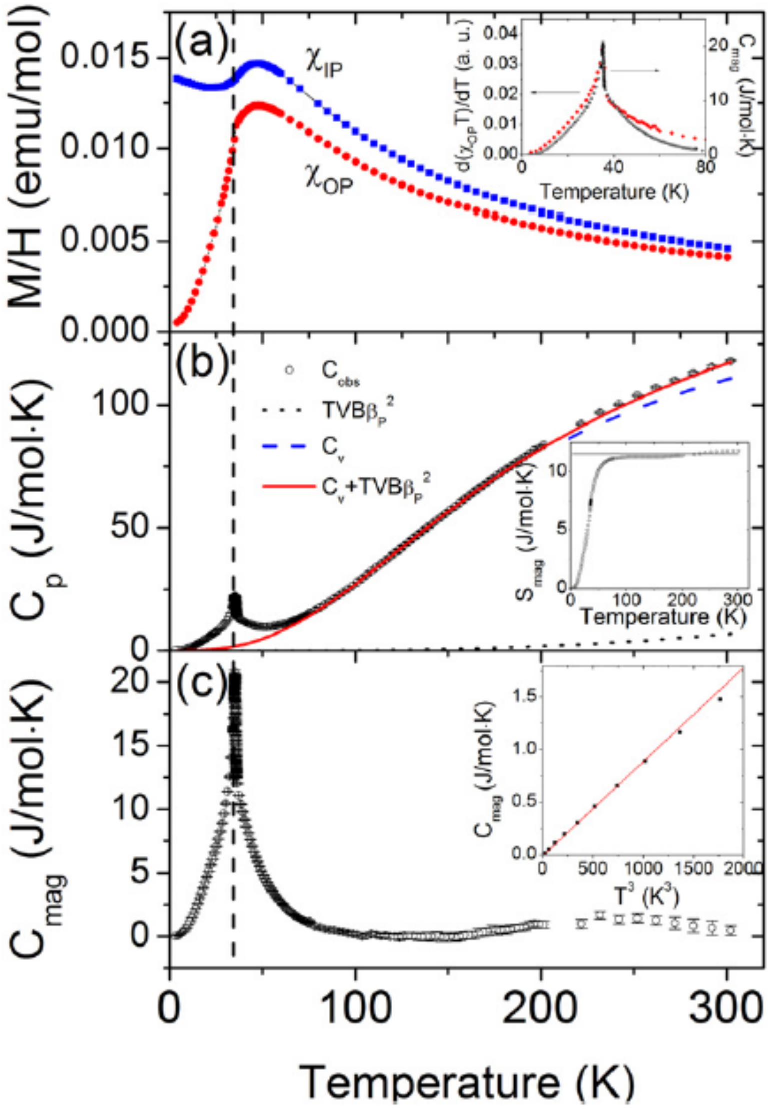
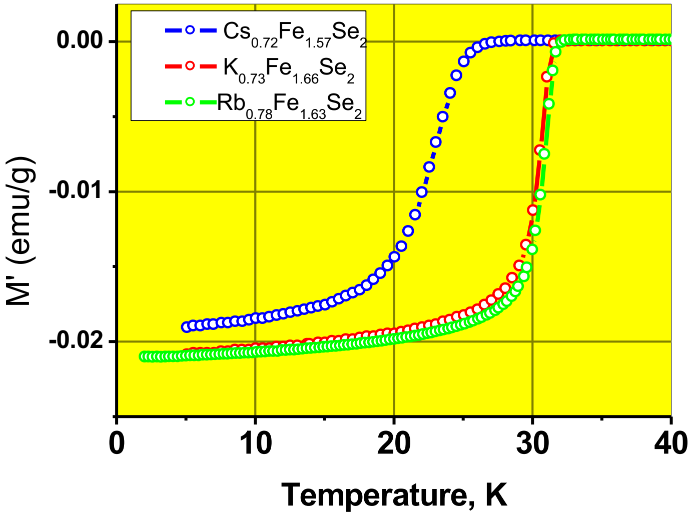
PSI Master School 2017

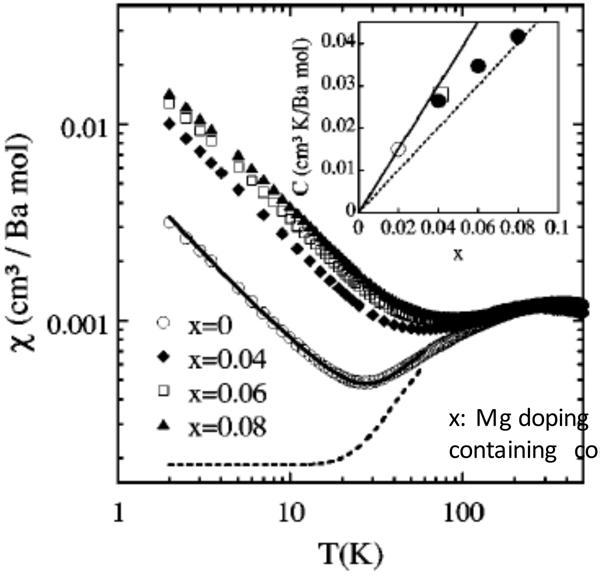
Introducing photons, neutrons and muons for materials characterization

Lecture 12: Magnetic diffraction

What is magnetic diffraction good for?

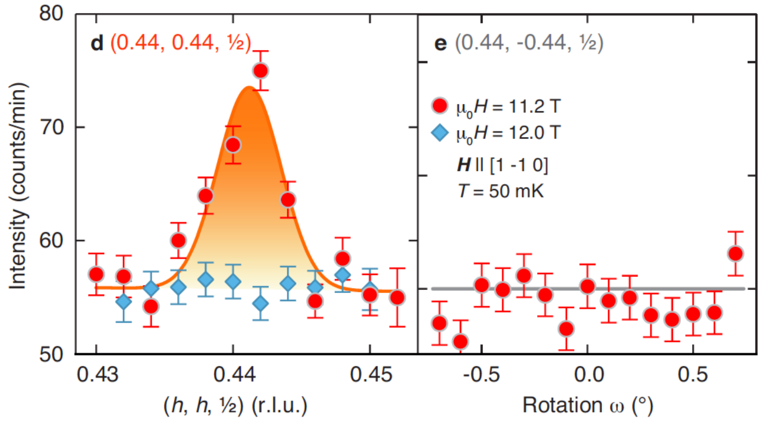




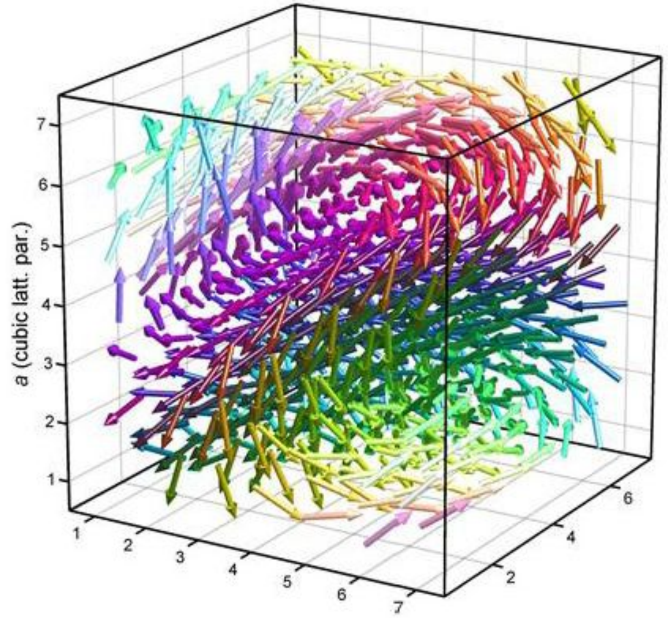


x: Mg doping of Ni containing compound

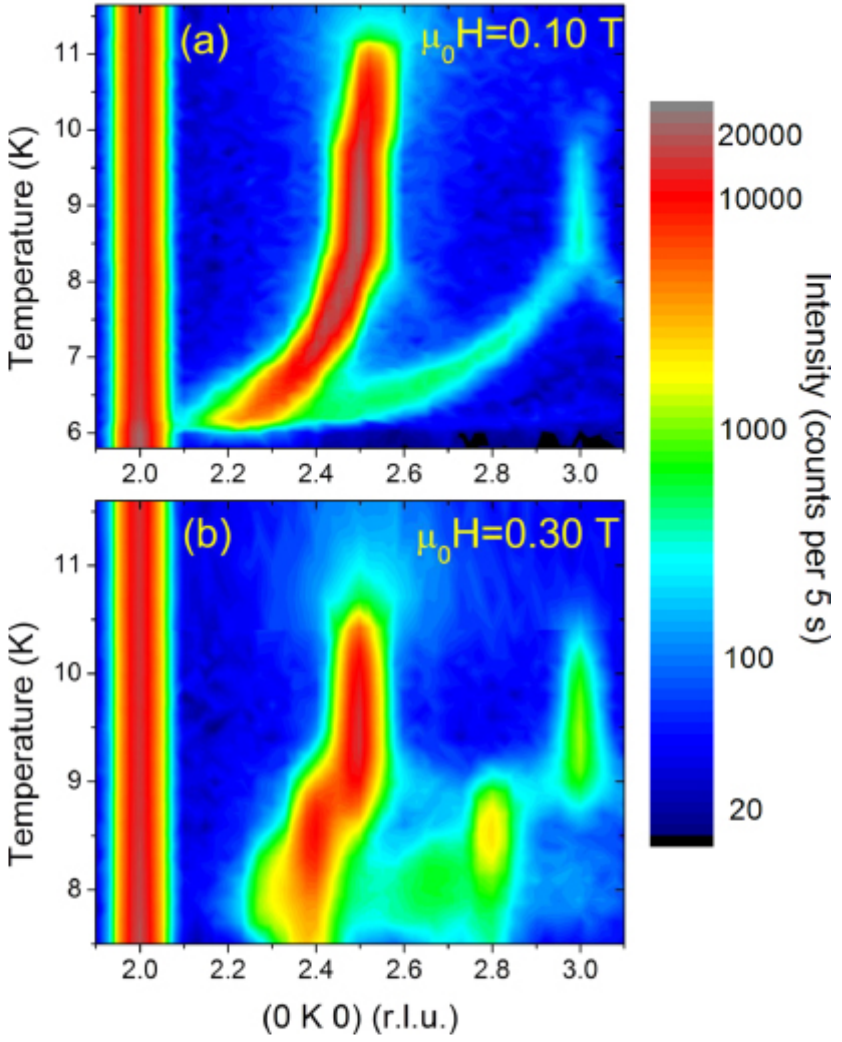
Things to learn from magnetic neutron diffraction



Presence or absence of magnetic order



Symmetry of magnetic order

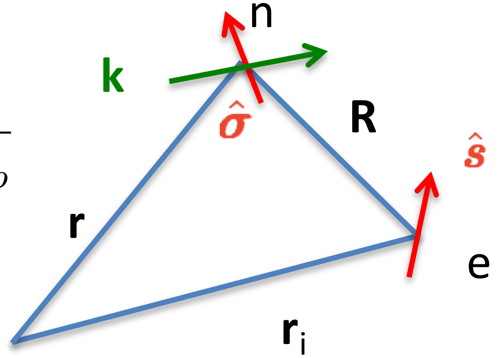


Identify magnetic phase transitions

Cross-section of magnetic neutron scattering

$$\boldsymbol{\mu}_n = 2\gamma\mu_n\frac{\hat{\boldsymbol{\sigma}}}{2} \qquad \mu_N = \frac{e\hbar}{2m_p}$$

$$\boldsymbol{\mu}_e = -2\mu_B\hat{\mathbf{s}}$$



Magnetic field from electron: $\mathbf{B}(\mathbf{R}) = \boldsymbol{\nabla} \times \left(\frac{\mu_0}{4\pi}\frac{\boldsymbol{\mu}_e \times \hat{\mathbf{R}}}{R^2}\right)$

