Neutron diffraction of magnetic materials

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- Inelastic scattering measures the forces between magnetic moments (i.e. the strength of the exchange interactions).

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- This moment is 1000 times smaller than the magnetic moment of an electron ($1\ \mu_B = 9.27 \times 10^{-24}\ Am^2$).

Magnetic moment of an atom

A free atom has both a spin and an orbital contribution to its magnetic moment.

$$\mu_S = 2\sqrt{S(S+1)}\mu_B$$

$$\mu_L = \sqrt{L(L+1)}\mu_B$$

The total moment is defined by the quantum number J, where $J = |L-S|$ for atoms with electron shells that are less than half filled and $J = |L+S|$ for electron shells that are more than half filled.

$$\mu_J = g\sqrt{J(J+1)}\mu_B$$

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

In a material with ordered magnetic moments, the projection, M_J, of J in a given direction of quantization takes one of $2J + 1$ states between $-J$ and $+J$.

$$\mu = gM_J\mu_B$$

Amplitude of magnetic scattering

The amplitude of magnetic scattering can be calculated theoretically by considering the dipole-dipole interaction between the neutron and the atomic moment (Halpern and Johnson 1939)

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$$p = \frac{\gamma}{2}\left(\frac{e^2}{mc^2}\right) = 0.2696 \times 10^{-12}\text{cm}$$

γ = neutron magnetic moment
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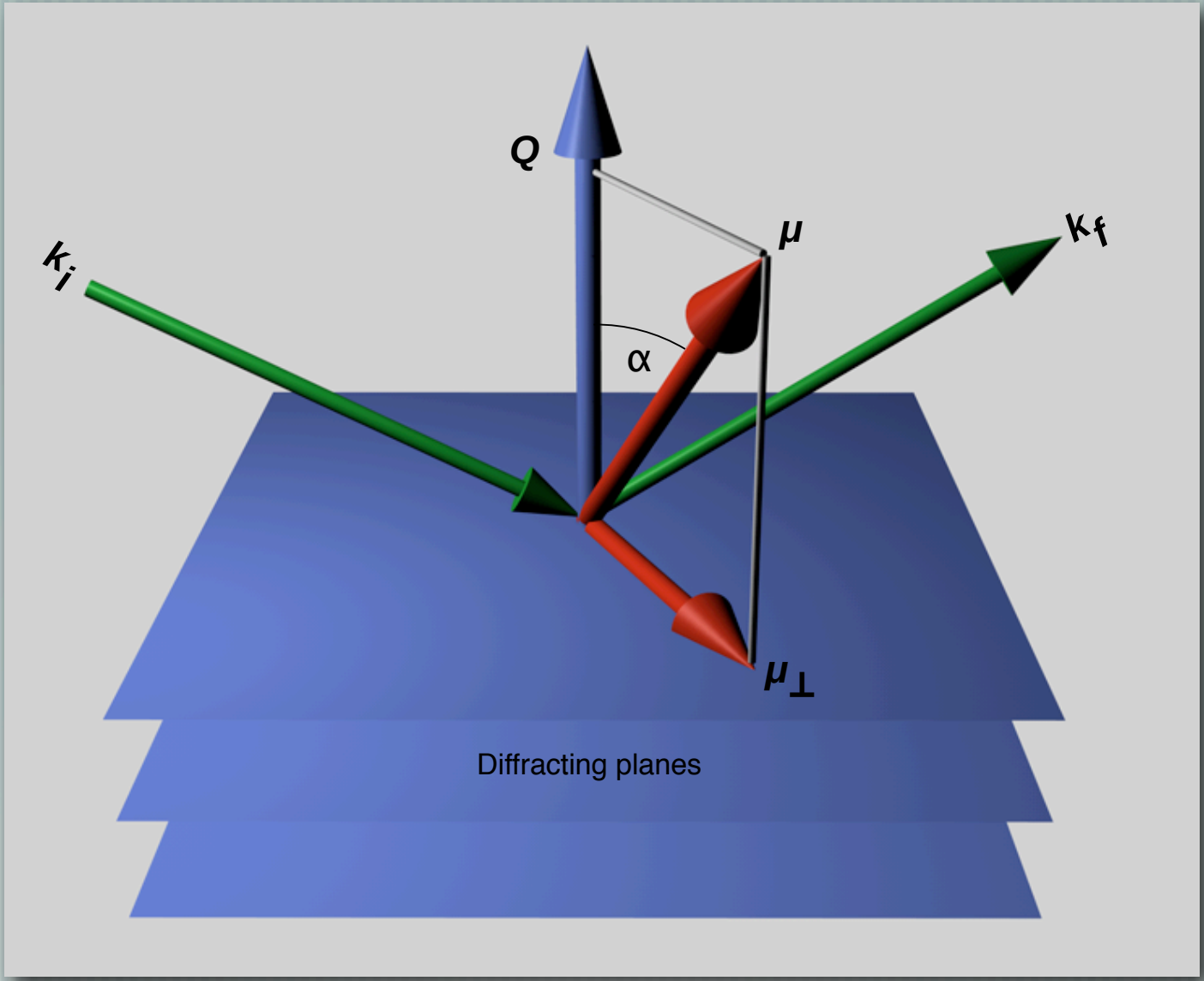
$$\boldsymbol{\mu}_\perp = \hat{\boldsymbol{Q}} \times \boldsymbol{\mu} \times \hat{\boldsymbol{Q}}$$

Component of
magnetic moment
perpendicular to $\boldsymbol{Q}$

Perpendicular component of μ



Magnetic form factors

Neutrons are scattered by the magnetization density of an atom. Since the magnetic moment originates from the electrons, interference between neutrons scattered from different parts of the electron cloud causes the amplitude of magnetic scattering to decrease with increasing Q.

$$f(\boldsymbol{Q}) = \langle j_0 \rangle + \left(\frac{g-2}{2}\right) \langle j_2 \rangle$$

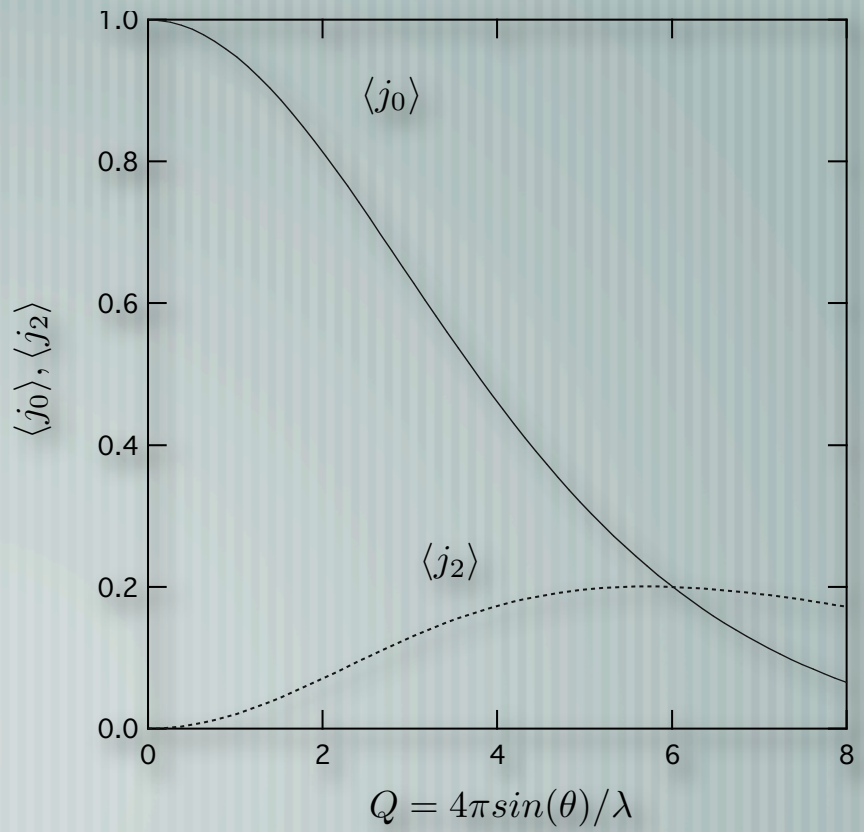
$$\langle j_0(s) \rangle = Ae^{-as^2} + Be^{-bs^2} + Ce^{-cs^2} + D$$

