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Neutron Diffraction

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Outline

- goals
- applications of diffraction
- some basic tools for diffraction
- diffraction instruments at PSI
- examples
- strengths and weaknesses
- summary

Goals of (Neutron) Diffraction

- structure (nuclear and magnetic)
- thermal motions
- occupation of interstitial sites
- multiphase compositions

Applications of Diffraction

- **material specification: multiphase**
- **structure/volume information as a function of temperature, pressure, light illumination, e.g**
- **complementary information to X-Rays (*nuclear density vs. electron-density)***
- **localization of light atoms in the presence of heavy ones such as Uranium**
- **neighbored atoms in the periodic table may be distinguished**
- **isotope effects (e.g. H/D, B^{11},…)**

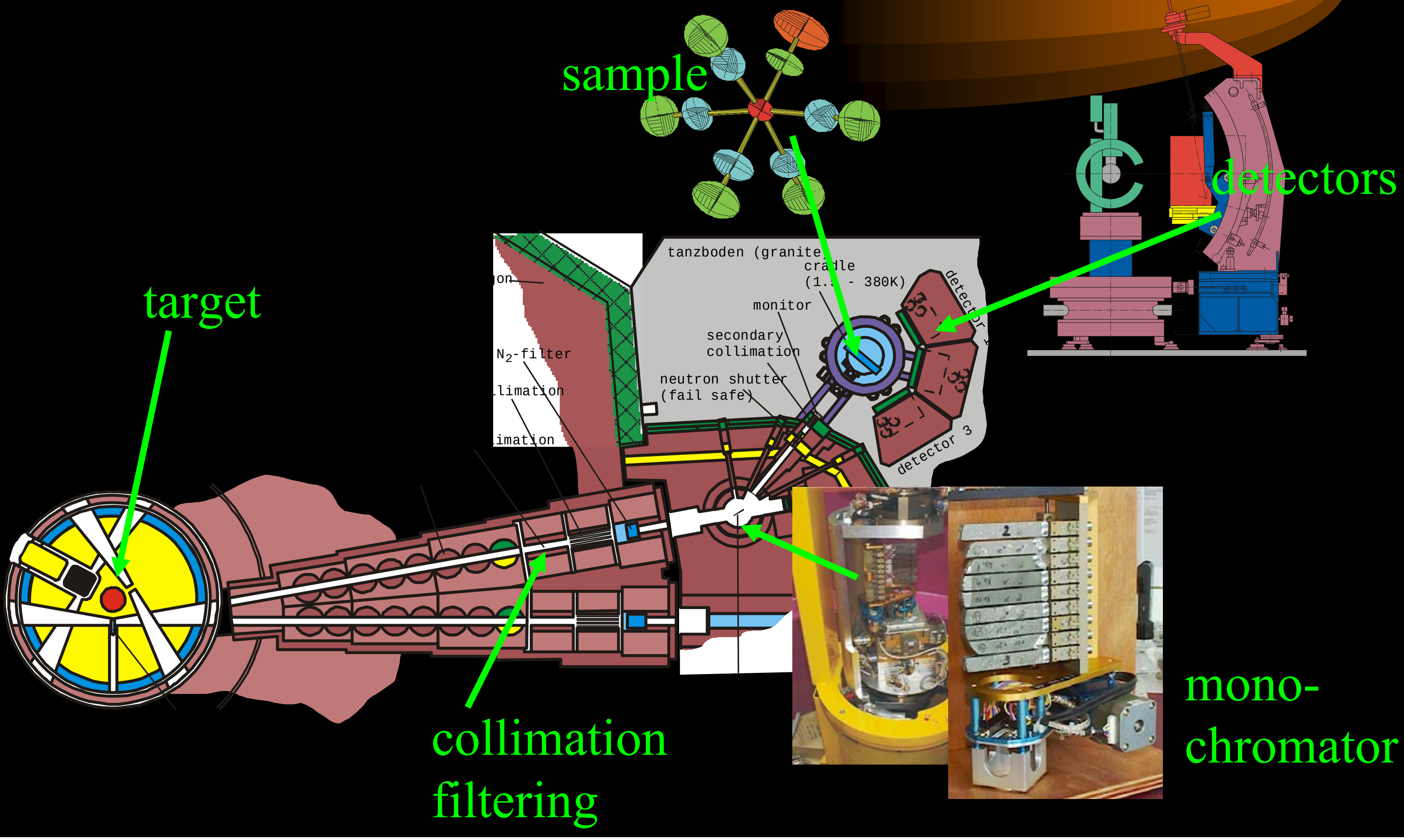
The Diffraction Method

- cross-section for diffraction
- reciprocal lattice and Ewald sphere construction
- structure factors and Bragg intensities
  Debye Waller factor as a correction example
- magnetic diffraction

