PSI Master School 2017

Introducing photons, neutrons and muons for materials characterization

Lecture 8: Neutron diffraction

Importance of nuclear neutron diffraction

- Structure determines physical properties
- Detailed knowledge of atomic positions and lattice symmetry is essential
- Structure is measured with elastic scattering: there is no energy transfer

Bragg peak scattering in Bravais lattice

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathrm{coh}} = \langle b\rangle^2 \sum_{j,j'} e^{-\imath \boldsymbol{Q}\cdot(\boldsymbol{R}_{j'}-\boldsymbol{R}_j)} \qquad \mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i$$

$r = R_{j'} - R_j$ and multiply with number of unit cell N_0
(assumption: only one type of atom with scattering length b on Bravais lattice)

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = N_0 \langle b\rangle^2 \sum_{\boldsymbol{r}} e^{\imath \boldsymbol{Q}\cdot\boldsymbol{r}}$$

Perform sum over r: $$\sum_{\boldsymbol{r}} e^{\imath \boldsymbol{Q}\cdot\boldsymbol{r}} = \frac{(2\pi)^3}{v_0} \sum_{\boldsymbol{\tau}} \delta(\boldsymbol{Q}-\boldsymbol{\tau})$$

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = N_0 \frac{(2\pi)^3}{v_0} \langle b\rangle^2 \sum_{\boldsymbol{\tau}} \delta(\boldsymbol{Q}-\boldsymbol{\tau})$$

Reminder: reciprocal lattice

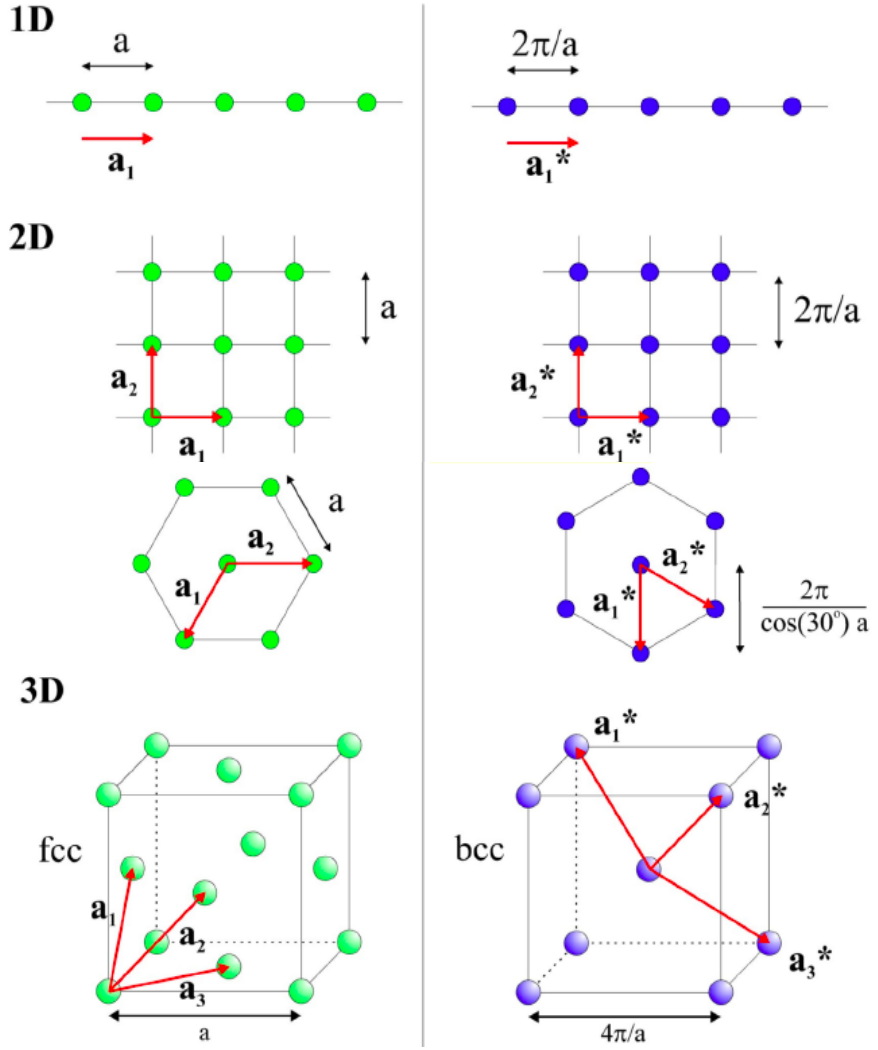
Lattice for “wave-vector space”

Connected with real space via Fourier transform

$$\mathbf{a}^\star = 2\pi \frac{\mathbf{b}\times\mathbf{c}}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})}$$

$$\mathbf{b}^\star = 2\pi \frac{\mathbf{c}\times\mathbf{a}}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})}$$

$$\mathbf{c}^\star = 2\pi \frac{\mathbf{a}\times\mathbf{b}}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})}$$



Bragg peak scattering in the non-Bravais case

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \sum_{j,j'} b_j b_{j'} \langle e^{-\imath \boldsymbol{Q}\cdot\hat{\boldsymbol{R}}_{j'}} e^{\imath \boldsymbol{Q}\cdot\hat{\boldsymbol{R}}_j} \rangle .$$

For a non-Bravais lattice the atomic positions are given by the position of the unit cell (lattice vector) plus relative position of the atom within unit cell

$$\boldsymbol{R} = \boldsymbol{l}_j + \boldsymbol{d}_\alpha$$

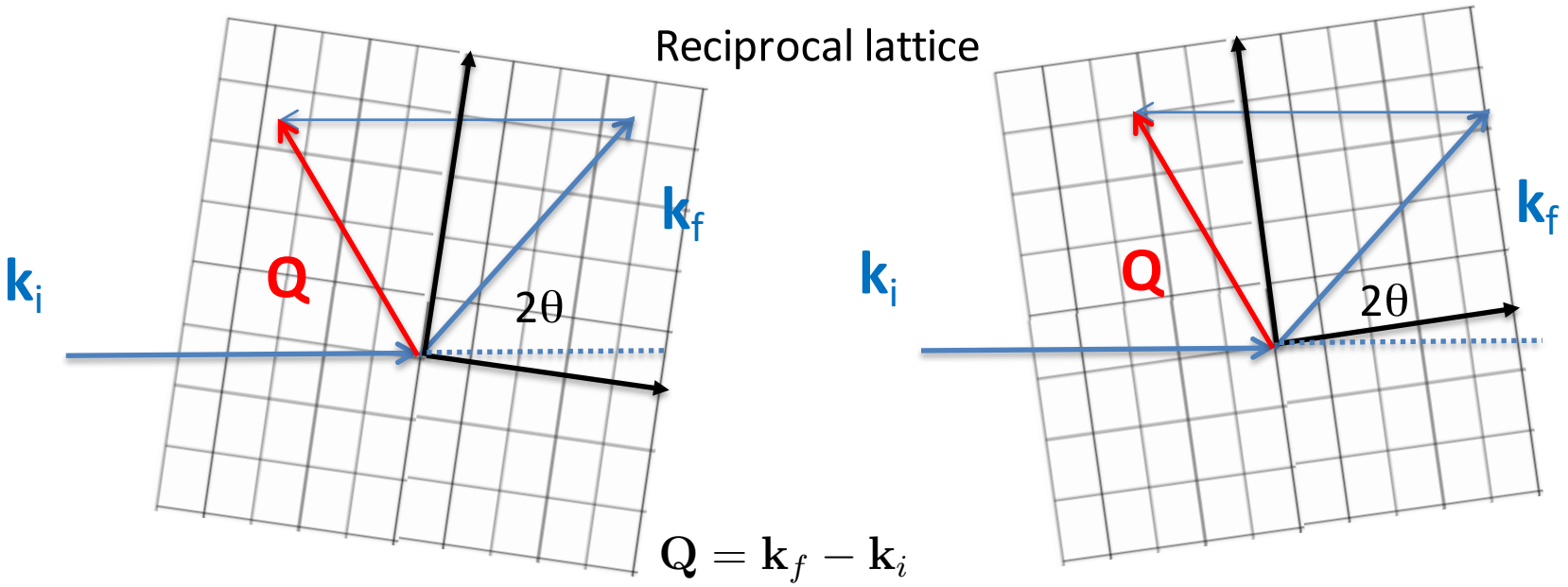
$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \sum_{j,j'} e^{\imath \boldsymbol{Q}\cdot(\boldsymbol{l}_j - \boldsymbol{l}_{j'})} \sum_{\alpha,\alpha'} b_\alpha b_{\alpha'} e^{\imath \boldsymbol{Q}\cdot(\boldsymbol{d}_\alpha - \boldsymbol{d}_{\alpha'})} .$$

using $$\sum_{\alpha,\alpha'} b_\alpha b_{\alpha'} e^{\imath \boldsymbol{Q}\cdot(\boldsymbol{d}_\alpha - \boldsymbol{d}_{\alpha'})} = \left| \sum_{\boldsymbol{d}} b_{\boldsymbol{d}} e^{\imath \boldsymbol{Q}\cdot\boldsymbol{d}} \right|^2$$

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = N_0 \frac{(2\pi)^3}{v_0} \sum_{\boldsymbol{\tau}} \left| F_N(\boldsymbol{\tau}) \right|^2 \delta(\boldsymbol{Q} - \boldsymbol{\tau})$$

$$F_N(\boldsymbol{\tau}) = \sum_{\boldsymbol{d}} b_{\boldsymbol{d}} e^{\imath \boldsymbol{\tau}\cdot\boldsymbol{d}}$$

Bragg scattering occurs in specific directions



Bragg condition: $Q = 2k_i \sin\Theta$

$\mathbf{Q} = \boldsymbol{\tau}$

Crystal has to be aligned accurately to observed Bragg scattering

Simple diffractometer offers the possibility the sample and change toe scattering angle

How to look for a Bragg peak?

