Introduction to Neutron Diffraction

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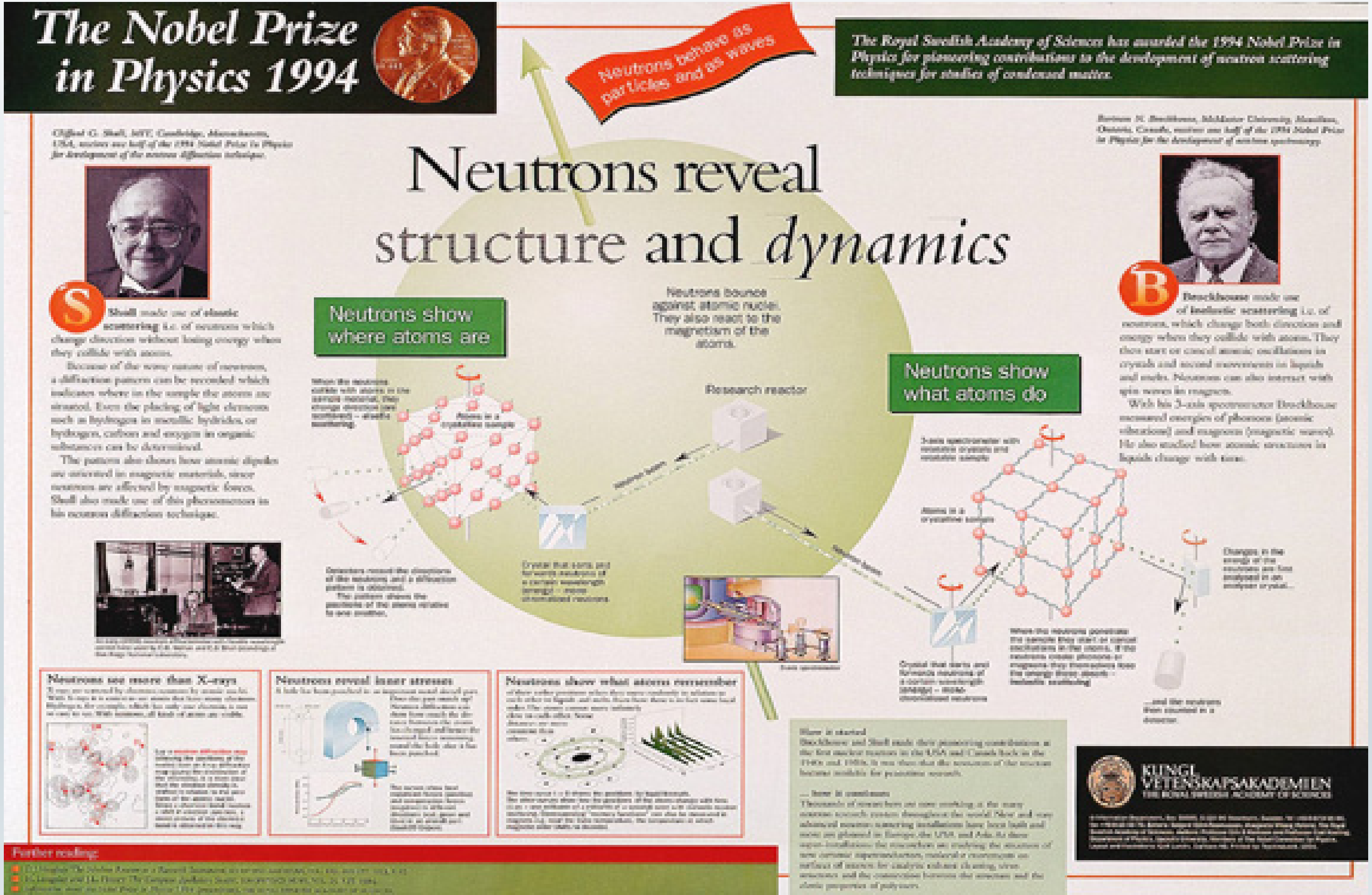
Outline

1. Characteristics of neutrons for diffraction
2. Diffraction equations: Laue conditions
3. Comparison neutrons – synchrotron X-rays
4. Magnetic neutron diffraction
5. Examples of neutron diffraction studies

Neutrons for what?

Neutrons tell you "where the atoms are and what the atoms do"
(Nobel Prize citation for Brockhouse and Shull 1994)



Particle-wave properties energy-velocity-wavelength ...

kinetic energy (E) velocity (v) temperature (T).

$$E = m_n v^2/2 = k_B\, T = p^2/2m_n = (\hbar k)^2/2m_n = (h/\lambda)^2/2m_n$$

momentum (p) $p = m_n v = \hbar\, k$

$\hbar = h/2\pi$

wavelength (λ)

wavevector (k) $k = 2\pi/\lambda = m_n v/\hbar$

Neutrons, a powerful probe

Matter is made up atoms, aggregated together in organised structures

The properties of matter and materials are largely determined by their structure and dynamics (behaviour) on the **atomic scale**

distance between atoms ~ 1 Å = 1/100 000 000 cm

Atoms are too small to be seen with ordinary light (wavelength approx. 4000-8000 Å)

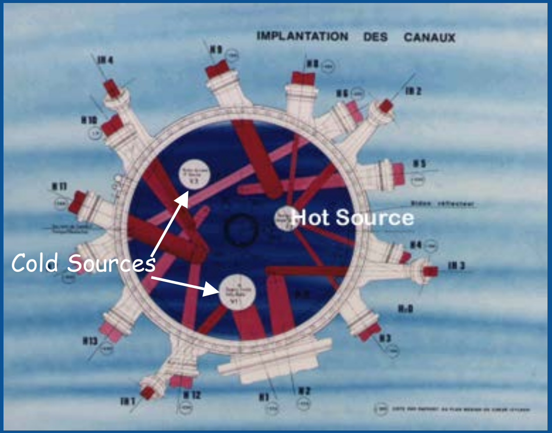
- **The wavelength of the neutron is comparable to atomic sizes and the dimensions of atomic structures, which explains why neutrons can « see » atoms.**
- **The energy of thermal neutrons is similar to the thermal excitations in solids.**
- **Neutrons are zero-charge particles and have a magnetic moment that interacts with the magnetic dipoles in matter.**

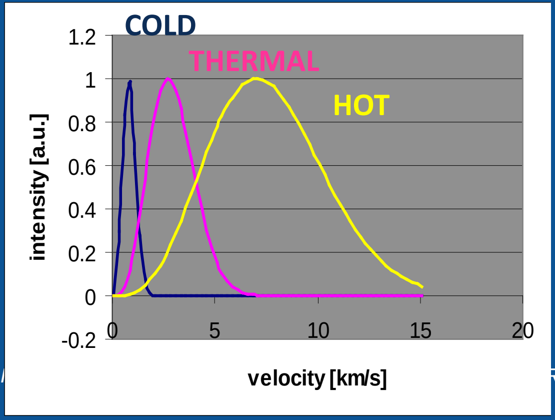
Techniques using neutrons can produce a picture of atomic and magnetic structures and their motion.

Particle-wave properties (Energy-Temperature-Wavelength)

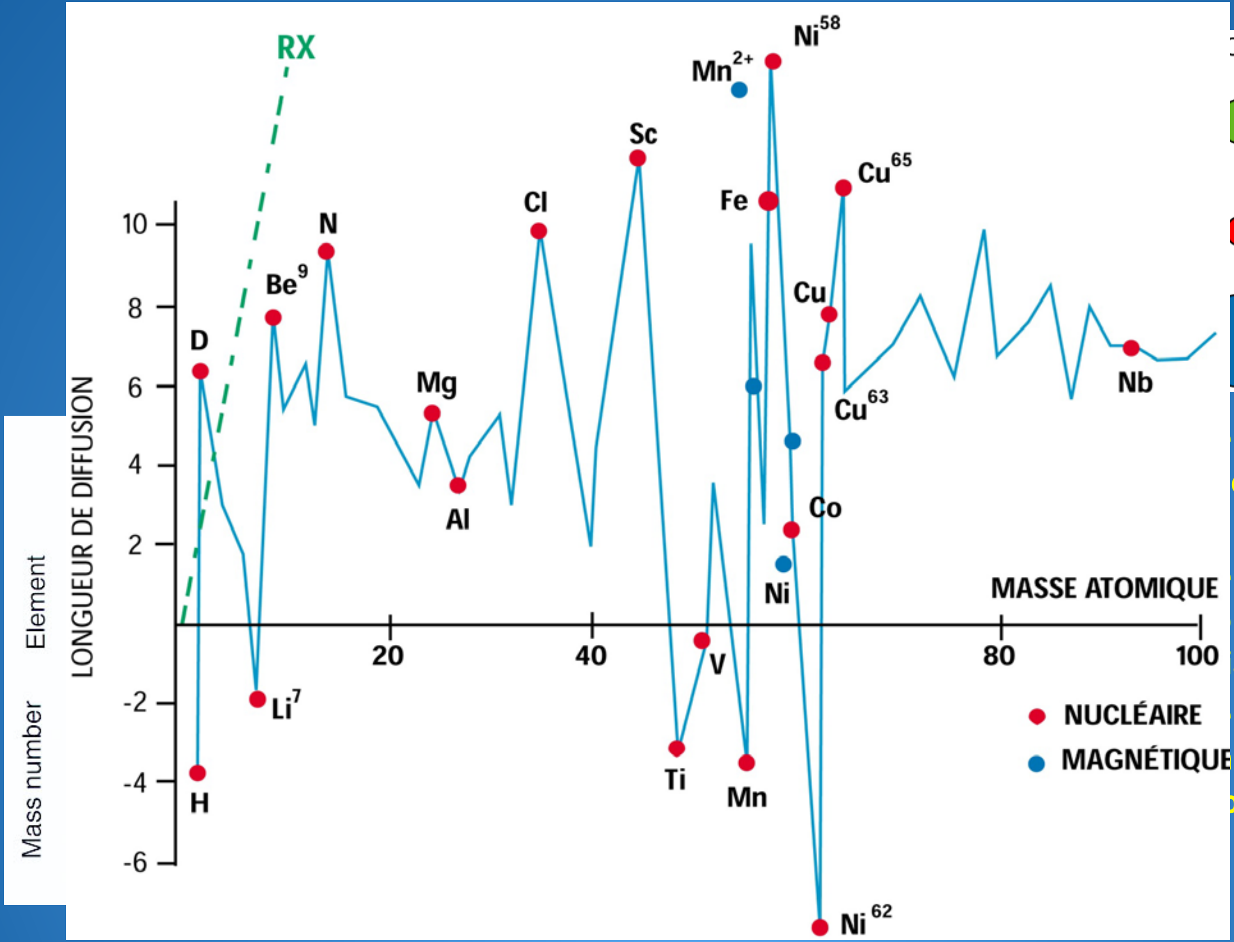
$$E = m_n v^2/2 = k_B\,T = (\hbar k)^2/2m_n \;;\quad k = 2\pi/\lambda = m_n v/\hbar$$

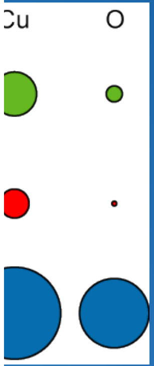
	Energy (meV)	Temp (K)	Wavelength (Å)
Cold	0.1 – 10	1 – 120	4 – 30
Thermal	5 – 100	60 – 1000	1 – 4
Hot	100 – 500	1000 – 6000	0.4 – 1





Scattering power of nuclei for neutrons





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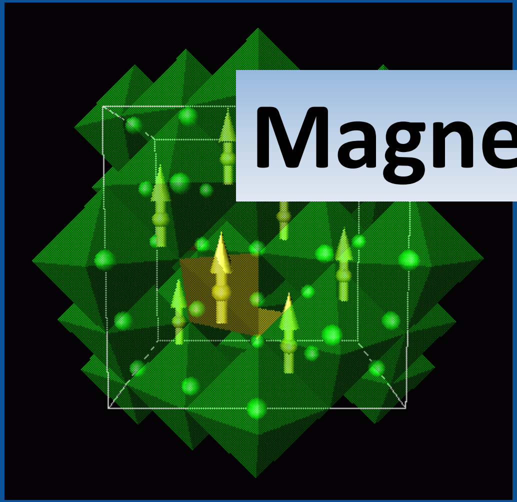
Neutrons for magnetism studies

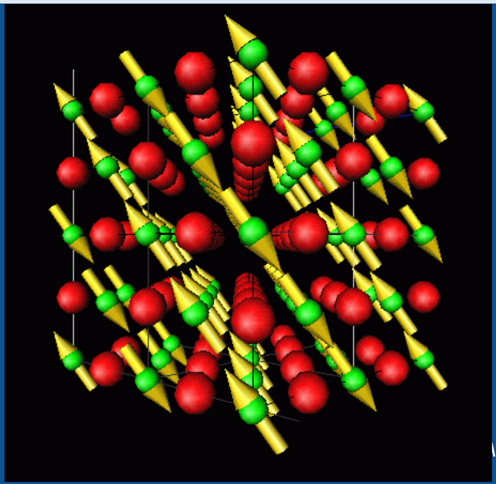
Neutrons are strongly scattered by magnetic materials

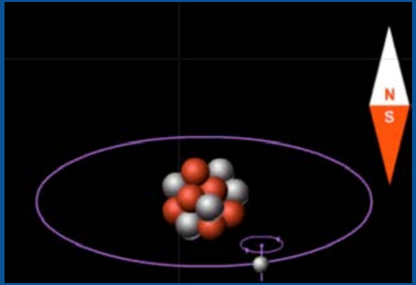
- Neutrons act as small magnets
- The dipolar magnetic moment of the neutron interacts strongly with the atomic magnetic moment
- Neutrons allow the determination of magnetic … neasure the … cision.