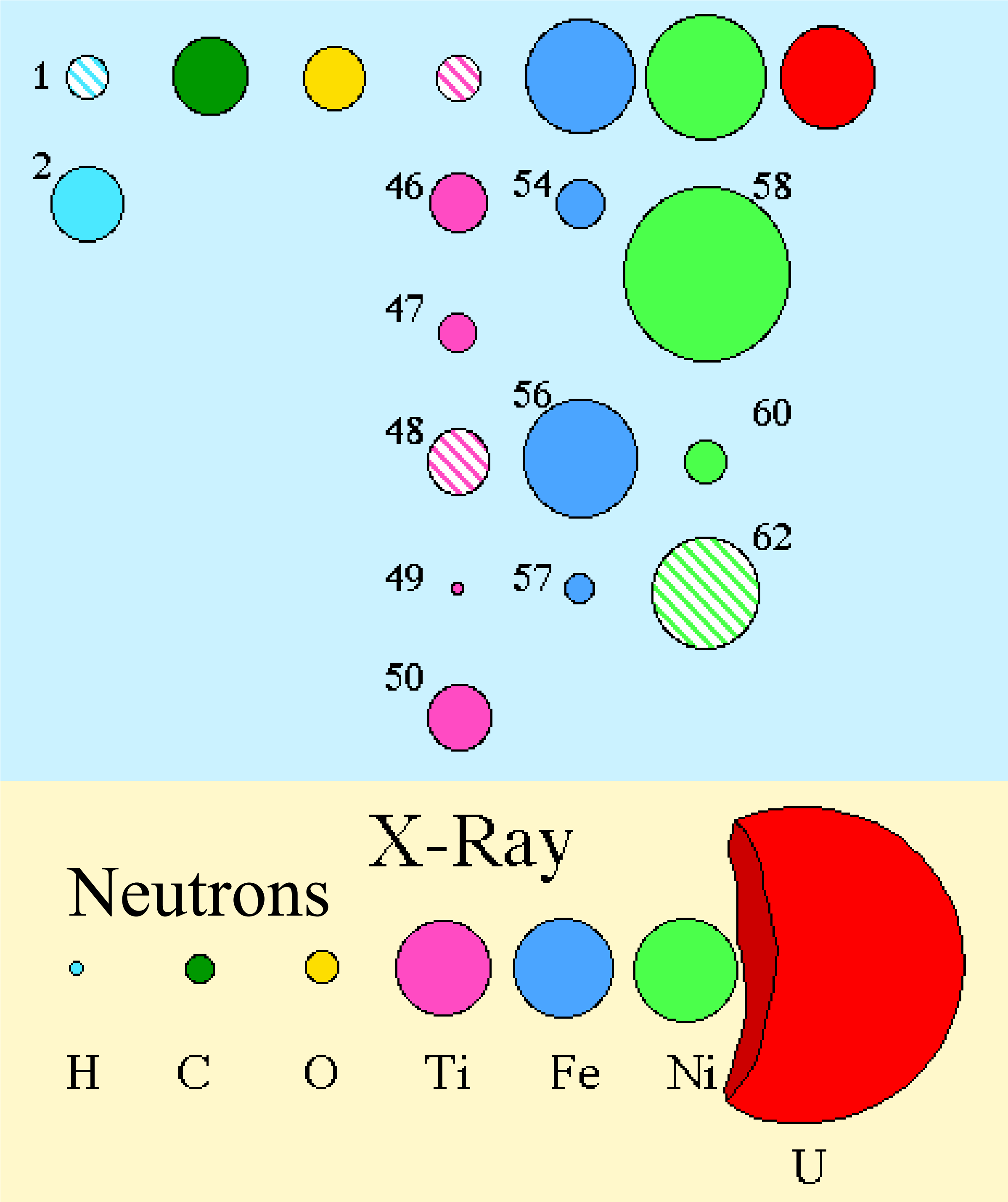
FOR MORE INFO...

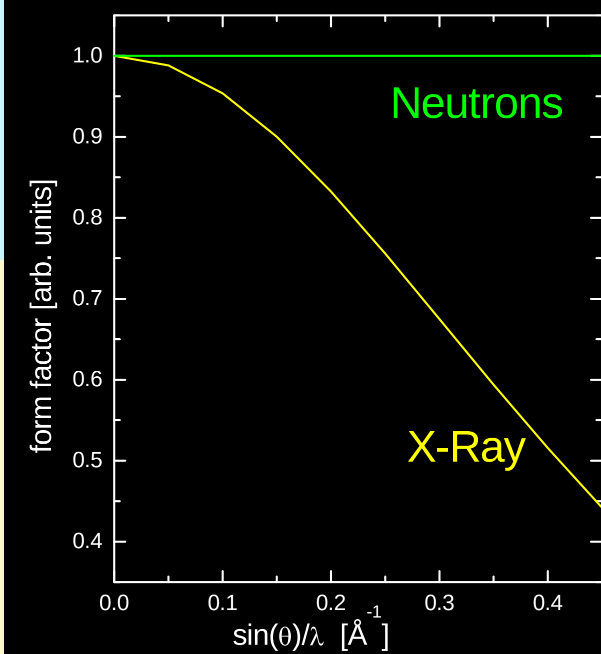
G.L. Squires, Thermal Neutron Diffraction, Dover 1996

Diffraction Setup



X-Rays? Neutrons?

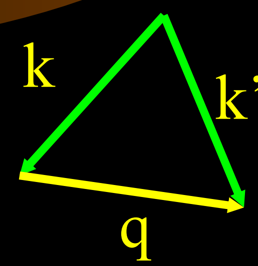




Diffraction Method ...

We are using:

- elastic scattering function S
  (momentum transfer q=k'-k, energy transfer ω=0)
- Born approximation: system undisturbed
- sample size is indefinite
- point symmetry of atoms
  yielding 3-dimensional symmetry (International tables)
  periodicity in real space: basic vectors a_1,a_2,a_3
- reciprocal space and Ewald sphere as a convenient definition



Elastic Scattering Function

scattering Density

$$V(\vec{\mathbf{r}}) = \frac{2\pi\hbar^2}{m}\rho\left(\vec{\mathbf{r}}\right)$$

$$\left\langle \vec{\mathbf{k}}'\middle| V \middle|\vec{\mathbf{k}}\right\rangle = \frac{m}{2\pi\cdot\hbar^2}\cdot\frac{2\pi\cdot\hbar^2}{m}\int d\vec{\mathbf{r}}\cdot\exp\left(-i\vec{\mathbf{k}}'\vec{\mathbf{r}}\right)\ \rho(\vec{\mathbf{r}})\exp(\ i\vec{\mathbf{k}}\vec{\mathbf{r}}),$$

incoming neutron with direction k

scattered neutron with direction k'