$$\langle j_2(s) \rangle = (Ae^{-as^2} + Be^{-bs^2} + Ce^{-cs^2} + D)s^2$$

$$s = \sin(\theta)/\lambda$$

A, B, C, D, a, b, c are constants that can be found at:

http://www.ill.fr/dif/ccsl/ffacts/ffachtml.html



Comparison of nuclear and magnetic scattering

Table 1.			Magnetic scattering amplitude p (10^{-12} cm)	
Atom or ion	Nuclear scattering amplitude b (10^{-12} cm)	Effective spin quantum number S	$\theta = 0$	$\sin\theta/\lambda = 0.25$ Å^{-1}
Cr^{2+}	0.35	2	1.08	0.45
Mn^{2+}	-0.37	5/2	1.35	0.57
Fe (metal)	0.96	1.11	0.6	0.35
Fe^{2+}	0.96	2	1.08	0.45
Fe^{3+}	0.96	5/2	1.35	0.57
Co (metal)	0.28	0.87	0.47	0.27
Co^{2+}	0.28	2.2	1.21	0.51
Ni (metal)	1.03	0.3	0.16	0.1
Ni^{2+}	1.03	1.0	0.54	0.23

Magnetic structure factor

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$$\boldsymbol{M}(\boldsymbol{Q}) = p \sum_{j=1}^{n_m} f_j(\boldsymbol{Q}) \boldsymbol{\mu}_j e^{i \boldsymbol{Q} \cdot \boldsymbol{r}_j}$$

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Magnetic interaction vector (component of M perpendicular to Q)

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Magnetic intensity

$$I_M(\boldsymbol{Q}) = \boldsymbol{M}_\perp(\boldsymbol{Q}) \cdot \boldsymbol{M}_\perp^*(\boldsymbol{Q})$$

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For simple structures, intensity is proportional to $\sin^2(\alpha)$

$$M_\perp^2(\boldsymbol{Q}) = \sin^2(\alpha) M(\boldsymbol{Q})^2$$

Domain and Powder Averaging

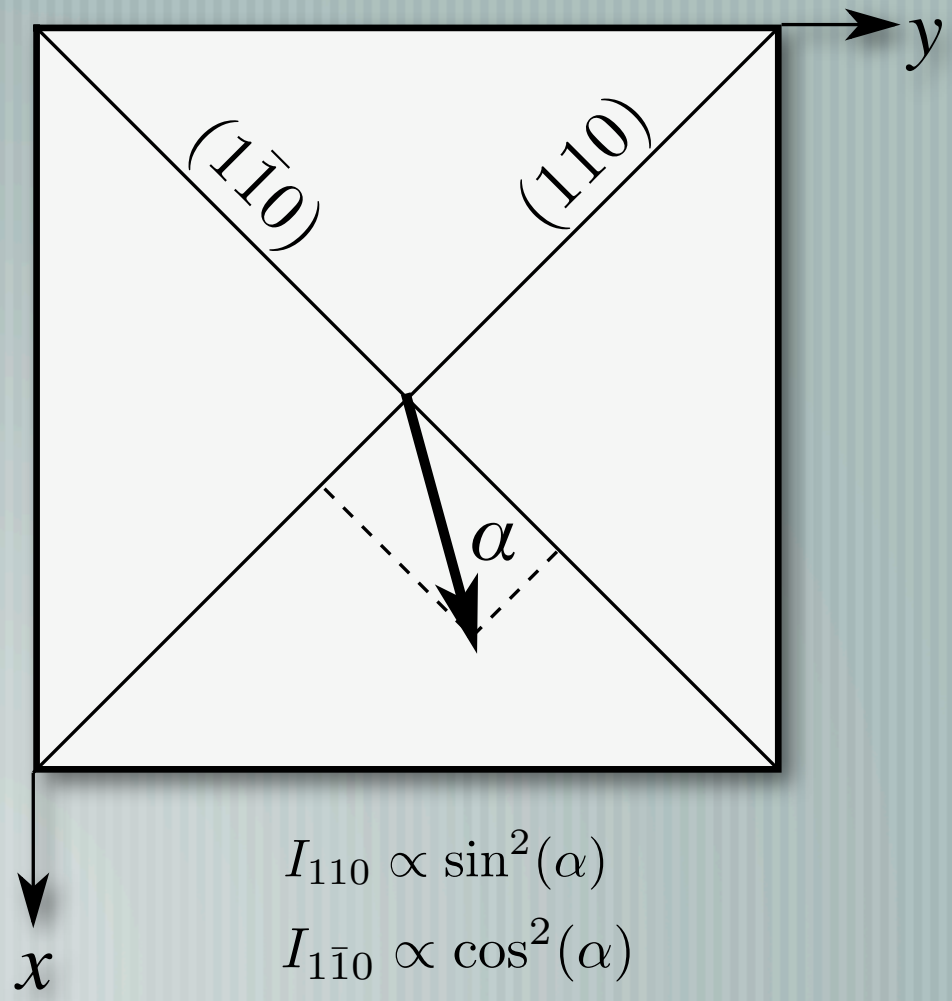
In a powder diffraction pattern, all symmetry related planes contribute to the intensity of a given peak. This can limit the amount of information that can be obtained about the orientation of magnetic moments.

For cubic symmetry:

$$< \sin^2(\alpha) >= 2/3$$

No orientation information can be obtained!

For tetragonal, hexagonal, trigonal symmetry, only the angle between the moments and the z axis can be determined.



$$I_{110} \propto \sin^2(\alpha)$$

$$I_{1\bar{1}0} \propto \cos^2(\alpha)$$

$$I_{tot} \propto \sin^2(\alpha) + \cos^2(\alpha) = 1$$

Classification and description of magnetic structures

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- It is essential to have a good grasp of this formalism before attempting to solve or refine magnetic structures.
- Most Rietvelt refinement programs use this formalism to describe and refine magnetic structures.