Magnetic Crystallography



Ferromagnetic and antiferromagnetic oxides





Outline

1. Characteristics of neutrons for diffraction
2. **Diffraction equations: Laue conditions**
3. Comparison neutrons – synchrotron X-rays
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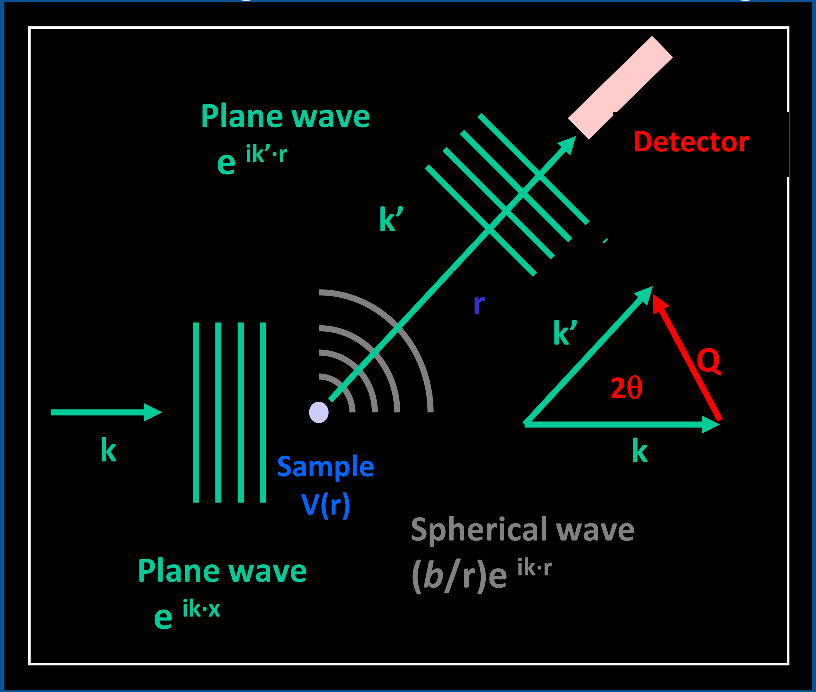
Interaction neutron-nucleus

Weak interaction with matter aids interpretation of scattering data

The range of nuclear force (~ 1fm) is much less than neutron wavelength so that scattering is "point-like"



- Fermi Pseudo potential of a nucleus in $\mathbf{r}_j$

$$V_j = \frac{2\pi\hbar^2}{m} b_j \delta(\mathbf{r} - \mathbf{r}_j)$$

Potential with a single parameter

Diffraction Equations

For diffraction part of the scattering the Fermi's golden rule resumes to the statement: **the diffracted intensity is the square of the Fourier transform of the interaction potential**

$$|\mathbf{k}'| = |\mathbf{k}| = 2\pi/\lambda$$

$$A(\mathbf{Q}) = \int V(\mathbf{r}) \exp(i\mathbf{Q}\cdot\mathbf{r}) d^3\mathbf{r} \quad \rightarrow \quad I(\mathbf{Q}) = A(\mathbf{Q})A^*(\mathbf{Q}) = |A(\mathbf{Q})|^2$$

$$\mathbf{Q} = \mathbf{k}' - \mathbf{k} = 2\pi(\mathbf{s} - \mathbf{s}_0)/\lambda = 2\pi\mathbf{s} = 2\pi\mathbf{h}$$

There are different conventions and notations for designing the scattering vector (we use here crystallographic conventions).

$$A_X(\mathbf{s}) = \int \sum \rho_{ej}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{R}_j) \exp(2\pi i \mathbf{s}\cdot\mathbf{r}) d^3\mathbf{r} = \sum f_j(\mathbf{s}) \exp(2\pi i \mathbf{s}\cdot\mathbf{R}_j)$$

$$f_j(\mathbf{s}) = \int \rho_{ej}(\mathbf{r}) \exp(2\pi i \mathbf{s}\cdot\mathbf{r}) d^3\mathbf{r}$$

Atomic form factor.

Scattering length

$$A_N(\mathbf{s}) = \frac{2\pi\hbar^2}{m} \int \sum b_j \delta(\mathbf{r} - \mathbf{R}_j) \exp(2\pi i \mathbf{s}\cdot\mathbf{r}) d^3\mathbf{r} \,\square\, \sum b_j \exp(2\pi i \mathbf{s}\cdot\mathbf{R}_j)$$

Diffraction Equations for crystals

In a crystal the atoms positions can be decomposed as the vector position of the origin of a unit cell plus the vector position with respect to the unit cell

$$\mathbf{R}_{lj} = \mathbf{R}_l + \mathbf{r}_j$$

$$A_N(\mathbf{s}) = \sum_{lj} b_j \exp(2\pi i \mathbf{s} \cdot \mathbf{R}_{lj}) = \sum_l \exp(2\pi i \mathbf{s} \cdot \mathbf{R}_l) \sum_{j=1,n} b_j \exp(2\pi i \mathbf{s} \cdot \mathbf{r}_j)$$

$$\sum_l \exp(2\pi i \mathbf{s} \cdot \mathbf{R}_l) = 0 \quad \textit{for general } \mathbf{s}$$

$$\sum_l \exp(2\pi i \mathbf{s} \cdot \mathbf{R}_l) = N \quad \textit{for } \mathbf{s} = \mathbf{H} \rightarrow \mathbf{H}\mathbf{R}_l = L_H \ \text{ integer}$$

$\mathbf{s} = \mathbf{H}$ Laue conditions: the scattering vector is a reciprocal lattice vector of the crystal

$$I_N(\mathbf{H}) \propto \left| \sum_{j=1,n} b_j \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j) \right|^2 = \left| F(\mathbf{H}) \right|^2$$

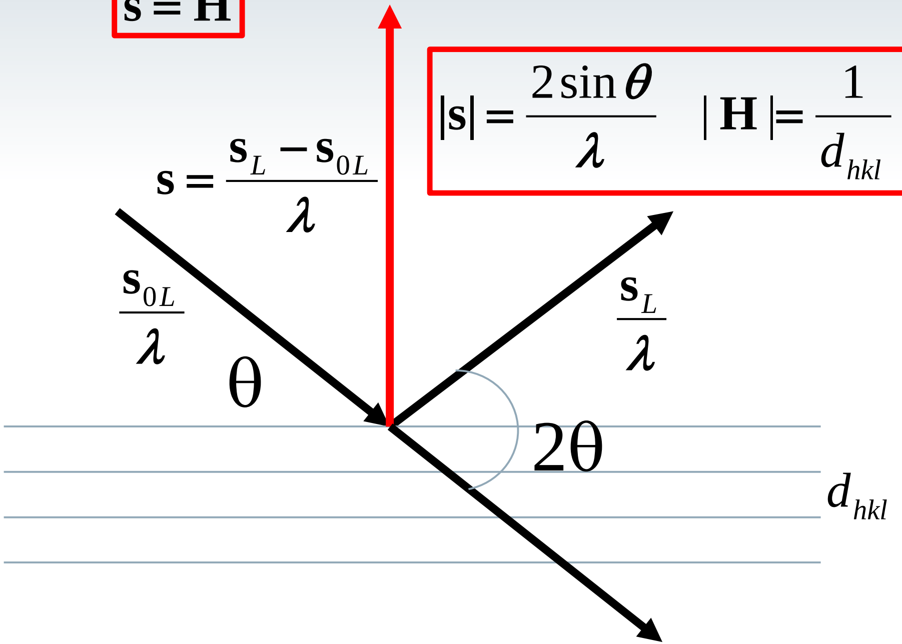
Diffraction Equations for crystals

The Laue conditions have as a consequence the Bragg Law

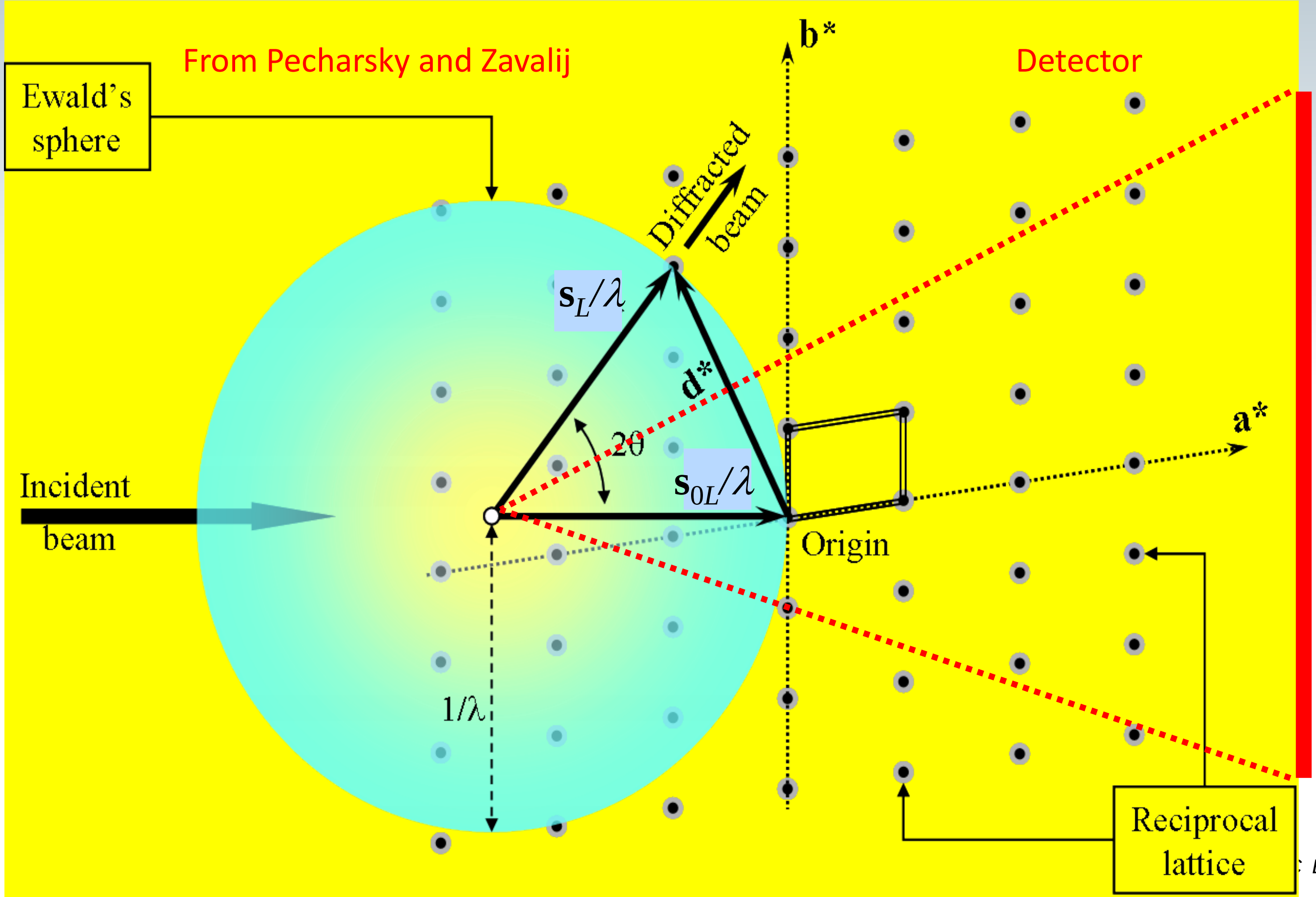
Laue conditions: the scattering vector is a reciprocal lattice vector of the crystal

$$\mathbf{s} = \mathbf{H}$$

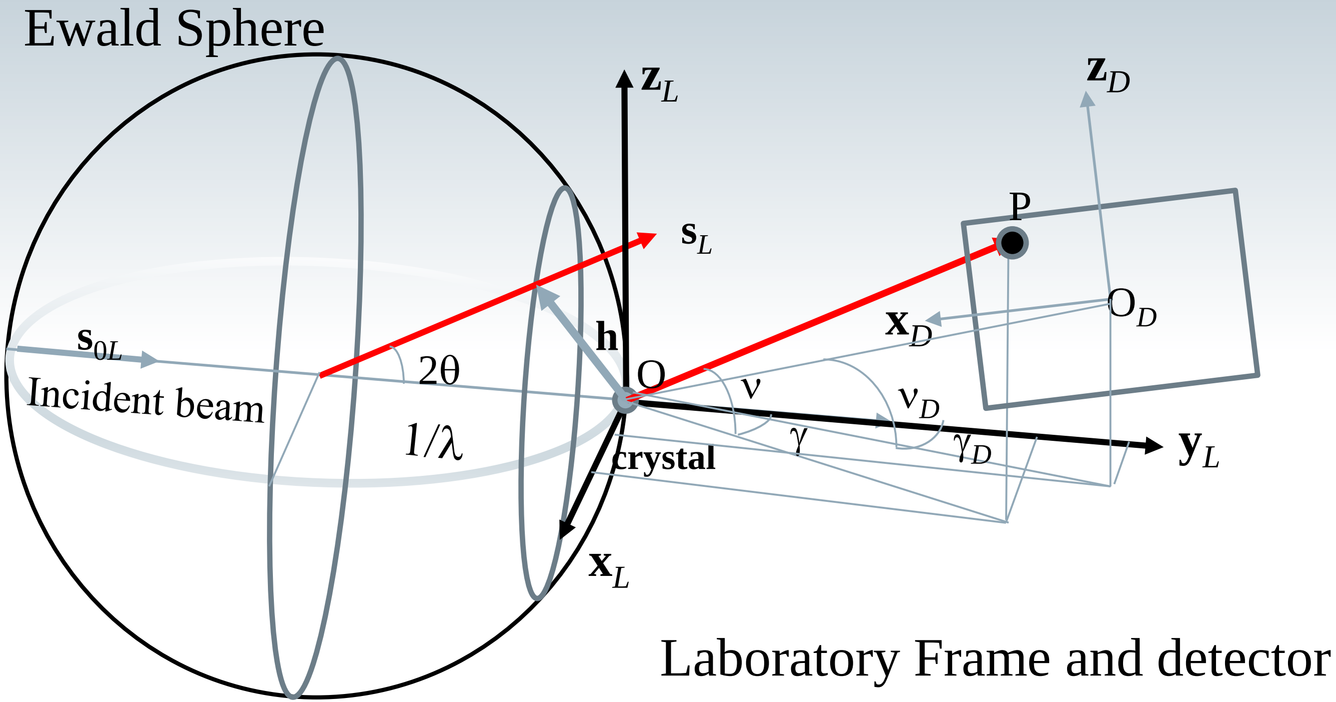
$$|\mathbf{s}| = \frac{2\sin\theta}{\lambda} \qquad |\mathbf{H}| = \frac{1}{d_{hkl}} \qquad \Rightarrow \qquad 2d_{hkl}\sin\theta = \lambda$$