|k'| = |k|

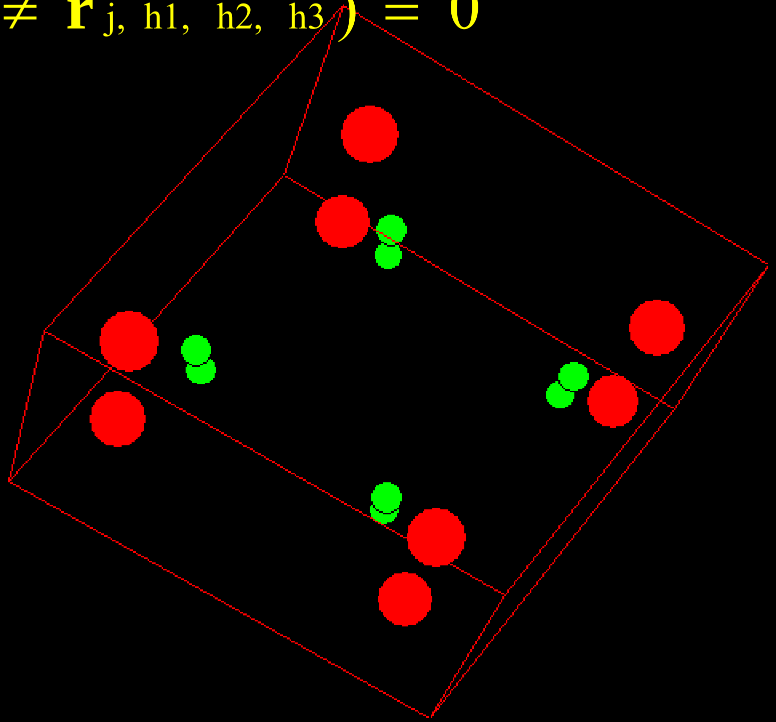
no energy transfer

Scattering Density: continuos -> atoms -> lattice

$$V(\vec{\mathbf{r}}) = \frac{2\pi \cdot \hbar^2}{m} \rho(\vec{r})$$

$$V(\vec{\mathbf{r}}_{j,\ h1,\ h2,\ h3}) = \frac{2\pi\hbar^2}{m} b_j$$

$$V(\vec{\mathbf{r}} \neq \vec{\mathbf{r}}_{j,\ h1,\ h2,\ h3}) = 0$$



Structure Factor: From the Continuum to Discrete Atoms

$$\langle \vec{k}' | V | \vec{k} \rangle = ?$$

$$V(\vec{\mathbf{r}}) = \frac{2\pi \cdot \hbar^2}{m} \rho(\vec{r}) \longrightarrow V(\vec{\mathbf{R}}_j) = \frac{2\pi\hbar^2}{m} \cdot b_j$$

$$V(\vec{\mathrm{r}} \neq \vec{\mathbf{R}}_j) = 0$$

$$\langle \vec{k}' | V | \vec{k} \rangle = \int \rho(\vec{r}) \cdot e^{i(\vec{k}-\vec{k}')\cdot\vec{r}} d\vec{r} = \sum_j^{atoms} b_j \cdot e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_j}$$

b_j: scattering “power”

Integral over ρ(r) replaced by sum over all atoms j at position R_j in the substance

R: Separation in Translation and Unit Cell Parts

$R_j = R_{hkl} + r_j$

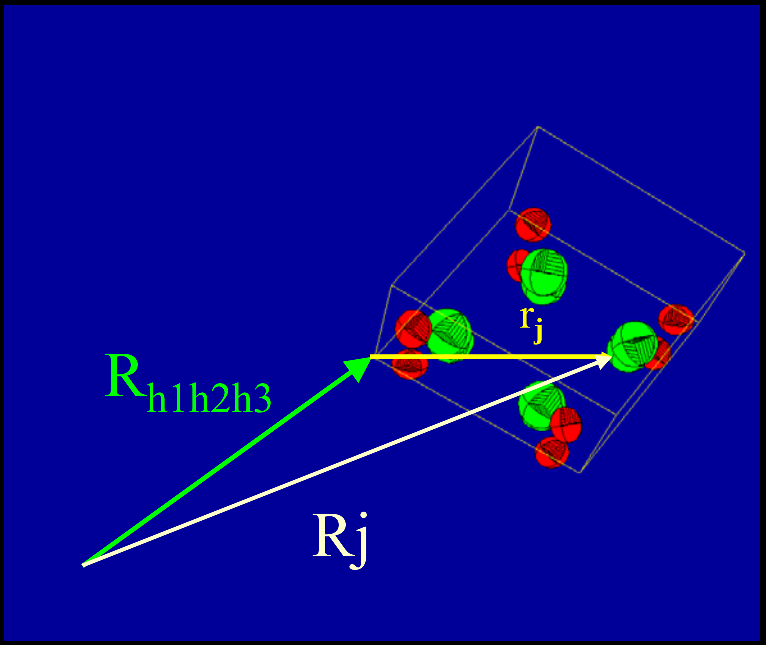
- translation symmetry

  R_{hkl} = $\mathbf{h_1}$*a_1 + $\mathbf{h_2}$*a_2 + $\mathbf{h_3}$*a_3

a_1,a_2,a_3	**lattice constants**
h1,h2,h3	**integers**

- atoms within unit cell

  $r_j = x_j * a_1 + y_j * a_2 + z_j * a_3$
  $(0 \geq x_j, y_j, z_j \geq 1)$
  position of atom *j* within the unit cell



And Finally:

$$\int \rho(\vec{r}) \cdot e^{i(\vec{k}-\vec{k}')\cdot\vec{r}} d\vec{r}$$

$$=$$

$$\sum_{h1h2h3}^{lattice} \sum_{j}^{atoms} b_j \cdot e^{i(\vec{k}-\vec{k}')\cdot(\vec{R}_{h1h2h3}+\vec{r}_j)} = \sum_{h1h2h3,j} e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_{h1h2h3}} \quad b_j e^{i(\vec{k}-\vec{k}')\cdot\vec{r}_j}$$

$$= F$$

maximal if n·2π=integer
(wave superposition)
yields
Laue conditions
Ewald sphere construction

