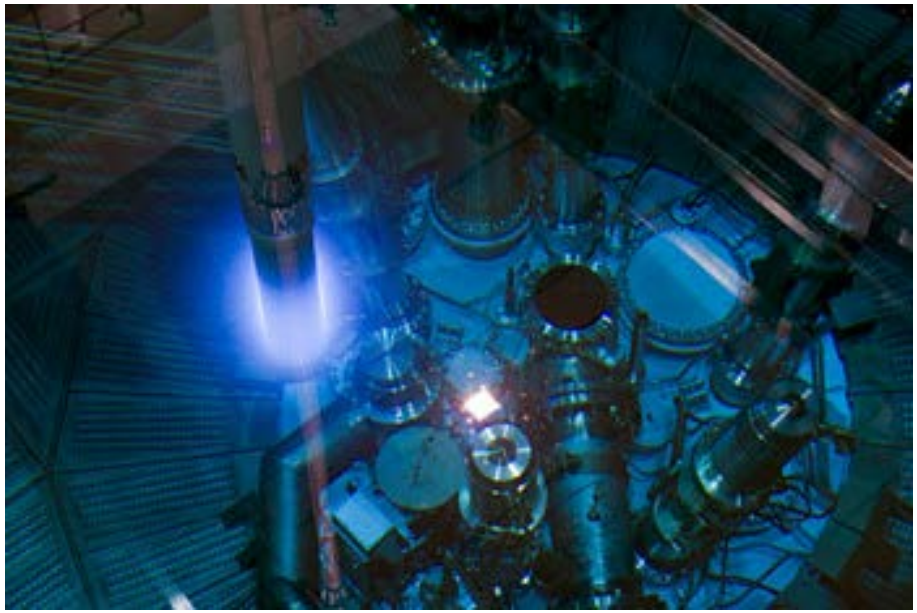
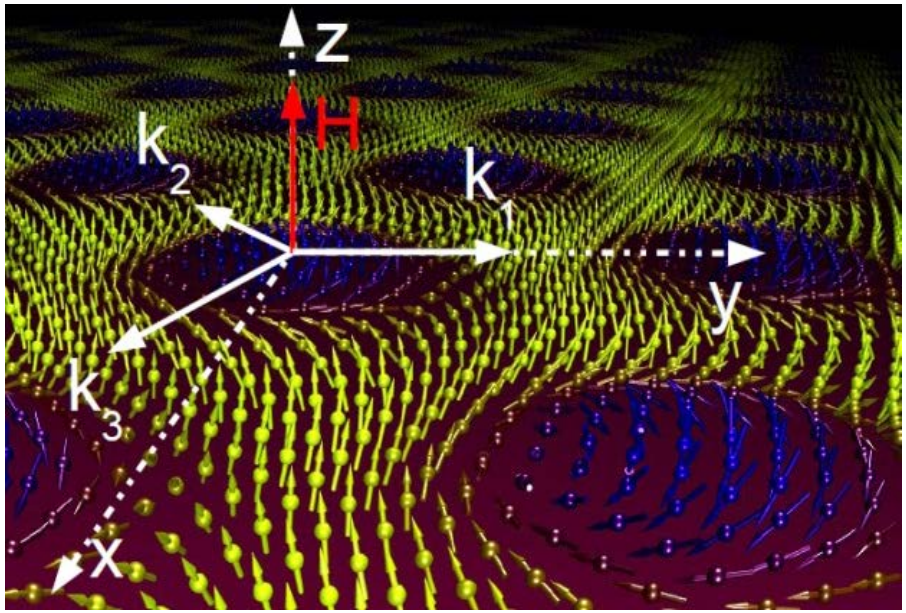
Physics with Neutrons I, WS 2015/2016





Lecture 8, 7.12.2015

Organization

Visit FRM II : 21.12.2015

10:15 – 13:00 (after the lecture)

Valid ID necessary!!!

Exam (after winter term)

- Registration: via TUM-Online between 16.11.2015 – 15.1.2015
- Email: sebastian.muehlbauer@frm2.tum.de for date arrangement
- 30min oral exam

4.2 Reminder: 32 Point groups

- Combinations of proper and improper rotations that leave one point fixed (intersection point of the axes)
- Classification of point symmetries: 32 Point groups

Crystal systems	Point groups: Non-centrosymmetric		Point groups: Centrosymmetric	Laue classes	Lattice point groups
Triclinic	1		$\bar{1}$	$\bar{1}$	$\bar{1}$
Monoclinic	2	m	2/m	2/m	2/m
Orthorhombic	222	mm2	mmm	mmm	mmm
Tetragonal	4	$\bar{4}$	4/m	4/m	4/mmm
	422	4mm, $\bar{4}$2m	4/mmm	4/mmm	
Trigonal	3		$\bar{3}$	$\bar{3}$	$\bar{3}$m
	32	3m	$\bar{3}$m	$\bar{3}$m	
Hexagonal	6	$\bar{6}$	6/m	6/m	6/mmm
	622	6mm, $\bar{6}$2m	6/mmm	6/mmm	
Cubic	23		m$\bar{3}$	m$\bar{3}$	m$\bar{3}$m
	432	$\bar{4}$3m	m$\bar{3}$m	m$\bar{3}$m	

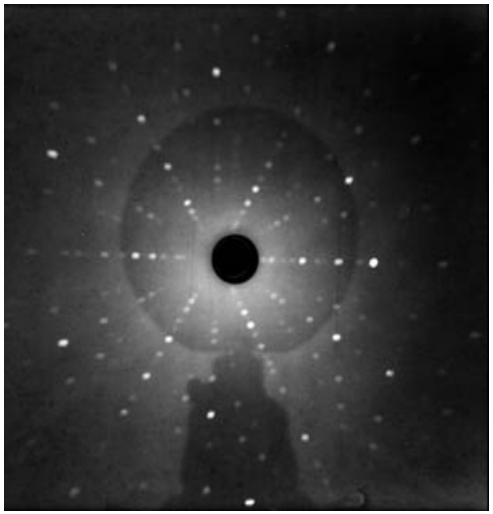
4.2 Reminder: Laue classes, Friedels law & Neumann Principle

Neumann Principle:
All physical properties reflect the symmetry of the point group

BUT:
Measurements do not always reflect the actual point group symmetry

- Diffraction always measures inensities, not the phase!
- Friedel´s law: Diffraction shows the symmetry as if there would be an additional center of inversion at the center $I_{hlk}=I_{-h-k-l}$
- Classification in 11 Laue classes

Laue forward scattering
Silicon single crystal, cubic, fcc, [111], three fold



4.2 Reminder: 14 Bravais lattices and 7 crystal classes

Allow for non-primitive unit cells: Classification according to unit cell symmetry

➡ 14 Bravais lattices and 7 crystal classes

The 7 lattice systems	The 14 Bravais lattices			
triclinic	P			
	$\alpha, \beta, \gamma \neq 90°$			
monoclinic	P	C		
	$\alpha \neq 90°$ $\beta, \gamma = 90°$	$\alpha \neq 90°$ $\beta, \gamma = 90°$		
orthorhombic	P	C	I	F
	$a \neq b \neq c$	$a \neq b \neq c$	$a \neq b \neq c$	$a \neq b \neq c$
tetragonal	P	I		
	$a \neq c$	$a \neq c$		
rhombohedral	P			
	$\alpha = \beta = \gamma \neq 90°$			
hexagonal	P			
cubic	P (pcc)	I (bcc)	F (fcc)	

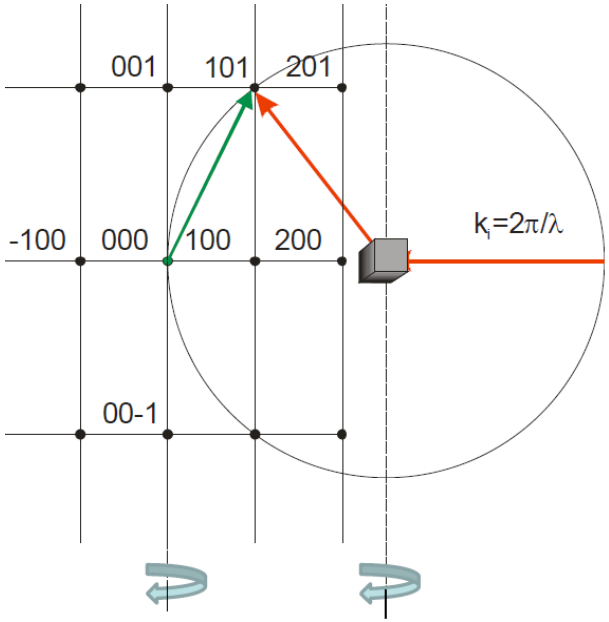
4.2 Reminder: 320 space groups

Table 1.9. The 230 three-dimensional space groups arranged by crystal systems and point groups. Space groups (and enantiomorphous pairs) that are uniquely determinable from the symmetry of the diffraction pattern and from systematic absences (see p. 159) are shown in bold-type. Point groups without inversion centres or mirror planes are emphasized by boxes

