MLZ Lab Course WS2023

Diffractometry with Neutrons

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Diffractometry – Overview

- **Motivation**
- **Crystallography – Structure Description**
  - Concept of Unit Cell and Space Groups
  - Concept of Reciprocal Space
- **Diffractometry – Structure Analysis**
  - General Concept
  - Instrumental Aspects
  - Sample Specific Aspects
  - Powder Diffraction
  - Single Crystal Diffraction
- **Summary**

Motivation for Diffractometry

Macroscopic features

Microscopic structure

- Mechanical properties
- Optical properties
- Electric properties
  - polarization
  - ion conductivity
  - superconductivity
- Magnetism

- Chemical elements/isotopes
- coordination of elements
- Type of atomic bonds, e.g. ionic, covalent
- Electron/nuclear distribution
- Disorder

Why Neutrons as a Probe

1932: Discovery of neutron by James Chatwick (Nobel Prize 1935)

DeBroglie wave-particle relationship:

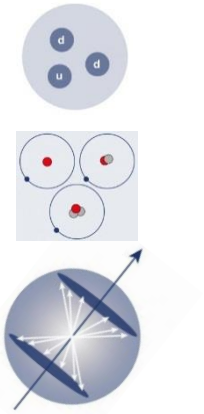
$$E = m_n v^2/2 = k_B T = (\hbar k)^2/2m_n$$

$$k = 2\pi/\lambda = m_n v/\hbar$$

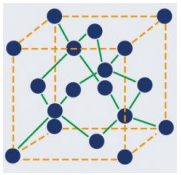
physical prop.	X-rays/γ	neutrons
mass [kg]	0	$1.673*10^{-27}$
energy [eV]	10^3 - 10^6	10^{-3} - 10^0 0.025 (thermal)
magn. moment	no	yes
wave length λ [Å]	0.3 - 20 1.5 (Cu-Kα)	0.3 - 20 1.8 (thermal)
typ. speed [m/s]	$3*10^8$	2500 (thermal)
Interaction with	e^- shell Z specific	nuclei/isotopes magnetic moment

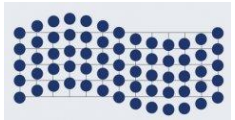
Neutrons are

- Electrically neutral
- Isotopically sensitive
- Magnetically sensitive



- Sensitive to atomic and magnetic structures
- Motion sensitive





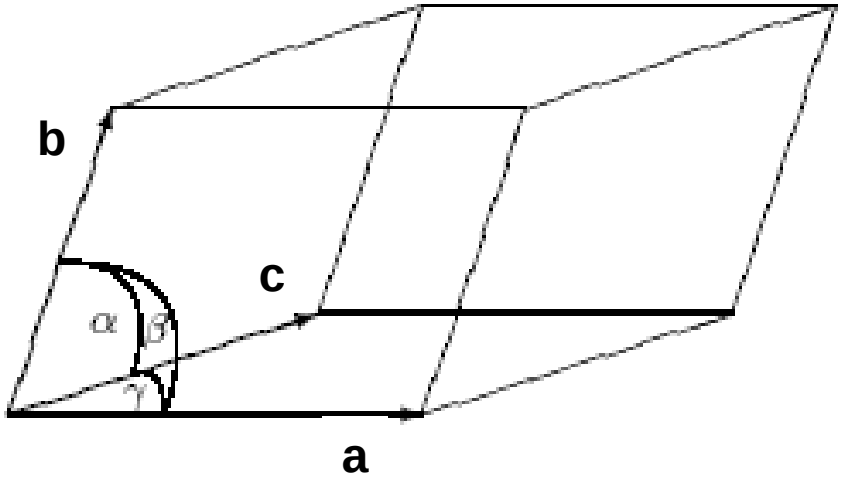
Crystallographic Definition of Structure

Three dimensional periodic arrangement of atoms/molecules

→ unit cell

Lattice vectors **a**, **b**, **c**

and constants *a, b, c*, α, β, γ



→ 7 crystal families

triclinic ($a \neq b \neq c$, α, β, γ ≠ 90°)
monoclinic ($a \neq b \neq c$, α, β = 90°, γ ≠ 90°)
trigonal $a = b \neq c$, α, β = 90°, γ = 120°)
cubic ($a = b = c$, α, β, γ = 90°)
orthorhombic ($a \neq b \neq c$, α, β, γ = 90°)
tetragonal ($a = b \neq c$, α, β, γ = 90°)
hexagonal ($a = b \neq c$, α, β = 90°, γ = 120°)

Beware:
Each family includes dedicated symmetry operations apply as well, not only metrics!

Crystallography

Crystal families

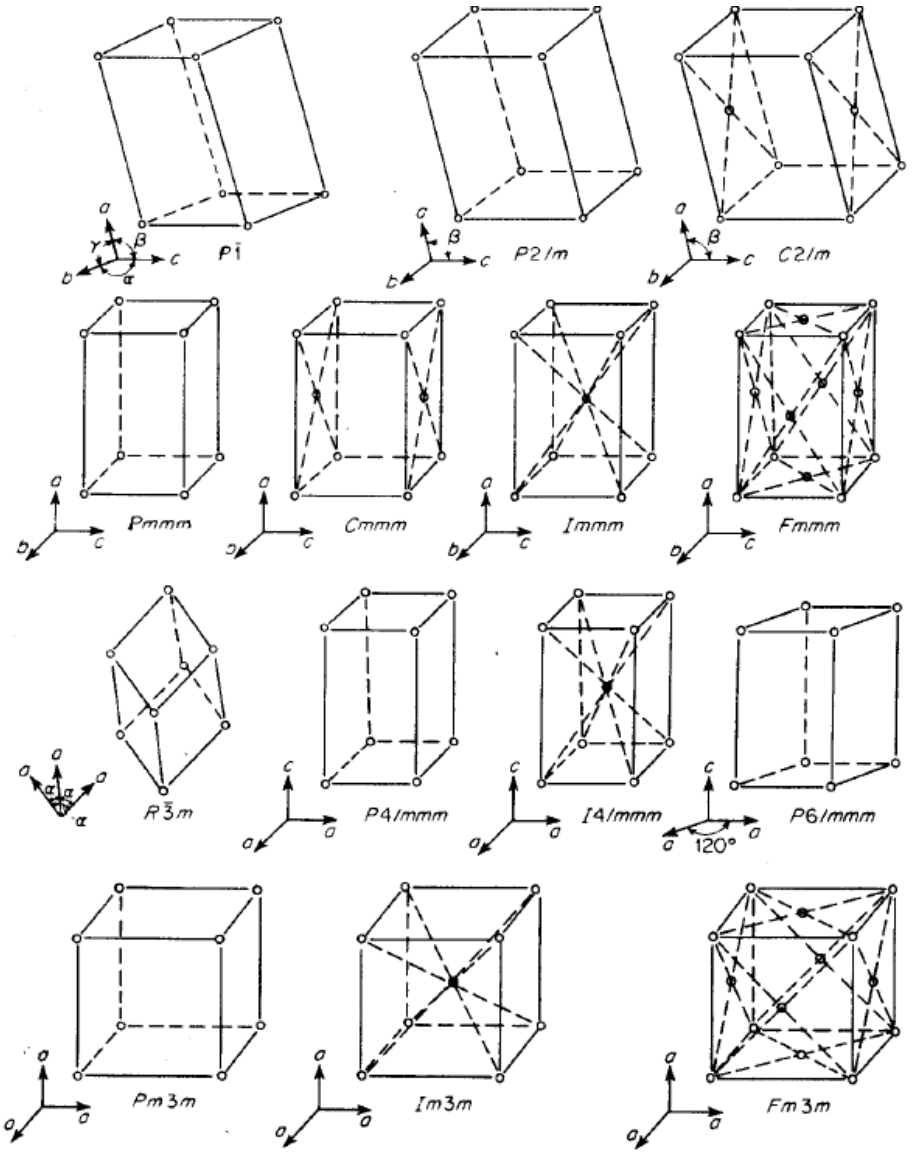
+

unit **cell centering**

(P, I, A, B, C, F, R)

↓

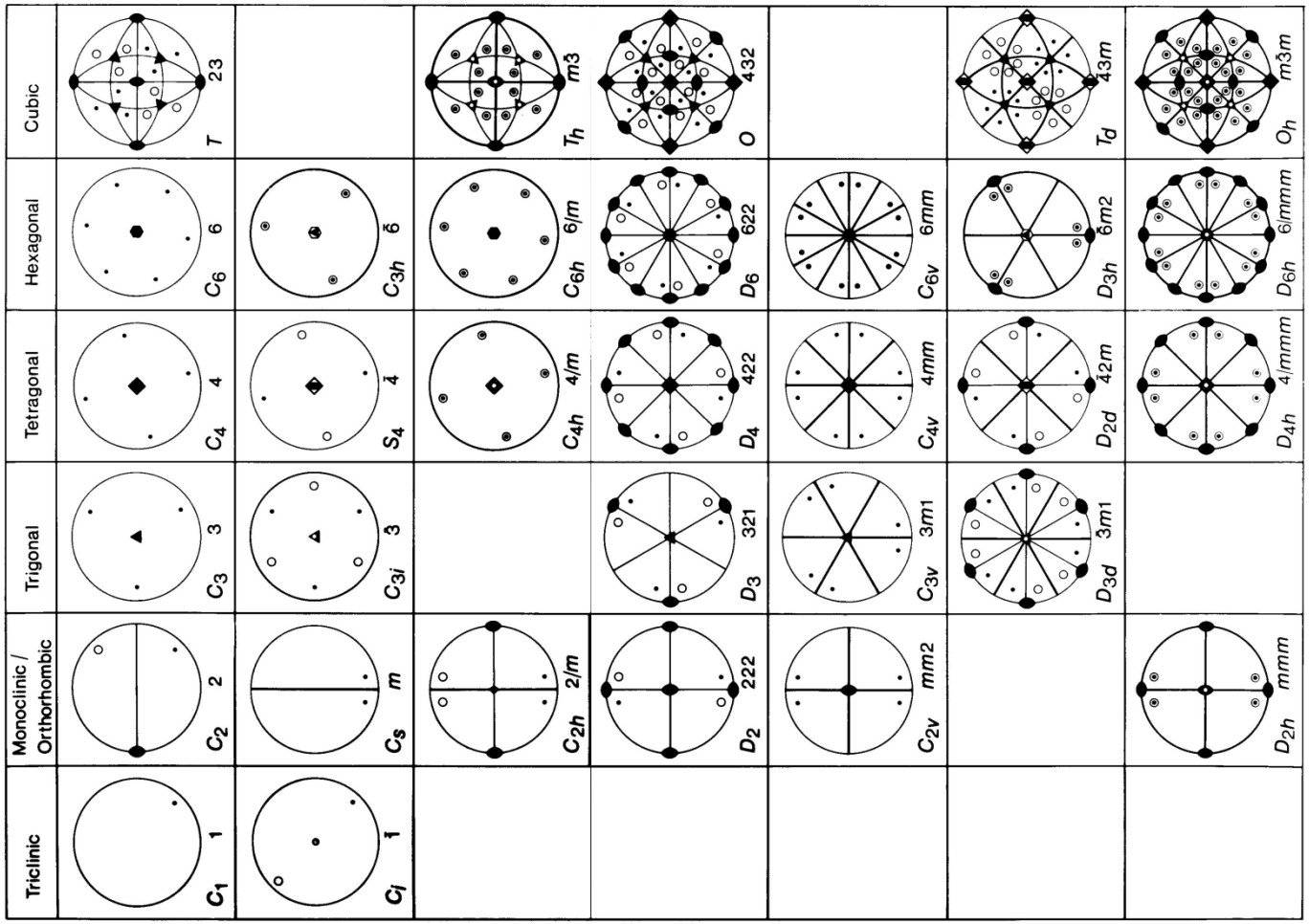
14 Bravais lattices



Crystallography

32 Point groups/Crystal classes

(point groups contain symmetry operations with at least one fixed point
⇒no glide planes, screw axes, translations)



4 fold axes,
3 fold axes
2 fold axes,
mirror planes, inv.

6 fold axes,
3 fold axes
2 fold axes,
mirror planes, inv.

4 fold axes,
2 fold axes,
mirror planes,
inversion

3 fold axes
2 fold axes,
mirror planes,
inversion

2 fold axes,
mirror planes,
inversion

inversion I:
-x –y -z

Crystallography

Crystal families + centring + symmetry elements

↓

230 crystallographic space groups

(Description by Hermann-Mauguin- or Schönfließ-Symbols)

Extensions

- **Magnetic space groups**
  (1651 groups accounting possible spin orientations of magnetic elements)
- **Quasicrystals**
  (n-dim. Crystallographic space groups, n>3)

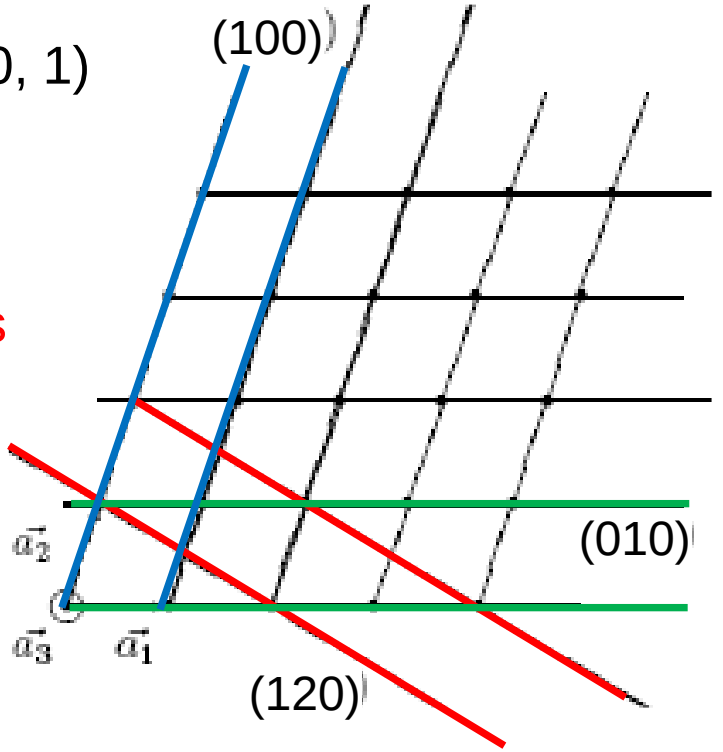
Concept of Reciprocal Space

Direct (=real) space: Unit Cell ↔ lattice vectors **a**, **b**, **c**

t = *u****a** + *v****b** + *w****c** translation vector, *u*, *v*, *w* ϵ ***Z***

x = *x****a** + *y****b** + *z****c** atomic coordinates, *x*, *y*, *z* ϵ [0, 1)

V= **a**(**b** x **c**) volume of unit cell



Reciprocal (=Q) space: reciprocal lattice vectors

a*=(**b** x **c**)/V, **b*** = (**c** x **a**)/V**, c***= (**a** x **b**)

Lattice plane with **Miller indices** *h*, *k*, *l* ϵ ***Z*** and

Q = 2π(*h****a*** + *k****b*** + *l****c***) = 2π **H**

H: normal vector of hkl plane

with **1/|H| = d_{hkl}** distance of (*h k l*) lattice plane, e.g. **cubic cell: $d_{hkl} = a\,l\sqrt{(h^2+k^2+l^2)}$**

Diffractometry - Concept

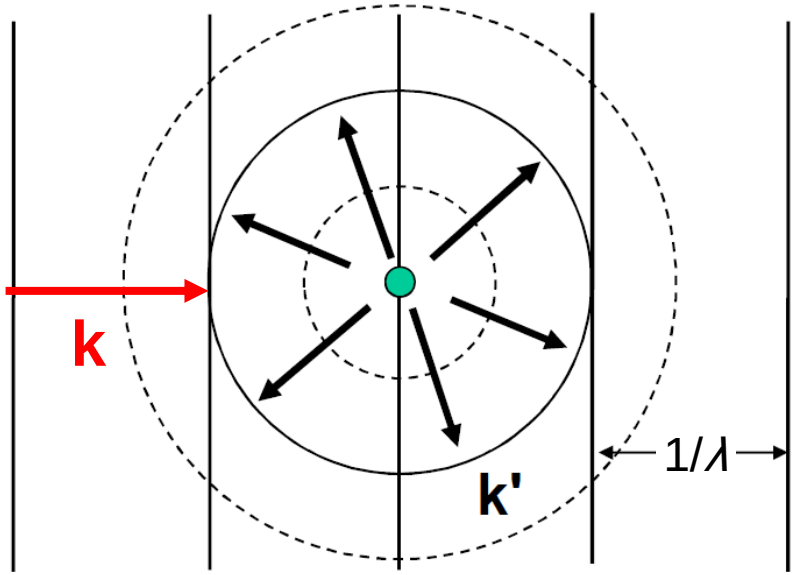
Scattering of Plane Wave

Radiation with wave vector k
|k|=$2\pi/\lambda$ (or $1/\lambda$ for crystallographers)

Radiation: el.-magn. waves, n°, e^-

radiation interacts with „scatterer“

in principle anything that makes the specific radiation to be scattered



scattered radiation with **k‘**:
spherical wave outgoing from scatterer‘s position (point source)

assume energy conservation $E = E'$ ⇔ **|k‘| = |k|** **elastic scattering**

⇨ Diffractometry

Diffractometry - Concept

Scattering of Plane Waves

more than one scatterer:

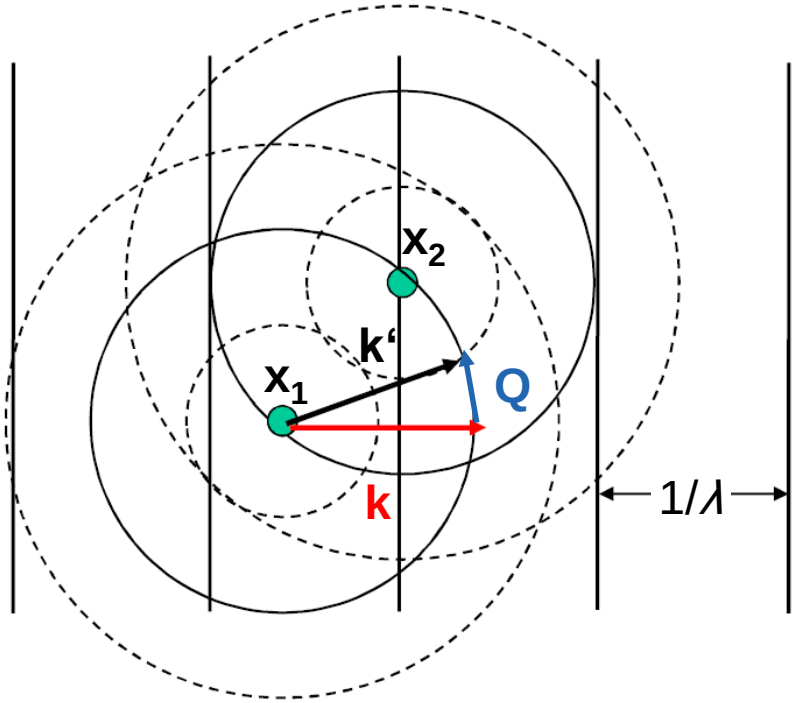
Interference with **k‘ = k** + **Q**
Q: scattering vector

phase shift between spherical waves
$\mathbf{Q}(\mathbf{x}_2 - \mathbf{x}_1)$

Scattering Amplitude $s(\mathbf{Q})$

$s(\mathbf{Q}) = s_1 \exp(i\mathbf{Q}\mathbf{x}_1) + s_2 \exp(i\mathbf{Q}\mathbf{x}_2)$

n scatterers in given volume: $s(\mathbf{Q}) = \sum_{j=1}^{n} s_j \exp(i\mathbf{Q}\mathbf{x}_j)$



