Neutrons and Magnetic Excitations

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Introduction

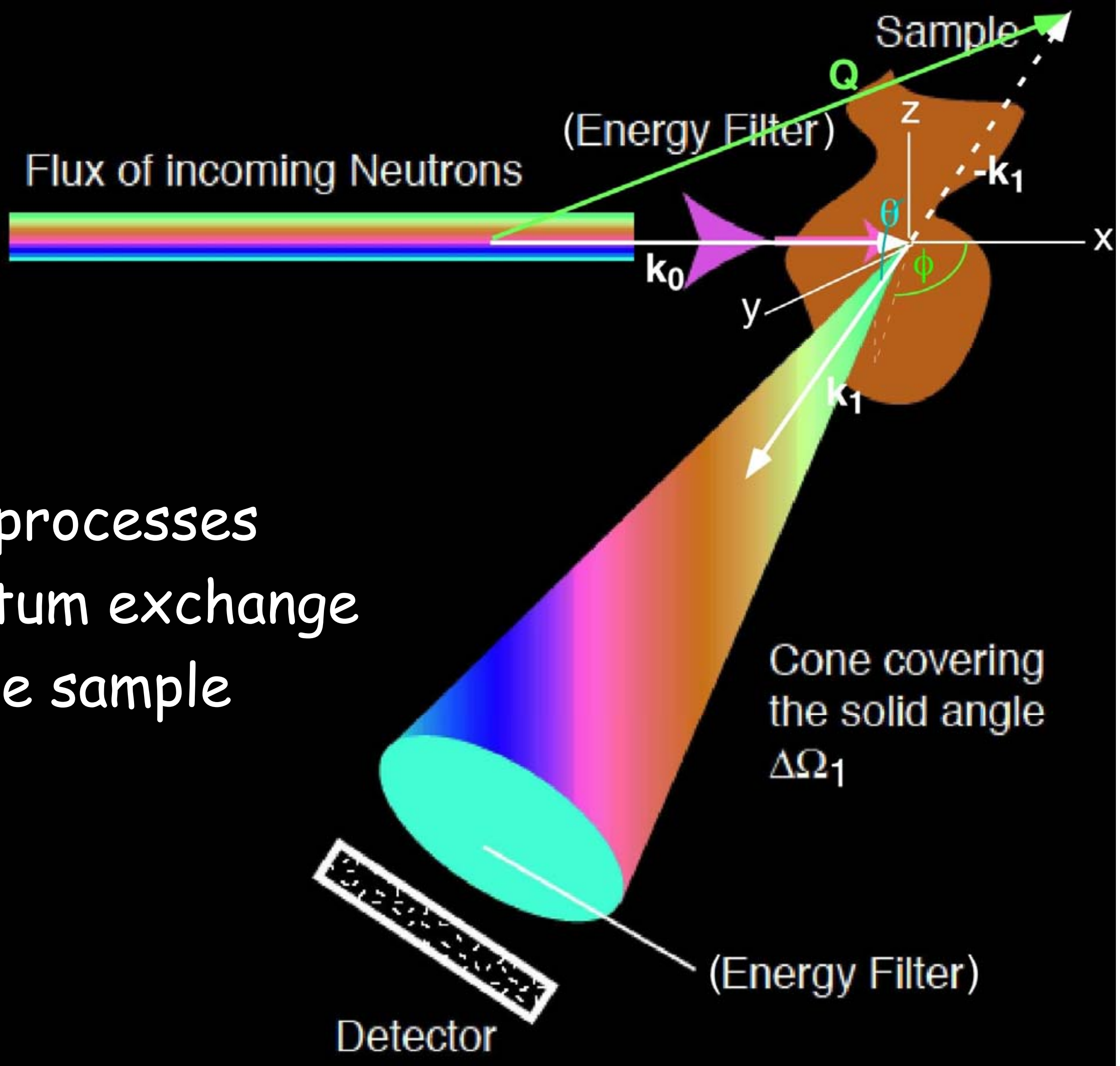
$$E = E_0 - E_1 = \frac{\hbar^2}{2m_n}\left(k_0^2 - k_1^2\right)$$

$$\vec{Q} = \vec{k}_0 - \vec{k}_1$$

$$\vec{Q}_x = |k_0| - |k_1| \sin\theta \cos\phi$$

$$Q_y = -|k_0| \sin\theta \sin\phi$$

$$Q_z = -|k_1| \cos\phi$$



INS: Measuring scattering processes involving energy and momentum exchange between the neutron and the sample

Introduction

Inelastic neutron scattering offers the ability to measure directly the interactions of magnetic moments with other magnetic moments and with the local environment.
A variety of problems can be investigated in a variety of systems:

- Single ion excitations
- crystal field measurements
- Spin dynamics in polymetallic clusters
- One dimensional spin chains
- Two dimensional square lattices
- Three dimensional systems

Introduction

The neutron has a small dipole moment that causes it to scatter from inhomogeneous internal fields produced by electrons

The magnetic scattering cross section is similar in magnitude to the nuclear cross section

Elastic magnetic scattering probes static magnetic structure

Inelastic magnetic scattering probes spin dynamics

Polarized neutrons can distinguish magnetic and nuclear scattering and specific spin components

The n^0 has a magnetic moment, due to some substructure of charged particles.

$$\vec{\mu} = -\gamma\,\mu_N\,\hat{\sigma} \qquad \gamma = 1.913, \quad \mu_N = \frac{\hbar e}{2\,m_p}$$

A crude estimate (non-relativistic quarks, no quarks-gluons interaction):

n^0 = ddu, with quarks in s states (no angular momentum)

The magnetic moment of a quark in a s state is due to its spin:

$$\vec{\mu}_Q = \frac{\hbar e_Q}{2\,m_Q}\vec{S}_Q \quad (Q = u, d;\ e_u = +2/3,\ e_d = -1/3,\ m_u \simeq m_d = 350\ \mathrm{MeV})$$

The spins of the three quarks add up to give the n^0 spin s = 1/2.

Racah algebra gives:

$$\mu_n = \frac{4}{3}\mu_{up} - \frac{1}{3}\mu_{down}$$

In good agreement with exp.

$$\frac{\mu_e}{\mu_N} = 960$$

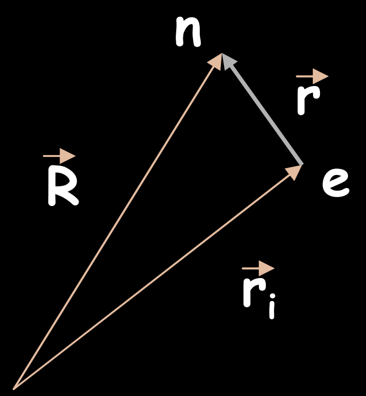
Magnetic interaction potential

A dipole in a magnetic field has potential energy

$$V(\mathbf{r}) = -\boldsymbol{\mu}\cdot\mathbf{B}(\mathbf{r}) = -\gamma\,\mu_N\,\hat{\sigma}\cdot\mathbf{B}(\mathbf{r})$$

The magnetic field that scatters the neutrons is due to currents and magnetic dipole moments of electrons.
For a single electron in $\mathbf{r}_i$, the field acting on a n^0 in $\mathbf{R} = \mathbf{r}_i + \mathbf{r}$ is:

$$\boldsymbol{B}_e(\boldsymbol{r}) = \frac{\mu_0}{4\pi}\nabla\times\frac{-g\,\mu_B\,\boldsymbol{s}_e\times\boldsymbol{r}}{r^3} - \frac{\mu_0}{4\pi}\frac{\mu_B}{\hbar}\left(\boldsymbol{p}_e\times\frac{\boldsymbol{r}}{r^3} + \frac{\boldsymbol{r}}{r^3}\times\boldsymbol{p}_e\right)$$



The total field $\mathbf{B}(\mathbf{r},t)$ in a sample of condensed matter is the sum of the fields generated by all the electrons and depends on the wave-function of the system .

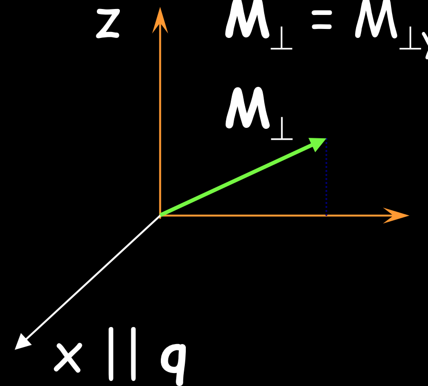
Magnetic cross-section

The matrix element defining the scattering amplitude is

$$|\langle \mathbf{k}', s', \lambda' | -\boldsymbol{\mu}\cdot\mathbf{B}(\mathbf{r}) | \mathbf{k}, s, \lambda\rangle| =$$

$$\mu_0 \, |\langle s' | \boldsymbol{\mu} | s\rangle \cdot \langle \lambda' | \mathbf{M}_\perp(\mathbf{q}) | \lambda\rangle|$$

$$\mathbf{M}_\perp = M_{\perp y}\,\mathbf{j} + M_{\perp z}\,\mathbf{k}$$



where $\mathbf{q} = \mathbf{k}-\mathbf{k}'$ and $\quad -\mu_0 \mathbf{M}_\perp(\mathbf{q}) = \int \mathbf{B}(\mathbf{r})\, e^{i\mathbf{q}\cdot\mathbf{r}}\, d\mathbf{r}$

The magnetic scattering of neutrons will therefore depends only on the transverse component of the magnetisation. Ex. #1. Why?

Then, the pdcs for scattering of n^0 in the $|\uparrow\rangle$ spin state into the spin state $\langle s'|$ at T = 0 is:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{s'} = \frac{k_f}{k_i}\left(\frac{\gamma r_0}{2\mu_B}\right)^2 (4\pi)^2 \sum_{\lambda'} \left| \langle \lambda' | \mathbf{M}_\perp(\mathbf{q}) | 0\rangle \cdot \langle s' | \hat{\boldsymbol{\sigma}} | \uparrow\rangle \right|^2 \delta(E_{\lambda'} - E_0 - \hbar\omega)$$

Ex. #2. Extend to non-zero temperatures

Magnetic cross-section

Recalling the matrix elements of the Pauli spin operators

$$\begin{pmatrix} \langle\uparrow|\hat{\sigma}_x|\uparrow\rangle & \langle\uparrow|\hat{\sigma}_x|\downarrow\rangle \\ \langle\downarrow|\hat{\sigma}_x|\uparrow\rangle & \langle\downarrow|\hat{\sigma}_x|\downarrow\rangle \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\begin{pmatrix} \langle\uparrow|\hat{\sigma}_y|\uparrow\rangle & \langle\uparrow|\hat{\sigma}_y|\downarrow\rangle \\ \langle\downarrow|\hat{\sigma}_y|\uparrow\rangle & \langle\downarrow|\hat{\sigma}_y|\downarrow\rangle \end{pmatrix} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$\begin{pmatrix} \langle\uparrow|\hat{\sigma}_z|\uparrow\rangle & \langle\uparrow|\hat{\sigma}_z|\downarrow\rangle \\ \langle\downarrow|\hat{\sigma}_z|\uparrow\rangle & \langle\downarrow|\hat{\sigma}_z|\downarrow\rangle \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

one has (initial spin state |↑>):

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\uparrow} = \frac{k_f}{k_i}\left(\frac{\gamma r_0}{2\mu_B}\right)^2 (4\pi)^2 \sum_{\lambda'} \left| \langle\lambda'|M_{\perp z}(\mathbf{q})|0\rangle \right|^2 \delta(E_{\lambda'} - E_{\lambda} - \hbar\omega)$$

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\downarrow} = \frac{k_f}{k_i}\left(\frac{\gamma r_0}{2\mu_B}\right)^2 (4\pi)^2 \sum_{\lambda'} \left| \langle\lambda'|M_{\perp x}(\mathbf{q})|0\rangle + i\langle\lambda'|M_{\perp y}(\mathbf{q})|0\rangle \right|^2 \delta(E_{\lambda'} - E_{\lambda} - \hbar\omega)$$

So, NSF scattering probes the components of $\mathbf{M}_{\perp}$ along the quantization axis of the n^0 spin, whilst SF scattering probes the components of $\mathbf{M}_{\perp}$ perpendicular to z.

Ex. #3. Work out the pdcs for ↓→↓ and ↓→↑ scattering

Magnetic cross-section unpolarised neutrons

If the beam is unpolarised we have:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\downarrow} = \frac{k_f}{k_i}\left(\frac{\gamma r_0}{2\mu_B}\right)^2 (4\pi)^2 \sum_{\lambda'} \left| \langle \lambda' \,|\, \mathbf{M}_\perp(\mathbf{q}) \,|\, 0 \rangle \right|^2 \delta(E_{\lambda'} - E_\lambda - \hbar\omega)$$

a) The spatial part of the matrix elements can be written in terms of $\mathbf{s}_\perp$, the electron spin component transverse to the momentum transfer $\mathbf{q}$.

$$\mathbf{M}_\perp(\mathbf{q}) = -2\mu_B \sum_n e^{i\mathbf{q}\cdot\mathbf{r}_n} \mathbf{s}_{\perp n}$$

b) Using the Fourier representation of the δ function, the pdcs at non-zero T can be written as the FT of a spin-spin time correlation function

$$\langle \mathbf{S}_\perp \cdot \mathbf{S}_\perp \rangle(\mathbf{q}, \omega) = \sum_{n,n'} e^{i\mathbf{q}\cdot(\mathbf{r}_{n'} - \mathbf{r}_n)} \int_0^\infty e^{-i\omega t'}\, dt' \sum_\lambda p(E_\lambda) \langle \lambda \,|\, \mathbf{s}_{\perp n}(0) \cdot \mathbf{s}_{\perp n'}(t) \,|\, \lambda \rangle$$

Spin-spin correlation function

For neutrons with initial spin state |↑>:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\uparrow} = A(\mathbf{q})\langle \mathbf{S}_{\perp}\cdot\hat{z}\ \mathbf{S}_{\perp}\cdot\hat{z}\rangle(\mathbf{q},\ \omega)$$

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\downarrow} = A(\mathbf{q})[\langle(\mathbf{S}_{\perp})_{\perp}\cdot(\mathbf{S}_{\perp})_{\perp}\rangle(\mathbf{q},\ \omega) + i\langle(\mathbf{S}_{\perp}\times\mathbf{S}_{\perp})\cdot\hat{\mathbf{z}}\rangle(\mathbf{q},\ \omega)]$$

$(\mathbf{S}_{\perp})_{\perp}$ is the component of the spin perpendicular to **q** and **z**.