Neutron-electron interaction: $V(\mathbf{R}) = -\boldsymbol{\mu}_n \cdot \mathbf{B}(\mathbf{R})$

Average over
neutron coordinates:

$$< \mathbf{k}_f|V(\mathbf{R})|\mathbf{k}_i >= \gamma r_e \boldsymbol{\sigma}[\underbrace{\hat{\mathbf{Q}} \times [\underbrace{\mathbf{S}_i \exp{(i\mathbf{Q}\mathbf{r}_i)}}_{\frac{1}{2\mu_B}\mathbf{M}(\mathbf{Q})} \times \hat{\mathbf{Q}}]}_{\frac{1}{2\mu_B}\mathbf{M}_{\perp}(\mathbf{Q})}]$$

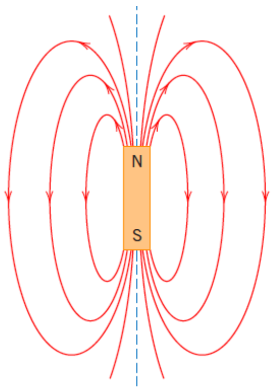
$$\mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i$$

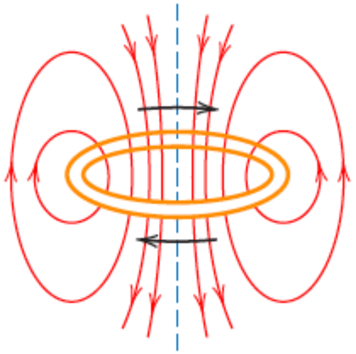
Magnetic operator $\frac{1}{2\mu_B}\mathbf{M}_{\perp}(\mathbf{Q})$

Cross-section of magnetic neutron scattering

$$\mathbf{B}_S = \boldsymbol{\nabla} \times \left(\frac{\mu_0}{4\pi}\frac{\boldsymbol{\mu}_e \times \hat{\mathbf{R}}}{R^2}\right)$$

$$\mathbf{B}_\mathbf{L} = \frac{\mu_0}{4\pi} I \frac{dI \times \hat{\mathbf{R}}}{R^2}$$





$$\mathbf{B} = \mathbf{B}_S + \mathbf{B}_L = \frac{\mu_0}{4\pi}\left(\boldsymbol{\nabla} \times \left(\frac{\boldsymbol{\mu}_e \times \mathbf{R}}{R^2}\right) - \frac{2\mu_B}{\hbar}\frac{\mathbf{p} \times \mathbf{R}}{R^2}\right)$$

Magnetic vs. nuclear scattering

Nuclear scattering length

$b_i \exp(i\mathbf{Q} \cdot \mathbf{r_i})$

short range and isotropic interaction

Magnetic scattering length

$$-\gamma r_e \boldsymbol{\sigma} \underbrace{[\hat{\mathbf{Q}} \times (\mathbf{S}_i \times \hat{\mathbf{Q}}) + \tfrac{i}{\hbar Q}(\mathbf{p}_i \times \hat{\mathbf{Q}})] \exp(i\mathbf{Q}\mathbf{r}_i)}_{\frac{1}{2\mu_B}\mathbf{M}_\perp(\mathbf{Q})}$$

long range and anisotropic interaction

Cross section of magnetic neutron scattering

$$\left(\frac{d^2\sigma}{d\Omega dE_f}\right) = (\frac{\gamma r_e}{2\mu_B})^2\frac{k_f}{k_i}S(\mathbf{Q},\omega)$$

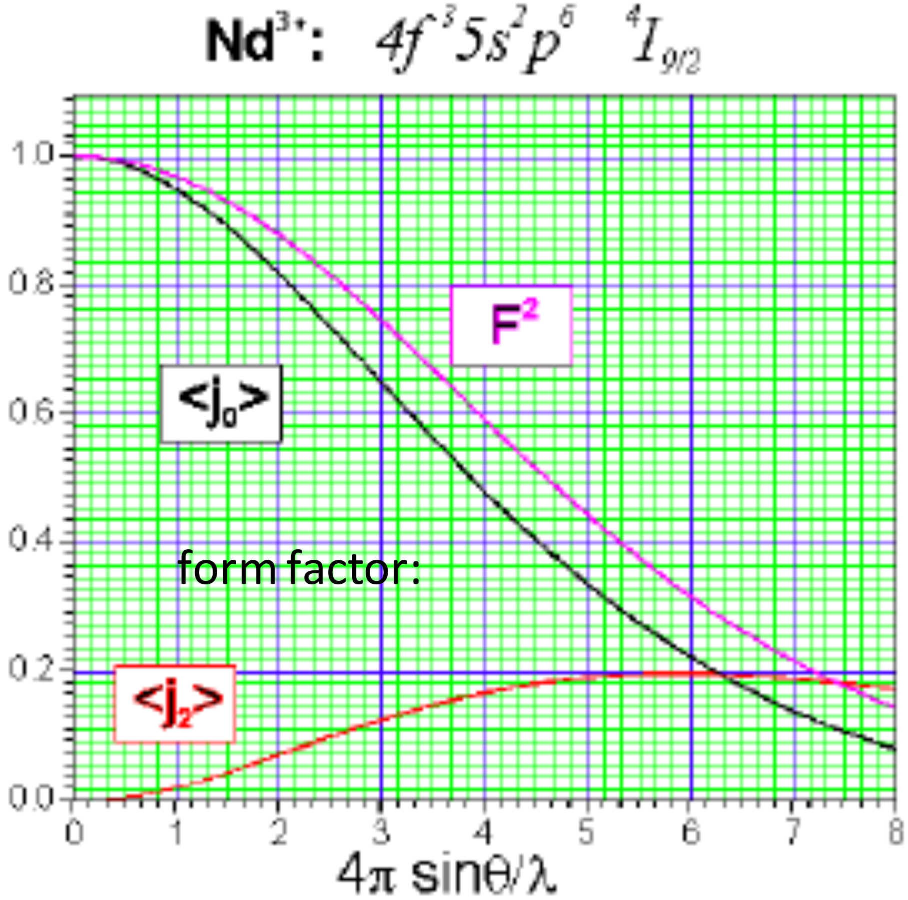
$$S(\mathbf{Q},\omega) = \sum_{\lambda_i,\lambda_f}\sum_{\alpha,\beta}(\delta_{\alpha,\beta} - \hat{Q}_\alpha\hat{Q}_\beta)$$

$$p_{\lambda_i} < \lambda_i|M_\alpha^+|\lambda_f >< \lambda_f|M_\beta|\lambda_i > \delta(E_f - E_i - \hbar\omega)$$

Cross-section is proportional to spin-spin correlation function

Only sensitive to the fluctuations perpendicular to the wave-vector transfer **Q**

Magnetic form factor



form factor:

$$F_d(\mathbf{Q}) = \int s_d(\mathbf{r}) \exp{(i\mathbf{Q}\cdot\mathbf{r})} d\mathbf{r}$$

Integral over the electron density of a single atom

Magnetic form factor always decreases with the wave-vector transfer

Magnetic form factor is different from structure factor

Cross-section and magnetic dynamical structure factor

$$\left(\frac{d^2\sigma}{d\Omega dE_f}\right) = \left(\frac{\gamma r_e}{8\pi\hbar}\right)^2 \frac{k_f}{k_i} \sum_{\alpha\beta}(\delta_{\alpha\beta} - \hat{Q}_\alpha \hat{Q}_\beta) \sum_{l'd'ld} g_{d'} g_d F^\star_{d'}(\mathbf{Q}) F_d(\mathbf{Q})$$

$$\times \int_{-\infty}^{\infty} \langle \exp(-i\mathbf{Q} \cdot \mathbf{R}_{l'd'}(0)) \exp(i\mathbf{Q} \cdot \mathbf{R}_{ld}(t)) \rangle$$

$$\times \langle S^\alpha_{l'd'}(0) S^\beta_{ld}(t) \rangle \exp(-i\omega t) dt$$

Spin-spin correlation function of the material

What are the various terms in the cross-section?

Magnetic neutron diffraction

Elastic scattering $\lim_{t\to\infty}\langle S_0^\alpha(0)S_i^\beta(t)\rangle = \langle S_0^\alpha\rangle\langle S_i^\beta\rangle$

$$(\frac{d\sigma}{d\Omega})_{\rm el} = N(\gamma r_e)^2[\frac{1}{2}gF(\mathbf{Q})]^2\exp(-2W)$$

$$\sum_{\alpha\beta}(\delta_{\alpha\beta} - \hat{Q}_\alpha\hat{Q}_\beta) \times \sum_i \exp(i\mathbf{Q}\cdot\mathbf{r}_i)\langle S_0^\alpha\rangle\langle S_i^\beta\rangle$$

Wave-vector dependence of scattering?

Strength of magnetic neutron scattering

Magnetic scattering length : $\gamma r_e \cdot S$

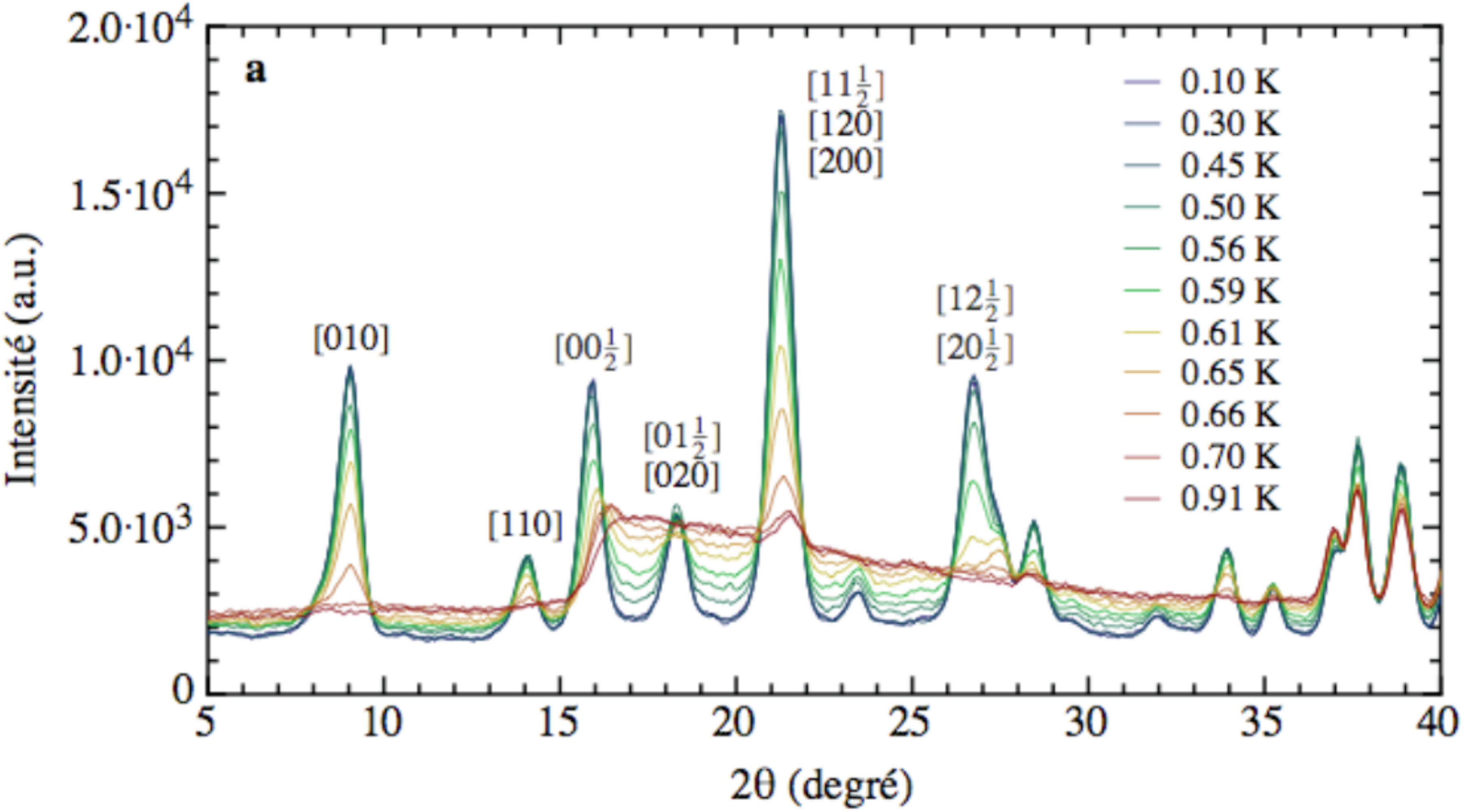
-1.91 classical electron radius

γr_e = $0.54 \cdot 10^{-12}$ cm (x S) = -5.4 fm (x S) [fm=10^{-13} cm]

Comparison of neutron scattering lengths, two examples:

	Mn^{3+} (S=2)	Cu^{2+} (S=1/2)
Magnetic	-10.8 fm	-2.65 fm
Nuclear	-3.7 fm	7.7 fm

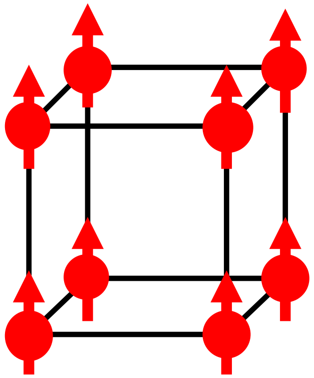
Strength of magnetic Bragg peaks



What are the nuclear and magnetic peaks?