Crystal system	Point group	Space groups
Triclinic	1	P1
	$\bar{1}$	$P\bar{1}$
Monoclinic	2	P2, $P2_1$, C2
	m	Pm, Pc, Cm, Cc
	2/m	P2/m, $P2_1/m$, C2/m, P2/c, $P2_1/c$, C2/c
Orthorhombic	222	P222, $P222_1$, $P2_12_12$, $P2_12_12_1$, $C222_1$, C222, F222, I222, $I2_12_12_1$
	mm2	Pmm2, $Pmc2_1$, Pcc2, $Pma2_1$, $Pca2_1$, $Pnc2_1$, $Pmn2_1$, Pba2, $Pna2_1$, Pnn2, Cmm2, $Cmc2_1$, Ccc2, Amm2, Abm2, Ama2, Aba2, Fmm2, Fdd2, Imm2, Iba2, Ima2
	mmm	Pmmm, Pnnn, Pccm, Pban, Pmma, Pnna, Pmna, Pcca, Pbam, Pccn, Pbcm, Pnnm, Pmmn, Pbcn, Pbca, Pnma, Cmcm, Cmca, Cmmm, Cccm, Cmma, Ccca, Fmmm, Fddd, Immm, Ibam, Ibca, Imma
Tetragonal	4	P4, $P4_1$, $P4_2$, $P4_3$, I4, $I4_1$
	$\bar{4}$	$P\bar{4}$, $I\bar{4}$
	4/m	P4/m, $P4_2/m$, P4/n, $P4_2/n$, I4/m, $I4_1/a$
	422	P422, $P42_12$, $P4_122$, $P4_12_12$, $P4_222$, $P4_22_12$, $P4_322$, $P4_32_12$, I422, $I4_122$
	4mm	P4mm, P4bm, $P4_2cm$, $P4_2nm$, P4cc, P4nc, $P4_2mc$, $P4_2bc$, I4mm, I4cm, $I4_1md$, $I4_1cd$
	$\bar{4}$m	$P\bar{4}2m$, $P\bar{4}2c$, $P\bar{4}2_1m$, $P\bar{4}2_1c$, $P\bar{4}m2$, $P\bar{4}c2$, $P\bar{4}b2$, $P\bar{4}n2$, $I\bar{4}m2$, $I\bar{4}c2$, $I\bar{4}2m$, $I\bar{4}2d$
	4/mmm	P4/mmm, P4/mcc, P4/nbm, P4/nnc, P4/mbm, P4/mnc, P4/nmm, P4/ncc, $P4_2/mmc$, $P4_2/mcm$, $P4_2/nbc$, $P4_2/nnm$, $P4_2/mbc$, $P4_2/mnm$, $P4_2/nmc$, $P4_2/ncm$, I4/mmm, I4/mcm, $I4_1/amd$, $I4_1/acd$
Trigonal–hexagonal	3	P3, $P3_1$, $P3_2$, R3
	$\bar{3}$	$P\bar{3}$, $R\bar{3}$
	32	P312, P321, $P3_112$, $P3_121$, $P3_212$, $P3_221$, R32
	3m	P3m1, P31m, P3c1, P31c, R3m, R3c
	$\bar{3}$m	$P\bar{3}1m$, $P\bar{3}1c$, $P\bar{3}m1$, $P\bar{3}c1$, $R\bar{3}m$, $R\bar{3}c$
	6	P6, $P6_1$, $P6_5$, $P6_3$, $P6_2$, $P6_4$
	$\bar{6}$	$P\bar{6}$
	6/m	P6/m, $P6_3/m$
	622	P622, $P6_122$, $P6_522$, $P6_222$, $P6_422$, $P6_322$
	6mm	P6mm, P6cc, $P6_3cm$, $P6_3mc$
	$\bar{6}$m	$P\bar{6}m2$, $P\bar{6}c2$, $P\bar{6}2m$, $P\bar{6}2c$
	6/mmm	P6/mmm, P6/mcc, $P6_3/mcm$, $P6_3/mmc$
Cubic	23	P23, F23, I23, $P2_13$, $I2_13$
	m$\bar{3}$	Pm$\bar{3}$, Pn$\bar{3}$, Fm$\bar{3}$, Fd$\bar{3}$, Im$\bar{3}$, Pa$\bar{3}$, Ia$\bar{3}$
	432	P432, $P4_232$, F432, $F4_132$, I432, $P4_332$, $P4_132$, $I4_132$
	$\bar{4}$3m	$P\bar{4}3m$, $F\bar{4}3m$, $I\bar{4}3m$, $P\bar{4}3n$, $F\bar{4}3c$, $I\bar{4}3d$
	m$\bar{3}$m	Pm$\bar{3}$m, Pn$\bar{3}$n, Pm$\bar{3}$n, Pn$\bar{3}$m, Fm$\bar{3}$m, Fm$\bar{3}$c, Fd$\bar{3}$m, Fd$\bar{3}$c, Im$\bar{3}$m, Ia$\bar{3}$d

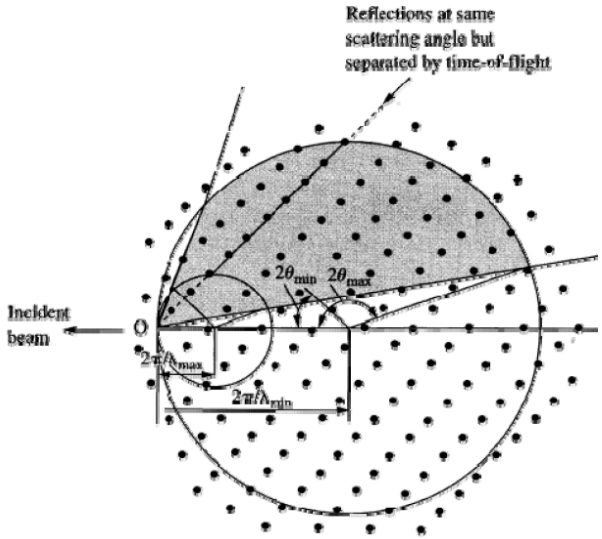
4.3 Diffraction: Monochromatic vs. TOF vs. Laue

Monochromatic beam



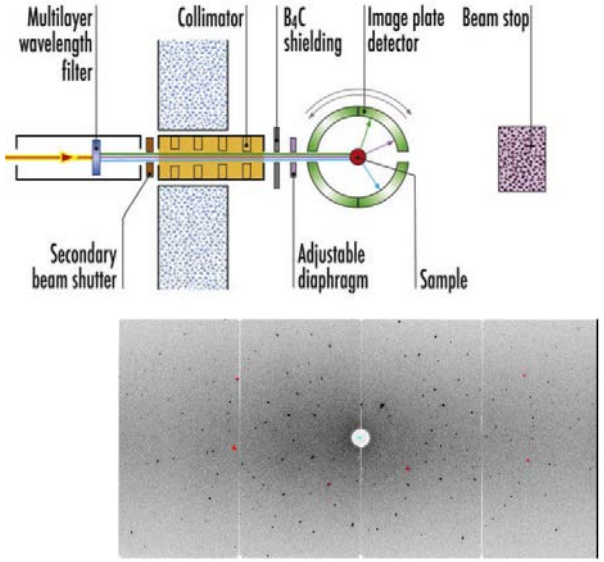
- Ewald construction
- Less intensity
- Rocking curve gives intensity of Bragg peak
- Clean data

Time-of-flight (TOF)



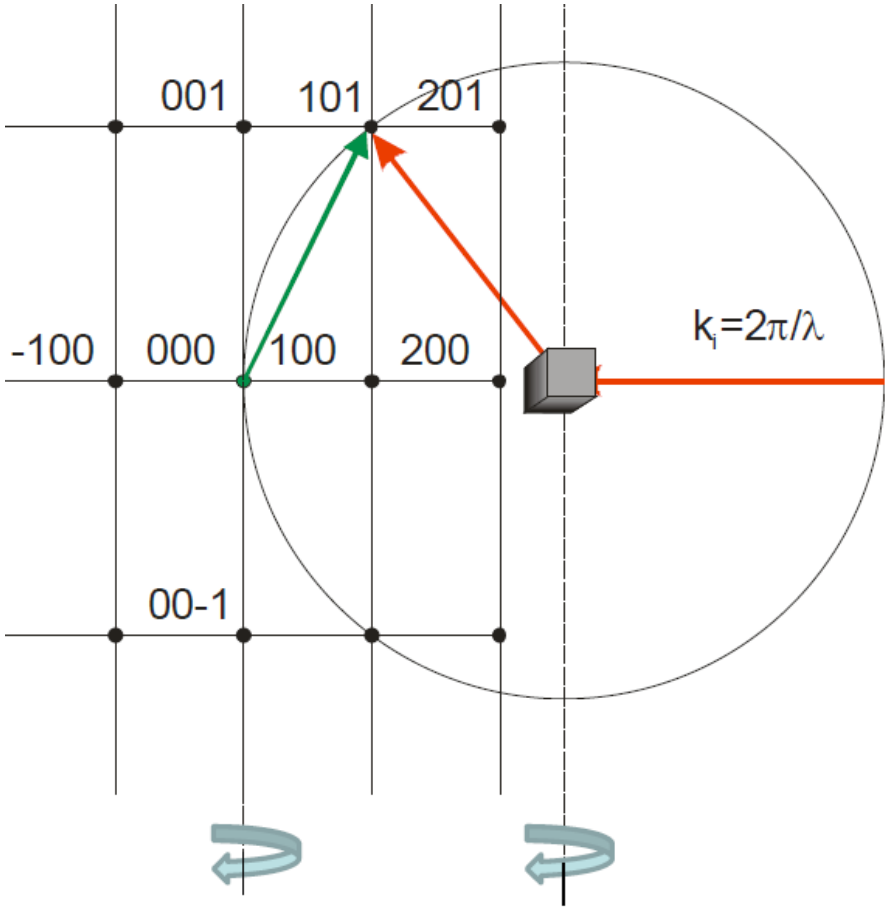
- Ewald construction for each wavelength in the beam
- Rocking curve distributed in time and detector
- Waste less neutrons