NSF→ correlations of the $\mathbf{S}_{\perp}$ component || to the initial dir. of polarization

SF→ correlations of the $\mathbf{S}_{\perp}$ component ⊥ to the initial dir. of polarization

$$A(\mathbf{q}) = \frac{k_f}{k_i}\frac{(\gamma r_0)^2}{2\pi\hbar}\,|F(\mathbf{q})|^2 \exp(-2W(\mathbf{q})) \qquad \gamma r_0 = 0.54\times 10^{-12}\ \mathrm{cm}$$

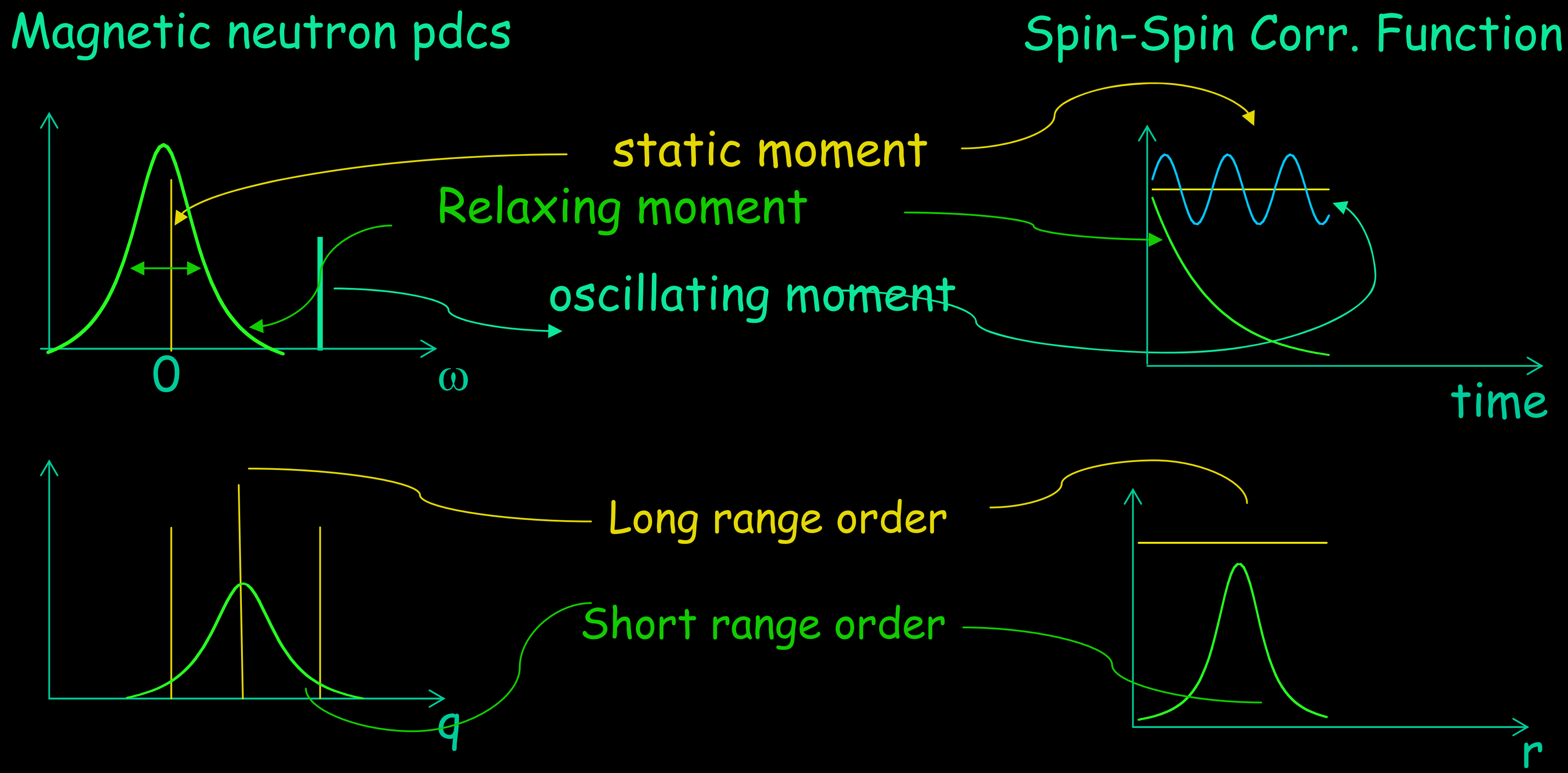
Spin density spread out: scattering decreases at high *q*

$$F(\mathbf{q}) = \int s(\mathbf{r})\exp(i\mathbf{q}\cdot\mathbf{r})\,d\mathbf{r}$$

The scalar function s(**r**) is the density of unpaired e⁻ divided by their number

Spin-spin correlation function

$\langle S_n^\alpha(0) S_{n'}^\beta(t) \rangle$ is the thermal average of the time dependent spin operator and corresponds to the van Hove correlation function: The probability of finding a spin $S_{n'}$ at site n' and at time t when the spin at position n is S_n at t=0



Γ : quasielastic broadening
κ : intrinsic linewidth

τ : lifetime
ξ : correlation length

$\Gamma = 1/\tau$
$\kappa = 1/\xi$

$$\frac{d^2\sigma}{d\Omega dE'} = A(\mathbf{q})\langle \mathbf{S}_\perp \cdot \mathbf{S}_\perp \rangle(\mathbf{q}, \omega)$$

or

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k_f}{k_i}(\gamma r_0)^2 \,|\, F(\mathbf{q}) \,|^2 \exp(-2W(\mathbf{q})) \sum_{\alpha,\beta}\left(\delta_{\alpha\beta} - \frac{q_\alpha q_\beta}{q^2}\right) S^{\alpha\beta}(\mathbf{q}, \omega)$$

$(\alpha, \beta = x, y, z)$

Ex. #4. Derive the above result.

$$S^{\alpha\beta}(\mathbf{q}, \omega) = \sum_{n,n'} e^{i\mathbf{q}\cdot(\mathbf{r}_{n'}-\mathbf{r}_n)} \int_0^\infty e^{-i\omega t'} dt' \sum_\lambda p(E_\lambda)\langle\lambda \,|\, s^\alpha{}_n(0)\, s^\beta{}_n(t) \,|\, \lambda\rangle$$

or, in terms of matrix elements:

$$S^{\alpha\beta}(\mathbf{q}, \omega) = \sum_{n,n'} e^{i\mathbf{q}\cdot(\mathbf{r}_{n'}-\mathbf{r}_n)} \sum_{\lambda\lambda'} p(E_\lambda)\langle\lambda \,|\, s^\alpha{}_{n'} \,|\, \lambda'\rangle\langle\lambda' \,|\, \mathbf{s}^\beta{}_n \,|\, \lambda\rangle\, \delta(E_{\lambda'} - E_\lambda - \hbar\omega)$$

Inelastic Magnetic Scattering

Squared form factor

DW factor

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k_f}{k_i}(\gamma r_0)^2 \,|\,F(\mathbf{q})\,|^2 \exp(-2W(\mathbf{q})) \sum_{\alpha,\beta}\left(\delta_{\alpha\beta} - \frac{q_\alpha q_\beta}{q^2}\right) S^{\alpha\beta}(\mathbf{q},\,\omega)$$

geometrical factor

Spin correlation function

For ions with unquenched orbital moment and for $q \to 0$

$$s_n^\alpha \longrightarrow \frac{1}{2}\, g J_n^\alpha \qquad \text{with} \qquad g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)},$$

J_n^α being an effective angular momentum operator

For a wide class of systems $S^{\alpha\beta}$ satisfies useful sum-rules

Detailed balance

$$S^{\alpha\beta}(\mathbf{q},\ \omega) = \exp(\hbar\omega / k_B T)\ S^{\alpha\beta}(-\mathbf{q},\ -\omega)$$

Total moment

$$\frac{\hbar}{\int d\mathbf{q}} \sum_{\alpha} \int S^{\alpha\alpha}(\mathbf{q},\ \omega)\, d\mathbf{q}\, d\omega = S(S+1)$$

First moment sum-rule

$$\hbar^2 \int S(\mathbf{q},\ \omega)\, \omega\, d\omega = -\frac{1}{3N} \sum_{n,n'} J_{nn'} \langle \mathbf{s}_n \cdot \mathbf{s}_{n'} \rangle (1 - \cos \mathbf{q} \cdot (\mathbf{r}_{n'} - \mathbf{r}_n))$$

Generalised susceptibility

The scattering function $S^{\alpha\beta}(q, \omega)$ is related to the generalized susceptibility $\chi^{\alpha\beta}$ by the fluctuation-dissipation theorem:

$$S^{\alpha\beta}(\mathbf{q}, \omega) = \frac{N\hbar}{\pi} \frac{1}{1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)} \mathrm{Im}\chi^{\alpha\beta}(\mathbf{q}, \omega)$$

$\chi^{\alpha\beta}$ determines the response of the system to the magnetic field established by the neutron:

$$M^{\alpha}(\mathbf{q}, \omega) = \chi^{\alpha\beta}(\mathbf{q}, \omega) H^{\beta}(\mathbf{q}, \omega)$$

We convert inelastic scattering data to $\chi^{\alpha\beta}$ to

- Compare with bulk susceptibility data
- Analyze the temperature dependence of the response
- Compare with theories

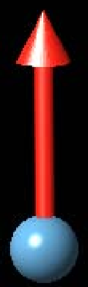
Note that: $$\chi(\mathbf{q}, 0) = \frac{1}{2\pi i} \int d\omega \frac{\mathrm{Im}\chi^{\alpha\beta}(\mathbf{q}, \omega)}{\omega}$$

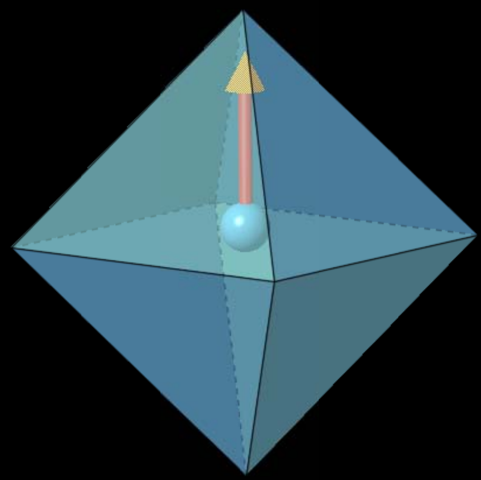
Single-ion Crystal Field Excitations

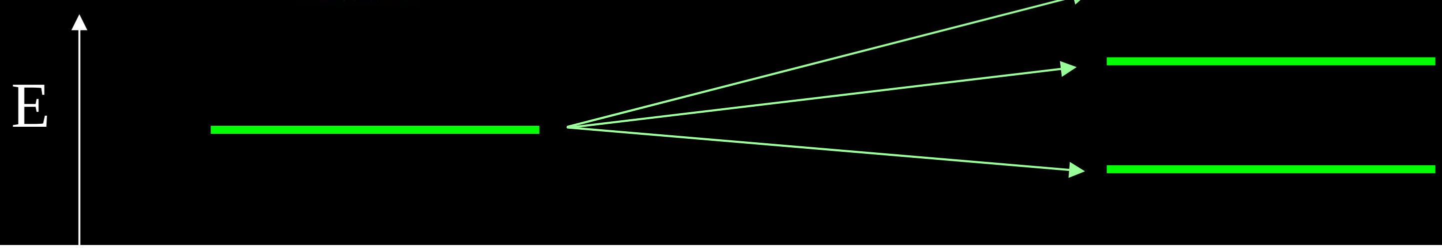
Weak coupling between magnetic ions: the excitation energies are independent from the scattering vector **q**. We have to deal with a single-ion problem.

Local charge symmetry lifts partially or totally the (2J+1)-fold degeneracy of the ground state multiplet

Isolated magnetic ion: complete rotational symmetry. The total angular momentum J is a good quantum number







Crystal Field Excitations

The surrounding ions produce an electric field (CF) to which the charges of the central ions adjusts.

CF weak (4f, 5f): smaller than the spin-orbit interaction. Each multiplet J can be considered as isolated. The eigenstates are linear combinations of the 2J+1 free--ion eigenstates $|LSJM_J\rangle$,

$$|\Gamma_n\rangle = \sum_{M=-J}^{J} a_n(M)\,|JM_J\rangle$$

The label Γ refers to the Bethe notation for the Irrep of the group of rotations.

CF intermediate (3d): if it is stronger than the spin-orbit interaction but weaker than the intra-atomic Coulomb electron-electron interaction. J is no more a good quantum number. The CF effects must be considered on the $|LSM_LM_S\rangle$ basis, then the SO corrections must be applied. L and S are good quantum numbers.

CF strong (4d, 5d): comparable to the intra-atomic Coulomb interaction. The CF modifies the state of each single electron. L is not a good quantum number.

Crystal Field Potential

If J is a good quantum number

$$H^{CF} = \sum_{k=0}^{\min(2\ell,2j)} \sum_{m=0}^{k} B_k^n \hat{O}_k^n$$

with k even and m equal to a multiple of the order of rotational symmetry around z

$J = 1, 3/2 \quad k = 0 \quad 2$

$J = 2, 5/2 \quad k = 0 \quad 2 \quad 4$

$J = 3, 7/2 \quad k = 0 \quad 2 \quad 4 \quad 6$

Examples of Stevens Operator Equivalents

$$\hat{O}_2^0 = 3\,S_z^2 - S\,(S+1)$$

$$\hat{O}_2^1 = \frac{1}{4}\,[S_z\,(S_+ + S_-) + (S_+ + S_-)\,S_z]$$

$$\hat{O}_2^2 = \frac{1}{2}\,[S_+^2 + S_-^2]$$

$$\hat{O}_4^0 = 35\,S_z^4 - [30\,S\,(S+1) - 25]\,S_z^2 - 6\,S\,(S+1) + 3\,S^2\,(S+1)^2$$

$$\hat{O}_4^1 = \frac{1}{4}\,\{[7\,S_z^2 - 3\,S\,(S+1) - 1]\,S_z\,(S_+ + S_-) + (S_+ + S_-)\,S_z\,[7\,S_z^2 - 3\,S\,(S+1) - 1]\}$$

$$\hat{O}_4^2 = \frac{1}{4}\,\{[7\,S_z^2 - S\,(S+1) - 5]\,(S_+^2 + S_-^2) + (S_+^2 + S_-^2)\,[7\,S_z^2 - S\,(S+1) - 5]\}$$

$$\hat{O}_4^3 = \frac{1}{4}\,[S_z\,(S_+^3 + S_-^3) + (S_+^3 + S_-^3)\,S_z]$$

$$\hat{O}_4^4 = \frac{1}{2}\,(S_+^4 + S_-^4)$$

CF and Stevens operator equivalents

Cubic symmetry, quantization axis along the 4-fold axis

$$H_C^{CF} = B_4\left(\hat{O}_4^0 + 5\,\hat{O}_4^4\right) + B_6\left(\hat{O}_6^0 - 21\,\hat{O}_6^4\right)$$

Tetragonal symmetry (D_{4h})

$$H_t^{CF} = B_2^0\,\hat{O}_2^0 + B_4^0\,\hat{O}_4^0 + B_4^4\,\hat{O}_4^4 + B_6^0\,\hat{O}_6^0 + B_6^4\,\hat{O}_6^4$$

Trigonal symmetry (D_{3d}), up to fourth order

$$H_{tr}^{CF} = B_2^0\,\hat{O}_2^0 + B_4^0\,\hat{O}_4^0 - \frac{2}{3}\,B_4\left(\hat{O}_4^0 + 20\sqrt{2}\,\hat{O}_4^3\right)$$

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k_f}{k_i}(\gamma r_0)^2 \, |F(\mathbf{q})|^2 \, \exp(-2W(\mathbf{q})) \sum_{\alpha,\beta}\left(\delta_{\alpha\beta} - \frac{q_\alpha q_\beta}{q^2}\right) S^{\alpha\beta}(\mathbf{q},\omega)$$

$$S^{\alpha\beta}(\mathbf{q},\omega) = \sum_{n,n'} e^{i\mathbf{q}\cdot(\mathbf{r}_{n'}-\mathbf{r}_n)} \sum_{\lambda\lambda'} p(E_\lambda)\langle\lambda|\mathbf{s}^{\alpha}{}_{n'}|\lambda'\rangle\langle\lambda'|\mathbf{s}^{\beta}{}_{n}|\lambda\rangle\delta(E_{\lambda'}-E_\lambda-\hbar\omega)$$

Single ion excitations: n'=n. N identical ion

$$S^{\alpha\beta}(\mathbf{q},\omega) = N\sum_{\lambda\lambda'} p(E_\lambda)\langle\lambda|\mathbf{s}^{\alpha}|\lambda'\rangle\langle\lambda'|\mathbf{s}^{\beta}|\lambda\rangle\delta(E_{\lambda'}-E_\lambda-\hbar\omega)$$