Debye-Weller factor

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \sum_{j,j'} b_j b_{j'} \langle e^{-\imath \boldsymbol{Q}\cdot\hat{\boldsymbol{R}}_{j'}} e^{\imath \boldsymbol{Q}\cdot\hat{\boldsymbol{R}}_j} \rangle .$$

The atoms thermally move around their equilibrium positions. As a consequence the scattered intensity falls off at higher momentum transfer **Q**, according to the so-called Debye-Waller factor

For cubic material $2W(\boldsymbol{Q}) = 2W(Q) = \frac{1}{3}Q^2\langle u^2\rangle$

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = N_0 \frac{(2\pi)^3}{v_0} e^{-2W(\boldsymbol{Q})} \sum_{\boldsymbol{\tau}} \left|F_N(\boldsymbol{\tau})\right|^2 \delta(\boldsymbol{Q}-\boldsymbol{\tau})$$

$$F_N(\boldsymbol{\tau}) = \sum_{\boldsymbol{d}} b_{\boldsymbol{d}} e^{\imath \boldsymbol{\tau}\cdot\boldsymbol{d}}$$

Summary nuclear Bragg scattering

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = N_0 \frac{(2\pi)^3}{v_0} e^{-2W(\boldsymbol{Q})} \sum_{\boldsymbol{\tau}} \left|F_N(\boldsymbol{\tau})\right|^2 \delta(\boldsymbol{Q}-\boldsymbol{\tau})$$

$$F_N(\boldsymbol{\tau}) = \sum_{\boldsymbol{d}} b_{\boldsymbol{d}} e^{i\boldsymbol{\tau}\cdot\boldsymbol{d}}$$

Location of Bragg peaks

Information about chemical lattice (lattice parameters and symmetry of space group)

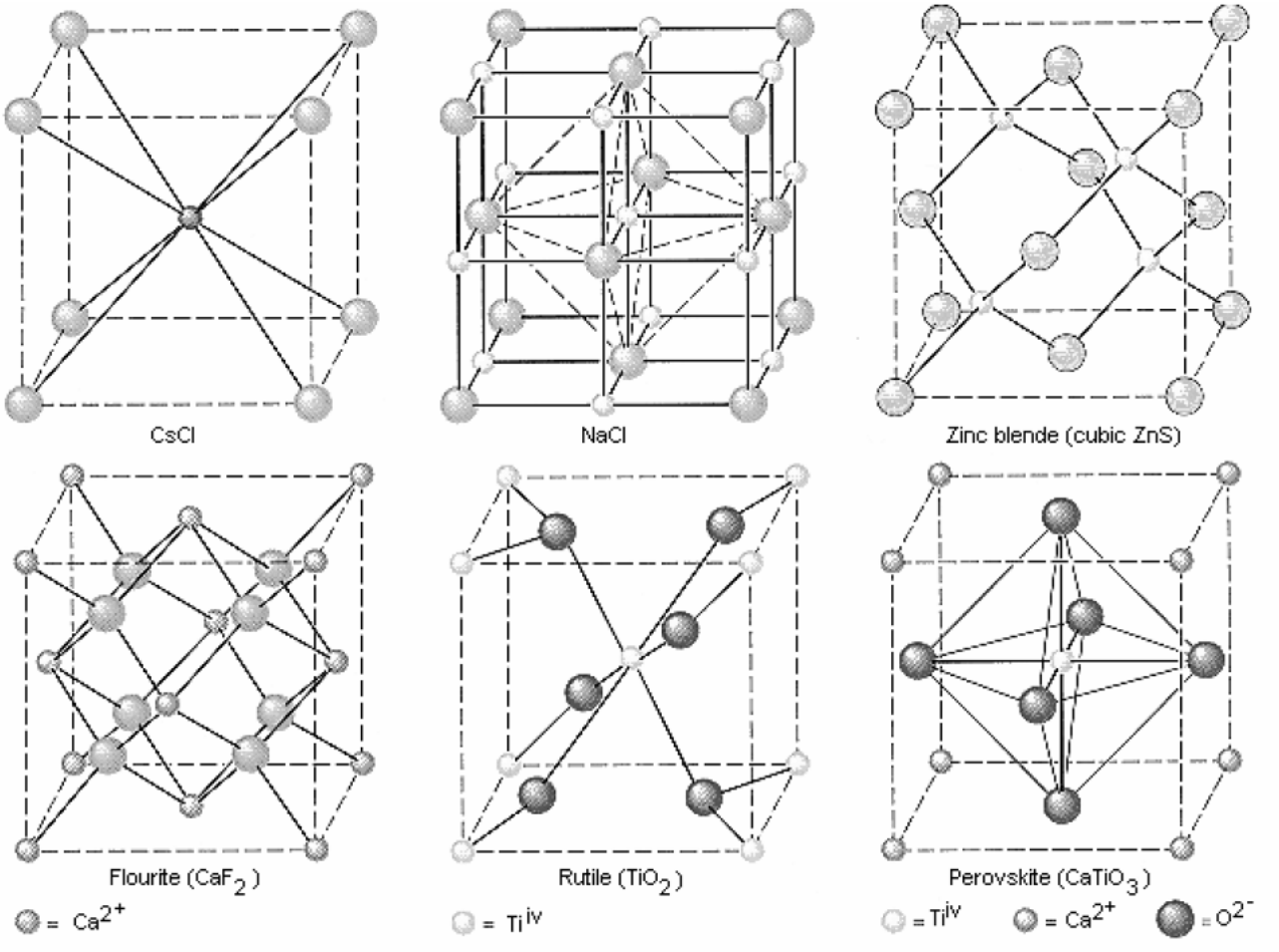
Debye-Waller factor

Information of atomic displacements from equilibrium positions

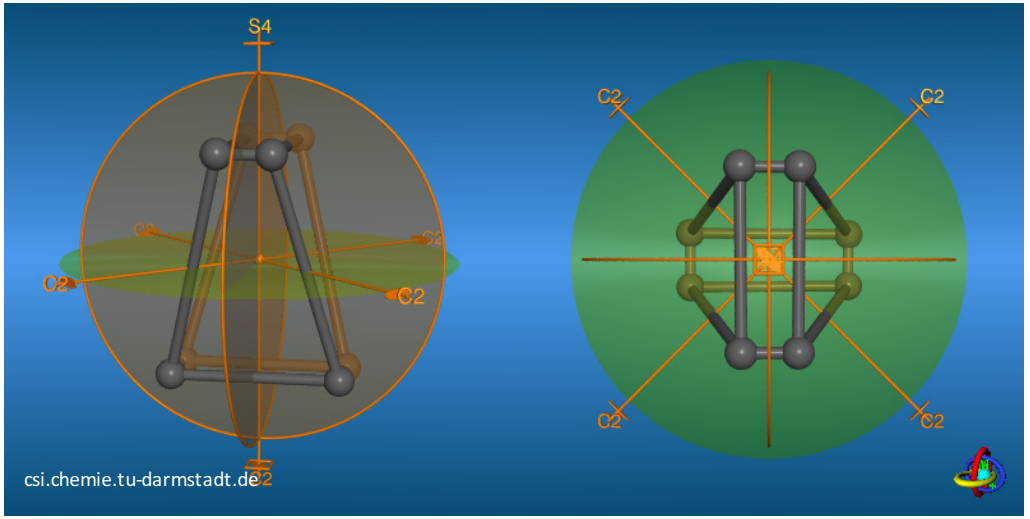
Intensities of Bragg peaks

Information about the species and location of atoms within unit cell

Excursion: symmetry



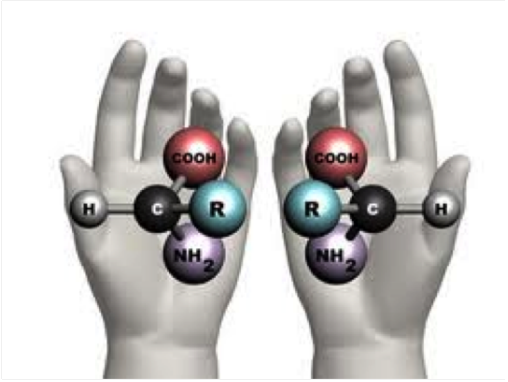
Point groups



Point groups determine local properties, such a magnetic moments, crystal fields etc

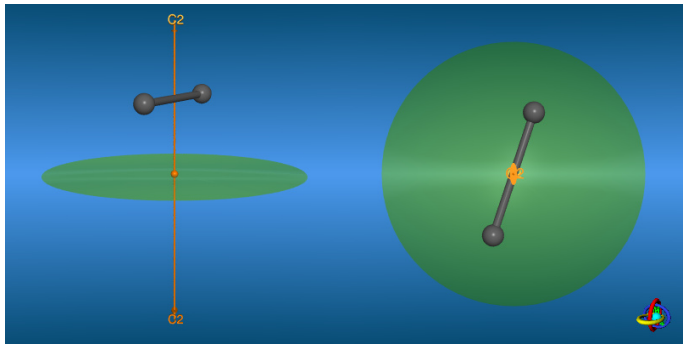
Basic symmetry operations:

- Rotations
- Mirror planes
- Inversion

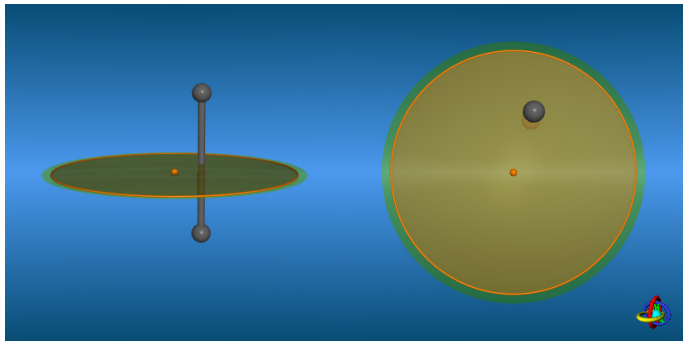


Basic symmetry operations

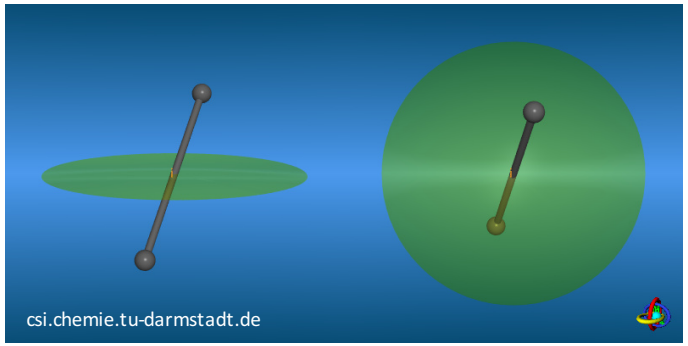
Rotation symmetry $\mathcal{R} = \begin{pmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix}$