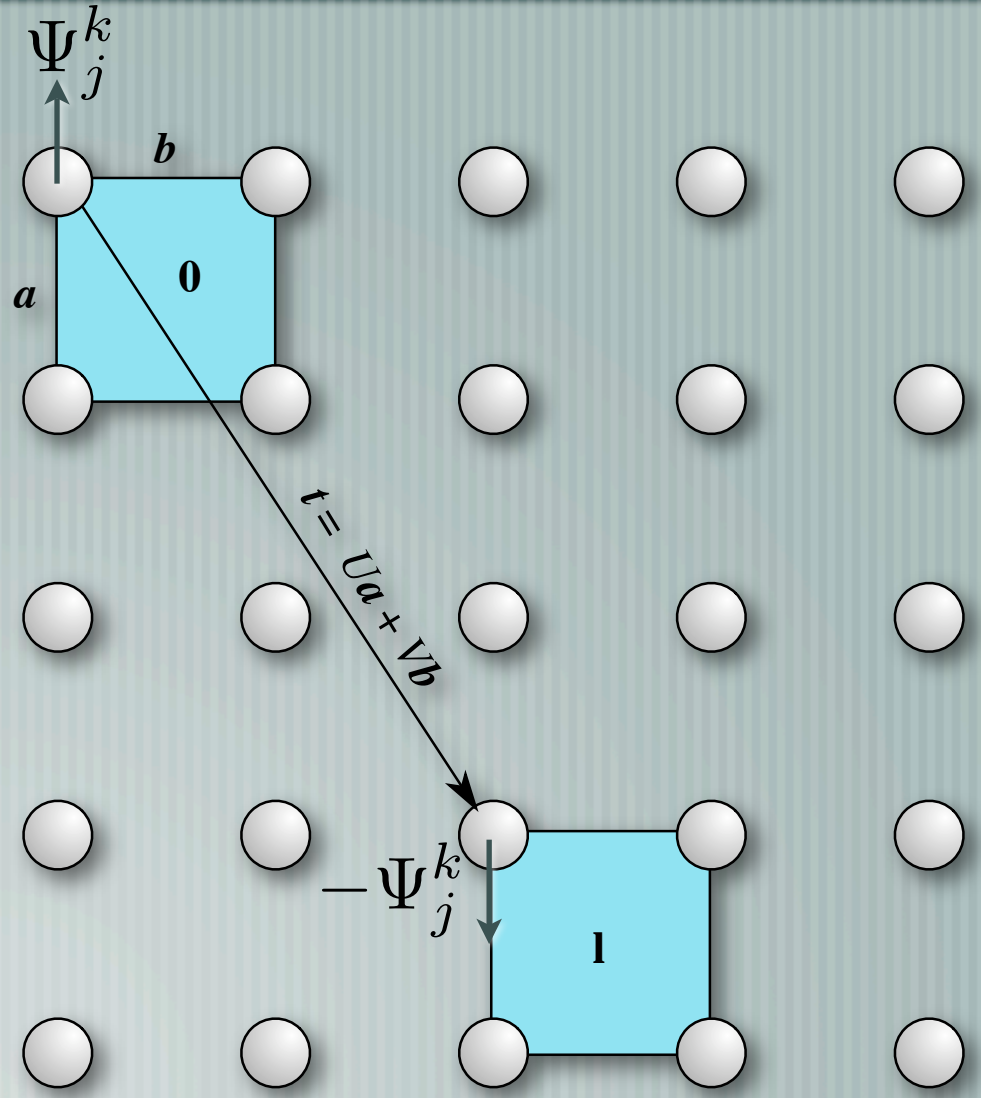
Basis vectors and propagation vectors

A basis vector is used to specify the magnetic moment on atom *j* in the 'zeroth' nuclear unit cell.

$$\boldsymbol{\Psi}_j^{\boldsymbol{k}} = [u, v, w] + i[u', v', w']$$

The magnetic moment on atom *j* within unit cell '*l*' is related to that in the 'zeroth' unit cell via a propagation vector, *k*, in reciprocal space, and the lattice vector, *t*:

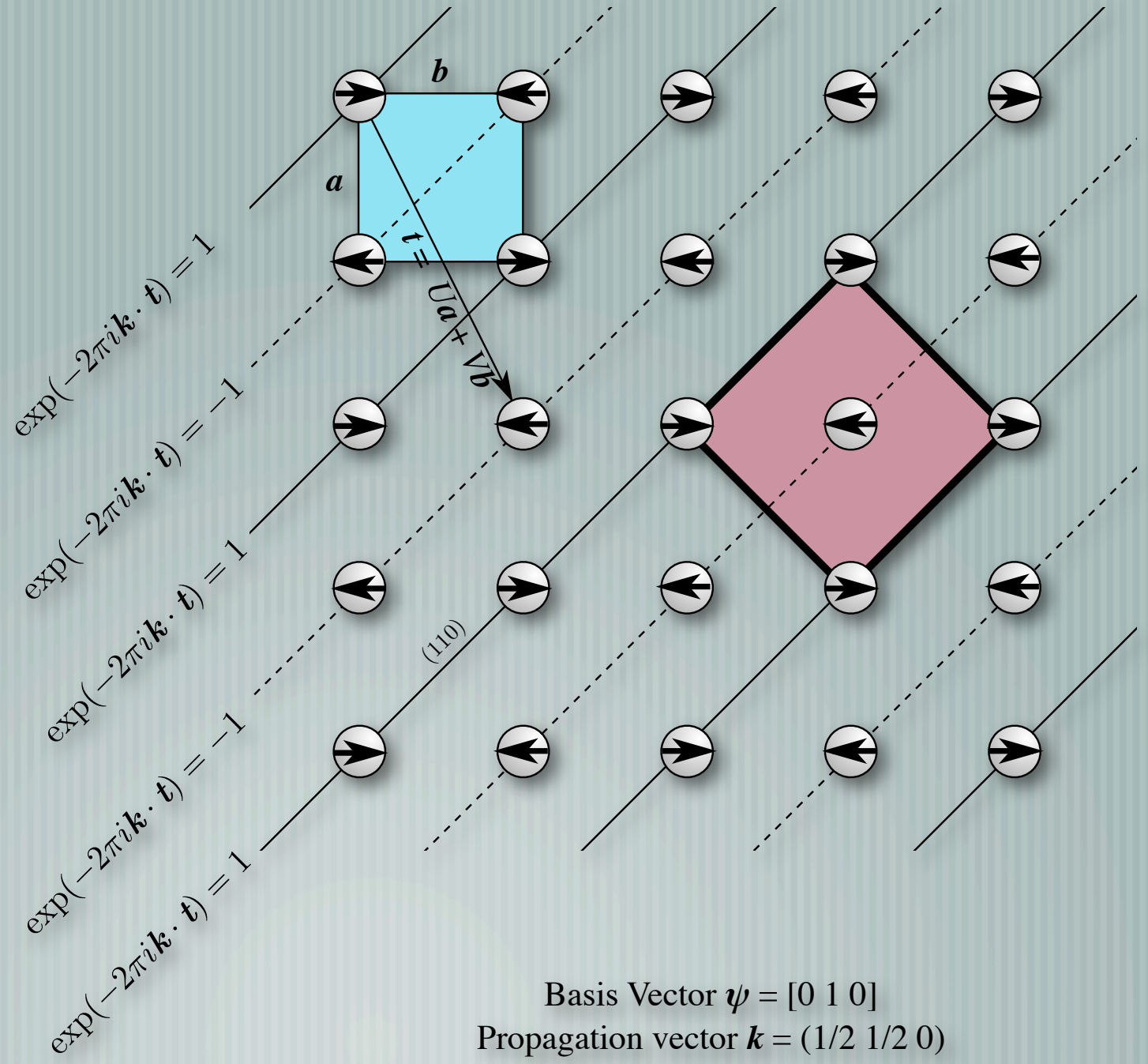
$$\boldsymbol{\mu}_{jl} = \boldsymbol{\Psi}_j^{\boldsymbol{k}} e^{-2\pi i \boldsymbol{k}\cdot\boldsymbol{t}}$$



For k = 0, the magnetic unit cell is the same size and shape as the nuclear unit cell.

For $k \neq 0$, the magnetic unit cell is larger than the nuclear unit cell.

e.g. for k = (0.5 0.5 0), periodicity of the structure normal to (110) is doubled.



Basis Vector ψ = [0 1 0]
Propagation vector k = (1/2 1/2 0)