Average in **q**-space for a polycrystalline sample:

$$\frac{1}{4\pi}\int_{4\pi}\sum_{\alpha,\beta}\left(\delta_{\alpha\beta}-\frac{q_\alpha q_\beta}{q^2}\right)S^{\alpha\beta}(\mathbf{q},\omega)\,d\Omega = \frac{1}{4\pi}\int_0^{\pi}\int_0^{2\pi}\sum_\alpha\left(1-\frac{q_\alpha^2}{q^2}\right)S^{\alpha\alpha}\sin\theta\,d\theta\,d\phi = \frac{2}{3}\sum_\alpha S^{\alpha\alpha}$$

So that

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k_f}{k_i}(\gamma r_0)^2 \left| F(\mathbf{q}) \right|^2 \exp(-2W(\mathbf{q})) \times$$
$$\times \frac{2}{3} N \sum_{\lambda,\lambda'} \sum_{\alpha} p(E_\lambda) \left| \langle \lambda | s^\alpha | \lambda' \rangle \right|^2 \delta(E_{\lambda'} - E_\lambda - \hbar\omega)$$

with

$$\sum_{\alpha} \left| \langle \lambda | s^\alpha | \lambda' \rangle \right|^2 = \left| \langle \lambda | s^z | \lambda' \rangle \right|^2 + \frac{1}{2}\left(\left| \langle \lambda | s_+ | \lambda' \rangle \right|^2 + \left| \langle \lambda | s_- | \lambda' \rangle \right|^2 \right)$$

Ex. #5: prove the above relation

Example

J = S = 5

$D=3B_2^0 = -25\ \mu eV$, $B_4^0 = 9\times10^{-4}\ \mu eV$, $B_4^4 = 7\times10^{-4}\ \mu eV$

$$S_+|m,S\rangle = \hbar\sqrt{(S-m)(S+m+1)}|m+1,S\rangle$$

$$S_-|m,S\rangle = \hbar\sqrt{(S-m+1)(S+m)}|m-1,S\rangle$$

$$S_z|m,S\rangle = \hbar m|m,S\rangle$$

$$S^2|m,S\rangle = \hbar^2 S(S+1)|m,S\rangle$$

$$\langle m',S|D\left(S_z^2-\frac{1}{3}S(S+1)\right)|m,S\rangle = D\left(m^2-\frac{1}{3}S(S+1)\right)\delta_{m',m}$$

$$\langle m',S|B_4^0\hat{O}_4^0|m,S\rangle = B_4^0\left[35m^4-(30S(S+1)-25)m^2-6S(S+1)+3S^2(S+1)^2\right]\delta_{m',m}$$

$$\langle m',S|B_4^4\hat{O}_4^4|m,S\rangle =$$

$$\frac{B_4^4}{2}\left(\sqrt{\prod_{i=0}^{3}(S-m-i)\prod_{i=1}^{4}(S+m+i)}\,\delta_{m+4,m}+\sqrt{\prod_{i=1}^{4}(S-m+i)\prod_{i=0}^{3}(S+m-i)}\,\delta_{m-4,m}\right)$$

Matrix elements

$M = -5, -4, -3 \ldots\ldots 4, 5$

$$\langle M'|H^{CF}|M\rangle = \begin{pmatrix}
-\frac{93183}{250} & 0 & 0 & 0 & 3.484 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -\frac{38067}{250} & 0 & 0 & 0 & 3.851 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \frac{5683}{250} & 0 & 0 & 0 & 4.080 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{74811}{500} & 0 & 0 & 0 & 4.158 & 0 & 0 & 0 \\
3.484 & 0 & 0 & 0 & \frac{28314}{125} & 0 & 0 & 0 & 4.080 & 0 & 0 \\
0 & 3.851 & 0 & 0 & 0 & \frac{63067}{250} & 0 & 0 & 0 & 3.851 & 0 \\
0 & 0 & 4.080 & 0 & 0 & 0 & \frac{28314}{125} & 0 & 0 & 0 & 3.484 \\
0 & 0 & 0 & 4.158 & 0 & 0 & 0 & \frac{74811}{500} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 4.080 & 0 & 0 & 0 & \frac{5683}{250} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 3.851 & 0 & 0 & 0 & -\frac{38067}{250} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 3.484 & 0 & 0 & 0 & -\frac{93183}{250}
\end{pmatrix}$$

Diagonalization of the matrix gives eigenvalues and eigenvectors

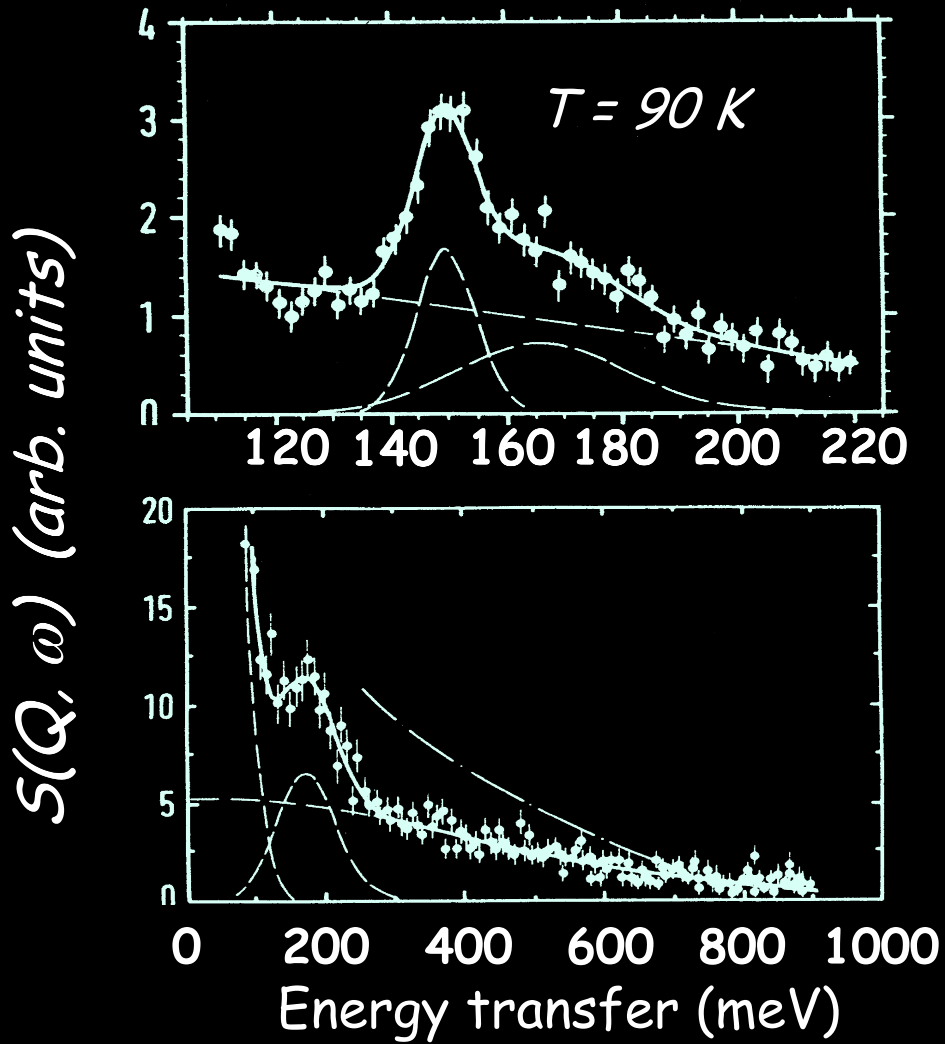
Eigenstates and transition probabilities

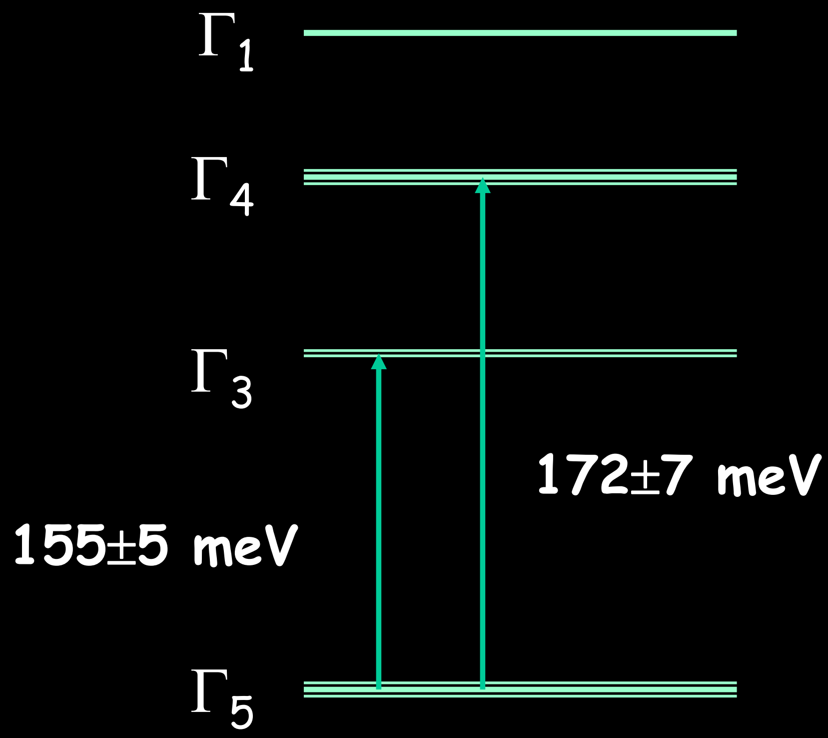
ENERGY (μeV)	Eigenfunctions
0	$\vert\lambda_{0-}> = 1.0 \vert 5,-5>$
0	$\vert\lambda_{0+}> = 1.0 \vert 5,5>$
220.45	$\vert\lambda_1> = \sqrt{2}\vert 5,4> + \sqrt{2}\vert 5,-4>$
220.46	$\vert\lambda_2> = \sqrt{2}\vert 5,4> - \sqrt{2}\vert 5,-4>$
395.45	$\vert\lambda_3> = -1.0 \vert 5,3>$
395.45	$\vert\lambda_4> = 1.0 \vert 5,-3>$
522.0	$\vert\lambda_5> = -\sqrt{2}\vert 5,-2> + \sqrt{2}\vert 5,2>$
522.63	$\vert\lambda_6> = -\sqrt{2}\vert 5,-2> - \sqrt{2}\vert 5,2>$
500.22	$\vert\lambda_7> = -1.0 \vert 5,-1>$
500.22	$\vert\lambda_8> = -1.0 \vert 5,1>$
624.98	$\vert\lambda_9> = -1.0 \vert 5,0>$

Transition probability from the ground state doublet to the 1st excited level

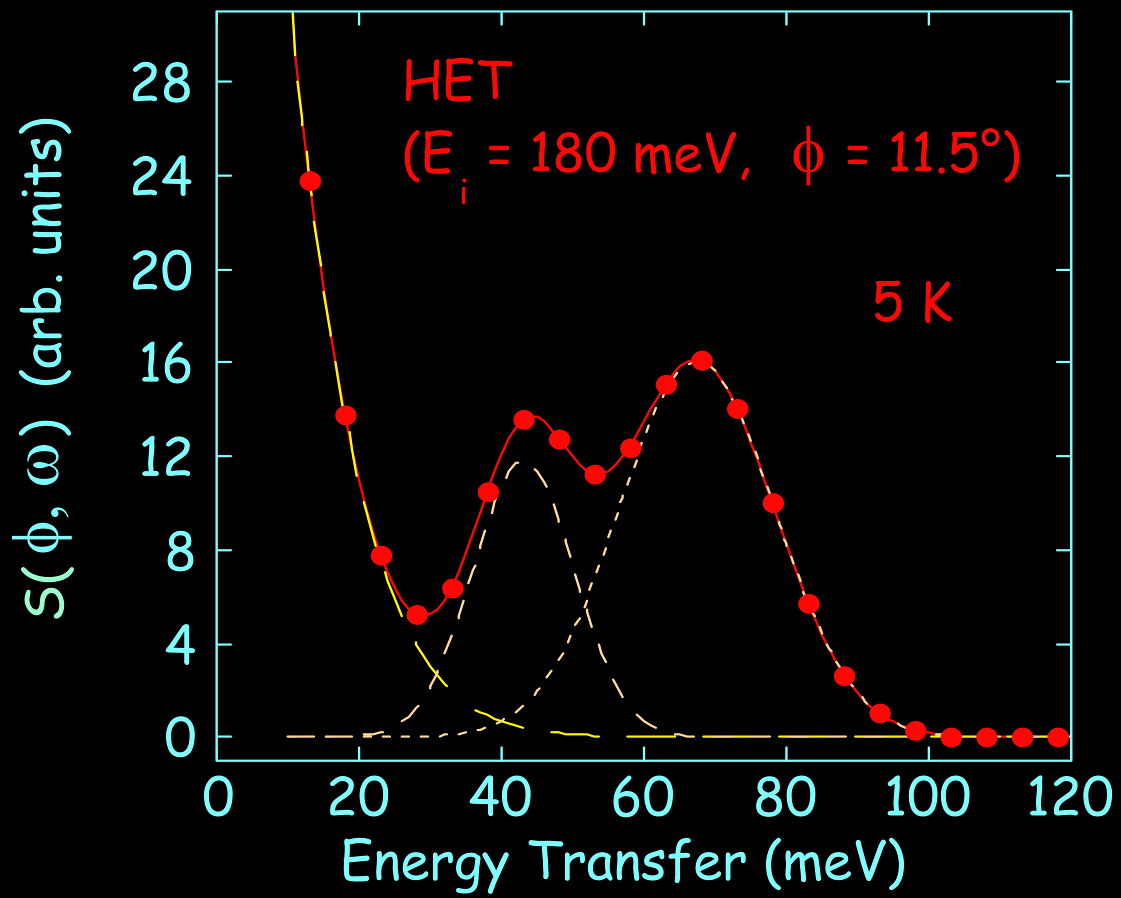
$$|\langle\lambda_1|S_\perp|\lambda_{0+}\rangle|^2 + |\langle\lambda_1|S_\perp|\lambda_{0-}\rangle|^2 = \frac{1}{2}\left(|\langle 5,4|S_-|5,5\rangle|^2 + |\langle 5,-4|S_+|5,-5\rangle|^2\right) = 10$$

UO_2 T > T_N

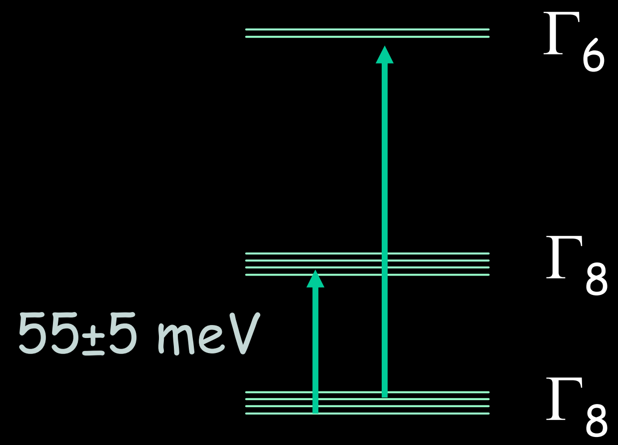

T = 90 K
S(Q, ω) (arb. units)
120 140 160 180 200 220
0 200 400 600 800 1000
Energy transfer (meV)