Ewald construction

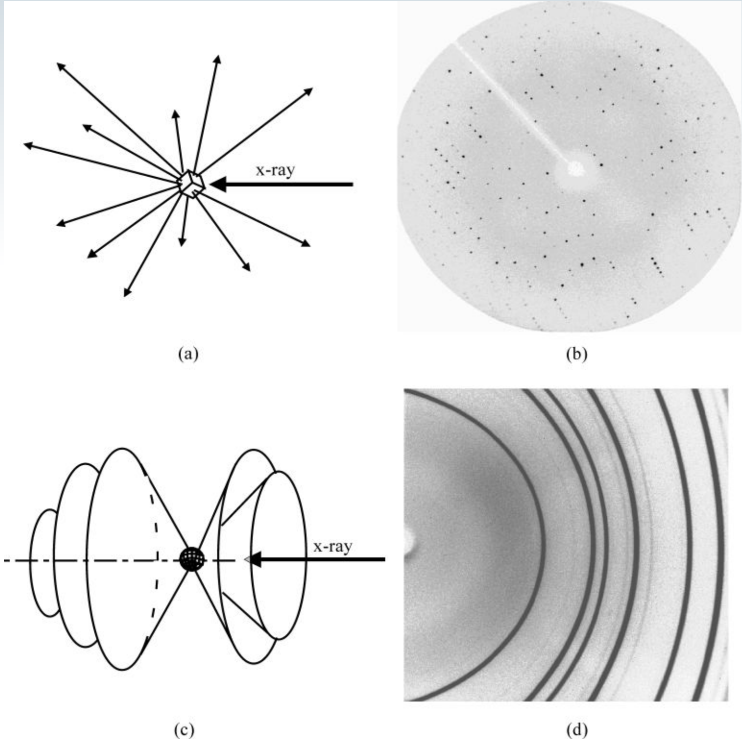


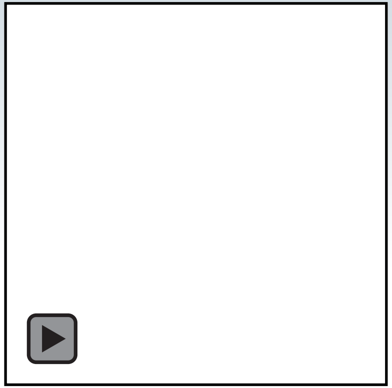
Ewald construction



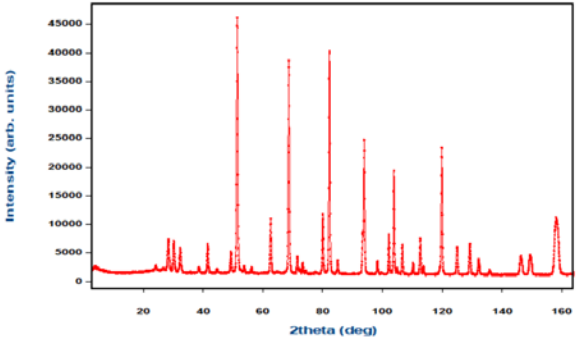
Diffraction patterns

Single Xtal - 2D image + scan –> 3D Int vs 2θ
Powder - 2D image –> 1D Int vs 2θ





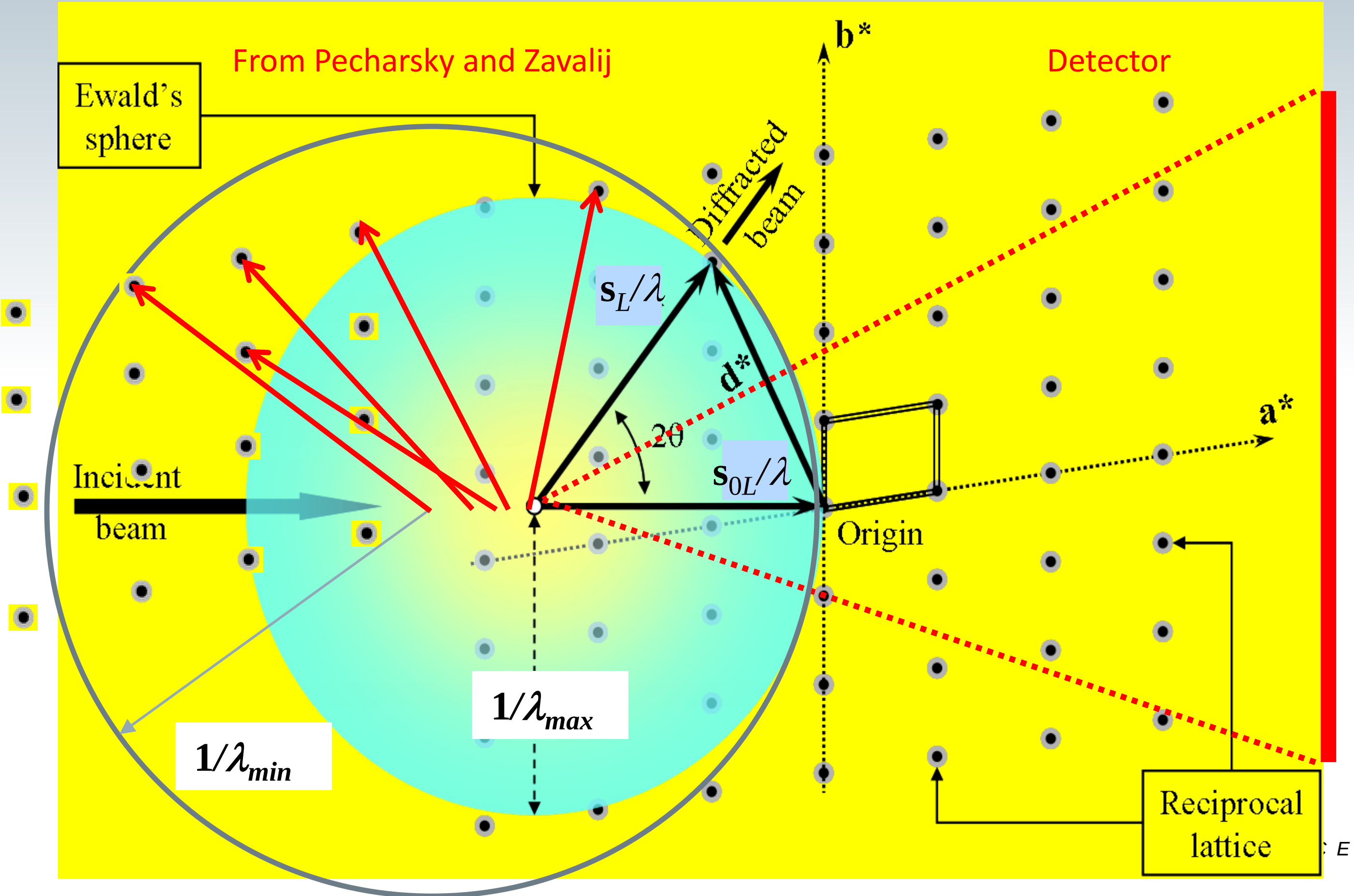
Single Crystal



Powder or polycrystalline solid

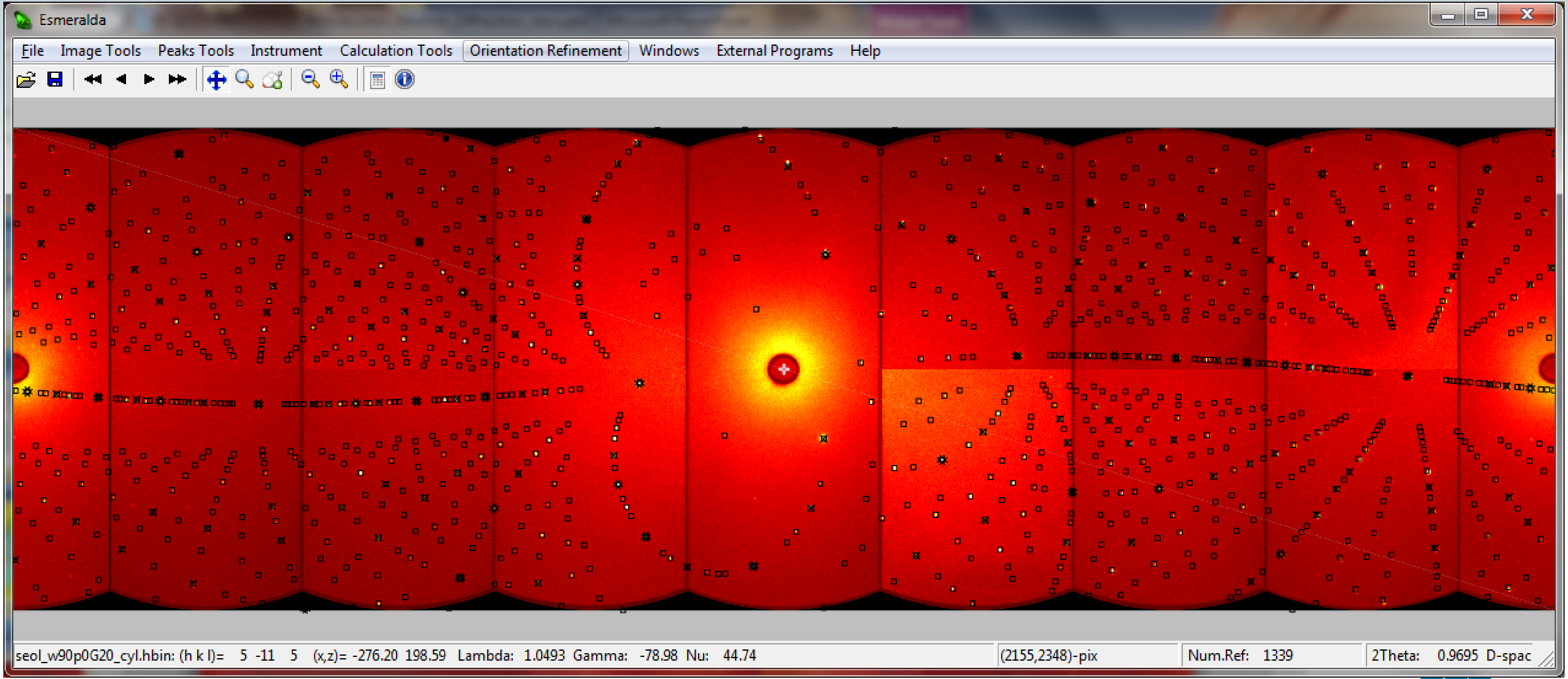
Courtesy of Jim

Ewald construction Laue



NEUTRONS FOR SOCIETY

Laue image obtained in Cyclops



Single Crystal and Powder Diffraction

Single Crystal diffraction allows to get with high precision subtle structural details: thermal parameters, anharmonic vibrations.
Drawbacks: big crystals for neutrons, extinction, twinning
Data reduction: Needs only the indexing and integration of Bragg reflection and obtain structure factors. List: $h\ \ k\ \ l\quad F^2\quad \sigma(F^2)$
Data Treatment: SHELX, FullProf, JANA, GSAS, …

Powder diffraction no problem with extinction or twinning.
Data reduction: minimalistic, needs only the profile intensities and their standard deviations
Data Treatment: FullProf, JANA, GSAS, TOPAS, …

$$y_{ci} = \sum_{\{\mathbf{h}\}} I_{\mathbf{h}} \Omega(T_i - T_{\mathbf{h}}) + b_i$$

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Why neutrons?

NEUTRON DIFFRACTION FOR FUNDAMENTAL AND APPLIED RESEARCH IN CONDENSED MATTER AND MATERIALS SCIENCE

Location of light elements and distinction between adjacent elements in the periodic table.