⇒ Structure factor $F(\mathbf{Q})$

Derivation of Bragg's Law from Scattering Vector

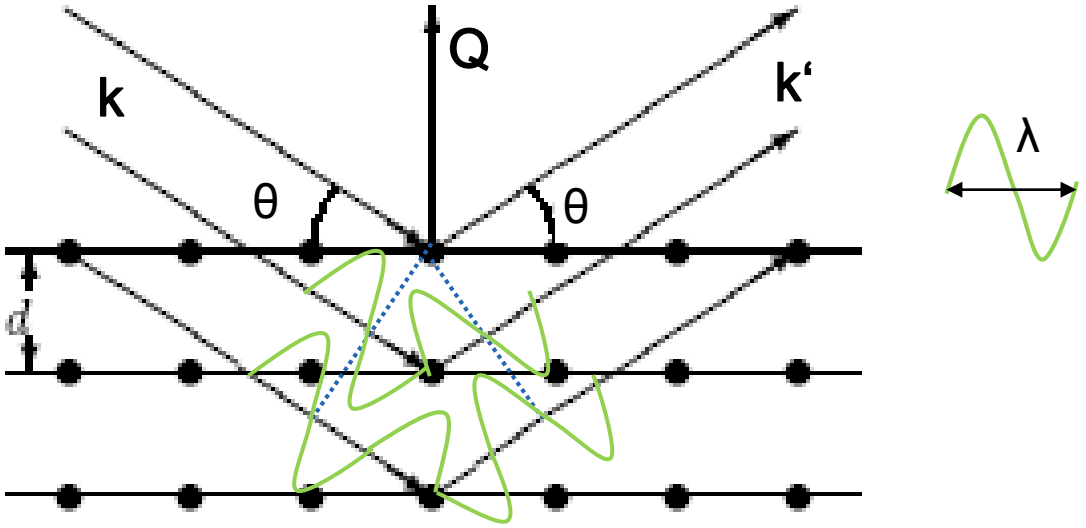
assume scattering vector $\mathbf{Q} = \mathbf{k'} - \mathbf{k} = 2\pi(h^*\mathbf{a}^* + k^*\mathbf{b}^* + l^*\mathbf{c}^*) = 2\pi\,\mathbf{H}$

distance of lattice plane $2\pi/|\mathbf{Q}| = d_{hkl}$; $|\mathbf{k}| = 2\pi/\lambda$, $\sphericalangle(\mathbf{k'}, \mathbf{k}) = 2\theta$

$$\mathbf{Q^2} = 4\pi^2/d_{hkl}^2$$

$$\Leftrightarrow (2d_{hkl} \sin\theta)^2 = \lambda^2$$ **squaric version of Bragg's Law**

constructive interference in crystal for integer *h, k, l* with phase shift of *n* λ between neighbored lattice planes of same H



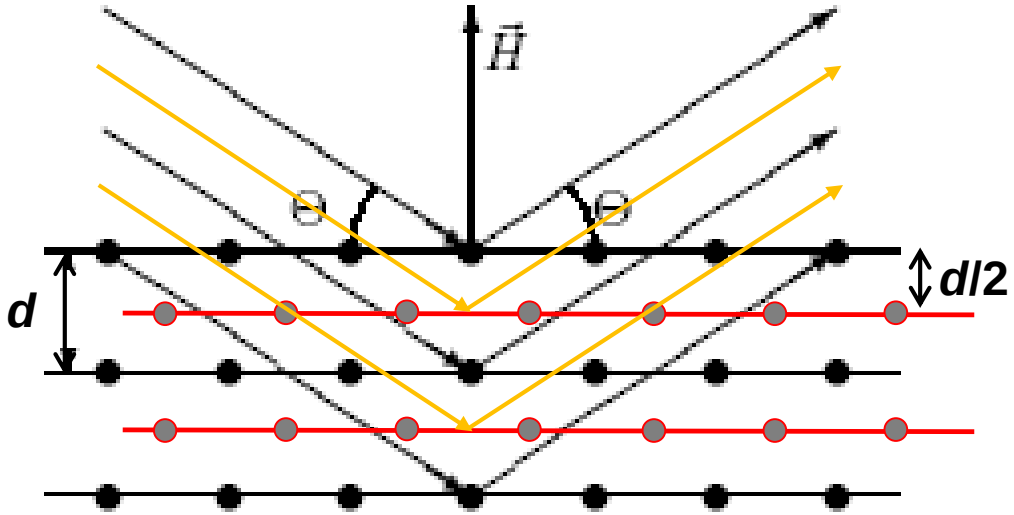
Effect of Centering for Structure factor

x = *x****a** + *y****b** + *z****c** , *x*, *y*, *z* ϵ [0, 1), rel. atomic coordinates
Q = 2π(*h****a*** + *k****b*** + *l****c***) = 2π **H**, scattering vector

$F(\mathbf{Q}) = \sum_{j=1}^{n} s_j \exp(i\,\mathbf{Q}\mathbf{x}_j) = \sum_{j=1}^{n} s_j \exp(2\pi i\,(hx_j + ky_j + lz_j)) =: F_{hkl}$

Constructive interference = phase shift of n*λ between layers of same orientation

Geometric approach



Insertion of additional identical layers of same **H**/|H| in distance ½d_{hkl}:

phase shift for neigbouring planes ½*n* → destructive interference for odd *n*

Effect of Centering for Structure factor

$\mathbf{x} = x^*\mathbf{a} + y^*\mathbf{b} + z^*\mathbf{c}$, $x, y, z \in [0, 1)$, rel. atomic coordinates
$\mathbf{Q} = 2\pi(h^*\mathbf{a^*} + k^*\mathbf{b^*} + l^*\mathbf{c^*}) = 2\pi\,\mathbf{H}$, scattering vector

$$F(\mathbf{Q}) = \sum_{j=1}^{n} s_j \exp(i\,\mathbf{Q}\mathbf{x}_j) = \sum_{j=1}^{n} s_j \exp(2\pi i\,(hx_j + ky_j + lz_j)) =: F_{hkl}$$

Constructive interference = phase shift of n*λ between layers of same orientation

Mathematical derivation, e.g. for bcc structure:

pattern in unit cell observed from (0 0 0) repeats at (½ ½ ½)

$$F(\mathbf{Q}) = \sum_{j=1}^{n} s_j \{\exp(i\,\mathbf{Q}\mathbf{x}_j)$$

$$= \tfrac{1}{2} \sum_{j=1}^{n/2} s_j \{\exp(i\,\mathbf{Q}\mathbf{x}_j) + \exp(i\,\mathbf{Q}(\mathbf{x}_j + (\tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2}))\}$$

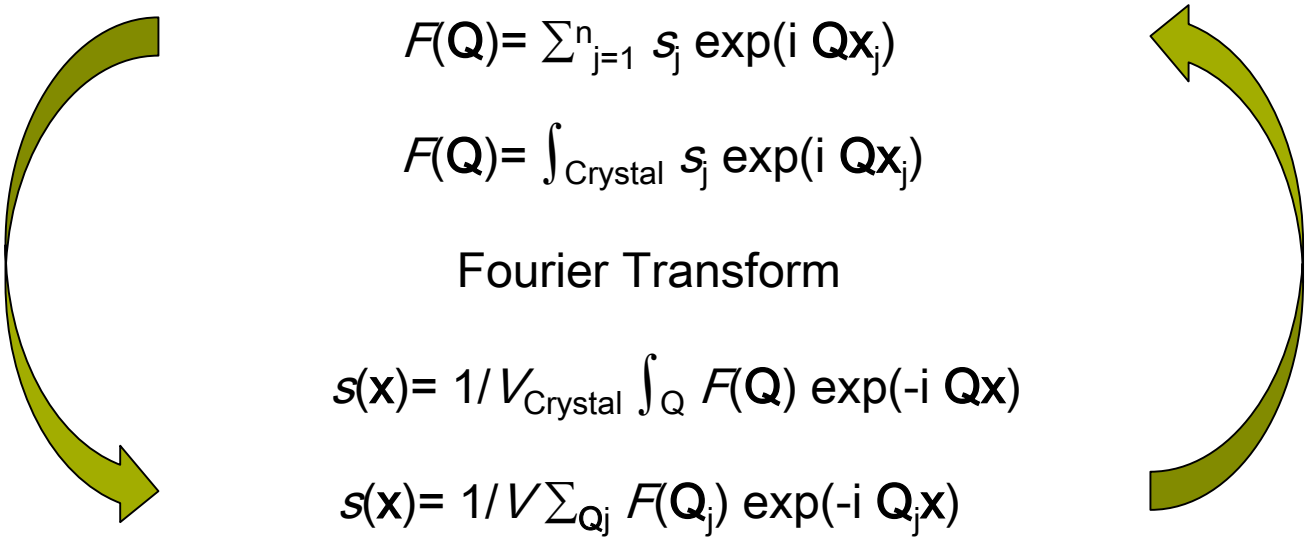
$$= \tfrac{1}{2} \{1 + \exp(\pi i\,(h+k+l))\} \sum_{j=1}^{n/2} s_j \exp(i\,\mathbf{Q}\mathbf{x}_j)$$

$$= \begin{cases} \sum_{j=1}^{n/2} s_j \exp(i\,\mathbf{Q}\mathbf{x}_j) & \text{for } h + k + l = 2n \\ 0 & \text{for } h + k + l \neq 2n \end{cases}$$

centered structures ⇔ extinction rules

Relationship between real space and reciprocal space

distribution of scattered wave amplitudes in Q space =Fourier transform of distribution of scattering objects in x (=real) space and vice versa!



more general: $s(x)$ = scattering density, e.g.

X-rays: form factor $f(Q)$ with $f(0)=Z$

Neutrons: nuclear and magnetic scattering lengths b

Phase problem of Crystallography

direct relationship between $F(\mathbf{Q})$ and $s(\mathbf{x})$, but:

only intensity $|F(\mathbf{Q})|^2$ measurable, no phase information

(except for special cases, e.g. resonant scattering)

$$I(\mathbf{Q}) = |F(\mathbf{Q})|^2 = F(\mathbf{Q})^* F(\mathbf{Q})^* = F(\mathbf{Q})^* F(-\mathbf{Q}) = I(-\mathbf{Q})$$ **Friedel pair**

Diffractometry - Concept

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Patterson function

$$I(\mathbf{Q}) = \int s(\mathbf{x}) \exp(i\mathbf{Q}\mathbf{x}) d\mathbf{x} \int s(\mathbf{x}') \exp(-i\mathbf{Q}\mathbf{x}') d\mathbf{x}'$$

$$= \iint s(\mathbf{x}) s(\mathbf{x}') \exp[i\mathbf{Q}(\mathbf{x}'-\mathbf{x})] d\mathbf{x} d\mathbf{x}' \text{ with } \mathbf{x}'-\mathbf{x} = \mathbf{r}$$

yields as Fourier transform

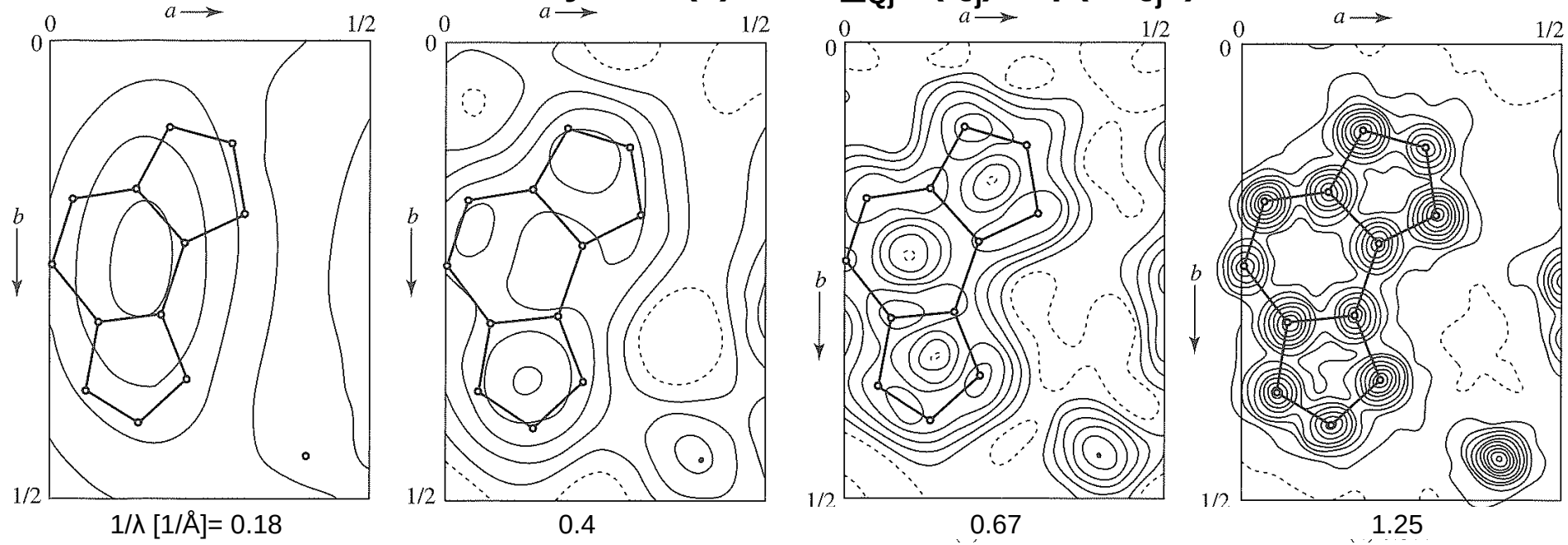
$$P(\mathbf{r}) = 1/N \sum I(\mathbf{Q}) \exp(i\mathbf{Q}\mathbf{r})$$

relative distances between electronic/nuclear densities

Diffractometry - Concept

Limitations of Diffractometry

- **averaging over V_{sample} and t**
- **only $I(Q)=|F(Q)|^2$ visible → „phase problem of crystallography“**
- **λ dependent resolution:** $2\pi/|Q_{max}|=d_{hkl,min} = \lambda/2\sin\theta_{max} > \lambda/2$
- **limited amount of $F(Q_j)$**
  → limited accuracy for $s(x)= 1/V \sum_{Qj} F(Q_j) \exp(-i\, Q_j x)$!



Electron density maps with different $d_{min} = \lambda/2\sin\theta_{max}$ for Mo-K_α radiation
from „Crystal Structure Analysis“; A. Blake, W. Clegg, et al.; IUCr Book Series, Oxford University Press (2009)

Diffractometry - Concept

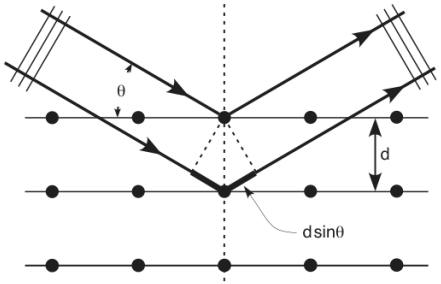
What can be extracted?

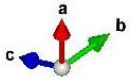
I. Collect **Bragg angles Θ_{hkl}** using

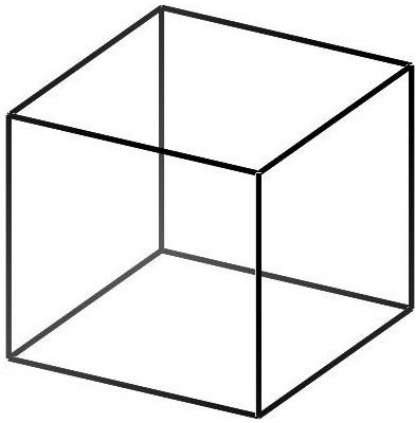
Bragg's Law $2d_{hkl}\sin(\Theta_{hkl})=\lambda$

↓

unit cell parameters







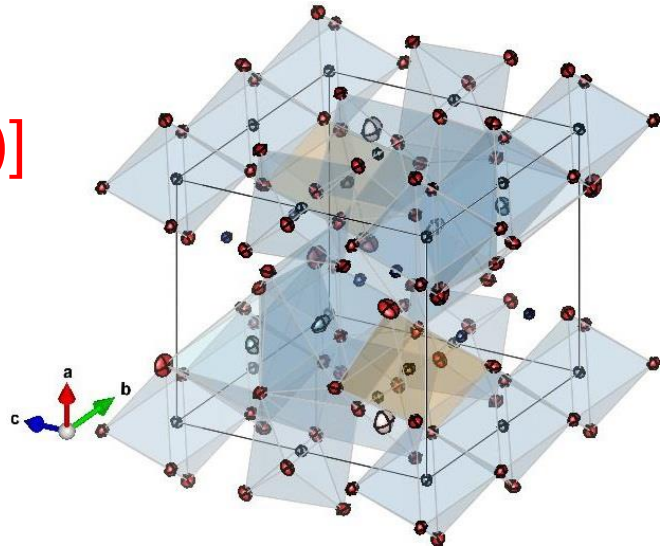
II. Collect **Reflection intensities $I_{hkl}\sim|F_{hkl}|^2$**

$$F_{hkl}=\Sigma_j T_j(\mathbf{Q})*occ_j*s_j(\theta_{hkl})*\exp[2\pi i(hx_j+ky_j+lz_j)]$$

↓

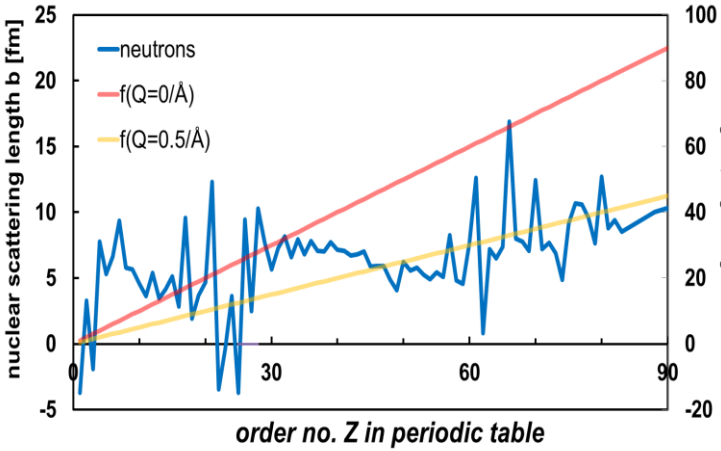
atomic positions

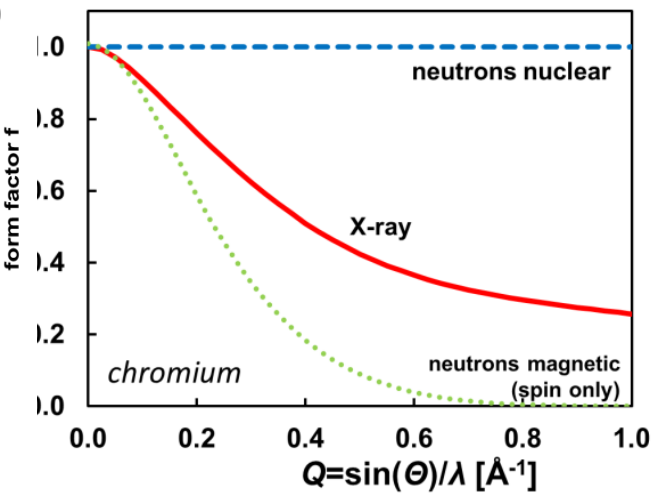
More accurate:
X-rays: electron densities
Neutrons: nuclear densities



Diffractometry - Concept

Consideration of the interaction character of $s_j(\theta_{hkl})$





M. Meven, G. Roth; Neutron Diffraction; ed. R. Dronskovski, S. Kikkawa, and A. Stein;; Handbook of Solid State Chemistry; Whiley Vol 3 (2017)