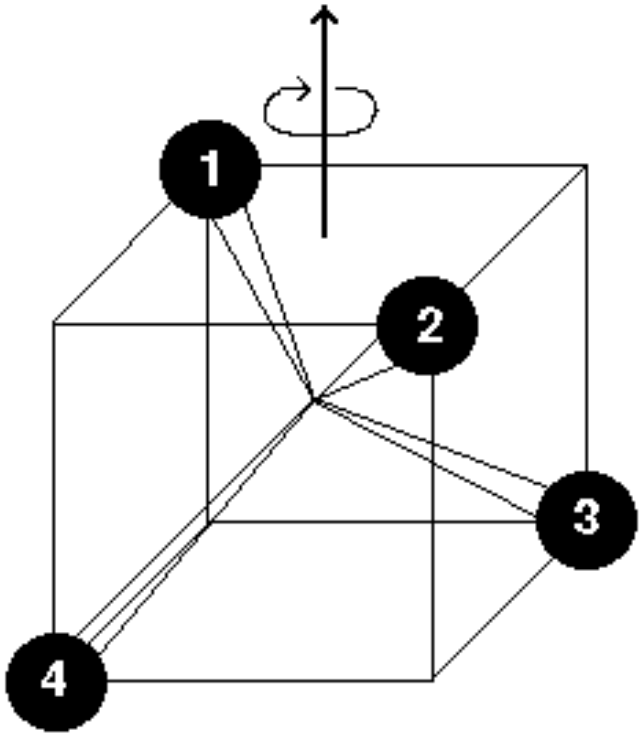
Mirror symmetry $\mathcal{R} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$



Inversion symmetry



Example of combined symmetry operations

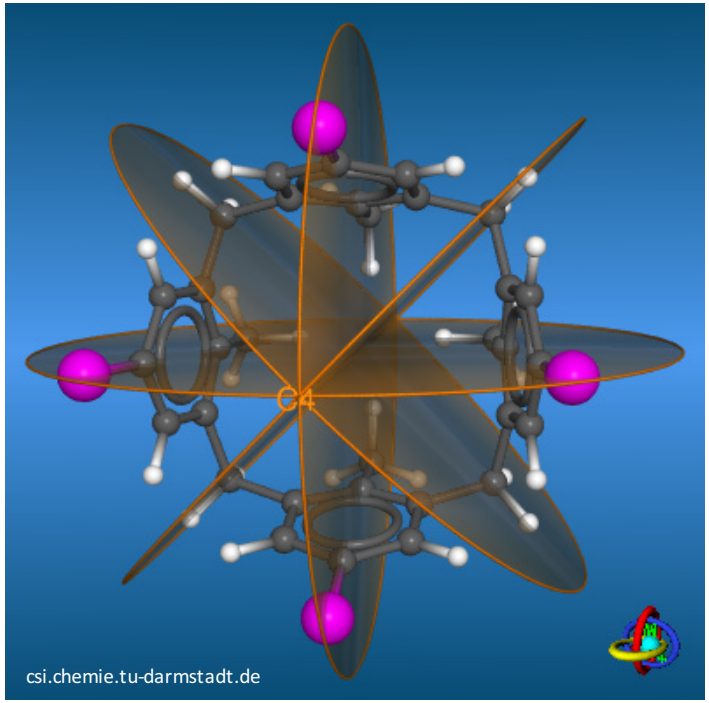


Symmetry operation S_4: four-fold rotation followed by a mirror operation perpendicular to the four-fold axis

Example

Point group C_{4v}

- Two-fold axis
- Four-fold axis
- Four mirror planes



$4mm$	1	2_z	4_z	4_z^{-1}	m_{xz}	m_{yz}	m_{xx}	$m_{x\overline{x}}$
1	1	2_z	4_z	4_z^{-1}	m_{xz}	m_{yz}	m_{xx}	$m_{x\overline{x}}$
2_z	2_z	1	4_z^{-1}	4_z	m_{yz}	m_{xz}	$m_{x\overline{x}}$	m_{xx}
4_z	4_z	4_z^{-1}	2_z	1	m_{xx}	$m_{x\overline{x}}$	m_{yz}	m_{xz}
4_z^{-1}	4_z^{-1}	4_z	1	2_z	$m_{x\overline{x}}$	m_{xx}	m_{xz}	m_{yz}
m_{xz}	m_{xz}	m_{yz}	$m_{x\overline{x}}$	m_{xx}	1	2_z	4_z^{-1}	4_z
m_{yz}	m_{yz}	m_{xz}	m_{xx}	$m_{x\overline{x}}$	2_z	1	4_z	4_z^{-1}
m_{xx}	m_{xx}	$m_{x\overline{x}}$	m_{xz}	m_{yz}	4_z	4_z^{-1}	1	2_z
$m_{x\overline{x}}$	$m_{x\overline{x}}$	m_{xx}	m_{yz}	m_{xz}	4_z^{-1}	4_z	2_z	1

List of point groups

Crystal System	Number of Point Groups	Herman-Mauguin Point Group	Schoenflies Point Group
Triclinic	2	$1, \bar{1}$	C_1, C_i
Monoclinic	3	$2, m, 2/m$	C_2, C_s, C_{2h}
Orthorhombic	3	$222, mm2, mmm$	D_2, C_{2v}, D_{2h}
Trigonal	5	$3, \bar{3}, 32$ $3m, \bar{3}m$	C_3, S_6, D_3 C_{3v}, D_{3d}
Hexagonal	7	$6, \bar{6}, 6/m, 622,$ $6mm, 62m, 6mm$	C_6, C_{3h}, C_{6h}, D_6 C_{6v}, D_{3h}, D_{6h}
Tetragonal	7	$4, \bar{4}, 4/m, 422,$ $4mm, \bar{4}2m$ $4/mmm$	C_4, S_4, C_{4h}, D_4 C_{4v}, D_{2d}, D_{4h}
Cubic	5	$23, m3, 432$ $\bar{4}32, m\bar{3}m$	T, T_h, O T_d, O_h

Space groups

point groups + lattice translations = space groups

$$(\mathcal{R}, \mathbf{t})(\mathbf{r}) = \mathcal{R}\mathbf{r} + \mathbf{t}$$

$$(\mathcal{R}_1, \mathbf{t}_1) \cdot (\mathcal{R}_2, \mathbf{t}_2) = (\mathcal{R}_1 \cdot \mathcal{R}_2, \mathcal{R}_1\mathbf{t}_1 + \mathbf{t}_2))$$

Crystal symmetry consists of

- Bravais lattices
- Choice of basis
- Translational symmetry

There are 230 space groups in three dimensions

→ International Tables for Crystallography (Hahn)

Space groups: international tables

http://it.iucr.org/

Home

International Tables for Crystallography

ISBN: 978-0-470-68575-4 doi: 10.1107/9780955360206000001

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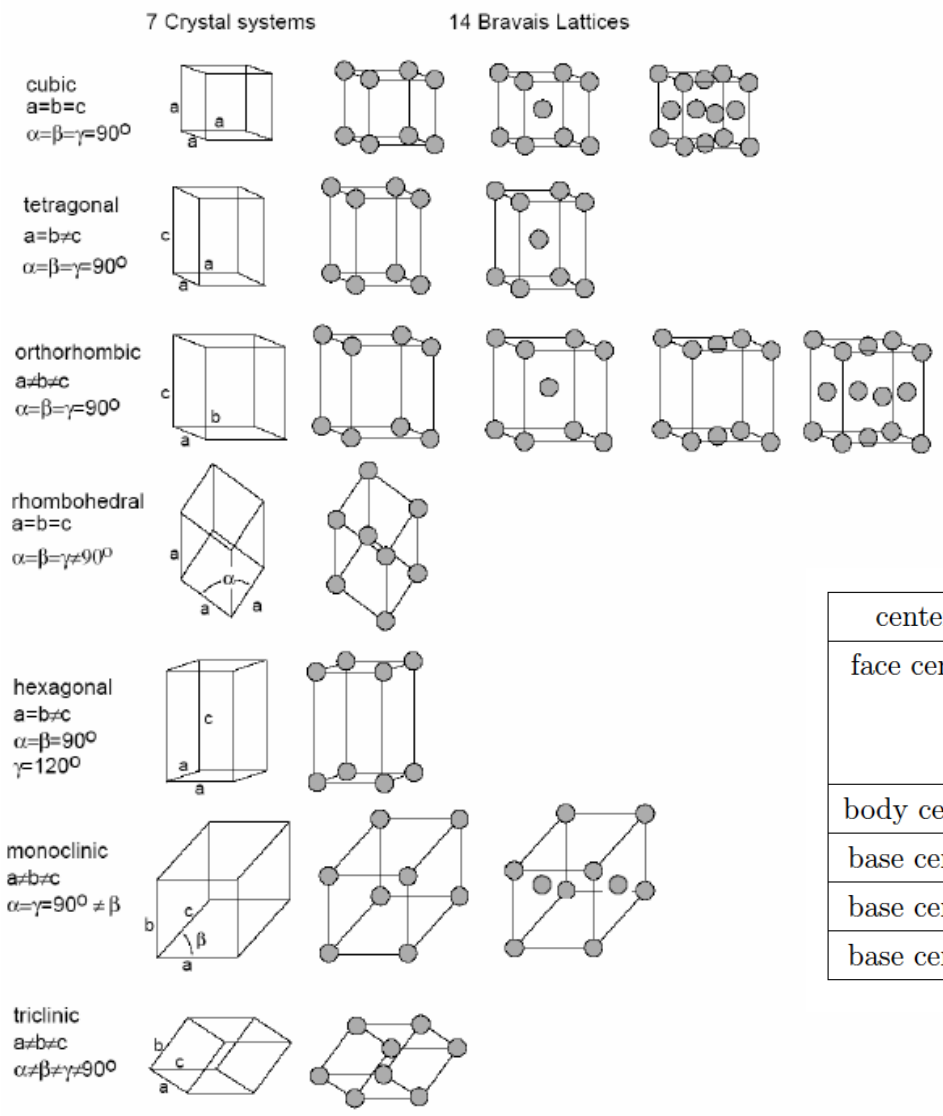
Reminder Bravais lattice