Examples are:

- **Oxygen positions in High-T_C superconductors and manganites**
- **Structural determination of fullerenes an their derivatives,**
- **Hydrogen in metals and hydrides**
- **Lithium in battery materials**
- **Determination of atomic site distributions in solid solutions**

Systematic studies of hydrogen bonding

Host-guest interactions in framework silicates

Role of water in crystals

Magnetic structures, magnetic phase diagrams and magnetisation densities

Relation between static structure and dynamics (clathrates, plastic crystals).

Aperiodic structures: incommensurate structures and quasicrystals

Why neutrons?

The complementary use of X-ray Synchrotron radiation and neutrons (1)

The advantages of thermal neutrons with respect to X-rays as far as <u>diffraction</u> is concerned are based on the following properties of thermal neutrons:

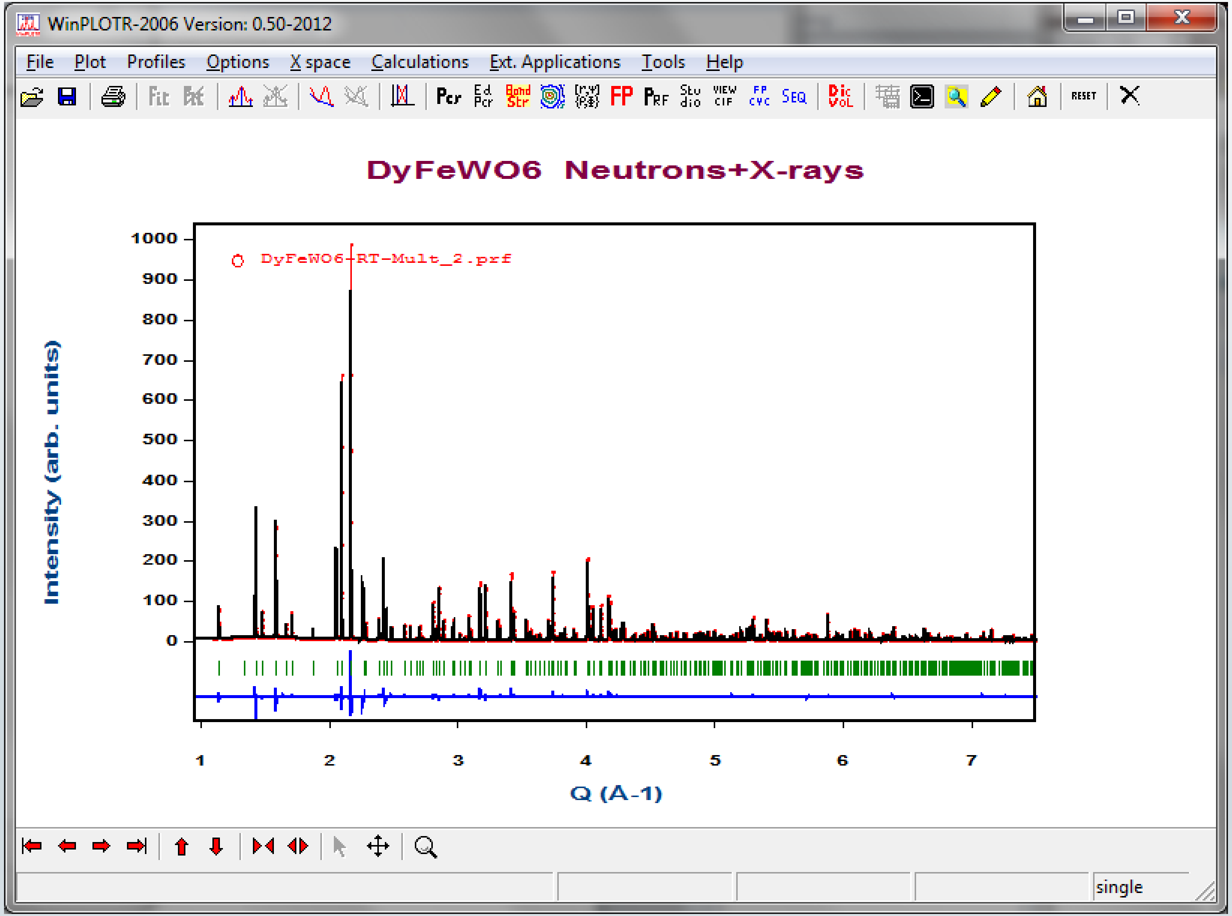
- **constant scattering power (b is Q-independent) having a non-monotonous dependence on the atomic number**
- **weak interaction (the first Born approximation holds) that implies simple theory can be used to interpret the experimental data**
- **the magnetic interaction is of the same order of magnitude as the nuclear interaction**
- **low absorption, making it possible to use complicated sample environments**

Why neutrons?

The complementary use of X-ray Synchrotron radiation and neutrons (2)

- **Powder diffraction with SR can be used for *ab initio* structure determination and microstructural analysis due to the current extremely high Q-resolution.**

- **Structure refinement is better done with neutrons (or using simultaneously both techniques) because systematic errors in intensities (texture effects) are less important and because scattering lengths are Q-independent in the neutron case.**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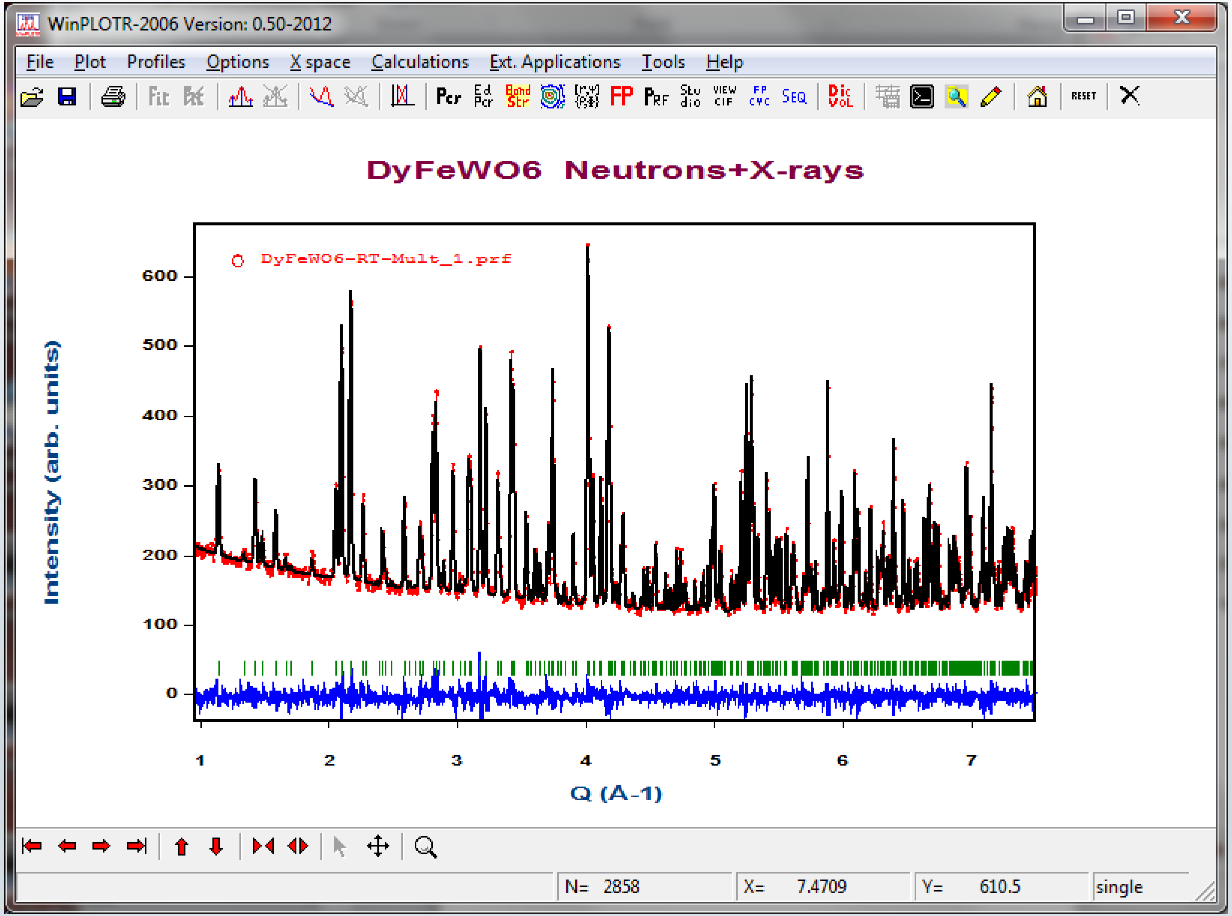
File Plot Profiles Options X space Calculations Ext. Applications Tools Help
DyFeWO6 Neutrons+X-rays
DyFeWO6-RT-Mult_2.prf
Intensity (arb. units)
0
100
200
300
400
500
600
700
800
900
1000
1
2
3
4
5
6
7
Q (A-1)
single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File Plot Profiles Options X space Calculations Ext. Applications Tools Help
DyFeWO6 Neutrons+X-rays
DyFeWO6-RT-Mult_1.prf
Intensity (arb. units)
Q (A-1)
N= 2858
X= 7.4709
Y= 610.5
single

Why neutrons?

The complementary use of X-ray Synchrotron radiation and neutrons (3)

- **Magnetic X-ray scattering allows in principle the separation of orbital and spin components. However, SR cannot compete with neutrons in the field of *magnetic structure determination* from powders.**

- **The contribution of SR to that field is on details of magnetic structures (already known from neutrons) for selective elements using resonant magnetic scattering (rare earths, U, ...)**

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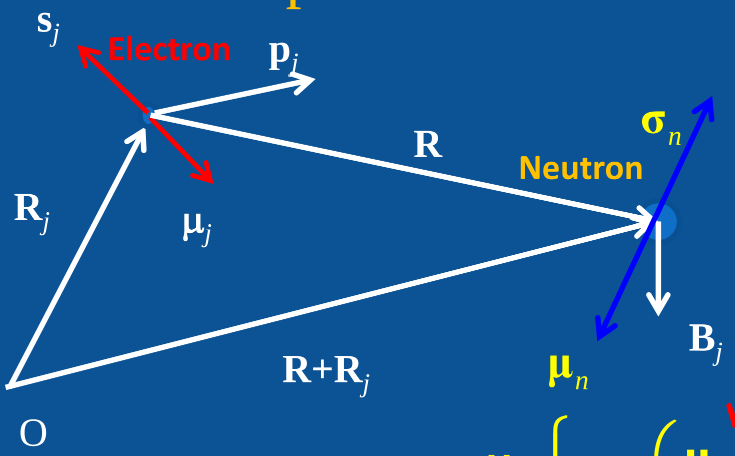
Magnetic scattering: magnetic fields

The interaction potential to be evaluated in the FGR is: $V_m^j = \boldsymbol{\mu}_j \mathbf{B}_j$

Magnetic field due to spin and orbital moments of an electron:



Magnetic vector potential of a dipolar field due to electron spin moment

$$\mathbf{B}_j = \mathbf{B}_{jS} + \mathbf{B}_{jL} = \frac{\mu_0}{4\pi}\left\{ \nabla \times \left(\frac{\boldsymbol{\mu}_j \times \hat{\mathbf{R}}}{R^2} \right) - \frac{2\mu_B}{\hbar} \frac{\mathbf{p}_j \times \hat{\mathbf{R}}}{R^2} \right\}$$

Biot-Savart law for a single electron with linear momentum **p**

Magnetic scattering: magnetic fields

Evaluating the spatial part of the transition matrix element for electron *j*:

$$\langle \mathbf{k}' | V_m^j | \mathbf{k} \rangle = \exp(i\mathbf{Q}\mathbf{R}_j) \left\{ \mathbf{e} \times (\mathbf{s}_j \times \mathbf{e}) + \frac{i}{\hbar Q} (\mathbf{p}_j \times \mathbf{e}) \right\} \qquad \mathbf{e} = \frac{\mathbf{Q}}{Q}$$

Where $\hbar\mathbf{Q} = \hbar(\mathbf{k} - \mathbf{k}')$ is the momentum transfer

Summing for all unpaired electrons we obtain:

$$\sum_j \langle \mathbf{k}' | V_m^j | \mathbf{k} \rangle = \mathbf{e} \times (\mathbf{M}(\mathbf{Q}) \times \mathbf{e}) = \mathbf{M}(\mathbf{Q}) - (\mathbf{M}(\mathbf{Q}).\mathbf{e}).\mathbf{e} = \mathbf{M}_\perp(\mathbf{Q})$$

$\mathbf{M}_\perp(\mathbf{Q})$ is the perpendicular component of the Fourier transform of the magnetisation in the scattering object to the scattering vector. It includes the orbital and spin contributions.

Scattering by a collection of magnetic atoms

We will consider in the following only elastic scattering.

We suppose the magnetic matter made of atoms with unpaired electrons that remain close to the nuclei.

