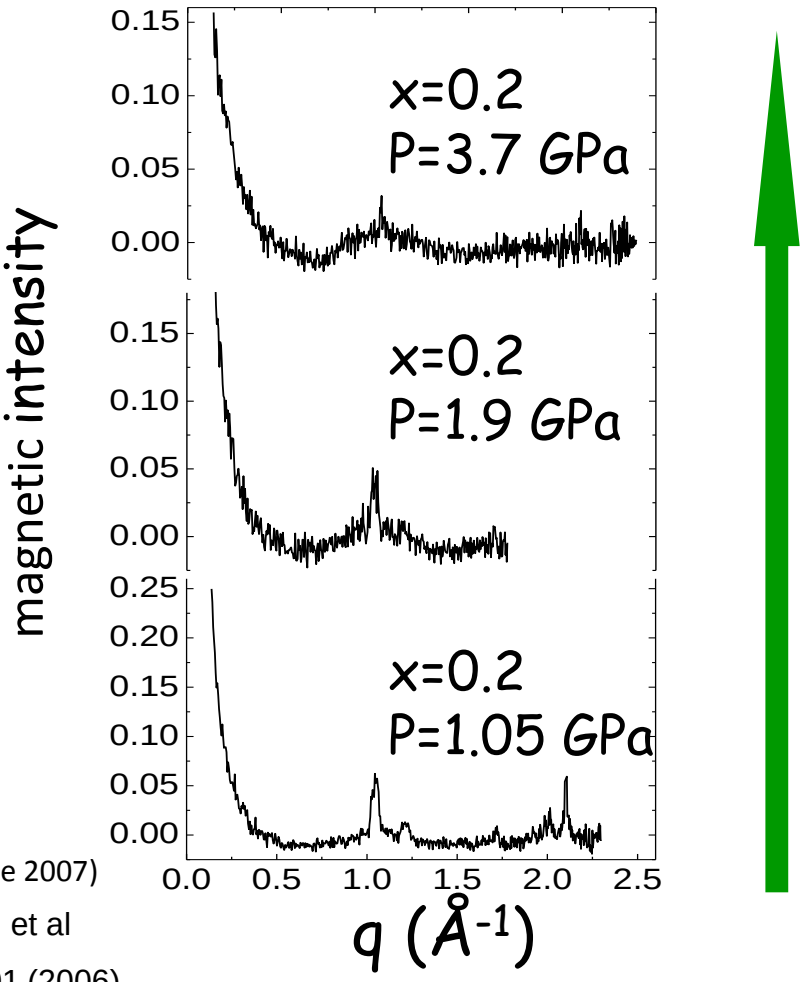
$(Tb_{1-x}La_x)_2Mo_2O_7$

Expanding the lattice

Chemical Pressure



Applied Pressure



A. Apetrei (thèse 2007)

A.Apetrei, I. M. et al

PRL **97**, 206401 (2006)

LRO induced by Tb/La dilution

LRO destroyed by pressure

Changing the band structure changes the magnetic frustration (sign of Mo-Mo interactions)

From the random state

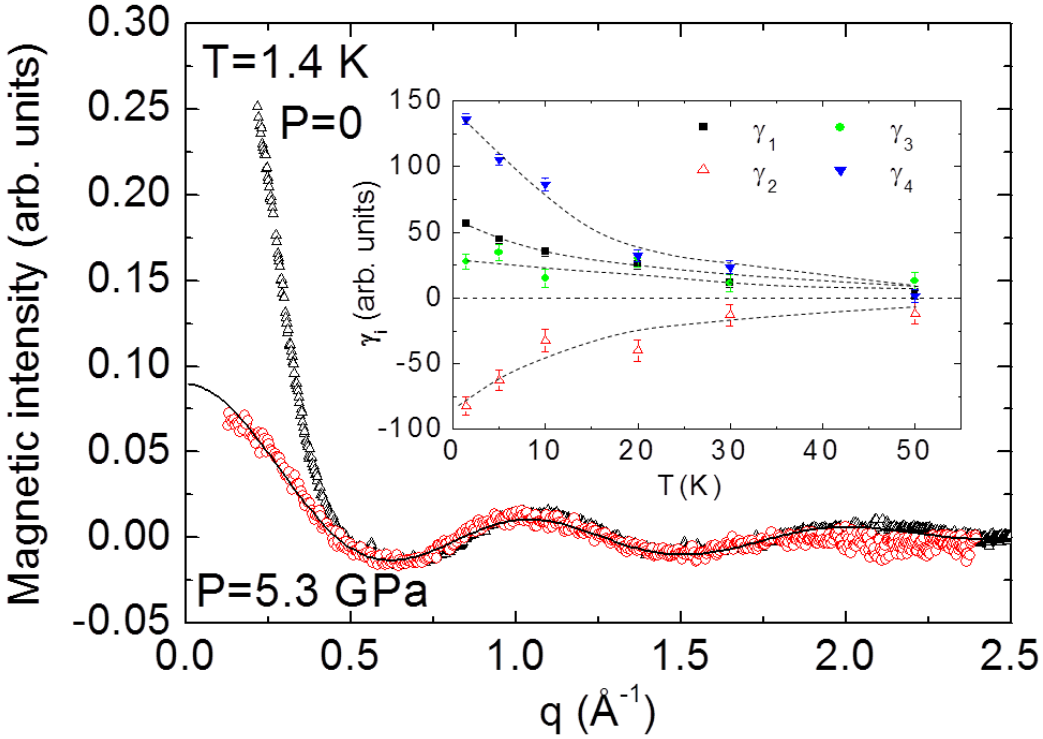
Look at the landscape!

RANDOM state
(paramagnetic/disordered)

SRO parameters

Statistical information on the first neighbour shells
(occupation/ relative spin orientations)

$Tb_2Mo_2O_7$ spin glass



A.Apetrei, I. M. et al

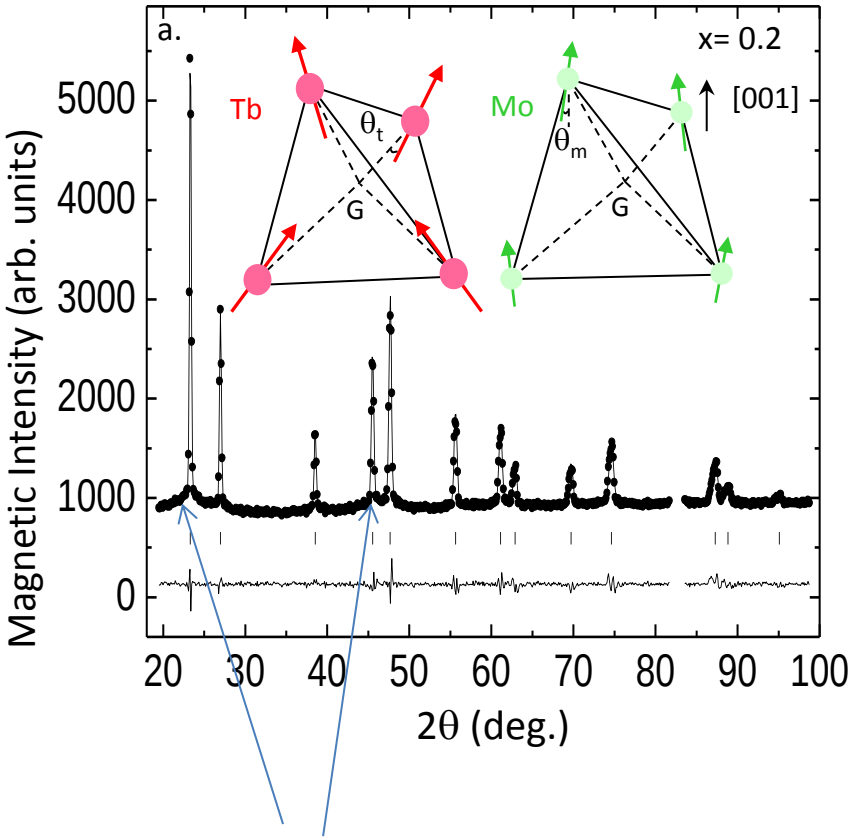
PRL **97**, 206401 (2006)

From the ordered state

model of the ordered state
(refined crystal/magnetic structure)

correlation length

Information on the mesoscopic structure

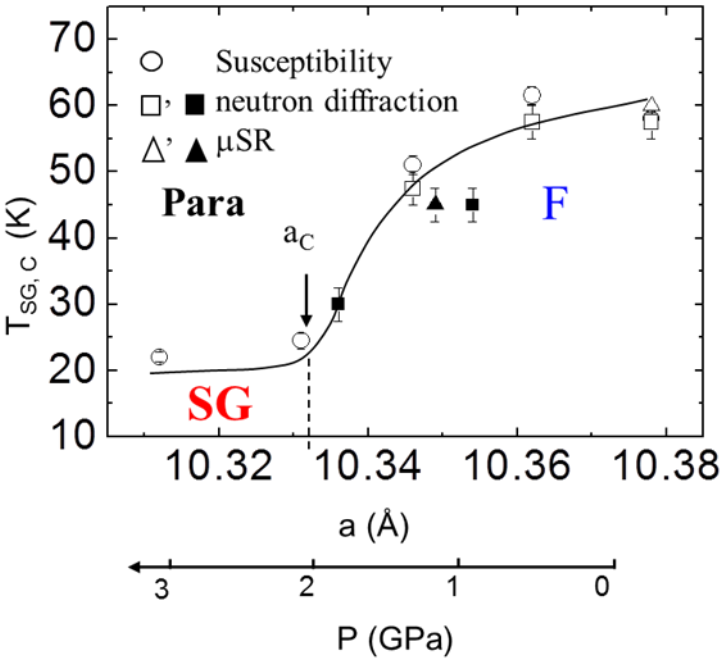


Diffuse scattering

The tricky cases

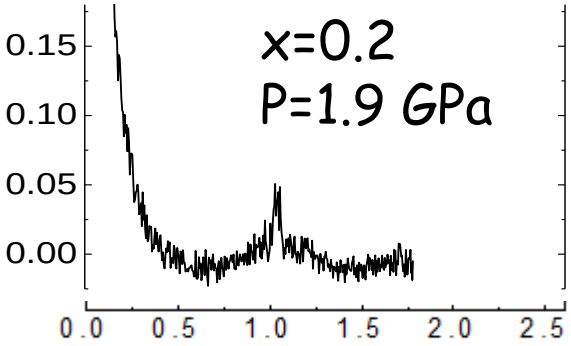
Quantum critical point

Induced by pressure or concentration

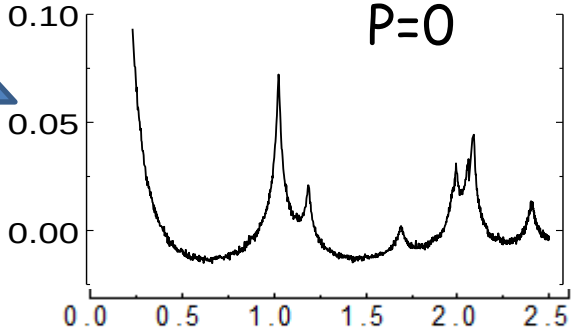


$(Tb_{1-x}La_x)_2Mo_2O_7$

Phase separation ?



mesoscopic structure ?



q (Å^{-1})

Several lengthscales

Type	Typical lengthscale	Example
local order Near neighbours	A few unit cells 1-10 Å	Binary alloys spin glasses
Mesoscopic structures	A few tenths of unit cells 10-100 Å	Critical phenomena
Long Range Order	Limited by exp. resolution > 500-1000 Å	Bragg

NO Time scale!