intensity

A Convenient Tool:
Reciprocal Lattice and Ewald-Sphere

$$e^{i(\vec{k}-\vec{k}')\vec{R}_{h1h2h3}}$$

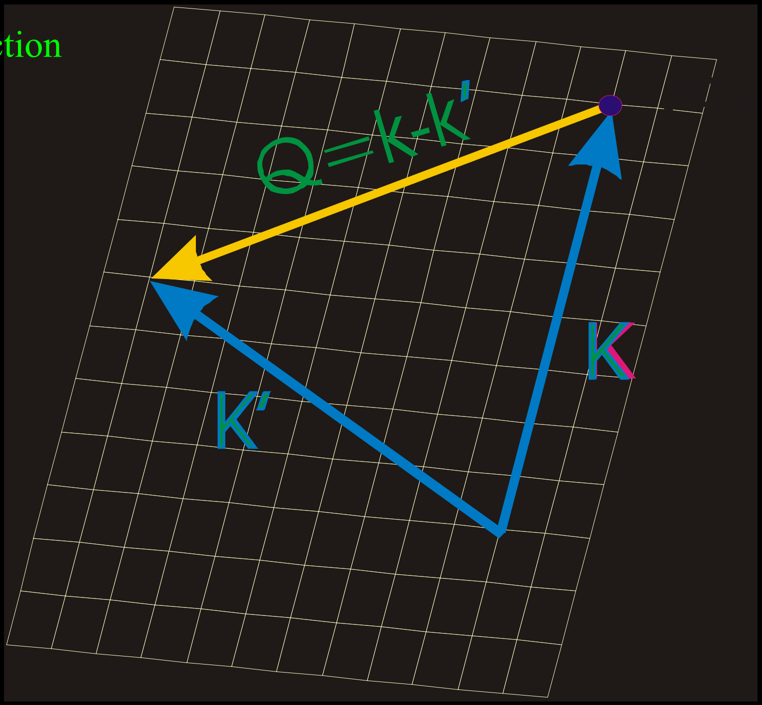
maximal if exponent is n·2π
(wave superposition)
=
Laue conditions
Ewald sphere construction

use reciprocal space:

$$\vec{a}_i \cdot \vec{a}_j{}^* = 2\pi \cdot \delta_{ij}$$

or

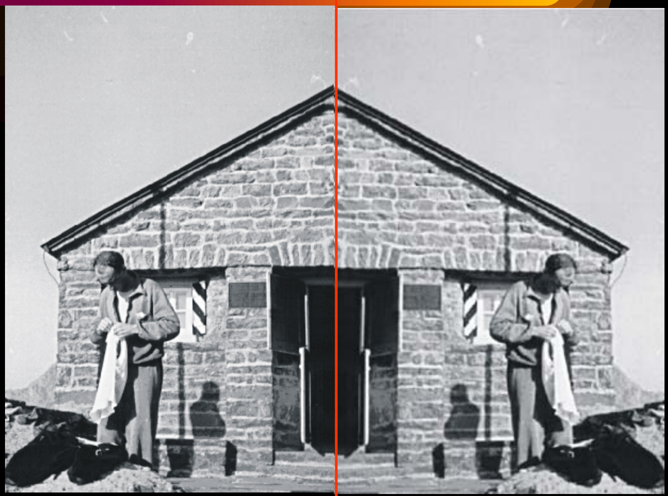
$$\vec{a}_1{}^* = 2\pi \cdot \frac{\vec{a}_2 x \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 x \vec{a}_3)} = 2\pi \cdot \frac{\vec{a}_2 x \vec{a}_3}{V_{unit}}$$

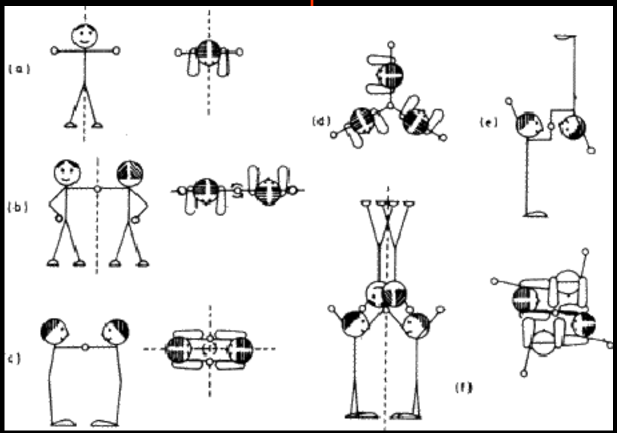


$Q_{hkl} = \mathbf{h}{*}a_1{}^* + \mathbf{k}{*}a_2{}^* + \mathbf{l}{*}a_3{}^*$

Symmetry: An addional help

Greek Geometry (Euklid)
Existence of symmetry was known,
but the importance not realized
(example: Mirror plane between figures)





A-M. Legendre (Lectures 1794)
Définition XVI: ***J`appelerai polyèdres symétriques deux polyèdre qui, ayant une base commune, sont construits semblablement, <u>l'un au-dessus</u> du plan, <u>l'autre au-dessous</u> avec cette condition que les sommets des angles solides homologues soient situés à égales distances du plan de la base, sure une même droite perpendiculaire à ce plan.***

Corrections: Debye Waller as an Example

$$Oscillator \quad around \quad \vec{r}_j(t) \quad : \vec{r}_j(t) = \vec{r}_j + \Delta\vec{r}_j(t)$$

to calculate :

$$\int \rho(\vec{r}) \cdot e^{i\vec{q}\cdot\vec{R}_j(t)} d\vec{r} = \int \rho(\vec{r}) \cdot e^{i\cdot\vec{q}\cdot\vec{R}_j} e^{i\cdot\vec{q}\Delta\vec{r}_j(t)} d\vec{r}$$

$$= \sum_{hkl}^{lattice} \sum_{j}^{atoms} e^{i\vec{q}\cdot(\vec{R}_{h1h2h3}+\vec{r}_j(t))} = \left\langle \sum e^{i\vec{q}\cdot\vec{R}_{h1h2h3}} b_j e^{i\vec{q}\cdot\vec{r}_j} e^{i\Delta\vec{r}_j(t)\vec{q}} \right\rangle$$

Corrections: Example Debye Waller (step by step calculation)

$$\int e^{i(\vec{k}-\vec{k}')\cdot\vec{R}}\, d\vec{r} = \sum_{hkl}^{lattice} \sum_{j}^{atoms} e^{i\vec{q}\cdot(\vec{H}_{hkl}+\vec{r}_j)} = e^{i\vec{q}\cdot\vec{H}_{hkl}}\, b_j\, e^{i\vec{q}\cdot\vec{r}_j(t)}$$

Vibrating: $\vec{r}_j(t) = \vec{r}_j + \Delta\vec{r}_j(t)$

to calculate: $e^{i\cdot\vec{q}\cdot\vec{r}_j(t)} = e^{i\cdot\vec{q}\cdot\vec{r}_j}\, e^{i\cdot\vec{q}\cdot\Delta\vec{r}_j(t)}$

$$e^{i\cdot\vec{q}\cdot\Delta\vec{r}_j(t)} = 1 + i\cancel{\left\langle \vec{q}\cdot\Delta\vec{r}_j \right\rangle} - \frac{1}{2}\cdot\left\langle (\vec{q}\cdot\Delta\vec{r}_j)^2 \right\rangle + \ldots$$

$$\frac{1}{2}\cdot\left\langle (\vec{q}\cdot\Delta\vec{r}_j)^2 \right\rangle = \frac{1}{2} q^2 \frac{\Delta r_j^{\,2}}{3}$$