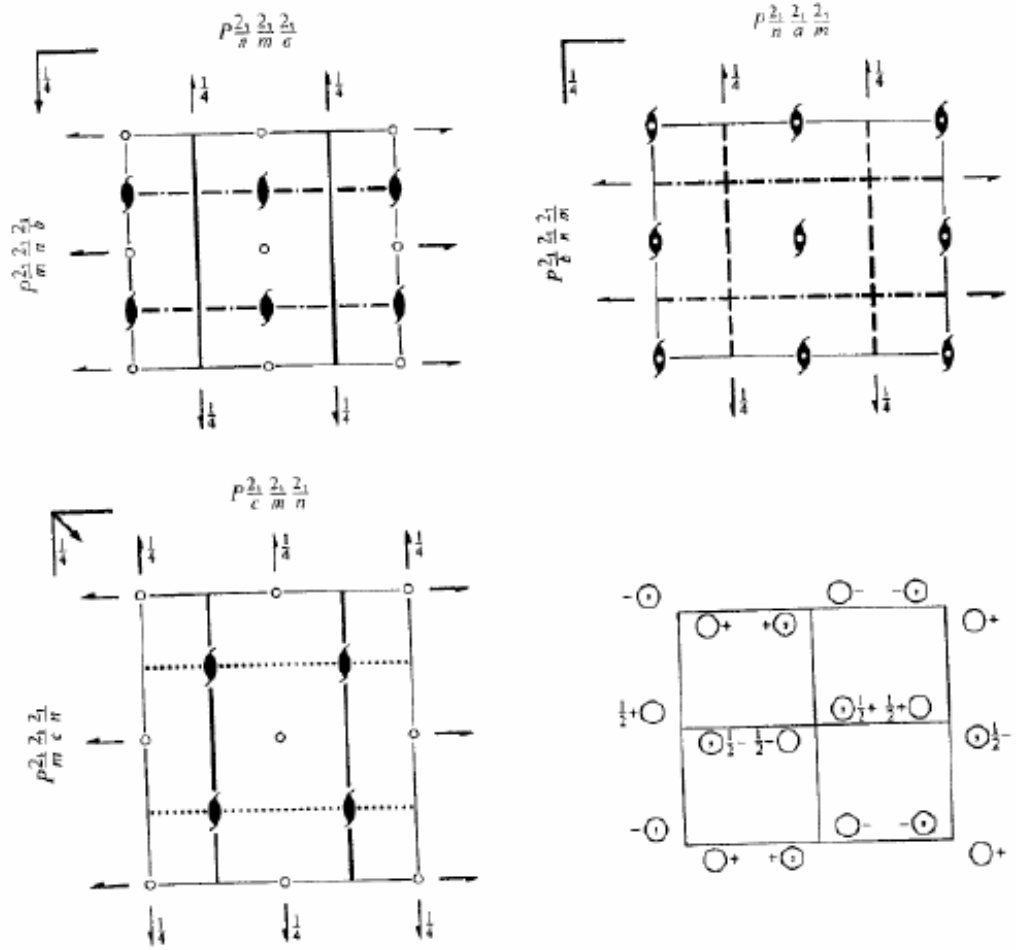
centering	symbol	centering vector(s)	lattice points per unit cell
face centered	F	$\frac{1}{2}(\mathbf{b}+\mathbf{c})$ $\frac{1}{2}(\mathbf{a}+\mathbf{c})$ $\frac{1}{2}(\mathbf{a}+\mathbf{b})$	4
body centered	I	$\frac{1}{2}(\mathbf{a}+\mathbf{b}+\mathbf{c})$	2
base centered	A	$\frac{1}{2}(\mathbf{b}+\mathbf{c})$	2
base centered	B	$\frac{1}{2}(\mathbf{a}+\mathbf{c})$	2
base centered	C	$\frac{1}{2}(\mathbf{a}+\mathbf{b})$	2

Important properties of a crystal structure

- Space group elements
- Centering
- Wyckoff positions
- Site symmetry
- Allowed Bragg peak positions

$Pnma$ D_{2h}^{16} mmm Orthorhombic

No. 62 $P\ 2_1/n\ 2_1/m\ 2_1/a$ Patterson symmetry $Pmmm$



Origin at $\bar{1}$ on 12_11

Asymmetric unit $0 \le x \le \frac{1}{2}$; $0 \le y \le \frac{1}{4}$; $0 \le z \le 1$

Symmetry operations

(1) 1
(2) $2(0,0,\frac{1}{2})$ $\frac{1}{4},0,z$
(3) $2(0,\frac{1}{2},0)$ $0,y,0$
(4) $2(\frac{1}{2},0,0)$ $x,\frac{1}{4},\frac{1}{4}$
(5) $\bar{1}$ $0,0,0$
(6) a $x,y,\frac{1}{4}$
(7) m $x,\frac{1}{4},z$
(8) $n(0,\frac{1}{2},\frac{1}{2})$ $\frac{1}{4},y,z$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3); (5)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
							General:
8	*d*	1	(1) x,y,z (5) $\bar{x},\bar{y},\bar{z}$	(2) $\bar{x}+\frac{1}{2},\bar{y},z+\frac{1}{2}$ (6) $x+\frac{1}{2},y,\bar{z}+\frac{1}{2}$	(3) $\bar{x},y+\frac{1}{2},\bar{z}$ (7) $x,\bar{y}+\frac{1}{2},z$	(4) $x+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}+\frac{1}{2}$ (8) $\bar{x}+\frac{1}{2},y+\frac{1}{2},z+\frac{1}{2}$	$0kl$: $k+l=2n$ $hk0$: $h=2n$ $h00$: $h=2n$ $0k0$: $k=2n$ $00l$: $l=2n$
							Special: as above, plus
4	*c*	. *m* .	$x,\frac{1}{4},z$	$\bar{x}+\frac{1}{2},\frac{3}{4},z+\frac{1}{2}$	$\bar{x},\frac{3}{4},\bar{z}$	$x+\frac{1}{2},\frac{1}{4},\bar{z}+\frac{1}{2}$	no extra conditions
4	*b*	$\bar{1}$	$0,0,\frac{1}{2}$	$\frac{1}{2},0,0$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$	hkl : $h+l,k=2n$
4	*a*	$\bar{1}$	$0,0,0$	$\frac{1}{2},0,\frac{1}{2}$	$0,\frac{1}{2},0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$	hkl : $h+l,k=2n$

Symmetry of special projections

Along [001] $p2gm$
$\mathbf{a}' = \frac{1}{2}\mathbf{a}$ $\mathbf{b}' = \mathbf{b}$
Origin at $0,0,z$

Along [100] $c2mm$
$\mathbf{a}' = \mathbf{b}$ $\mathbf{b}' = \mathbf{c}$
Origin at $x,\frac{1}{4},\frac{1}{4}$

Along [010] $p2gg$
$\mathbf{a}' = \mathbf{c}$ $\mathbf{b}' = \mathbf{a}$
Origin at $0,y,0$

Maximal non-isomorphic subgroups

I [2] $Pn2_1a$ ($Pna2_1$, 33) 1; **3**; 6; 8
[2] $Pnm2_1$ ($Pmn2_1$, 31) 1; 2; 7; 8
[2] $P2_1ma$ ($Pmc2_1$, 26) 1; 4; 6; 7
[2] $P2_12_12_1$ (19) 1; 2; 3; 4
[2] $P112_1/a$ ($P2_1/c$, 14) 1; 2; 5; 6
[2] $P2_1/n11$ ($P2_1/c$, 14) 1; 4; 5; 8
[2] $P12_1/m1$ ($P2_1/m$, 11) 1; 3; 5; 7

IIa none

IIb none

Maximal isomorphic subgroups of lowest index

IIc [3] $Pnma$ ($\mathbf{a}' = 3\mathbf{a}$) (62); [3] $Pnma$ ($\mathbf{b}' = 3\mathbf{b}$) (62); [3] $Pnma$ ($\mathbf{c}' = 3\mathbf{c}$) (62)

Minimal non-isomorphic supergroups

I none

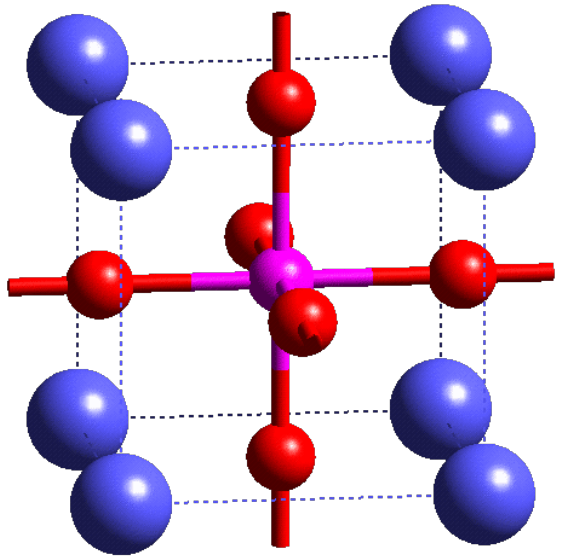
II [2] $Amma$ ($Cmcm$, 63); [2] $Bbmm$ ($Cmcm$, 63); [2] $Ccme$ ($Cmce$, 64); [2] $Imma$ (74); [2] $Pcma$ ($\mathbf{b}' = \frac{1}{2}\mathbf{b}$) ($Pbam$, 55); [2] $Pbma$ ($\mathbf{c}' = \frac{1}{2}\mathbf{c}$) ($Pbcm$, 57); [2] $Pnmm$ ($\mathbf{a}' = \frac{1}{2}\mathbf{a}$) ($Pmmn$, 59)

Example crystal structure

$SrTiO_3$: Pm-3m (No. 221)

Atom	site	x	y	z
Sr	1b	0.5	0.5	0.5
Ti	1a	0	0	0
O	3d	0.5	0	0

8	*g*	.3*m*	x,x,x $x,x,\bar{x}$	$\bar{x},\bar{x},x$ $\bar{x},\bar{x},\bar{x}$	$\bar{x},x,\bar{x}$ $x,\bar{x},x$	$x,\bar{x},\bar{x}$ $\bar{x},x,x$		
6	*f*	4*m*.*m*	$x,\frac{1}{2},\frac{1}{2}$	$\bar{x},\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},x,\frac{1}{2}$	$\frac{1}{2},\bar{x},\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},x$	$\frac{1}{2},\frac{1}{2},\bar{x}$
6	*e*	4*m*.*m*	$x,0,0$	$\bar{x},0,0$	$0,x,0$	$0,\bar{x},0$	$0,0,x$	$0,0,\bar{x}$
3	*d*	4/*mm*.*m*	$\frac{1}{2},0,0$	$0,\frac{1}{2},0$	$0,0,\frac{1}{2}$			
3	*c*	4/*mm*.*m*	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$			
1	*b*	$m\bar{3}m$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$					
1	*a*	$m\bar{3}m$	$0,0,0$					



Perovskite structure

Two classes of neutron diffraction experiments

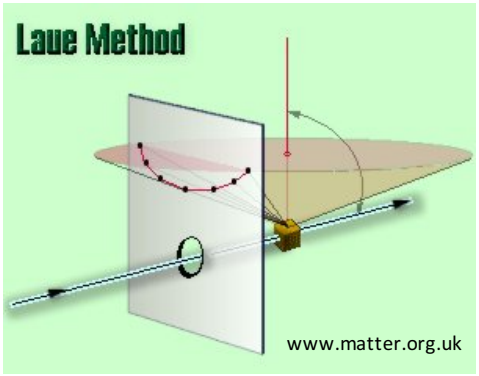
- Monochromatic beam
  - powder neutron diffraction
  - single crystal neutron diffraction