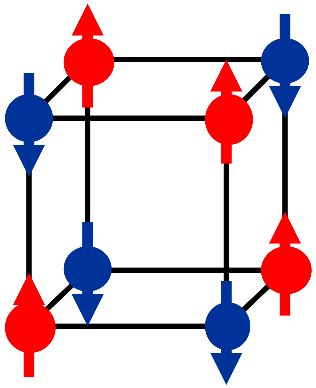
Example of commensurate structures

Magnetic modulation is a integer ratio of the nuclear unit cell



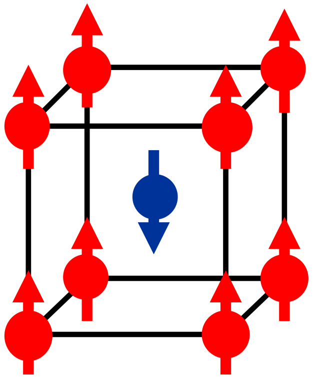
ferromagnet

k=(0,0,0)



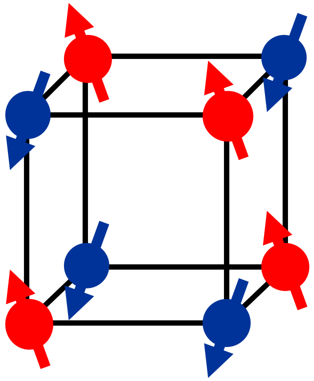
antiferromagnet

k=(1/2,1/2,1/2)



antiferromagnet

k=(0,0,0)



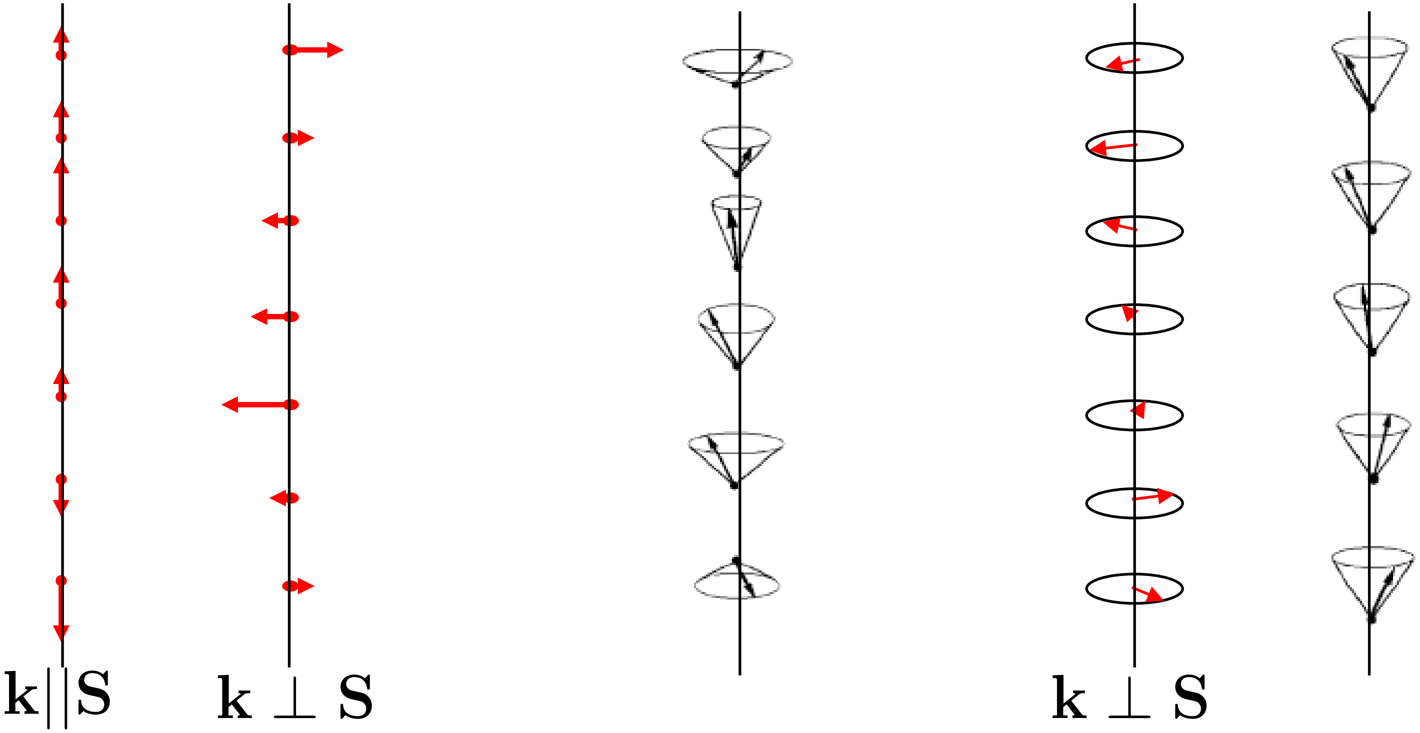
ferrimagnet
(non-collinear)

k=(1/2,1/2,1/2)

- Most insulators are antiferromagnets
- Breaking of translational symmetry: magnetic unit cell can be larger than chemical unit cell

Examples of incommensurate structures

Magnetic modulation is NOT a integer ratio of the nuclear unit cell



Longitudinal/transverse modulated structures

spiral structures (non-collinear)

helix structures (non-collinear)

Incommensurate structures are stabilized by susceptibility that diverges at an incommensurate wave-vector

Magnetic neutron diffraction from ferromagnet

$$(\frac{d\sigma}{d\Omega})_{\rm el} = N(\gamma r_e)^2[\frac{1}{2}gF(\mathbf{Q})]^2\exp(-2W)$$

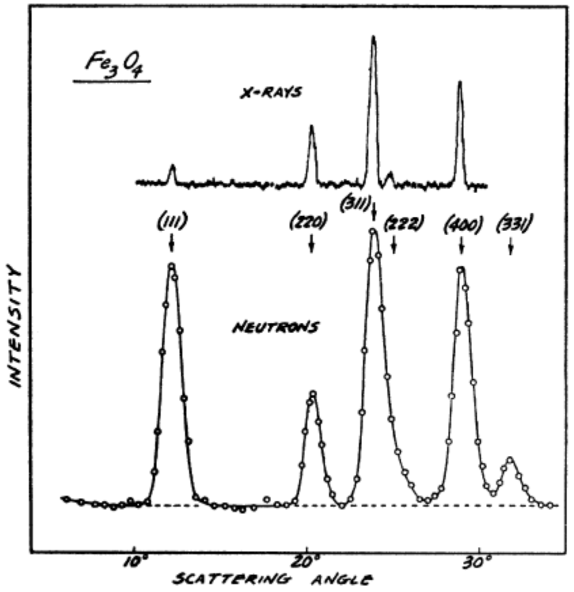
$$\sum_{\alpha\beta}(\delta_{\alpha\beta} - \hat{Q}_\alpha\hat{Q}_\beta) \times \sum_i \exp(i\mathbf{Q}\cdot\mathbf{r}_i)\langle S_0^\alpha\rangle\langle S_i^\beta\rangle$$

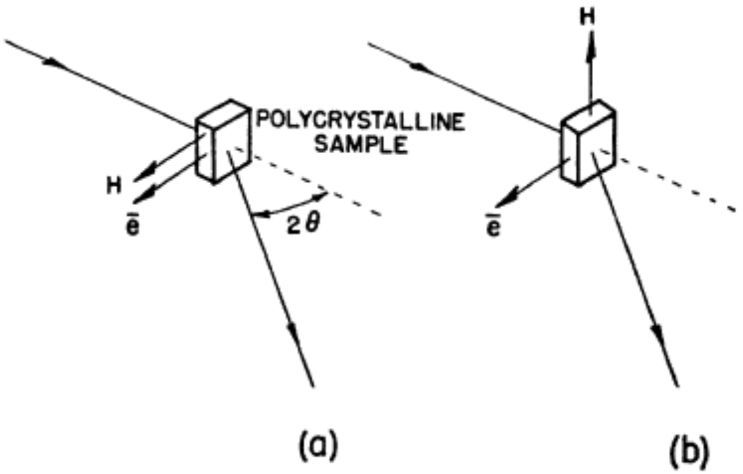
Example: ferromagnet with moments along z-axis

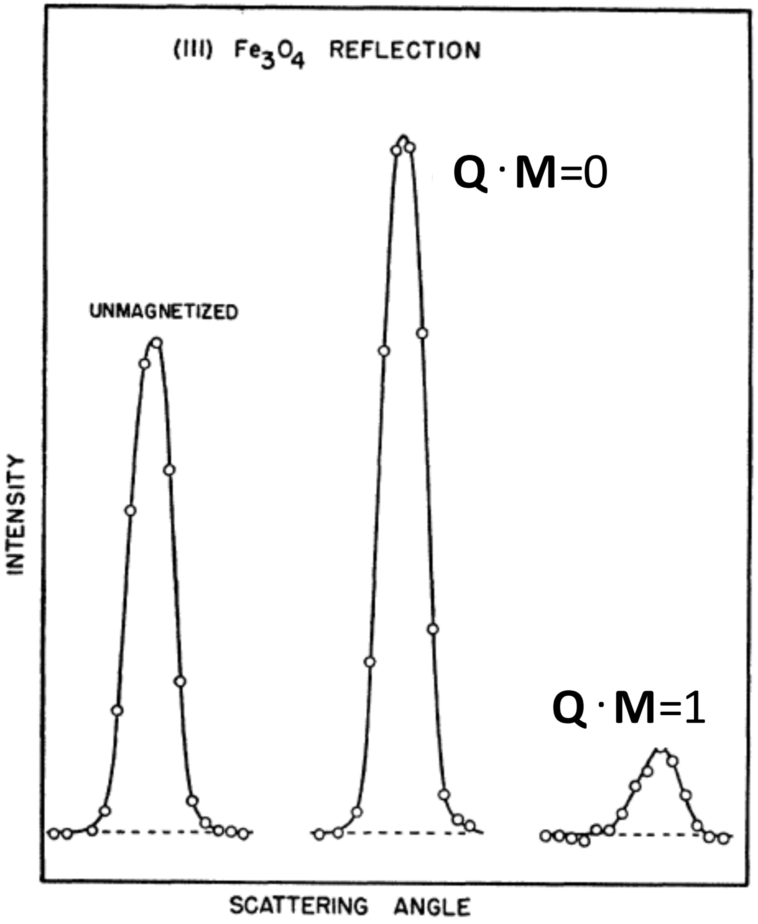
$$(\frac{d\sigma}{d\Omega})_{\rm el} = \frac{(2\pi)^3}{V_0}N(\gamma r_e)^2[\frac{1}{2}gF(\mathbf{Q})]^2\exp(-2W)(1-\hat{Q}_z^2)\langle S_i^z\rangle^2\delta(\mathbf{Q}-\boldsymbol{\tau})$$

What are the various terms in the cross-section?