Vector position of electron *e*: $\mathbf{R}_e = \mathbf{R}_{lj} + \mathbf{r}_{je}$

The Fourier transform of the magnetization can be written in discrete form as

$$\mathbf{M}(\mathbf{Q}) = \sum_{e} \mathbf{s}_e \exp(i\mathbf{Q}\cdot\mathbf{R}_e) = \sum_{lj} \exp(i\mathbf{Q}\cdot\mathbf{R}_{lj}) \sum_{e_j} \exp(i\mathbf{Q}\cdot\mathbf{r}_{je})\mathbf{s}_{je}$$

$$\mathbf{F}_j(\mathbf{Q}) = \sum_{e} \mathbf{s}_{je} \exp(i\mathbf{Q}\cdot r_{je}) = \int \boldsymbol{\rho}_j(\mathbf{r}) \exp(i\mathbf{Q}\cdot\mathbf{r}) d^3\mathbf{r}$$

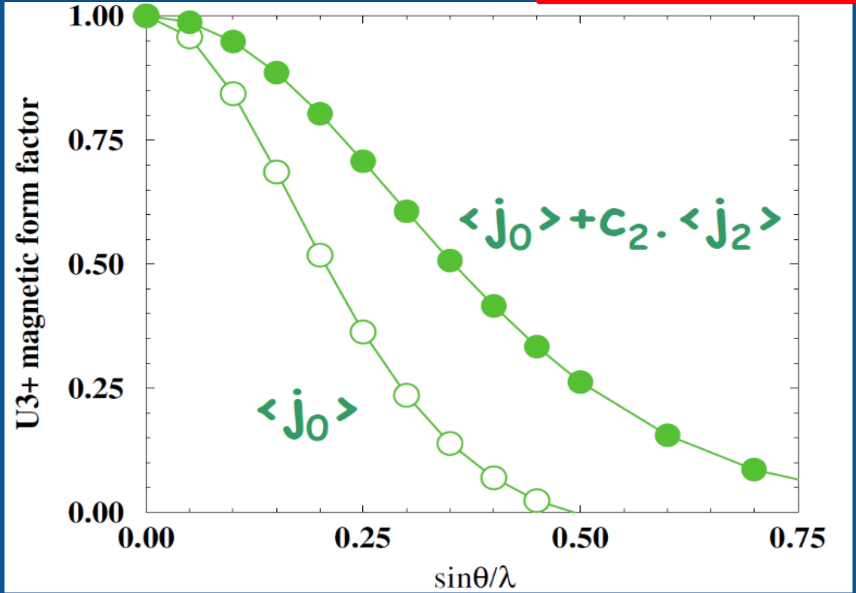
$$\mathbf{F}_j(\mathbf{Q}) = \mathbf{m}_j \int \rho_j(\mathbf{r}) \exp(i\mathbf{Q}\cdot\mathbf{r}) d^3\mathbf{r} = \mathbf{m}_j f_j(Q)$$

$$\mathbf{M}(\mathbf{Q}) = \sum_{lj} \mathbf{m}_{lj} f_{lj}(Q) \exp(i\mathbf{Q}\cdot\mathbf{R}_{lj})$$

Scattering by a collection of magnetic atoms

$$\mathbf{F}_j(\mathbf{Q}) = \sum_e \mathbf{s}_{je} \exp(i\mathbf{Q}\cdot r_{je}) = \int \boldsymbol{\rho}_j(\mathbf{r}) \exp(i\mathbf{Q}\cdot\mathbf{r}) d^3\mathbf{r}$$

$$\mathbf{F}_j(\mathbf{Q}) = \mathbf{m}_j \int \rho_j(\mathbf{r}) \exp(i\mathbf{Q}\cdot\mathbf{r}) d^3\mathbf{r} = \mathbf{m}_j f_j(Q)$$



If we use the common variable s=sinθ/λ, then the expression of the form factor is the following:

$$f(s) = \sum_{l=0,2,4,6} W_l \langle j_l(s) \rangle$$

$$\langle j_l(s) \rangle = \int_0^\infty U^2(r) j_l(4\pi s r) 4\pi r^2 dr$$

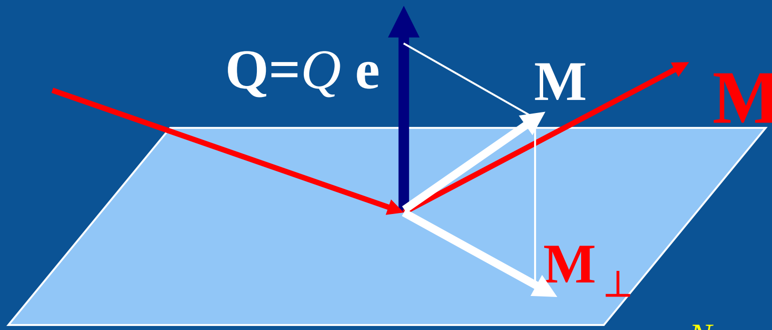
$$\langle j_l(s) \rangle = s^2 \left(A_l \exp\{-a_l s^2\} + B_l \exp\{-b_l s^2\} + C_l \exp\{-c_l s^2\} + D_l \right) \qquad for \quad l = 2,4,6$$

$$\langle j_0(s) \rangle = A_0 \exp\{-a_0 s^2\} + B_0 \exp\{-b_0 s^2\} + C_0 \exp\{-c_0 s^2\} + D_0$$

Magnetic scattering

$\mathbf{M}_\perp(\mathbf{Q})$ is the perpendicular component of the Fourier transform of the magnetisation in the sample to the scattering vector.

$$\mathbf{M}(\mathbf{Q}) = \int \mathbf{M}(\mathbf{r}) \exp\left(i\mathbf{Q}\cdot\mathbf{r}\right) d^3\mathbf{r}$$



Magnetic interaction vector

$$\mathbf{M}_\perp = \mathbf{e} \times \mathbf{M} \times \mathbf{e} = \mathbf{M} - \mathbf{e}\,(\mathbf{e} \cdot \mathbf{M})$$

$$\left(\frac{d\sigma}{d\Omega}\right) = (\gamma r_0)^2 \mathbf{M}_\perp^* \mathbf{M}_\perp$$

Magnetic structure factor: $\mathbf{M}(\mathbf{H}) = p \sum_{m=1}^{N_{mag}} \mathbf{m}_m f_m(H) \exp(2\pi i \mathbf{H}\cdot\mathbf{r}_m)$

Neutrons only see the components of the magnetisation that are perpendicular to the scattering vector

Elastic Magnetic Scattering by a crystal

For a general magnetic structure that can be described as a Fourier series:

$$\mathbf{m}_{lj} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}j} \; exp\{-2\pi \, i\mathbf{k}\mathbf{R}_l\}$$

$$\mathbf{M}(\mathbf{h}) = \sum_{lj}\sum_{\mathbf{k}} \mathbf{S}_{\mathbf{k}j} \exp(-2\pi i\mathbf{k}\mathbf{R}_l) f_{lj}(h) \exp(2\pi i\mathbf{h}\cdot\mathbf{R}_{lj})$$

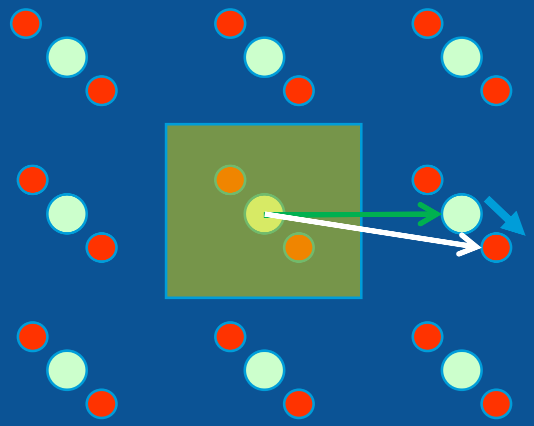
$$\mathbf{M}(\mathbf{h}) = \sum_{j} f_j(h) \exp(2\pi i\mathbf{h}\cdot\mathbf{r}_j) \sum_{\mathbf{k}} \mathbf{S}_{\mathbf{k}j} \sum_{l} \exp(2\pi i(\mathbf{h}-\mathbf{k})\cdot\mathbf{R}_l)$$

$$\mathbf{M}(\mathbf{h}) = \sum_{j} \mathbf{S}_{\mathbf{k}j} f_j(Q) \exp(2\pi i(\mathbf{H}+\mathbf{k})\cdot\mathbf{r}_j)$$

The lattice sum is only different from zero when **h-k** is a reciprocal lattice vector **H** of the crystallographic lattice. The vector **M** is then proportional to the magnetic structure factor of the unit cell that now contains the Fourier coefficients $\mathbf{S}_{\mathbf{k}j}$ instead of the magnetic moments $\mathbf{m}_j$.

Diffraction Patterns of magnetic structures

Portion of reciprocal space



Magnetic reflections

Nuclear reflections

h = **H**+**k**

Magnetic reflections: indexed by a set of propagation vectors {**k**}

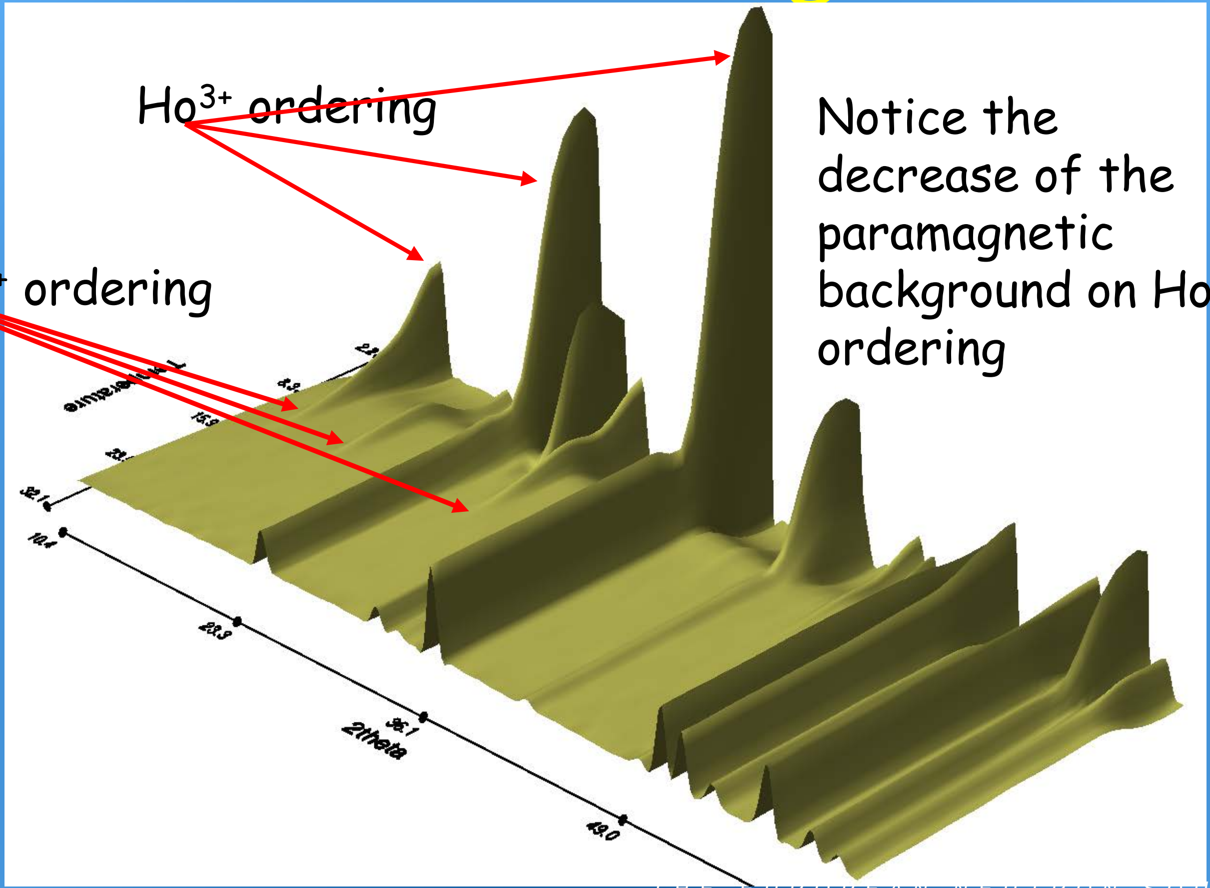
h is the scattering vector indexing a magnetic reflection