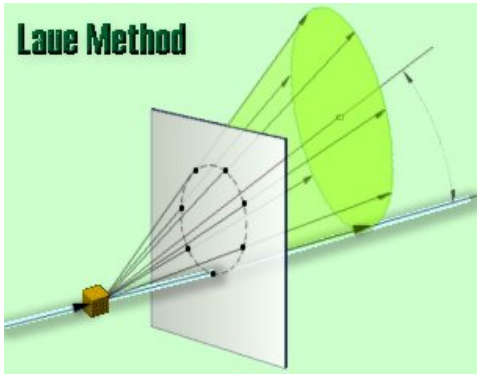
- Polychromatic beam
  - Laue diffraction
  - Time-of-flight diffraction

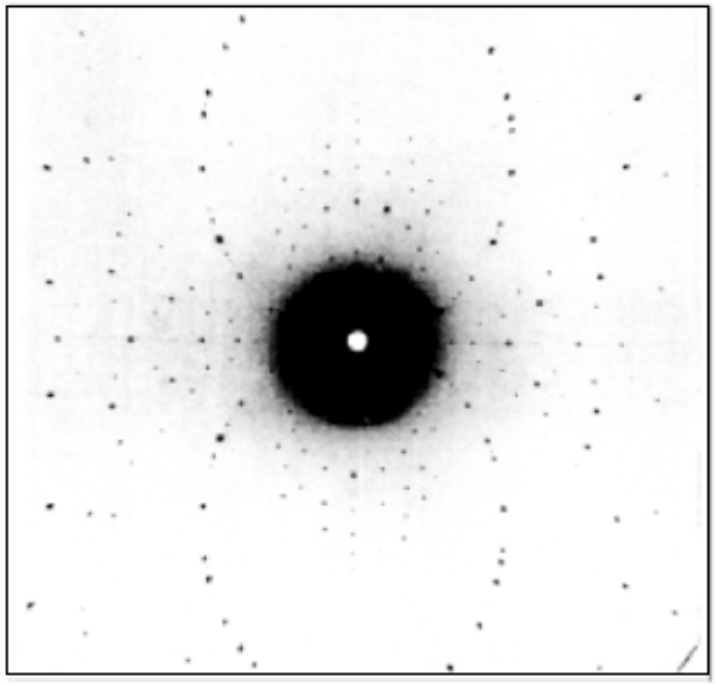
Laue measurements

Polychromatic beam fulfills the Bragg conditions for many reciprocal lattice vectors

$$Q = 2k_i \sin 2\Theta$$



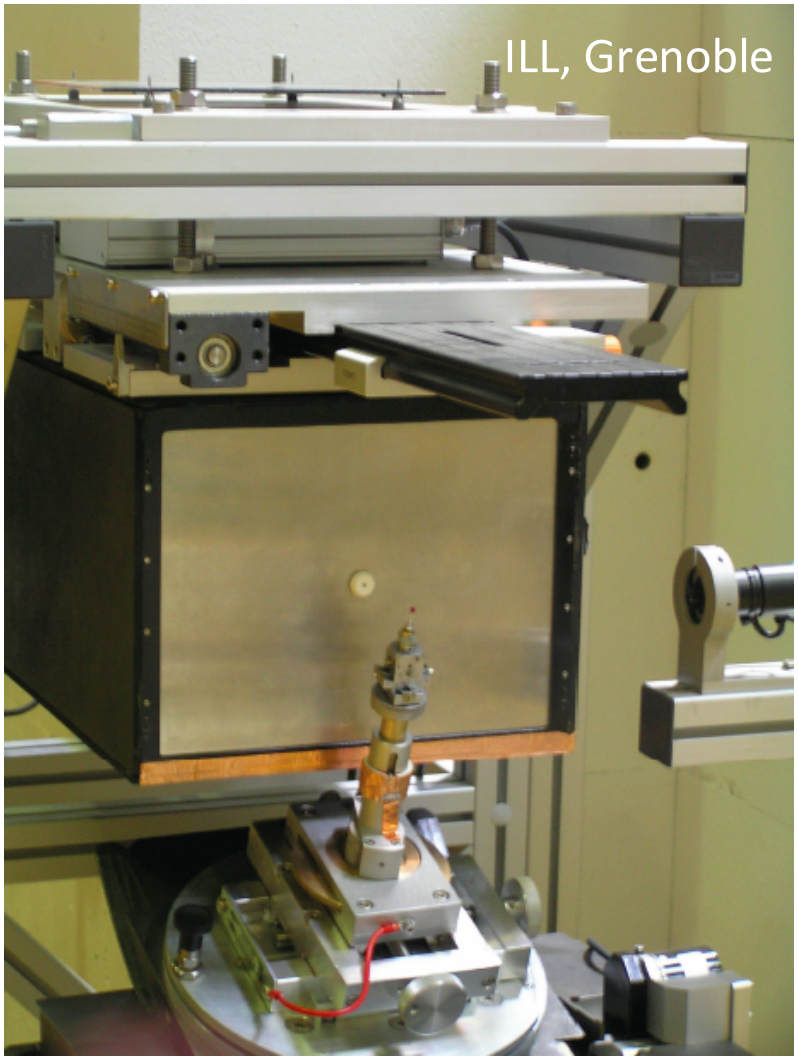




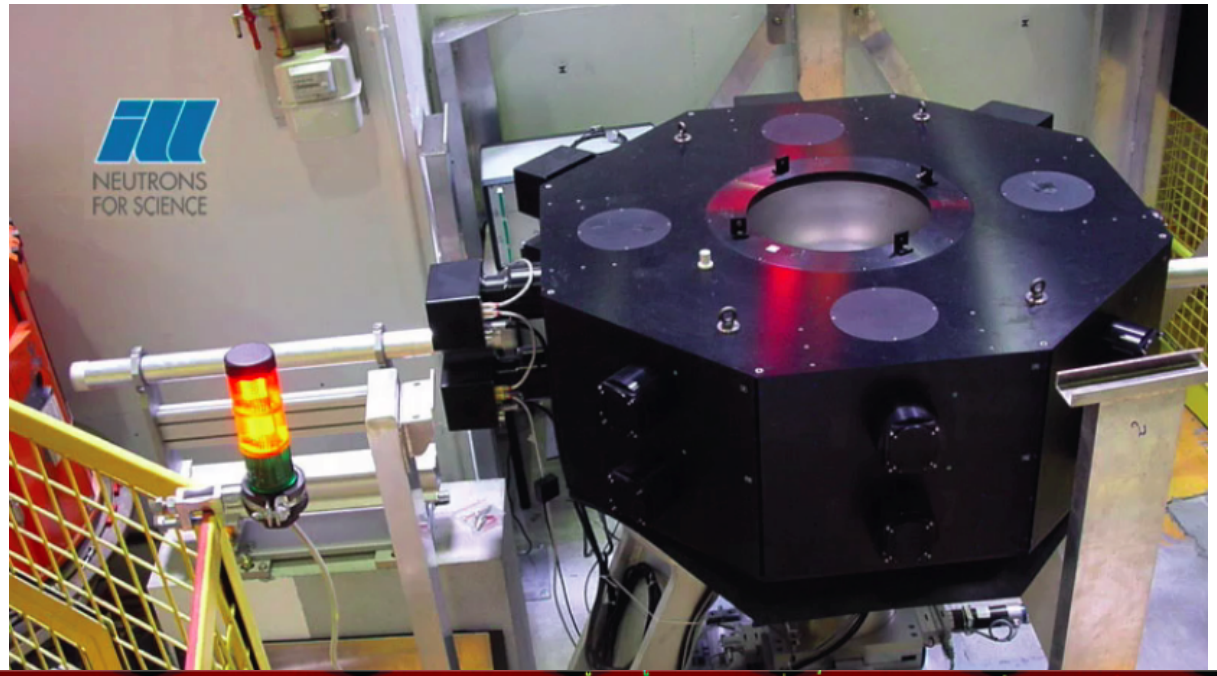
Systematic absences and symmetry of reciprocal lattice become immediately visible

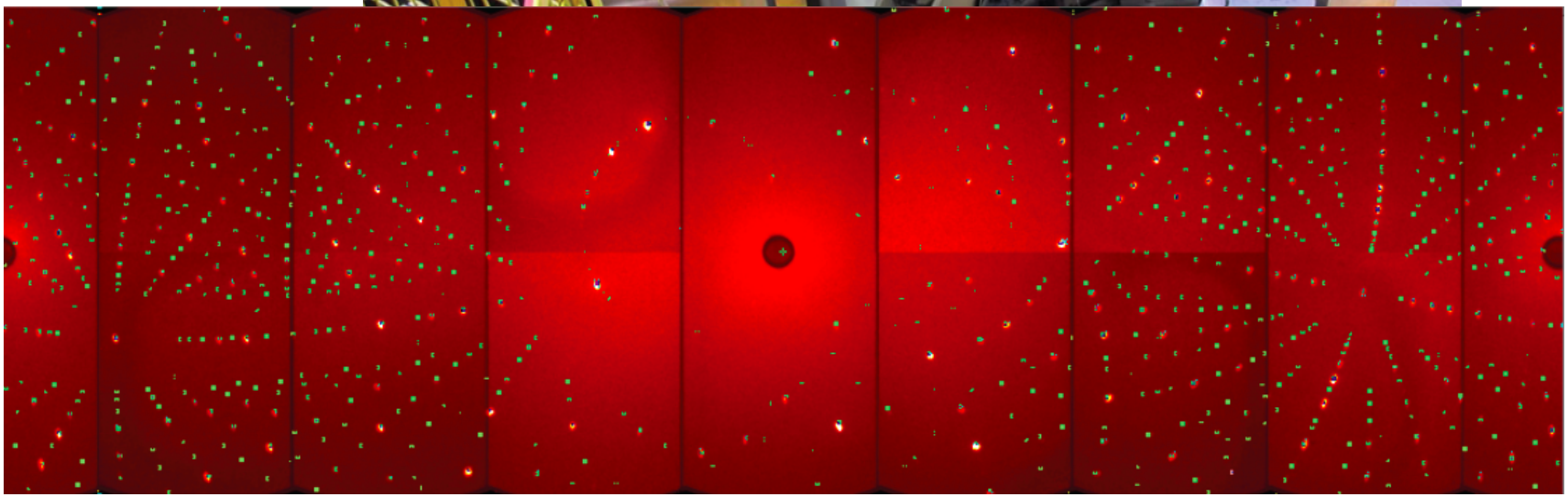
Experiments are usually carried out with image plates and thus the intensity cannot be be analyzed quantitatively