Example: ferromagnet Fe_3O_4







C.G. Shull, E.O. Wollan, W.C. Koehler, Phys. Rev. **84,** 912 (1951)

Neutron diffraction from antiferromagnets

Commensurate collinear antiferromagnet

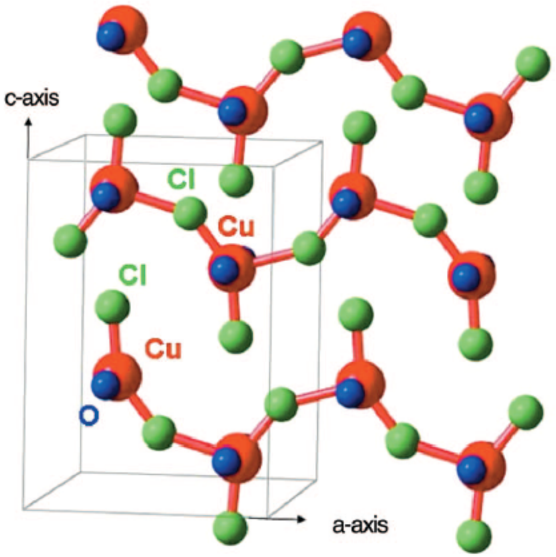
$$\langle S_i^\eta \rangle = \pm 1, \langle S_i^y \rangle = 0, \langle S_i^z \rangle = 0$$

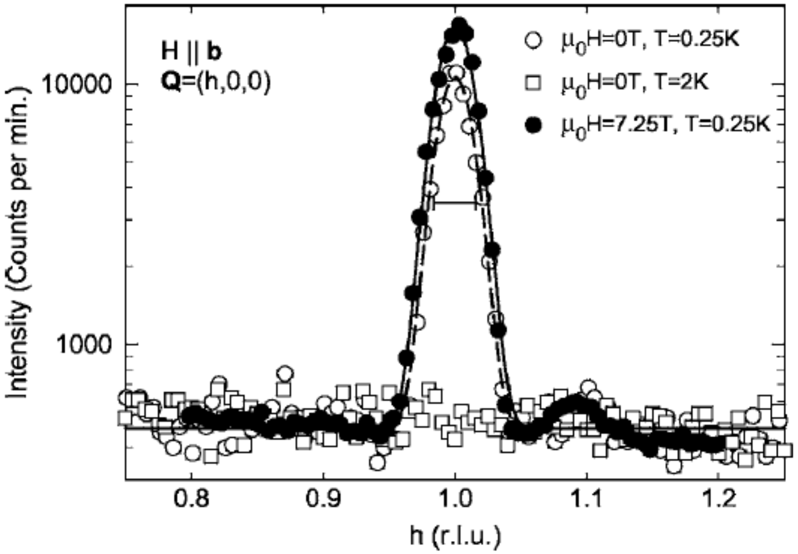
$$\sigma_d = \pm 1$$

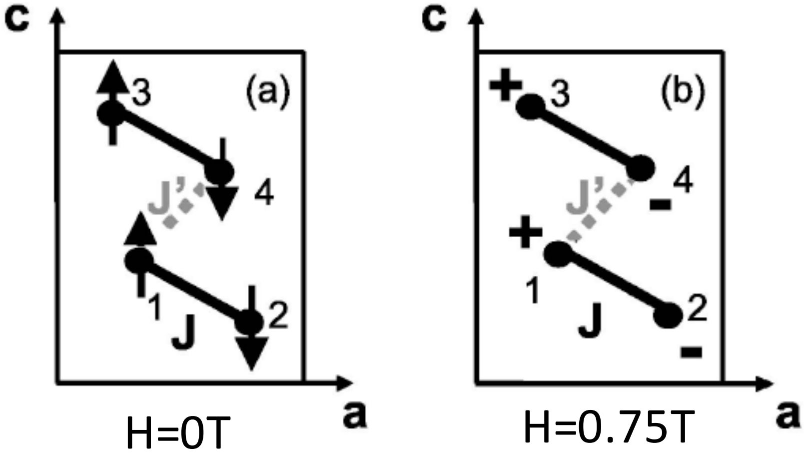
$$(\tfrac{d\sigma}{d\Omega})_{\mathrm{el}} = \tfrac{(2\pi)^3}{V_{0m}} N_m (\gamma r_e)^2 |F_M(\mathbf{Q})|^2 \exp(-2W)(1 - (\hat{\mathbf{Q}} \cdot \hat{\boldsymbol{\eta}})^2)\delta(\mathbf{Q} - \boldsymbol{\tau}_m)$$

$$F_M(\mathbf{Q}) = \tfrac{1}{2} g \langle S^\eta \rangle F(\mathbf{Q}) \textstyle\sum_d \sigma_d \exp(i\mathbf{Q}_m \cdot \mathbf{d})$$

Example antiferromanget



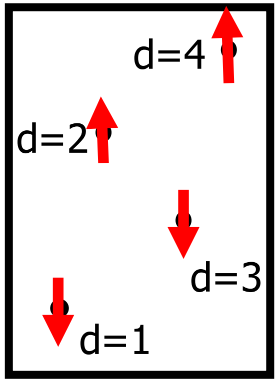




- Magnetic order below about 1K with **k**=0
- Non Bragg peaks along b* reciprocal axis at H=0.75T

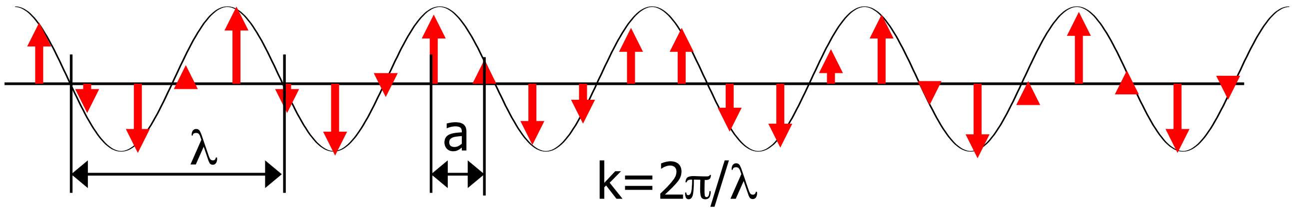
Y. Chen et al, Phys. Rev. B **75**, 214409 (2007).

Example: cross-section incommensurate magnetic structure



order in unit cell

Example: Transverse-modulated spin structure



propagation of magnetic structure is given by **Q**

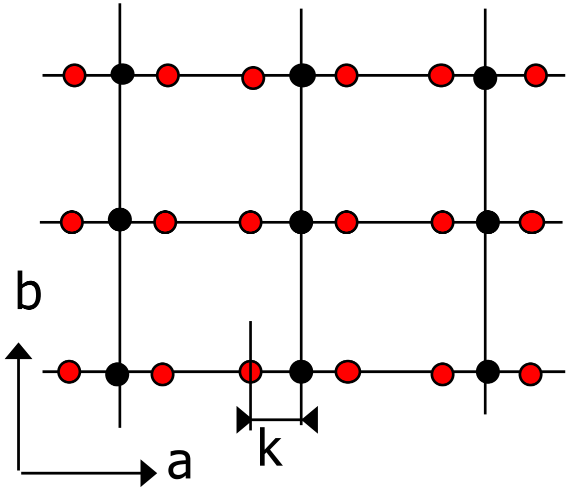
$$m^{\alpha}_{\mathbf{d}+\mathbf{R}} = \psi^{\alpha}_{d} \exp(i2\pi\mathbf{k}\cdot(\mathbf{d}+\mathbf{R})) + (\psi^{\alpha}_{d})^{*} \exp(-i2\pi\mathbf{k}\cdot(\mathbf{d}+\mathbf{R}))$$

Determination of magnetic structure from diffraction experiment

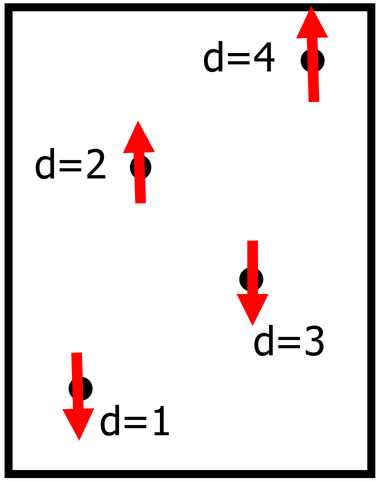
$$\frac{d^2\sigma}{dE d\Omega} \propto \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{Q}_{\alpha}\hat{Q}_{\beta}) S^{\alpha\beta}(Q,\omega)$$

Example: cross-section incommensurate magnetic structure

$$S(\mathbf{Q}) = N\left[|F_\perp(\boldsymbol{\tau})|^2\delta((\boldsymbol{\tau}-\mathbf{k})-\mathbf{Q}) + |F_\perp(-\boldsymbol{\tau})|^2\delta((\boldsymbol{\tau}+\mathbf{k})-\mathbf{Q})\right]$$



Magnetic Bragg peaks occur at satellite positions around Bragg peaks of the reciprocal lattice of the nuclear lattice

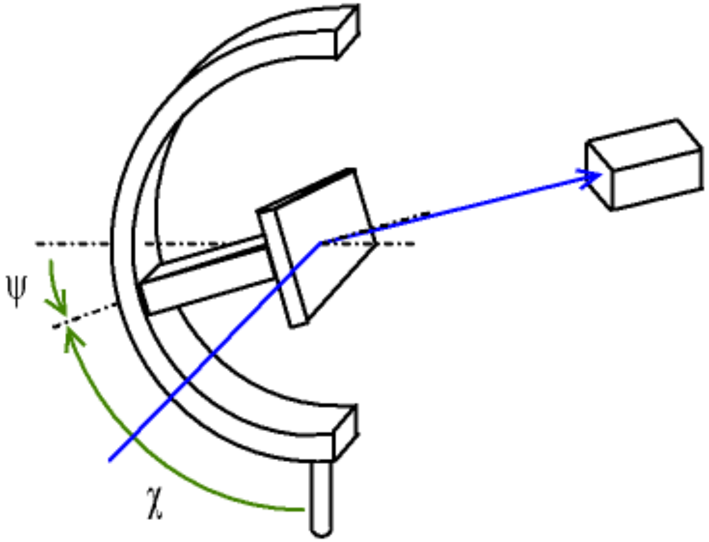


Spin ordering in unit cell from relative intensities of magn. Bragg peaks

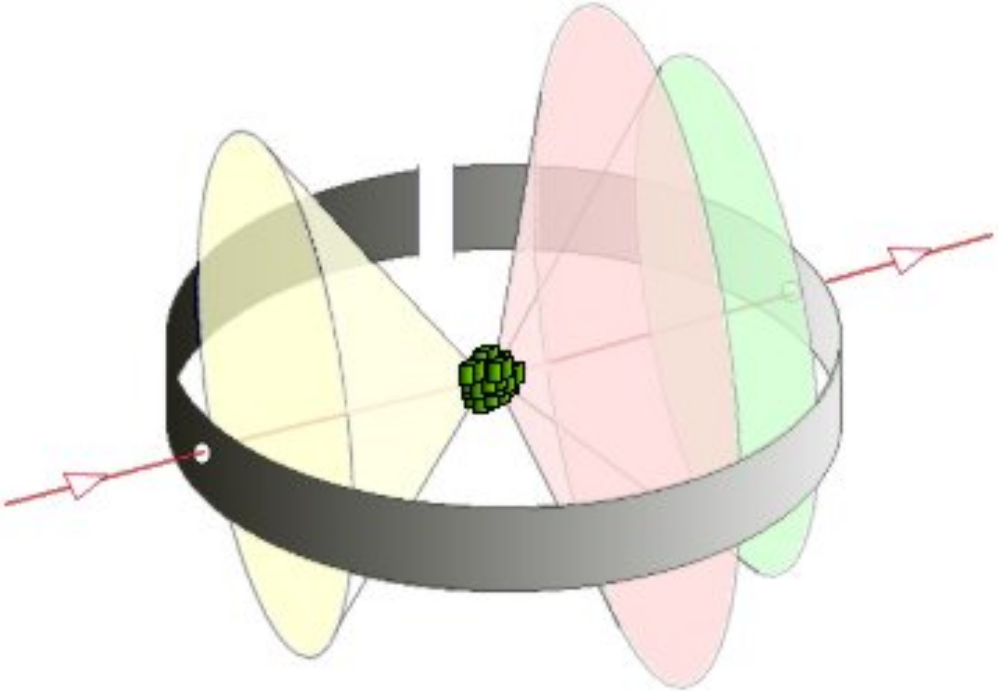
$$F^\alpha(\mathbf{Q}) = \sum_d \psi_d^\alpha \exp(i\mathbf{Q}\cdot\mathbf{d})$$