Complex magnetic structures

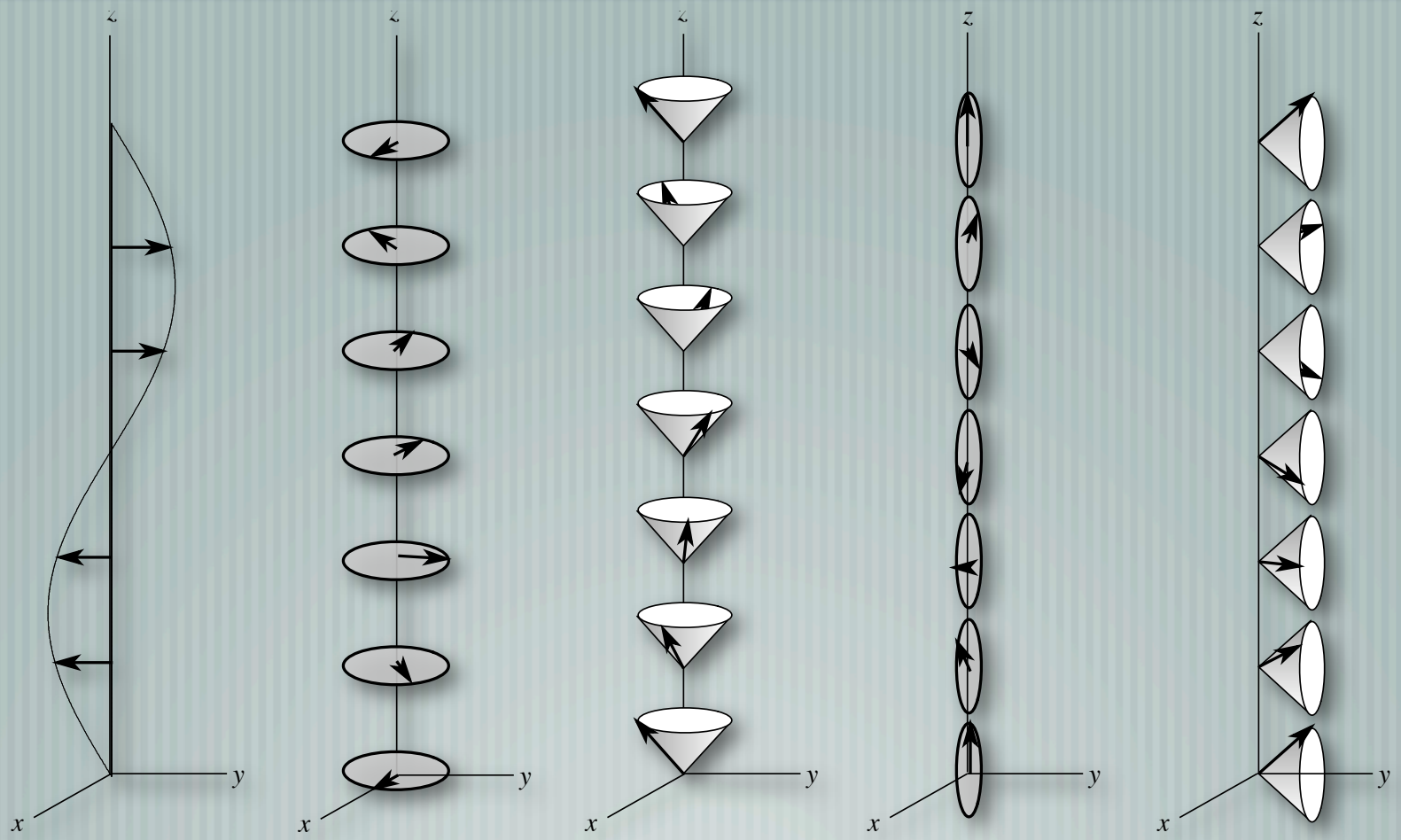
If the basis vectors are complex, the magnetic structure must be described as the sum of +*k* and -*k* components, so that the magnetic moment on each atom is real.

$$\boldsymbol{\mu}_{jl} = \boldsymbol{\Psi}_j^{\boldsymbol{k}}[\cos(-2\pi\boldsymbol{k}\cdot\boldsymbol{t}) + i\sin(-2\pi\boldsymbol{k}\cdot\boldsymbol{t})] + \boldsymbol{\Psi}_j^{\boldsymbol{-k}}[\cos(2\pi\boldsymbol{k}\cdot\boldsymbol{t}) + i\sin(2\pi\boldsymbol{k}\cdot\boldsymbol{t})]$$

$$\boldsymbol{\Psi}_j^{\boldsymbol{-k}} = \boldsymbol{\Psi}_j^{\boldsymbol{k}*} = [u, v, w] - i[u', v', w']$$

$$\boldsymbol{\mu}_{jl} = 2[u, v, w]\cos(-2\pi\boldsymbol{k}\cdot\boldsymbol{t}) + 2[u', v', w']\sin(-2\pi\boldsymbol{k}\cdot\boldsymbol{t})$$

Helical structures



(a) Sinusoidal (b) Screw Spiral (c) Conical Spiral (d) Cycloidal Spiral (e) Conical Cycloid

$$\boldsymbol{\mu}_{jl} = 2[1,0,0]\cos(-2\pi \boldsymbol{k}\cdot\boldsymbol{t}) + 2[0,1,0]\sin(-2\pi \boldsymbol{k}\cdot\boldsymbol{t})$$

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- Free software (e.g. BasIreps, SARAh) is available to do the hard work for you!
- Greatly simplifies the task of solving/refining magnetic structures using neutron diffraction.

Example: hematite (Fe_2O_3)

You need just 3 pieces of information to determine all possible magnetic structures:

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You need just 3 pieces of information to determine all possible magnetic structures:

1. Crystallographic space group of paramagnetic phase (R-3c)
2. Propagation vector ($k = 0$)
3. Wyckoff sites of magnetic atoms:

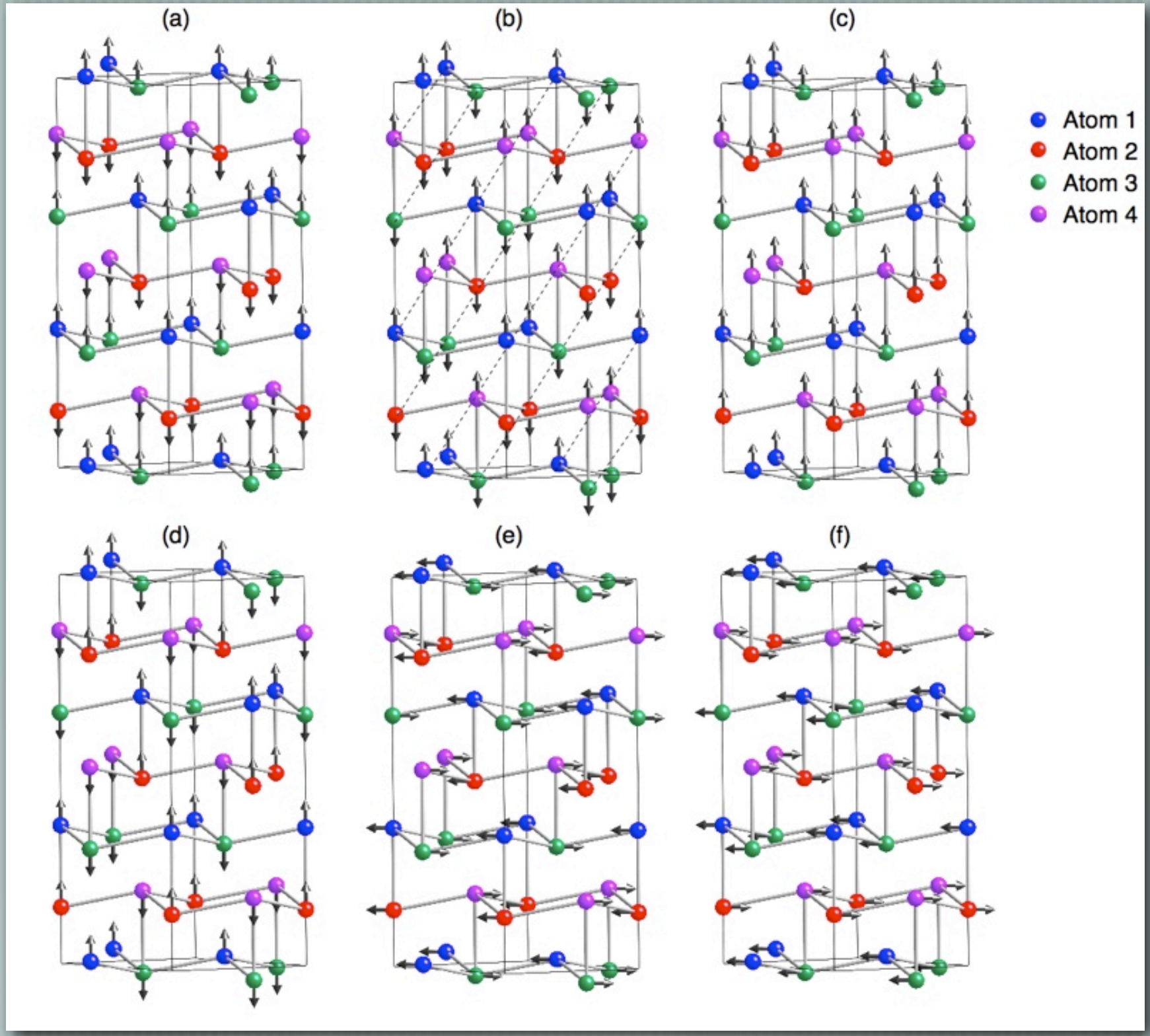
   Atom 1 at (0, 0, 0.3553)
   Atom 2 at (0, 0, 0.1447)
   Atom 3 at (0, 0, 0.6447)
   Atom 4 at (0, 0, 0.8553)