Example: neutron Laue instrument



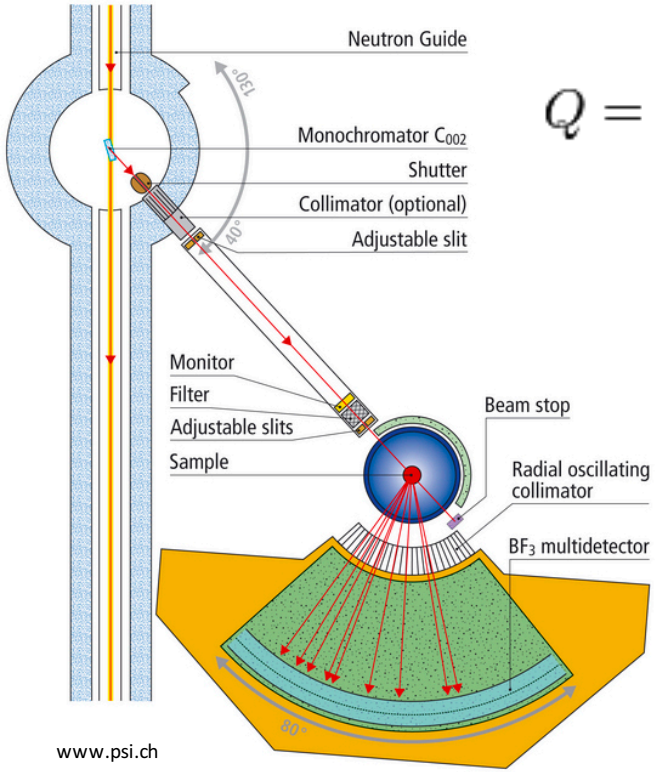
Modern neutron Laue instrument





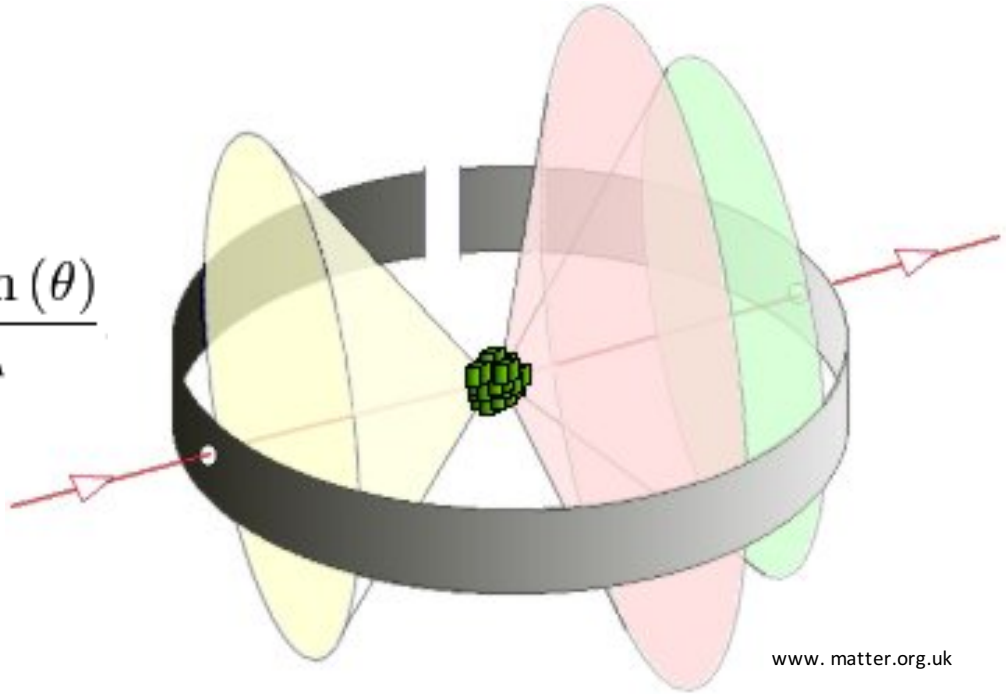
Neutron powder diffraction

- Many materials are not available as crystals
- Polycrystalline have no orientation
- Bragg peaks are easy to find
- Data is often easier to analyze

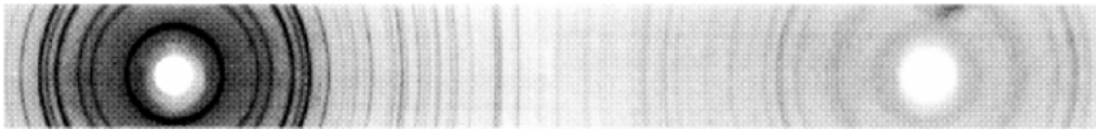


www.psi.ch

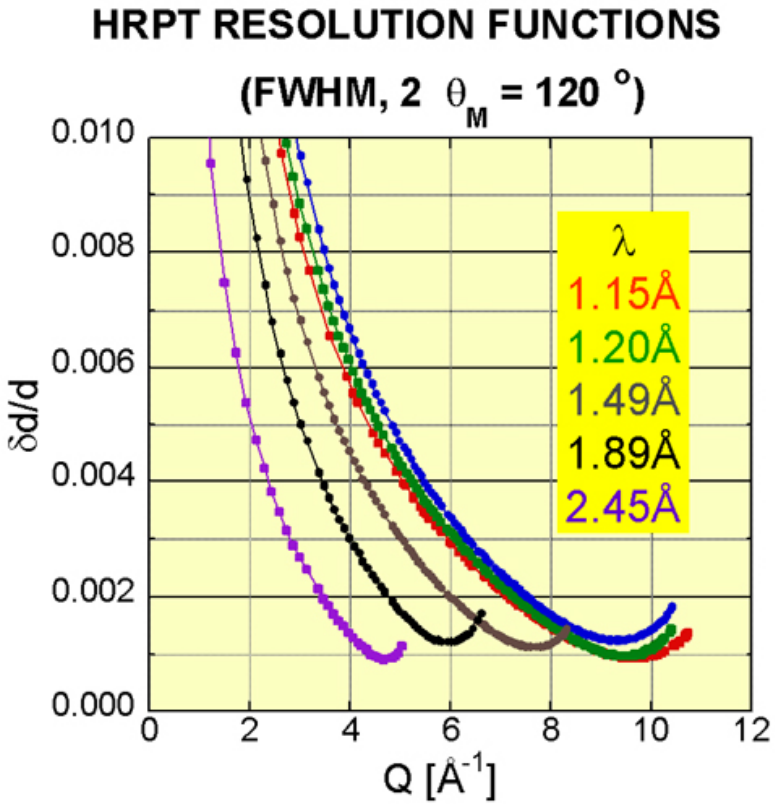
$$Q = \frac{4\pi \sin(\theta)}{\lambda}$$

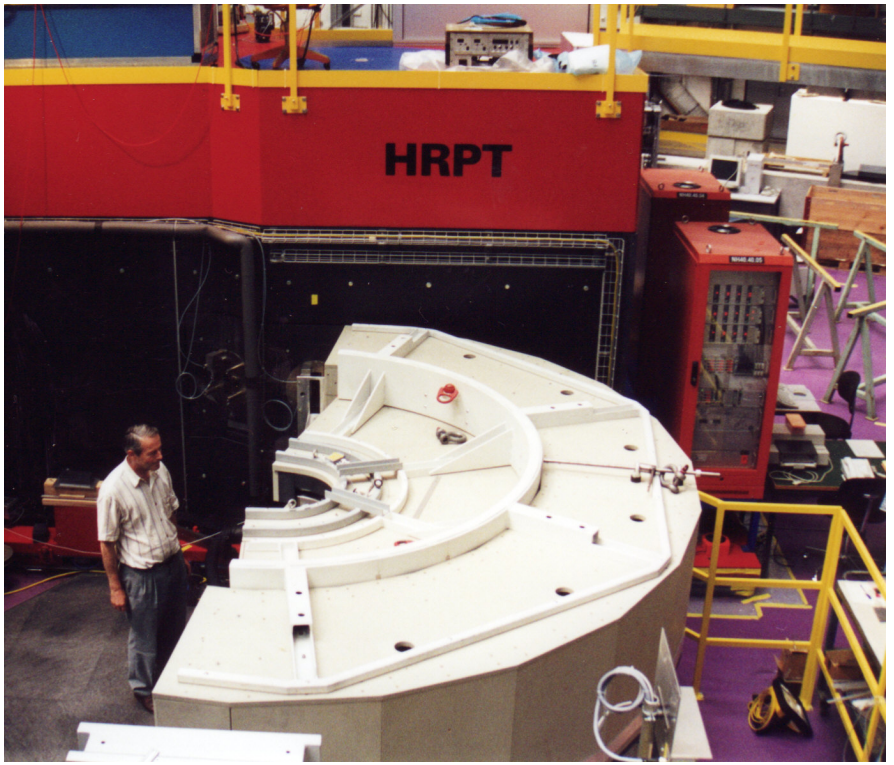


www. matter.org.uk



Resolution powder neutron diffraction





Phase problem

Neutron diffraction measures intensities, but not the structure factors

$$I \;\alpha\; \left|F_N(\boldsymbol{\tau})\right|^2 \qquad\qquad F_N(\boldsymbol{\tau}) = \sum_{\boldsymbol{d}} b_{\boldsymbol{d}} e^{i\boldsymbol{\tau}\cdot\boldsymbol{d}}$$

Structure factors are measured without the phase

Structure cannot be simply obtained from a Fourier Transform of structure factors, because the phases are not measured