F(Q) are different for Ψ_d vectors possible by symmetry

Techniques for (unpolarized) magnetic diffraction



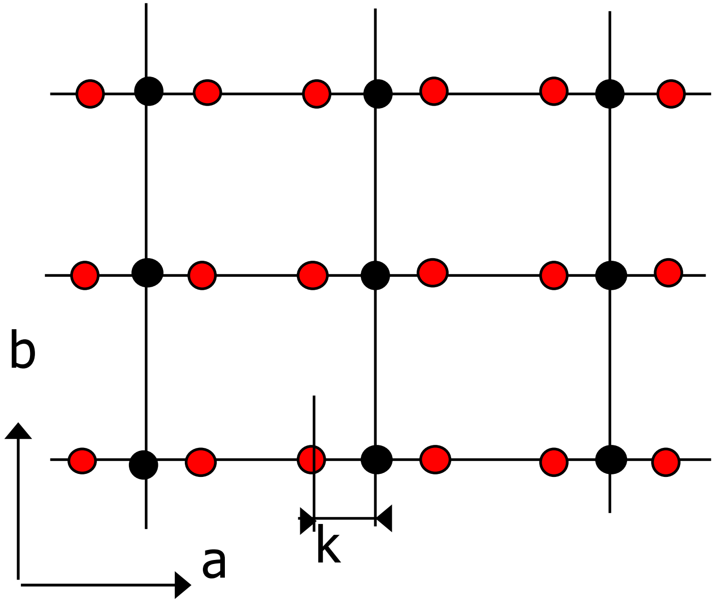
Four-circle single-crystal diffraction



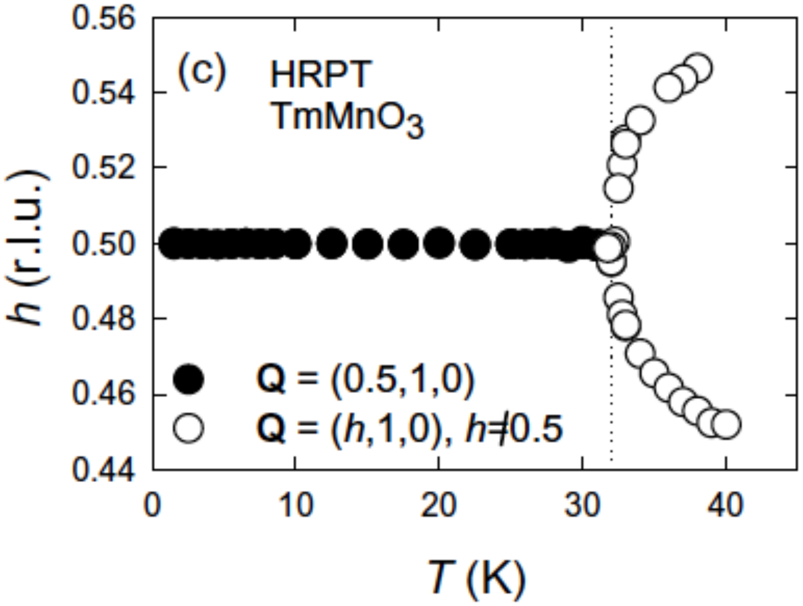
Powder diffraction

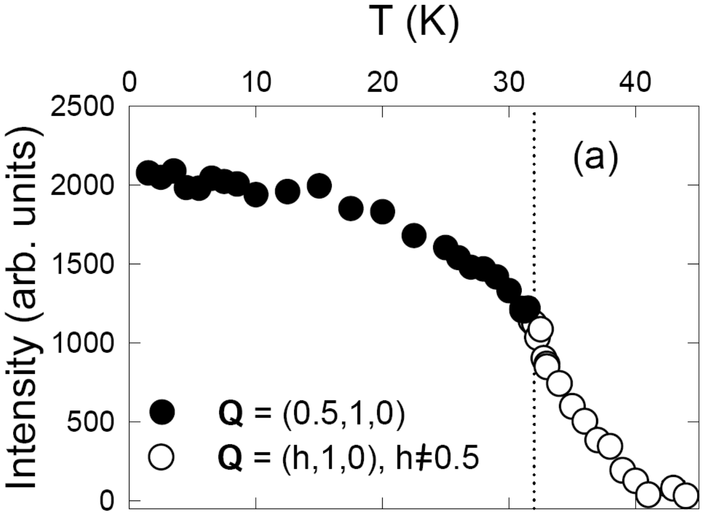
Symmetry aspects of magnetic structure determination

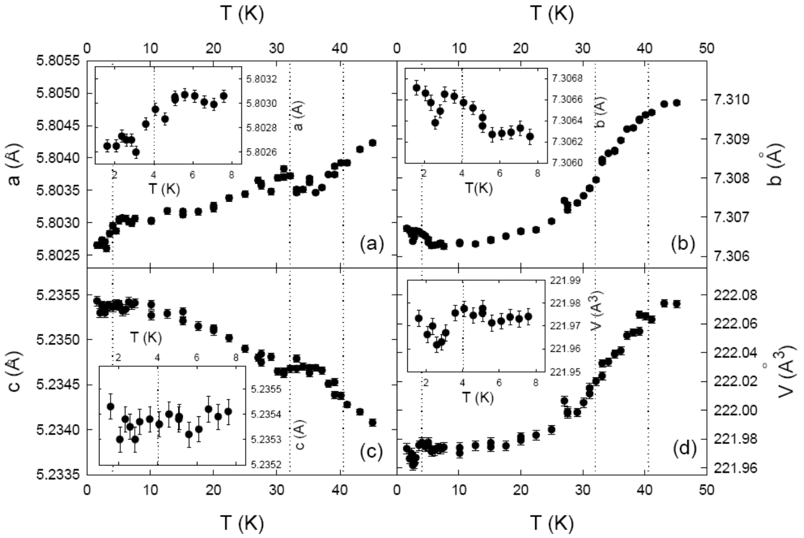
1) ordering wave-vector **k** is the modulation vector of the magnetic structure
2) Magnetic Bragg peaks are satellite peaks of the reciprocal lattice peaks **N** +/- **k**



Example: $TmMnO_3$







1) Incommensurate magnetic order above 30K

2) Commensurate order below 30K

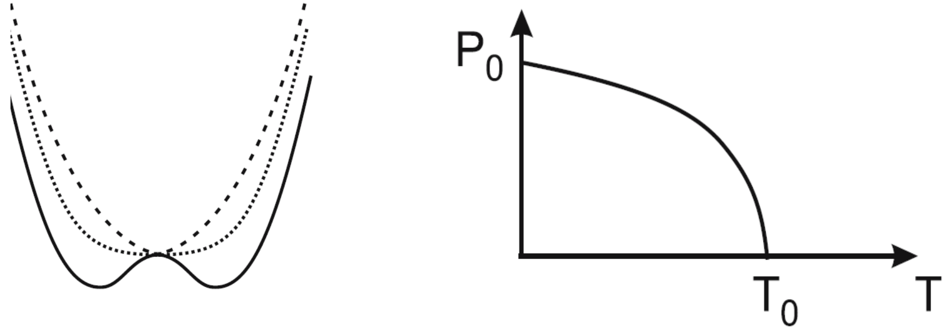
3) Order parameter can be measured with neutron diffraction

V. Pomjakushin et al, New J. Phys. **11**, 043019 (2009).

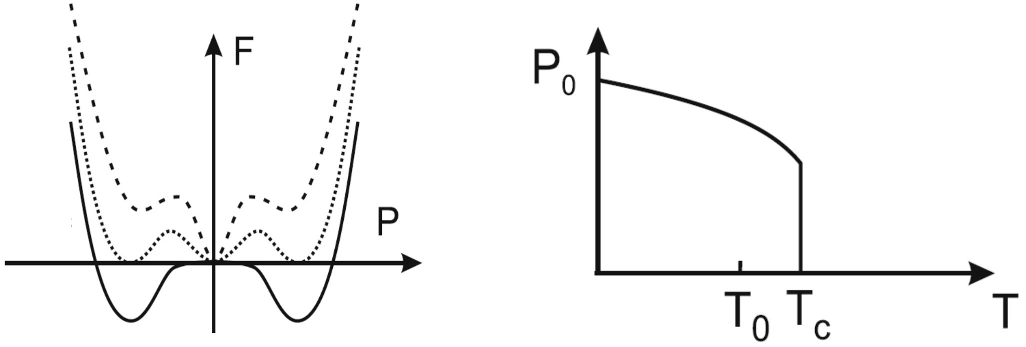
First and second order magnetic transitions

Landau theory for a magnet: $F(T,M) = F_0(T) + \alpha_2(T)M^2 + \alpha_4(T)M^4 + \cdots$