Γ1
Γ4
Γ3
Γ5
172±7 meV
155±5 meV

NpO_2 T > T_0



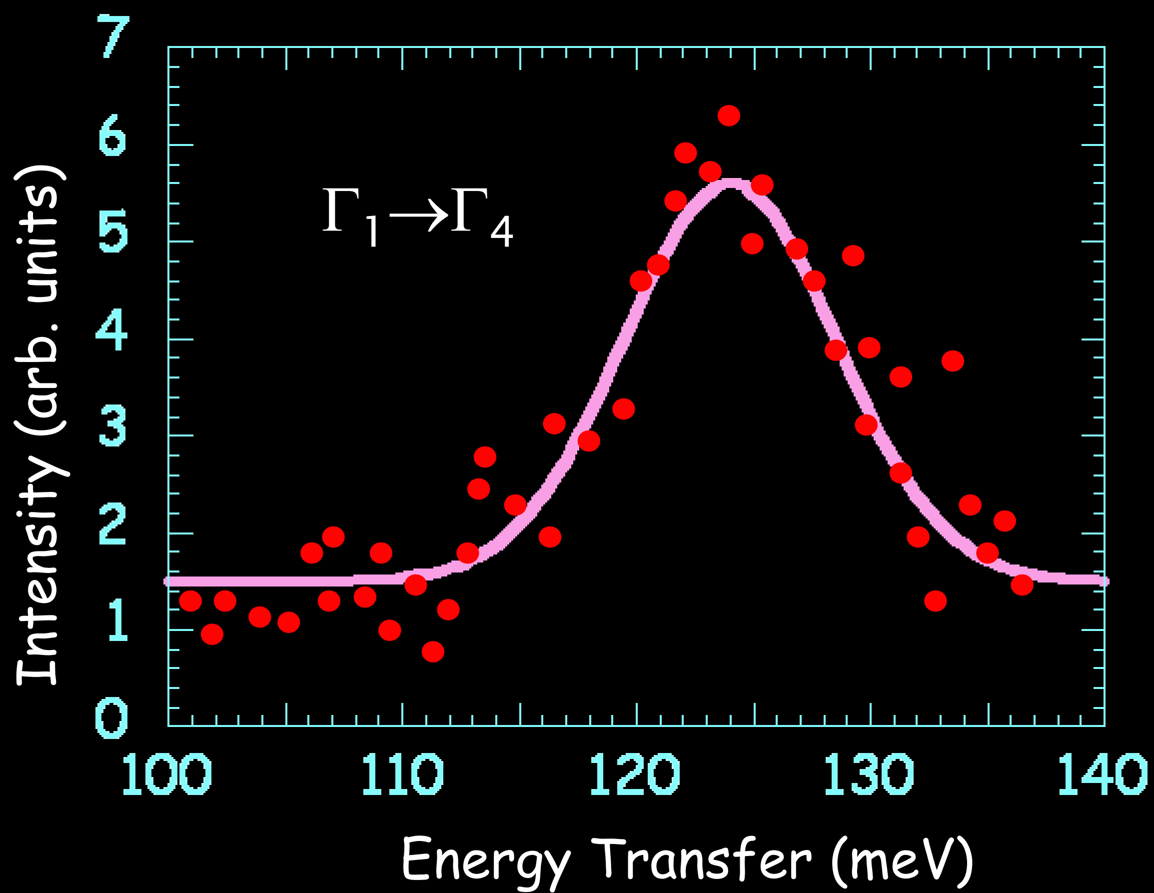
CF-phonon bound state

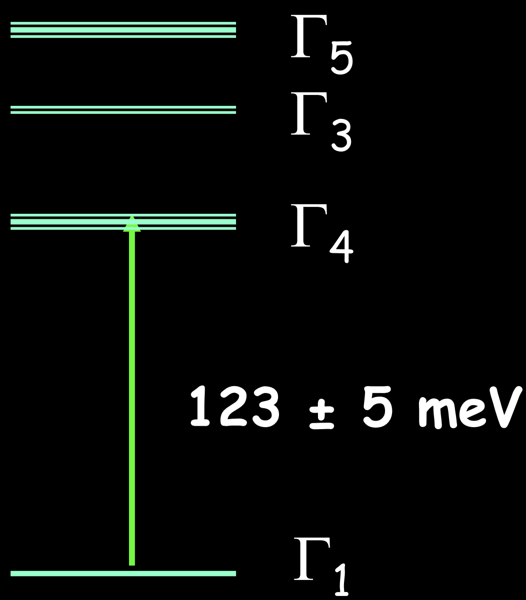


PuO_2

Experiment carried out at LANSCE using 75 grams of $^{242}PuO_2$

Magnetic excitation observed at 123 meV



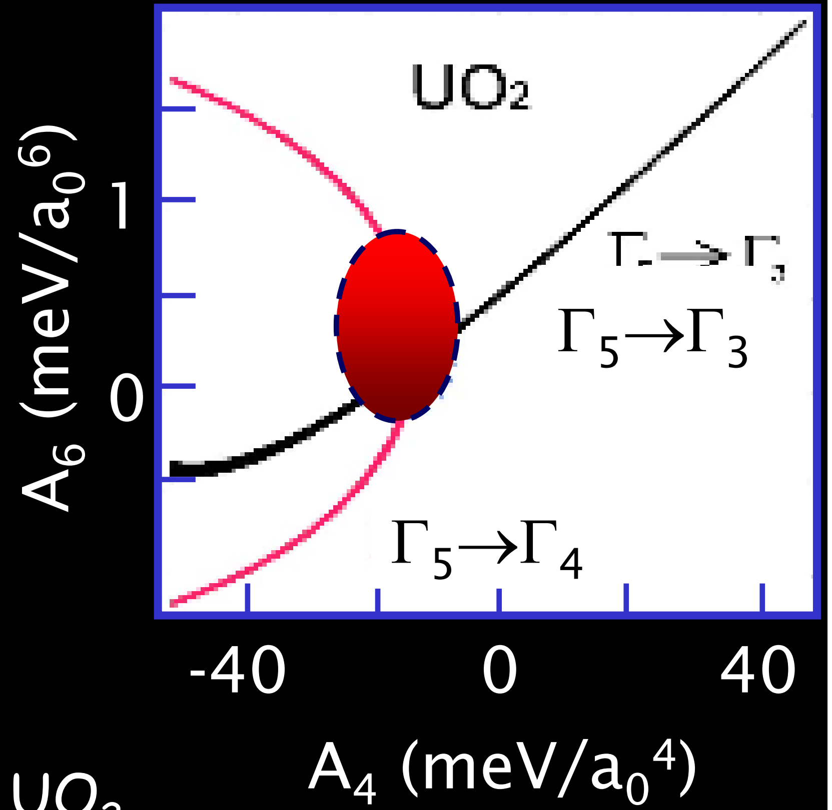


UO_2 Paramagnetic phase

Possible solutions of the disequations

$$165 \text{ meV} < E_{\Gamma_4} - E_{\Gamma_5} < 179 \text{ meV}$$

$$150 \text{ meV} < E_{\Gamma_3} - E_{\Gamma_5} < 160 \text{ meV}$$



in terms of the CF parameters A_4 and A_6 of UO_2.

The dashed ellipse delimitate the region within which the true CF parameters are located with high degree of confidence

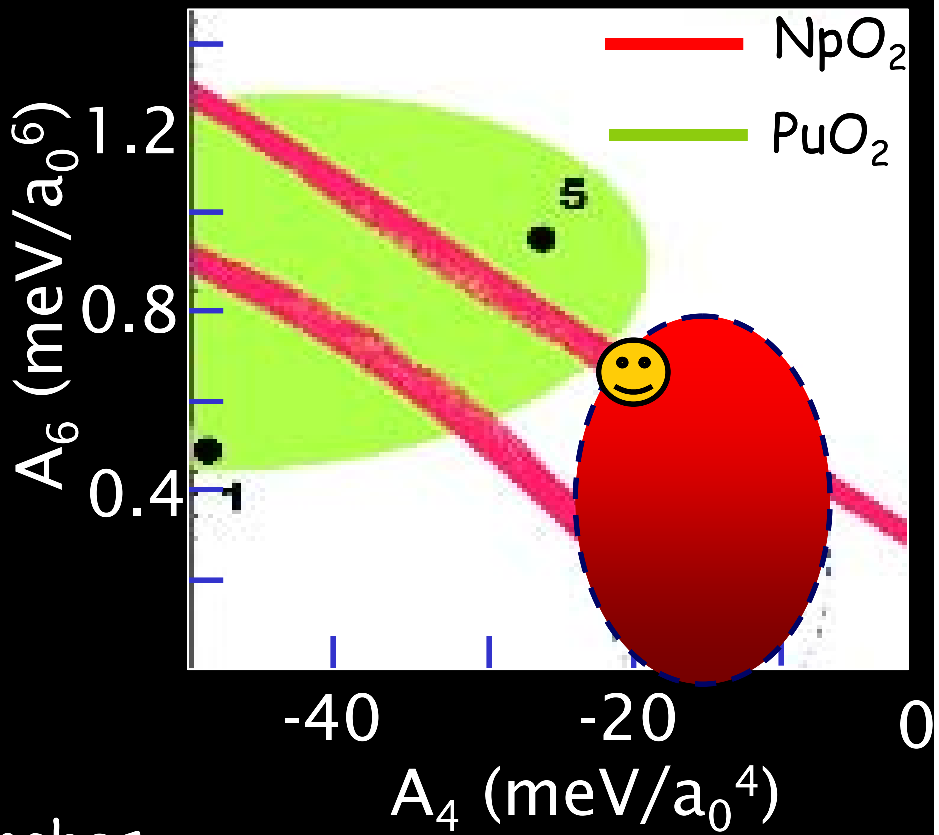
PuO_2 NpO_2

Possible solutions of the disequations

$50\ \text{meV} < E_{\Gamma_8(1)} - E_{\Gamma_8(2)} < 60\ \text{meV}$

$118\ \text{meV} < E_{\Gamma_4} - E_{\Gamma_1} < 128\ \text{meV}$

in terms of the CF parameters A_4 and A_6 of PuO_2 and NpO_2



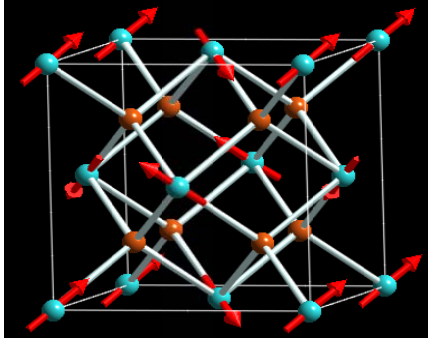
NpO_2: ∞ solutions divided into 2 branches

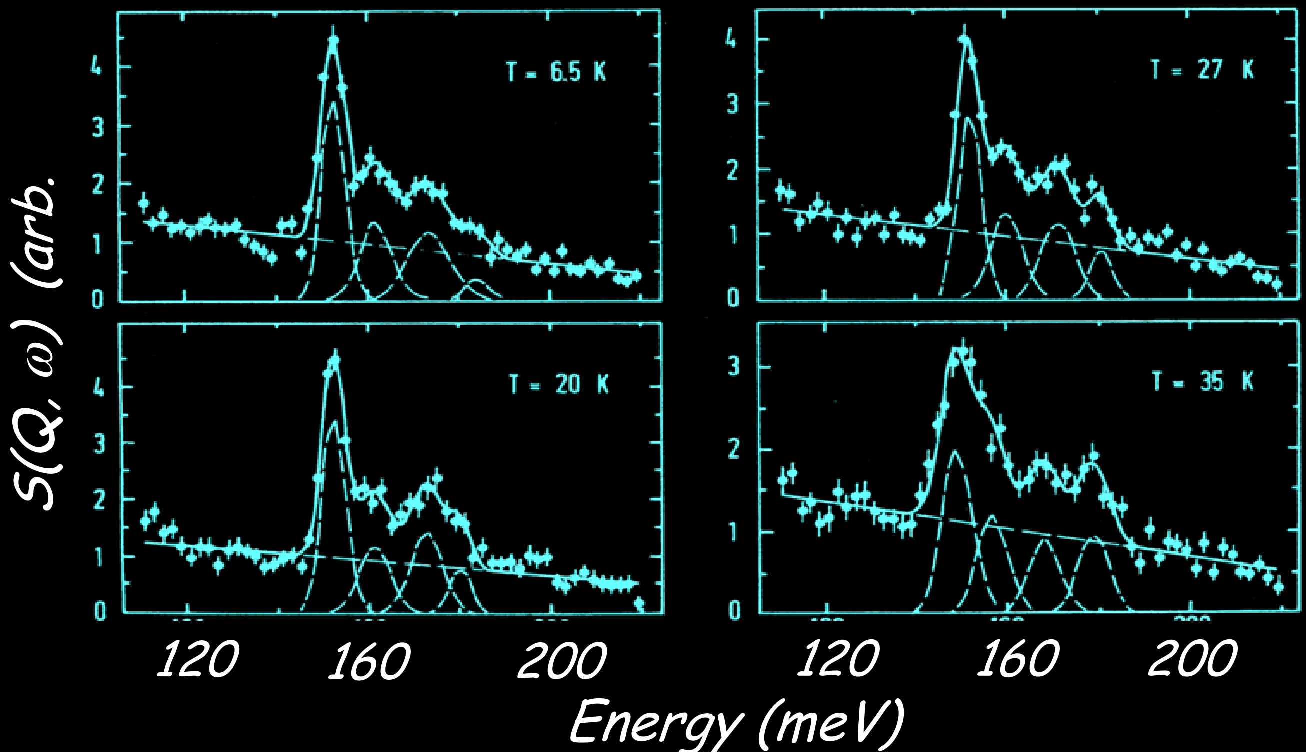
PuO_2: ∞ solutions covering a region of the A_4-A_6 plane

Dashed ellipse: zone of confidence for UO_2 parameters

☺ Common solutions for U. Np. Pu

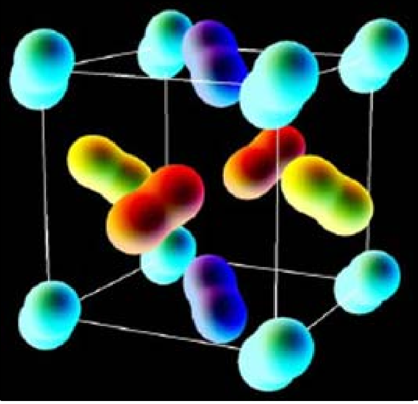
UO_2 Ordered phase





The cubic CF levels are split by the distortion.

$$H = H_{cub} + B_2^2O_2^2 + B_4^2O_4^2 + B_6^2O_6^2 + B_6^6O_6^6$$



Intermultiplet transitions in f-electron systems

We assume that a nf^m configuration is well separated in energy from other configurations: interactions within the *nf shell are dominant*. The appropriate base states are Slater determinants, with elements

$$\psi_{n\ell m_\ell m_s}(\mathbf{r}) = \frac{1}{r} R_{n\ell}(r)\, Y_{\ell m_\ell}(\theta,\phi)\, \chi_{m_s s}$$

In spherical symmetry these states are degenerate. The intra-atomic Coulomb repulsion remove the degeneracy.

As the Coulomb repulsion is diagonal in the basis $|\gamma SLM_L M_S\rangle$, the

nf^m configuration splits into Russell-Saunders terms ^{2S+1}L, which are $(2S+1)(2L+1)$ times degenerate.