Laue (polychromatic beam)



- Essentially white beam
- More Bragg peaks (not stronger)
- Hard to get intensities
- Large background

4.3 Diffraction: Ewald construction for single crystal diffraction

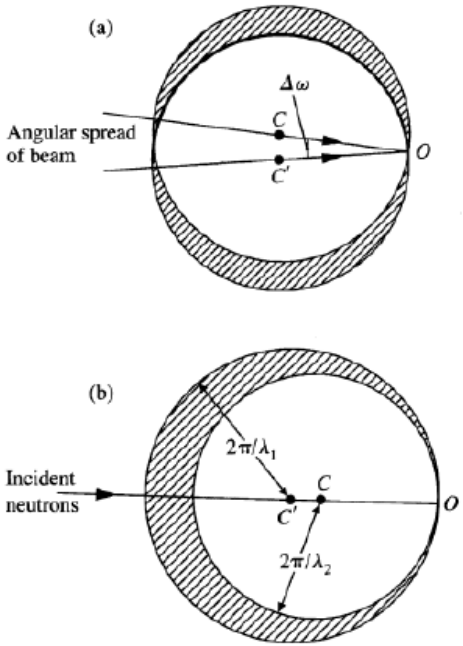


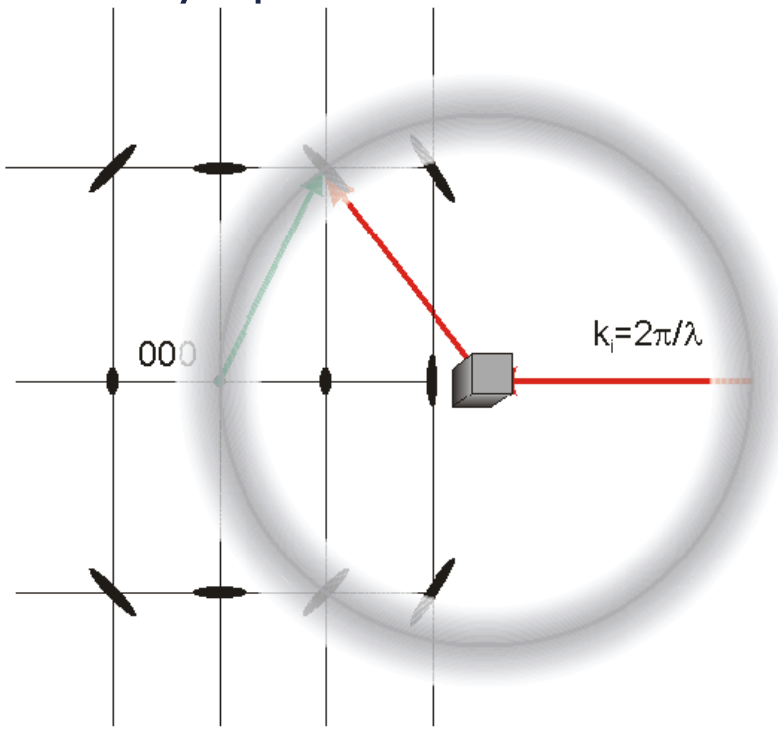
Ewald construction:

- Sphere around center of crystal (in real space)
- Origin of reciprocal space on transmitted beam at the edge of Ewald sphere
- Rotation of crystal (real space) corresponds to a rotation of reciprocal space

4.3 Diffraction: Ewald construction including resolution effects

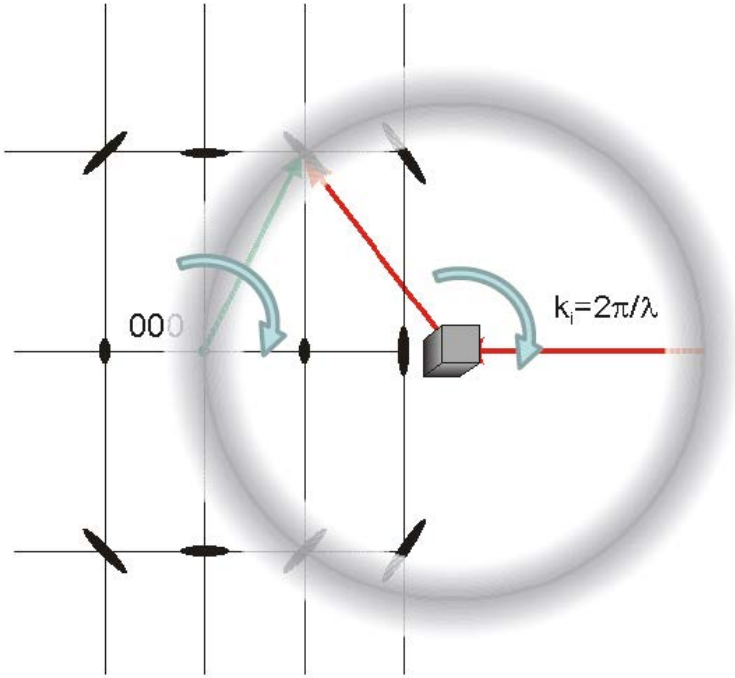
- Mosaic spread of the sample (no perfect crystal)
- Finite spread of incoming beam (wavelength spread)
- Finite collimation of the incoming beam
  - Ewald construction for real samples: Fuzzy sphere

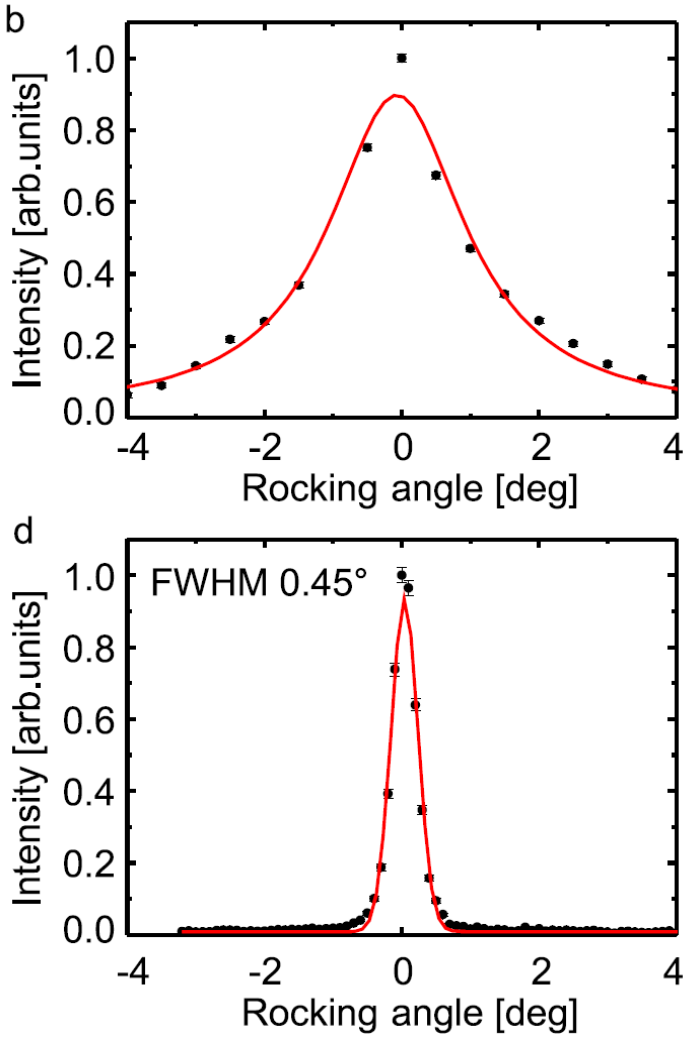




4.3 Diffraction: Crystal rotation method

- Solution: Measurement of **integrated intensity** and not **peak intensity**
- Fuzziness integrated out
  - Rocking scan