$b > 0$



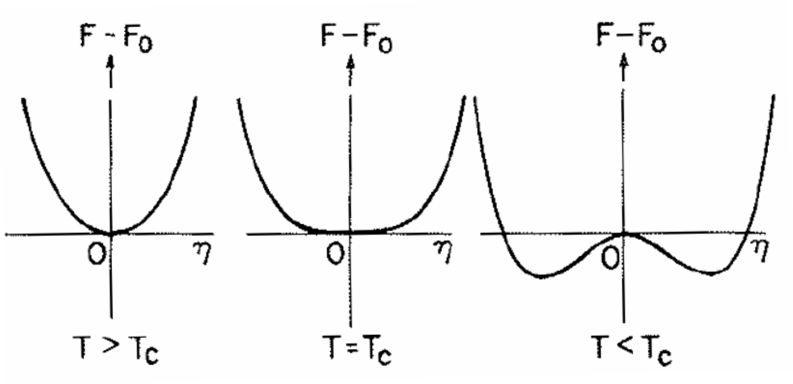
$b < 0$



Continuous phase transition

- Landau theory of free energy

$$F(T,M) = F_0(T) + \alpha_2(T)M^2 + \alpha_4(T)M^4 + \cdots$$



- time reversal symmetry → only even powers of M
- α_2 changes sign at transition
- Free energy is unstable for M non zero for T < T_c (M minimizes the free energy F(T):

$$M^2 \propto (T_c - T)$$

Inverse susceptibility

$$F = \alpha_2(T)M^2 + \alpha_4(T)M^4 - MH + \ldots$$

For small H the magnetization M is

$$M = 2\alpha_2(T)H \;\Rightarrow\; \alpha_2 = \tfrac{1}{2}\chi^{-1}$$

The coefficient, α_2, of M^2 is proportional to the inverse susceptibility:

$$F = \tfrac{1}{2}\chi^{-1}M^2 + \ldots$$

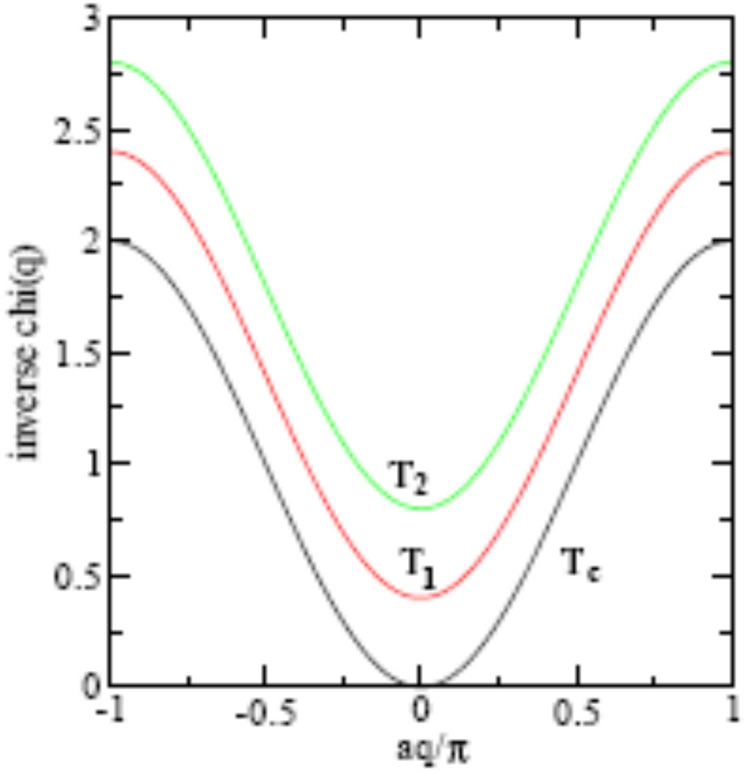
α_2 changes sign at transition → the susceptibility diverges
at a continuous transition.

More generally: for all Fourier components:

$$F = \tfrac{1}{2}\sum_k \chi^{-1}(k)|M(k)|^2$$

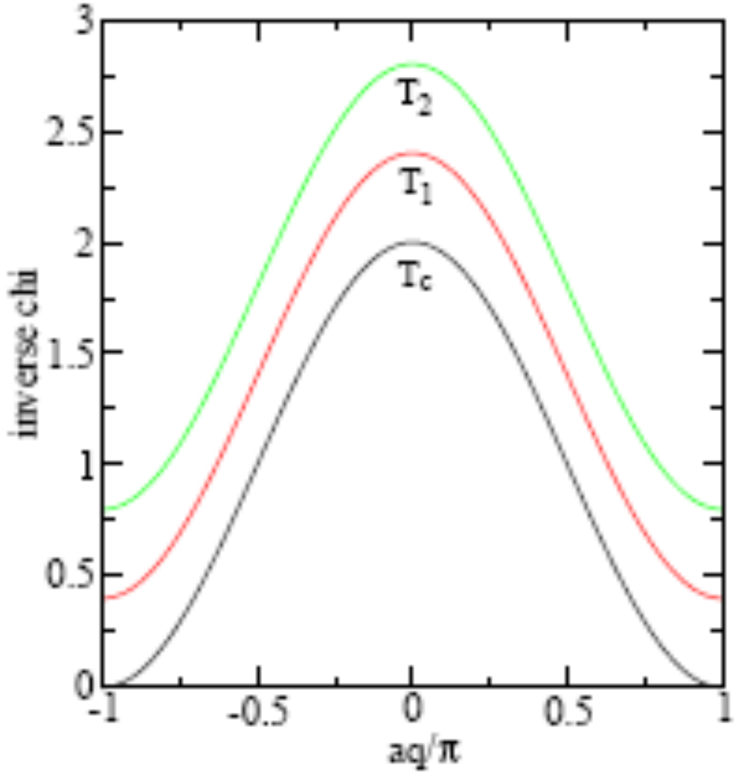
Inverse susceptibility

Ferromagnet



the instability occurs at q=0

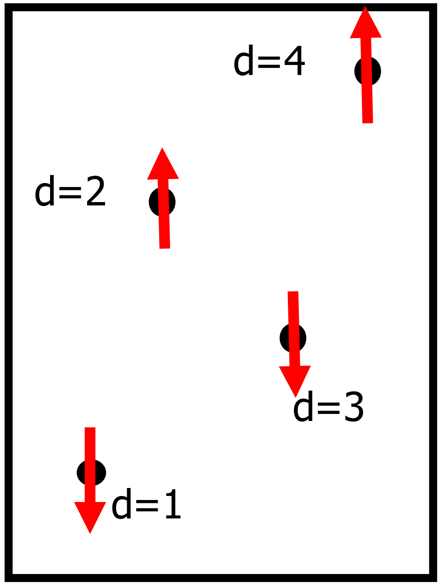
Antiferromagnet



The instability occurs at wave-vector q=π/a

Several magnetic ions in the unit cell

$$\mathbf{S}(\mathbf{r_d}, \mathbf{R}) = \mathbf{S}(\mathbf{r_d}) \exp(-i\mathbf{k} \cdot \mathbf{R})$$



Define spin vector describing all spins in the unit cell:

$$\mathbf{s} = [\mathbf{S}_1, \mathbf{S}_2, ...]$$

Then free energy can be written as:

$$F = F_{\gamma\delta}\, \mathbf{s}_\gamma\, \mathbf{s}_\delta$$

One of the eigenvalue of *F* that becomes first zero. The susceptibility of the associated eigenvector diverges and the system orders.

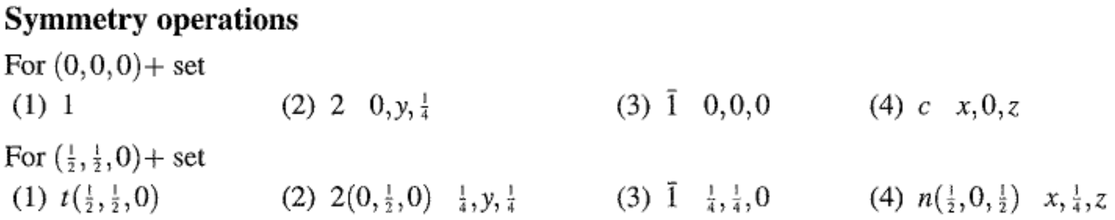
Magnetic order at a second order phase transition
Is described by one irreducible representation.

Irreducible representation

1) Little group is the subgroup of symmetry operations that leave the ordering wave-vector **k** invariant
2) The irreducible representations are matrix representations that cannot be decomposed into other representations
3) Basis vectors of irreducible representations are possible magnetic structures

Example: magnetic order on square lattice

C2/c: 1, 2_b, -1, m_{ac}



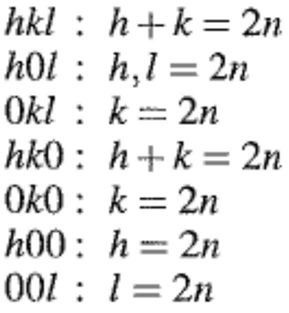
Symmetry operations

For (0,0,0)+ set

(1) 1 (2) 2 $0,y,\frac{1}{4}$ (3) $\bar{1}$ 0,0,0 (4) *c* $x,0,z$

For $(\frac{1}{2},\frac{1}{2},0)$+ set

(1) $t(\frac{1}{2},\frac{1}{2},0)$ (2) $2(0,\frac{1}{2},0)$ $\frac{1}{4},y,\frac{1}{4}$ (3) $\bar{1}$ $\frac{1}{4},\frac{1}{4},0$ (4) $n(\frac{1}{2},0,\frac{1}{2})$ $x,\frac{1}{4},z$



$hkl : h+k=2n$
$h0l : h,l=2n$
$0kl : k=2n$
$hk0 : h+k=2n$
$0k0 : k=2n$
$h00 : h=2n$
$00l : l=2n$

$r_1=(0\ \ 0.7499\ \ 0.25)$

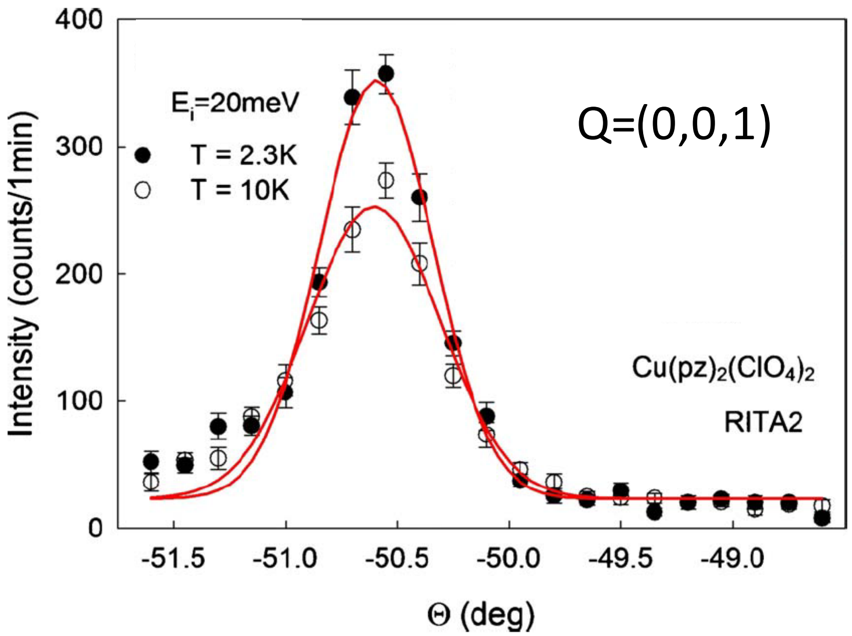
$r_2=(0\ \ 0.2501\ \ 0.75)$

$r_3=(0.5\ \ 0.2499\ \ 0.25)$

$r_4=(0.5\ \ 0.7501\ \ 0.75)$

Ordering wave-vector: k=(0,0,0)

Little group: 1, 2_b, -1, m_{ac}



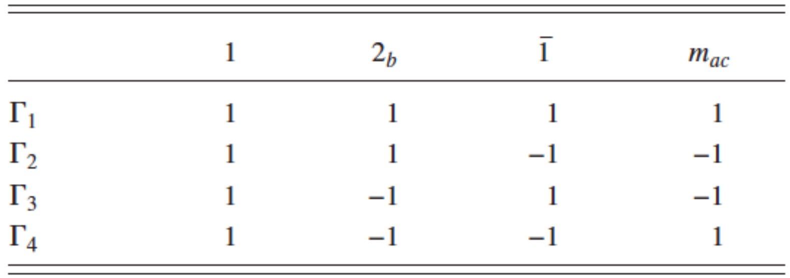
Q=(0,0,1)

Example: magnetic order on square lattice

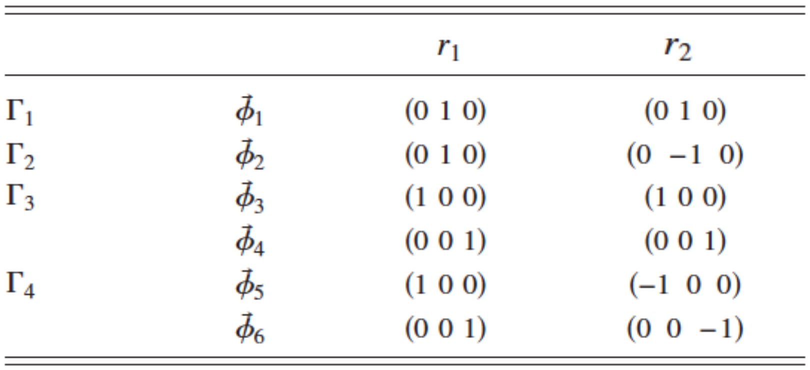
C2/c: 1, 2_b, -1, m_{ac}

Ordering wave-vector: k=(0,0,0)