The energy of the terms is given by linear combinations of Slater integrals $F^{(k)}$ $(k = 0, 2, 4, 6)$

$$F^{(k)} = e^2 \int_0^\infty dr_i \int_0^\infty dr_j \frac{r_<^k}{r_>^{k+1}} \left(R_{nf}(r_i) R_{nf}(r_j)\right)^2$$

Intermultiplet transitions in f-electron systems

Example: $4f^2$

$F_2 = F^{(2)}/225;\ F_4 = F^{(4)}/1089;\ F_6 = 25F^{(6)}/184041$

$E(^3H) = F_0 - 25F_2 - 51F_4 - 13F_6$

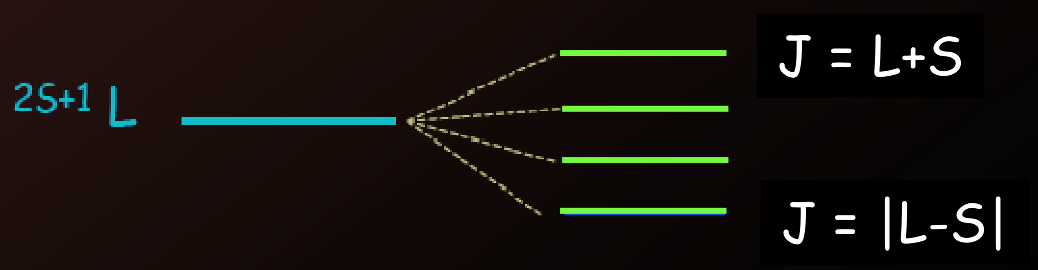
$E(^3F) = F_0 - 10F_2 - 33F_4 - 286F_6$

$E(^1G) = F_0 - 30F_2 + 97F_4 + 78F_6$

Spin-orbit interaction (diagonal in J, small compared to Coulomb)

$$H_{SO} = \sum_i \xi_i(r)\, \ell_i \cdot s_i = \zeta\, L \cdot S$$

where ζ is a radial integral of $\xi(r)$. The SO interaction lifts the degeneracy of the ^{2S+1}L terms, and leads to the formation of J multiplets



L and S are not good quantum numbers; if the SO is strong, levels with the same J but different L and S are mixed: IC

Example $^3H \rightarrow {}^3H_4,\ {}^3H_5,\ {}^3H_6$

Intermultiplet transitions in f-electron systems

The CF removes the degeneracy of the J multiplets

If the CF is strong, J-mixing occurs

The parameters determining the multiplets structure are known for free ions. Measurements of intermultiplet transitions by INS provide a tool for their determination in

- Metal systems with unstable magnetic moments
- Mixed valence systems
- Heavy Fermion systems with strong f-conduction band hybridization
- Sytems with f-electrons on the verge of delocalization

Coulomb transitions: $\Delta L \neq 0$ give information on Coulomb intra-atomic repulsion, Are influenced by the environment and probe intra-atomic correlations.

Spin-orbit transitions: $\Delta L = 0$, $\Delta S = 0$, $\Delta J = \pm 1, \pm 2 \ldots$
probe the spin-orbit coupling

INS cross section for spin-orbit transitions separated by an energy gap Δ

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{k_f}{k_i} r_0^2 G(\mathbf{Q}, J, J')d(\hbar\omega - \Delta)$$

$$G(Q, J, J') = \sum_{k'} \frac{3}{k'+1}\left[A(k'-1,k') + B(k'-1,k')\right]^2 + \sum_{k} \frac{3}{2k+1}\left[B(k,k)\right]^2 \qquad (k = 2, 4, 6 \quad k' = 1, 3, 5, 7)$$

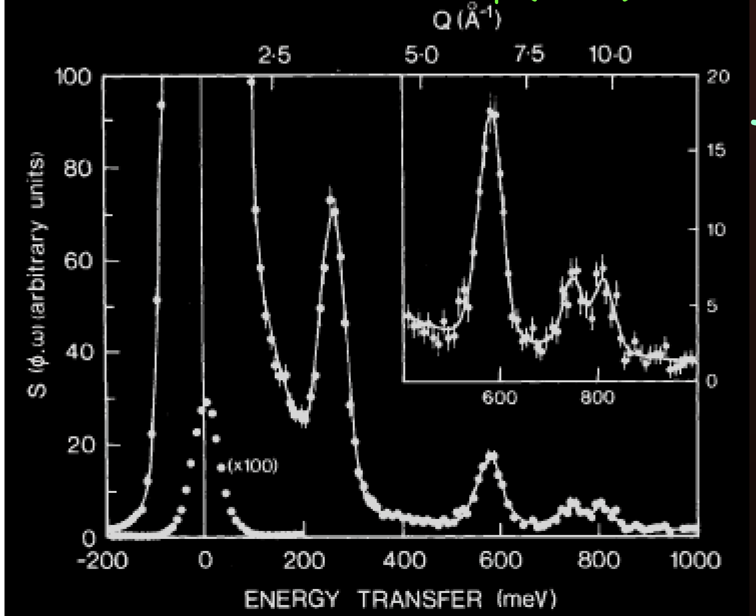
The quantities A(k,k’) and B(k,k’) are associated to radial integrals

$$\langle j_k(Q)\rangle = \int_0^\infty j_k(QR)\, r^2 R_f^2(r)$$

Intermultiplet transitions in f-electron systems

Pr metal, A.D. Taylor et al., PRL, 61, 1309 (1988)

Ground State $^3H_4$ ($4f^2$)



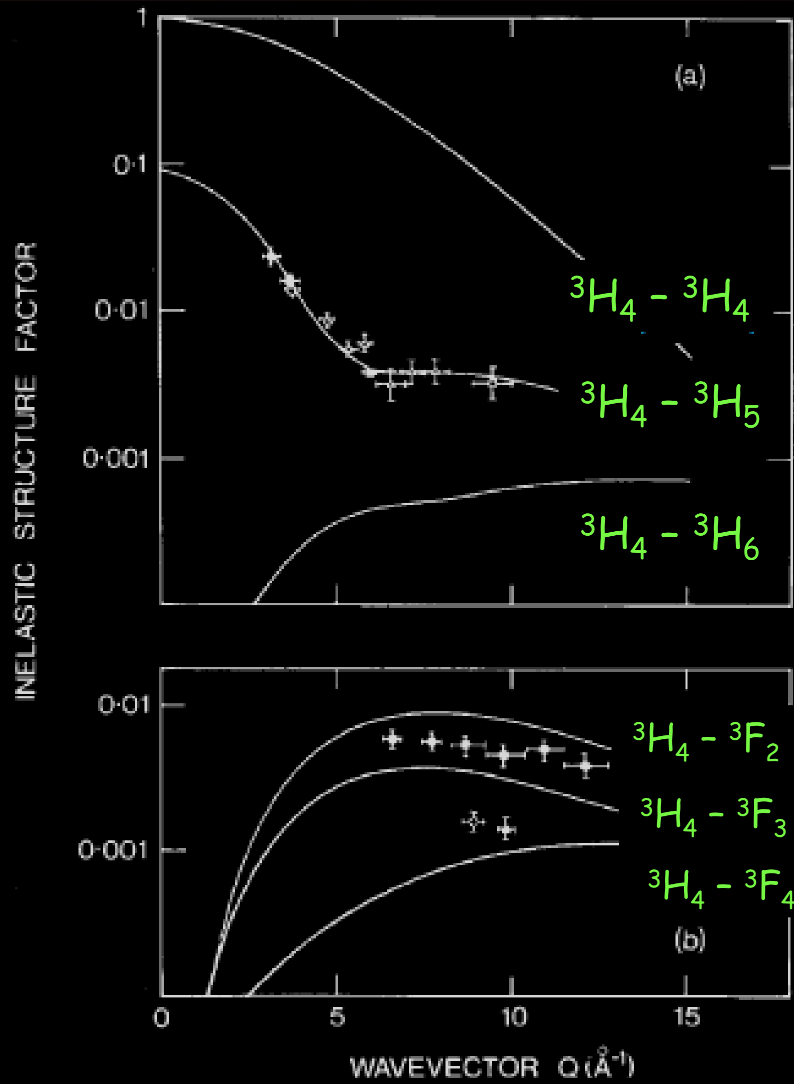
Transition	E (meV)
$^3H_4$ - $^3H_5$	261 meV
$^3H_4$ - $^3H_6$	529 meV
$^3H_4$ - $^3F_2$	578 meV
$^3H_4$ - $^3F_3$	751 meV
$^3H_4$ - $^3F_4$	809 meV

F_2 = 36.0 meV

F_4 = 5.69 meV

F_6 = 0.55 meV

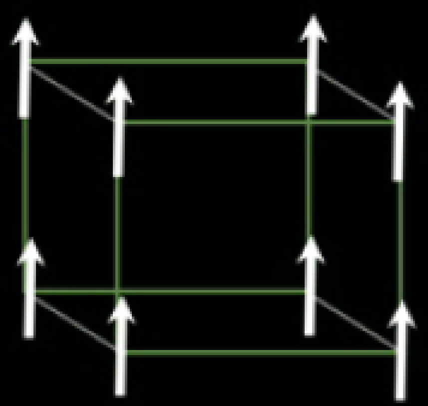
ζ = 92.2 meV



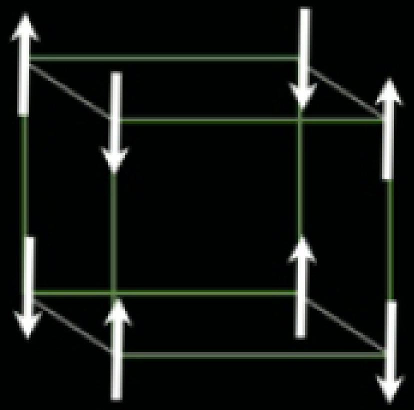
Q-dep of transition probabilities

F_2 is reduced to 90% of the free-ion value, due to screening effects in the metal

Collective excitations



Ferromagnetic: $J_{ij}>0$

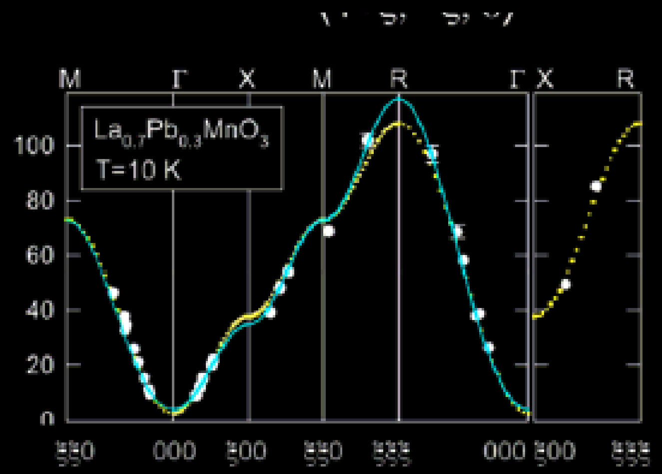


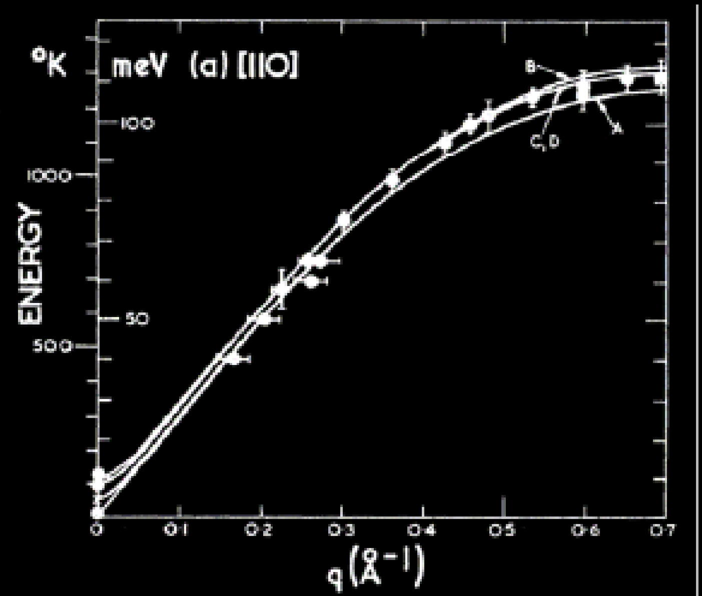
Antiferromagnetic: $Jij<0$

- In most magnetic systems, there is a coupling between neighboring spins
  - e.g. Heisenberg exchange

$$H_{ex} = -\sum_{i,j} J_{ij}\,\vec{S}_i . \vec{S}_j$$

- When one spin changes direction, it induces a wave-like disturbance of all the neighboring spins.



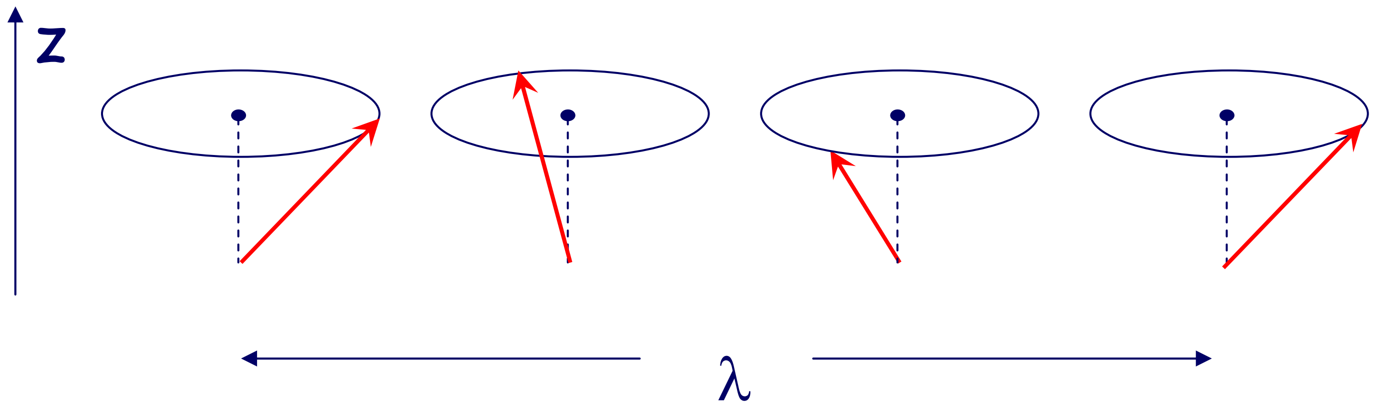


Ferromagnetic:
$E(k) = 4JS(1\text{-}\cos ka)$

Antiferromagnetic:
$E(k) = 4JS \sin ka$

Consider the magnetic moment at site i. Be z the direction of the static moment in an ordered structure. A spin wave corresponds to a precession of the spins about the z axis, with a spatial phase difference determined by a quasi-momentum vector $q = 2\pi/\lambda$:

- S_i^z and $[(S_i^x)^2 + (S_i^y)^2]$ eigenvalues are time independent
- $[(S_i^x)^2 + (S_i^y)^2]$ expectation values are site independent
- S_i^x and S_i^y expectation values are zero



INS cross section for spin waves (ferromagnet)

$$\frac{d^2\sigma}{d\Omega dE} = (\gamma r_0)^2 \frac{K_f}{K_i} \frac{(2\pi)^3}{v_0} \left[\frac{1}{2} g f(\vec{Q})\right]^2 \frac{1}{2} S(1 + \frac{Q_z^2}{Q^2}) e^{-2W} \times$$