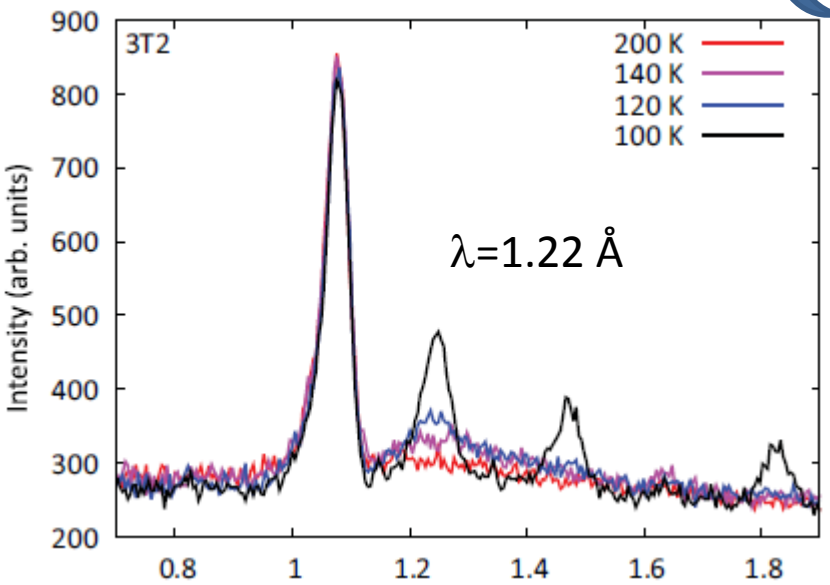
Energy integration (diffraction)

instantaneous correlations!

$$\int_{-\lambda_i}^{\infty} S(q,\omega)d\omega$$

Question :

What does the spectrometer measure ?



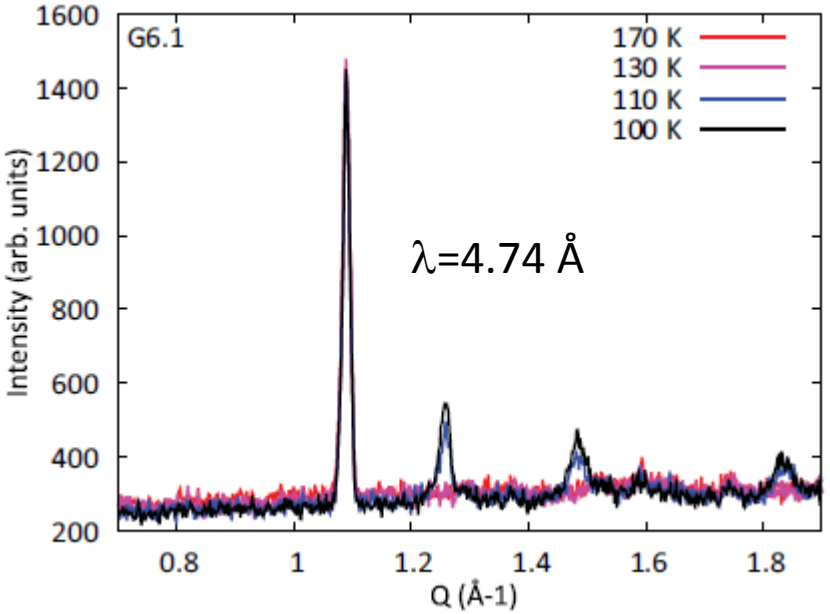


FIG. 7. (Color online) Observed and FULLPROF calculated NPD patterns at several temperatures. Above T_N a strong diffuse scattering is observed on the patterns recorded on 3T2 spectrometer (top) with $\lambda = 1.225$ Å. This scattering is not visible on the G6.1 patterns (bottom) for which $\lambda = 4.74$ Å.

PHYSICAL REVIEW B 84, 054455 (2011)

Frustration-driven magnetic order in hexagonal $InMnO_3$

X. Fabrèges,[1,2] I. Mirebeau,[1] S. Petit,[1] P. Bonville,[3] and A. A. Belik[4]

Local chemical order

- Deviation from random distribution
- Short range order parameters
- Nuclear Diffuse scattering
- Pair potentials
- **Example 1**: (single crystal) : **TiC vacancies**
- **Example 2** : polycrystal: **Fe-Cr alloys**
- How improve the data quality?
- How improve the data treatment ?

  The modern tool : pdf

Local chemical order

Alloy: Ac_A Bc_B

$C_A+C_B=1$

Long Range Order

Order parameter S

n: ratio of A atoms « well placed »

$c_A<n<1$ $0<S<1$

$$S = \frac{n - c_A}{c_B}$$

Surstructure

I Bragg $\propto S^2$

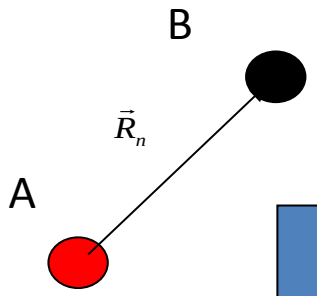
Short Range Order

All sites are statistically equivalents

$P_A=c_A$; $P_B=c_B$

S=0

Conditional Probability P_{AB}



$$\alpha(\vec{R}_n) = 1 - \frac{P_{AB}(\vec{R}_n)}{c_B}$$

SRO parameters α_n (Cowley-Warren)

Local Order parameters

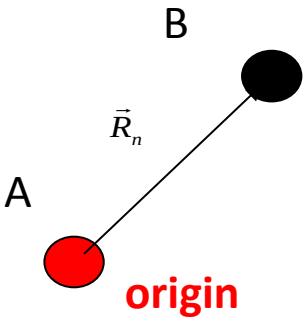
SRO parameters α_n (Cowley-Warren)

Alloy Ac_A Bc_B

$C_A+C_B=1$

$c_A < 0.5$

Conditional Probability P_{AB}



$$\alpha(\vec{R}_n) = 1 - \frac{P_{AB}(\vec{R}_n)}{c_B}$$

$$-\frac{c_A}{c_B} < \alpha < 1$$

$P_{AB}(\vec{R}_n) > c_B$	$\alpha(\vec{R}_n) < 0$	order
$P_{AB}(\vec{R}_n) < c_B$	$\alpha(\vec{R}_n) > 0$	clustering
$P_{AB}(\vec{R}_n) = c_B$	$\alpha(\vec{R}_n) = 0$	Random

$$\alpha(0) = 1$$

Calibration of the nuclear cross section
(checks the consistency of the measurement)

$$\alpha(\vec{R}_n) \to 0; n \to \infty$$

Fitting constraints

$$1 + \sum_{i=1}^{\infty} N_i \alpha_i = 0$$

Sum Rule (virtual) :
Grand Canonical space

Chemical order parameters and nuclear diffuse scattering

Cowley-Warren model

Alloy : A B

A: c_A

B : c_B

Cowley Phys.Rev. 77,669, (1950)
Warren X ray diffraction (1968)

$$I(\vec{Q}) = N(c_A b_A + c_B b_B)^2 . \sum_n \exp(i\vec{Q}.\vec{R}_n) + N(b_A - b_B)^2 . \sum_n < \sigma_0 \sigma_n > \exp(i\vec{Q}.\vec{R}_n)$$

Bragg: average lattice

Diffuse scattering : deviation

Diffuse cross section from chemical SRO

$$\frac{d\sigma_N}{d\Omega} = c_A c_B (b_B - b_A)^2 \sum_n \alpha(\vec{R}_n) \cos(\vec{Q}.\vec{R}_n)$$

Laue background

Périodic Modulation
In reciprocal space

Scattering Vector $\vec{Q} = \frac{2\pi}{\lambda}\vec{s} - \vec{s}_0$

Order parameters and pair potentials

Mean field model

Clapp et Moss Phys. Rev. 142, 418, (1966), et suivants

$$H = \frac{1}{2}\sum_{i,j}[V_{ij}^{AA}\sigma_i^A\sigma_j^A + V_{ij}^{BB}\sigma_i^B\sigma_j^B + V_{ij}^{AB}(\sigma_i^A\sigma_j^B + \sigma_i^A\sigma_j^B)]$$

Effective pair potential

$$V_{ij} = V_{ij}^{AB} - \frac{1}{2}(V_{ij}^{AA} + V_{ij}^{BB})$$

$V_{ij} < 0$ Order, AF

$V_{ij} > 0$ Segregation, F

Hamiltonien Ising

$$H = -\frac{1}{4}\sum_{i,j} V_{ij}\overline{\sigma}_i\overline{\sigma}_j$$

$$\alpha(\vec{Q},T) = \frac{C}{1 + \frac{2c_A c_B V(\vec{Q})}{kT}}$$

Diffuse cross section

⇩

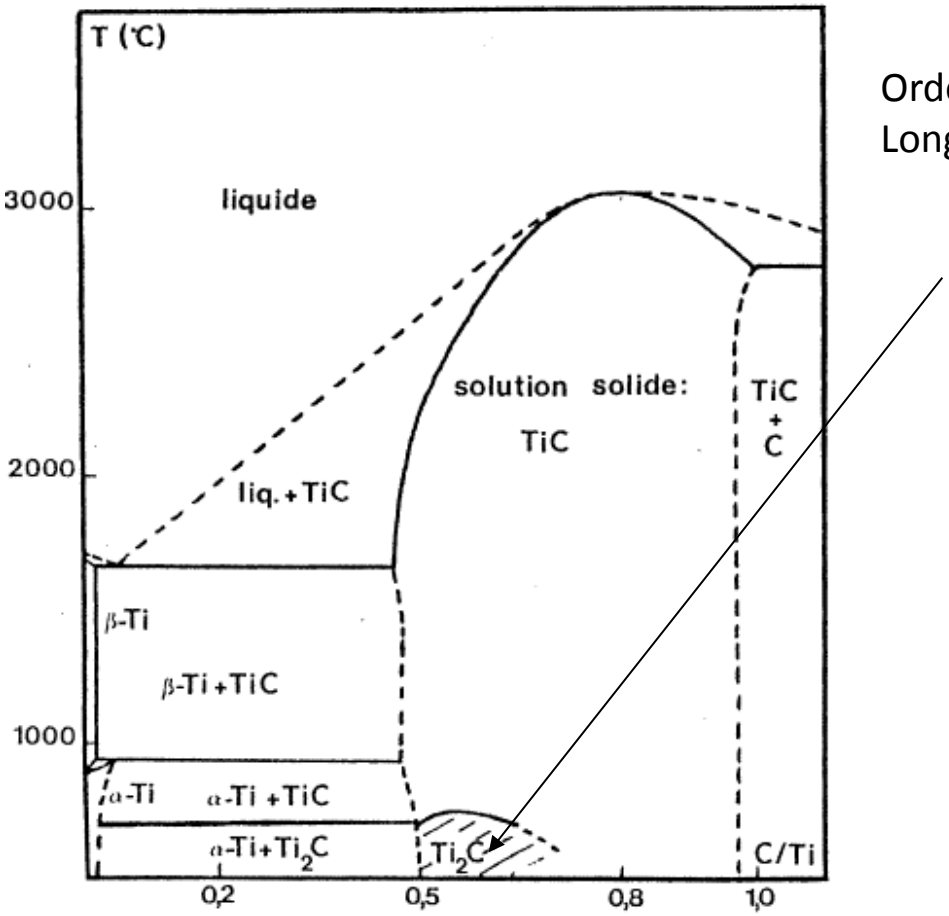
Effective pair potentials (~mev)