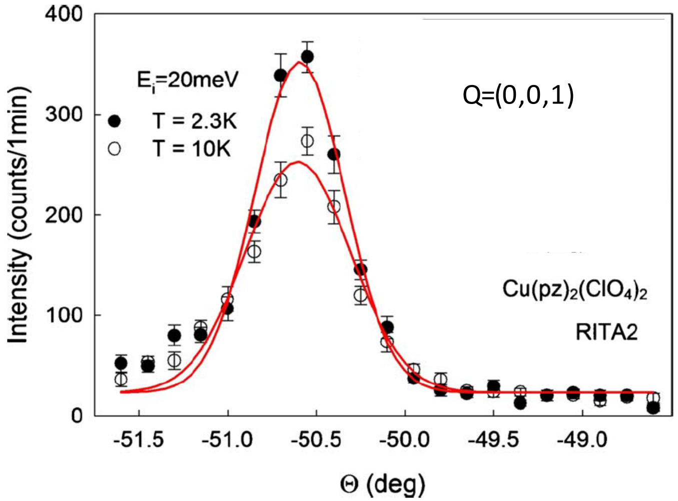
Little group: 1, 2_b, -1, m_{ac}

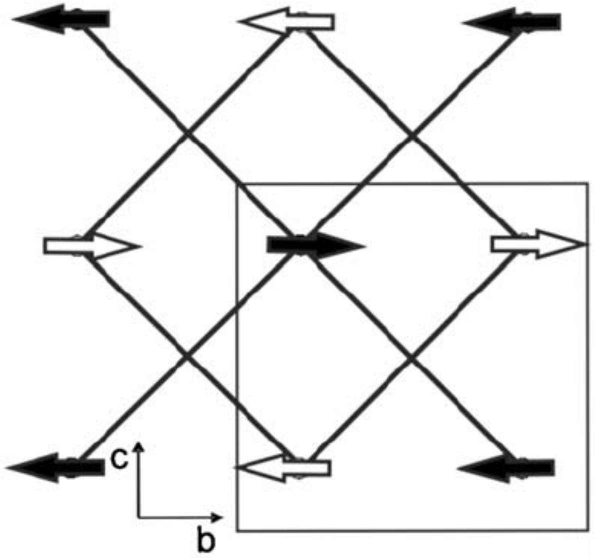


	1	2_b	$\bar{1}$	m_{ac}
Γ_1	1	1	1	1
Γ_2	1	1	−1	−1
Γ_3	1	−1	1	−1
Γ_4	1	−1	−1	1



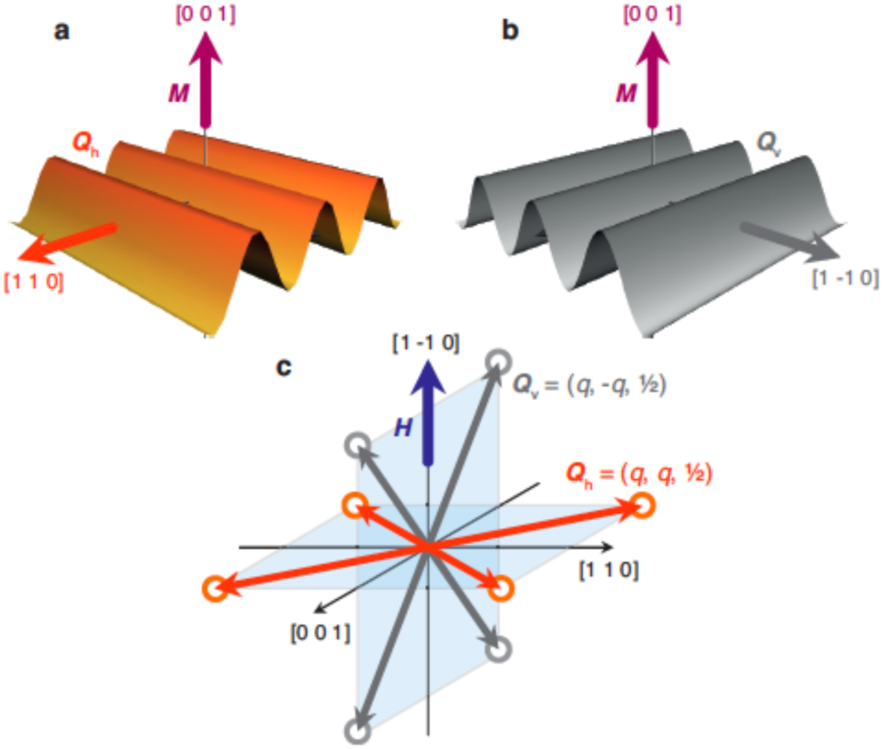
		r_1	r_2
Γ_1	$\vec{\phi}_1$	(0 1 0)	(0 1 0)
Γ_2	$\vec{\phi}_2$	(0 1 0)	(0 −1 0)
Γ_3	$\vec{\phi}_3$	(1 0 0)	(1 0 0)
	$\vec{\phi}_4$	(0 0 1)	(0 0 1)
Γ_4	$\vec{\phi}_5$	(1 0 0)	(−1 0 0)
	$\vec{\phi}_6$	(0 0 1)	(0 0 −1)



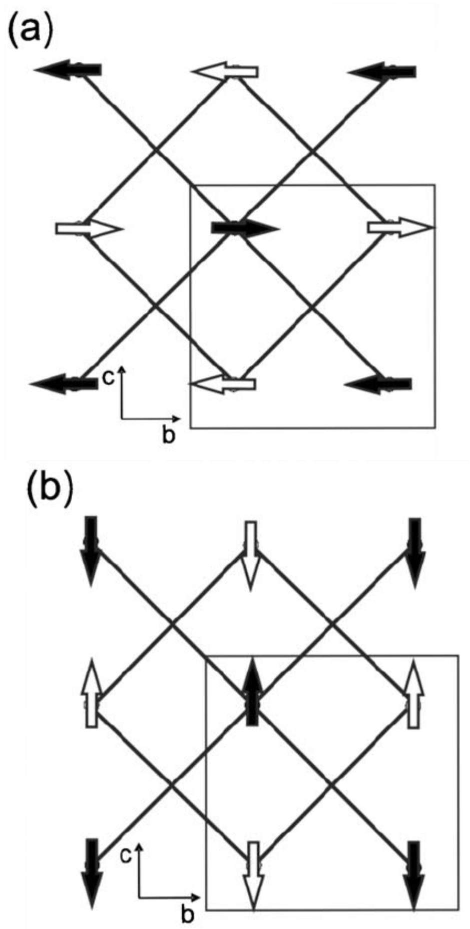


Magnetic domains

Q-domains



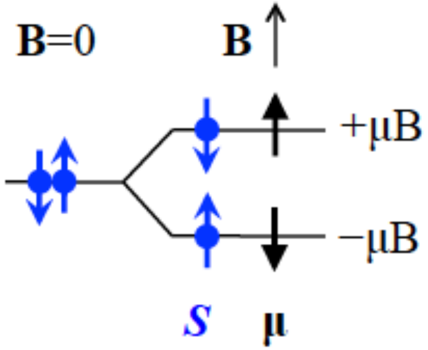
Domains of moment orientation



Polarized diffraction

Polarization $\mathbf{P} = 2\langle \mathbf{S} \rangle$

$$\mathrm{P} = \frac{n_\uparrow - n_\downarrow}{n_\uparrow + n_\downarrow}$$



$\hbar\omega_L = 2\mu\mathrm{B}$

$$b_l = A_l + B_l \boldsymbol{\sigma} \cdot \mathbf{I}_l$$

Nuclear scattering (plus nuclear magn.)

$$-\gamma r_e \boldsymbol{\sigma} \cdot \mathbf{M}_\perp$$

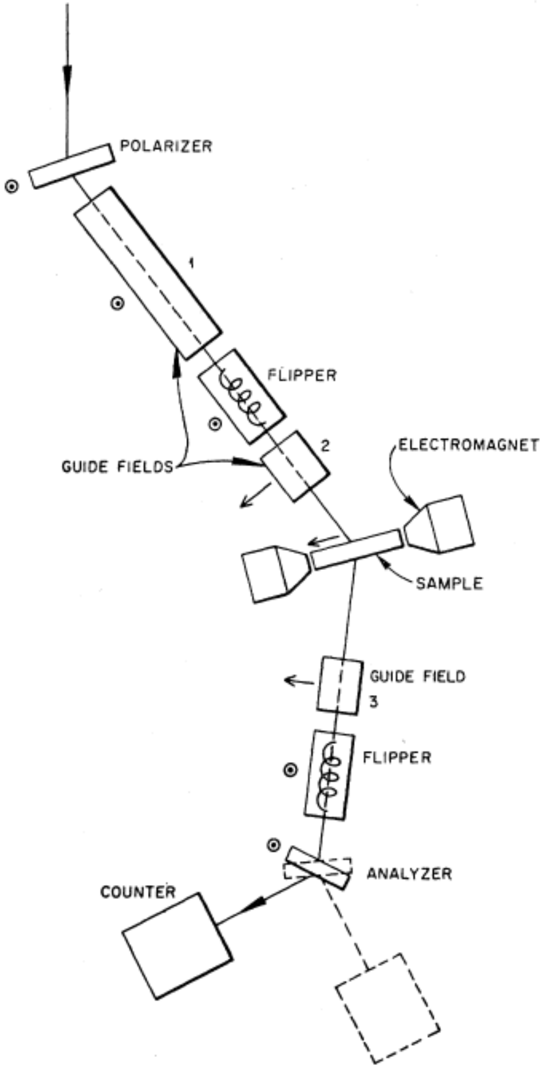
In case of electronic magnetism

u: spin up
v: spin down

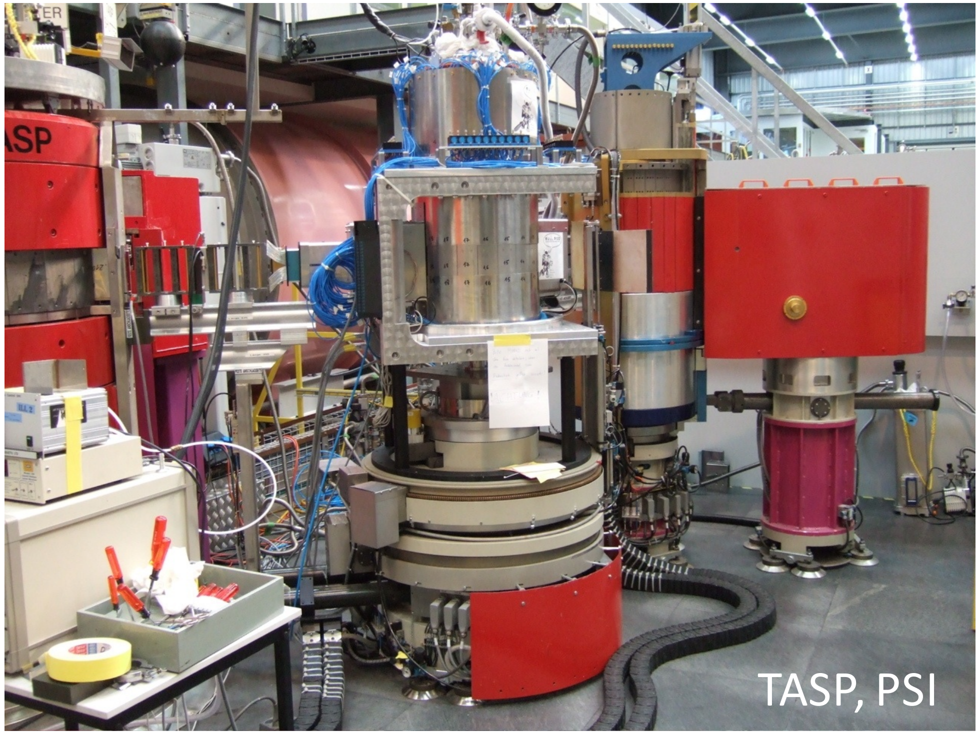
different spin-dependent cross-sections
(longitudinal polarization experiments)

$$u \to u,\ v \to v,\ u \to v,\ v \to r$$

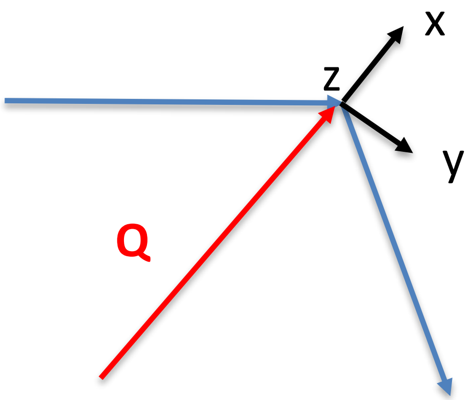
Instrumentation of polarized scattering



Moon et al, Phys. Rev. **181**, 920 (1968)