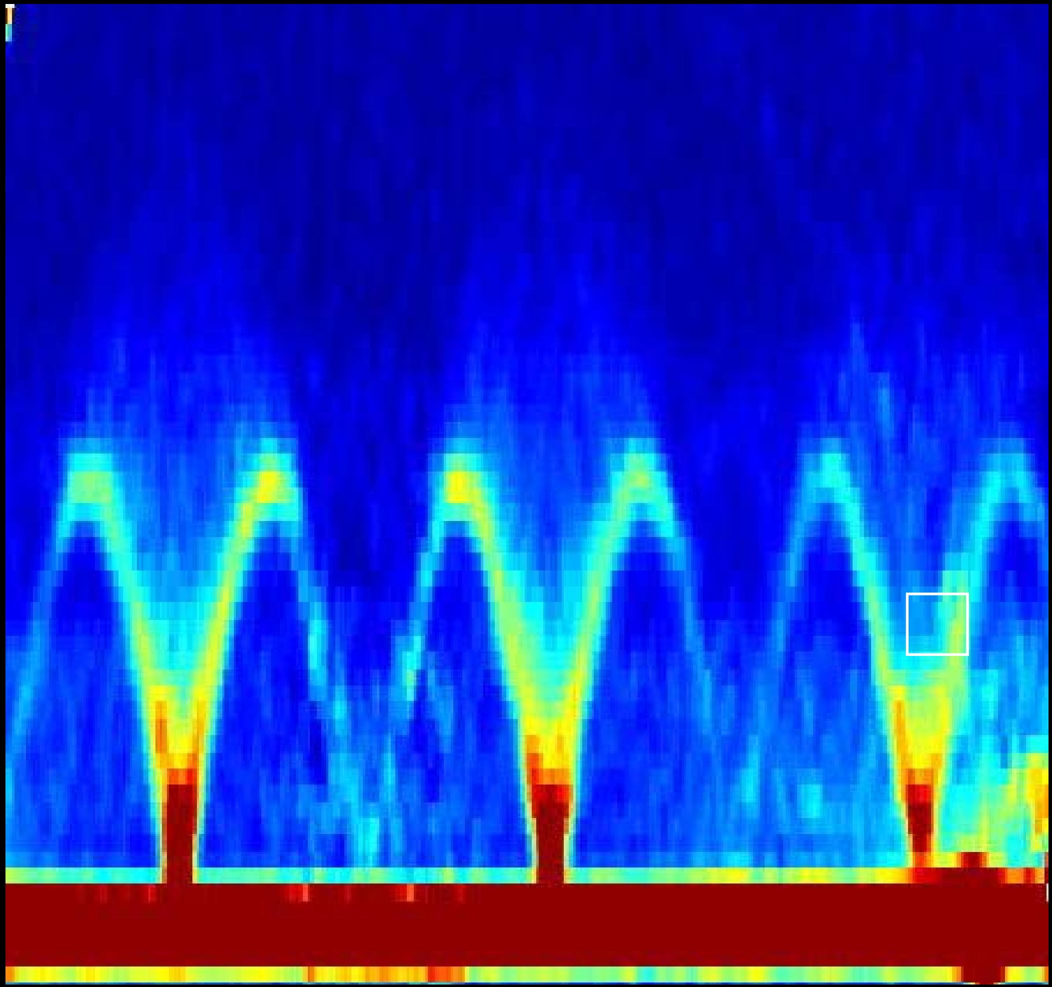
$$\times \sum_{\tau} \sum_{\vec{q}} \left\{ \delta(\vec{Q} - \vec{q} - \vec{\tau}) \delta(\hbar\omega_q - \hbar\omega) < n_q + 1 > + \delta(\vec{Q} + \vec{q} - \vec{\tau}) \delta(\hbar\omega_q + \hbar\omega) < n_q > \right\}$$

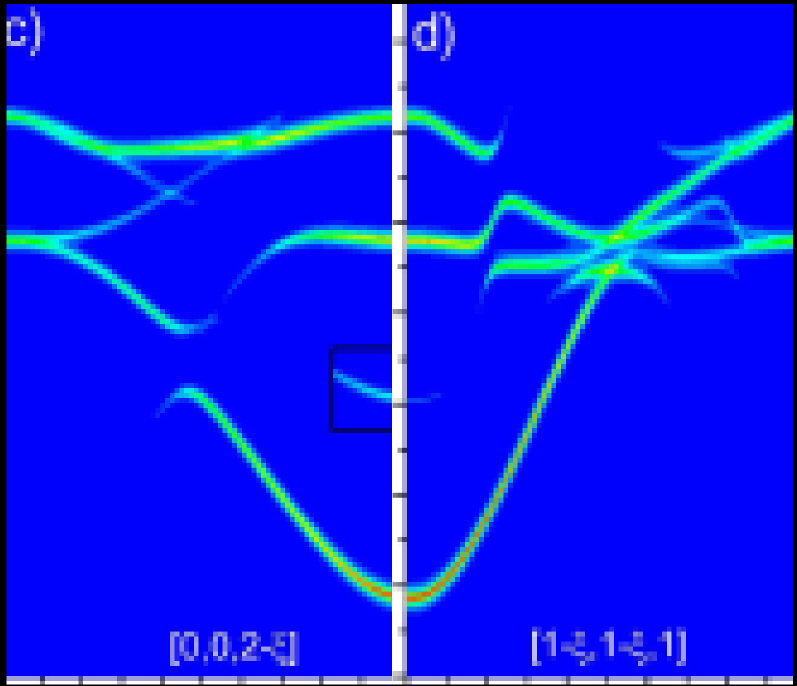
$$< n >= \frac{1}{e^{\hbar\omega / K_B T} - 1} \qquad < n + 1 >= \frac{e^{\hbar\omega / K_B T}}{e^{\hbar\omega / K_B T} - 1}$$

The scattering correspond to the creation or to the annihilation of one magnon. Scattering only occurs if

$$\frac{\hbar^2}{2m_n}(K_i^2 - K_f^2) = \pm\hbar\omega_q \qquad \vec{K}_i - \vec{K}_f = \vec{\tau} \pm \vec{q}$$

Collective excitations





Comparison of magnon and phonon scattering intensities:

- the intensity for magnon scattering decreases with the square of the form factor
- Phonon scattering intensity increases as Q^2
- SW excitations only in the magnetic ordered phase
- an external magnetic field, affect the intensity, provided it is strong enough to produce a domain reorientation:

$$1 + \frac{Q_\eta^2}{Q^2} = \begin{cases} 1 & ; \mathbf{B} \perp \mathbf{Q} \\ 2 & ; \mathbf{B} \parallel \mathbf{Q} \end{cases}$$

For B = 0, the directional average of $(1+Q_\eta^2/Q^2)$ depends on the symmetry.

In a cubic crystal, the average is 4/3.

Time of Flight Spectrometers

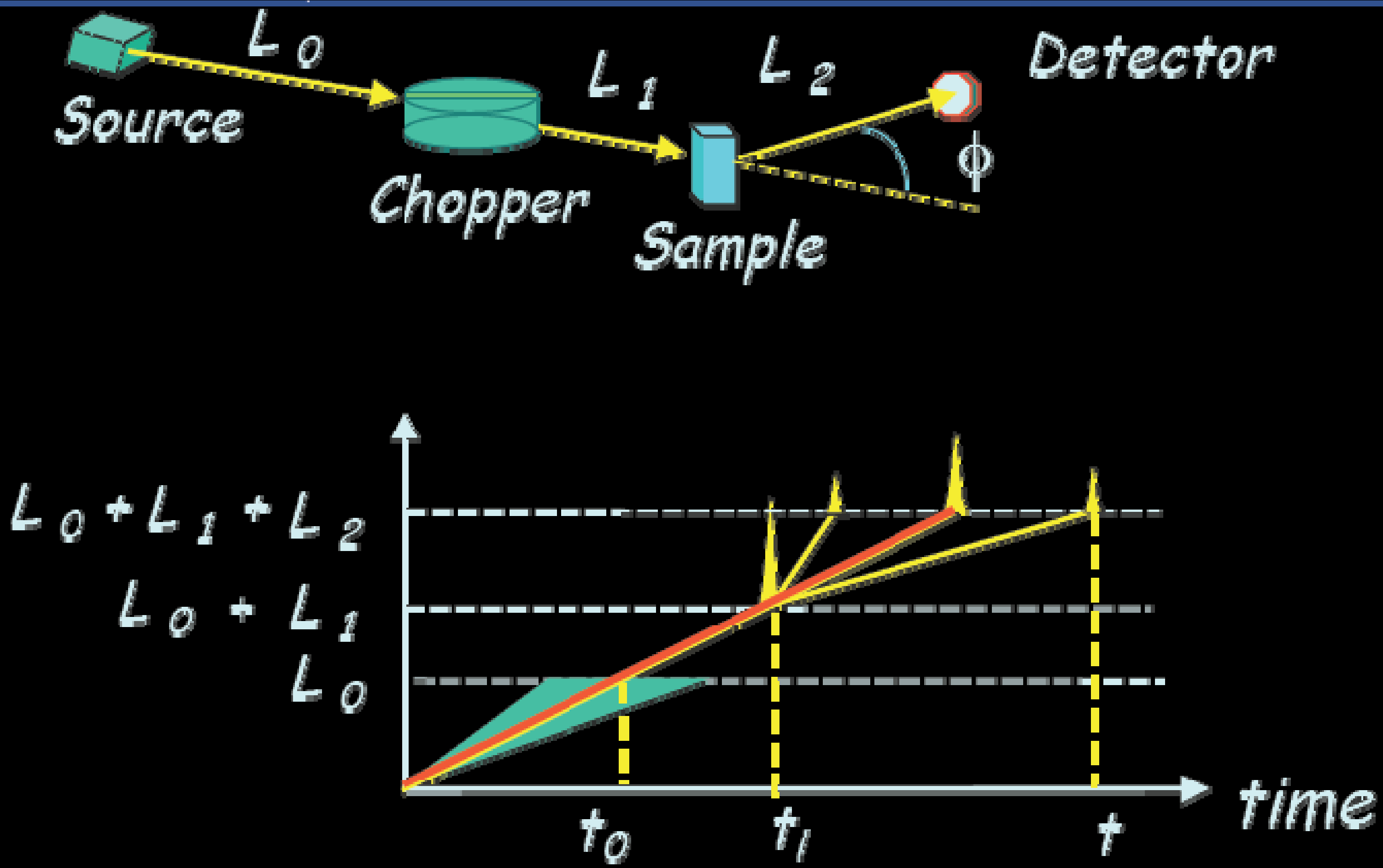
Thermal neutrons have velocity of the order of km/s

Their energy can be determined by measuring time-of-flight over a distance of a few metres.

Direct Geometry: the incident energy is defined by a crystal or a chopper and the final energy is scanned by time-of-flight

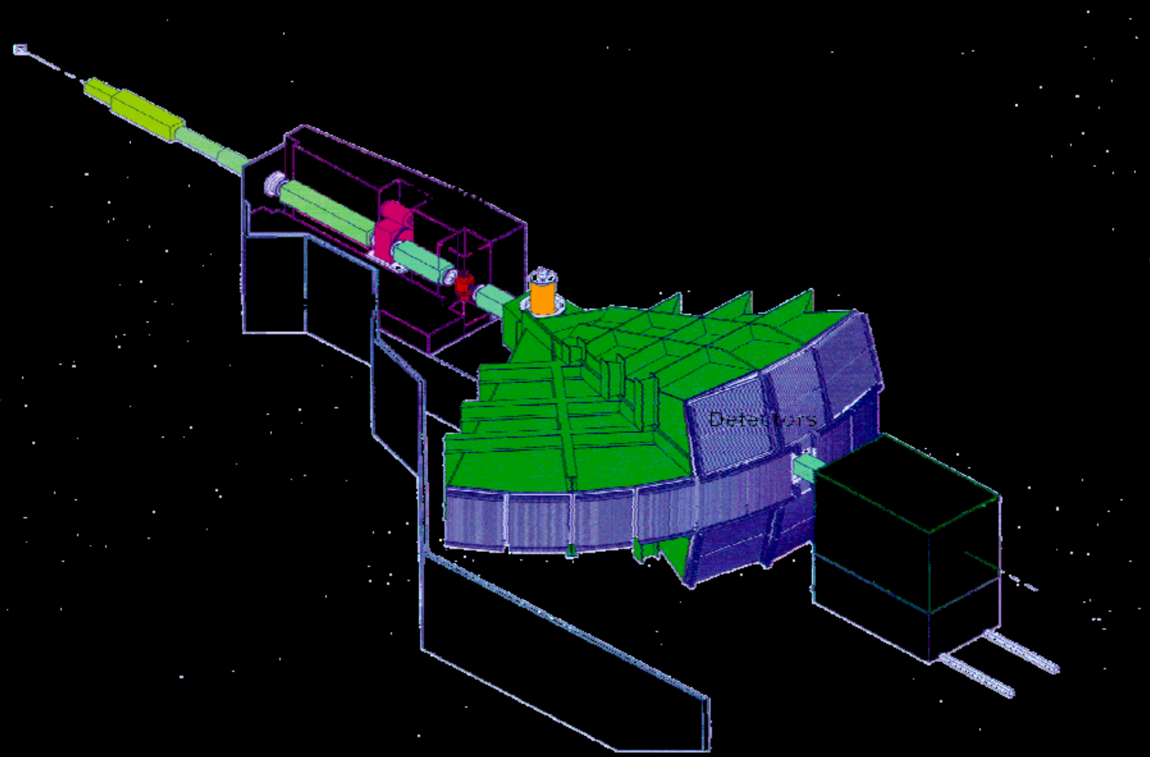
Inverted Geometry: the final energy is defined by a crystal or a filter and the incident energy is scanned by time-of-flight

Direct Geometry TOF Spectrometer



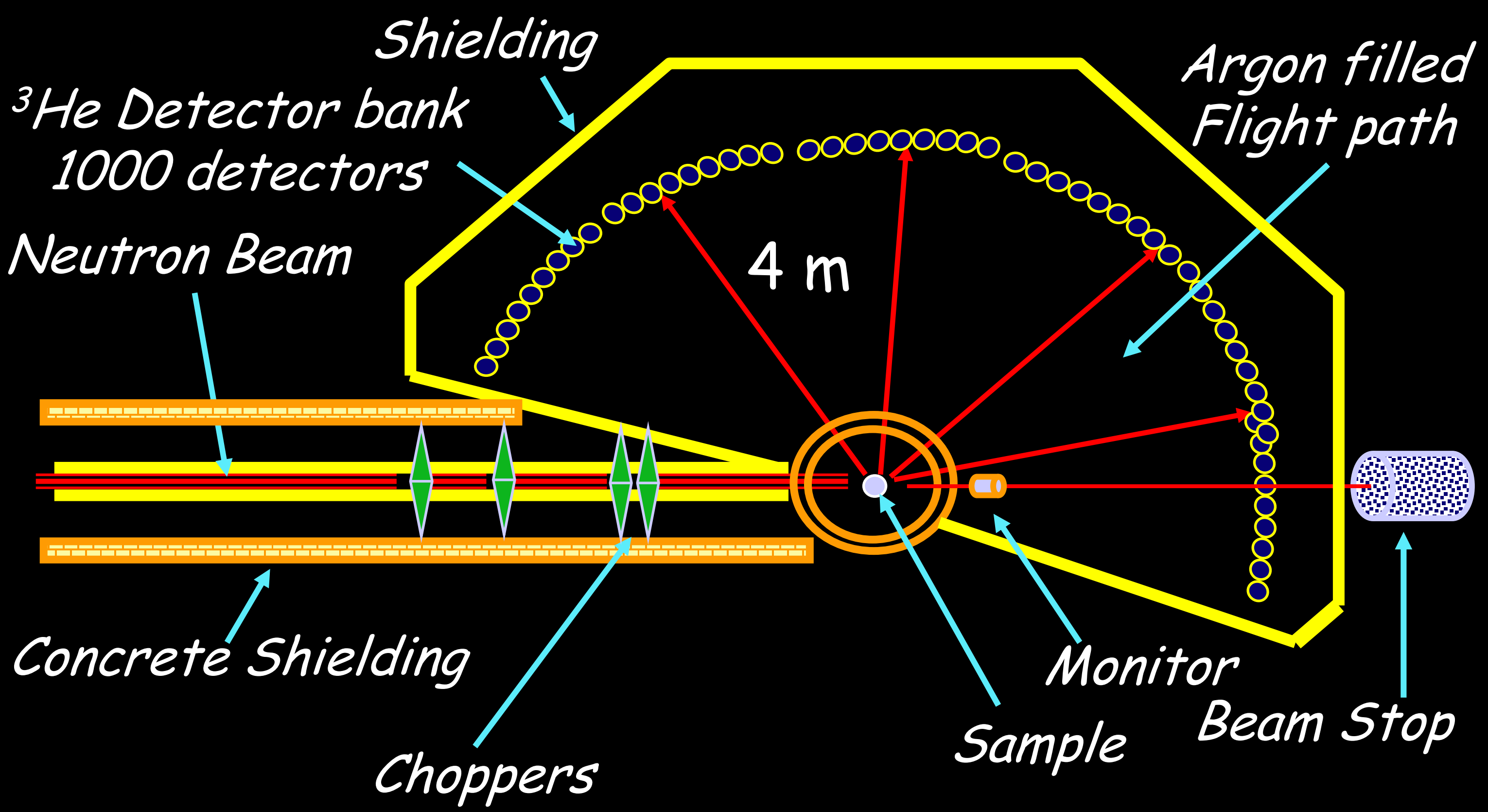
$$E_f = \frac{1}{2} m_n \frac{L_2^2}{(t - t_1)^2}$$