Example:

isotrop: $\Delta x^2 = \Delta x^2 = \Delta x^2 = \dfrac{\Delta\vec{r}_j^{\,2}}{3}$

$$\left\langle \vec{q}\cdot\Delta\vec{r} \right\rangle^2 = q^2\cdot\Delta r^2\cdot\left\langle \cos^2\vartheta\cdot\sin^2\varphi \right\rangle = q^2\frac{\Delta r_j^{\,2}}{3}$$

$$q = \frac{4\pi}{\lambda}\sin\Theta$$

$$W = \frac{q^2}{2}\frac{\Delta\vec{r}_j^{\,2}}{3} = \frac{8\pi^2\sin^2\Theta}{\lambda^2}\frac{\Delta\vec{r}_j^{\,2}}{3}$$

$$e^{-W} = 1 - W + \frac{W^2}{2} - \ldots$$

$$\int e^{i(\vec{k}-\vec{k}')\cdot\vec{R}}\, dr = \sum_{hkl}^{lattice} \sum_{j}^{atoms} e^{i\vec{q}\cdot(\vec{H}_{hkl}+\vec{r}_j)} = e^{i\vec{q}\cdot\vec{H}_{hkl}}\, b_j\, e^{i\vec{q}\cdot\vec{r}_j}\, e^{-W}$$

Easier: Folding Functions in Real Space Multiplying Functions in Reciprocal Space

$$\vec{R}_j \longleftrightarrow F_{hkl}$$

$$F_{hkl} = \int \rho(\vec{r}) \cdot e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_j} d\vec{r}$$

$$\vec{r}_j(t) = \vec{r}_j + \Delta\vec{r}_j(t)$$

$$F_{hkl}' = F_{hkl} \cdot \int e^{i(\vec{k}-\vec{k}')\cdot\Delta\vec{r}_j} d\vec{r}$$

$$e^{-W} = \int e^{i(\vec{k}-\vec{k}')\cdot\Delta\vec{r}_j} d\vec{r}$$

isostropic:

$$W = \frac{q^2}{2}\frac{\Delta\vec{r}_j^{\,2}}{3} = \frac{8\pi^2 \sin^2\Theta}{\lambda^2}\frac{\Delta\vec{r}_j^{\,2}}{3}$$

$$F'_{hkl} = \int \rho(\vec{r}) \cdot e^{i(\vec{k}-\vec{k}')\cdot\vec{R}} dr = \sum_{h1h2h3}^{lattice} \sum_{j}^{atoms} b_j e^{i\vec{q}\cdot(\vec{R}_{h1h2h3}+\vec{r}_{j(t)})} = F_{hkl}\ e^{-W}$$

Magnetic Scattering (I)

$$\hat{\mu} = -\mu_B(\hat{L} + 2\hat{S}) \quad \longleftrightarrow \quad \hat{\mu}_N$$

where

$\hat{L} = \vec{r} \times \hat{p}$: orbital angular momentum operator

$\hat{S}$: spin angular momentum operator

Field of a single electron with speed v_e :

$$\hat{U}_m = \hat{\mu}\vec{H} = -\gamma\mu_N\hat{\sigma}\cdot\vec{H}$$

$$\vec{H} = curl\,\frac{\vec{\mu}_e x \vec{R}}{|R|^3} - \frac{e}{c}\frac{\vec{v}_e x \vec{R}}{|R|^3}$$

γ : gyromagnetic ratio

c : speed of light

e : electron charge

$\hat{\sigma}$: Pauli spin operator

$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ $\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$ $\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

Magnetic Scattering (II)

$$F_M(\vec{q}_{hkl}) = \sum_{hkl}^{lattice} \sum_{j}^{atoms} b_{Mj}(\vec{q}_{hkl}) \cdot e^{i \cdot \vec{q} \vec{r}_j} \cdot T_j(\vec{q}_{hkl})$$

$$b_{Mj}(\vec{q}_{hkl}) = \frac{e^2\gamma}{m_e c^2} \cdot f_{Mj}(\vec{q}_{hkl}) \cdot \vec{\sigma} \cdot \vec{m}_{\perp j}(\vec{q}_{hkl})$$

b_{Mj} : magnetic scattering amplitude

f_{Mj} : magnetic form factor

$T_j(\vec{q}_{hkl})$: Debye Waller

$\frac{1}{2}\vec{\sigma}$: spin of sampling neutron

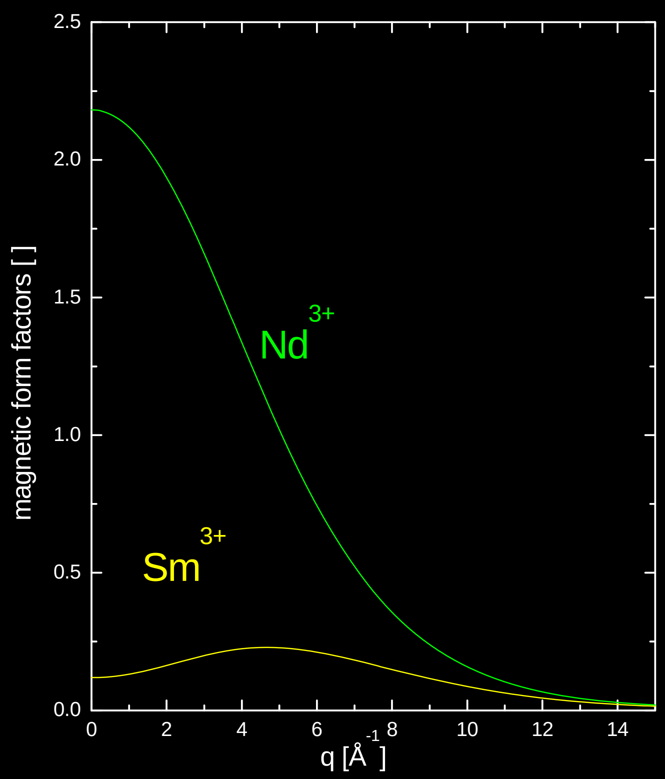
$\vec{m}_{\perp j}(\vec{q}_{hkl})$: projection of magnetic moment m_j to the z-axis (perpendicular to $\vec{k}, \vec{k}'$)