⇩

Stability of the phase diagrams

Local order of carbon vacancies

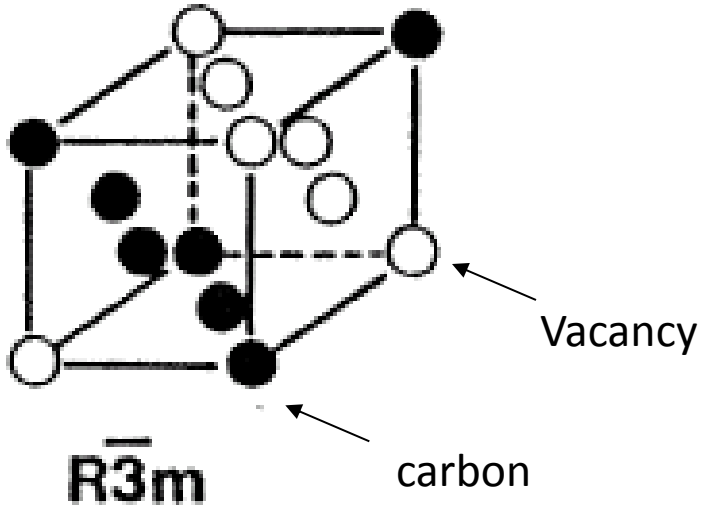
Phase Diagram TiC_x



Ordered Phase Ti_2C

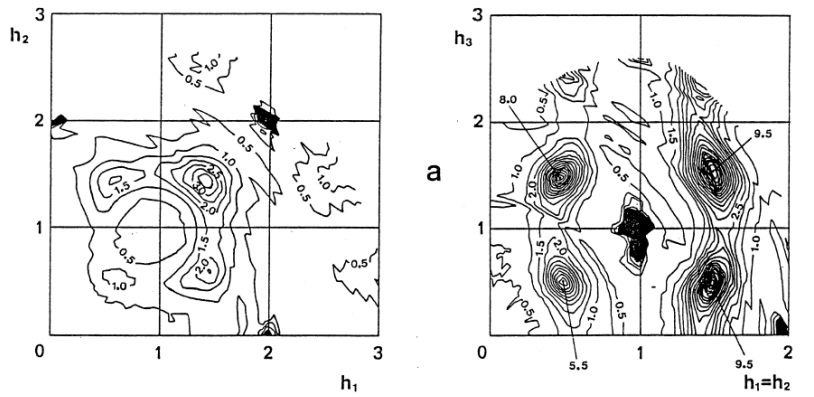
Long Range Order of carbon vacancies in a fcc lattice

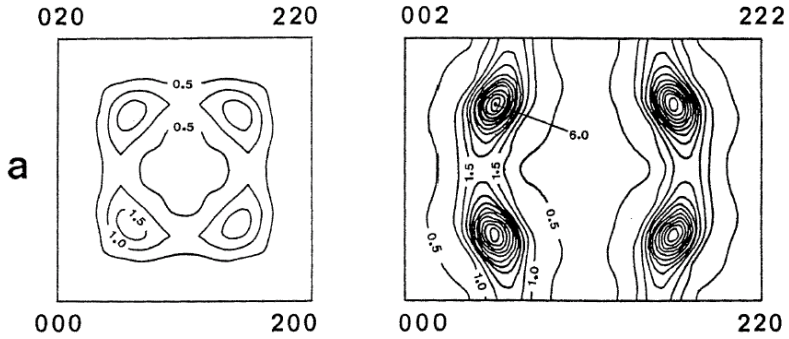
Propagation vector K= ½ ½ ½

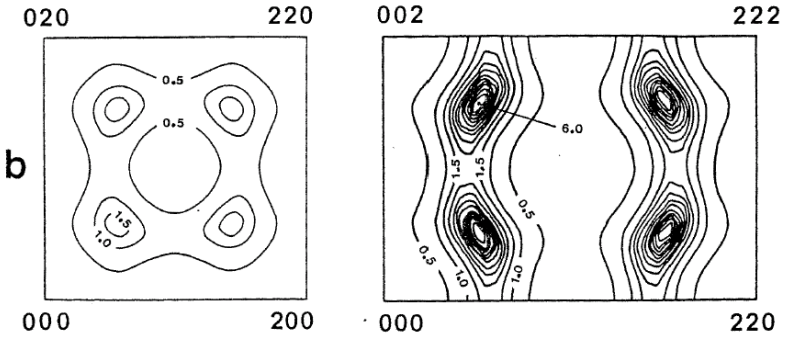


Local Order in solid solution ?

Ordre local order of carbon vacancies in $TiC_{0.64}$







B. Beuneu, R. Caudron (Onera)

T. Priem (thèse 1988)

Intensity measured in situ : T=900 °C

local order + lattice distortions

Maxima at hkl positions ½ ½ ½

~30 parameters

Intensity from **local order**, calculated from the SRO parameters : 20 α

20 SRO parameters

Intensity calculated by the Mean field (Clapp-Moss) model

4 pair potentials (2 main)

V_1=15; V_2=48; V_3=-4; V_4=8 meV

2 potentials

From single crystal to polycrystal

$$< \cos(\vec{Q}.\vec{R}) >= \frac{\sin QR}{QR}$$

$$\alpha(\vec{R}_i) = \alpha_i$$ i^{th} shell of radius R_i

$$\frac{d\sigma_N}{d\Omega} = c_A c_B (b_B - b_A)^2 \sum_i N_i \alpha_i \frac{\sin QR_i}{QR_i}$$

Loss of the periodicity

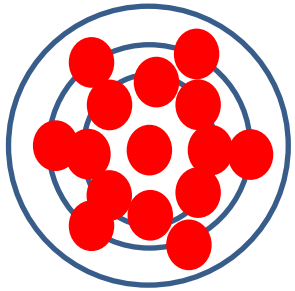
- Shifts of the positions of the diffuse maxima
- Fit of a few α's only

FeCr alloys

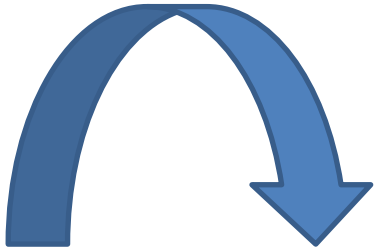
Fe_{1-x}-Cr_x alloys: why are they interesting ?

First and unique example of short range order inversion in a solid solution

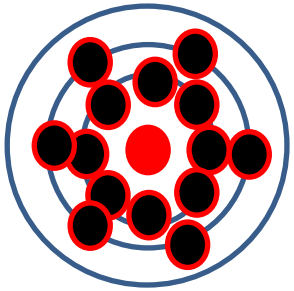
$x > x_c$ clustering



$x \sim x_c$ random



$x < x_c$ ordering

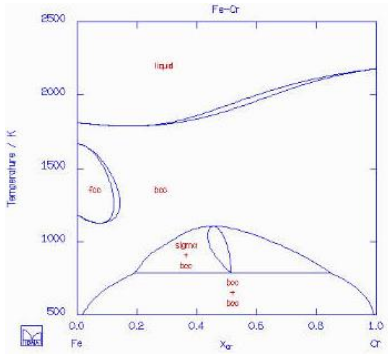


origin:
anomaly of the band structure : local magnetism of Cr

M. Hennion J. Phys. F (1982)

Possible applications in metallurgy

~ 700 papers and 800 citations/year about FeCr

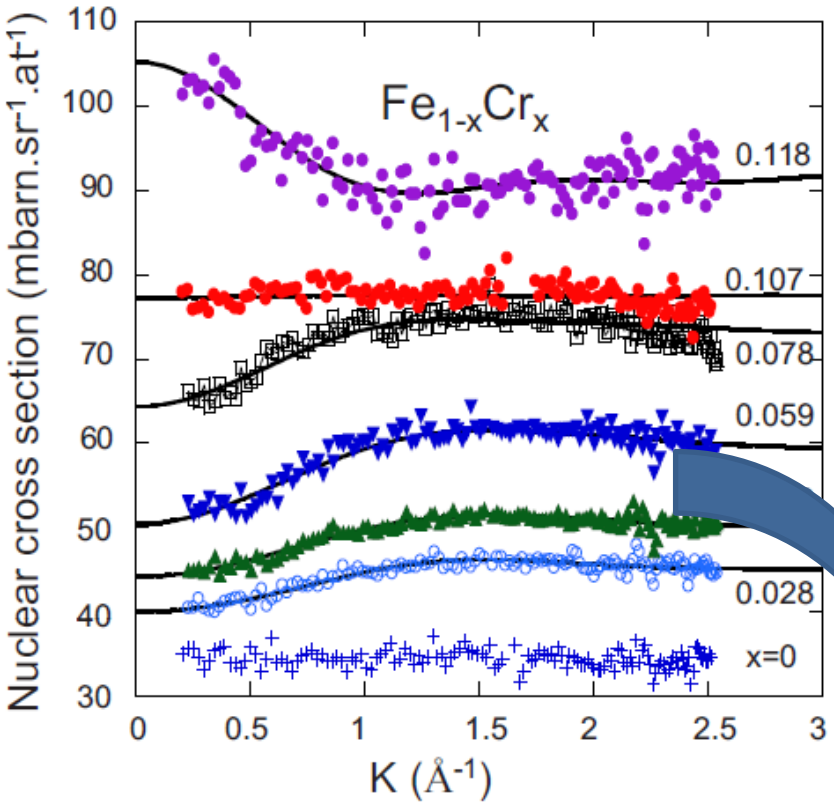


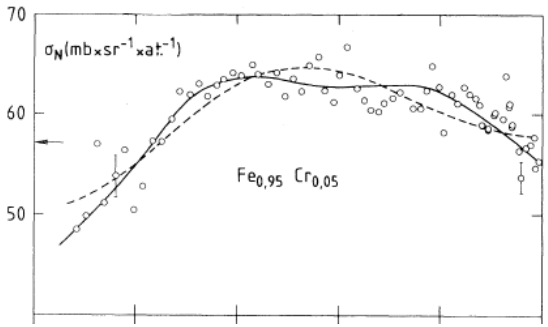
Physical consequences

- Resistivity
- Bulk modulus
- Aging (irradiation)
- Formation energy

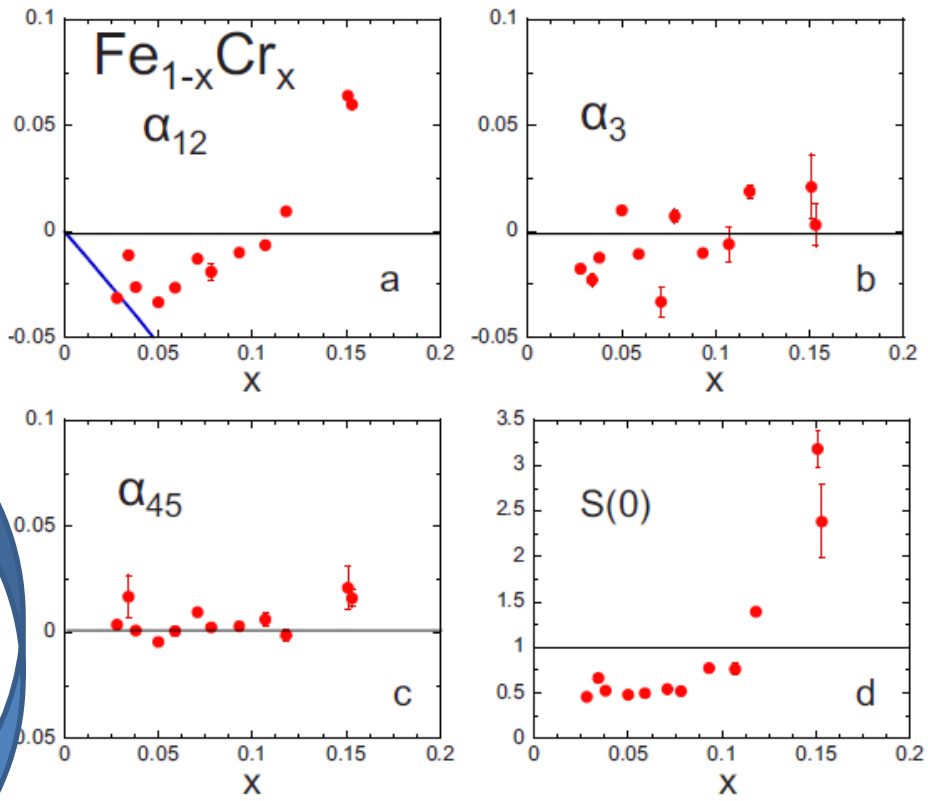
Direct probe : Neutron diffuse scattering