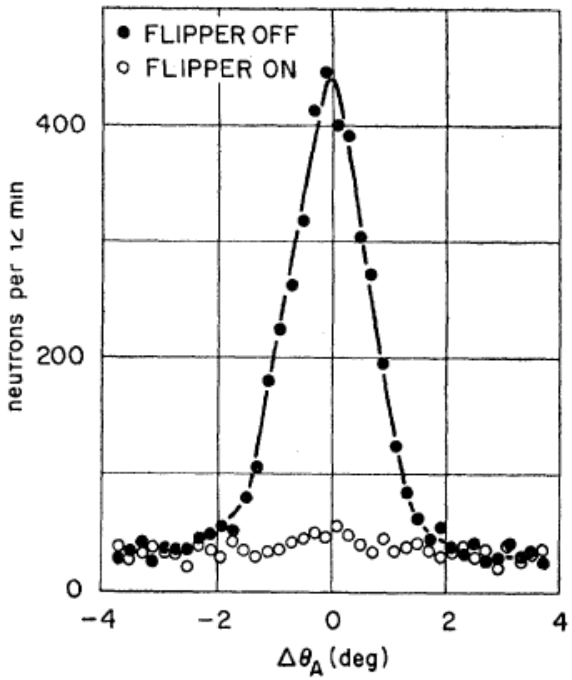


Polarized magnetic diffraction



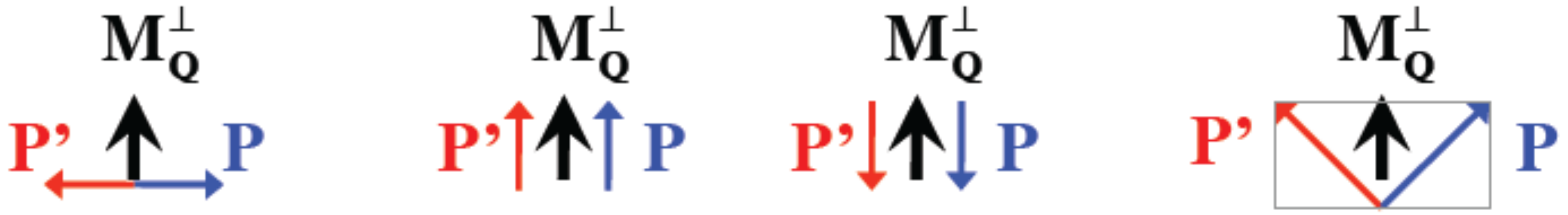
x-axis parallel to **Q**
y-axis perpendicular to **Q**
z-axis perpendicular to scattering plane

neutron polarization along z



Moon et al, Phys. Rev. **181**, 920 (1968)

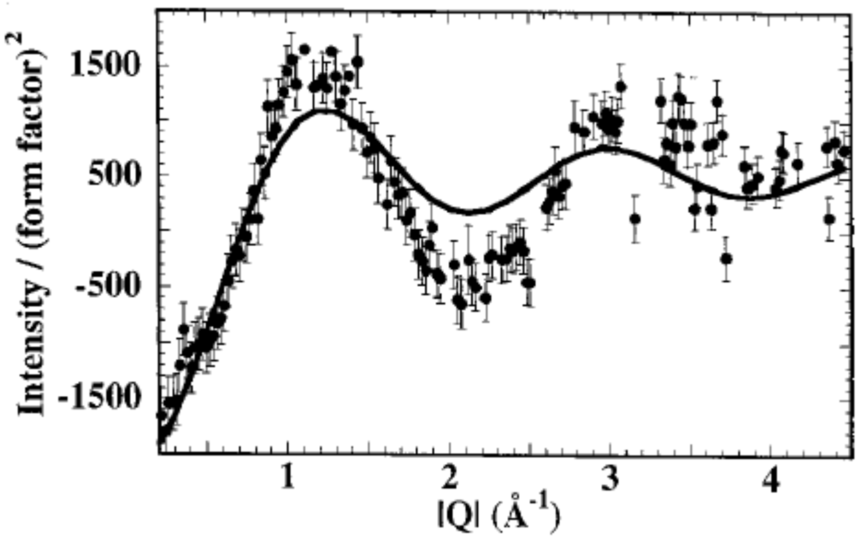
$$\begin{aligned} \langle + |\, \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{M}}^{\perp}_{\mathbf{Q}} | + \rangle &= \mathbf{M}^{\perp}_{z,\mathbf{Q}} \\ \langle - |\, \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{M}}^{\perp}_{\mathbf{Q}} | + \rangle &= \mathrm{i}\mathbf{M}^{\perp}_{y,\mathbf{Q}} \end{aligned}$$



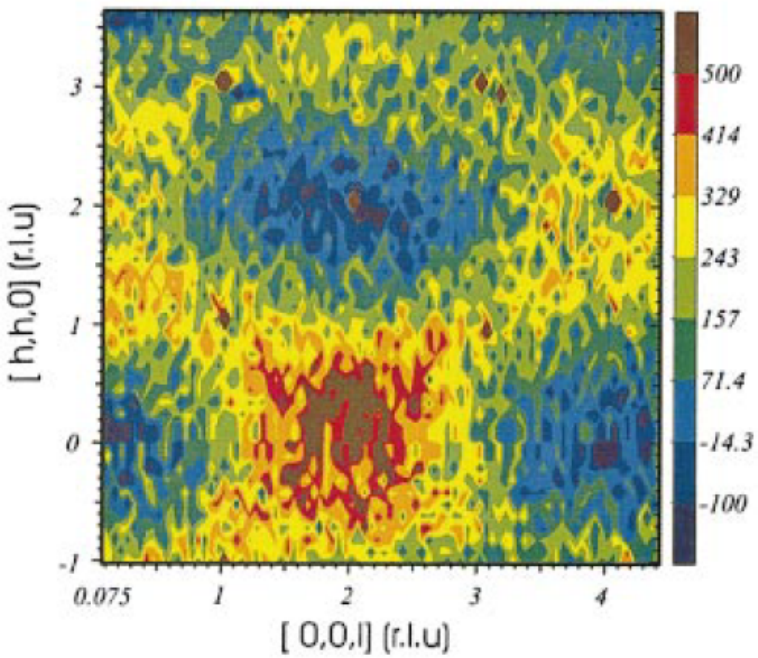
Example: $Tb_2Ti_2O_7$

Diffuse scattering from short range correlations (even at T~50mK)

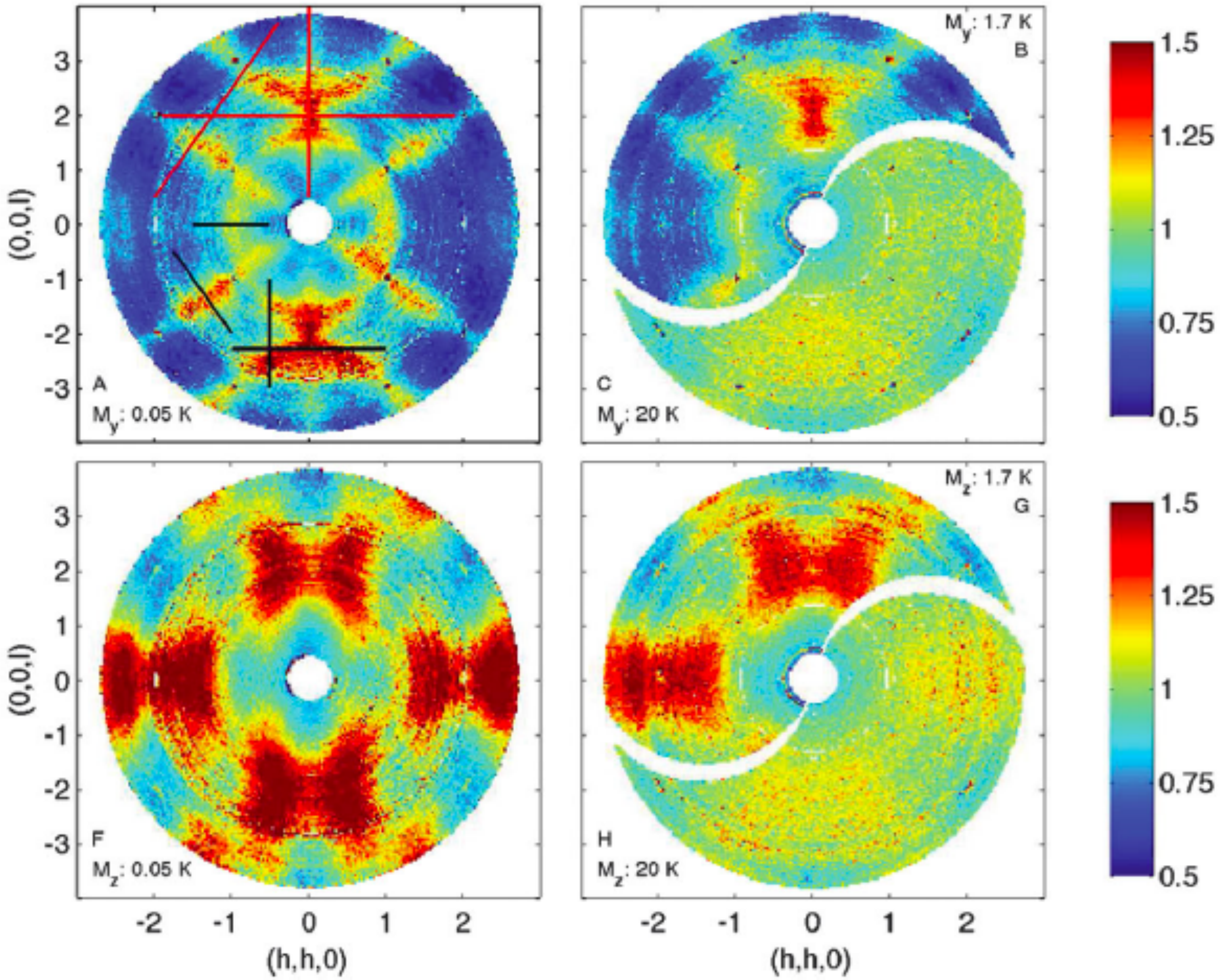
Broad scattering as a function of wave-vector → no long range order



J. Gardner et al, Phys. Rev. B 64, 224416 (2001).



Polarized measurement of diffuse scattering



Fennell et al, Phys. Rev. Lett. **109**, 017201 (2012).

M_y: spin-flip scattering
M_z: non spin-flip scattering