→ Fitting of models to the observed data is necessary

Powder diffraction analysis

$$I_i = a + 2b\theta_i + m_{\mathrm{hkl}} \left|F_N(\boldsymbol{\tau})\right|^2 L(\theta_i) \exp\left(-4\ln 2\left(\frac{2\theta_i - 2\theta_{\mathrm{hkl}}}{\Gamma_i}\right)^2\right)$$

$$L(\theta) = 1/(\sin\theta \sin 2\theta)$$

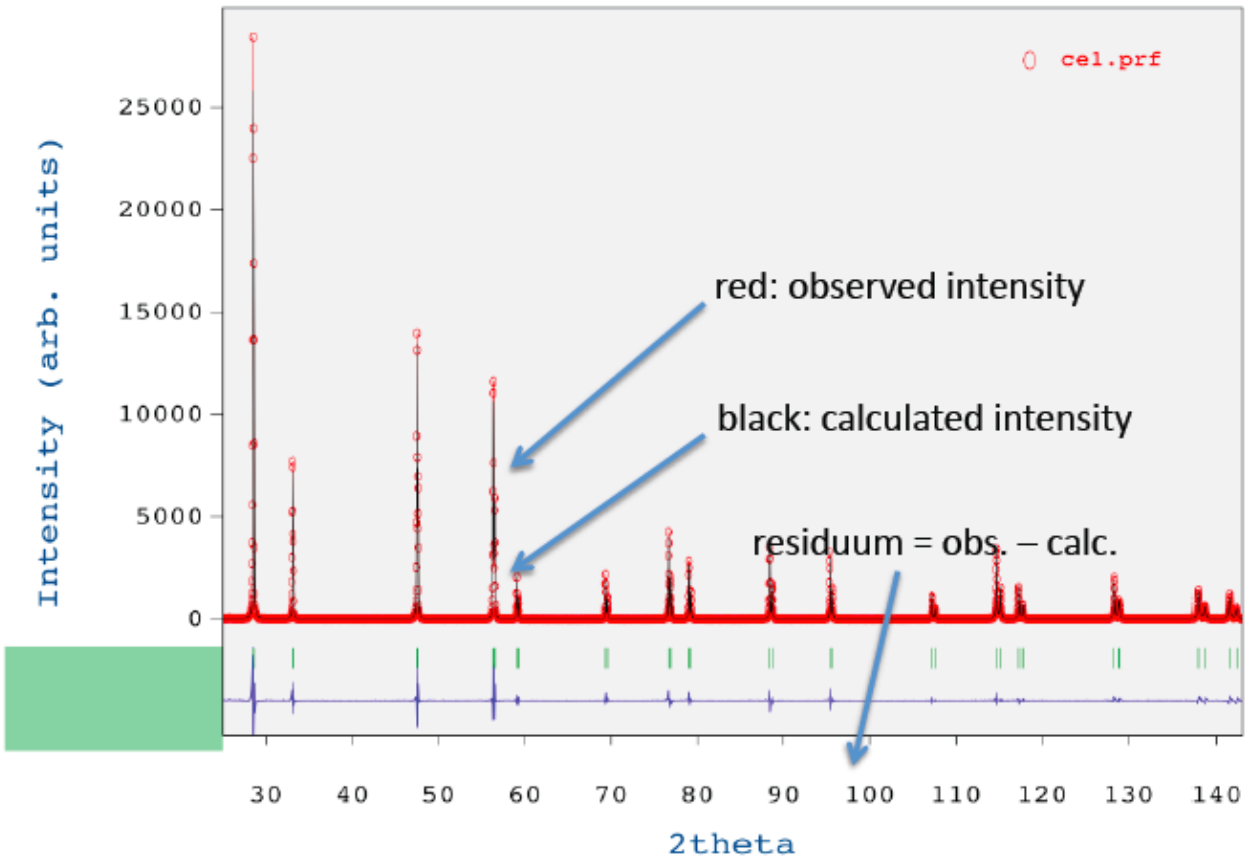
Lorentz factor arising from the Debye-Scherrer cones intersecting powder sample

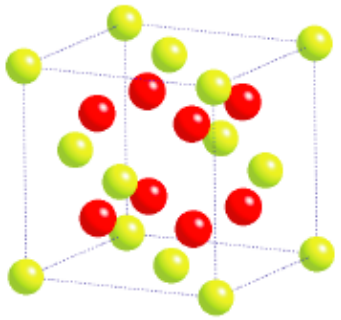
$$\Gamma(2\theta) = \sqrt{U\tan^2\theta + V\tan\theta + W}$$

Bragg peaks are broadened by resolution (finite wave-length distribution etc)

Additional information may be extracted about strain, preferred orientation etc through a peak shape analysis

Example CeO_2

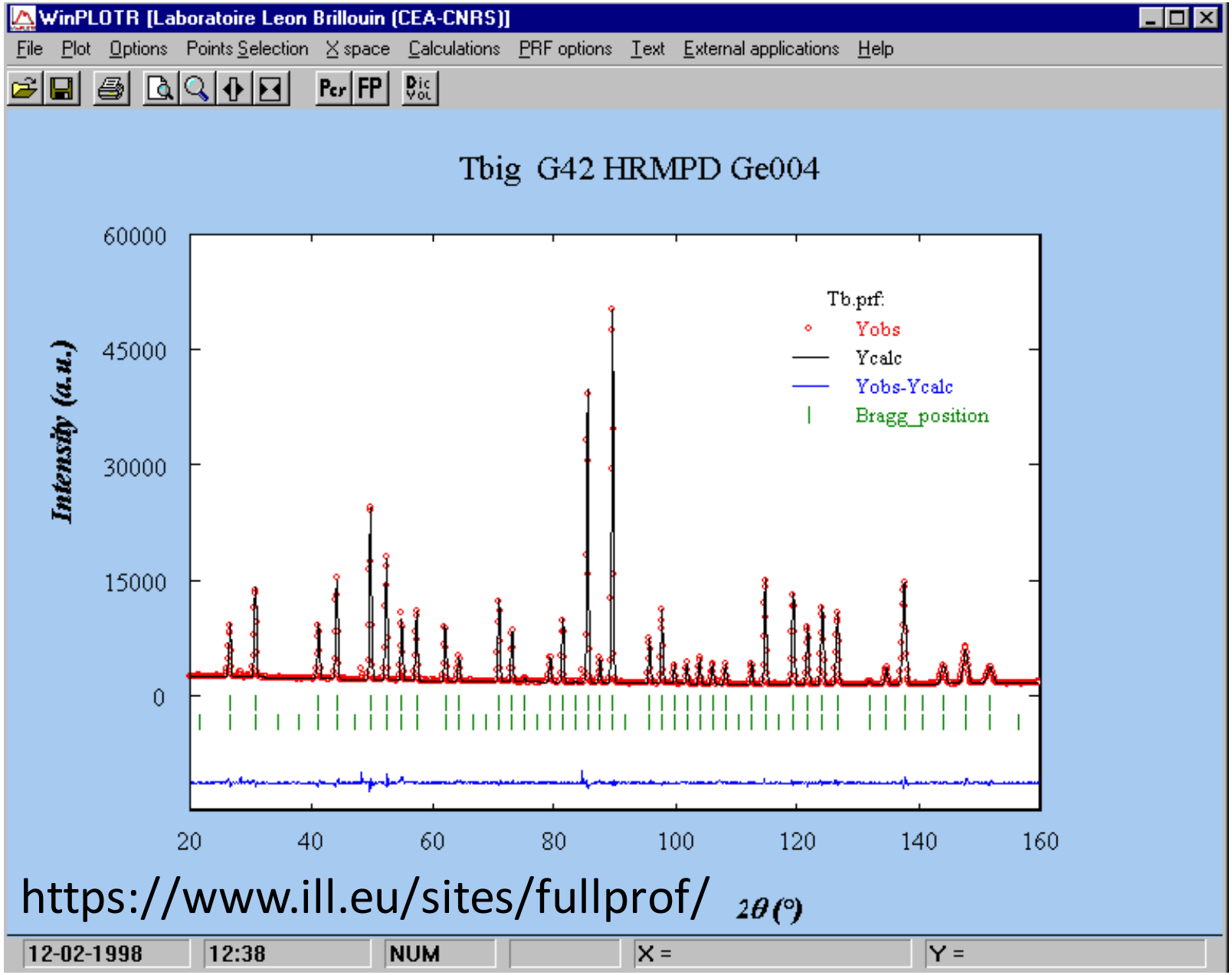




CeO_2 cubic Fm3m
Ce: 0, 0, 0
O: ¼, ¼, ¼,

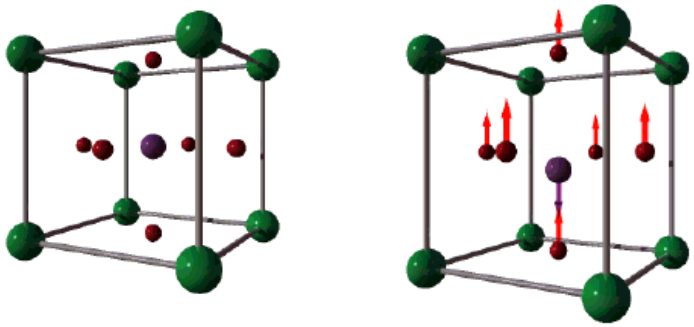
Minimize $$\chi^2 = \sum_i w_i \left(I_i^{\text{obs}} - I_i^{\text{cal}}\right)^2$$

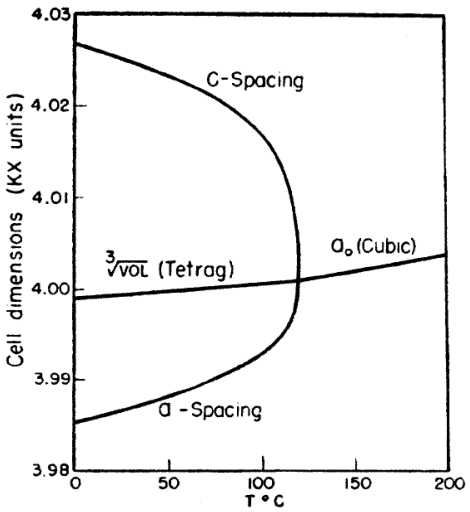
Fullprof Rietfeld fitting program



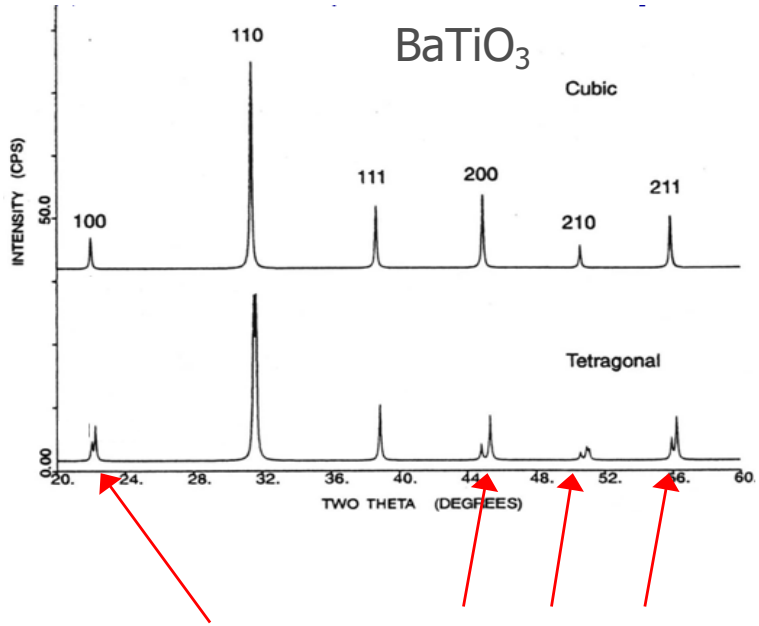
Temperature dependence of crystal structures