Permitted basis functions

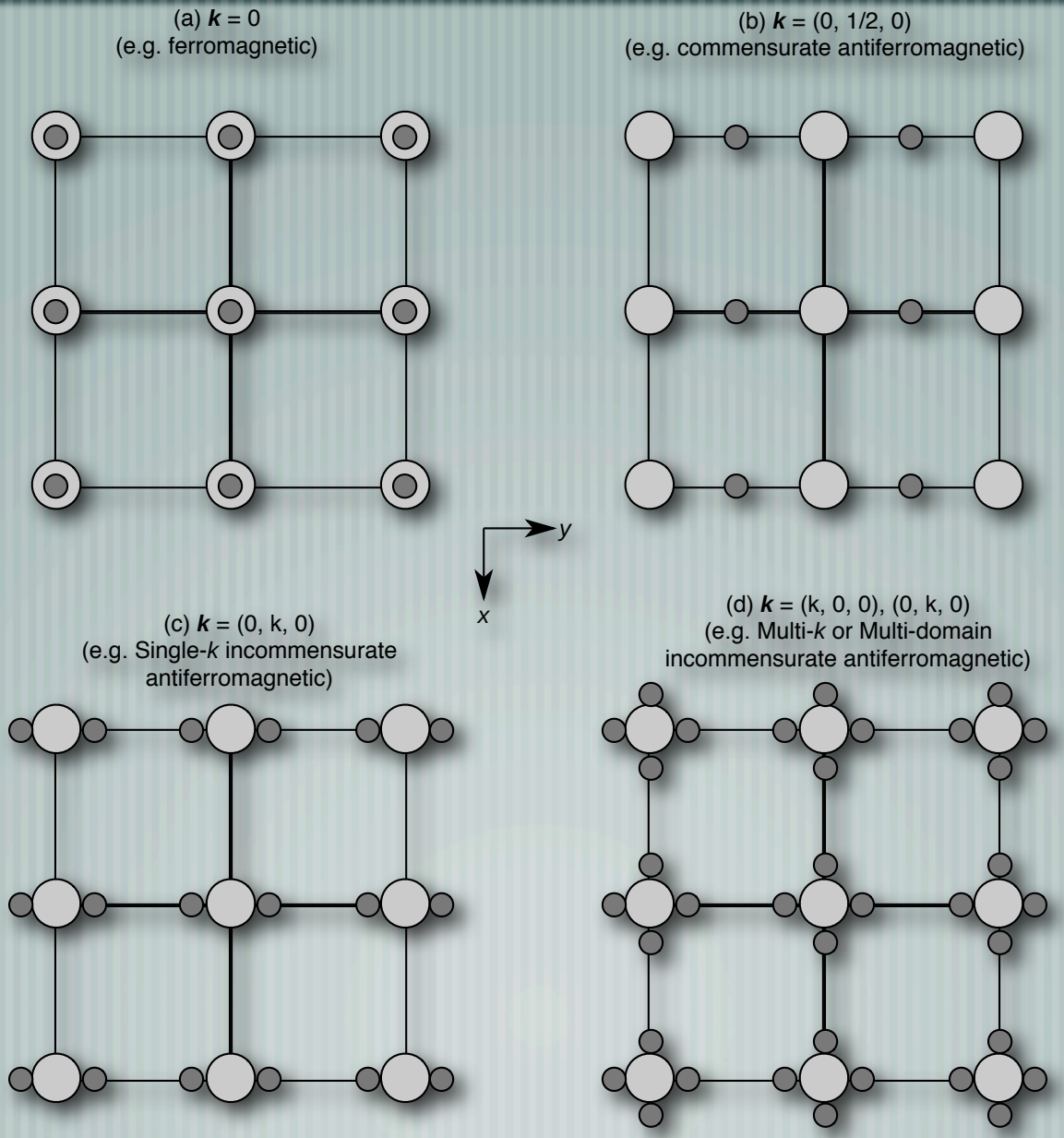
Magnetic ordering transition is driven by one irreducible representation (IR).

The magnetic structure is a linear combination of the permitted basis functions for the active IR.

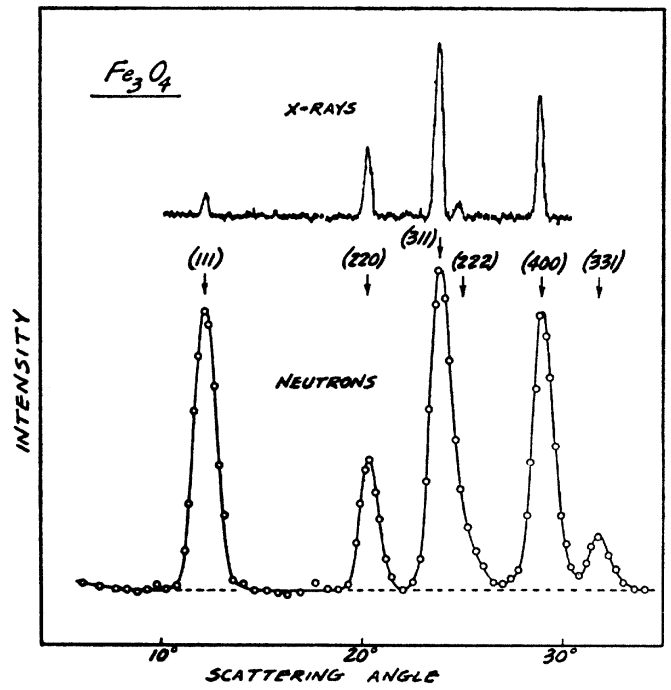
IR		Atom 1 (0, 0, 0.3553)	Atom 2 (0, 0, 0.1447)	Atom 3 (0, 0, 0.6447)	Atom 4 (0, 0, 0.8553)
Γ_1		[0 0 1]	[0 0 -1]	[0 0 1]	[0 0 -1]
Γ_2		[0 0 1]	[0 0 -1]	[0 0 -1]	[0 0 1]
Γ_3		[0 0 1]	[0 0 1]	[0 0 1]	[0 0 1]
Γ_4		[0 0 1]	[0 0 1]	[0 0 -1]	[0 0 -1]
Γ_5	ν_1	Re: [1.5 0 0] Im: [-0.87 -1.73 0]	Re: [0 0 0] Im: [0 0 0]	Re: [-1.5 0 0] Im: [0.87 1.73 0]	Re: [0 0 0] Im: [0 0 0]
	ν_2	Re: [0 1.5 0] Im: [1.73 0.87 0]	Re: [0 0 0] Im: [0 0 0]	Re: [0 -1.5 0] Im: [-1.73 -0.87 0]	Re: [0 0 0] Im: [0 0 0]
	ν_3	Re: [0 0 0] Im: [0 0 0]	Re: [0 1.5 0] Im: [1.73 0.87 0]	Re: [0 0 0] Im: [0 0 0]	Re: [0 -1.5 0] Im: [-1.73 -0.87 0]
	ν_4	Re: [0 0 0] Im: [0 0 0]	Re: [1.5 0 0] Im: [-0.87 -1.73 0]	Re: [0 0 0] Im: [0 0 0]	Re: [-1.5 0 0] Im: [0.87 1.73 0]
Γ_6	ν_1	Re: [1.5 0 0] Im: [-0.87 -1.73 0]	Re: [0 0 0] Im: [0 0 0]	Re: [1.5 0 0] Im: [-0.87 -1.73 0]	Re: [0 0 0] Im: [0 0 0]
	ν_2	Re: [0 1.5 0] Im: [1.73 0.87 0]	Re: [0 0 0] Im: [0 0 0]	Re: [0 1.5 0] Im: [1.73 0.87 0]	Re: [0 0 0] Im: [0 0 0]
	ν_3	Re: [0 0 0] Im: [0 0 0]	Re: [0 1.5 0] Im: [1.73 0.87 0]	Re: [0 0 0] Im: [0 0 0]	Re: [0 1.5 0] Im: [1.73 0.87 0]
	ν_4	Re: [0 0 0] Im: [0 0 0]	Re: [1.5 0 0] Im: [-0.87 -1.73 0]	Re: [0 0 0] Im: [0 0 0]	Re: [1.5 0 0] Im: [-0.87 -1.73 0]