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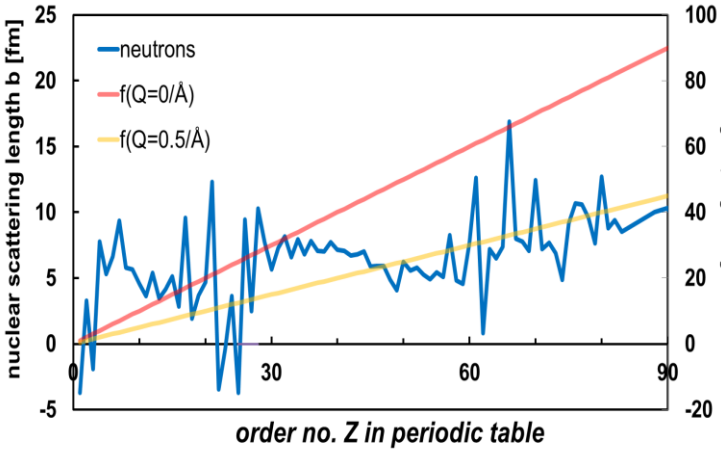
$$F_{hkl} = \Sigma_j T_j(\mathbf{Q}) * occ_j * \mathbf{s_j(\theta_{hkl})} * \exp[2\pi i(hx_j + ky_j + lz_j)]$$

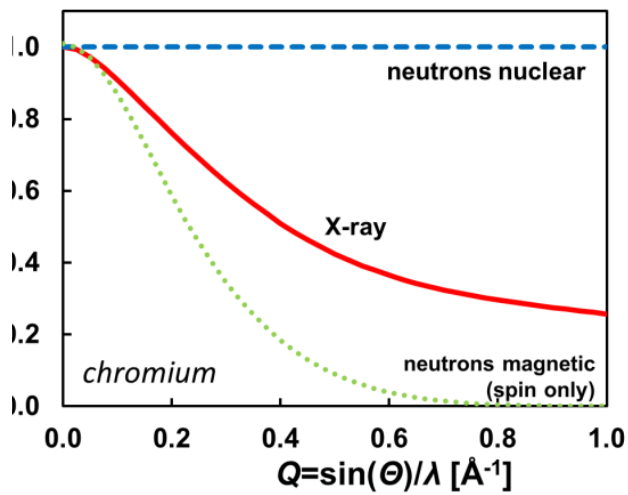
↓ *static or non static in sin(Θ)/λ !*

- **electron density distributions comparable to wavelength → Q dependence**
- **nuclei 10^5 times smaller than atoms = point scatterer → no Q depencence**
- **strong contrast variation between F_{hkl} from X-ray and neutron diffraction!**

Diffractometry - Concept

Consideration of the interaction character of $s_j(\theta_{hkl})$





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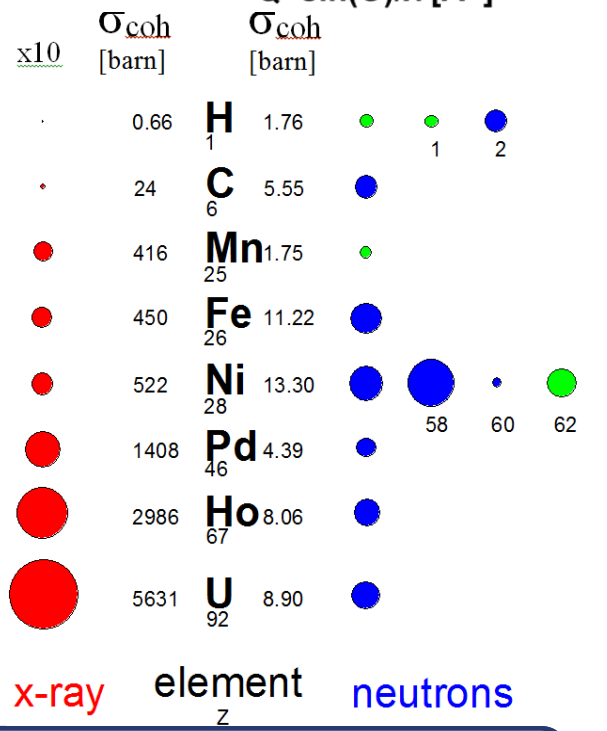
static in sin(Θ)/λ !↓

- **vacancies,** probability for atom on site i: $p_i < 1$
- **occ. disorder,** $occ_j * s_j = p_1 * s_{A1} + p_2 * s_{A2} + p_3 * s_{A3} + \ldots$, $\Sigma\, p_{Ai} = 1$
- **Q independent effect**
- **tunable with isotope mixture (neutrons)**



T. Brückel, A Neutron Primer in Neutron Scattering, Lectures of the JCNS Laboratory course, ed. T. Brückel, G. Heger, D. Richter, G. Roth and R. Zorn, Schriften des Forschungszentrums Jülich, Reihe Schlüsseltechnologien Bd. 15, pp 2:1-32 (2010).

Diffractometry - Concept

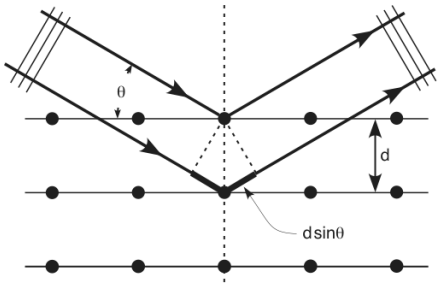
What can be extracted?

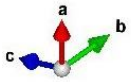
I. Collect **Bragg angles Θ_{hkl}** using

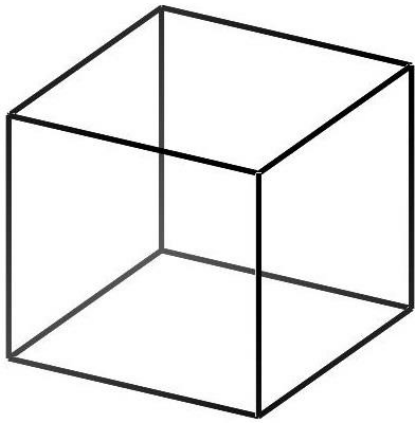
Bragg's Law $2d_{hkl}\sin(\Theta_{hkl})=\lambda$

↓

unit cell parameters







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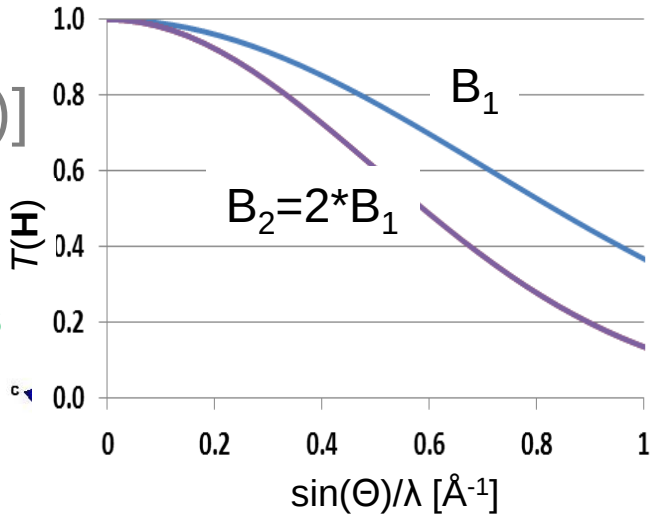
$$F_{hkl}=\Sigma_j \mathbf{T_j(Q)}*occ_j*s_j(\theta_{hkl})*\exp[2\pi i(hx_j+ky_j+lz_j)]$$

↓ **Q dependent**, *decreases with sin(Θ)/λ !*



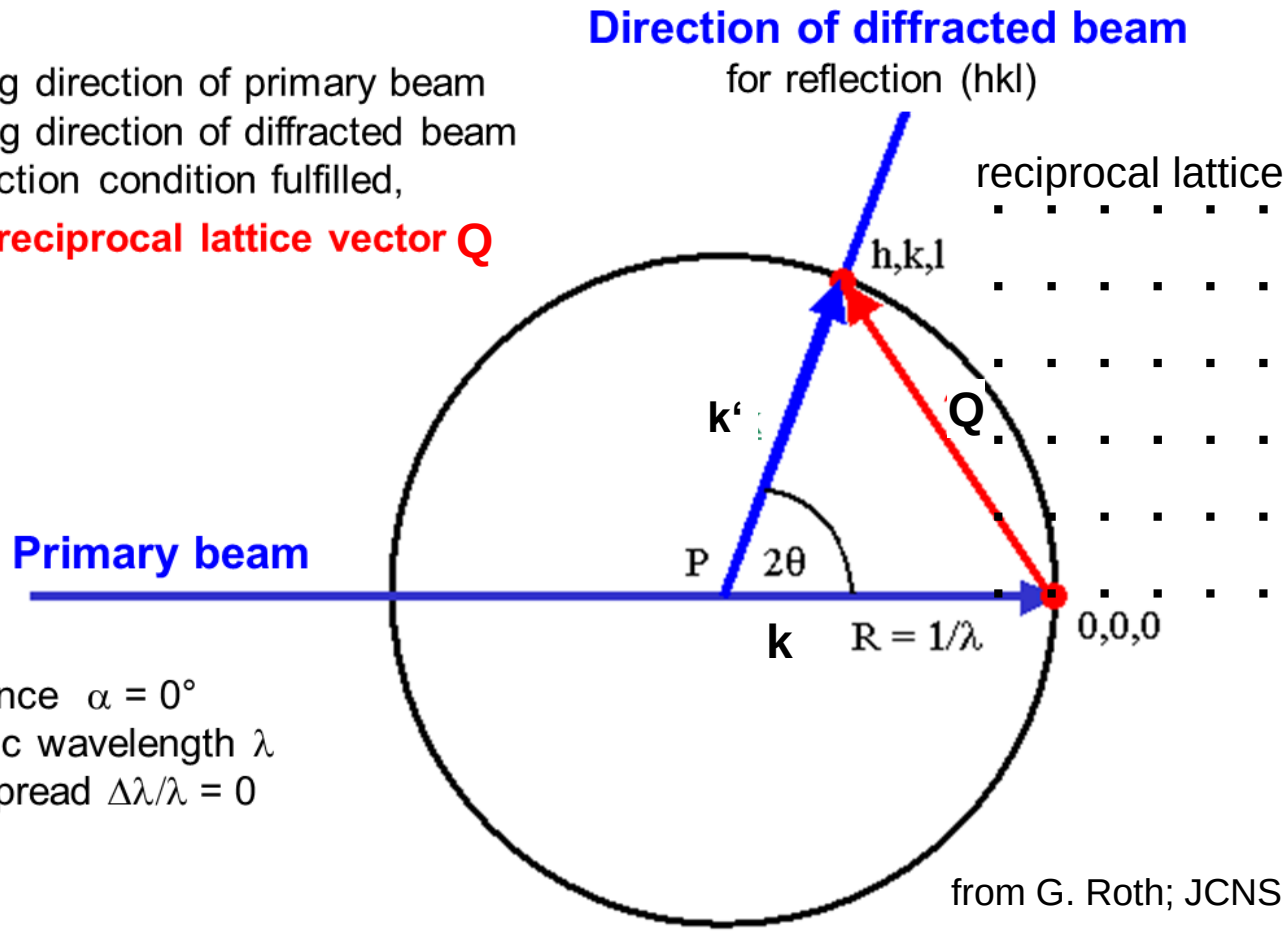
Debye Waller factors aka **mean square displacements** caused by statistical oszillations around mean positions

- **isotropic:** $T(\mathbf{H})=\exp\{-B(\sin\Theta_{hkl}/\lambda)^2\}$ with $\mathbf{B_i}$
- **anisotropic: 6 displacement parameters $\mathbf{U_{ij}}$**
- **static and dynamic disorder or anharmonicities**

Instrumental Aspects

introduce Ewald sphere for discussion

k : Vector along direction of primary beam
k' Vector along direction of diffracted beam
Bragg-reflection condition fulfilled,
if k-ko is a **reciprocal lattice vector Q**



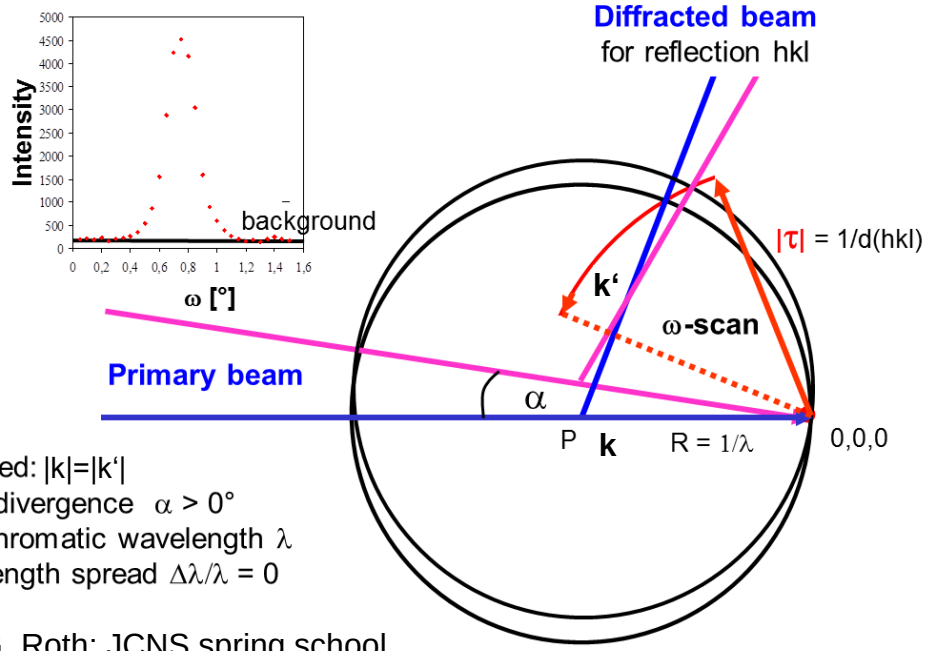
Assumed:
Beam divergence $\alpha = 0°$
Monochromatic wavelength λ
Wavelength spread $\Delta\lambda/\lambda = 0$

from G. Roth; JCNS spring school

***I*(hkl) measurable: Q touches Ewald sphere & detector is at same position**

Instrumental Aspects

- **Beam divergence**
  - spacial divergence monochromator quality & size, collimation



Assumed: |k|=|k‘|
Beam divergence $\alpha > 0°$
Monochromatic wavelength λ
Wavelength spread $\Delta\lambda/\lambda = 0$

from G. Roth; JCNS spring school

⇒ Ewald sphere broadens

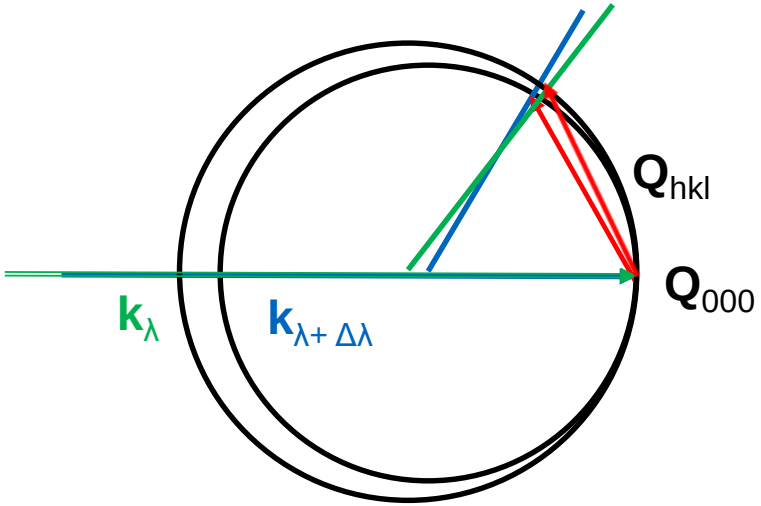
⇒ Bragg‘ Law fulfilled in
$(\theta_{hkl}, \theta_{hkl} + \alpha)$

Instrumental Aspects

- **Beam divergence**
  - **Energy resolution $\Delta\lambda/\lambda$**

    ⇒ broadens thickness of Ewald sphere in dependence of θ (typ. 10^{-3} - 10^{-2} for neutron diffractometers)

    ⇒ Bragg‘ Law fulfilled in (λ, λ+Δλ) → additional $\Delta\theta_E$



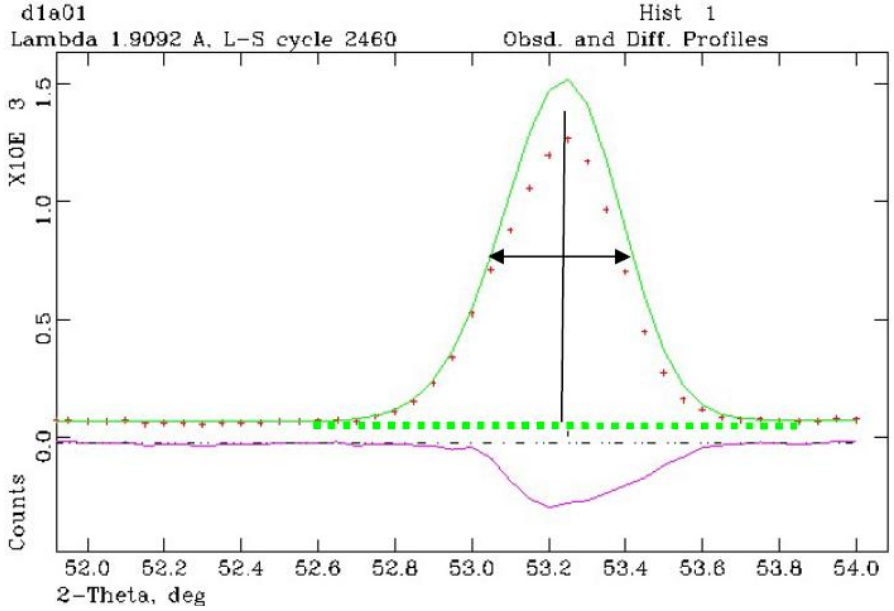
Instrumental Aspects

- **Beam divergence usually dependent on 2θ**
  $K_{\alpha1}/K_{\alpha2}$ split for high 2θ (X-ray tube) or
  instrument with monochromator

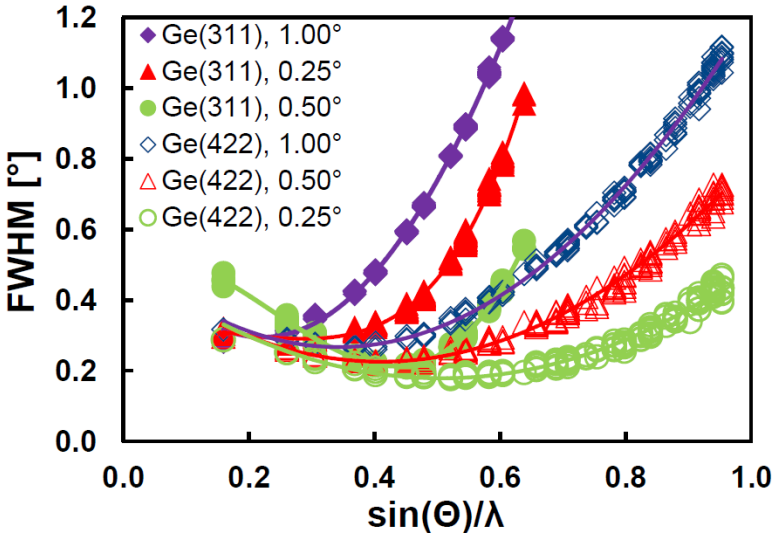
⇒ **determine instrumental resolution empirically, e.g.**

Caglioti formula: $FWHM^2_{instrument} = w + v \tan(\theta) + u \tan^2(\theta)$

Caglioti, Paelotti and Ricci, Nucl. Instrum. Methods, 35,223 (1958)



FWHM definition (full width at half maximum)



Resolution NSCD HEIDI

Instrumental Aspects

- **Beam divergence Δθ**
  usually Q dependent!

  Lorenz factor L = 1/sin(2Θ)
  relative time the reflection spot stays in Ewald sphere depends on θ

- **Polarisation factor P = ½ (1 + cos²(2Θ))** (X-ray lab. beam tube)
  Diffracted X-rays become polarized, (unpolarised) neutrons not!