Onset of ferroelectricity is associated with chemical phase transition, change of lattice





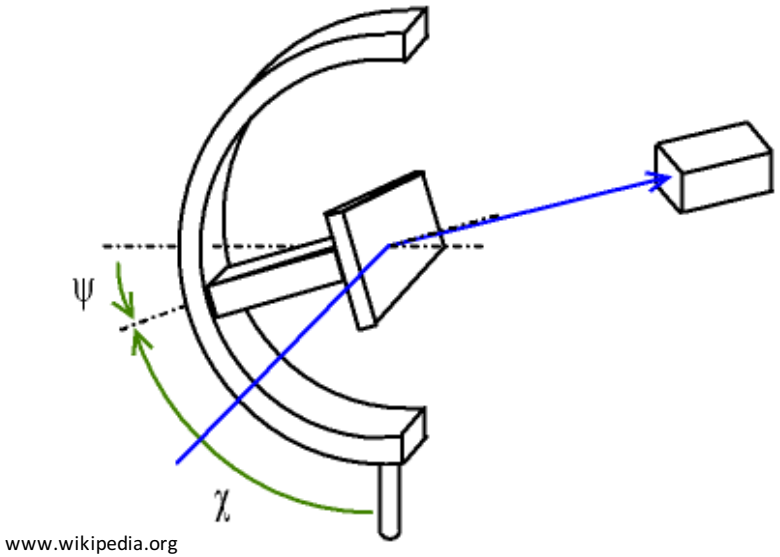
Megaw et al



Splitting of nuclear Bragg peaks

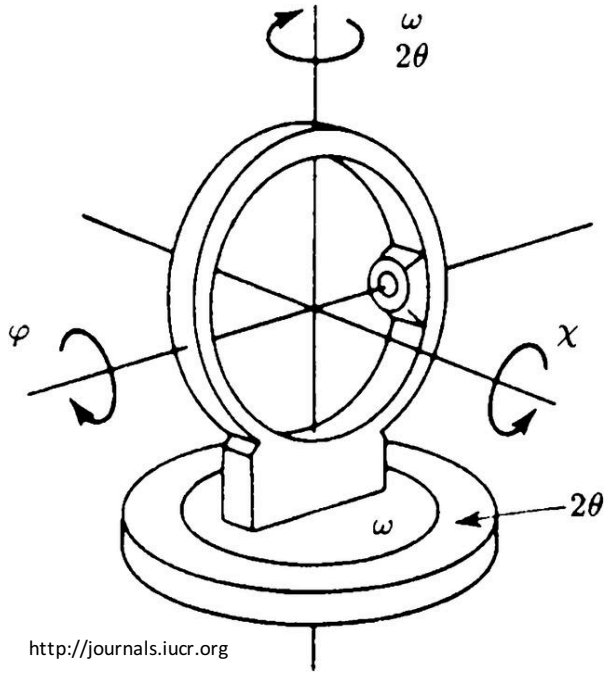
- loss of all 3-fold rotation axes
- loss of inversion symmetry
- loss of some 4-fold rotation axes

Single crystal diffraction



www.wikipedia.org

four angles are needed
to access all directions in
reciprocal space for
horizontal scattering plane

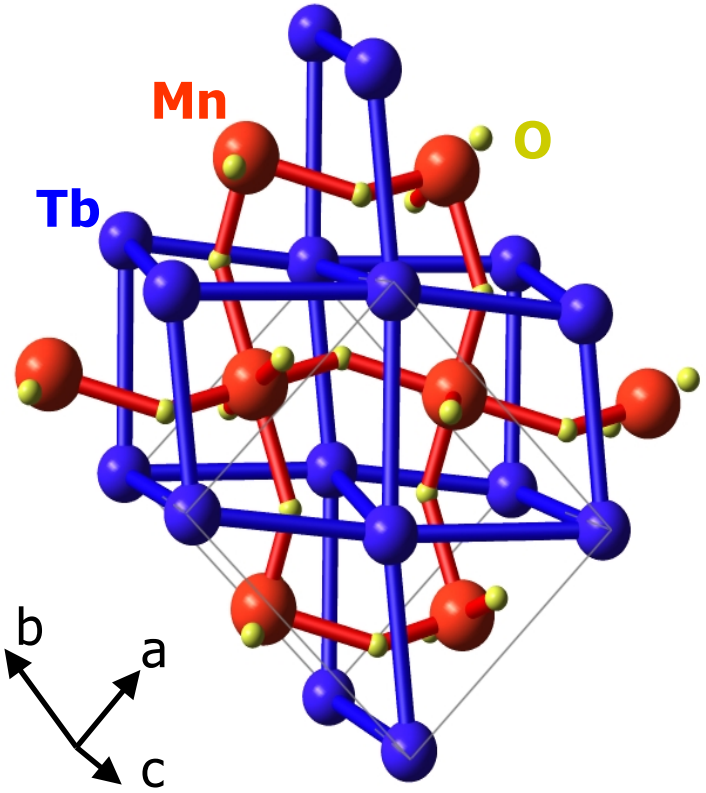


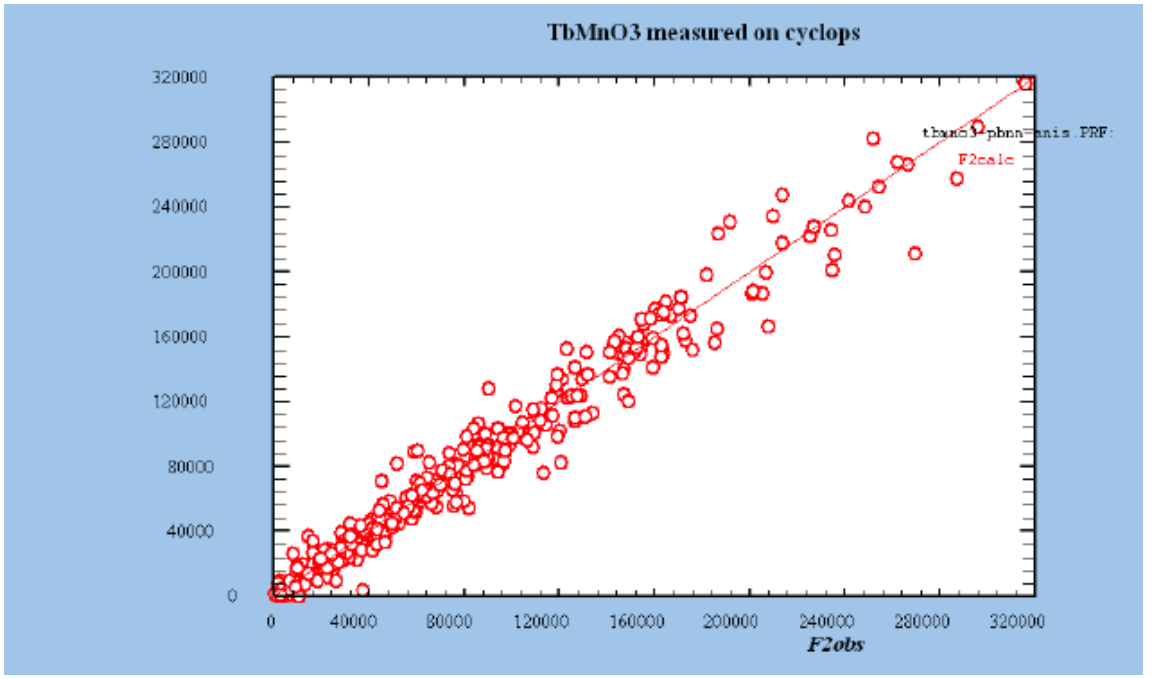
http://journals.iucr.org

- Monochromatic beam
- Horizontal scattering plane

Lifting arm detectors allow limited access to 3D
reciprocal space only with omega and 2Theta angles

Example $TbMnO_3$





Small-angle diffraction

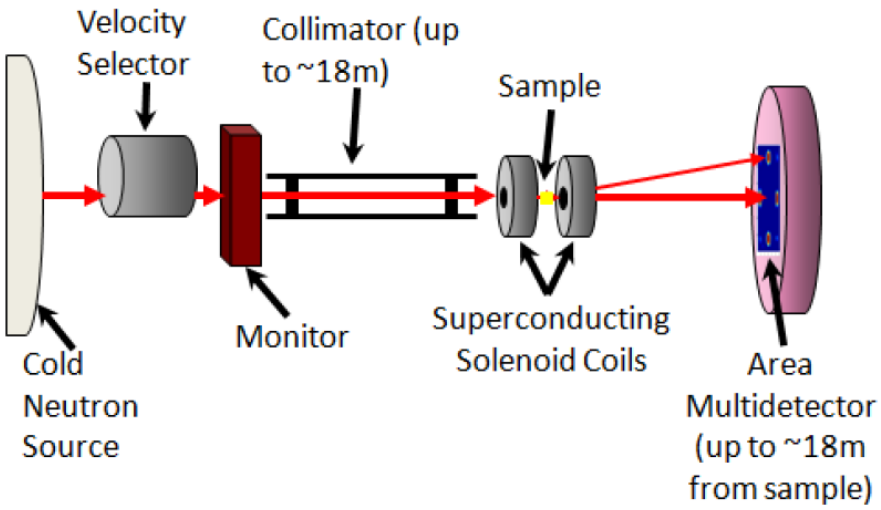
- For a unit cell of 1 nm and neutron wave-length of 5 Angstrom, lowest angle peaks are at $2\Theta = 29^{o}$

$$(n)\lambda = 2d\sin(\theta)$$

- If a unit cell is large, then 2 Theta becomes small

  for d=20nm → $2\Theta \sim 1^{o}$

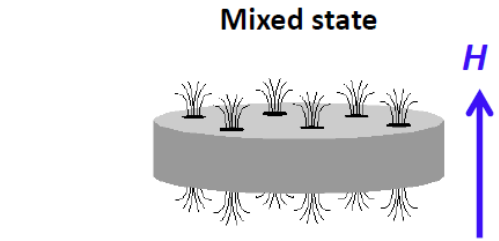
- Such low-angle scattering experiment are performed on small-angle neutron scattering (SANS) instruments



SANS instrument

SANS-I beamline at Paul Scherrer Institute, Villigen (Switzerland).

Measurement of structure of a flux lattice in a superconductor



Vortices penetrate the bulk. Each carries one *flux quantum*

$$\Phi_0 = \frac{h}{2e}$$

$$(n)\lambda = 2d\sin(\theta)$$

d ~ 14nm → θ ~ 1°