Magnetic Scattering (III)

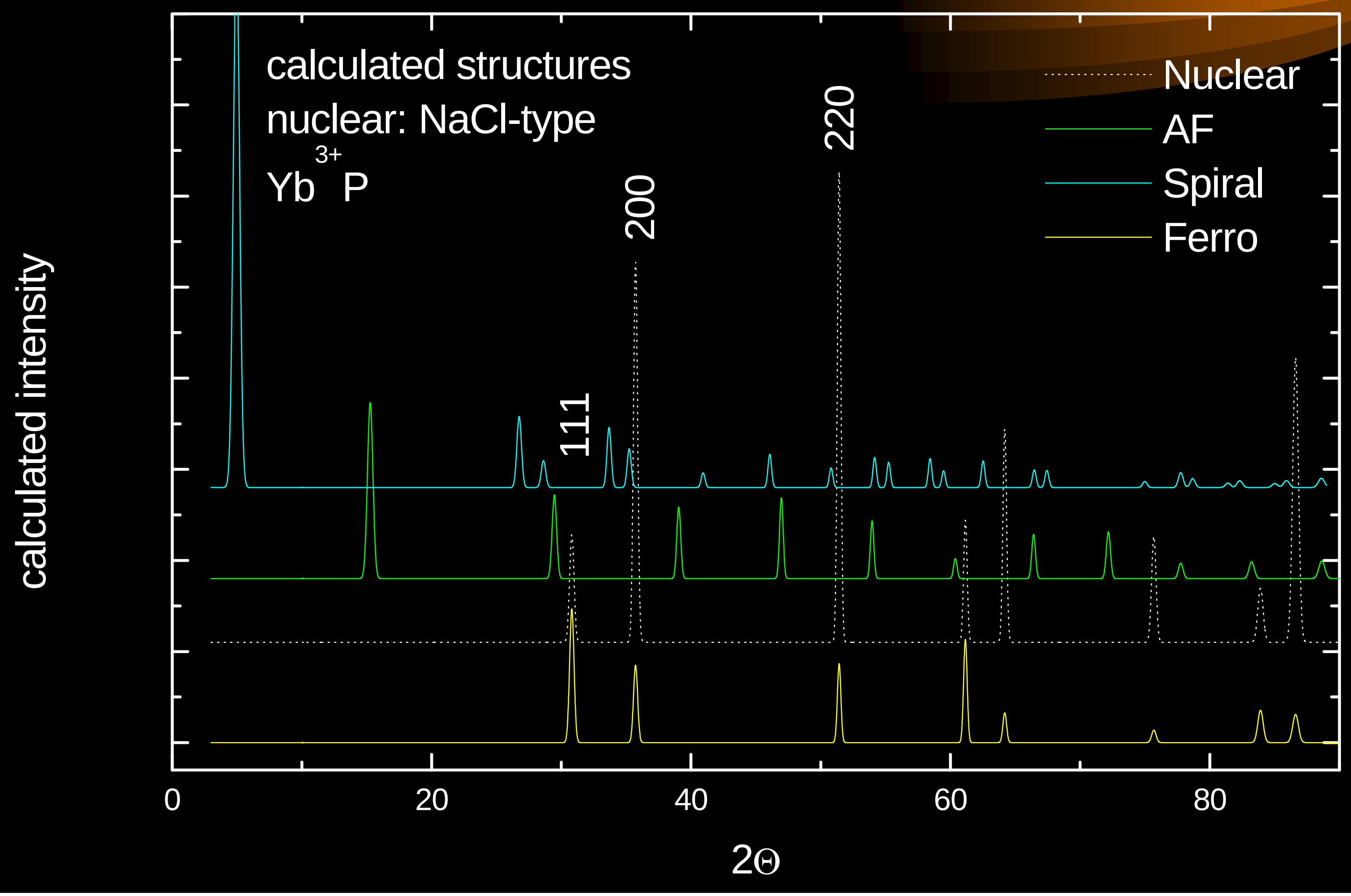
$$f_{Mj}(\vec{q}_{hkl}) = \int_{unit-cell} M_j(\vec{r}) e^{i\cdot\vec{q}\vec{r}} d\vec{r}$$

with the normlised magnetization density

$$f_{Mj}(0) = \int_{unit-cell} M_j(\vec{r}) \cdot d\vec{r} = 1.$$



Magnetic Diffraction: Calculated Powder Patterns



Nuclear and Magnetic: The Sum

unpolarised neutrons : incoherent superposition :

$$I(\vec{q}_{hkl}) = |F_n + F_m|^2 \approx |F_n|^2 + |F_m|^2 = I_{nuclear} + I_{magnetic}$$

polarized neutrons : coherent superposition :

incoming neutrons: spin up (+) or down (-)

$$I^{\pm}(\vec{q}_{hkl}) = |F_n \pm F_m|^2 = |F_n|^2 + |F_m|^2 \pm 2|F_n \cdot F_m|$$