- **LP factor** merged factor of L and P

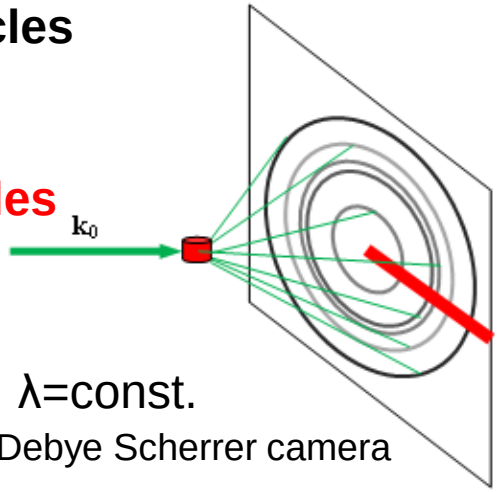
Powder vs. SC Diffractometry

Powder sample: many randomly oriented crystalline particles

Example: angular dispersive design (λ=const.)

⇨ **many Bragg peaks at same time on Debye Scherrer circles**

parallel measurement of I_{hkl}



λ=const.

Debye Scherrer camera

Powder vs. SC Diffractometry

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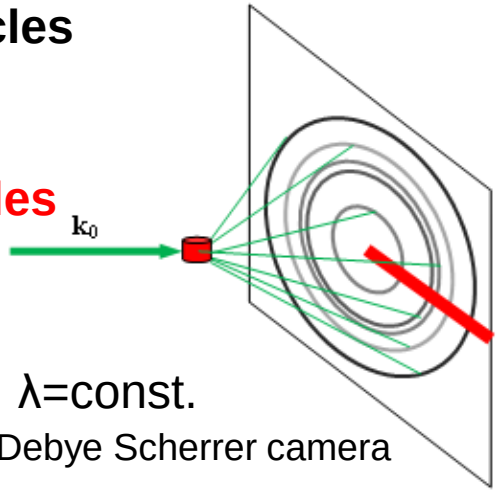


λ=const.

Debye Scherrer camera

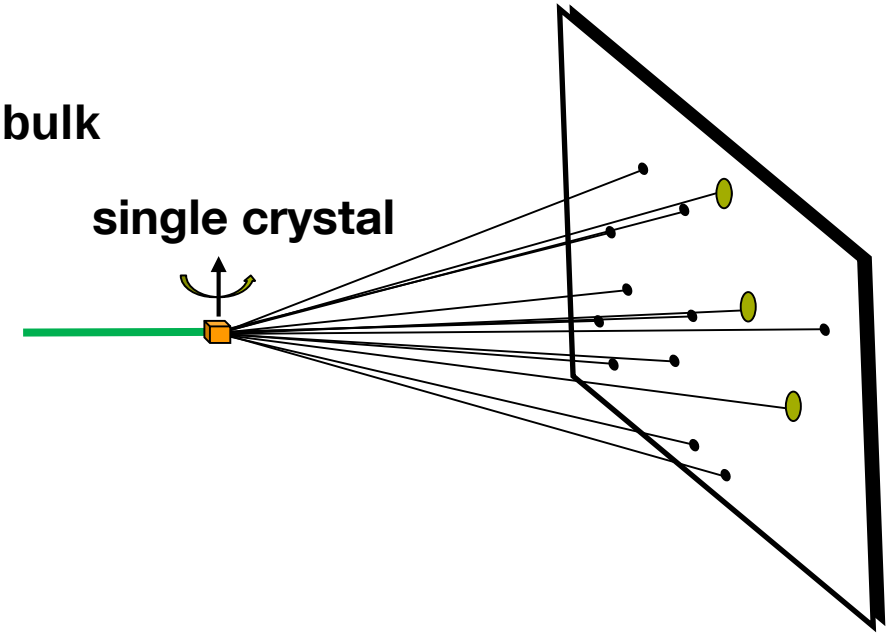
Single Crystal: One large perfectly oriented bulk

- angular dispersive design

(λ=const., $2d_{hkl}\sin(\Theta)=\lambda$)

⇨ only one set of planes per time

sequential measurement of I_{hkl}



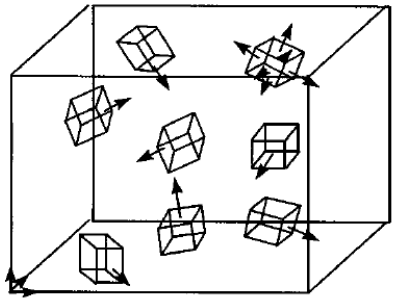
Sample specific Aspects

Powder Microstructure

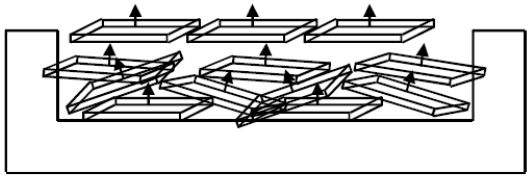
- **Texture**
  ideally total random distribution of crystallites not always possible

  ⇒

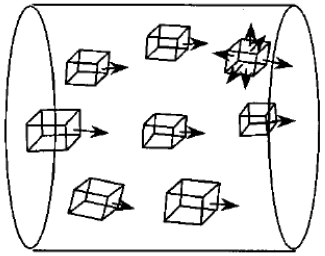
  I(Q) varies on Debye-Scherrer circle!



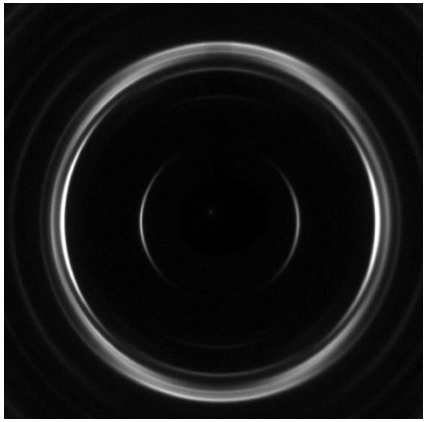
Loose powder



Platelike particles pressed in a recess



Metal wire



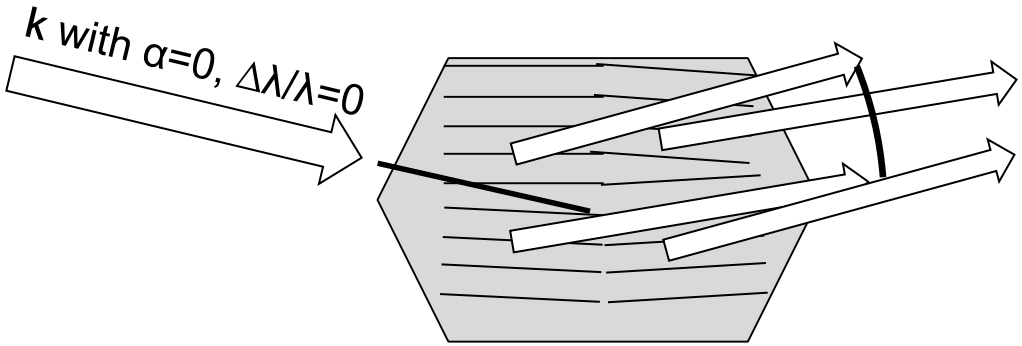
- **Crystallite size *D***
  limited volume of coherent scattering:
  FWHM(2θ) ~ λ/D /cos(θ) Scherrer Equation (Lorentian)

- **Micro strain ε**
  fluctuations in lattice constants: FWHM(2θ) ~ $<\varepsilon>$ tan(θ) (Gaussian)

Sample specific Aspects

Single Crystals

- **Mosaicity**
  thanks to entropy there is no crystal free of any faults impurities, dislocations, stacking faults generate grains



variation of grain orientation
$\Delta\omega > 0$

Mosaic spread

Mosaic spread $\Delta\omega > 0 \Rightarrow$ peak broadening
→ rotate sample in diffraction plane to get full volumetric intensity (ω scan)

$FWHM^2_{total} = \alpha^2_{instrument} + \Delta\omega^2_{sample}$ (Special case: twinning)

Effect can be strongly anisotropic, graphite as extreme example!

- Twinning (Arrangement of grains follows specific crystallographic grain boundaries)

Sample specific Aspects

Radiation & direction dependent interaction weakens scattered intensities

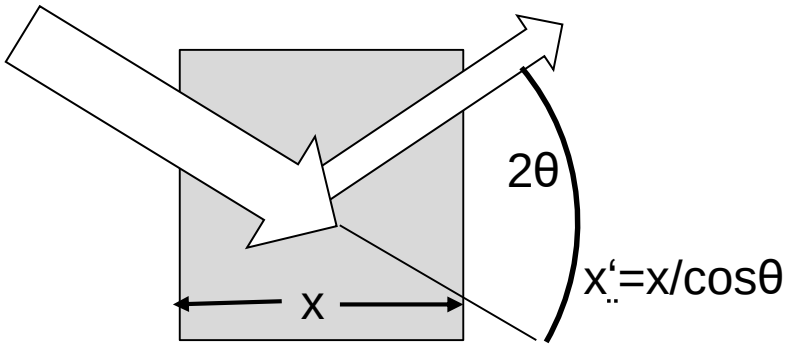
X-rays: electron densities, Neutrons: core, phonons

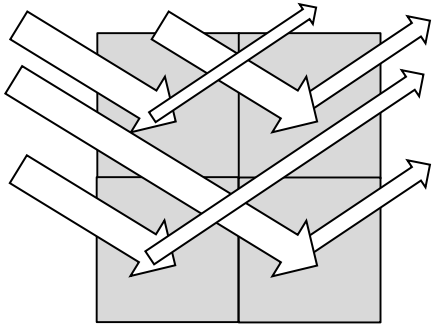
Absorption $I(Q) = I_0(Q)\exp(-\mu x)$; $\mu=\sum_{j,\ unit\ cell} \sigma_j^{abs} n_j$ linear absorption coefficient

σ_j^{abs} abs. cross section (E and element/isotope specific), n_j particle density

Numerical solution

calculate mean path length x^t through sample for each I(Q)





for each segment:

$I_k(Q)= I_0/k \exp(-\mu x_k)$

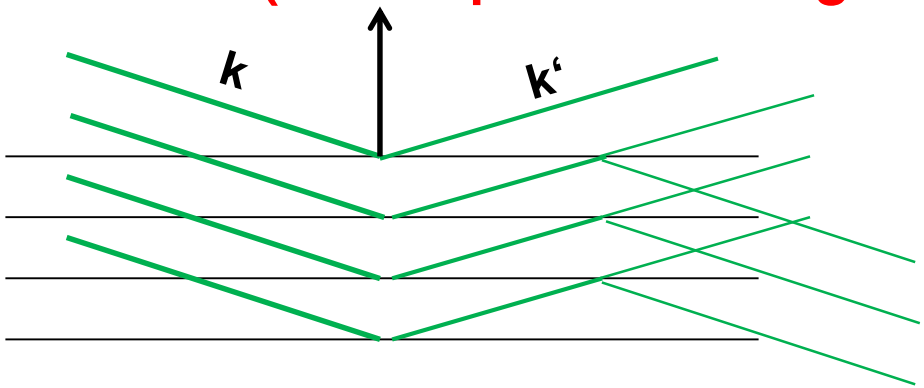
$I(Q) = \sum_k I_k = I_0 \exp(-\mu x^t)$

Empiric solution

„absorption map“ measuring same I(Q) for various ψ angles and Q

Sample specific Aspects

Extinction (= multiple scattering on identical planes)



unwanted backscattering of diffracted beam towards **k**

⇒ intensity loss in I(Q)
up to 50% or more

Effect depends on crystal quality and crystal size

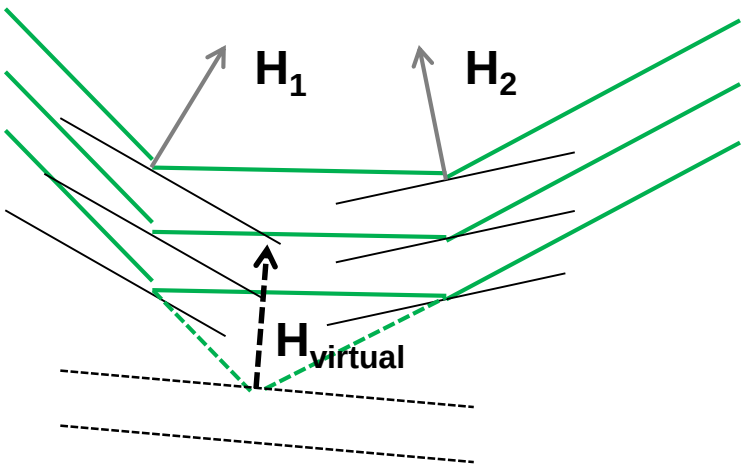
⇒ ψ scans for empirical correction or mathematical modelling

Numerical correction by extinction parameter
isotropic E_{iso} / anisotropic E_{ij}

high risk alternative: increase by shock freezing

Sample specific Aspects

„Renninger“-Effect (= multiple scattering on different planes)



$H_{virtual} = (H_1 + H_2)$

unwanted intensity gain in I(Q)

can bias space group determination
for extinct but not vanishing reflections

Effect is influenced by crystal quality and crystal size

⇒ ψ scans for test or mathematical modelling („Umweg“, Rosmanith)

Note: Except mosaicity/texture all effects also depend on wavelength/brillance

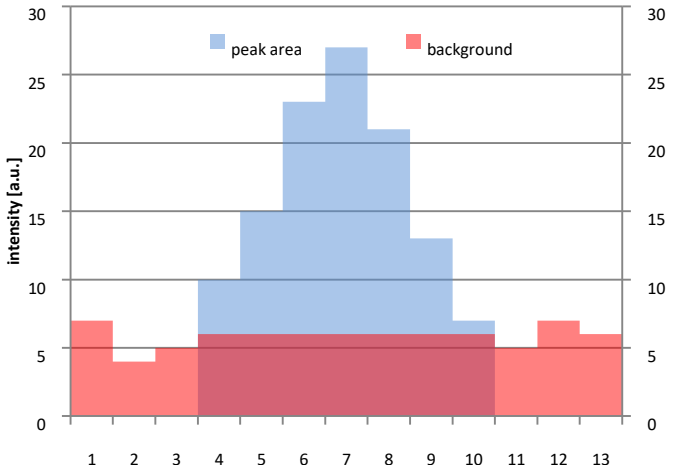
Consideration of Statistics

- **Measure full peak profiles → integral I_{hkl}**
  well defined/full volumentric information
- **Choose enough time *t* to minimize error of I_{netto}:**

⇨ profile spit in peak $P = \sum I_P$ &background $B = \sum I_B$

$I_{netto} = P - (t_P/t_B)B$

$\sigma^2 = P + (t_P/t_B)^2 B;\ t = t_P + t_B$



single crystal peak and single point detector

⇨ set *t* to achieve $I_{netto}/\sigma > 20$ (e.g.) for most reflections (= 5% error)
(or other reasonable value and combine pre-scan + final scan

⇨ **Error of I_{netto} depends strongly on background (H/D problem!)**

- **Consider instrumental error : McCandlish factor *mc***
  $\sigma^2 \rightarrow \sigma^2 + (mc\ I_{netto})^2$
- **Diffraction exeriment:**
  Compromize between max. Q space/no. of reflections and max. accuracy

Structure Determination→ Structure Refinement Principle

- **Collection** of a diffractogram (powder) or Bragg data set (single crystal)
- **Correction** of raw data (remove instrumental and sample effects, if possible)
- **Comparison & Refinement**

  I. Compare diffractogram / set of measured intensities I_{exp} with expected/calculated diffractogram / set of $|F_{calc}|^2=I_{calc}$ for both given parameters from structure model and instrument and

  II. Calculate $R(I)=\sum|I_{calc}-I_{exp}|^2/\sum I^2_{exp}$ **to estimate quality of agreement** other sophisticated „agreement factors“ might also apply

  III. Estimate shift of free parameters for improvement of structure model and recalculate I_{calc} and all other related parameters

  IV. Repeat steps until R and other statistical parameters reach minimum

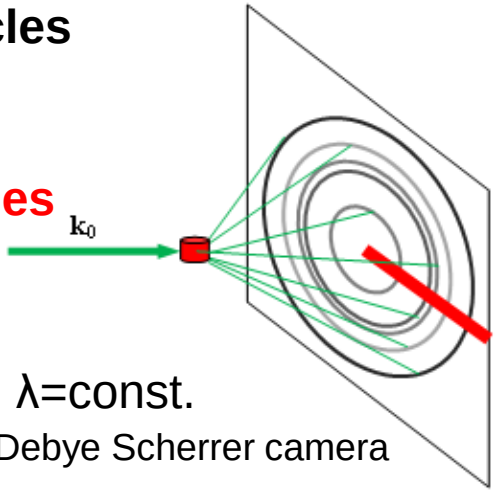
Attention! Wrong starting parameters/insufficient information (e.g. low no. of reflections, large errors) can yield misleading /wrong results

Powder Diffractometry

Powder sample: many randomly oriented crystalline particles

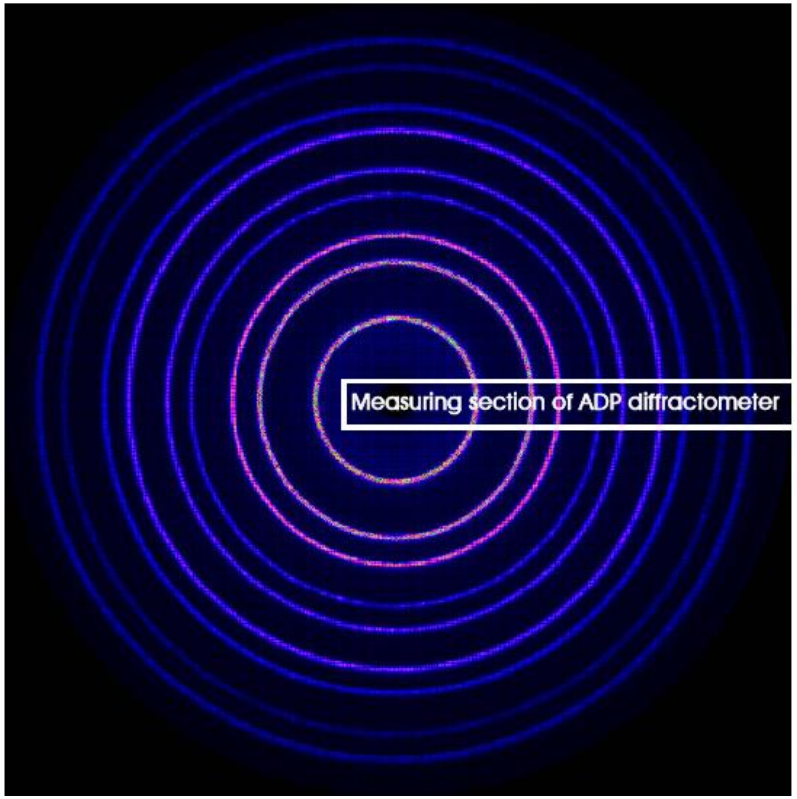
Example: angular dispersive design (λ=const.)