MAPS@ISIS

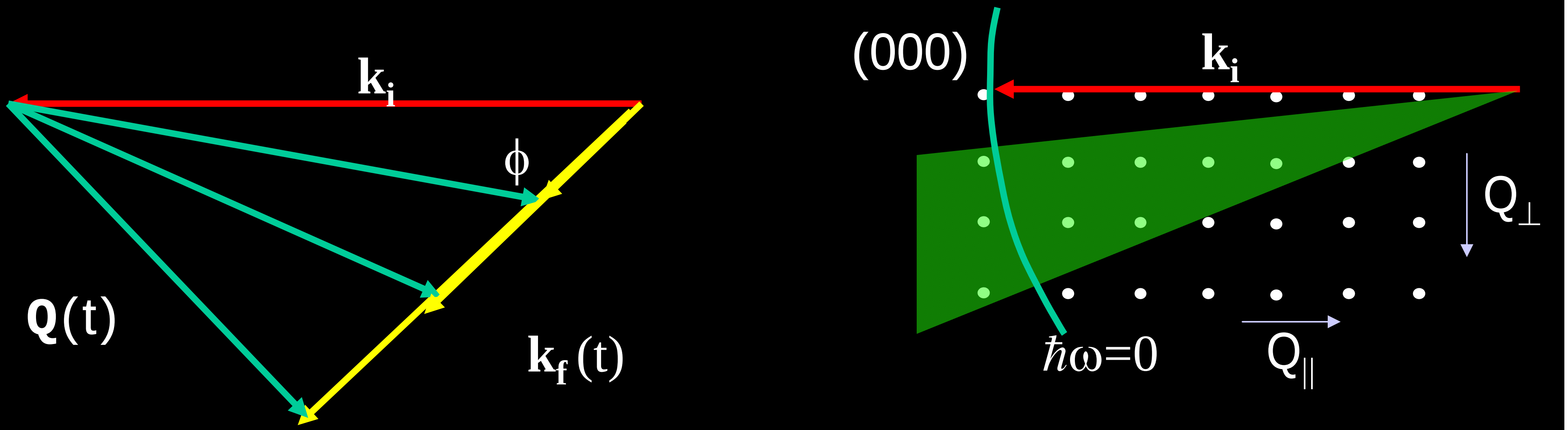


- Broad simultaneous coverage of (Q,ω) space
- Coupled measurement trajectories

IN5 at the Institut Laue Langevin



Kinematical triangle

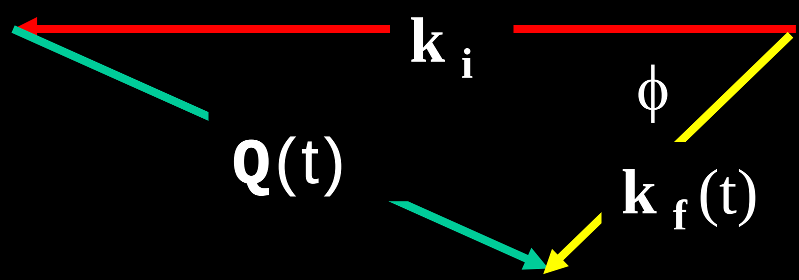


From the scattering triangle we can see that an array of detectors will trace out a sector in reciprocal space

Trajectory in kinematical space

Apply the cosine rule

$$\mathbf{Q}^2 = \mathbf{k}_i^2 + \mathbf{k}_f^2 - 2\mathbf{k}_i\mathbf{k}_f \cos\phi$$

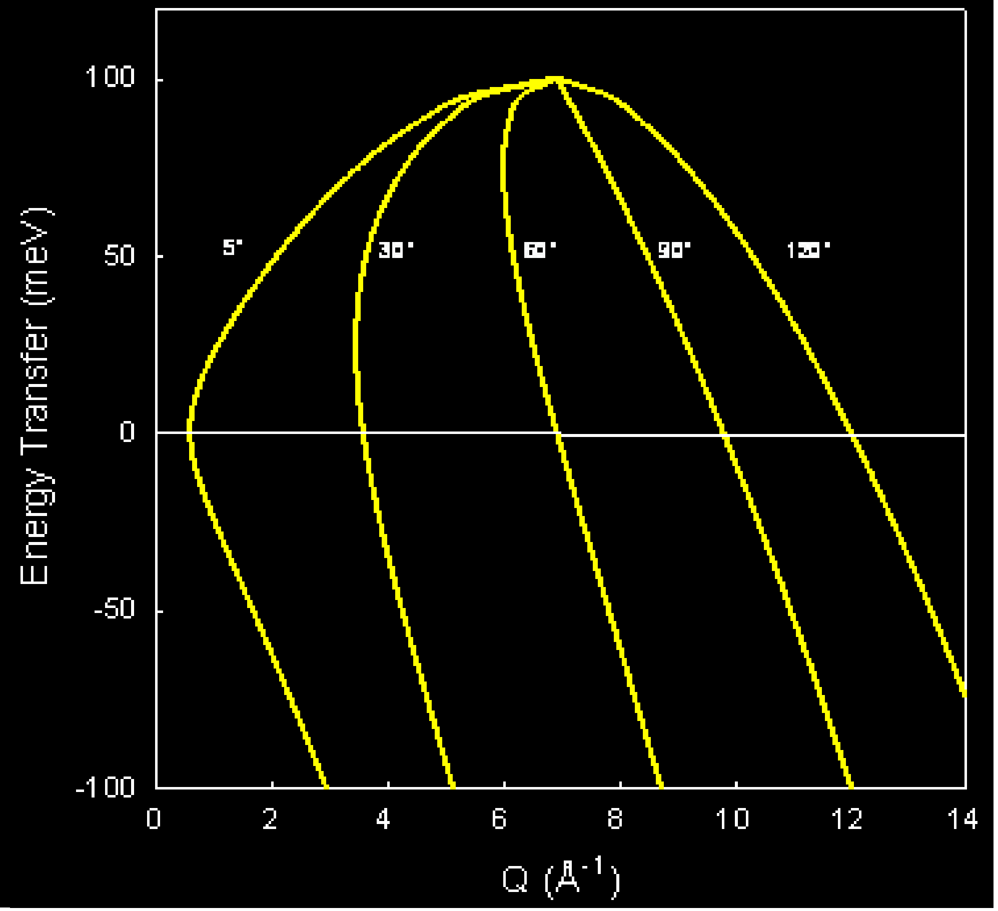


Convert to energy

$$\frac{\hbar^2\mathbf{Q}^2}{2m} = E_i + E_f - 2\left(E_i E_f\right)^{1/2}\cos\phi$$

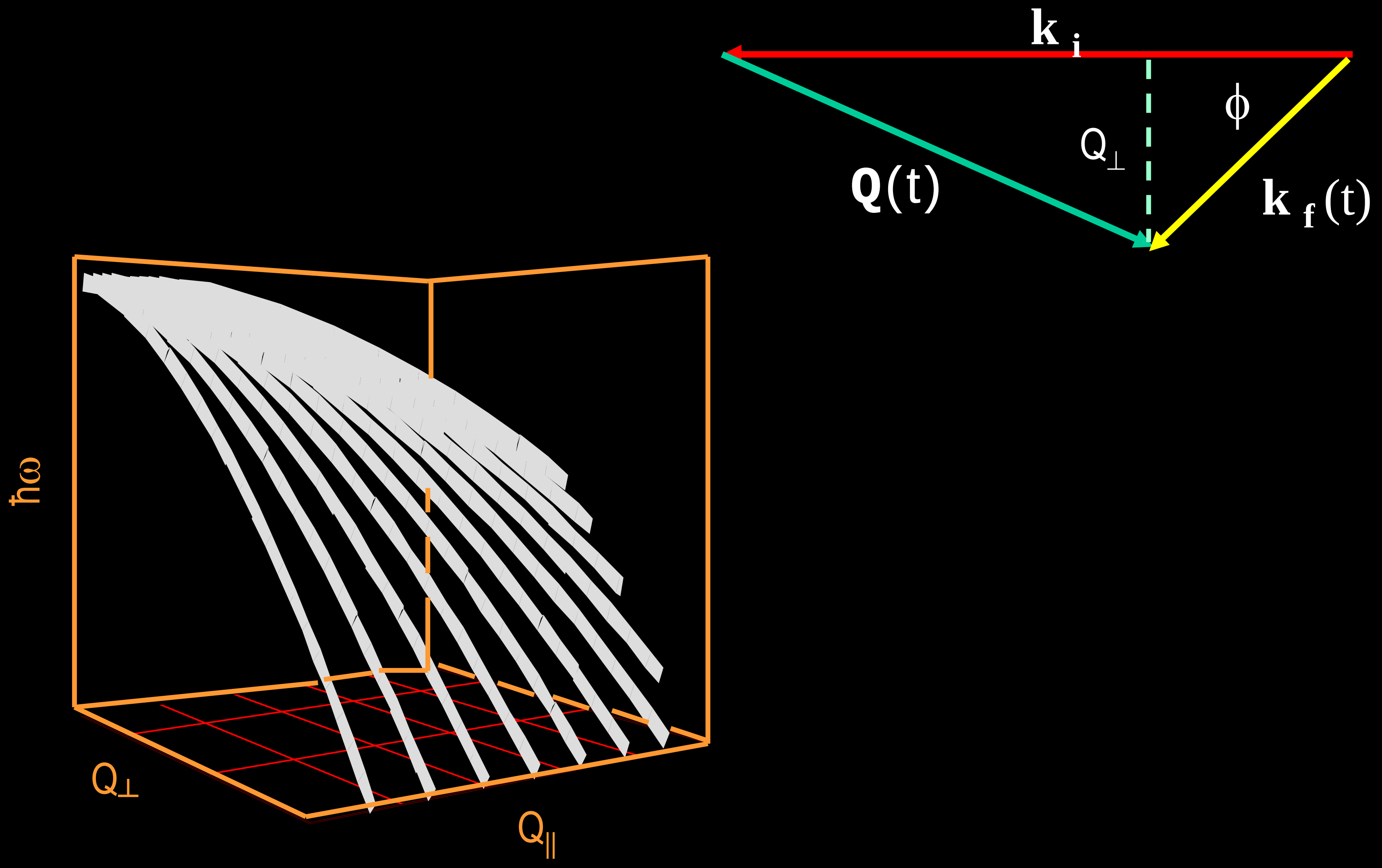
Eliminate E_f

$$\frac{\hbar^2\mathbf{Q}^2}{2m} = 2E_i - \hbar\omega - 2\cos\phi\left[E_i\left(E_i - \hbar\omega\right)\right]^{1/2}$$



Each detector traces a parabolic trajectory trough (Q,ω) space

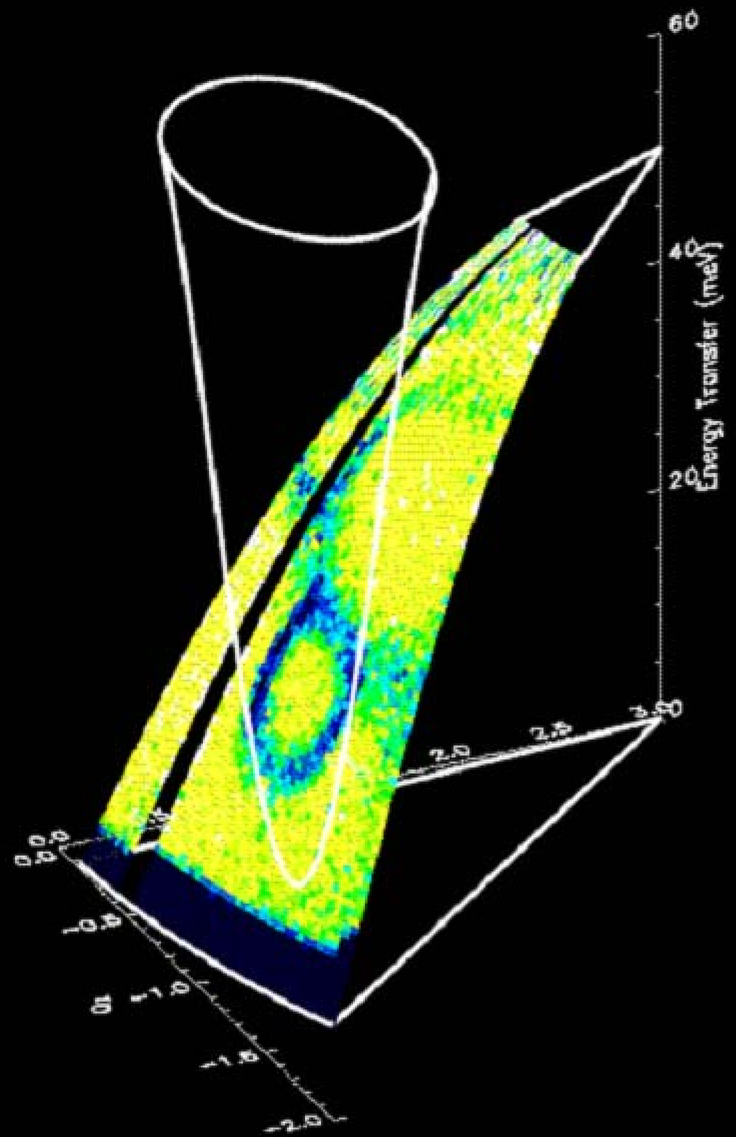
The detector array produces a surface in ($Q_{||}$,$Q_{\perp}$,ω) space