flipping ratio can be changed

Elastic Diffuse Magnetic Scattering from Paramagnets: Example Yb^{3+}

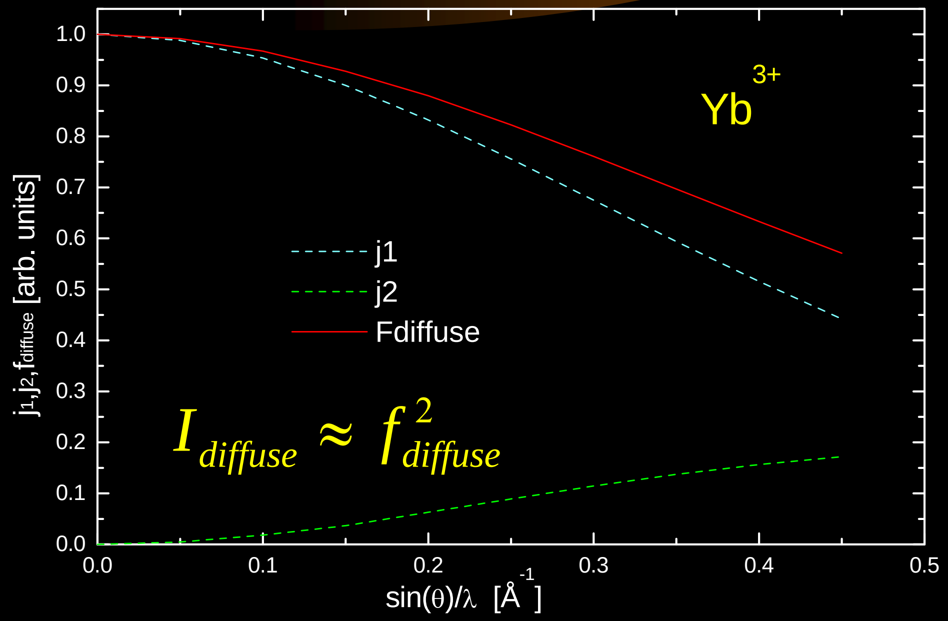
Yb^{3+} : S=1/2, L=3, J=7/2

Dipole approximation:

$$f_{diffuse}(q) = \langle j_o(q) \rangle + \langle j_2(q) \rangle \cdot \frac{J(J+1)+L(L+1)-S(S+1)}{3J(J+1)-L(L+1)+S(S+1)}$$

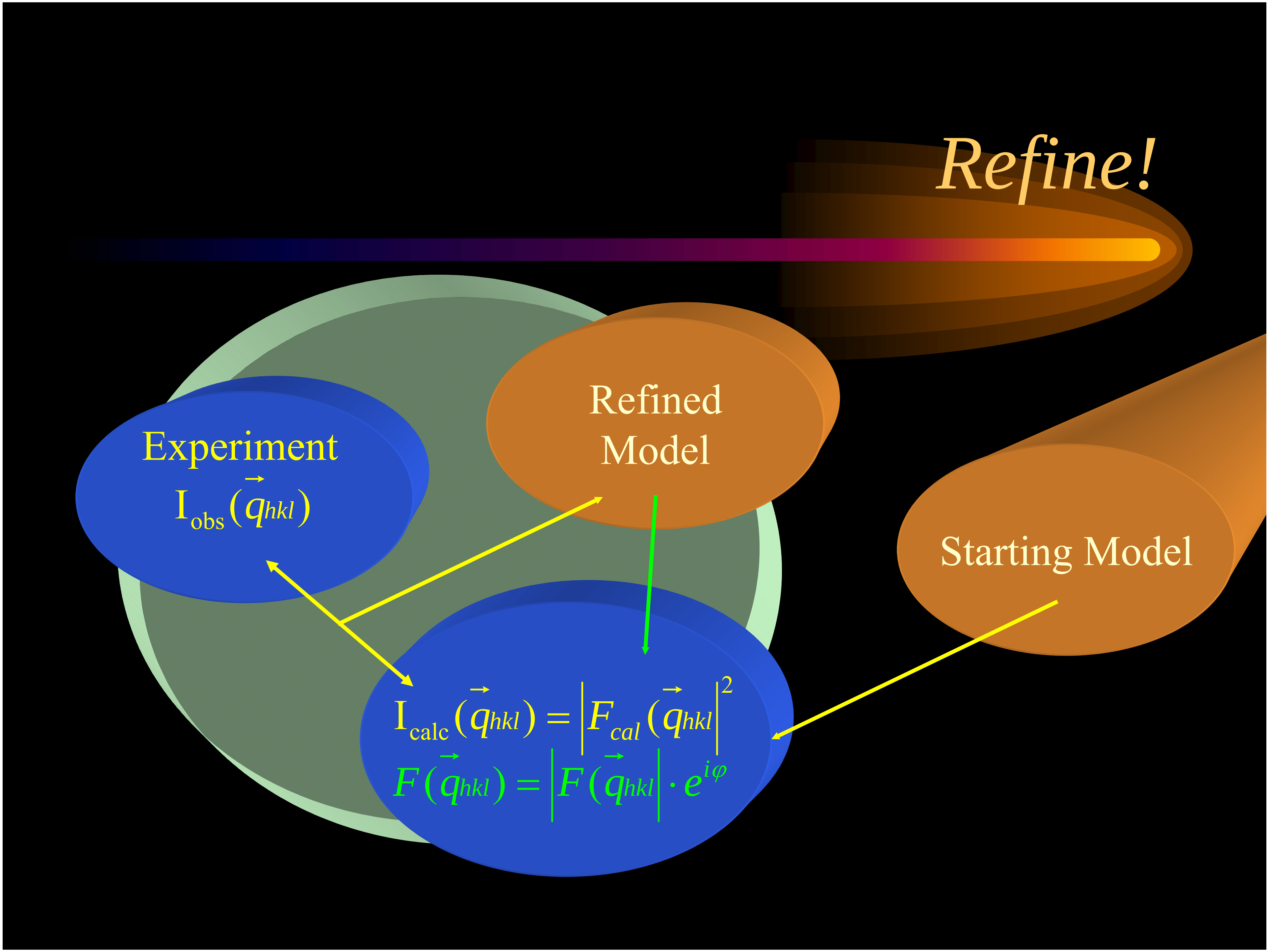
$\langle j_\nu(q) \rangle$: calculated by relativistic Dirac – Fock Approx.
cf. J. Brown, Int.Tables for Crystallography C (Kluver 1992) p.391

$$f_d = \langle j_o \rangle + \langle j_2 \rangle \cdot \frac{\frac{7}{2}\cdot\frac{9}{2} + 3\cdot 4 - \frac{1}{2}\cdot\frac{3}{2}}{3\cdot\frac{7}{2}\cdot\frac{9}{2} - 3\cdot 4 + \frac{1}{2}\cdot\frac{3}{2}}$$



$$I_{diffuse} \approx f_{diffuse}^2$$

Ref.: P.Fischer in: Magnetic Neutron Scattering, Ed. A. Furrer, World Scientific (1995), Singapore, ISBN 981-02-2353-6