⇨ **many Bragg peaks at same time on Debye Scherrer circles**

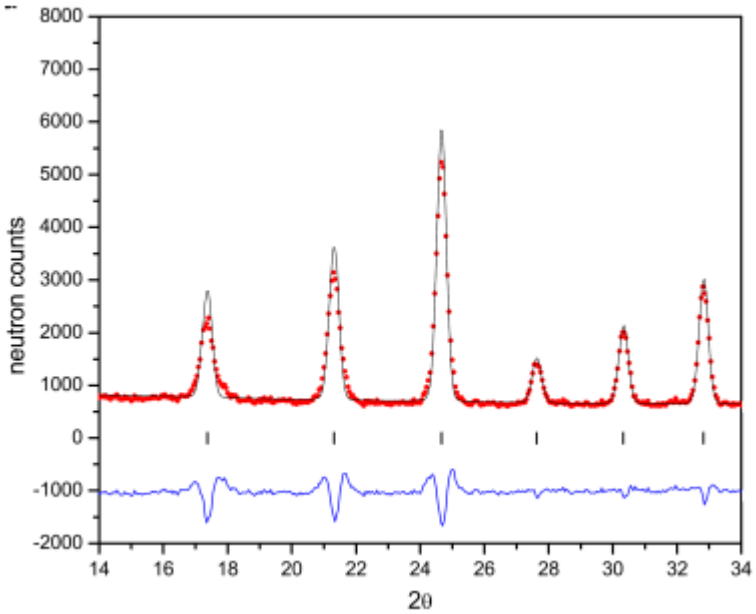


λ=const.

Debye Scherrer camera

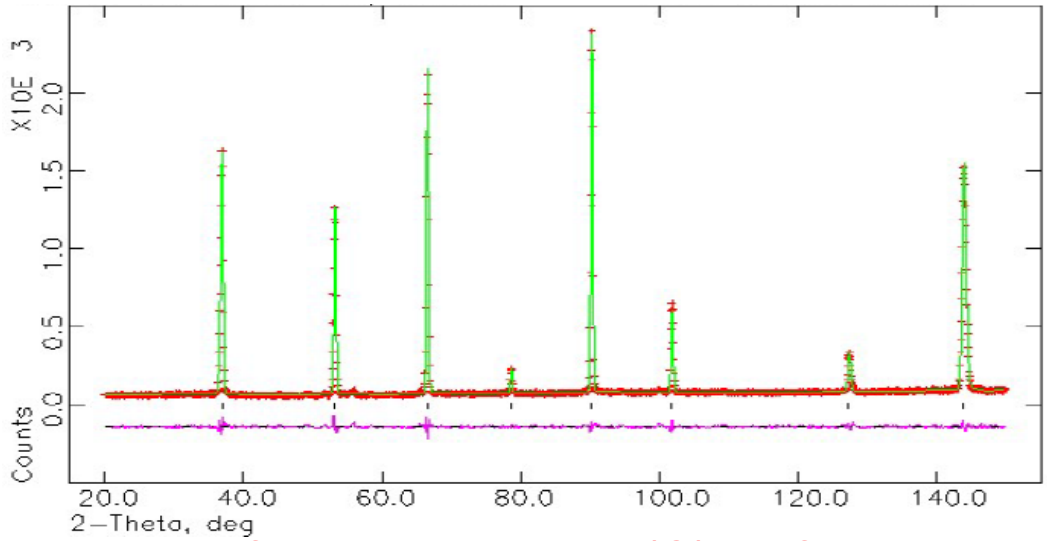


Debye Scherrer circles from powder diffraction



Profile analysis with Rietfeld procedure

Powder Structure Refinement → Rietveld

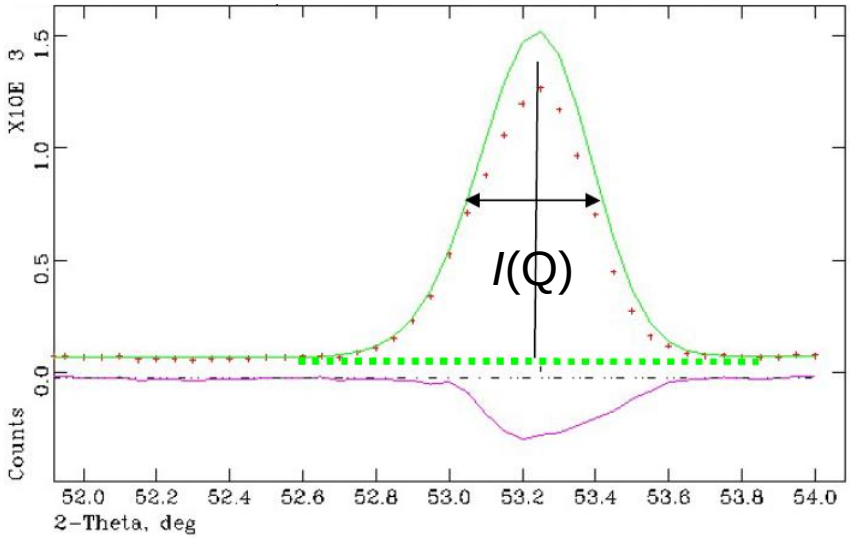


Diffractogram: *collection of background and I(Q) profile intensities in 2θ region*

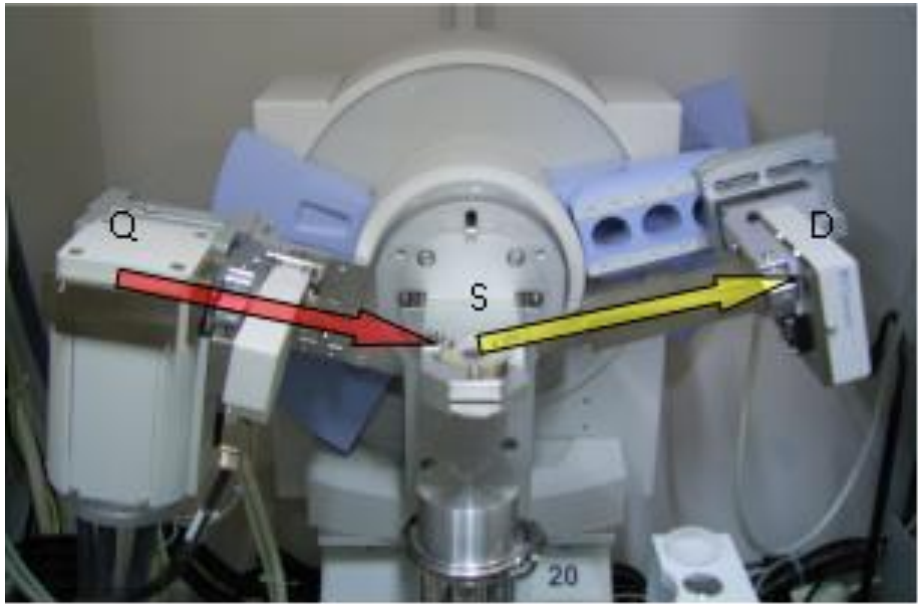
I(Q) = m LP A O E S $|F(Q)|^2$ with

- m: Multiplicity
- LP: LP factor
- A: absorption factor
- E: extinction factor
- Q: Bragg vector |Q|

I(Q) profile convolutions of instrumental and crystal specific parameters



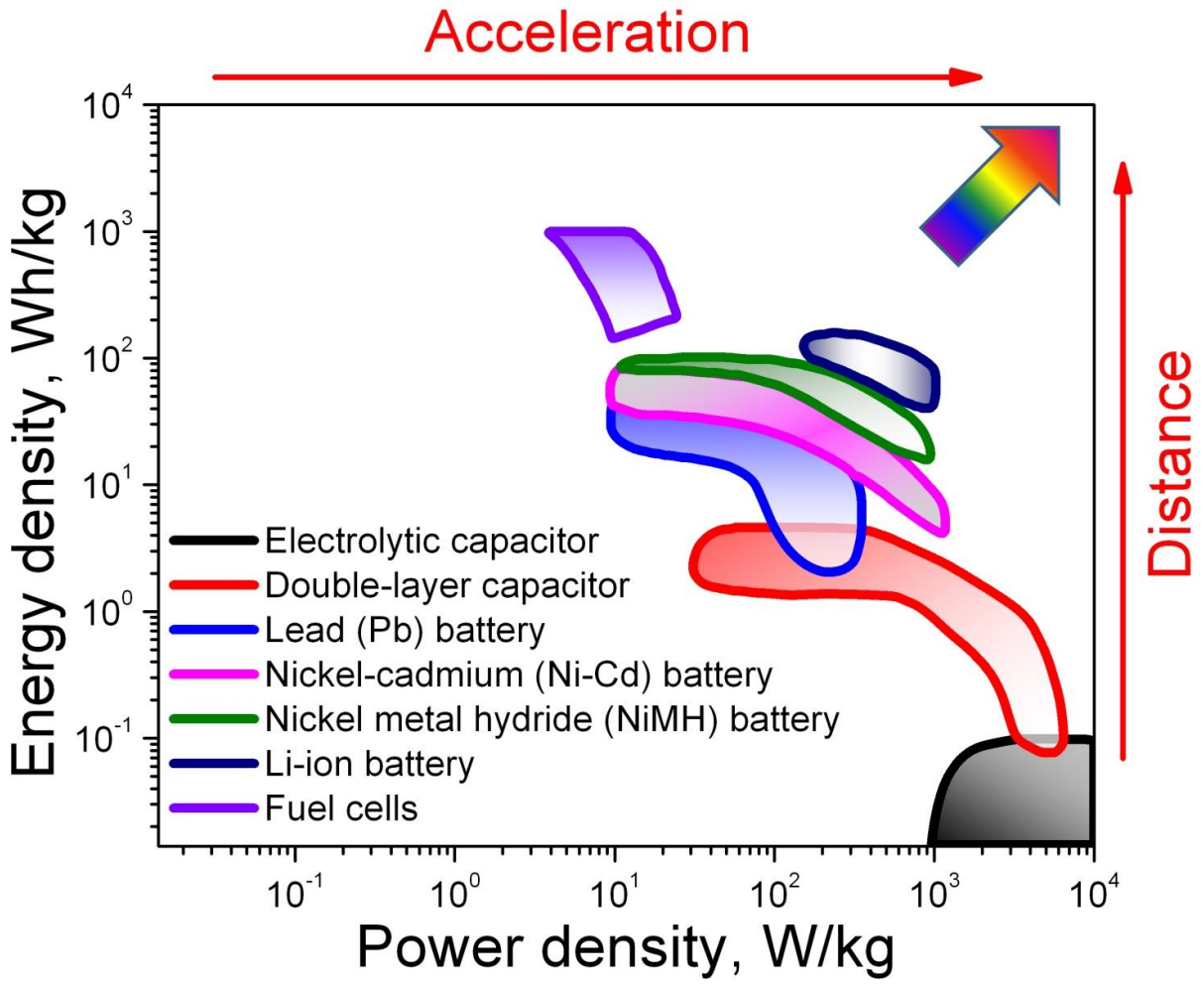
Instrumentation



left: laboratory X-ray diffractometer with $\theta/2\theta$ geometry (Bragg-Brentano),
right: Neutron diffractometer SPODI

(Q: source, S: sample, D: detector, M: monochromator).

Energy: Li-ion Battery Technology – Why Lithium?

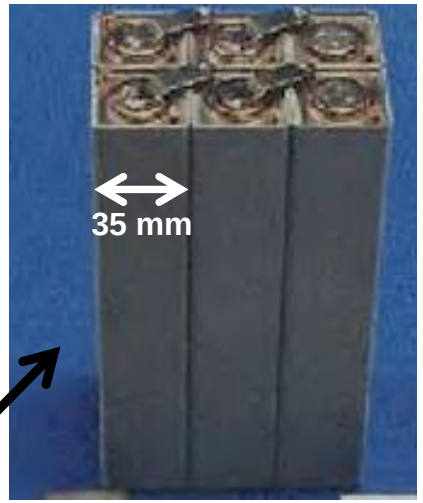


A. Senyshyn et al. (FRM II & KIT), Journal of power sources, 245, 678 – 683 (2014)

ZEBRA Battery – (Zero Emission Battery Research Activities) Na-(Ni/FeCl) Battery

Properties:

- high energy density (100-120 Wh/kg, lead accu. 30 Wh/kg)
- high reliability > 1000 cycles
- low cost of material (Ni, Fe)
- operating temperature: 270 ºC – 350 ºC



hybrid railway locomotives

V. Zinth, S. Seidlmayer, N. Zanon, G. Crugnola, M. Schulz, R Gilles, M. Hofmann, Journal of The Electrochemical Society 162, A384 (2015)

ZEBRA Battery – Charge cycle

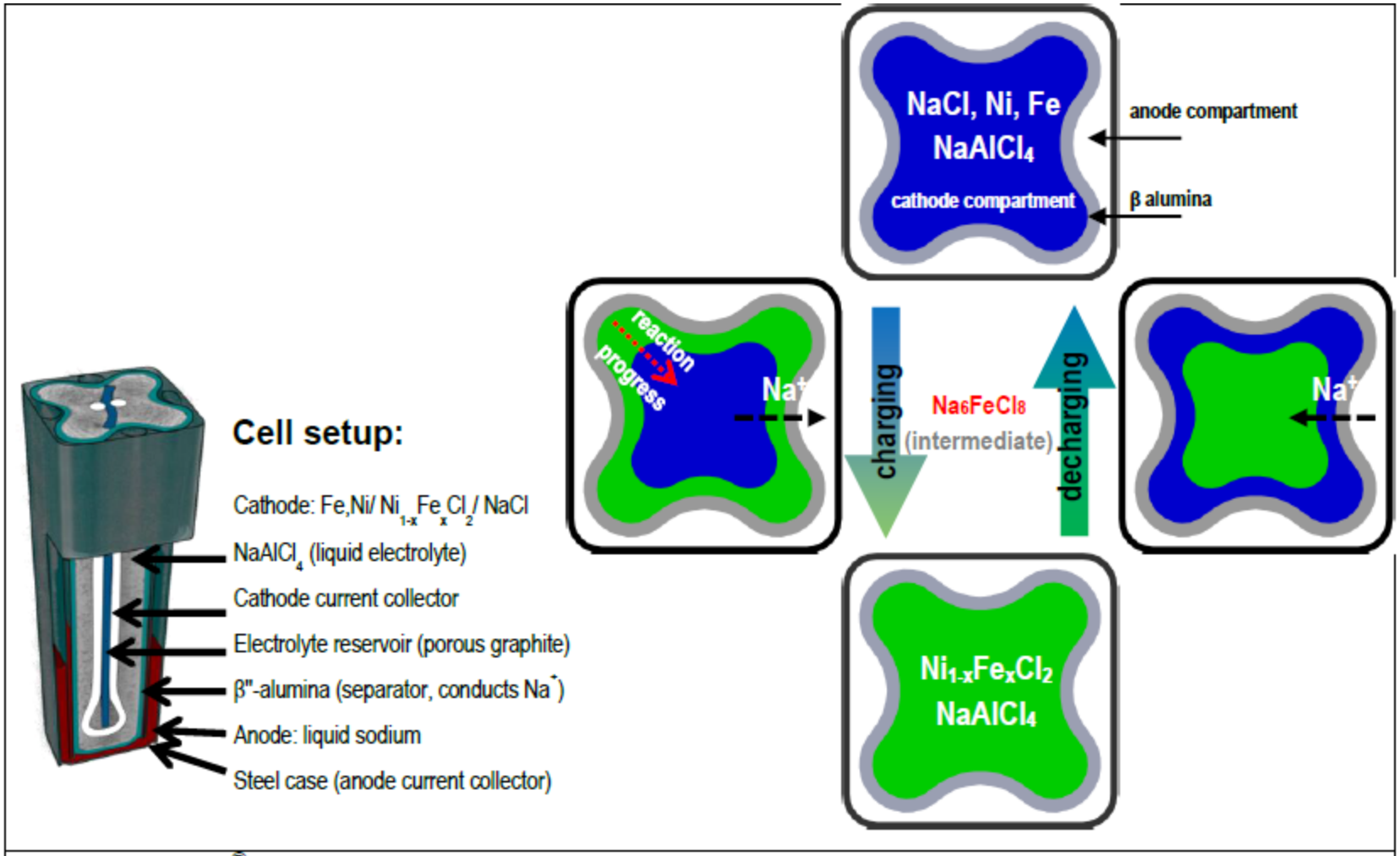


Fig. 25: *ZEBRA® power cell; left: cell design (35*35*240 mm³) [HOF12]; right: reaction process*

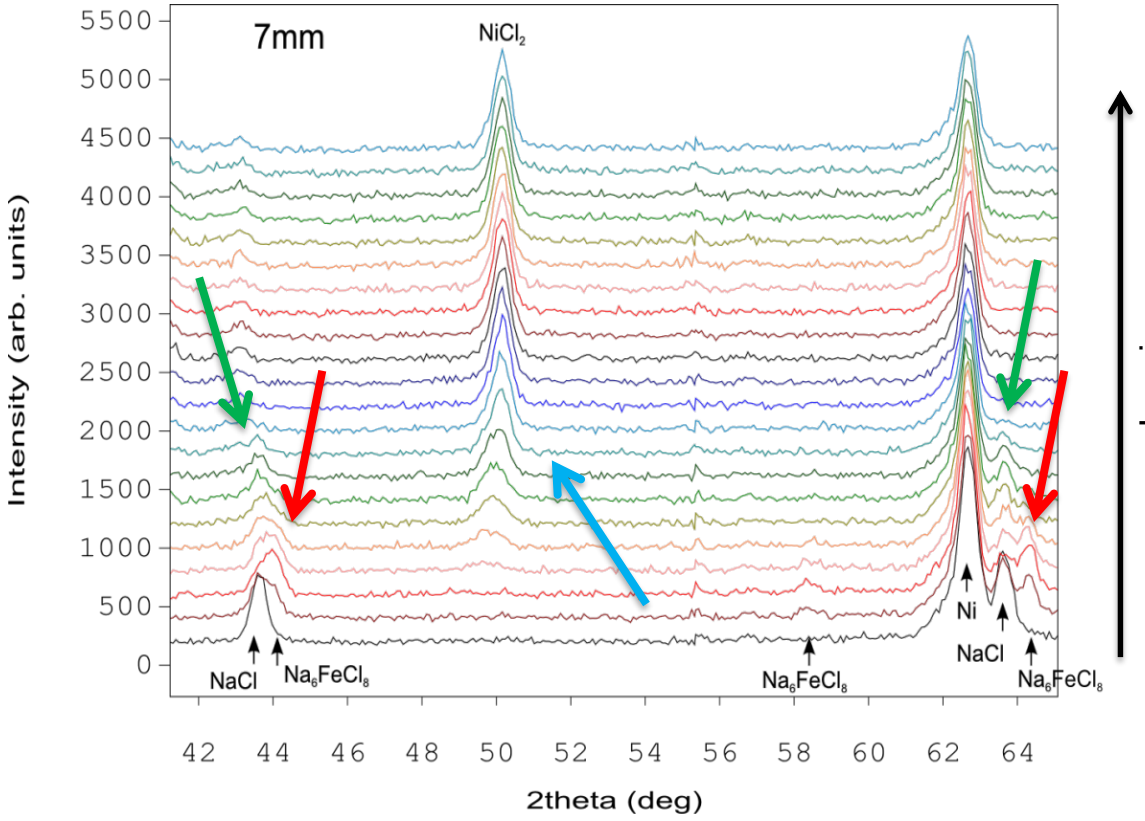
In Situ Spatially Resolved Neutron Diffraction of a Sodium Metal Halide Battery

Measurement at 7 mm (Position 1)

- Limited 2θ range
- 6 min for every diffractogram repeated every 26 min

Observations:

- NaCl reacts to Na_6FeCl_8
- NaCl and Na_6FeCl_8 disappear
- Formation of $Ni_{1-x}Fe_xCl_2$