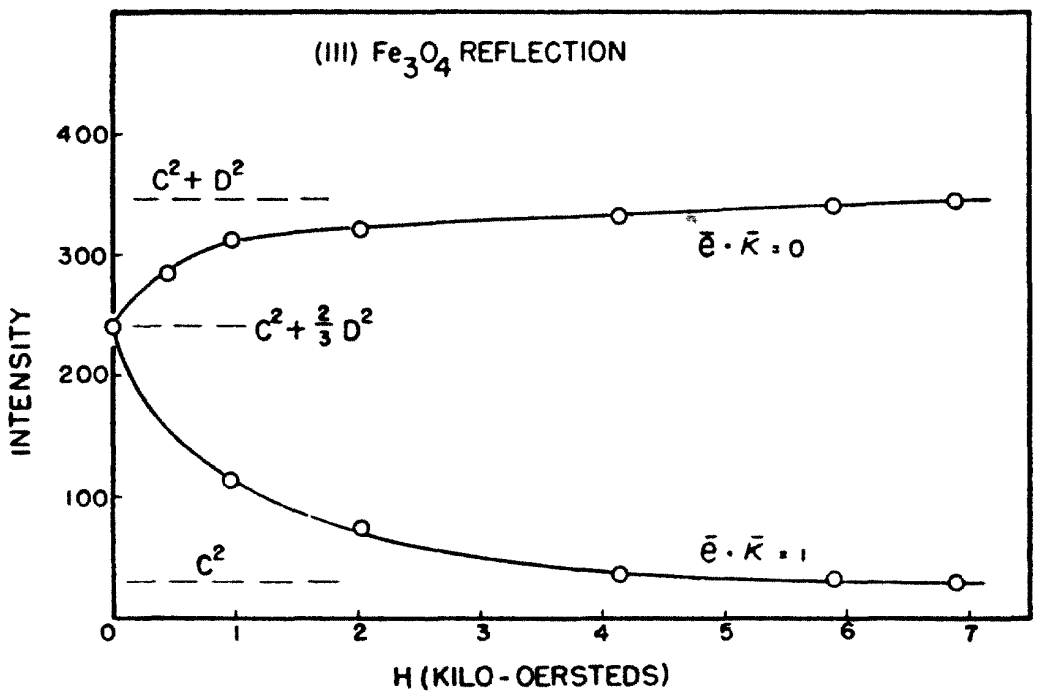

(a)
(b)
(c)
(d)
(e)
(f)
Atom 1
Atom 2
Atom 3
Atom 4

Magnetic neutron diffraction patterns

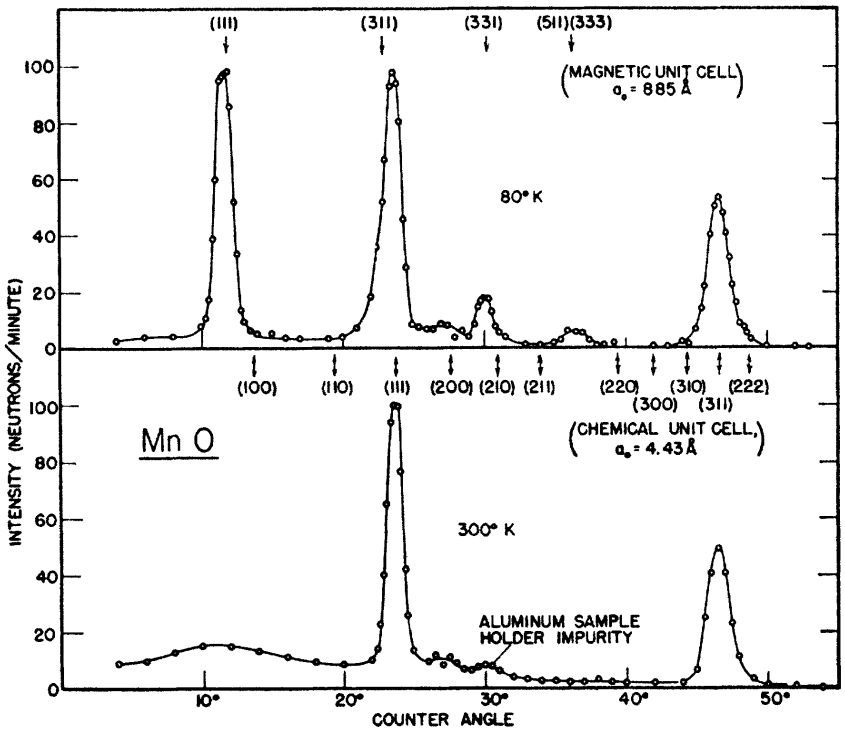


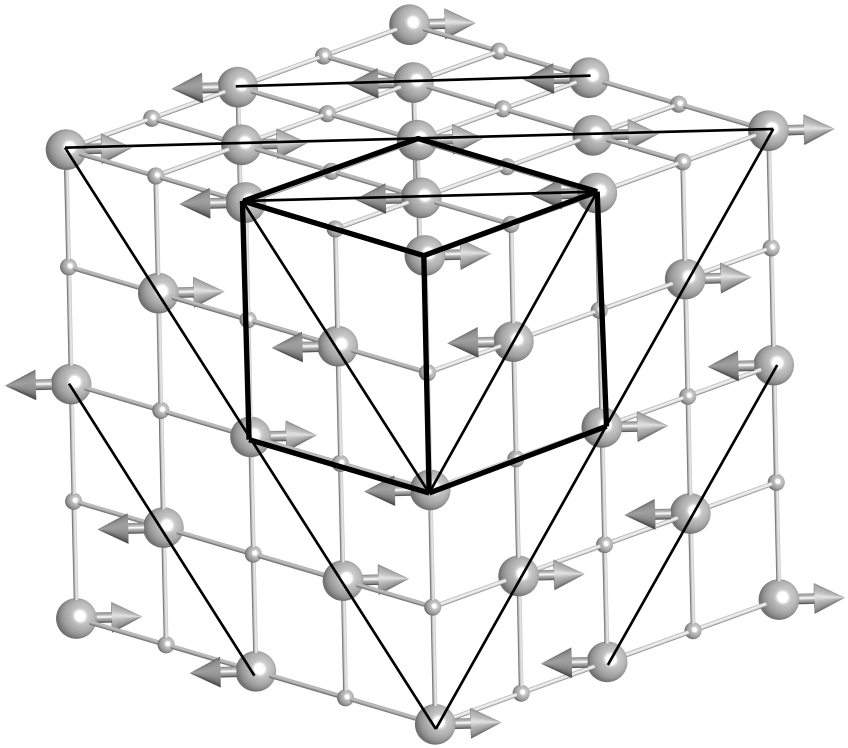
Example: Magnetite ($k = 0$)