H is a reciprocal vector of the crystallographic structure

k is one of the propagation vectors of the magnetic structure

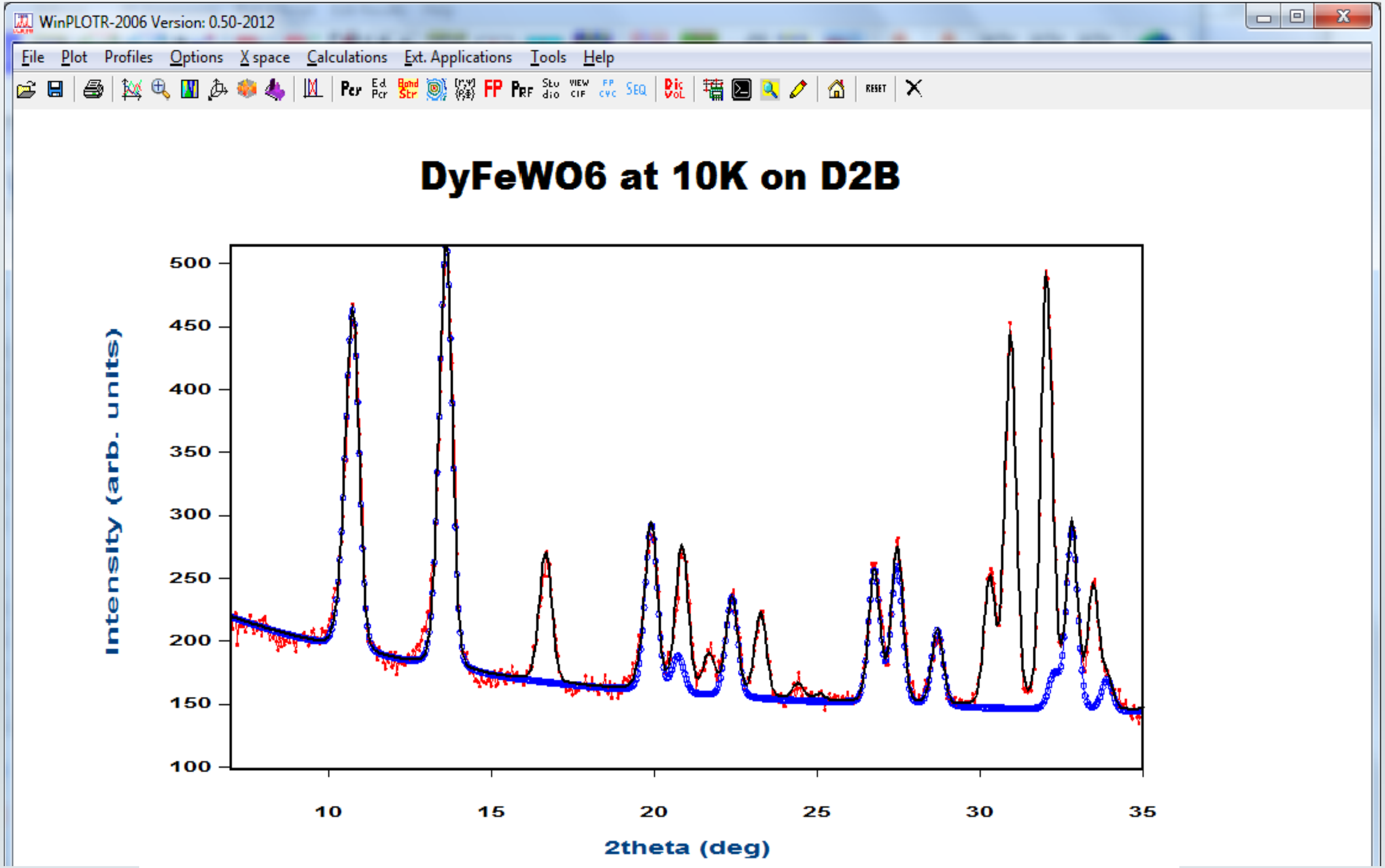
(**k** is reduced to the Brillouin zone)

Diffraction Patterns of magnetic structures



Notice the decrease of the paramagnetic background on Ho^{3+} ordering

Magnetic refinement on D2B



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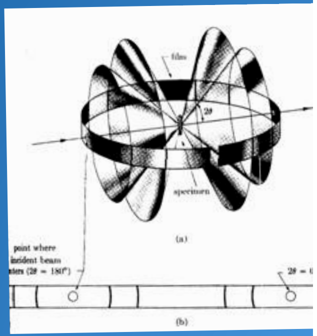
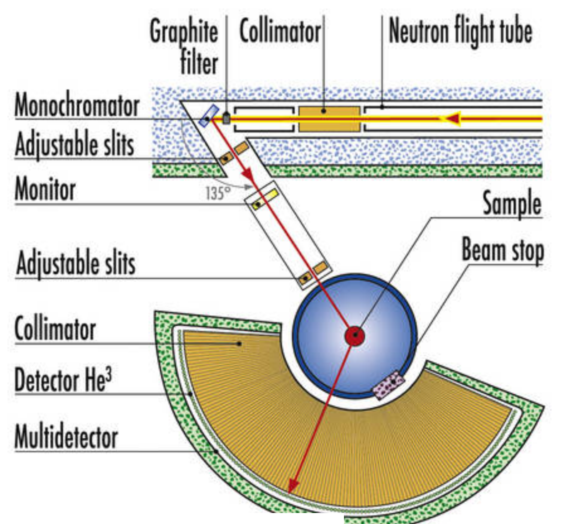
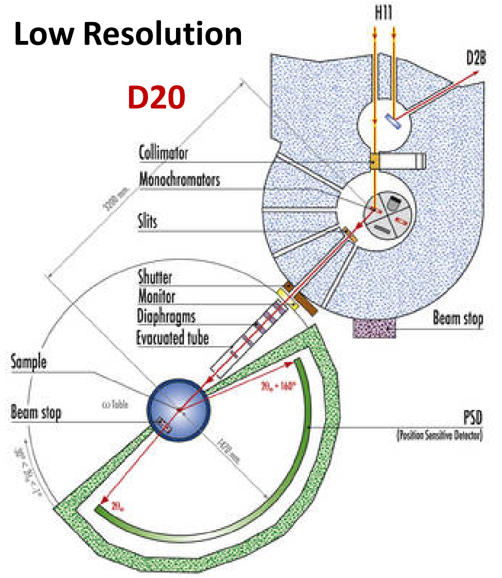
Two Axes Diffractometers: Powders and Liquids



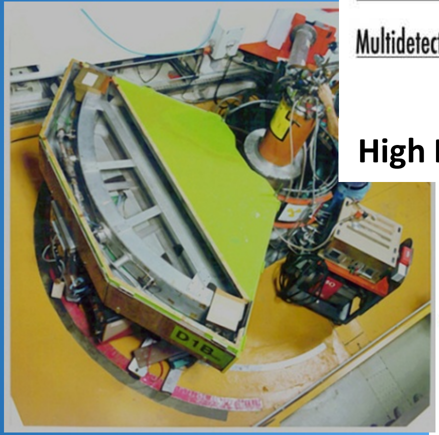


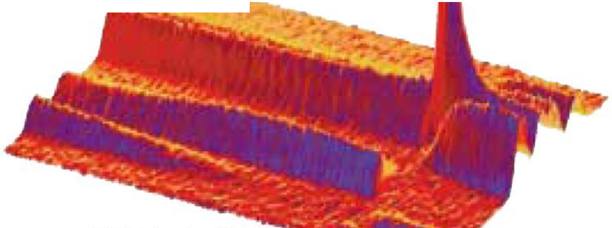
High Resolution D2B



Low Resolution

D20

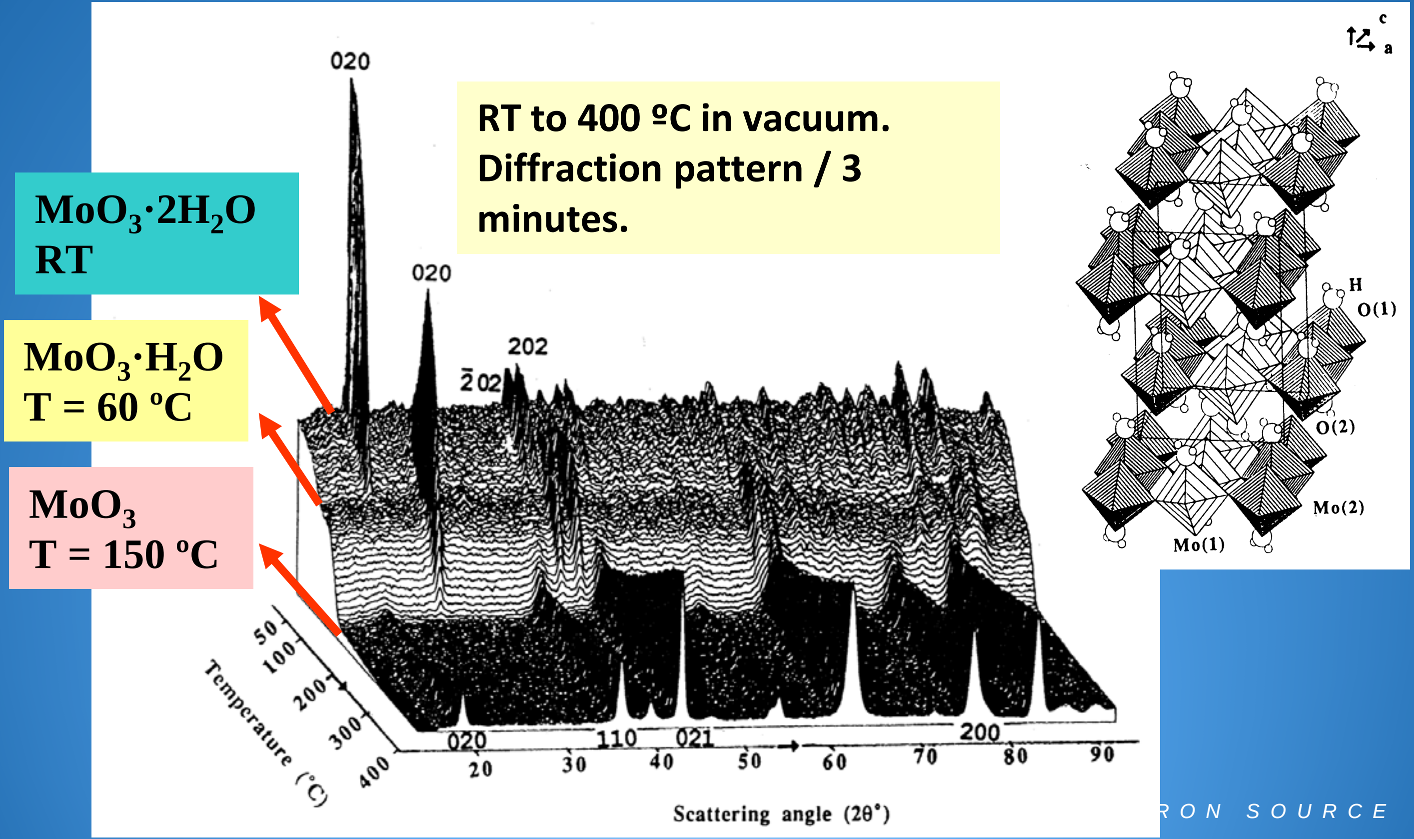




A 3-D plot of a portion of the diffraction patterns during SHS of Ti_3SiC_2 as the reaction progresses (left to right)

Real time powder diffraction on D1B

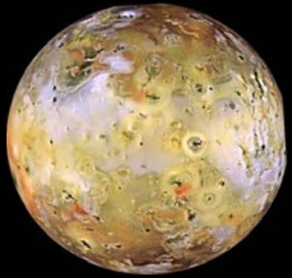
Dehydration of $MoO_3 \cdot 2H_2O$ [N. Boudjada et al.; *J. Solid State Chem.* **105**, 211 (1993)]



Some Applications: Liquid state → D4

Earth

Mars



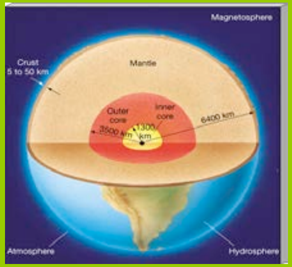
Io

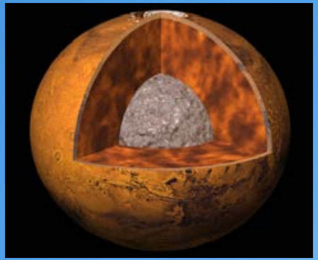
Ganymede

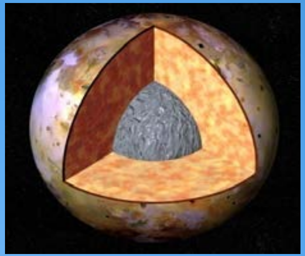
What they have in common …?

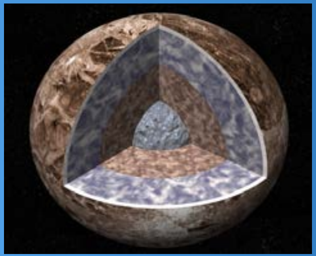
Metallic cores

Proximity in Solar System









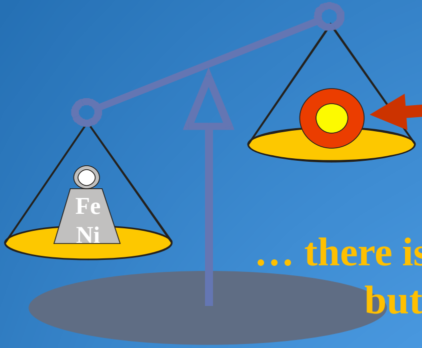
Fluid Outer Core: from 3000 to 5200 km

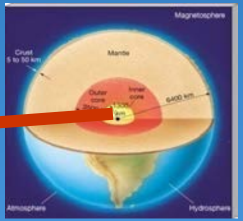
Primarily Fe with some Ni

Thanks to Gabriel Cuello

Some Applications: Liquid state

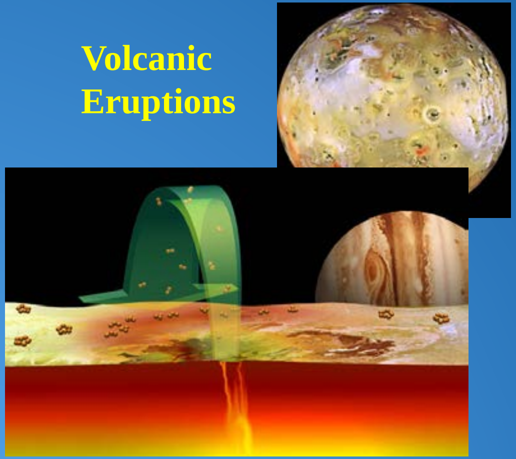
But ρ is 5-10% less than pure Fe+Ni …

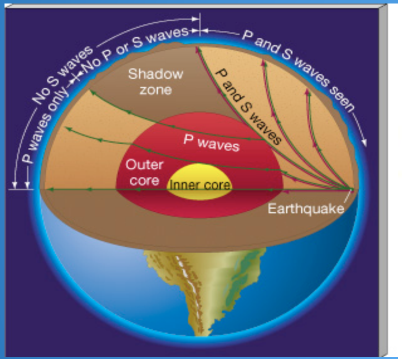


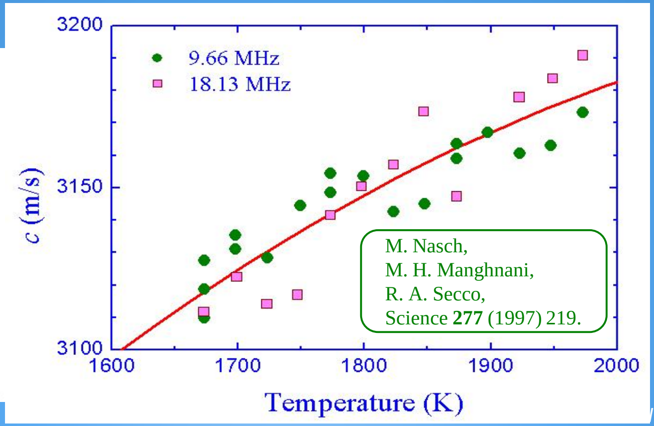


… there is some light element,
but which? S? O? H? Si?