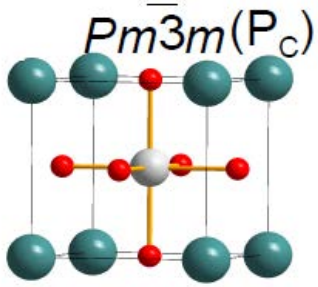




4.3 Diffraction: Example I – Powder Diffraction on Ferroelectrica

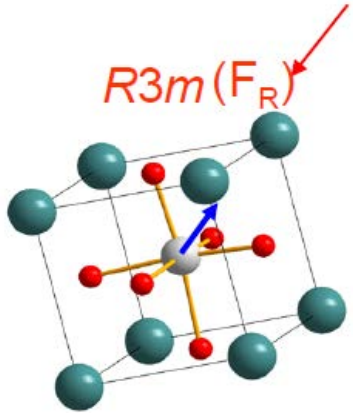
Ferroelectricity: Standard system $PbZr_{1-x}Ti_xO_3$

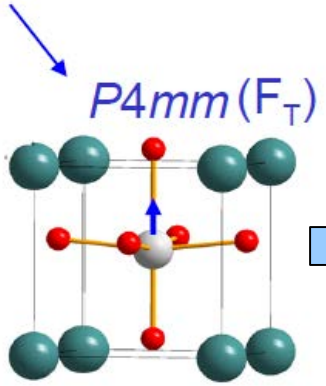
Pb^{2+}
Zr^{4+}/ Ti^{4+}
O^{2-}



→ Centrosymmetric space group

No polar axis! No ferrolelectricity! Center for positive and negative charge coincide





→ Non-centrosymmetric space group

polar axis [111] polar axis [001]

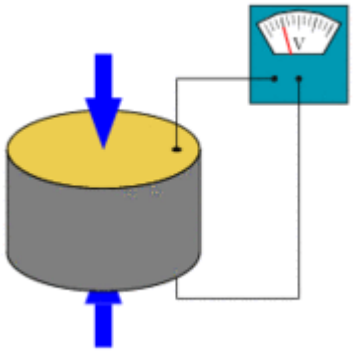
Displacement of Zr/Ti atom by 5%

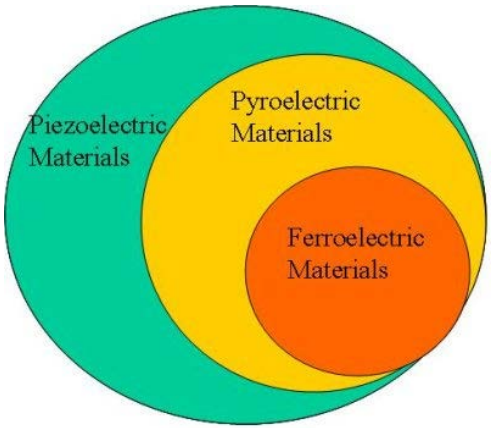
Dipole in the unit cell, finite polarization

$$\vec{P} = \frac{1}{V}\sum_i q_i \vec{r}_i$$

4.3 Diffraction: Example I – Powder Diffraction on Ferroelectrica

Ferroelectricity

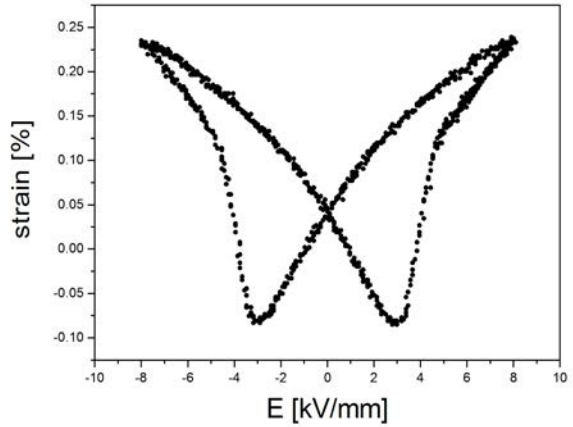




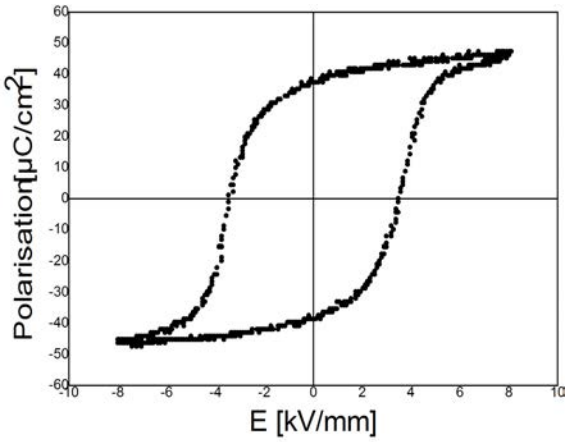
Piezoelectrics
stress → el. polarisation
E-field → strain

Pyroelectrics
change in polarization with temperature

Ferroelectrics
polarization can be switched in electric field
strain and polarisation hysteresis



strain hysteresis of 94%
$Bi_{1/2}Na_{1/2}TiO_3$ - 5% $BaTiO_3$- 1%
$K_{1/2}Na_{1/2}NbO_3$



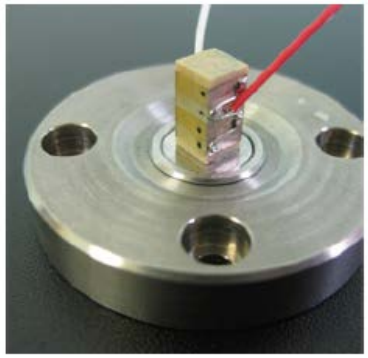
polarisation hysteresis of 94%
$Bi_{1/2}Na_{1/2}TiO_3$ - 5% $BaTiO_3$- 1%
$K_{1/2}Na_{1/2}NbO_3$

4.3 Diffraction: Example I – Powder Diffraction on Ferroelectrica

Applications of Piezo- , Pyro and Ferroelectrics

Actuators, sensors, transducers:

Fuel injectors, ultrasound transducers, speakers, strain gauges, ink jet printers, piezo motors...



Electronic applications:

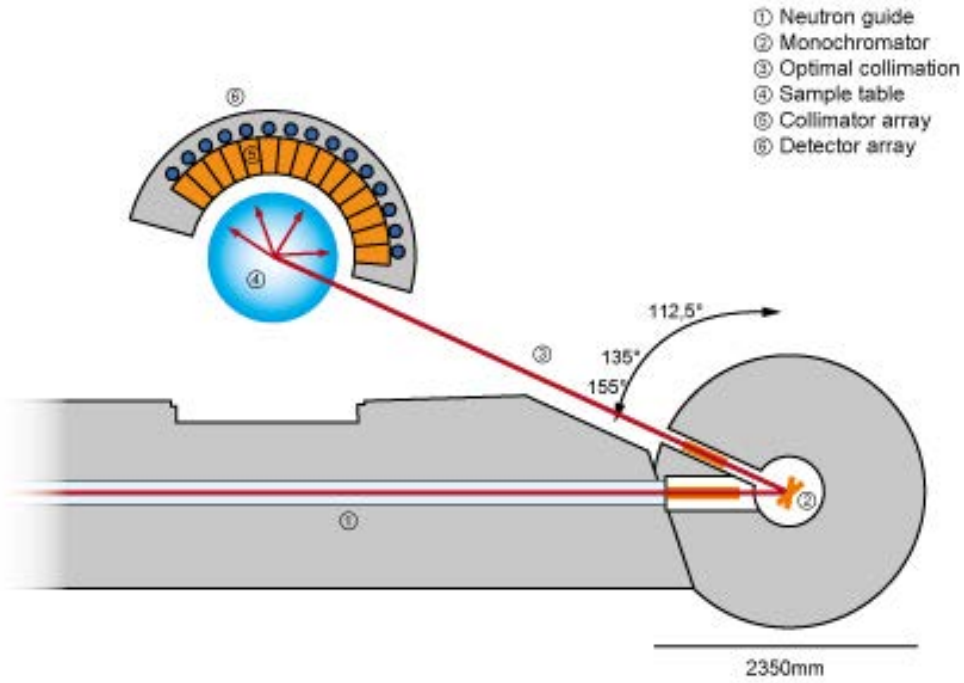
Capacitors, ferroelectric RAM...

- Research: Lead-free alternative to standard system $PbZr_{1-x}Ti_xO_3$
- Crystallographic structure and symmetry matters!