FeCr alloys : Short range order inversion





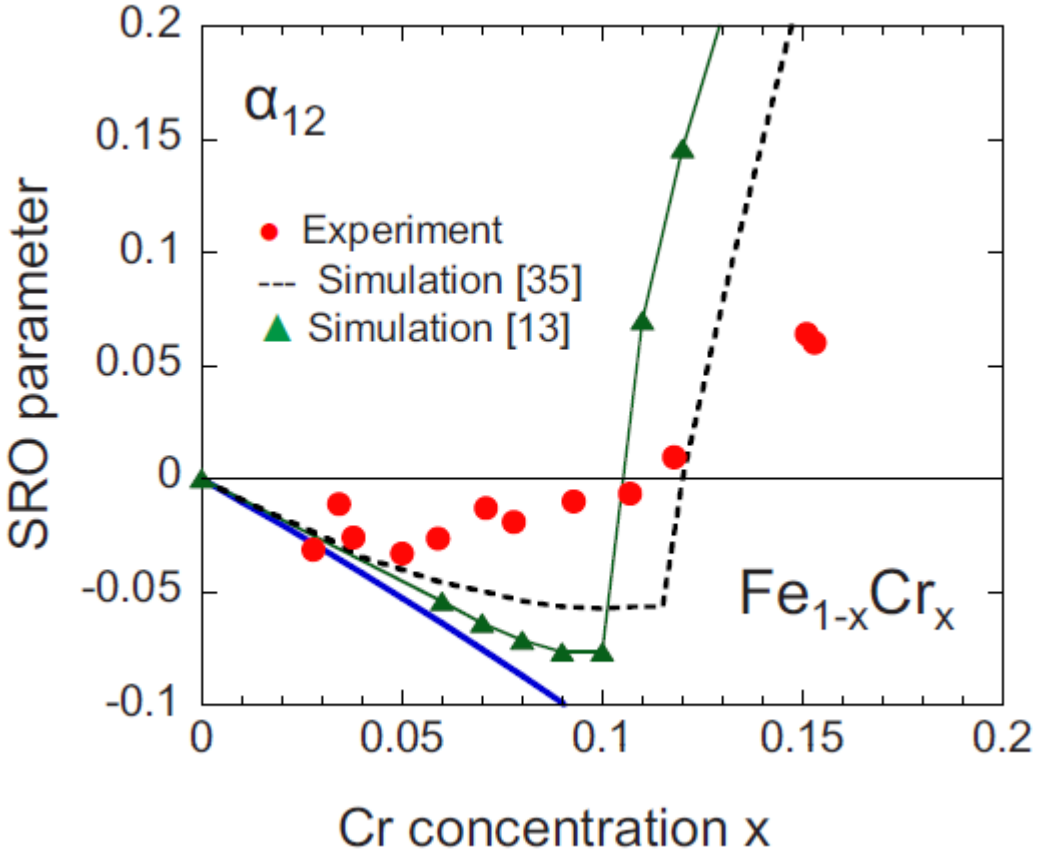
G. Parette, I. M. Phys. Rev. B (2010)

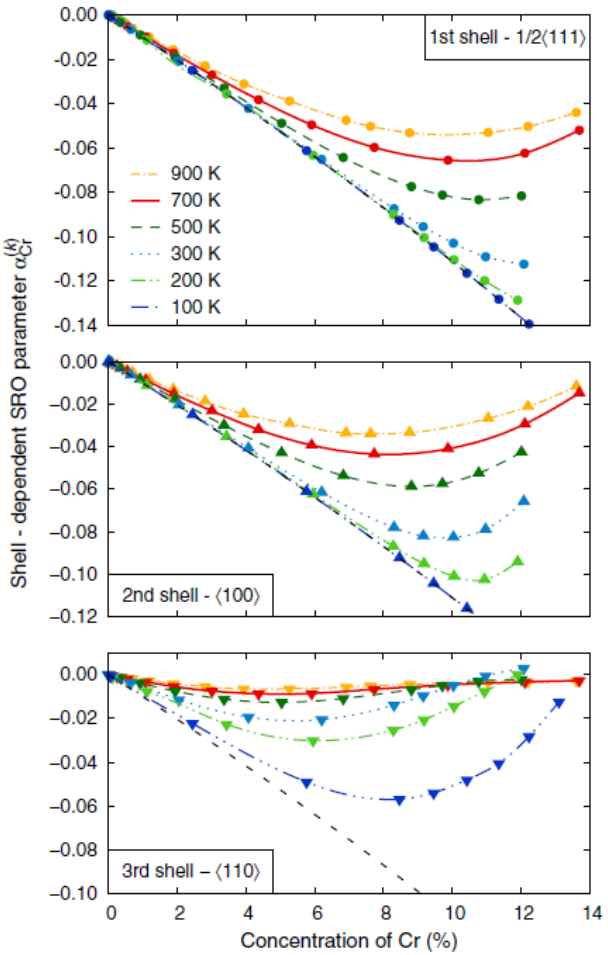


signal/background ratio increased by a factor ~20 with respect to first measurements

IM, M. Hennion, G. Parette, PRL(1984)

$Fe_{1-x}Cr_x$, SRO parameters and Monte-Carlo Sim.



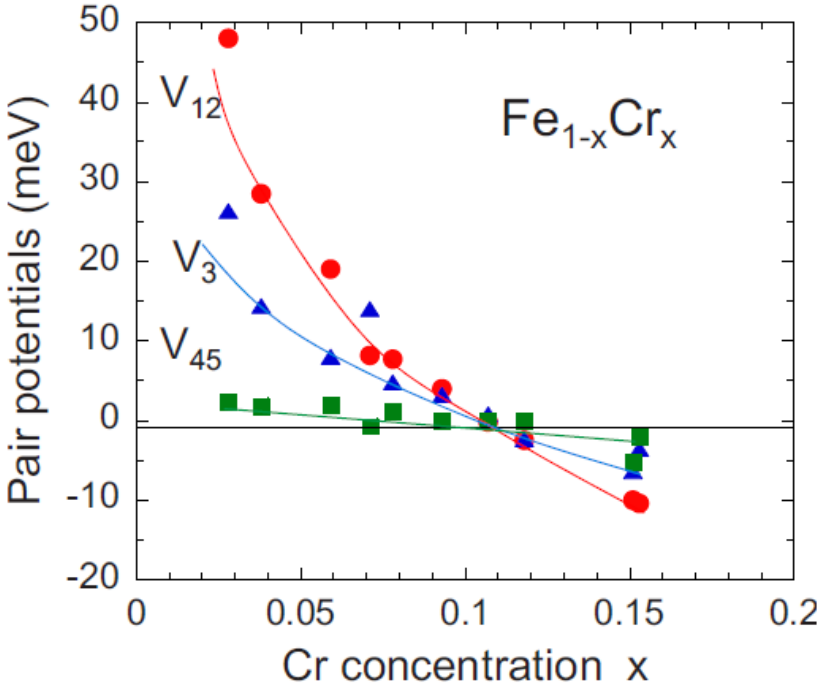


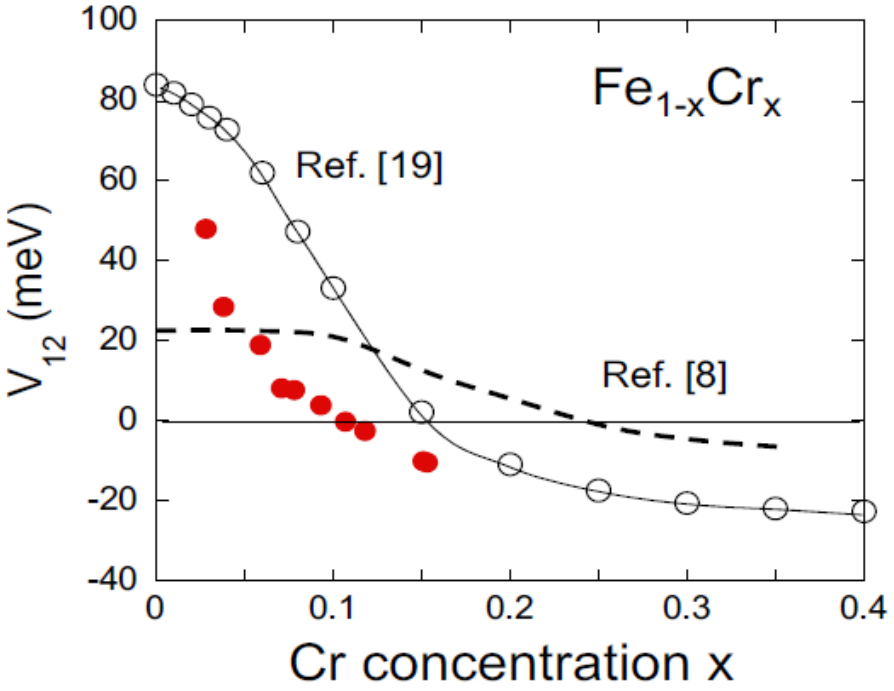
Simulation

A.Caro et al Phys. Rev. Lett. **95**, 075702, (2005).

P. Erhart et al Phys. Rev B(2008)

$Fe_{1-x}Cr_x$, pair potentials and ab initio models





Ab initio calculations:

[8] M. Hennion J. Phys. F (1983)
[19] Ruban et al Phys. Rev . B (2008)

How to improve the data quality?

The secrets:

- Decrease environmental background

Vacuum chamber..

- Take care of all corrections

•Background (Cd and empty sample holder)
•transmission
• angle dependent absorption
• multiple scattering
•Detector efficiency

- Calibrate the cross section in absolute scale

Vanadium sample (Corrected)

- Think about possible artefacts
- find the suitable conditions

- diffuse Magnetic scattering?
  play with H and (q, H) angle, polarized neutrons..
- inelastic (play with T)
- Thermodynamical conditions (quench, in situ..)

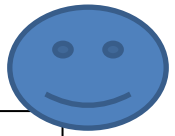
How to improve the data treatment ? The pdf

Pair Distribution Function (for nuclear scattering)

See P. Bordet , JDN15

Measured: from the **TOTAL** powder cross section S(Q) , corrected and normalized by $\langle b \rangle^2$

$$G(r) = 4\pi r[\rho(r) - \rho_0] = \frac{2}{\pi}\int_0^\infty Q[S(Q) - 1]\,\sin(Qr)\,\mathrm{d}Q$$



Needs
High statistics
and
large Q_{max}

Calculated: from a structural model

$$G_c(r) = \frac{1}{r}\sum_i\sum_j\left[\frac{b_i b_j}{\langle b\rangle^2}\delta(r - r_{ij})\right] - 4\pi r\rho_0$$