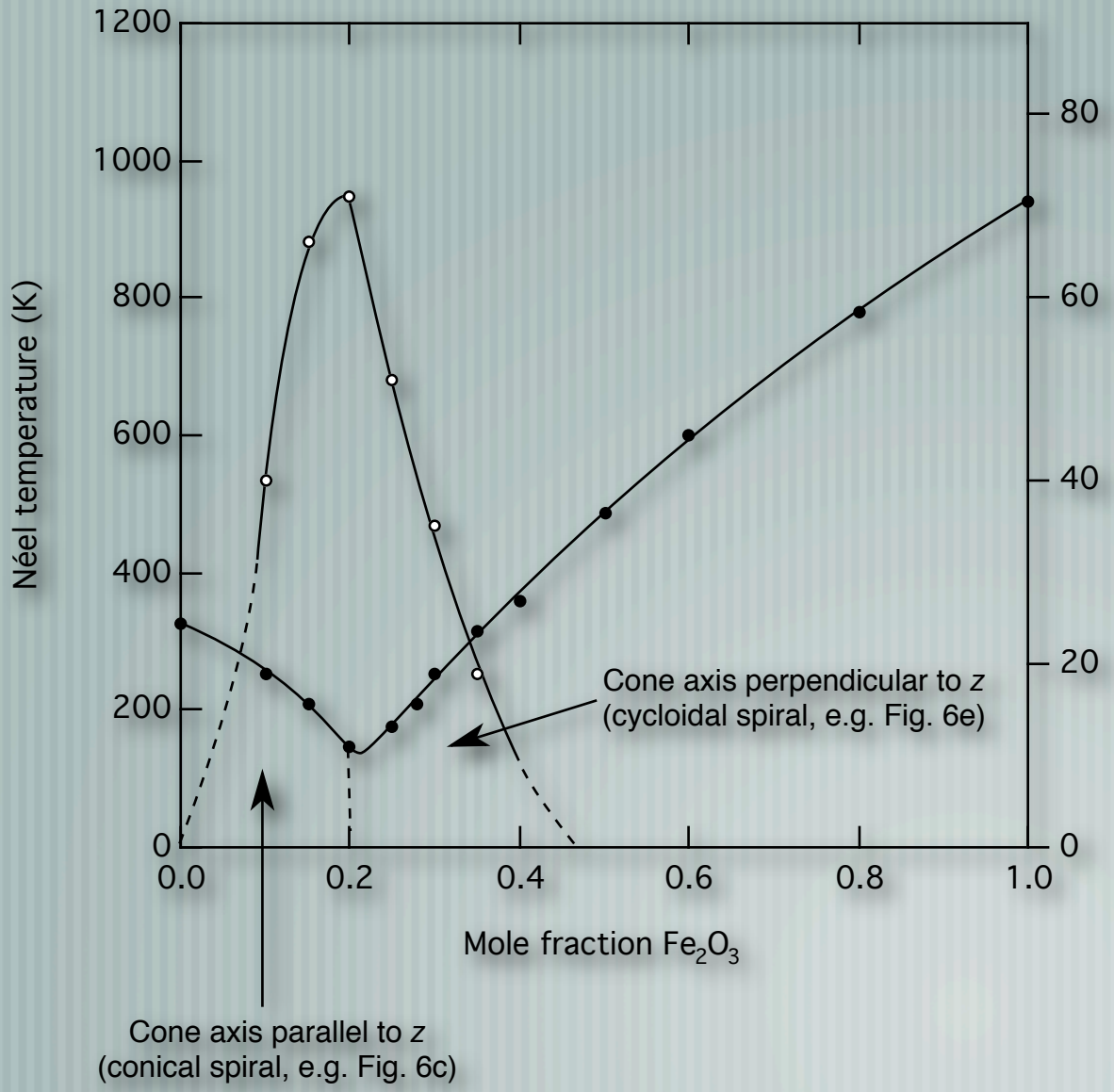


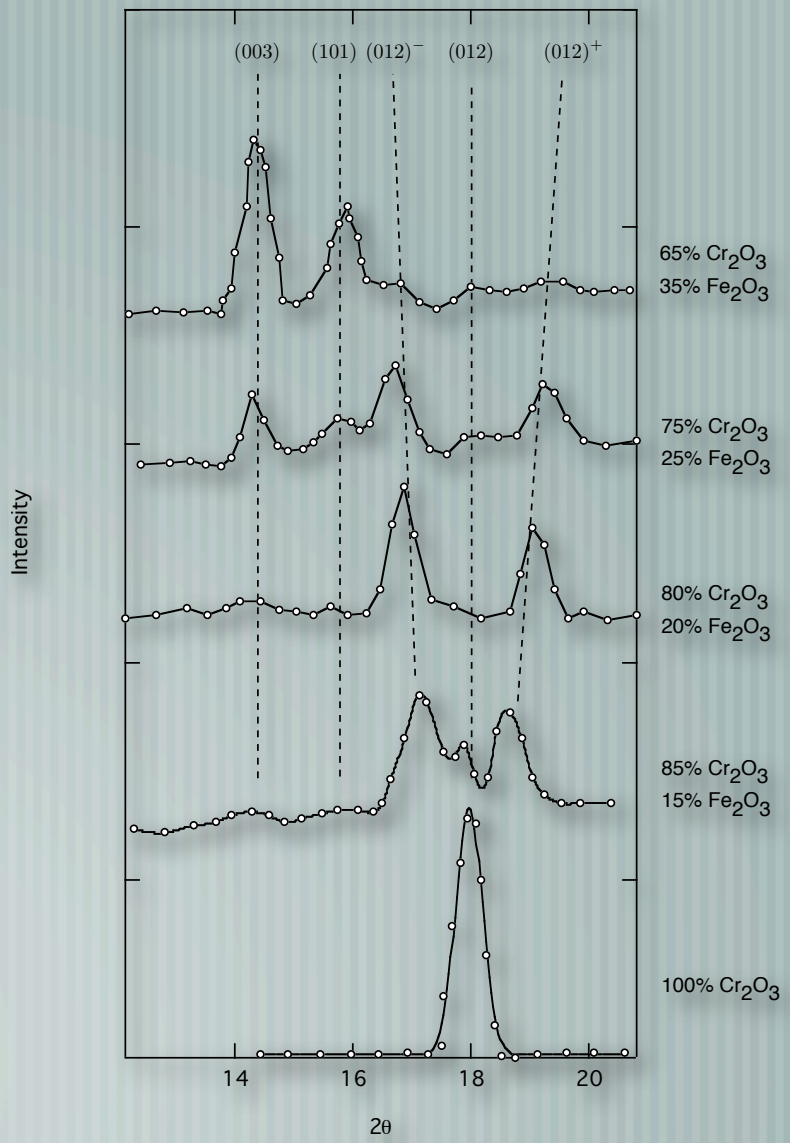
Example: MnO k = (.5 .5 .5)





Example: Cr_2O_3-Fe_2O_3 ($k \neq 0$)