4.3 Diffraction: Example I – Powder Diffraction on Ferroelectrica

Lead free piezoelectric ceramic $Bi_{1/2}Na_{1/2}TiO_3$

Powder difffraction + structural refinement at SPODI @ MLZ

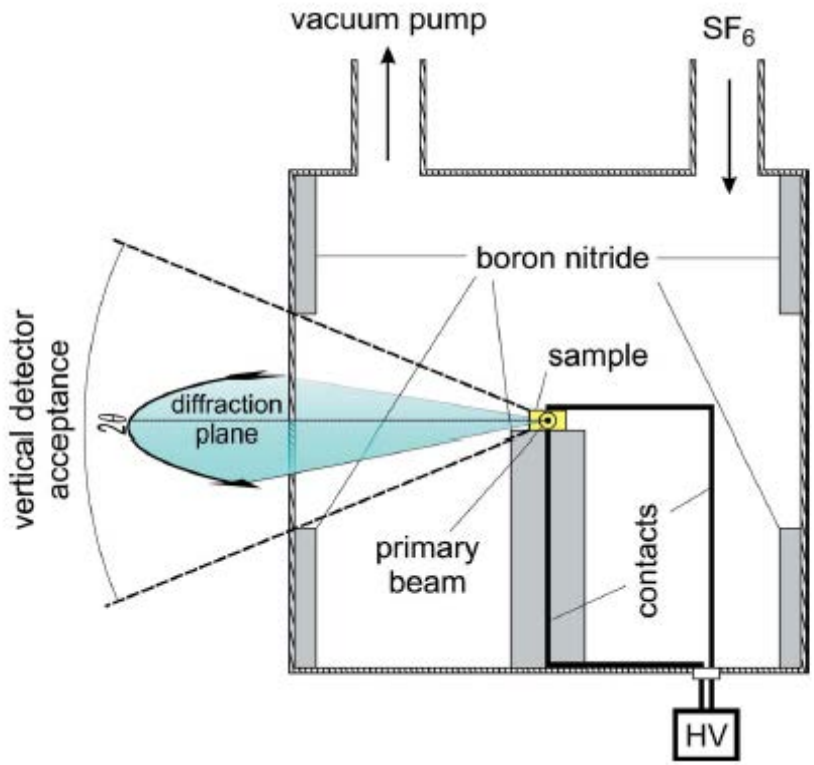


4.3 Diffraction: Example I – Powder Diffraction on Ferroelectrica

Lead free piezoelectric ceramic $Bi_{1/2}Na_{1/2}TiO_3$

➡ Strong recoverable strain of 0.45%
comparable to lead compounds

➡ In situ diffraction under E-field



4.3 Diffraction: Example I – Powder Diffraction on Ferroelectrica

Lead free piezoelectric ceramic $Bi_{1/2}Na_{1/2}TiO_3$

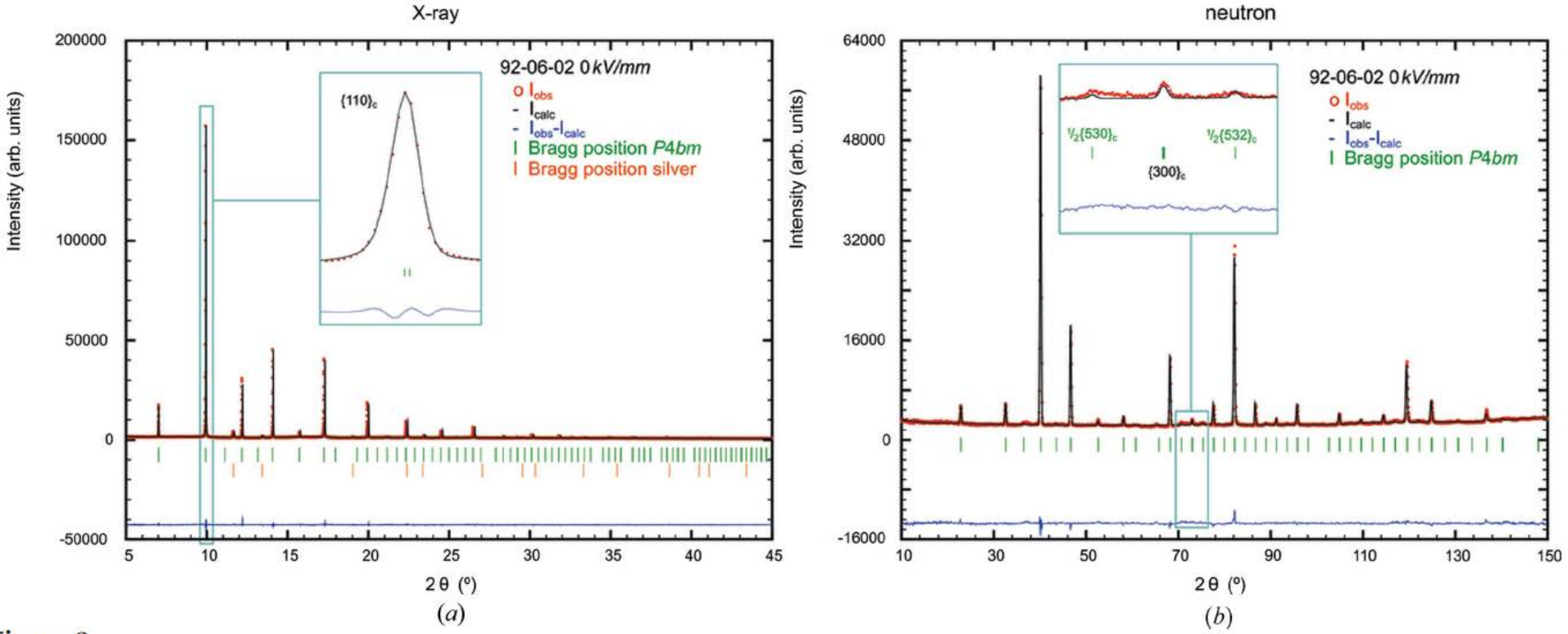
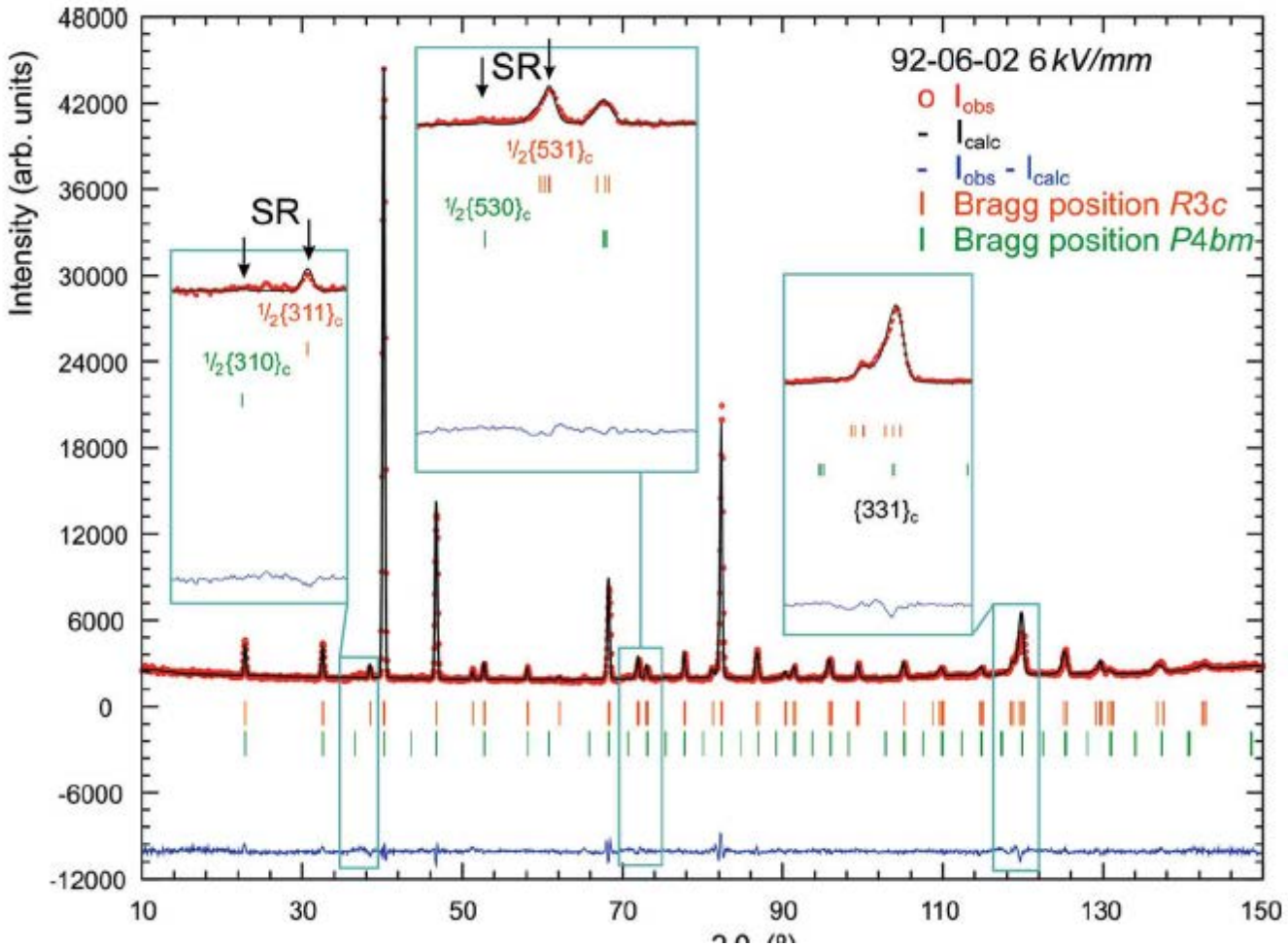


Figure 2
Combined Rietveld refinement with (*a*) X-ray diffraction and (*b*) neutron diffraction data. The insets show the (*a*) $\{110\}_c$ reflection and (*b*) broadened superstructure reflections.