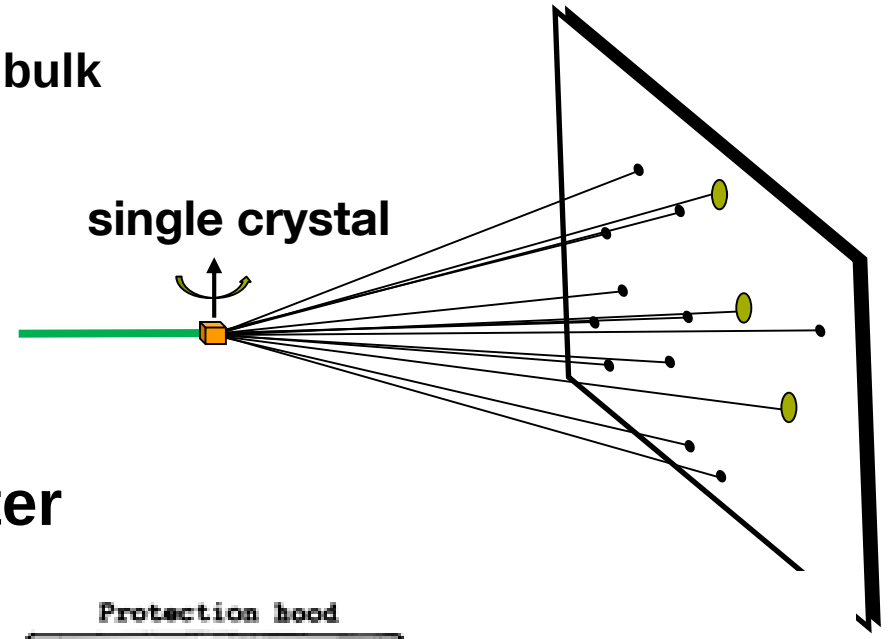
Veronika Zinth et al., Journal of the Electrochemical Society 162 (3), A 384 – A391 (2015)

Single Crystal Diffractometry

Single Crystal: One large perfectly oriented bulk

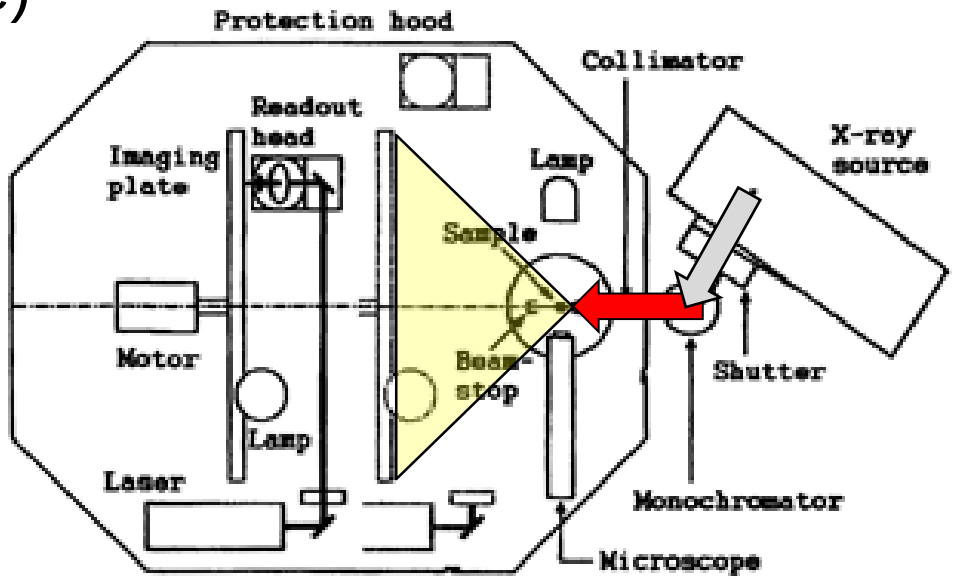
- angular dispersive design
(λ=const., $2d_{hkl}\sin(\Theta)=\lambda$)

⇨ only one set of planes per time



X-ray Single Crystal Diffractometer

Image plate system (IPDS/Stoe)



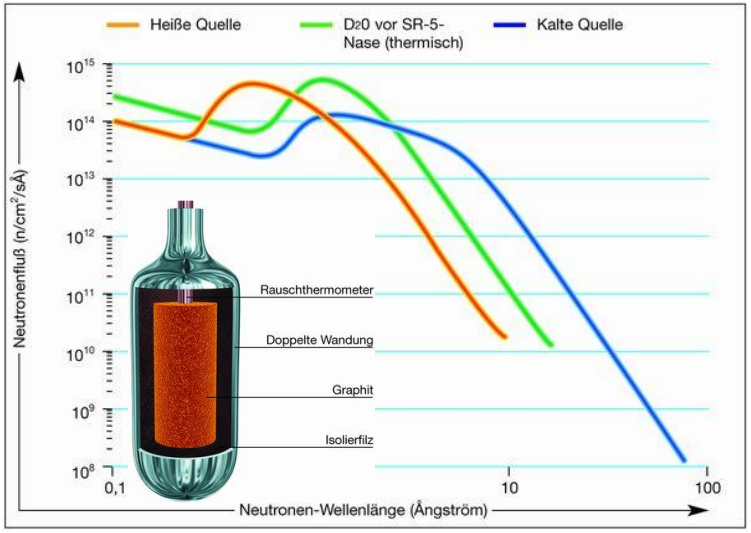
+ fast, no reflections can be missed

- limited profile analysis

Single Crystal Diffractometry

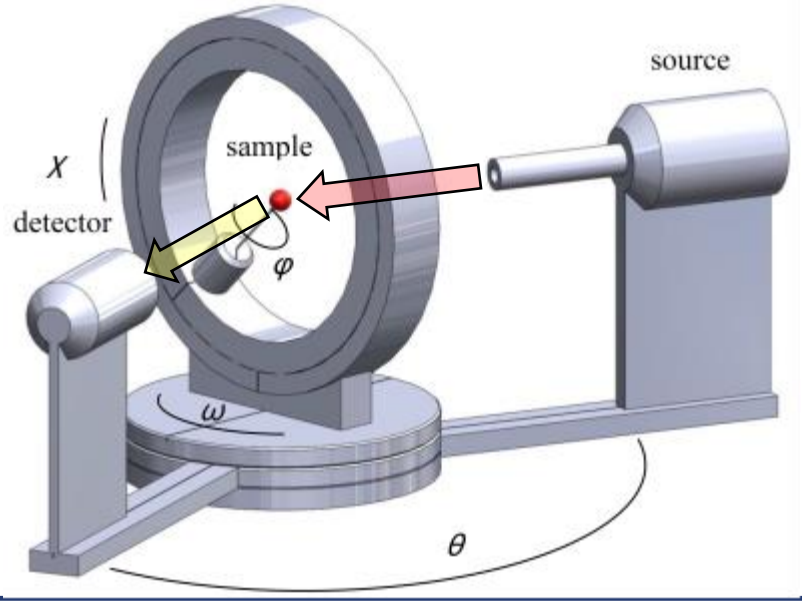
Neutron Single Crystal Diffractometer

- Single point detector system (HEiDi@FRM II)
- Use hot source to increase flux for *short* λ, e.g.
  - λ = 1.17 Å, flux = 1.4*10^7 n°/cm²/s → **loss 20%**
  - λ = 0.55 Å, flux = 3.0*10^6 n°/cm²/s → **gain 900%**
- Temperature range: 2 K < T < 1300 K



Traditional 4 circle setup

- Single detector on 2Θ circle
- Eulerian cradle for sample orientation (ω, χ, φ)



Time of Flight (TOF) Diffractometer

Bragg + *de Broglie*

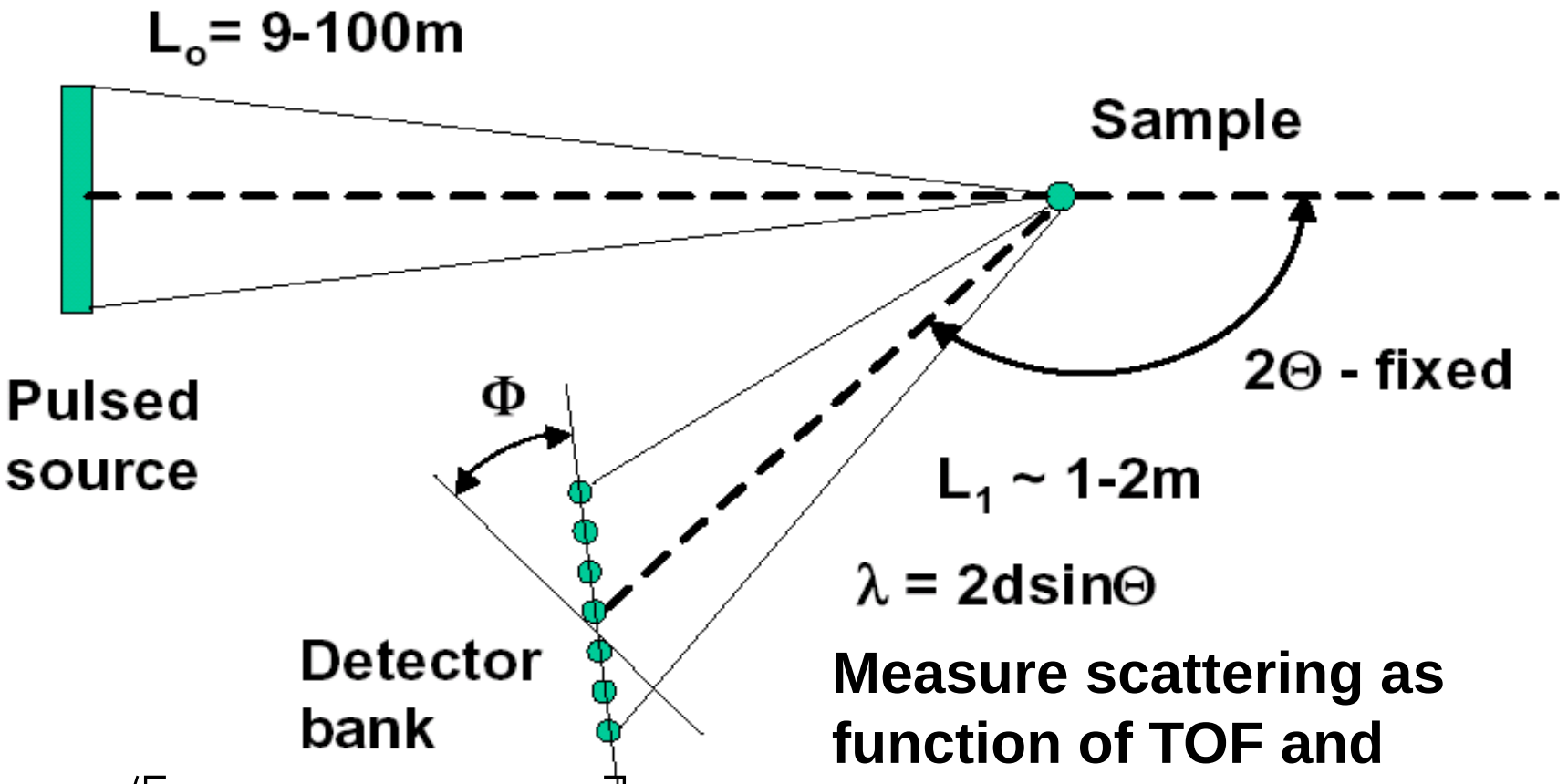
$2d_{hkl} \sin\Theta = \lambda$ + $h/\lambda = m_n v = m_n L/t$; $\lambda = h/m_n v = t*h/(m_n L)$

$$t = \frac{2m_n}{h} L d_{hkl} \sin\theta$$

→ **ideal for limited movability of sample (sample environment)**

- use a pulsed beam with a broad spectrum of neutron energies/wavelengths
- separate different energies (velocities) by time of flight

Time of Flight (TOF) Diffractometer



$$d = t \Big/ \left[\frac{m}{h} (L_0 + L_1) 2 \sin\theta \right]$$

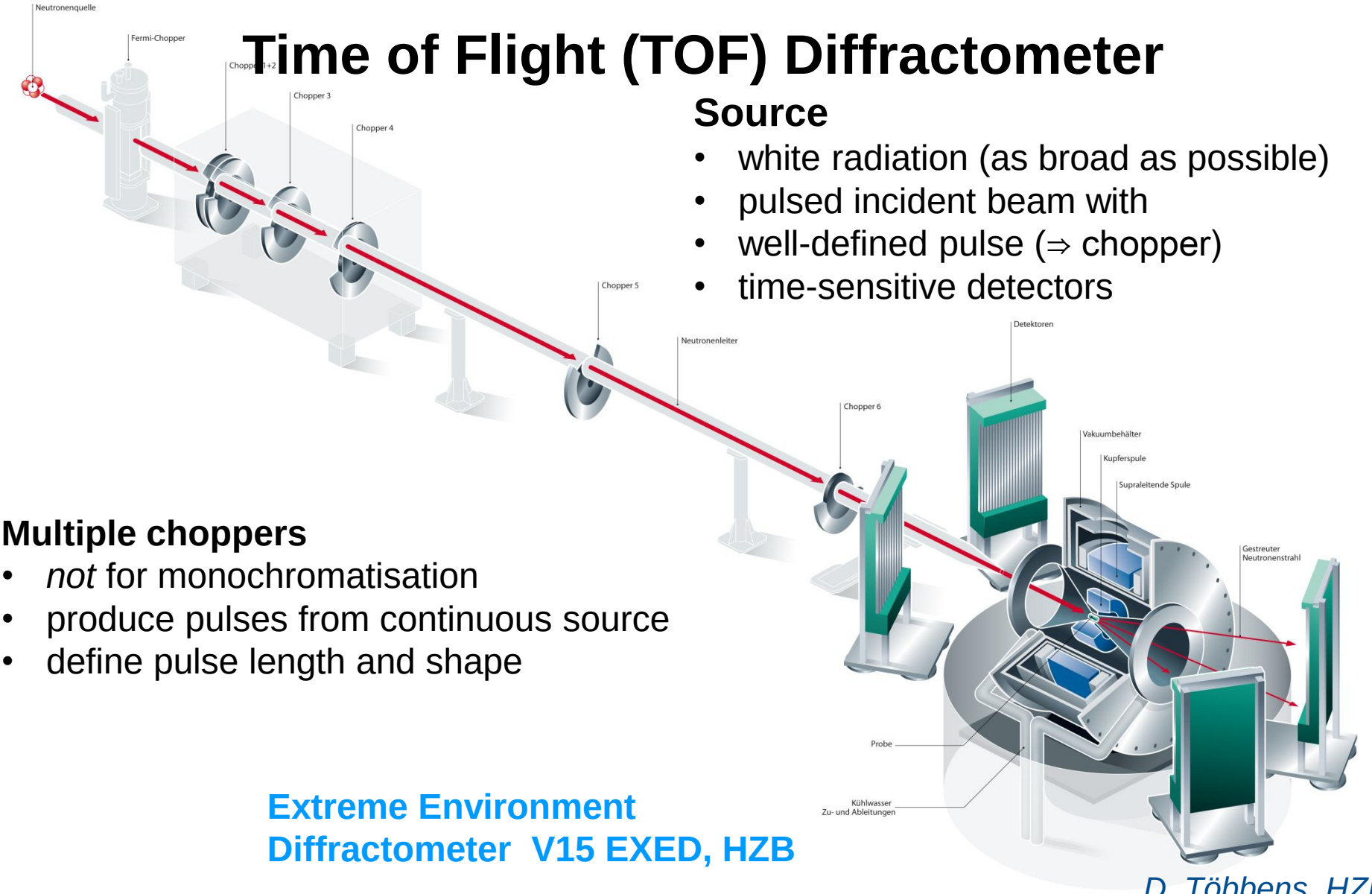
Measure scattering as function of TOF and scattering angle 2θ

D. Többens, HZB

Time of Flight (TOF) Diffractometer

Source

- white radiation (as broad as possible)
- pulsed incident beam with
- well-defined pulse (⇒ chopper)
- time-sensitive detectors



Multiple choppers

- *not* for monochromatisation
- produce pulses from continuous source
- define pulse length and shape

Extreme Environment Diffractometer V15 EXED, HZB

D. Többens, HZB

Single Crystal Diffractometry

Complex 3d framework structure in Phosphates - Brazilianite

- Monoclinic yellowish crystals preferrably found in Brazil, SG P21/n
- Ideal composition $NaAl_3(PO_4)_2(OH)_4$
- only few structure studies based on x-ray diffraction available:
  - Chains of edge sharing **$AlO_4(OH)_2$**- and **$AlO_3(OH)_3$-octahedra**
  - Chains connected via corner sharing **PO_4-tetrahedra**
  - Strongly distorted Na polyhedron with coordination number: 9
  - energetically unfavorable H bond assumed (X-ray diffraction): **O(2)-H(2)...O(9) with angle 113°**

Location of H bonds in Brazilianite?

► **Neutron single crystal diffraction**

Brazilianite sample on aluminum pin (1mm) for measurement on HEiDi/MLZ

Single Crystal Diffractometry

Complex 3d framework structure in Phosphates - Brazilianite

	Prismatic	Prismatic
Crystal shape		
Crystal size (mm³)	4.2 × 3.6 × 2.8	0.35 × 0.32 × 0.20
Crystal color	Translucent pink	Translucent pink
Unit-cell constants	a = 11.243(2) Å	a = 11.2448(5) Å
	b = 10.154(2) Å	b = 10.1539(6) Å
	c = 7.115(1) Å	c = 7.1031(3) Å
	β = 97.32(2)°	β = 97.351(4)°
Max. 2θ (°)	80.07	72.67
	$-18 \le h \le 18$	$-18 \le h \le 18$
	$-16 \le k \le 16$	$-13 \le k \le 13$
	$-11 \le l \le 11$	$-11 \le l \le 11$
No. measured reflections	6321	20604*
No. unique reflections	3461	2968
No. unique refl. with $F_o > 4\sigma(F_o)$	2844	2430
No. refined parameters	211	169
R_{int}	0.0261	0.0392
R_1 (F) with $F_o > 4\sigma(F_o)$	0.0290	0.0325
R_1 (F) for all the unique refl.	0.0462	0.0548
wR_2 (F^2)	0.0474	0.0487
S	1.343	1.422
Weighting scheme: a, b	0.01, 0	0.01, 0
Residuals (fm/Å³)	+0.9/–0.9	+0.4/–0.4

Comparison **X-ray** vs. **neutron** diffraction

- *similar range of reciprocal space*
- ***with neutrons:***
  - ***more insight into light element behaviour (H, O)***
  - ***H positions and anisotropic displacements***

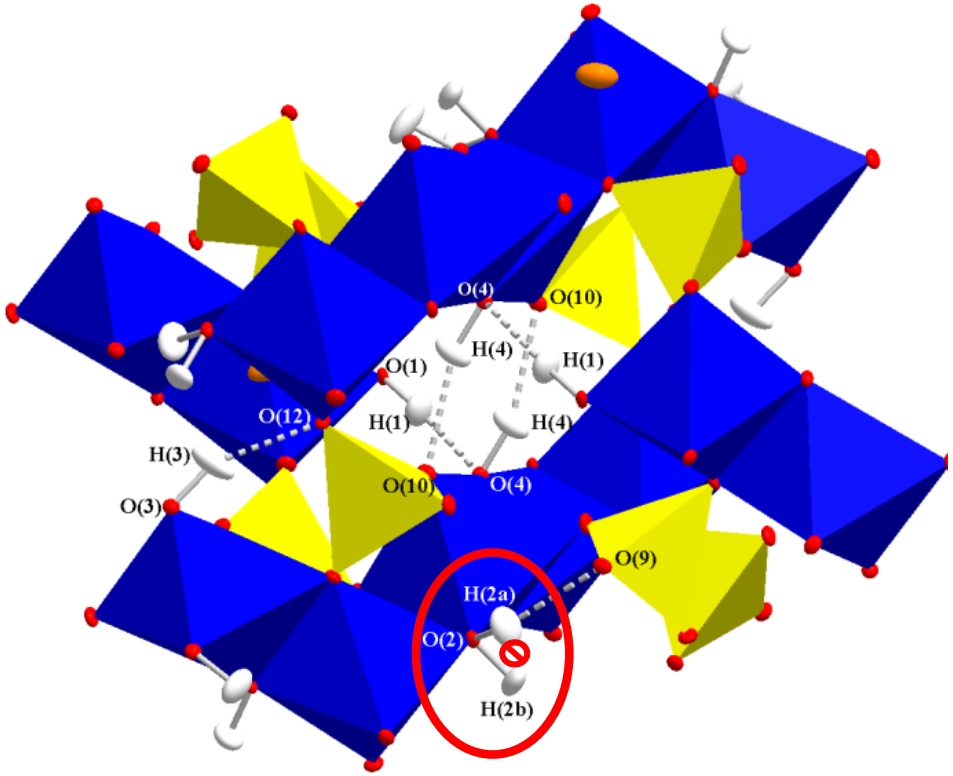
Principal root-mean-square components (R1, R2, R2 x 10² A) at RT; upper: X-ray diffraction, lower: Neutron diffraction