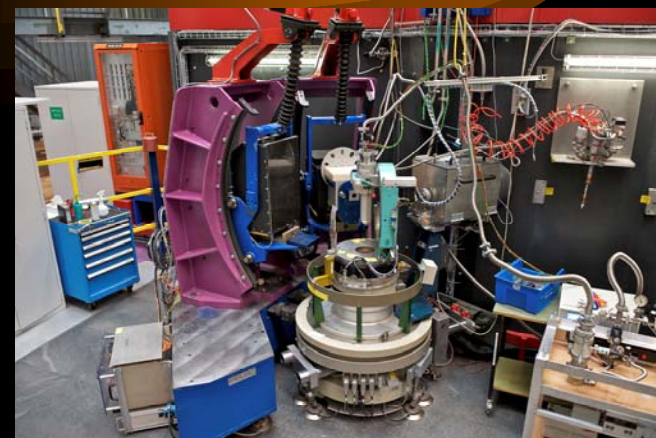


Refine!
Refined Model
Experiment
$I_{obs}(\vec{q}_{hkl})$
Starting Model
$I_{calc}(\vec{q}_{hkl}) = \left|F_{cal}(\vec{q}_{hkl}\right|^2$
$F(\vec{q}_{hkl}) = \left|F(\vec{q}_{hkl}\right| \cdot e^{i\varphi}$

Diffraction Instruments at PSI

- HRPT
  high resolution powder diffraction
- DMC
  medium resolution high intensity
  powder diffraction
- TriCS
  single crystal diffraction

Diffraction Instruments at PSI...

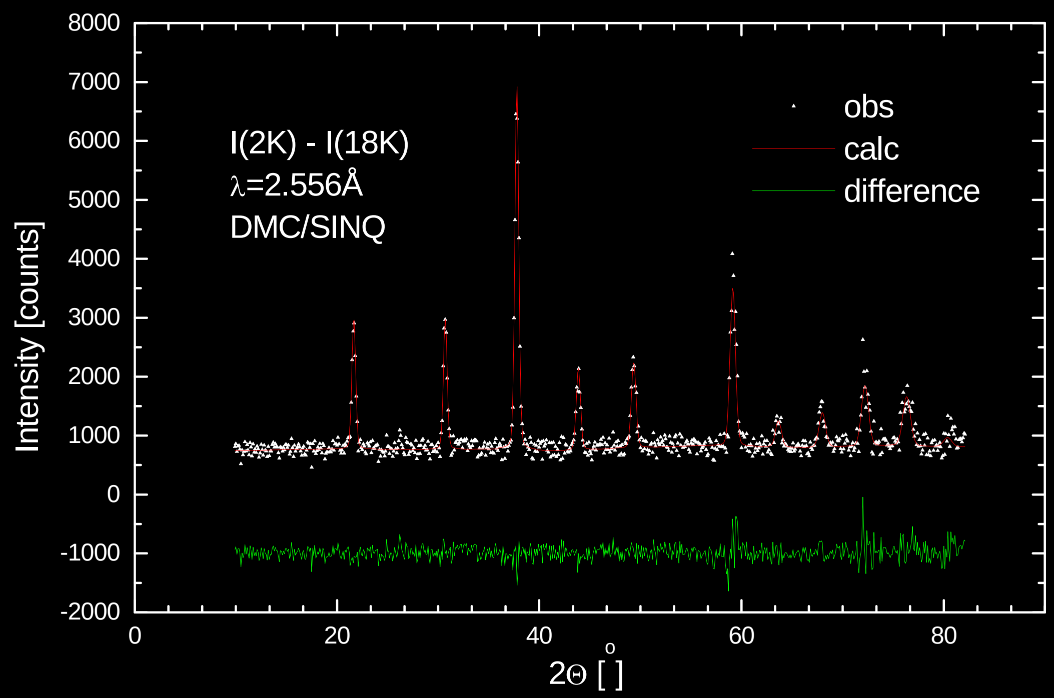


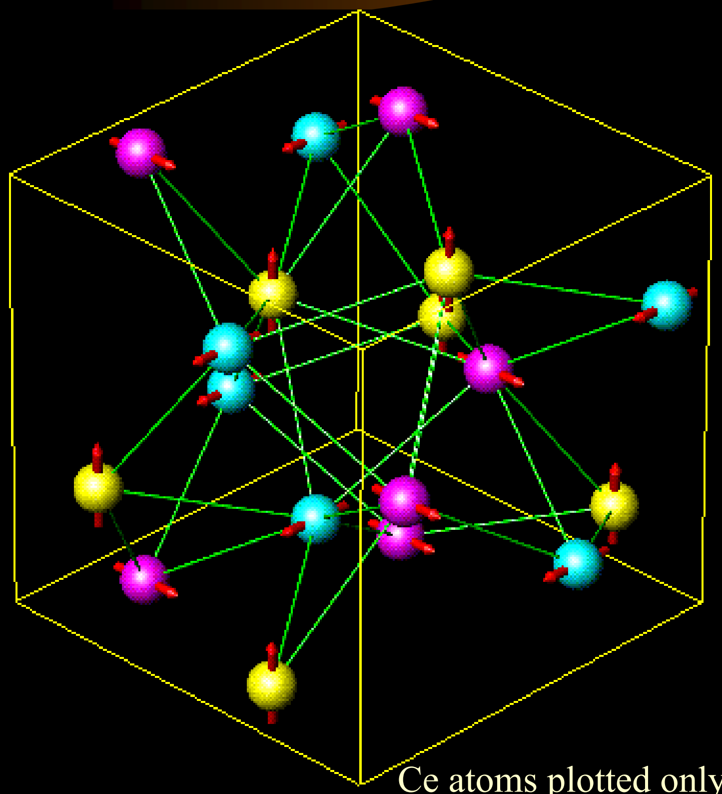
DMC
Powder Diffractometer
Cold Neutrons
$\lambda > 2$ Å

HRPT
Powder Diffractometer
Thermal Neutrons
1 **Å** >λ > 2.5 **Å**

TriCS
Single Crystal Diffractometer
thermal neutrons
λ = 1.18 Å, 2.3 Å

$Ce_3Cu_3Sb_4$: Powder Diffraction at DMC





Ce atoms plotted only!

T. Herrmannsdörfer et. al., Solid State Comm. (sub. 1999)

TriCS Layout