Combination of X-ray and neutron data, Rietveld refinement

4.3 Diffraction: Example I – Powder Diffraction on Ferroelectrica

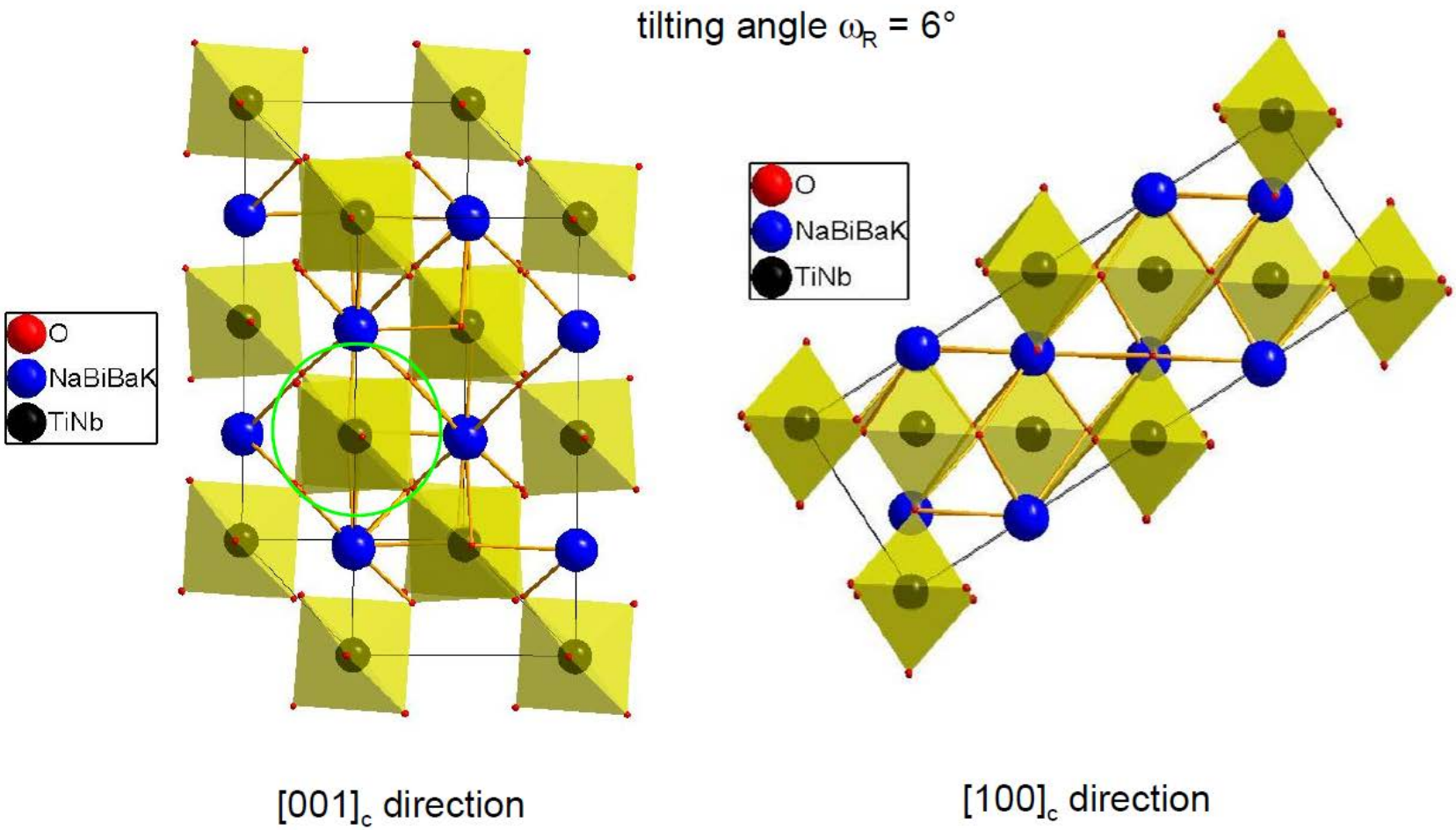
Lead free piezoelectric ceramic $Bi_{1/2}Na_{1/2}TiO_3$



Weak superstructure reflections (oxygen) can be resolved only by neutrons!

4.3 Diffraction: Example I – Powder Diffraction on Ferroelectrica

Lead free piezoelectric ceramic $Bi_{1/2}Na_{1/2}TiO_3$



Weak superstructure reflections (oxygen) can be resolved only by neutrons!

4.3 Diffraction: Example I – Powder Diffraction on Ferroelectrica

Lead free piezoelectric ceramic $Bi_{1/2}Na_{1/2}TiO_3$

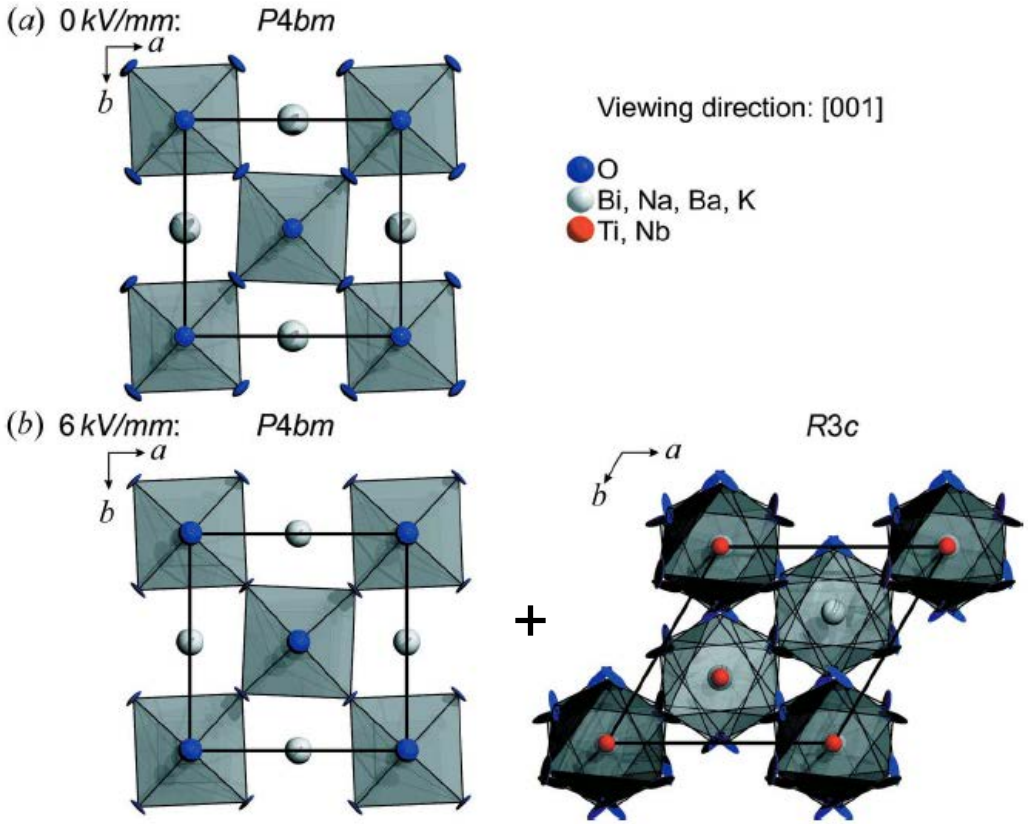


Figure 3
Illustration of the unit cell with ADPs for the O atoms of (*a*) *P4bm* in the unpoled state and (*b*) *P4bm* and *R3c* at 6 kV mm^{-1}.

Table 3
Structural parameters.

0 kV mm^{-1}, *P4bm*	
a (Å)	5.52166 (3)
c (Å)	3.90541 (4)
V (Å^3)	119.0712 (16)
V_c (Å^3)	59.54
Tetragonal distortion (%)	0.0258 (16)
ω_t (°)	2.25 (11)
P_s (μC cm^{-2})	4 (2)
R_B (ND/XRD)	7.92/7.48
χ^2 (ND/XRD)	3.51/1.14
6 kV mm^{-1}, *P4bm*	
a (Å)	5.51020 (10)
c (Å)	3.9186 (4)
V (Å^3)	118.977 (12)
V_c (Å^3)	59.49
Tetragonal distortion (%)	0.572 (12)
P (μC cm^{-2})	5 (4)
Phase fraction (%)	29.13 (16)
ω_t (°)	2.39 (12)
R_B (ND)	7.58
χ^2 (ND)	2.58
6 kV mm^{-1}, *R3c*	
a (Å)	5.50818 (9)
c (Å)	13.5286 (10)
V (Å^3)	355.47 (3)
V_c (Å^3)	59.24
α_r (°)	89.90
Rhombohedral distortion (%)	0.269 (9)
P (μC cm^{-2})	11 (6)
Phase fraction (%)	70.87 (16)
s	0.007 (2)
t	0.004 (3)
d	0.0009 (5)
e	0.0154 (8)
ω_r (°)	6.106 (6)
$\zeta \times 10^2$	−0.75 (7)
R_B (ND)	5.53
χ^2 (ND)	2.58

Reversible structural phase transition under electrical field is the cause for lage ferroelectric strain!