Peaks of G(r)
- position: interatomic distances r_{ij}
- intensity : stucture factor $b_i b_j$
- width : r_{ij} distribution, Debye-Waller, occupation disorder

local magnetic order

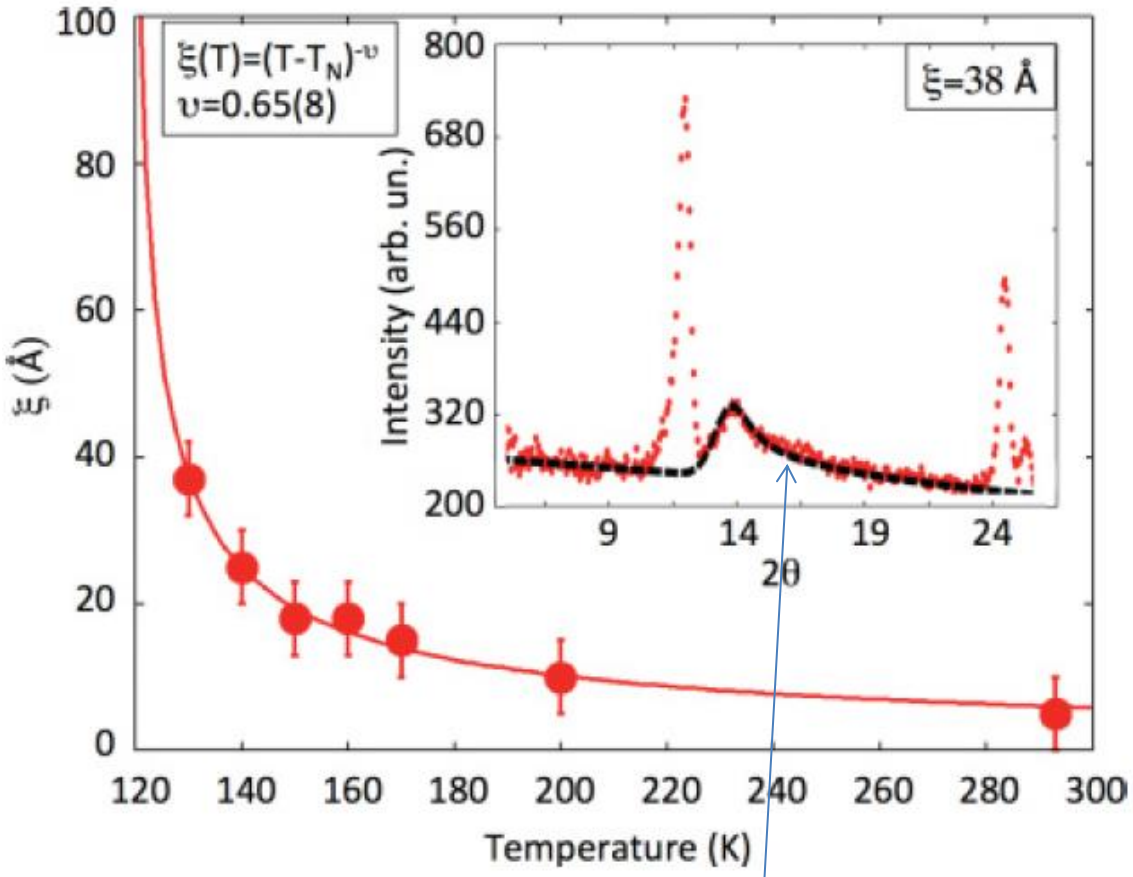
- Diffuse scattering and …
  - magnetic fluctuations : ***above*** T_c
  - spin waves : ***below*** T_c
  - critical behaviour: ***around*** T_c
- Choose the right Q-scale
- Diffuse scattering in spin ices

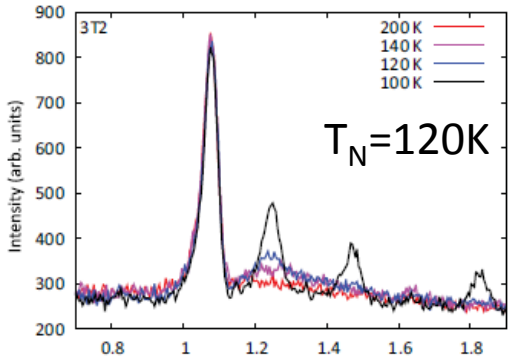
local constraints

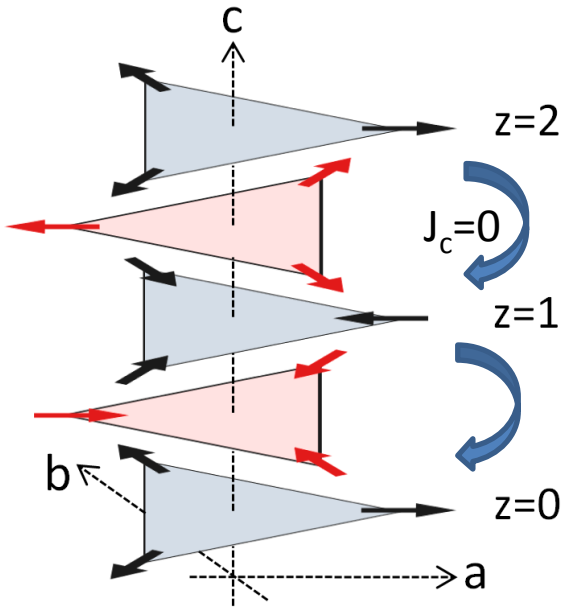
Diffuse scattering and magnetic fluctuations : $T>T_C$

2D fluctuations above T_N in $InMnO_3$

$T<T_N$ magnetic order with K=(0 0 1/2)



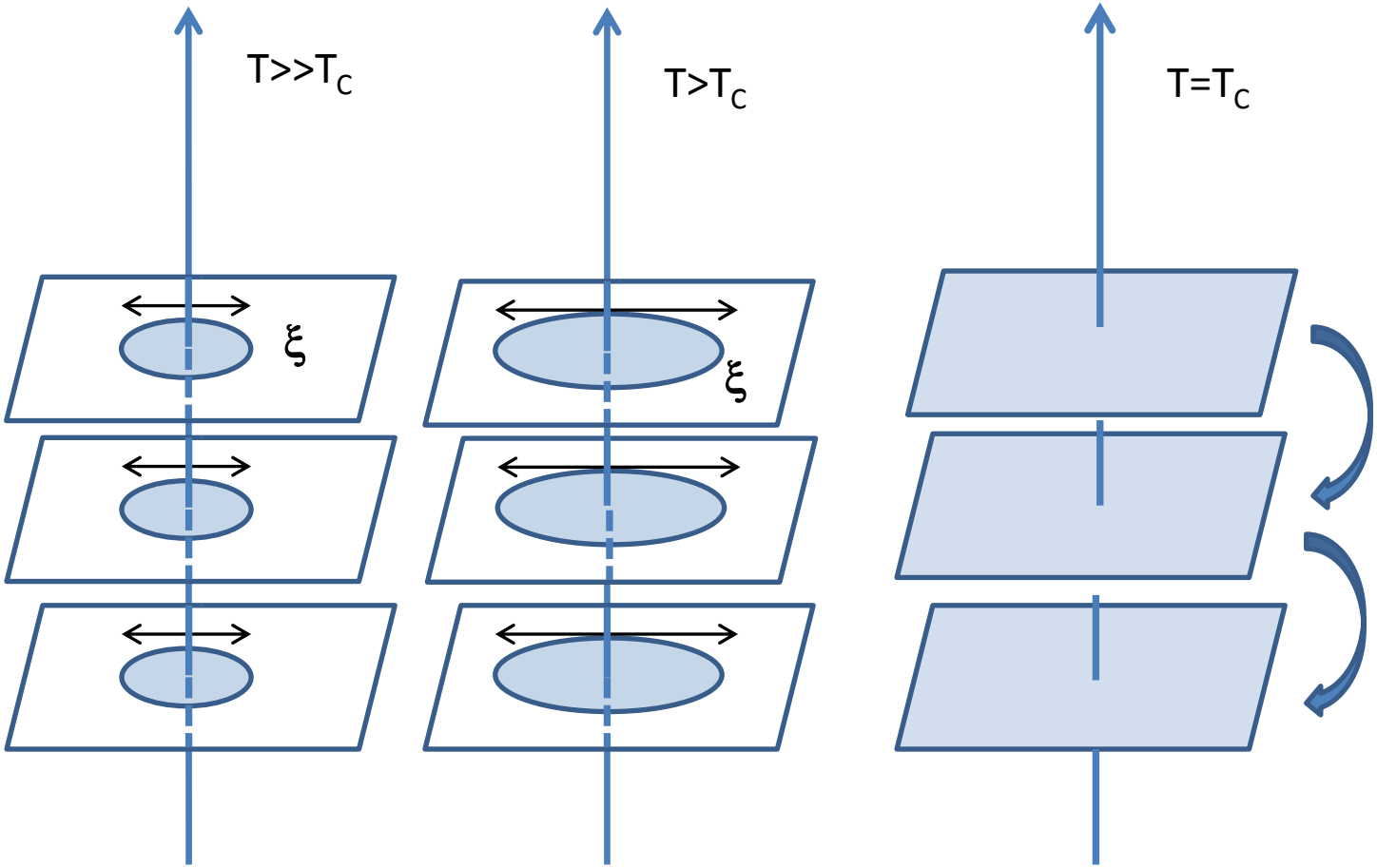




X. Fabrèges et al Phys. Rev. B (2011)

$T>T_N$
Fit by a 2d Warren function
Phys.Rev (1941)

From 2D to 3D order

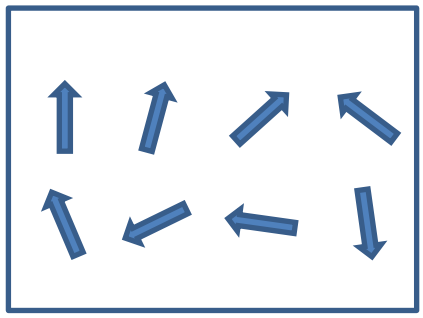


Divergence of ξ
associated with 3d order
(coupling between the planes)

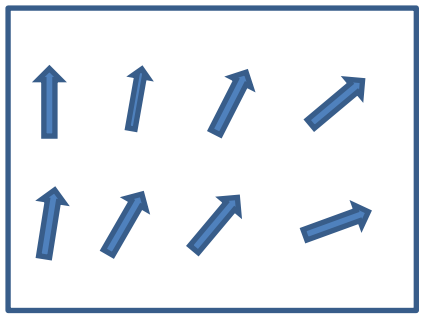
Collapse of the 2D diffuse scattering
and onset of Bragg peaks

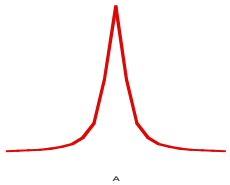
Diffuse scattering and critical behaviour : $T \sim T_C$

How diffuse scattering collapses on Bragg peaks: the scaling laws

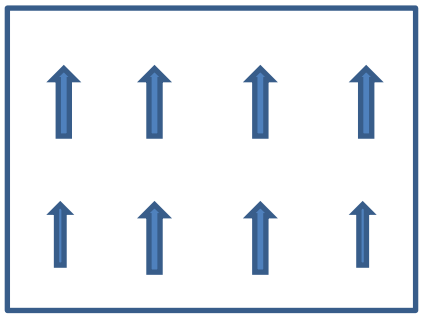


$T >> T_C$





$T \sim T_C$



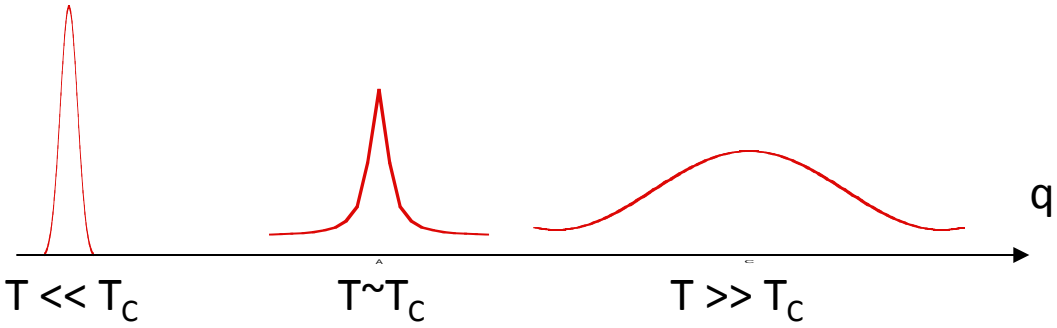
$T << T_C$

Towards a transition

Chemical : transition to a superstructure

Magnetic : Ferro or AF transition

Towards a critical point at T_C



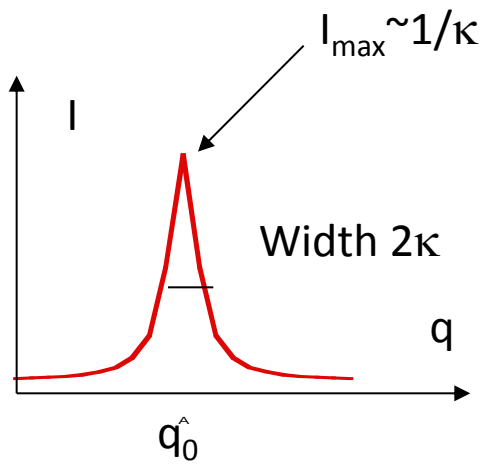
$$< \vec{S}_0 \vec{S}_r > \sim e^{-\kappa R} \Rightarrow I(q) = A \frac{\kappa}{\kappa^2 + (q - q_0)^2}$$