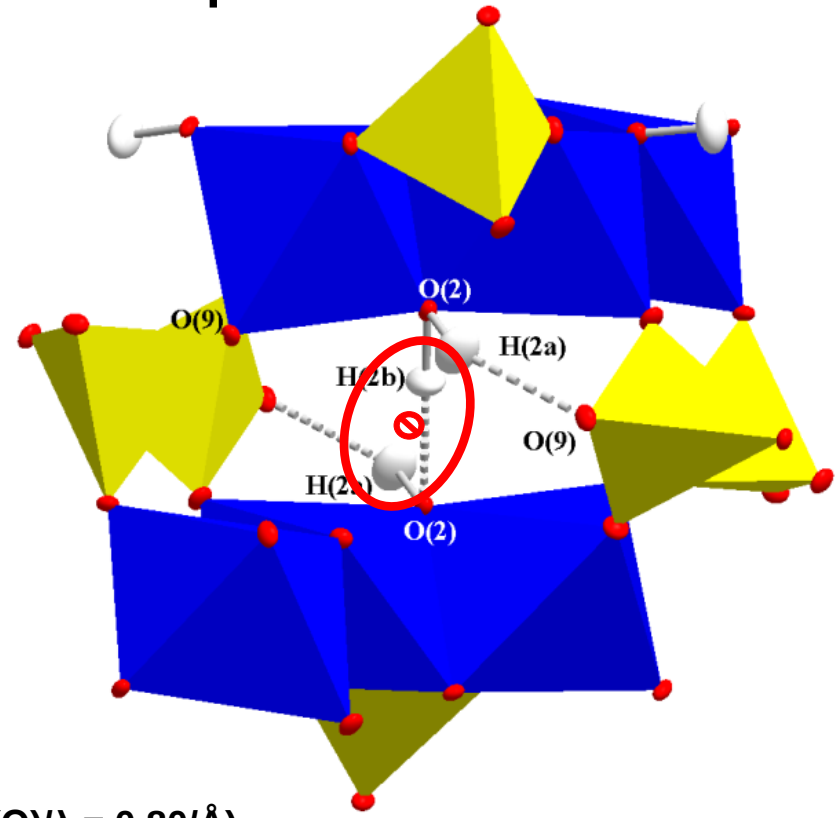
Site	R1	R2	R3	R1/R3
Na	20.4(1)	13.0(1)	11.6(2)	1.76
Al(1)	8.2(1)	8.1(1)	6.5(2)	1.26
Al(2)	8.1(1)	7.5(1)	7.1(1)	1.14
Al(3)	8.1(1)	7.7(1)	6.3(2)	1.27
P(1)	7.8(1)	7.0(1)	6.48(8)	1.21
P(2)	7.4(1)	6.9(1)	6.40(8)	1.16
O(1)	9.6(3)	7.8(3)	6.9(4)	1.38
O(2)	9.2(3)	8.5(3)	8.0(3)	1.15
O(3)	9.9(2)	8.0(4)	7.4(3)	1.34
O(4)	9.5(3)	8.5(3)	7.5(3)	1.26
O(5)	10.9(3)	9.4(3)	7.5(3)	1.45
O(6)	8.9(3)	8.3(3)	8.0(3)	1.12
O(7)	9.4(3)	8.4(3)	7.0(4)	1.34
O(8)	10.5(2)	8.7(3)	7.4(3)	1.42
O(9)	10.4(2)	8.5(3)	7.1(4)	1.48
O(10)	10.6(2)	8.4(3)	6.9(4)	1.53
O(11)	10.5(2)	9.6(3)	7.8(4)	1.34
O(12)	9.6(3)	8.5(2)	7.8(3)	1.23

Site	R1	R2	R3	R1/R3
Na	19.9(1)	12.8(2)	11.3(2)	1.76
Al(1)	7.7(1)	6.9(1)	5.8(3)	1.32
Al(2)	7.2(2)	6.6(2)	5.3(2)	1.36
Al(3)	7.0(1)	6.4(2)	5.2(3)	1.35
P(1)	6.9(1)	5.8(2)	5.1(1)	1.34
P(2)	6.6(2)	5.5(2)	5.1(2)	1.29
O(1)	9.7(1)	6.2(2)	5.66(9)	1.71
O(2)	9.1(1)	6.93(7)	6.3(2)	1.44
O(3)	8.54(6)	7.5(1)	6.6(2)	1.30
O(4)	8.0(1)	7.8(1)	6.3(2)	1.26
O(5)	10.3(1)	8.2(1)	5.48(9)	1.89
O(6)	8.1(1)	7.5(1)	5.29(9)	1.52
O(7)	8.37(6)	7.1(1)	5.57(9)	1.50
O(8)	10.0(1)	8.4(1)	5.39(9)	1.87
O(9)	9.9(1)	7.6(1)	5.9(2)	1.67
O(10)	9.8(1)	7.7(1)	5.9(2)	1.66
O(11)	9.5(1)	9.4(1)	5.8(2)	1.64
O(12)	9.4(1)	7.42(7)	6.0(2)	1.56
H(1)	18.0(1)	14.8(1)	9.9(2)	1.82
H(2a)	19.9(3)	15.5(3)	10.5(4)	1.90
H(2b)	21.8(4)	13.6(3)	9.5(5)	2.30
H(3)	23.4(1)	15.7(2)	10.2(2)	2.28
H(4)	19.1(1)	14.9(2)	10.6(2)	1.79

Single Crystal Diffractometry

Complex 3d framework structure in Phosphates - Brazilianite





Single Crystal Neutron Diffraction reveals (Q_{max}: sin(Θ)/λ = 0.80/Å)

- **Single H(2) position generates "unphysical" displacement parameter**
- **Split position of H(2), 2 energetically favorable mutually exclusive H bonds**

  O(2)-H(2a)...O(9) with angle 151°and O(2)-H(2b)...O(2) with angle 171°.
- **No lower symmetry found → locally disordered structure**

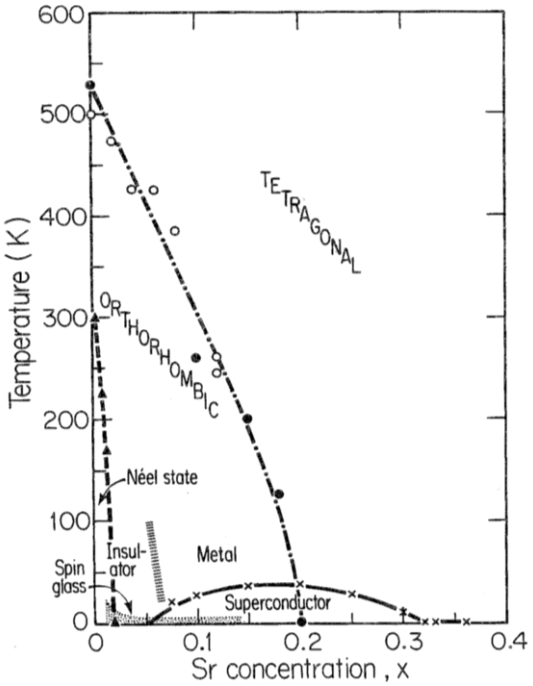
G. Diego Gatta et al., American Mineralogist **98**, 1624-1630 (2013)

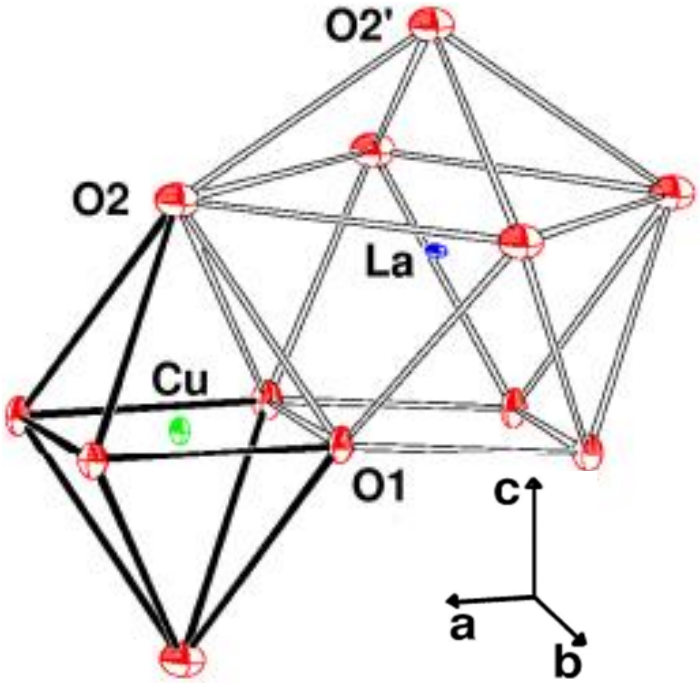
Single Crystal Diffractometry

HT Superconductor - $(La/Sr)_2CuO_4$

- **Simplest HT superconductor with layered perovskite structure**
- **only 4 elements**
- **Sr content changes**

  HTT-LTO transition temp.





Comparison scatt. factors

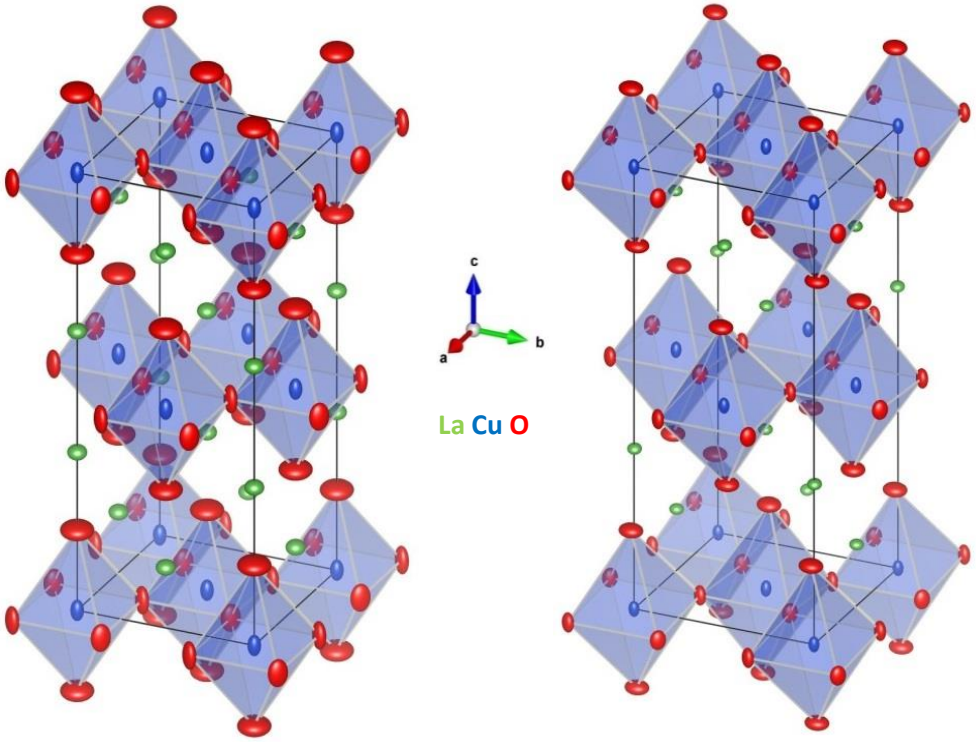
Atoms	f(2Θ=0)=Z	b[fm]
La	57	8.24
Cu	29	7.718
O	8	5.803

Oxygen contribution to total intensity about 50 times smaller for X-ray than for neutron diffraction!

→**Accurate determination of super structure reflections with X-ray diffraction very difficult!**

Single Crystal Diffractometry

HT Superconductor - $(La/Sr)_2CuO_4$



F4/*mmm* ←t2→ F*mmm* ←k2→ A*bma*/B*mab* twin

Phase transition at $T_{HTT-LTO}$=540 K

Above: tetragonal $a = b \neq c$

F4/mmm (HTT)
Extinction rules:**(uuu)** and **(ggg)**

$h+k,\ k+l,\ h+l = 2n$

Below: orthorhombic $a \neq b \neq c$
Attention $a > b$ *or* $a < b$

Abma/Bmab (LTO)
Extinction rules: **(uuu) and (ggg)**

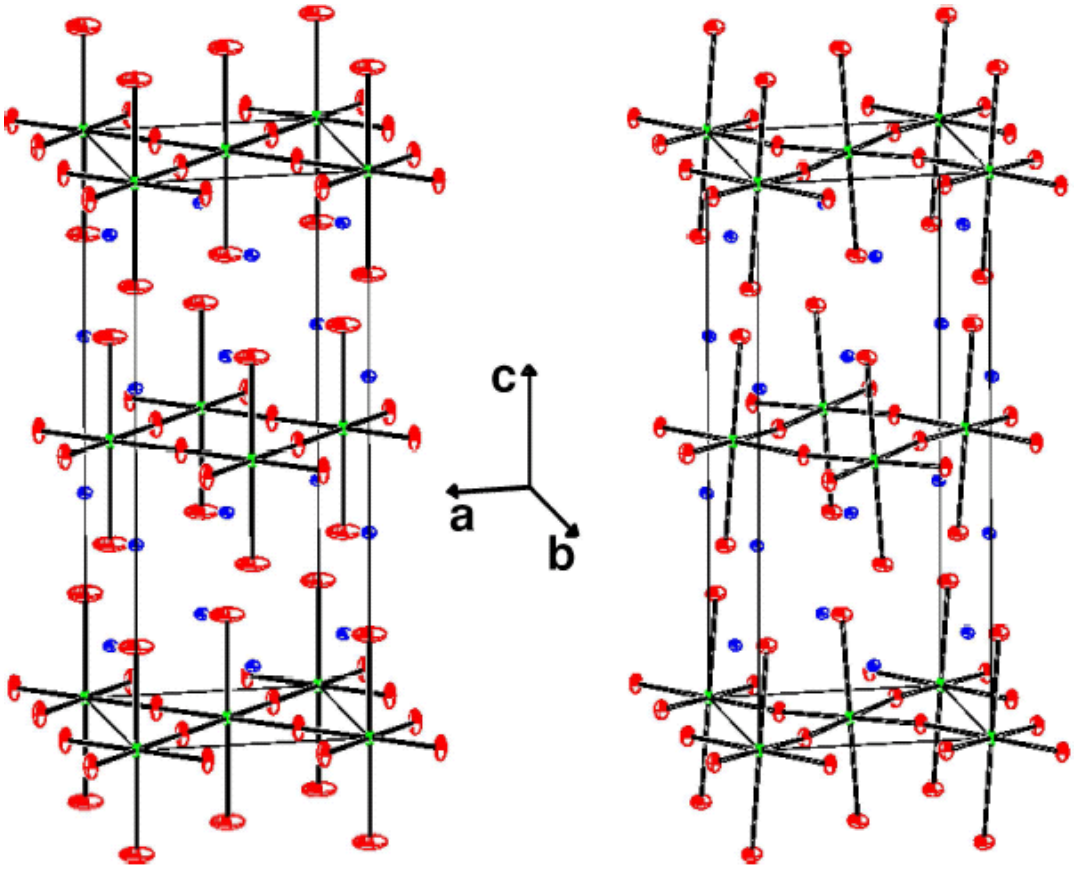
and for (l≠0):

Abma: (ugg) and **(guu) or**
Bmab: (gug) and **(ggu)**

New reflections ⇒ superstructure

Single Crystal Diffractometry

HT Superconductor - $(La/Sr)_2CuO_4$



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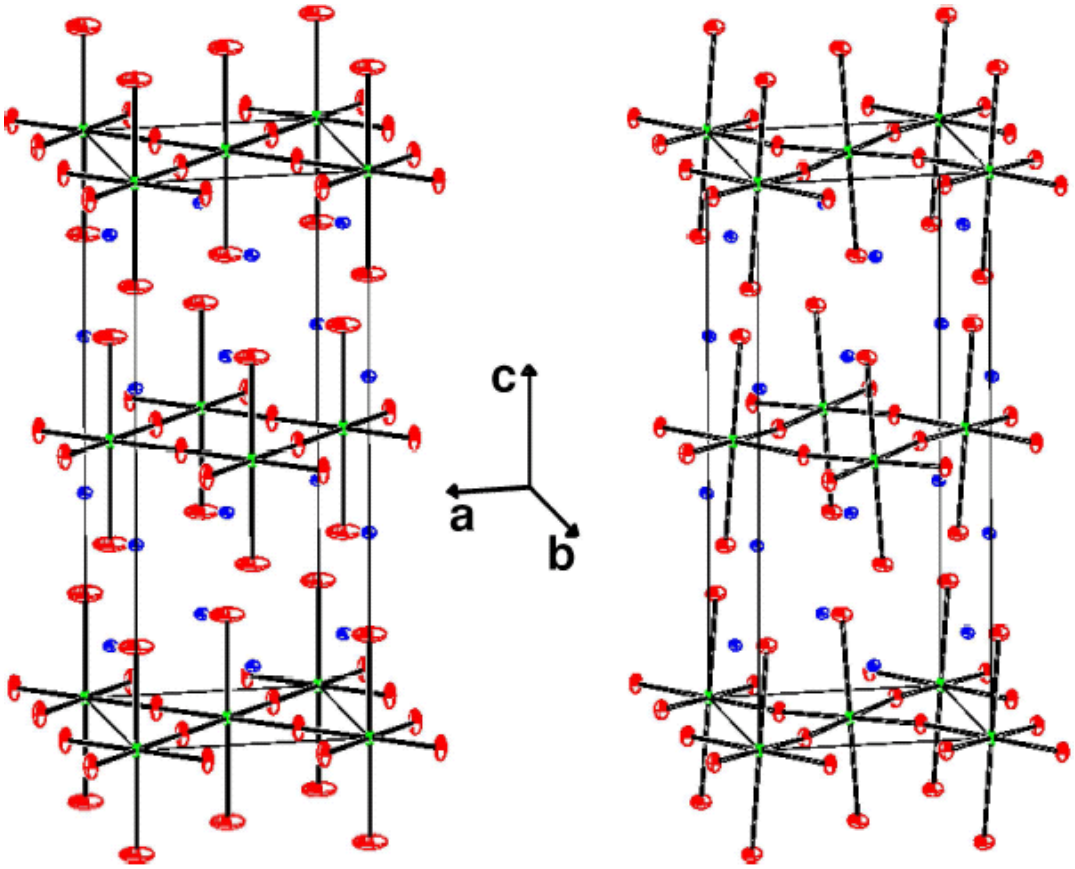
and for (l≠0):

Abma: (ugg) and **(guu) or**
Bmab: (gug) and **(ggu)**

New reflections ⇒ superstructure

Single Crystal Diffractometry

HT Superconductor - $(La/Sr)_2CuO_4$



F4/*mmm* ←t2→ F*mmm* ←k2→ A*bma*/B*mab* twin

Phase transition at $T_{HTT-LTO}$=540 K

Above: tetragonal $a = b \neq c$

F4/mmm (HTT)
Extinction rules:**(uuu)** and **(ggg)**

$h+k,\ k+l,\ h+l = 2n$

Below: orthorhombic $a \neq b \neq c$
Attention $a > b$ *or* $a < b$

Abma/Bmab (LTO)
Extinction rules: **(uuu) and (ggg)**

and for (l≠0):