Volcanic
Eruptions





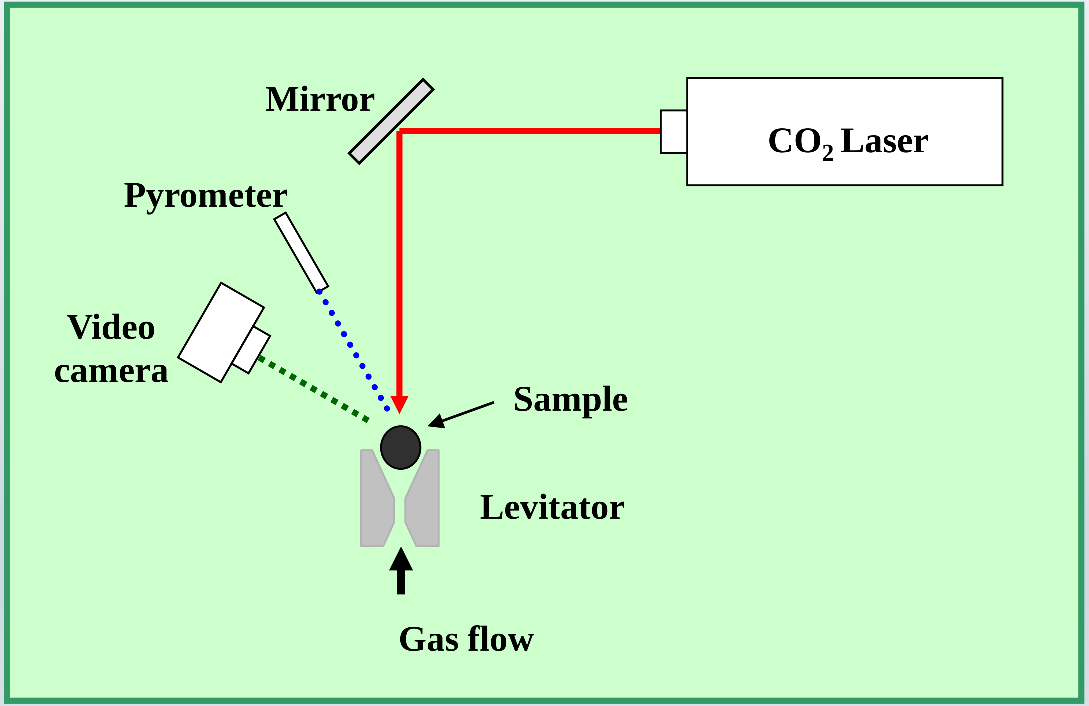


Hypothesis:

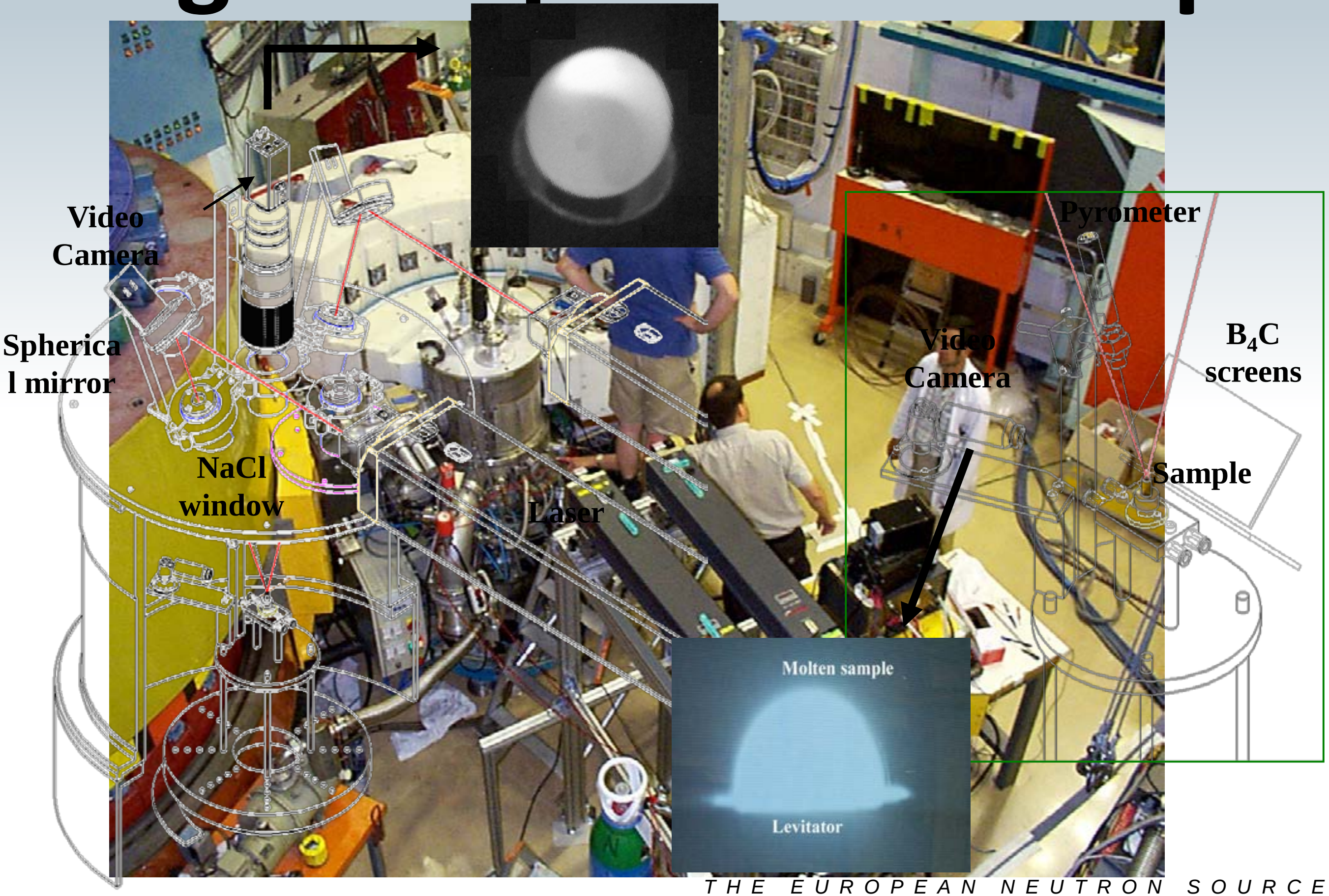
The light element helps aggregating clusters, which in turn are disaggregated by heating the system.

Levitation of Liquids

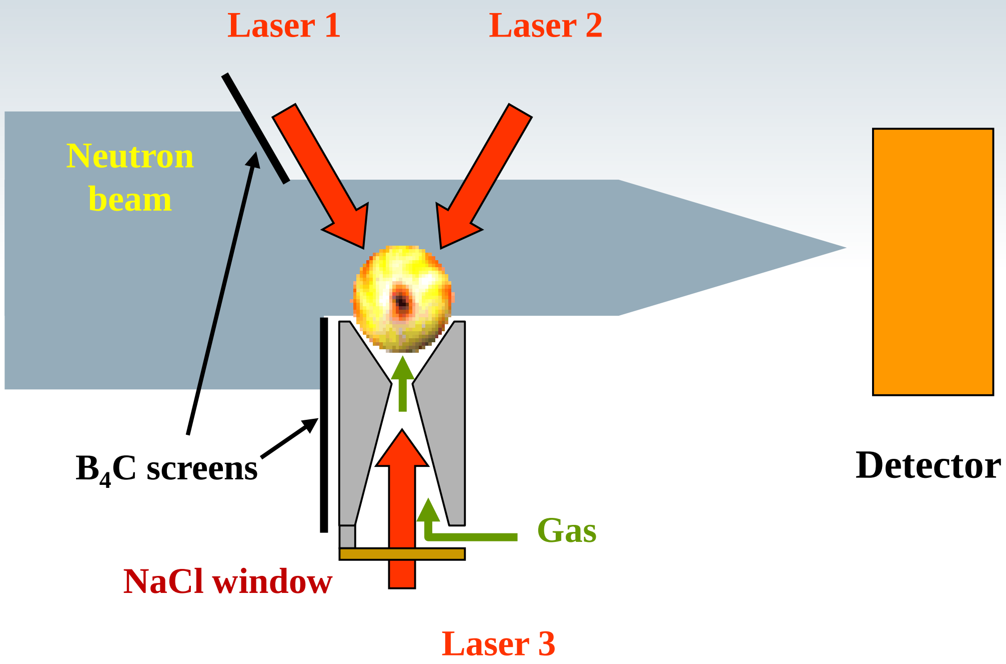
Principle of the aerodynamic levitation and laser heating