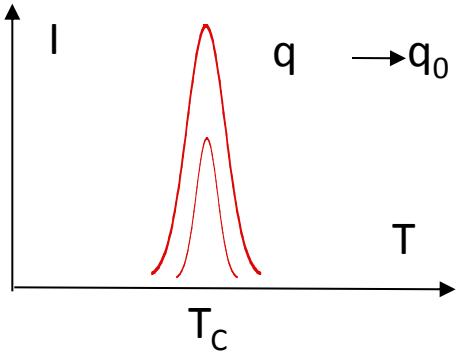
$$A = A(T)$$

$$\kappa = \frac{1}{\xi} \sim \left(\frac{T - T_C}{T_C}\right)^{\nu}$$

ξ: correlation length

$$T \Rightarrow T_C \quad \kappa \Rightarrow 0 \quad \xi \Rightarrow \infty$$

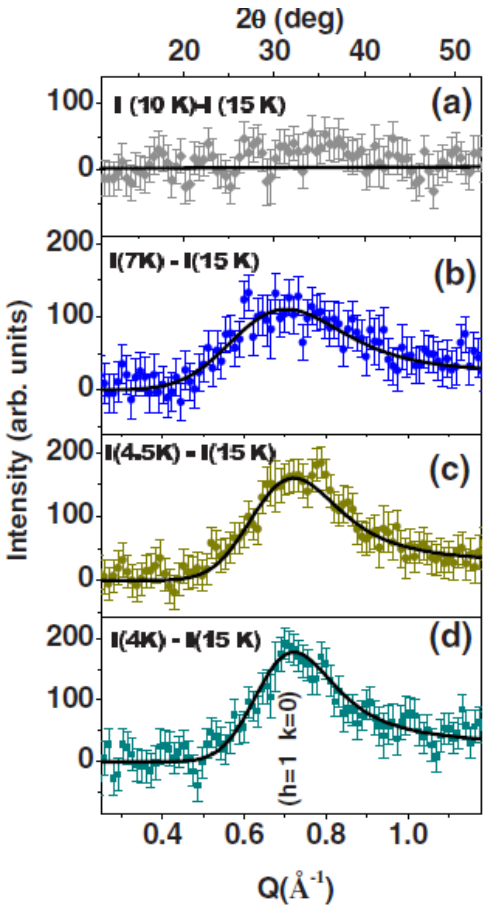




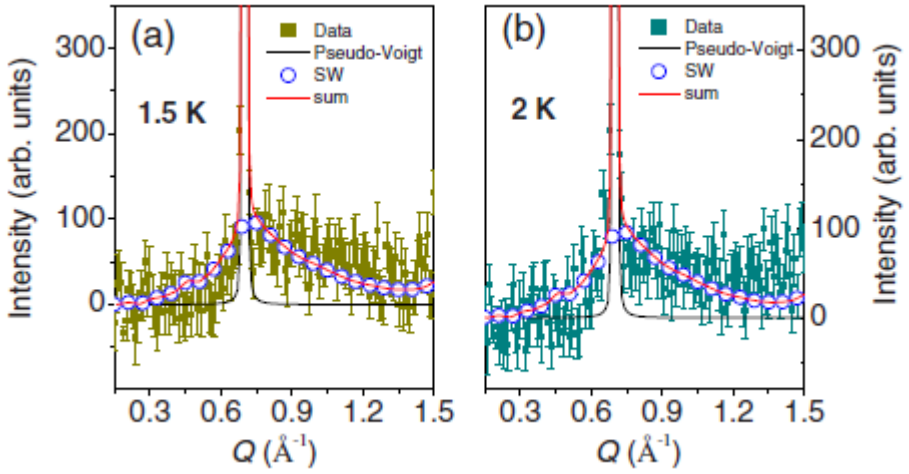
Diffuse scattering and spin waves $T<T_C$

$Zn_2VO(PO4)_2$: Quantum fluctuations in a S=1/2, 2d- Antiferromagnet

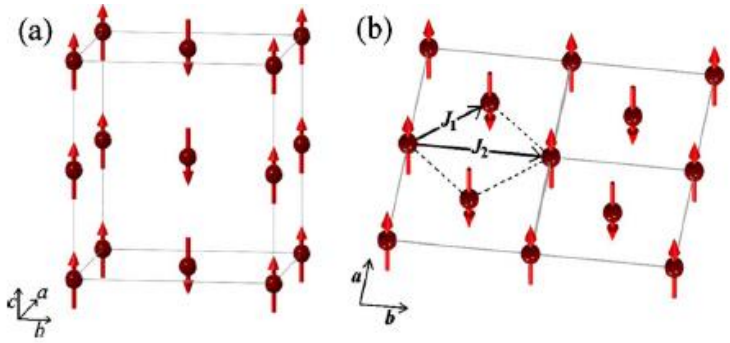
Above T_N



Below T_N



2d signal coexist with 3d order!



Why?

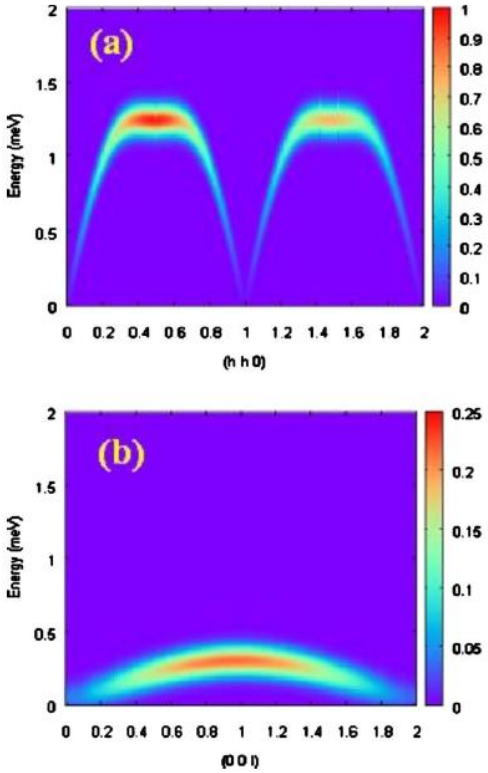
S. M. Yusuf et al PRB (2010)

Diffuse scattering and spin waves $T<T_C$

$Zn_2VO(PO4)_2$: Quantum fluctuations in a S=1/2, 2d- Antiferromagnet

T=0 Calculation of the SW spectrum

$$H = J_1 \sum_{i,\delta} (S_i S_{i+\delta}) + J_2 \sum_{i,\xi} (S_i S_{i+\xi}) + J_\perp \sum_{i,\delta_\perp} (S_i S_{i+\delta_\perp}) - D \sum_i (S^z)^2,$$

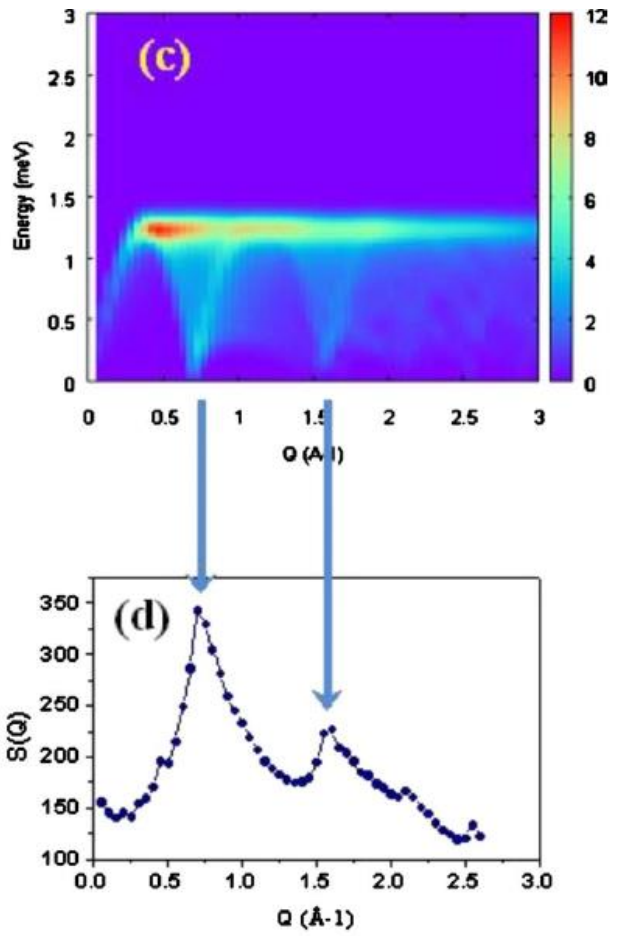


S. M. Yusuf et al PRB (2010)

Sum over energies in the range 0-E_i at constant Q modulus

program from S. Petit

Powder average and projection in S(q) plane



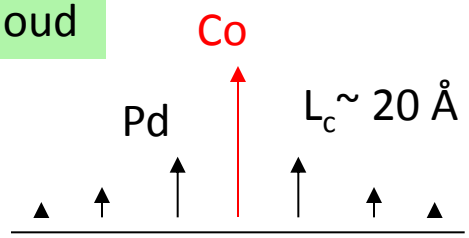
Chose the right Q scale

Towards a ferromagnetic transition: from Diffuse scattering to SANS

Example: $Pd_{1-x}Co_x$ alloys

Giant moments/polarization cloud

$M \sim 10\mu_B$/ atom Co

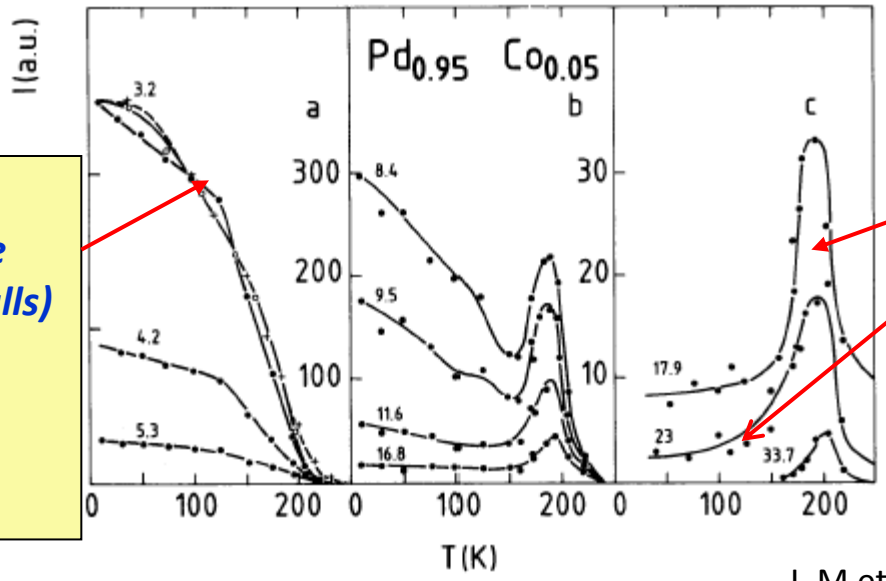


q~1 Å^{-1}

diffuse scattering ***probes local inhomogeneities (above Tc)***

x>0.1% : Ferro transition
T_C increases by 40K per Co %

Neutron intensity vs. T at Constant q



q~10^{-3} Å^{-1}
SANS probes large defects (Bloch walls)

I (q) ∝ q^{-4}

I(T) ∝ M^2(T)

q~10^{-2} Å^{-1}
SANS probes:
- ***the critical region***
- ***the spin waves***

I (q) ∝ κ / (κ^2+q^2)

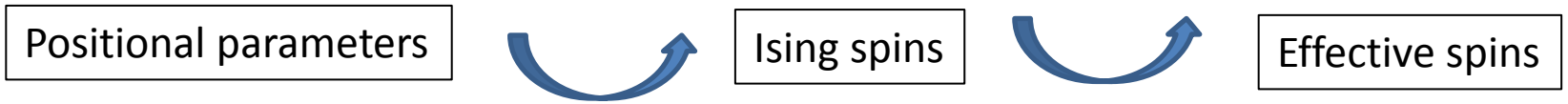
peak of I(T) at T_C

I. M et al J. Mag. Mag. Mat **54**, 997 (1986)

Diffuse scattering in Spin ices

Describe the diffuse scattering from a locally ordered state

- Local constraints : ice rules
- Entropy
- conservation laws and pinch points
- mapping



Water ice

Spin ice

Spin liquids..