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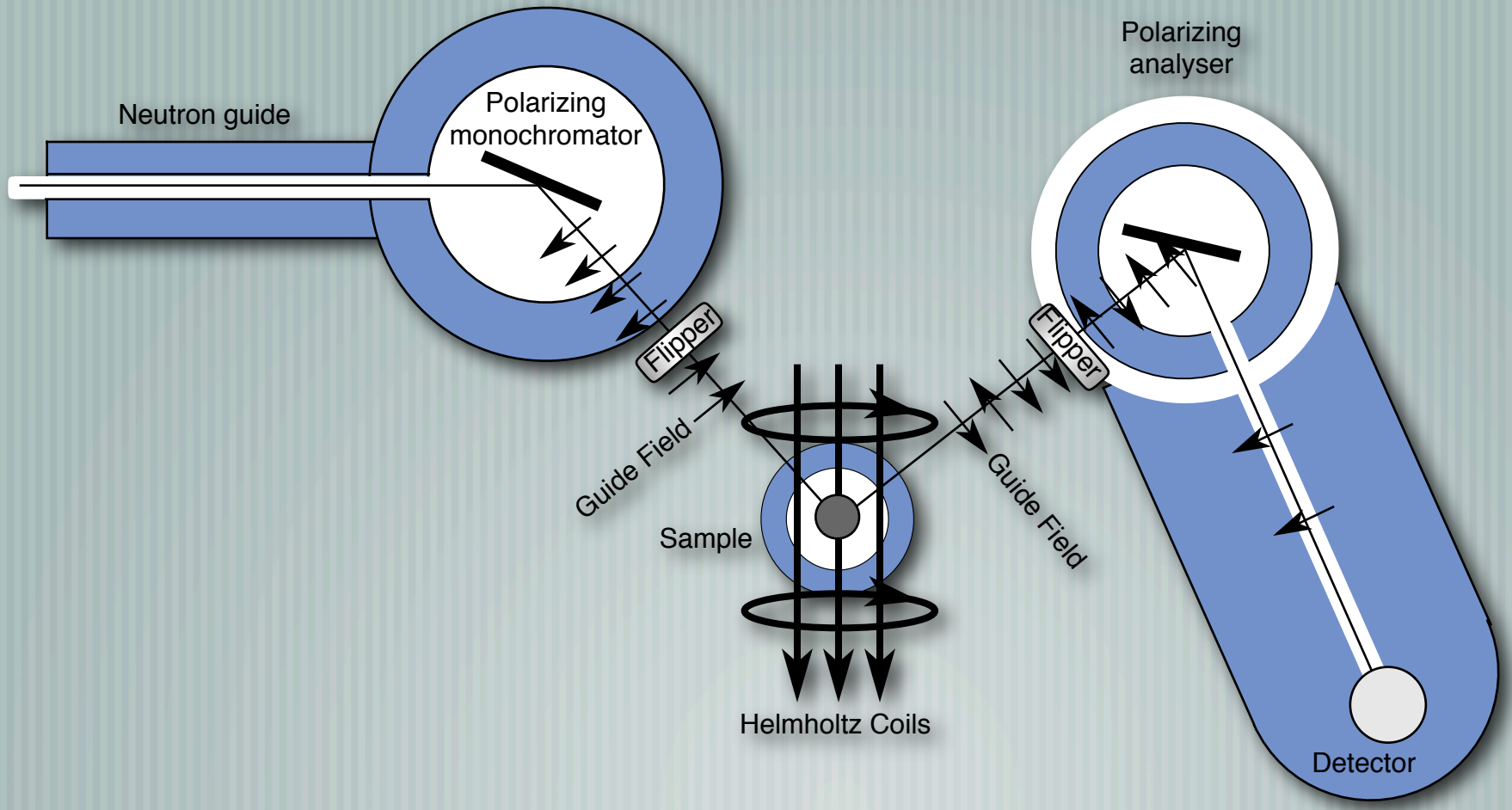
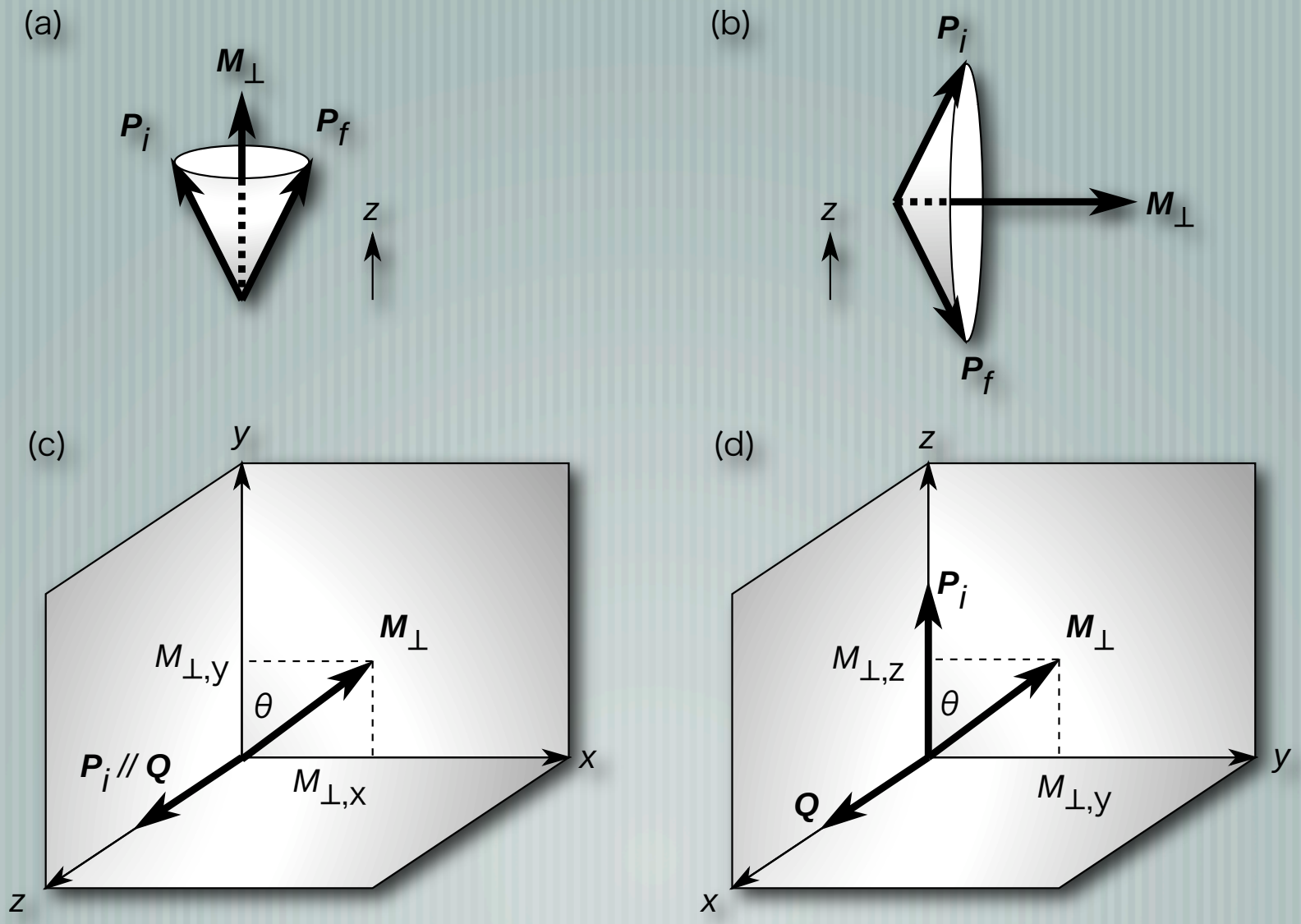
- Limited orientational information due to domain or powder averaging for certain symmetries.
- Some structures cannot be resolved unambiguously using unpolarised neutrons.

Experimental Setup



Spin flip (sf) and non spin flip (nsf)



Spin flip (sf) and non spin flip (nsf)

Incident spin \ Diffracted spin	$\uparrow$	$\downarrow$
$\uparrow$	$\sigma^{++} = \lvert F + M_{\perp,z}\rvert^2$	$\sigma^{+-} = \lvert M_{\perp,x} + iM_{\perp,y}\rvert^2$
$\downarrow$	$\sigma^{-+} = \lvert M_{\perp,x} - iM_{\perp,y}\rvert^2$	$\sigma^{--} = \lvert F - M_{\perp,z}\rvert^2$

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- Structure solution/refinement is made easy using the basis vector/ propagation vector formalism.
- Representational analysis can be used to predict the possible range of magnetic structures.
- There are limits to the information that can be obtained using unpolarised neutrons and powdered samples.
- Most of these can be overcome using polarisation analysis.

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