Abma: (ugg) and **(guu) or**
Bmab: (gug) and **(ggu)**

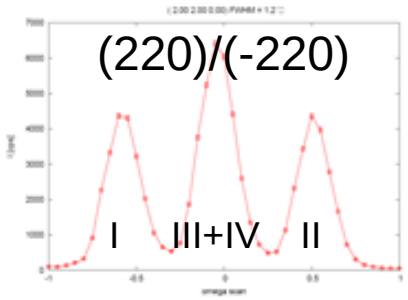
New reflections ⇒ superstructure

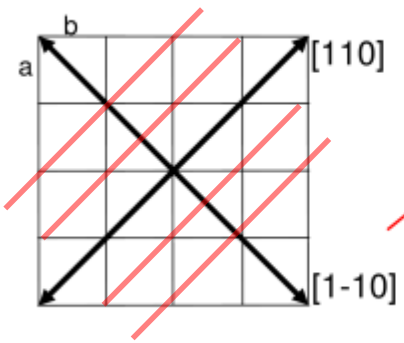
Intensity of superstructure reflections: $F_{hkl}=F_{hkl}(La,Cu) + F_{hkl}(O1)+F_{hkl}(O2)$
h uneven: $F_{hkl}=F_{hkl}(O1)+F_{hkl}(O2)$; $F_{hkl}(O2)\sim s(O)\sin(2\pi\ hx_{O2})*\cos(2\pi\ lz_{O2}) \approx s(O)\sin(2\pi\ hx_{O2})$

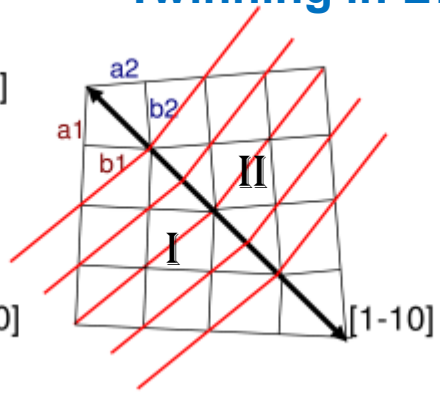
Single Crystal Diffractometry

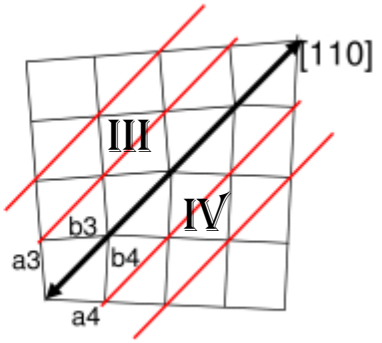
HT Superconductor - $(La/Sr)_2CuO_4$

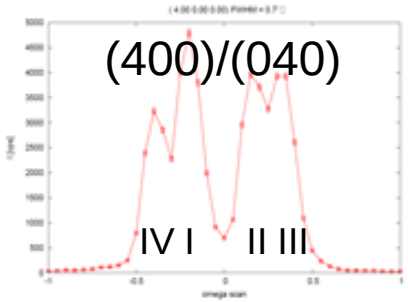
Crystal Growth in HTT phase ↔ Twinning in LTO Phase

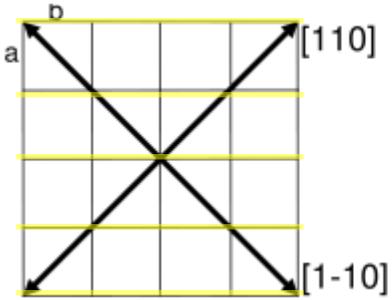


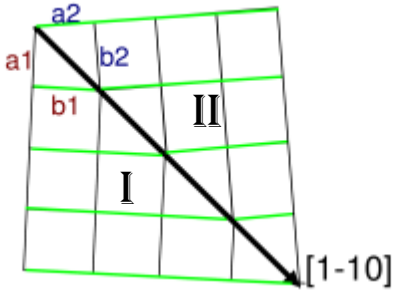


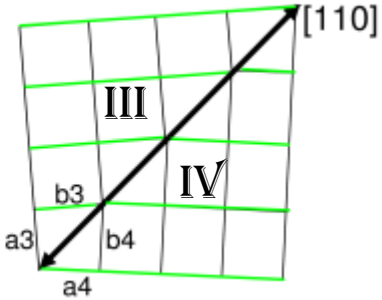


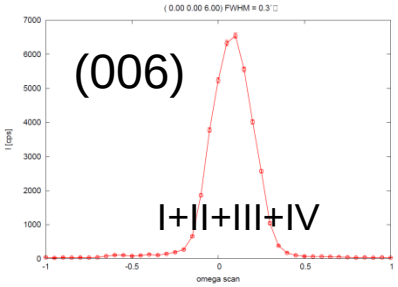












- Reflection Splitting corresponds to Δab
- no *d* difference for (220)/(-220) → **no splitting for powder**
- *d* difference for (400)/(040) → **only two peaks for powder**

Only single crystal diffraction tells the whole truth!

Single Crystal Diffractometry

Magnetic compounds - $EuFe_2As_2$

New Group of HTSL

- 1111- and 122-FeAs compounds
- Layered structure with FeAs planes
- Structural phase transition T-O

I4/mmm (tetragonal)

↓

Fmmm (orthorhombic)

- magnetic order of undoped compounds

→ **strong similarities to HTSL cuprates**

$EuFe_2As_2$

- AF order of Fe^{2+} below $T_{T\text{-}O}$≈190 K, ***k***=(1 0 1)
- AF order of Eu^{2+} below 19 K, ***k***=(0 0 1)
- $Eu_{0.5}K_{0.5}Fe_2As_2$: Tc=31 K,
- $EuFe_2As_{1.4}P_{0.6}$ Tc=26 K + AF order of Eu^{2+}

Coexistance of SC and magnetism?
Check nuclear and magnetic structure with NSCD

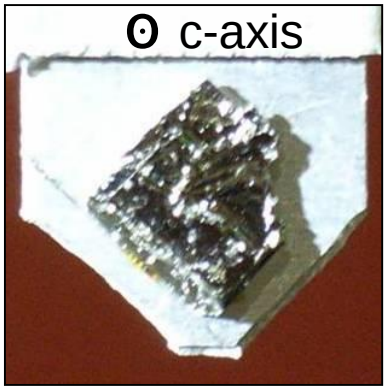
Growth of large single crystals

- Sn melt at about 1050°C
- plate like
- "Auffächerung"

→ tensionless mount on Al sample holder using grease

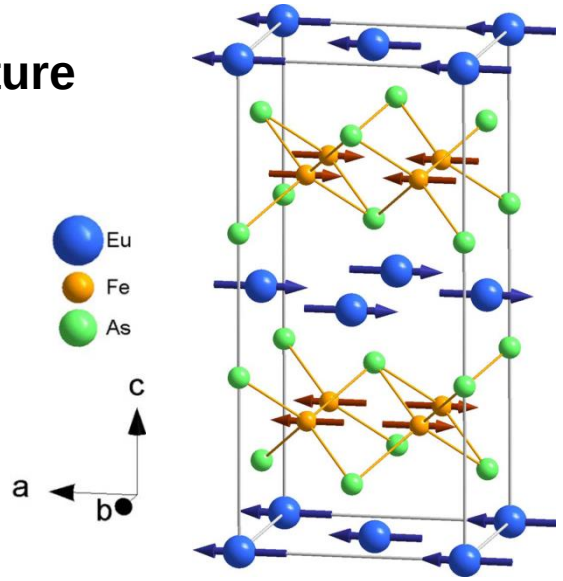
- **Eu strong absorber**

→ λ = 0.87 Å



Fmmm structure

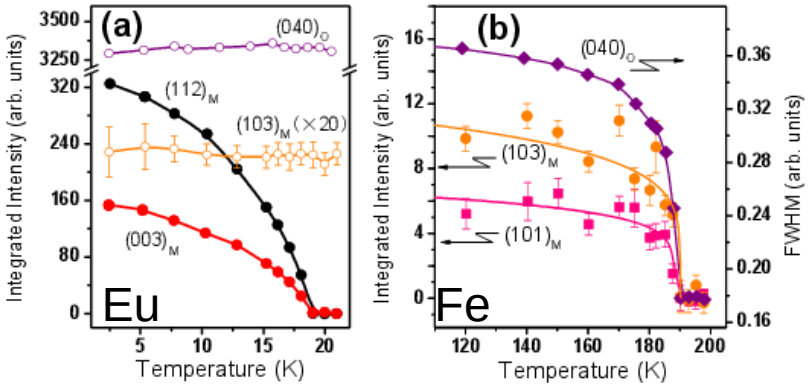
at T=2.5 K

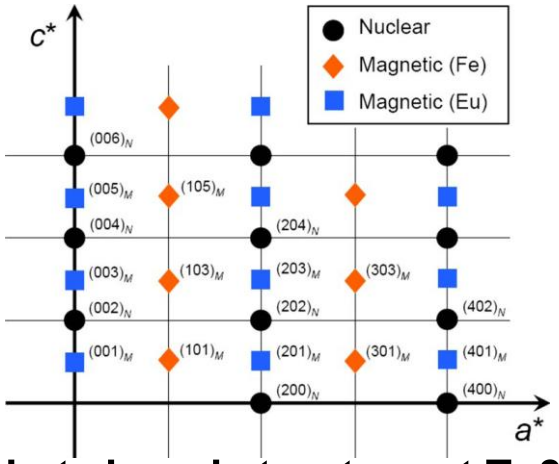


Single Crystal Diffractometry

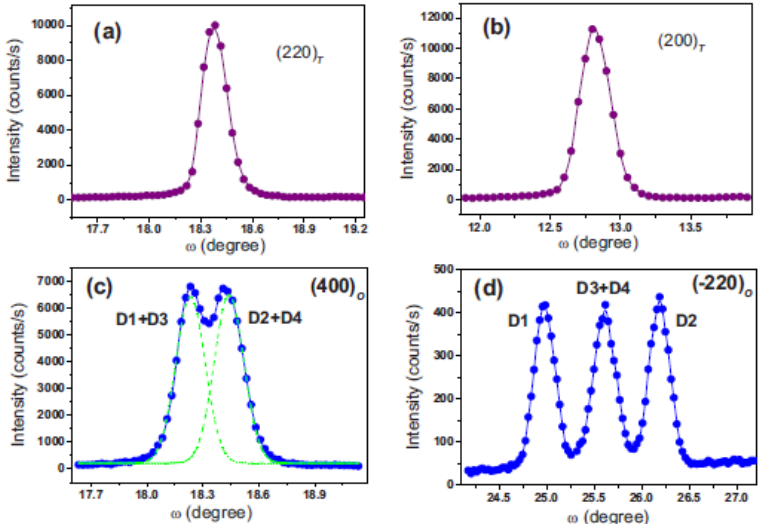
Magnetic compounds - $EuFe_2As_2$

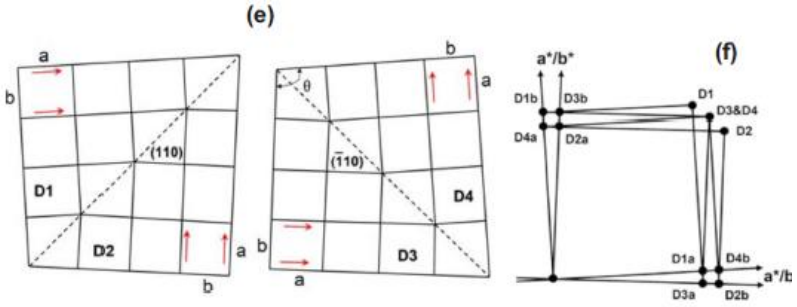
1. Step: Determination of magnetic order temperature





2. Step: Collection of all nuclear & magnetic reflections in twinned structure at T=2.5K



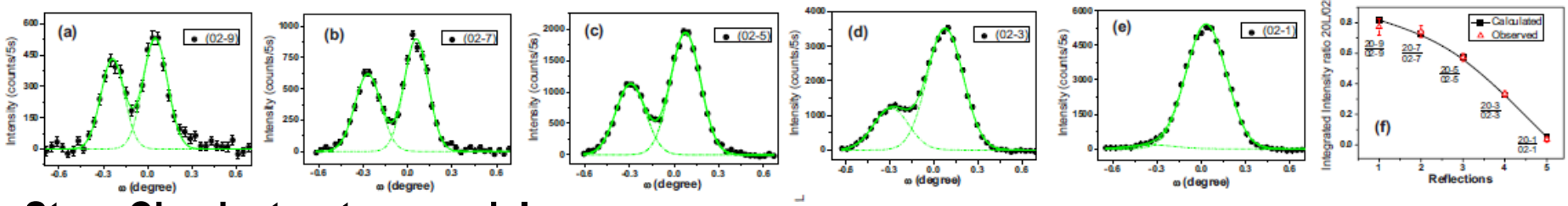


Use twin law to determine the volume contributions of all 4 domain types to all reflections!

Single Crystal Diffractometry

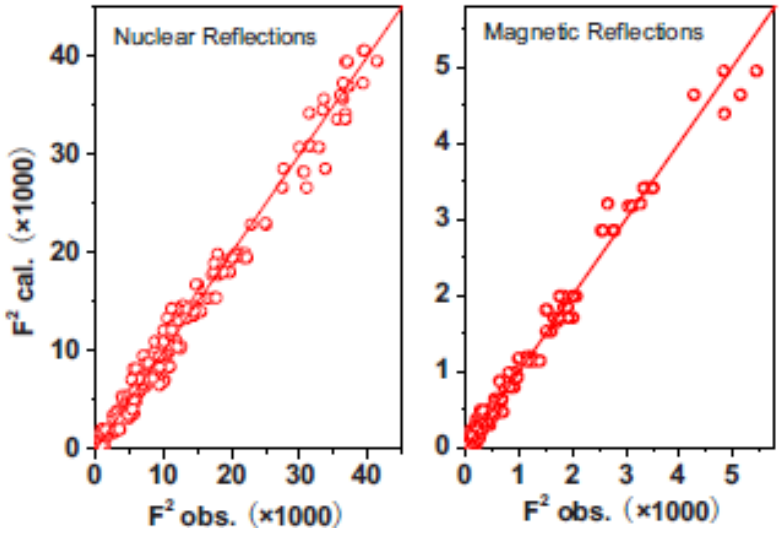
Magnetic compounds - $EuFe_2As_2$

3. Step: Alignment of direction of magn. moments with domain structure/sample orientation



4. Step: Check structure model

Atom/site	x	y	z	B (Å^2)
Eu (4*a*)	0	0	0	0.81(3)
k, $M_a(\mu_B)$	(0,0,1), 6.8(3)			
Fe (8*f*)	0.25	0.25	0.25	0.26(3)
k, $M_a(\mu_B)$	(1,0,1), 0.98(8)			
As (8*i*)	0	0	0.363(5)	0.25(3)
a, b, c (Å): 5.537(2), 5.505(2), 12.057(2)				
Number of reflections (Nuclear): 280				
RF^2, RF^{2W}, $RF(\%)$, χ^2 Nuclear: 9.34, 9.67, 6.22, 7.1				
Number of reflections (Magnetic): 228				
RF^2, RF^{2W}, $RF(\%)$, χ^2 Magnetic: 9.42, 7.68, 6.53, 5.7				



*Y. Xiao et al., Phys. Rev. B **80**, 174424 (2009).*

Phase Diagram of Eu Magnetic Ordering in Sn Flux Grown $Eu(Fe_{1-x}Co_x)_2As_2$ Single Crystals

Member of Iron Pnictide Family

- **2 magnetic sublattices (Eu, Fe/Co)**
- **strong Co dependence of**
  - **structural phase transition T_S**
    I4/mmm → Fmmm
  - **supression of Fe-SDW transition T_{SDW}**
  - **ground state magnetic Eu^{2+} order**
    - indirect Eu^{2+}-Eu^{2+} RKKY interaction
    - direct Eu^{2+}-Fe^{2+} interaction
    - $EuCo_2As_2$: $T_{FM}(Eu^{2+})$= 39 K (Ballinger et al.)
  - **superconductivity by chemical substitution**
    $Eu(Fe_{1-x}Co_x)_2As_2$: $0.10 \leq x \leq 0.18$ (SC + AFM/FM)

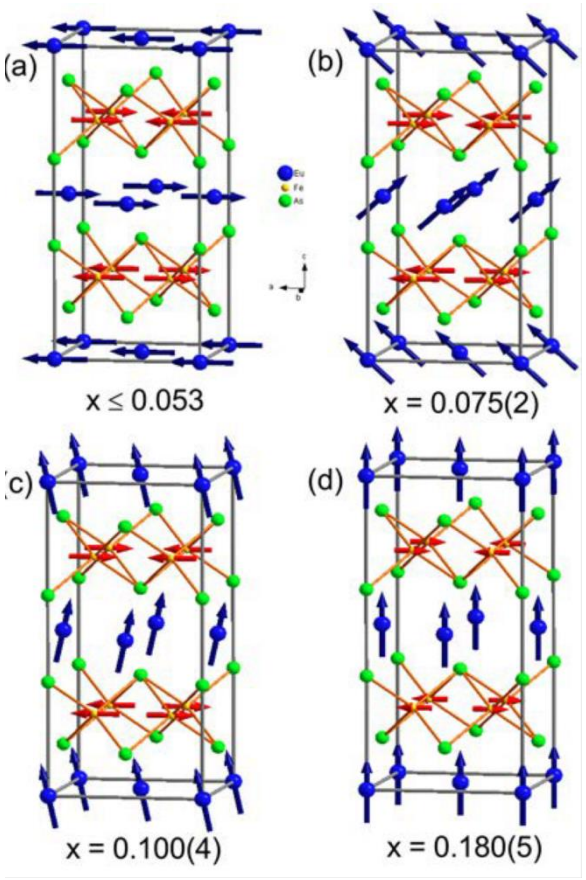
Detailed Study of Magnetic Order vs. Co Content with Detailed Single Crystal Neutron Diffraction

(HEIDI@MLZ, DNS@MLZ, TRiCS@PSI, D23@ILL)

- **short wavelengths to overcome Eu absorption**
- **Eu: AF ⇒ FM transition at x=0.180(5)**
- **Fe: AFM not affected**

W. T. Jin et al.; Phys. Rev. B 94, 184513 (2016)

AF ⇒ FM Evolution with Co Content



determined by single crystal neutron diffraction

Diffractometry - Summary

	Powder	Single Crystal
X-Rays	sample mass µg	sample size µm
	very fast, in situ experiments	fast (1/2 - 2 days)
	(intrinsic & resolution dep.) reflection overlapp	very high angular resolution, anisotropic effects
	intensity damping by temperature factor *and* structure factor!	
	weak interaction with light elements (H, N, O, etc.)	
	no discrimination of neighbouring elements (e.g. Co, Fe, Cu)	
	large absorption effects, polarization effects	
	limited sample environment (T, H)	
	e- density maps - characterization of chemical bonds	
Neutrons	sample mass mg	sample size mm
	fast, in situ experiments	slow (3 days -7 days)
	reflection overlap	good angular resolution/anisotropic effects
	Q dependent intensity damping *only* by temperature factor	
	strong interaction with light elements, isotope specific!	
	discrimination of neighbouring elements and isotopes (H/D)	
	weak absorption effects, no polarization effects (unless pol. neutrons)	
	core and spin density maps, magnetic ordering!	

Diffraction - Summary

Structure Description → Crystallography

- Successful concept of space groups for description of structural properties, e.g. phase transitions, symmetry restrictions of solid matter on atomic scale
- developed about 100 years ago and still new features, e.g. quasi crystals

Structure Determination → Diffractometry

- Contribution to almost any compound of scientific interest
- Different radiations for different questions (X-ray, XFEL, neutron, electron)
- Accessible at any laboratory/sophisticated sources for special applications
- Powder diffraction: Very fast ↔ Single crystal diffraction: Very detailed
- different techniques (angular dispersive, energy dispersive, e.g. TOF) available
- Limitation: averaging technique

Thank you for your attention!