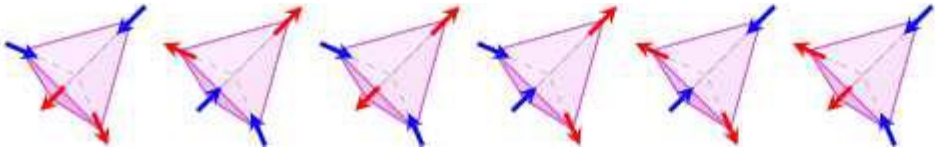
The ice rules

$$\mathcal{H} = \sum_{i,j} J_{zz} S_i^z S_j^z$$

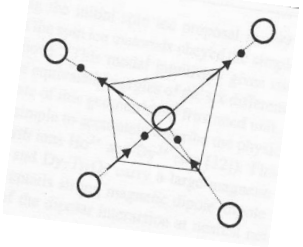
spins along <111 axes>, J_{ZZ} ferro

Two in- two out

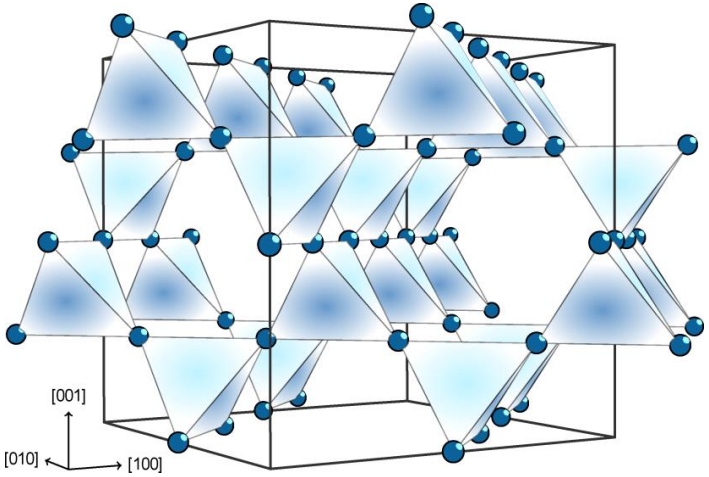
Spin ice



Real ice



Pyrochlore lattice with loosely connected tetrahedra



Frozen, disordered state with ground state entropy (akin to real ice)

Conservation laws and diffuse scattering

2 conditions for the energy

2in-2out state yields a non divergent field

$$\nabla.\mathbf{M} = 0$$

Free energy is determined by the entropy, maximized by states with M=0

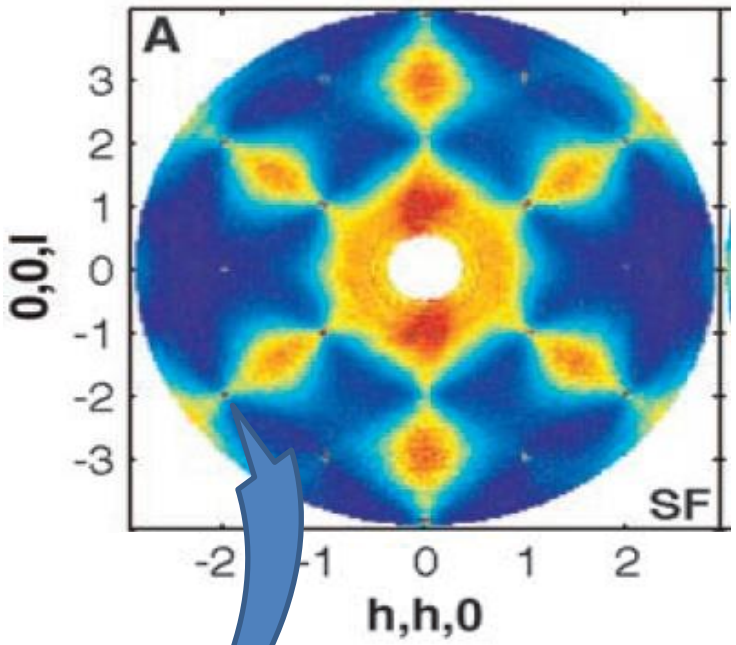
$$F_{\rm tot}(\mathbf{M}(\mathbf{r}))/T = \text{const} + \int d^d r K |\mathbf{M}(\mathbf{r})|^2/2.$$

The magnetic GS is a Coulomb Phase

Correlations are ***dipolar*** and ***anisotropic***

PINCH POINTS

T. Fennell
Science (2009)
Review J. Phys. F (2012)



Nearby (002)

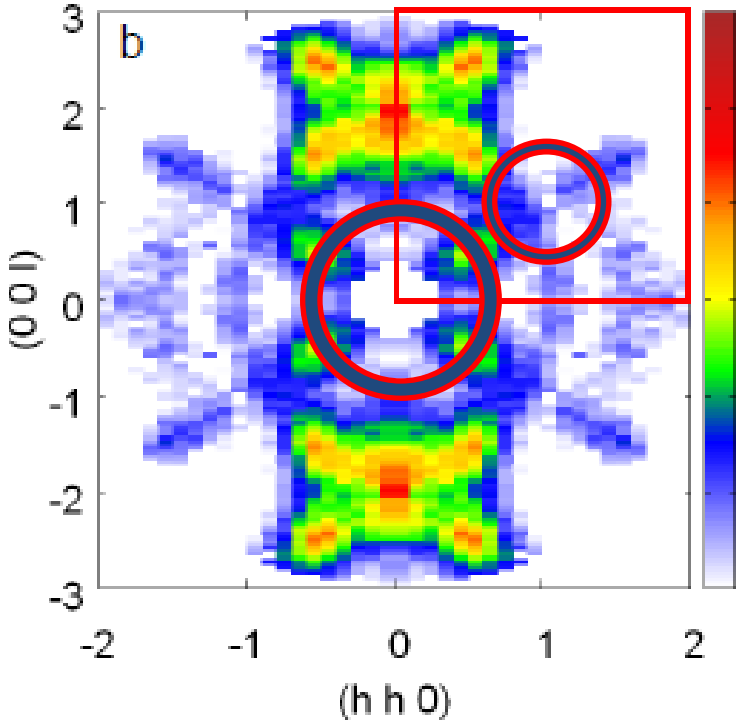
$$S^{yy}(q_h, q_k, q_l) \propto \frac{q_{l-2}^2 + \xi_{\rm ice}^{-2}}{q_{l-2}^2 + q_h^2 + q_k^2 + \xi_{\rm ice}^{-2}}$$

Diffuse scattering in spin Ice and spin liquid

$Tb_2Ti_2O_7$ - 50 mK

Spin liquid
(fluctuating and AF)

no spectral weight at Q=0
½ ½ ½ maxima : AF correlations

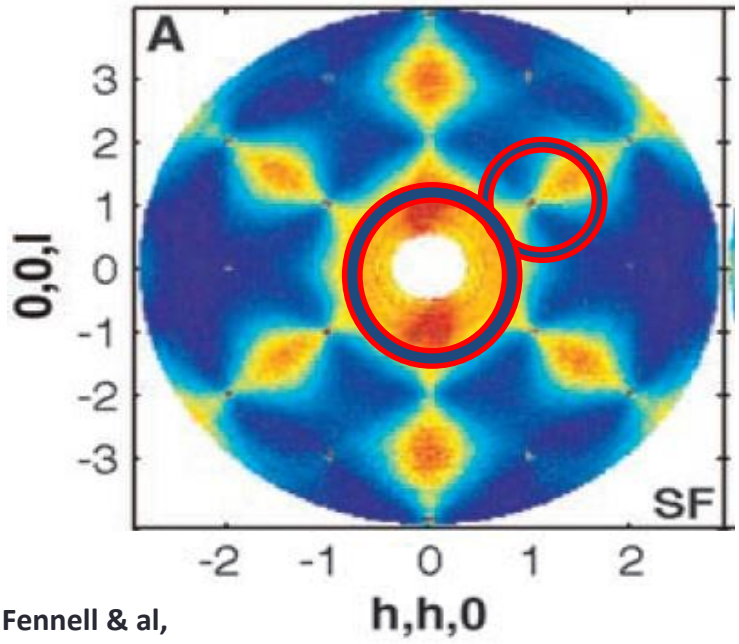


S.Petit & al, PRB 86 (2012)
S. Guitteny et al PRL(2013)

$Ho_2Ti_2O_7$ - 50 mK

Classical spin ice
(static and Ferro)

strong spectral weight at Q=0



T.Fennell & al,
Science 326 (2009)

Pinch points in both!

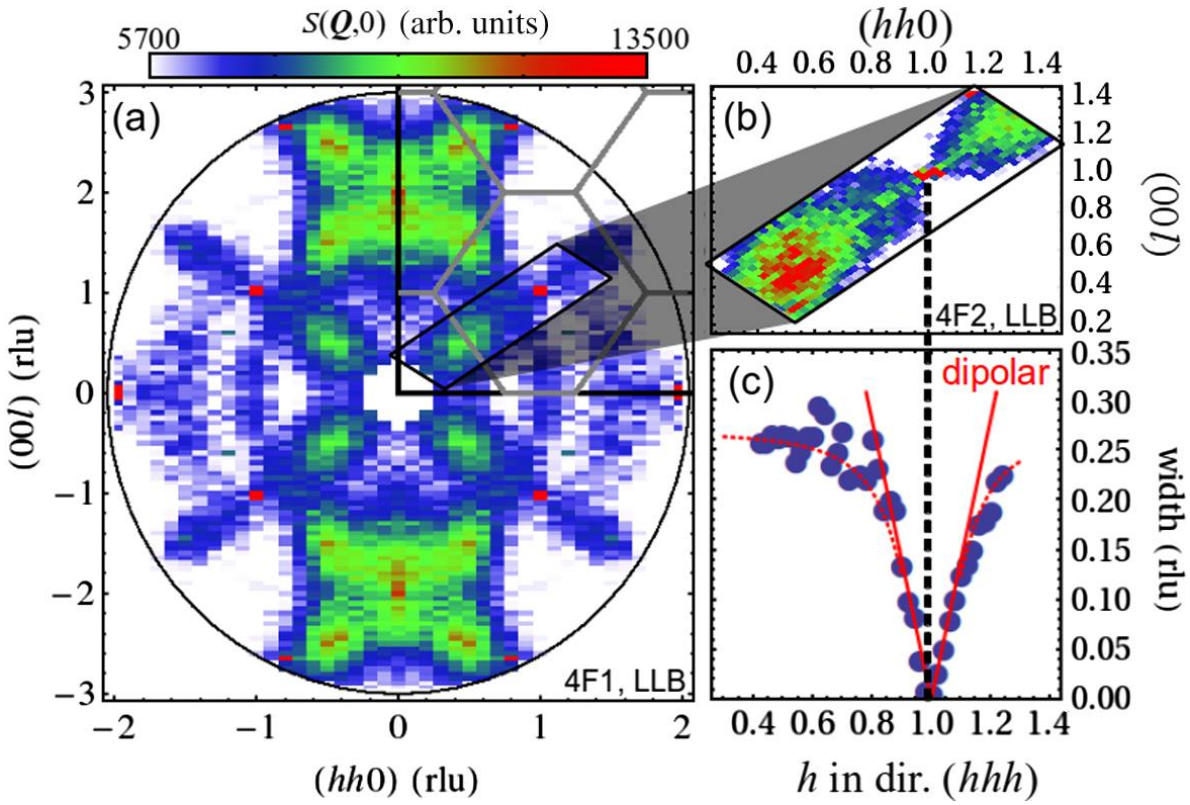
Analysis of the pinch points

Strongly anisotropic correlations of algebric nature

conservation law in TTO spin liquid analogous to the ice rules

see also
T. Fennell et al
PRL (2012)