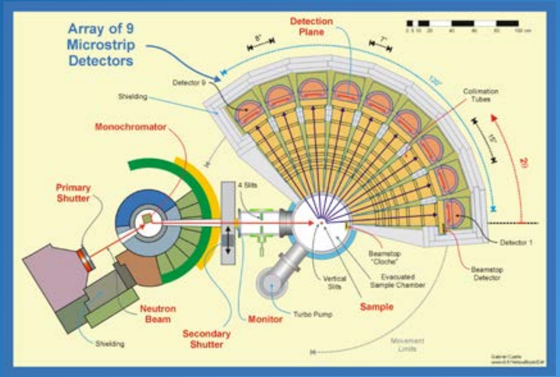
High Temperature Setup



Three Lasers Setup



Some Applications: Liquid state



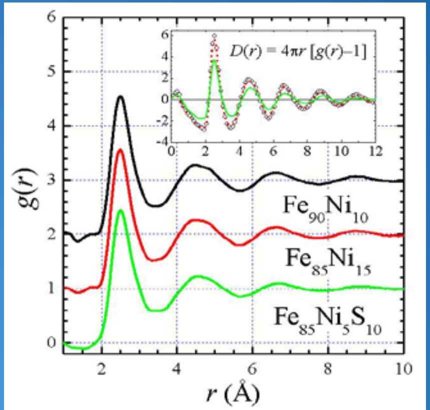
FeNi and FeNiS alloys

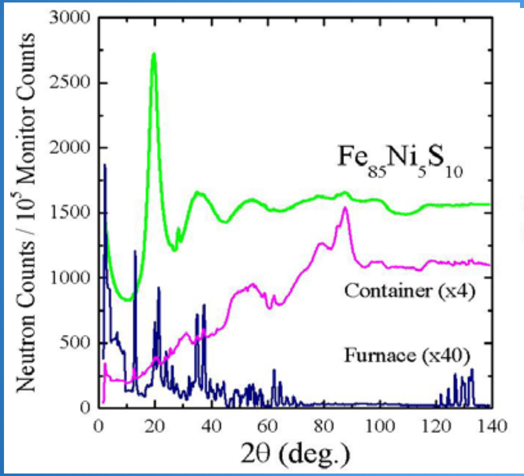
Liquid state

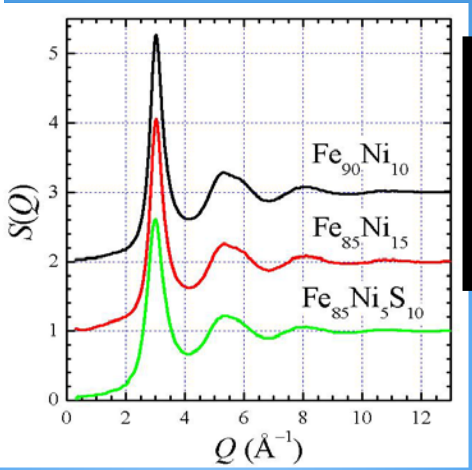
High temperature

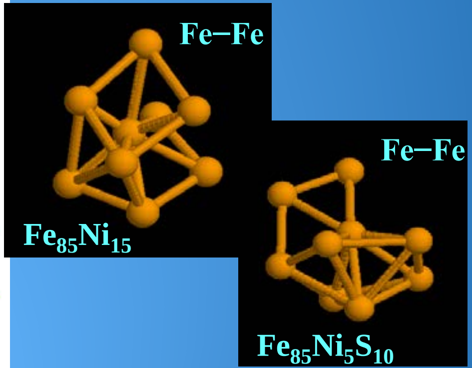
Special furnace

Two-axis diffractometer



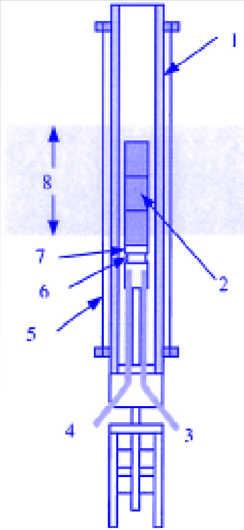


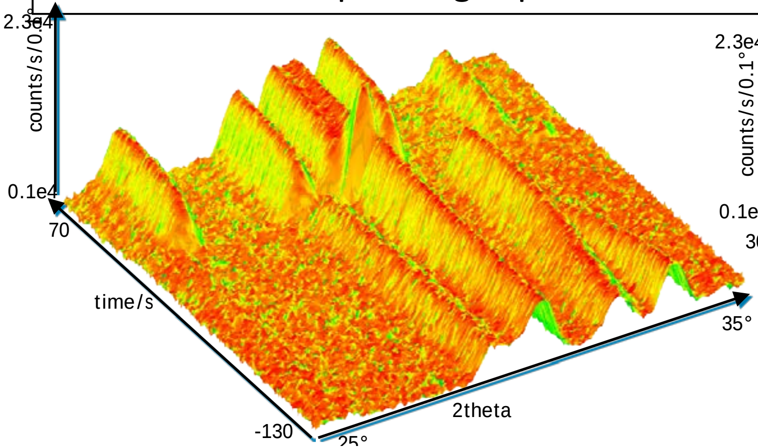


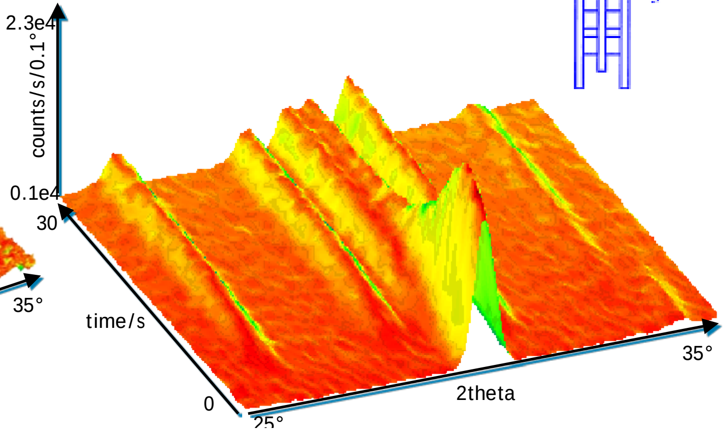


Self-propagating High-T Synthesis (SHS) D20

- Titanium silicon carbide Ti_3SiC_2
- Self-propagating High-temperature Synthesis (SHS)
  - Riley, Kisi et al.: 3 Ti : 1 Si : 2 C, 20 g pellet in furnace
  - Heating from 850 C to 1050 C at 100 K/min
  - Acquisition time 500 ms (300 ms)
- Hot isostatic pressing expensive







Thanks to
Thomas Hansen

D.P. Riley, E.H. Kisi, T.C. Hansen, A. Hewat, *J. Am. Ceramic Soc.* **85** (2002) 2417-2424.

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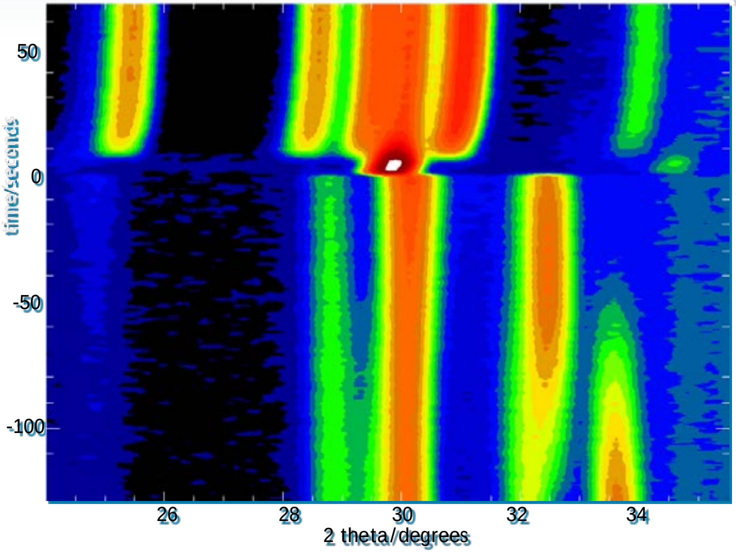
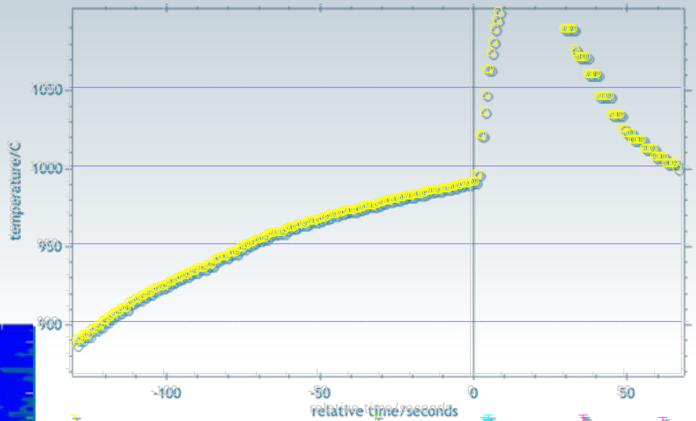
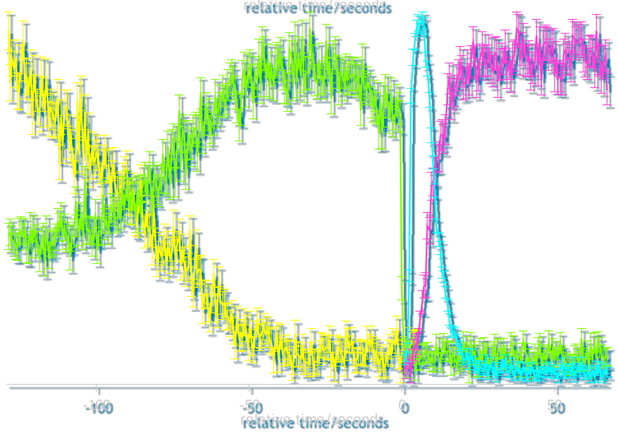
SHS: pre-ignition

- Ti α-β transition
  - starting at 870 C
- Pre-ignition:
  - TiC_x growth during 1 min
- Melting (?) in 0.5 s

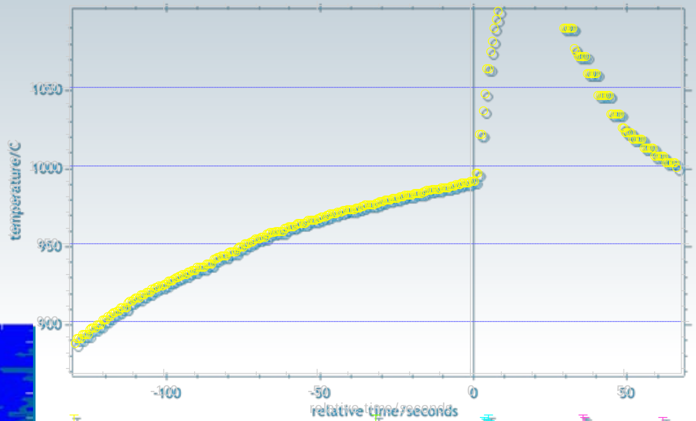


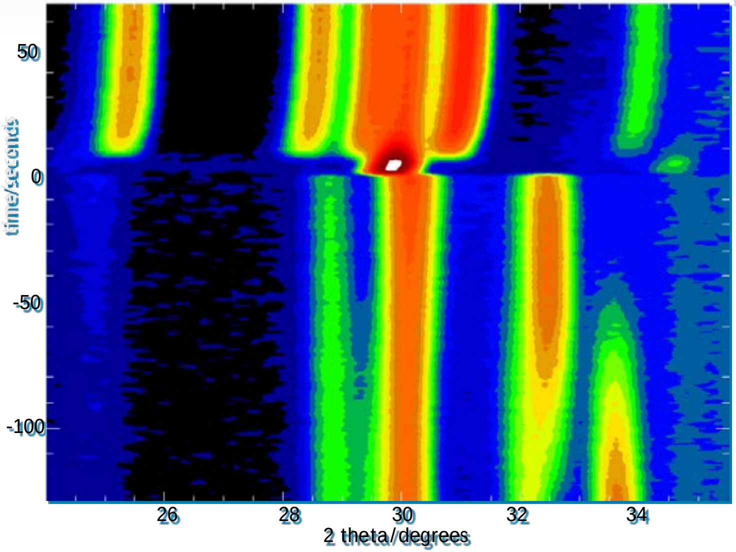


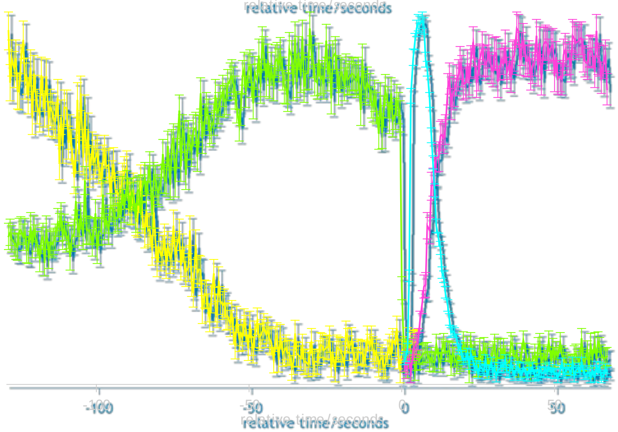


SHS: intermediate product

- Intermediate phase
  - TiC, Si substituted
  - formed in 0.5 s, 2s delay
  - Heating up to 2500 K
  - afterwards decay in 5 s

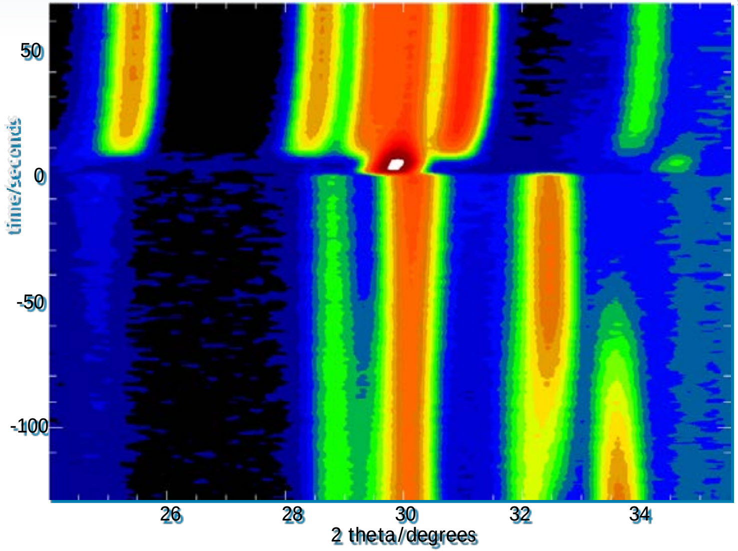


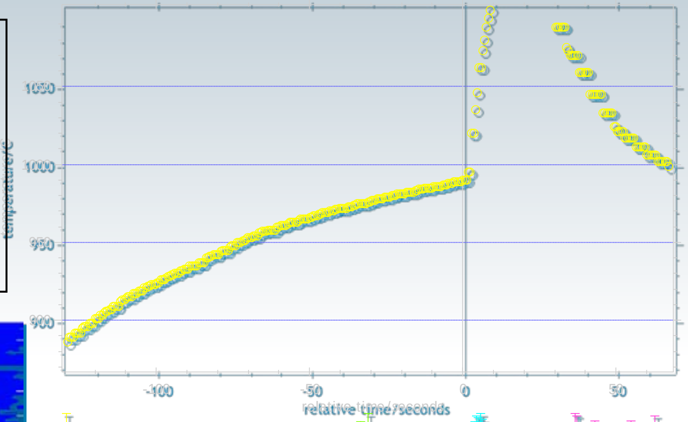


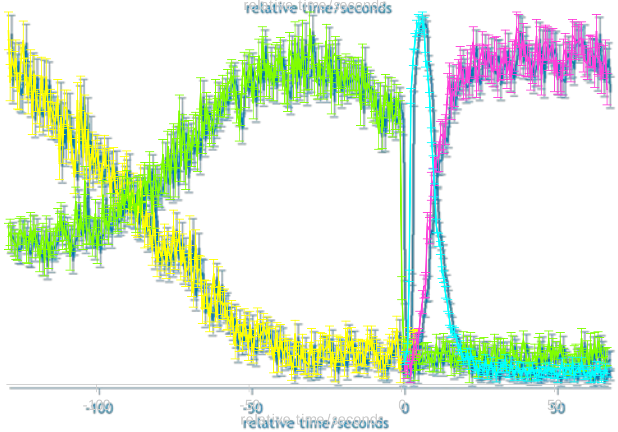


SHS: final product

- Product Ti_3SiC_2
  - starts after 5 s incubation
  - time constant about 5 s







Thank you for your attention

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