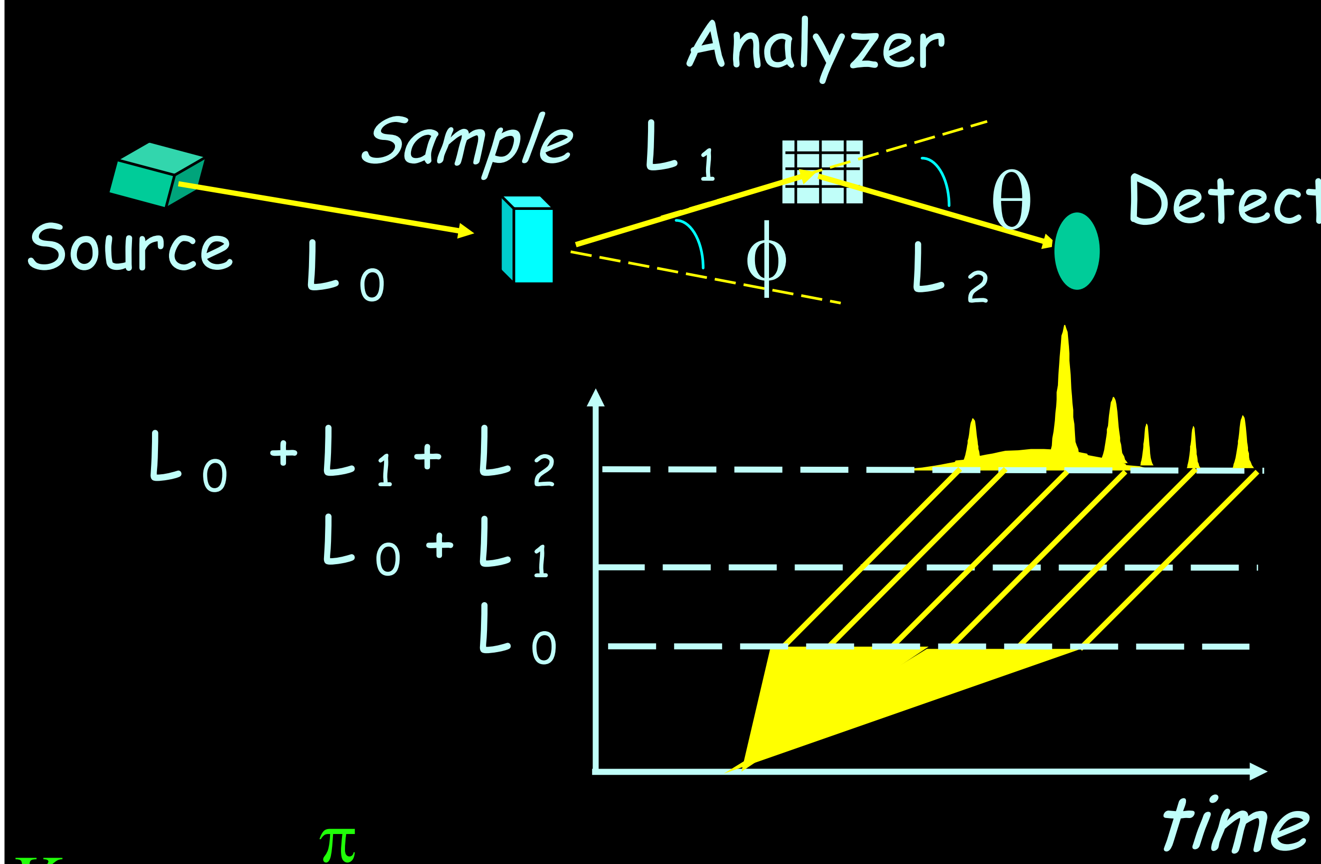
Ferromagnetic spin wave in a 3 dimensional magnetic system.
The spin wave will emerge like a 'cone' from a reciprocal lattice point.

Where that 'cone' intersects with the surface in $(Q_{||}, Q_{\perp}, \omega)$ space, scattering will be observed.

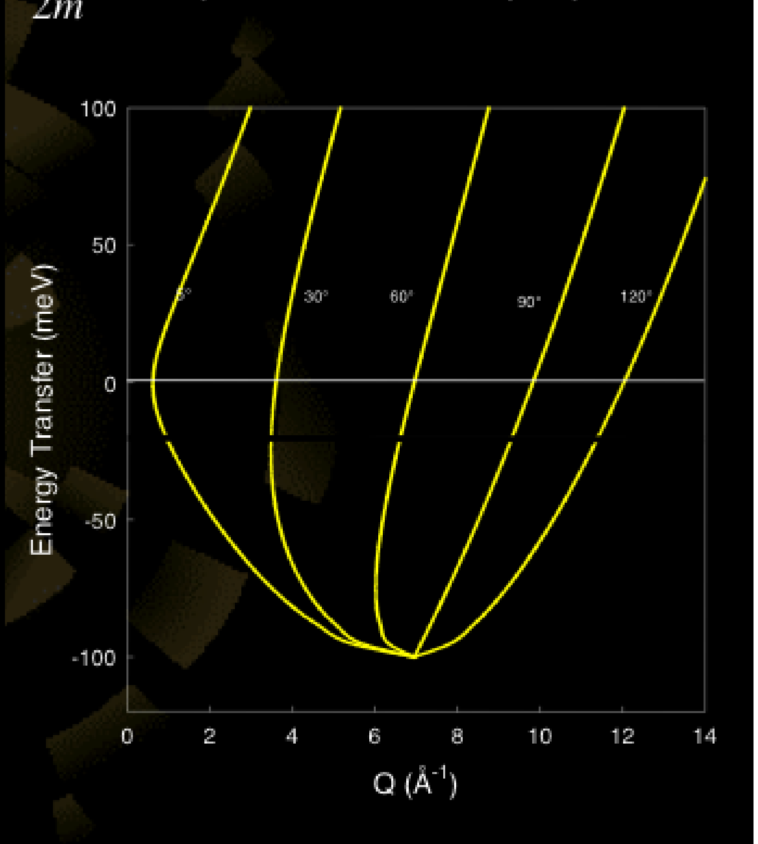
'Cuts' can the be performed in software during data analysis.



Inverse Geometry Chopper Spectrometers



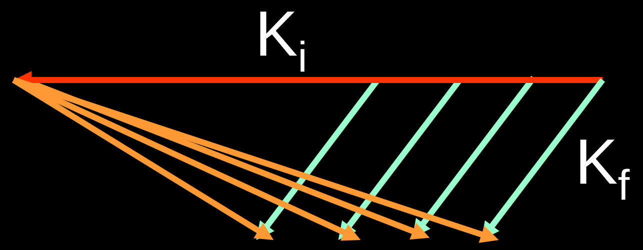
$$\frac{\hbar^2 Q^2}{2m} = 2E_f + \hbar\omega - 2\cos\phi\left[E_f\left(E_f + \hbar\omega\right)\right]^{1/2}$$

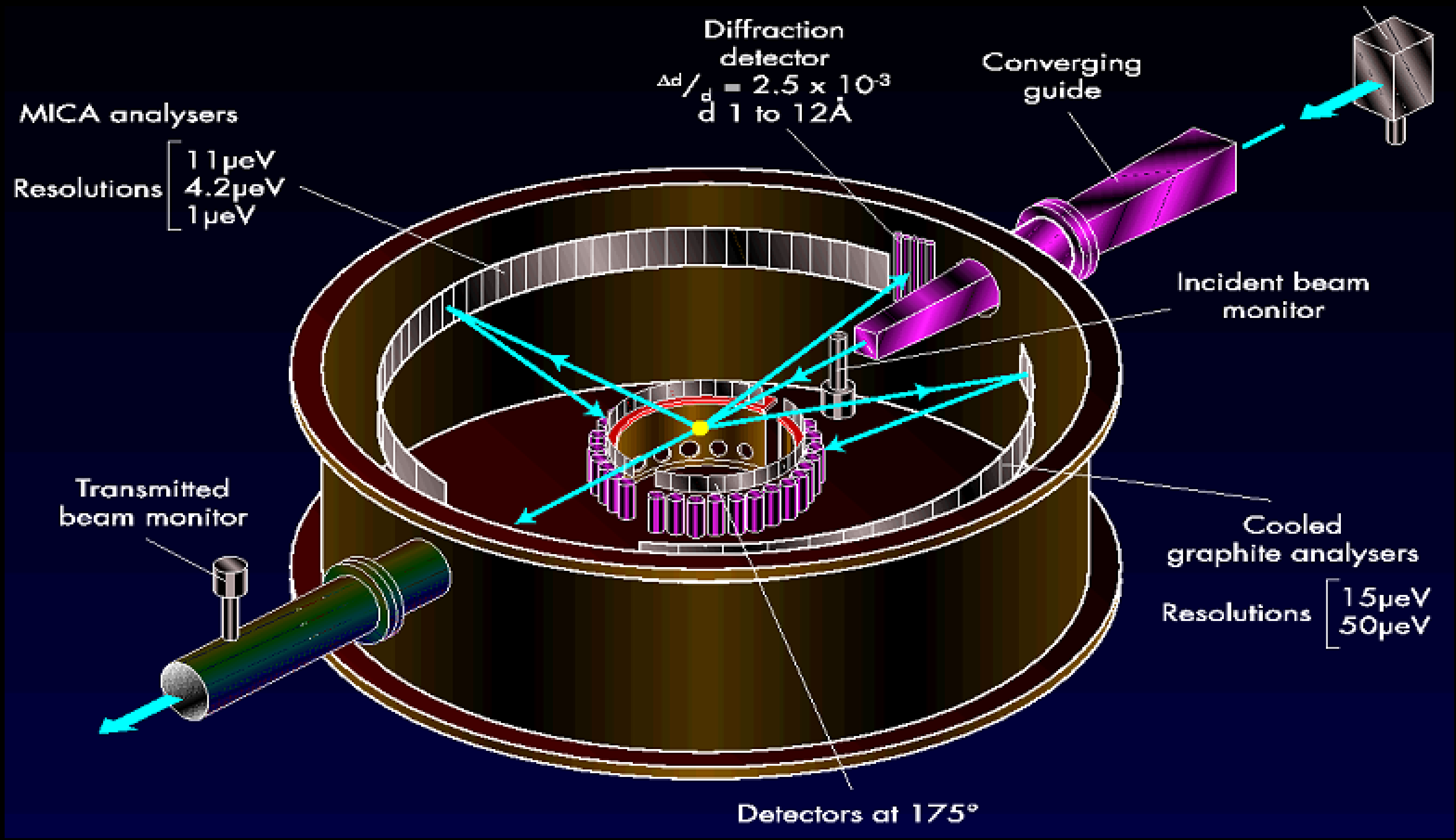


$$K_f = \frac{\pi}{d_A \sin\theta_A}$$

$$K_i = \frac{m_n L_0}{\hbar t - m_n (L_1 + L_2)\, d_A \sin\theta_A/\pi}$$

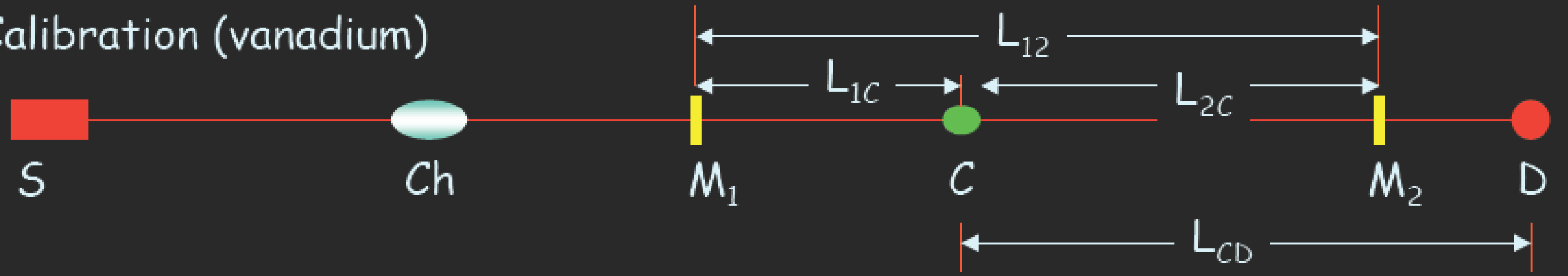
IRIS, RAL


K$_i$
K$_f$


Diffraction detector
$\Delta d/d = 2.5 \times 10^{-3}$
d 1 to 12Å
Converging guide
MICA analysers
Resolutions
11μeV
4.2μeV
1μeV
Incident beam monitor
Transmitted beam monitor
Cooled graphite analysers
Resolutions
15μeV
50μeV
Detectors at 175°

Energy calibration

Calibration (vanadium)



Incident wavevector: $$K_i = \frac{m_n}{\hbar}\,\frac{L_{12}}{t_2 - t_1} = 1.588\,\frac{L_{12}\,(\mathrm{mm})}{(t_2 - t_1)\,(\mu s)}$$

Time of arrival at the sample: $$t_C = t_1 + \frac{t_2 - t_1}{L_{12}}\,L_{1C}$$

Calibration of energy scale: the centre, t_e, of the vanadium elastic peak is determined first. The effective distance between the sample C and a given counter D is

$$L_{CD} = \frac{t_e - t_C}{t_2 - t_1}\,L_{12}$$

Wavevector and energy of neutrons detected at time t_j :

$$K_j = 1.588\,\frac{L_{CD}\,(\mathrm{mm})}{(t_j - t_C)\,(\mu s)}\,\text{Å}^{-1} \qquad E_j = 5.2131\,\frac{L_{CD}^2\,(\mathrm{mm}^2)}{(t_j - t_C)^2\,(\mu s)^2}\,\mathrm{meV}$$

Intensity calibration

Intensity histogram recorded with constant δt.
Time-to-energy conversion:

$$\delta E_j = -\frac{m_n L_{CD}^2}{(t_j - t_C)^3}\,\delta t$$

the cross-section is distorted

Counting strategy

C_j = counts in the j-th channel for sample +holder
H_j = counts in the j-th channel for holder
V_j = counts in the j-th channel for V standard
B_j = counts in the j-th channel for background
n_X = monitor counts (X = C, H, V, B)
$\eta_j(E)$ = detector efficiency
$\eta_M(E)$ = monitor efficiency

Intensity calibration

$$\frac{C_j}{n_C} - \frac{H_j}{n_H} = N_C \frac{d^2\sigma}{d\Omega dE_j} \Delta\Omega \; \Delta E_j \frac{\eta_j(E_j)}{\eta_M(E_0)}$$

$$\frac{V_j}{n_V} - \frac{B_j}{n_B} = N_V \left(\frac{d^2\sigma}{d\Omega dE_j}\right)_V \Delta\Omega \; \Delta E_j \frac{\eta_j(E_j)}{\eta_M(E_0)}$$

$$\sum_i \left(\frac{V_j}{n_V} - \frac{B_j}{n_B}\right) = N_V \left(\frac{d\sigma}{d\Omega}\right)_V \Delta\Omega \; \frac{\eta_j(E_0)}{\eta_M(E_0)}$$

Intensity calibration

$$\frac{d^2\sigma}{d\Omega dE_j} = \frac{N_V}{N_C} \frac{\frac{C_j}{n_C} - \frac{H_j}{n_H}}{\sum_j \left(\frac{V_j}{n_V} - \frac{B}{n_B}\right)} \left(\frac{d\sigma}{d\Omega}\right)_V \frac{\eta_j(E_j)}{\eta_M(E_0)} \frac{(t_j - t_C)^3}{m_n L_{CD}^2 \delta t}$$

$$N_V = 0.70 \times 10^{23} \text{ at} / \text{cm}^3$$

$$\left(\frac{d\sigma}{d\Omega}\right)_V = \frac{\sigma_V}{4\pi} = 0.3804 \text{ barn} / \text{sr}$$

Concluding remarks

INS accounts for the detailed atomic motions and magnetic excitations - individual or collective - within a many-body system.

Microscopic motions or excitations may occur in vastly different time and length scales, typically ps to ms and sub-nm to μm: INS necessitates a wide coverage in the energy (*E*) and wavevector (*Q*) space with good resolutions.

Interpretation of INS data can be a challenge facing experimentalists. Researchers nowadays have to apply methods of theoretical modeling and simulations that require high degree of sophistication and substantial amount of computing resources.