S.Guitteny & al, PRL 111 (2013)



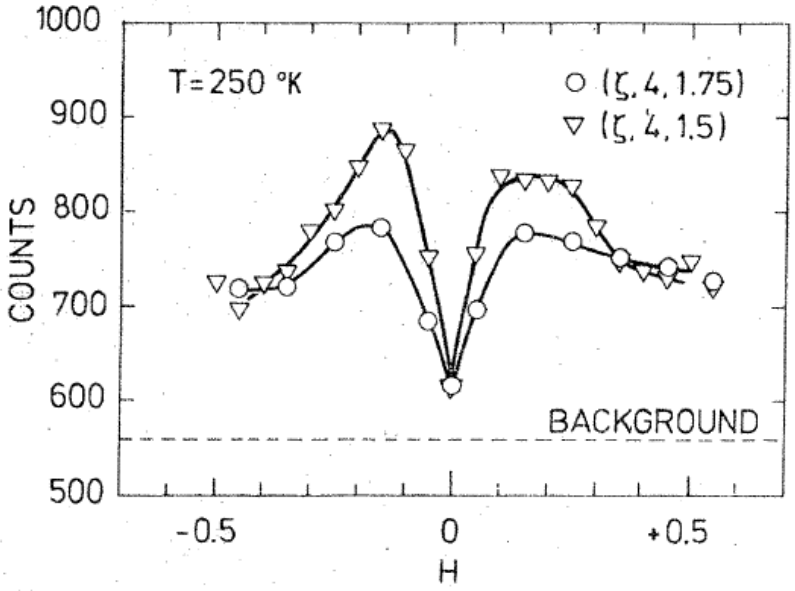
$\xi_{\perp}$ ~ 80 Å **(perpendicular to the pinch point)**

$\xi_{//}$ ~ 8 Å **(along <111>)**

Other local constraints and pinch points

ferroelectrics

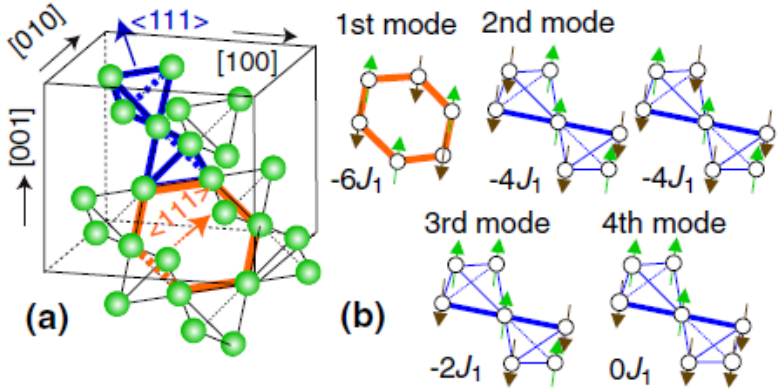
Positional Correlations between H-atoms



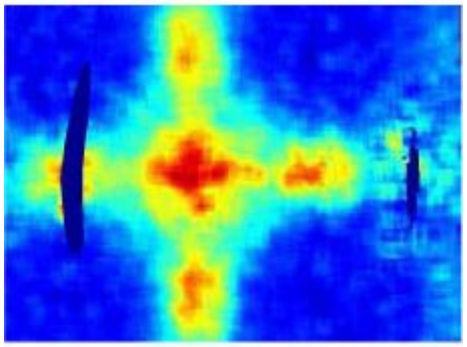
Youngblood PRB (1978)

spinels

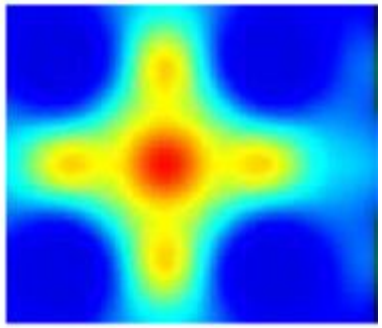
« Molecular modes »



Tomiyasu, PRL (2013)



Exp



Calc.

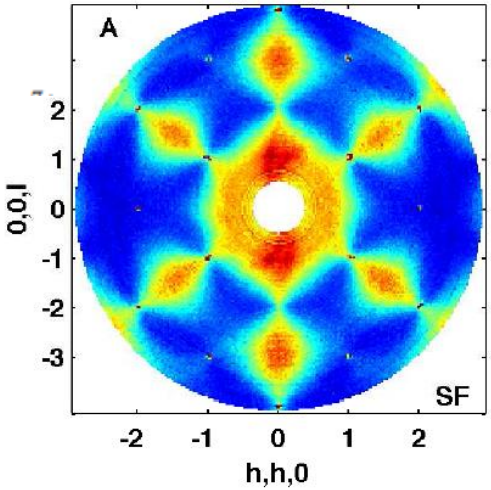
Simulate the diffuse scattering in spin ices

$Ho_2Ti_2O_7$ Spin ice:

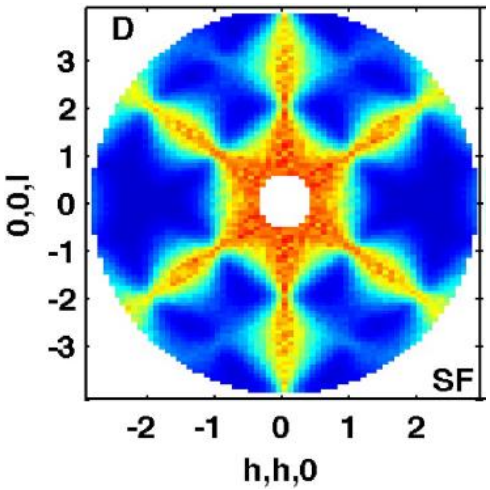
$$H = -J \sum_{\langle ij \rangle} \mathbf{S}_i^{z_i} \cdot \mathbf{S}_j^{z_j}$$

Fennell et al Science(2009)
Bramwell et al PRL(2001)

Exp.



Monte-Carlo simulations of the near-neighbour model

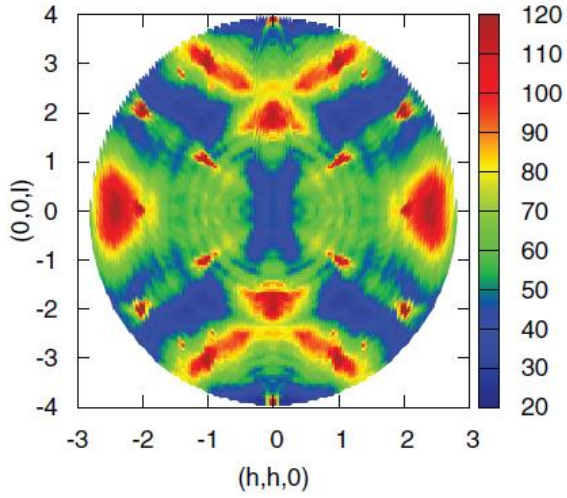


$Tb_2Ti_2O_7$ Spin liquid

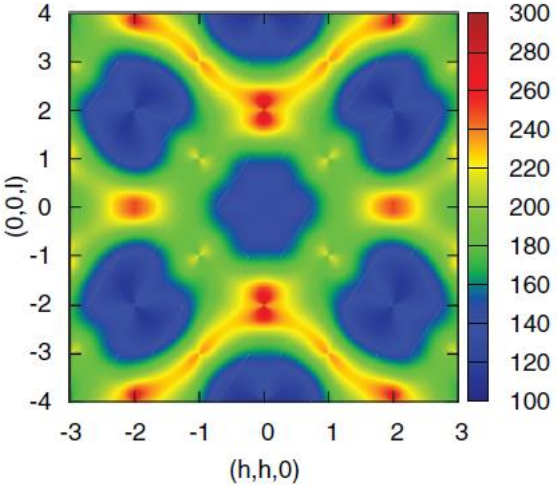
complex Hamiltonian
with
several Energy terms

P. Bonville et al PRB (2014)

Exp.



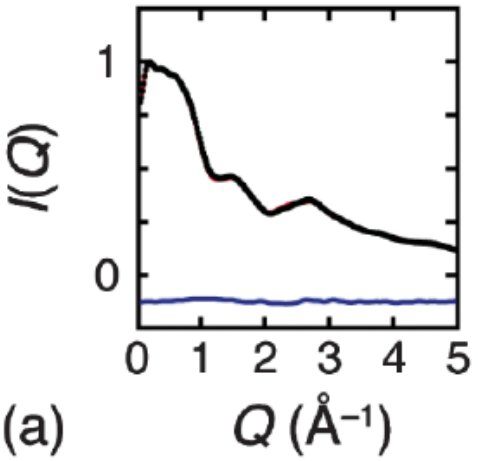
Mean field calculation



Simulate the diffuse scattering in frustrated magnets

Recent attempt in geometrically frustrated systems : an empirical solution to fit the diffuse scattering

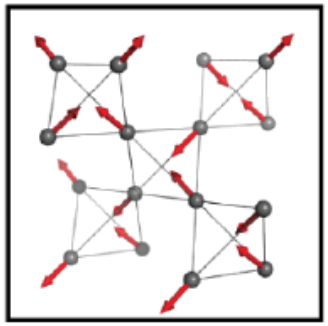
Paddison and Goodwin PRL(2012)



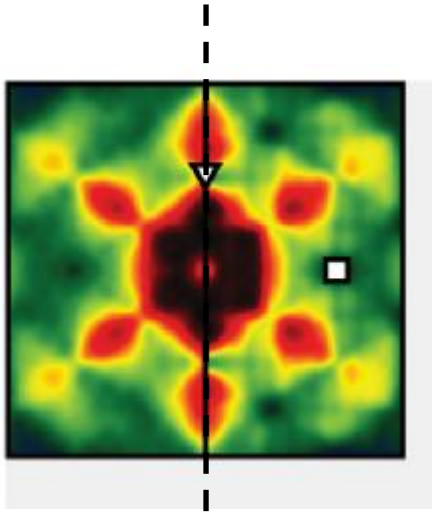
- Calculate powder data from exact model

- Fit this data by Reverse Monte Carlo technique using additionnal constraint (minimize local variance of spin orientations)

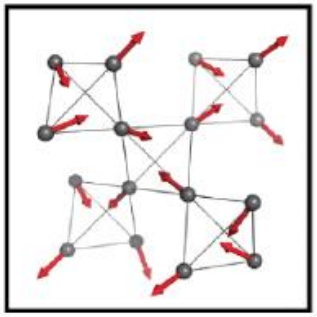
- Rebuild the 3d pattern (single crystal)



Ideal spin ice



RMC rebuilt



Message to bring back

Diffuse scattering is crucial in many studies of condensed matter physics.
For example:

$T >> T_C$
local chemical order

- informs on pair potentials which governs physical properties,
- allows one to predict phase diagrams, with applications to material science

T~Tc

Studies of critical phenomena and scaling laws

T=0

zero point fluctuations and GS entropy

- Low spin values, low dimensions, geometrical frustration
- Local constraints yield general features (such as pinch points)

No a priori description!

New physical cases stimulate new approaches