4.3 Diffraction: Example I – Powder Diffraction on Ferroelectrica

Lead free piezoelectric ceramic $Bi_{1/2}Na_{1/2}TiO_3$

0 kV/mm

purely tetragonal *P4bm*

- $\omega_T = 2.53°$, $a^0a^0c^+$
- $P_T \approx 4\ \mu C/cm^2$
- a = 5.5249(1) Å, c = 3.9068(2) Å
- a/c =1.000 √2

R3c = ferroelectric acitive phase

observed at 2 compositions: 94-5-1, 92-6-2

M. Hinterstein et al., J. Appl. Cryst. 43, 1314-1321 (2010)
L. A. Schmitt et al., J Mater Sci 46:4368–4376 (2011)

3 kV/mm

66 % tetragonal phase *P4bm*

- $\omega_T = 2.7°$, $a^0a^0c^+$
- $P_T \approx 5\ \mu C/cm^2$
- a = 5.5186(1)Å, c = 3.9009(2) Å
- a/c = 1.0004 √2

34 % rhombohedral phase *R3c*

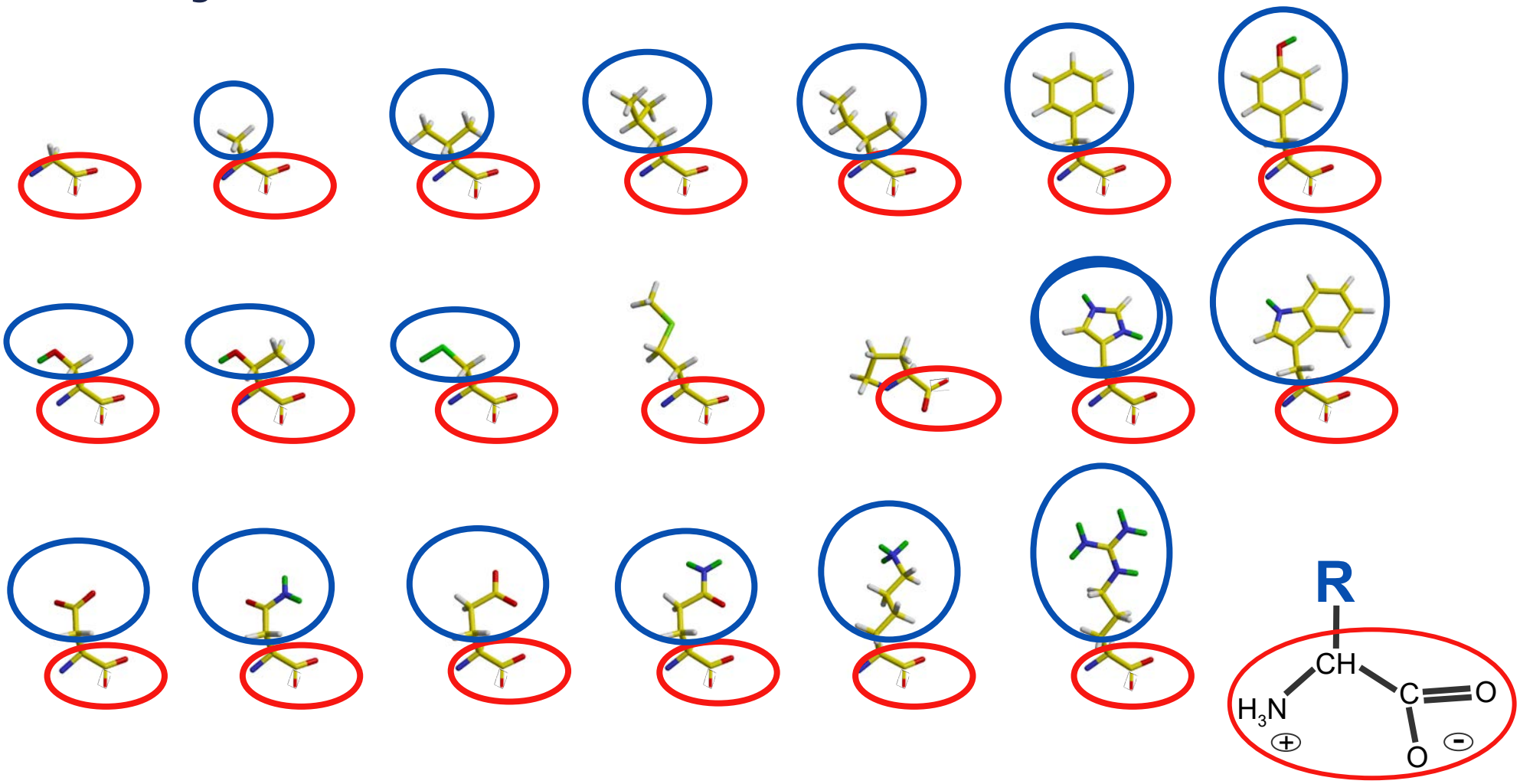
- $\omega_R = 8.7°$, $a^-a^-a^-$
- $P_R \approx 40\ \mu C/cm^2$
- a = 5.5025(1), c = 13.5929(1)

Reversible structural phase transition under electrical field is the cause for lage ferroelectric strain!

4.3 Diffraction: Example II – Protein Crystallography

Protein Structure:

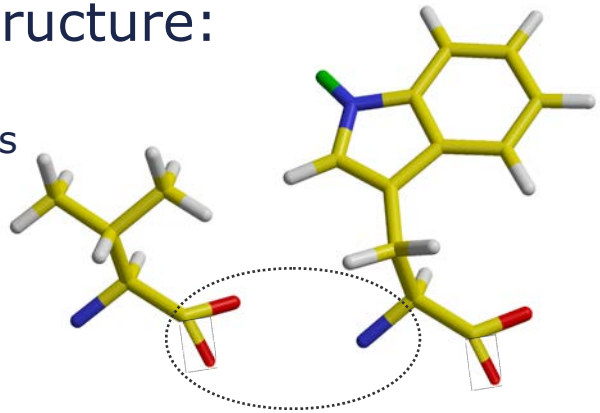
Building blocks 20 α-L amino acids



4.3 Diffraction: Example II – Protein Crystallography

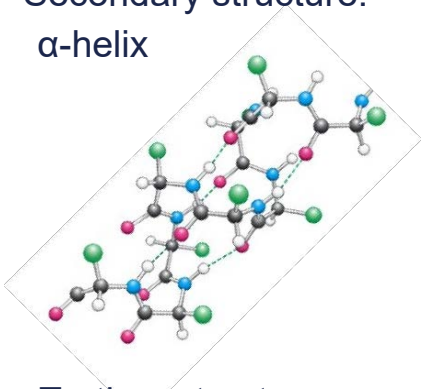
Protein Structure:

Building blocks:
20 α-L amino acids

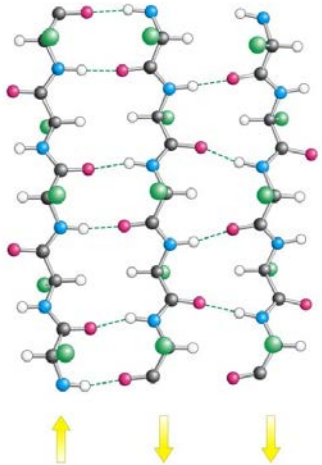


Secondary structure:

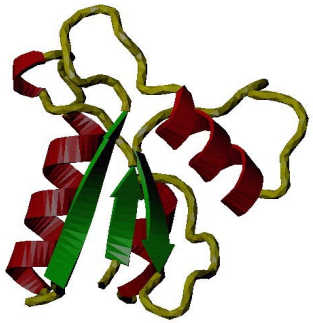
α-helix



β-sheet



Tertiary structure:



Interactions:

Backbone:

→ Covalent bonds

Secondary structure:

→ H-bonds

Tertiary structure:

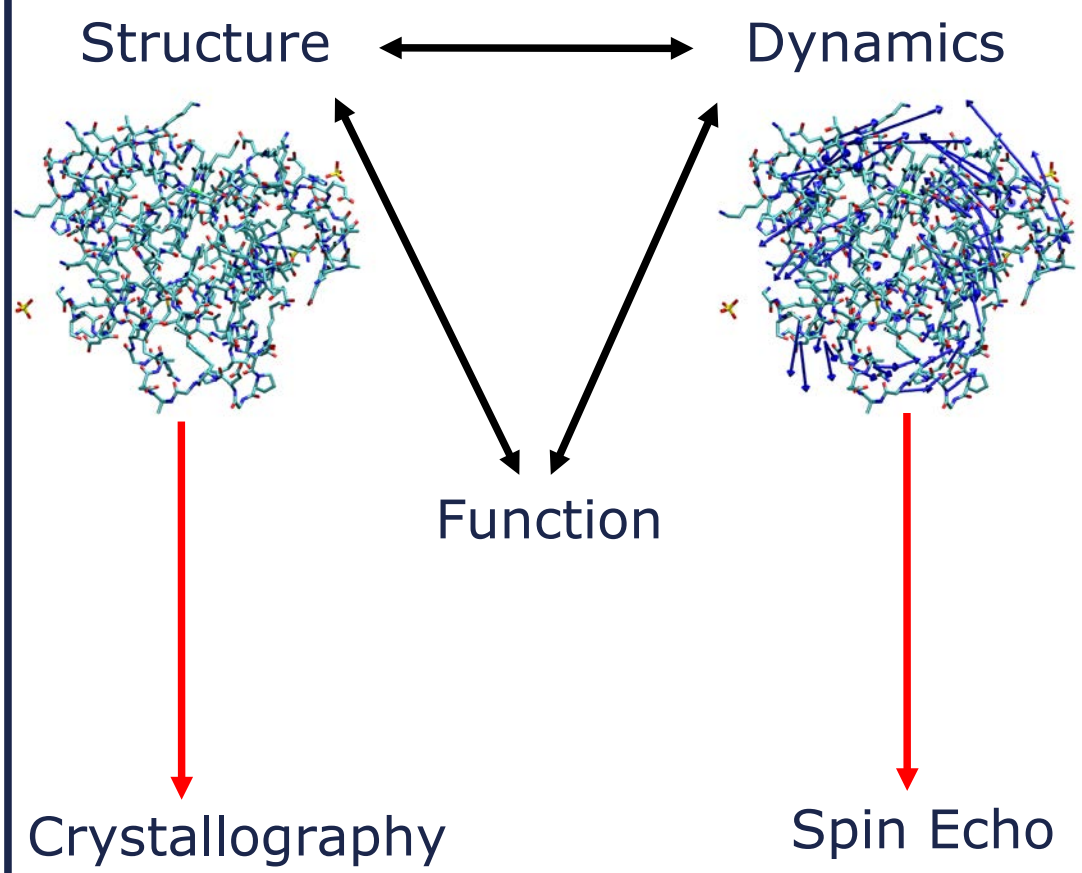
→
Hydrophobic interaction
Electrostatic interaction
Van-der-Waals interaction
H-bonds
Covalent bonds (S-S)

4.3 Diffraction: Example II – Protein Crystallography

Protein function:

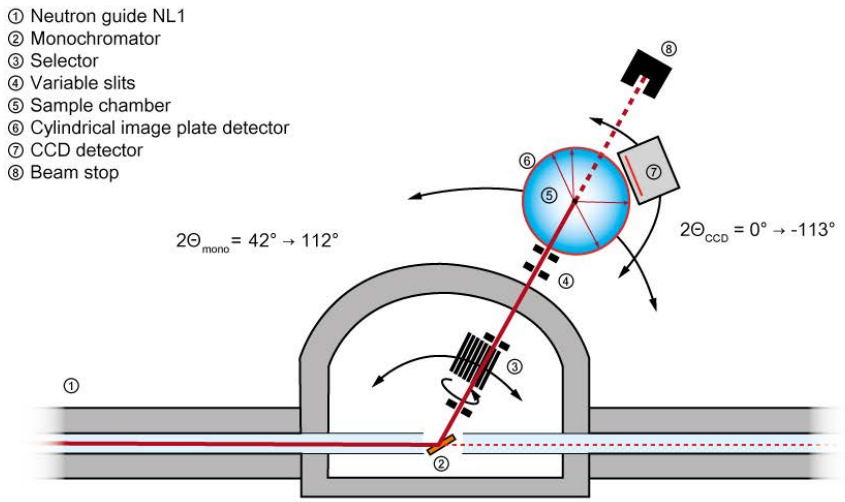
- Enzymes: catalysis of nearly all chemical reactions in the cell
- Coordinated motion: muscle proteins
- Immune system: antibodies
- Receptors, generation and transmission of nerve impulses
- Transport and storage
- Mechanical support

Molecular biophysics:



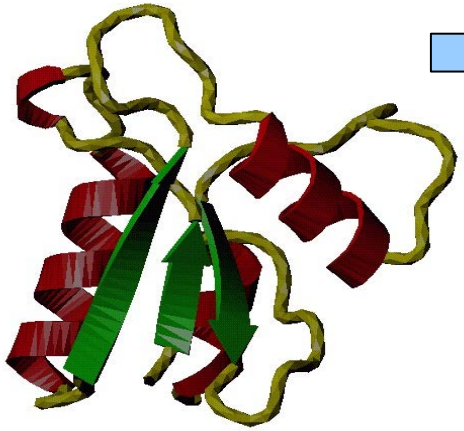
4.3 Diffraction: Example II – Protein Crystallography

Instrument Biodiff@MLZ



Samples:

- <u>Protein crystals</u>
  20.000 atoms per unit cell
  Sample volume ~ 1mm^3
  Deuterated samples
  Produced by genetically engineered E-coli / yeast

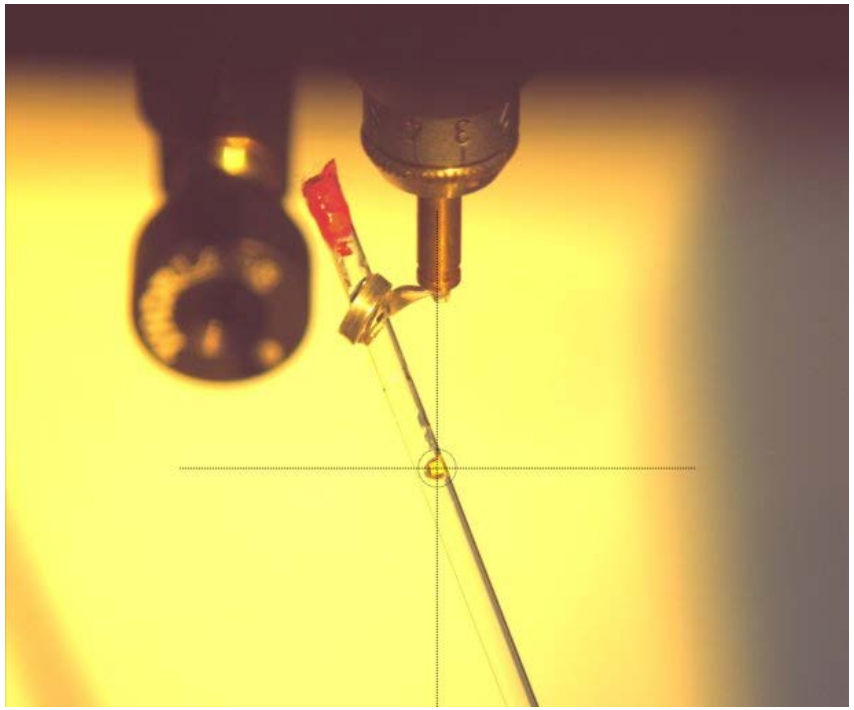


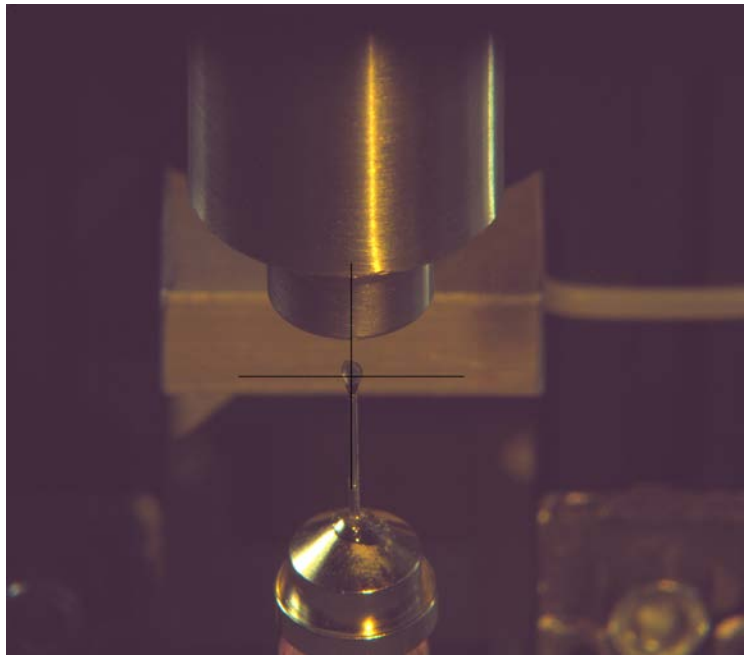
Challenges:

- Small sample volume vs. big unit cell
  Crystals sensitive to drying (5s!!)
  Some proteins don´t crystallize (NMR)

4.3 Diffraction: Example II – Protein Crystallography

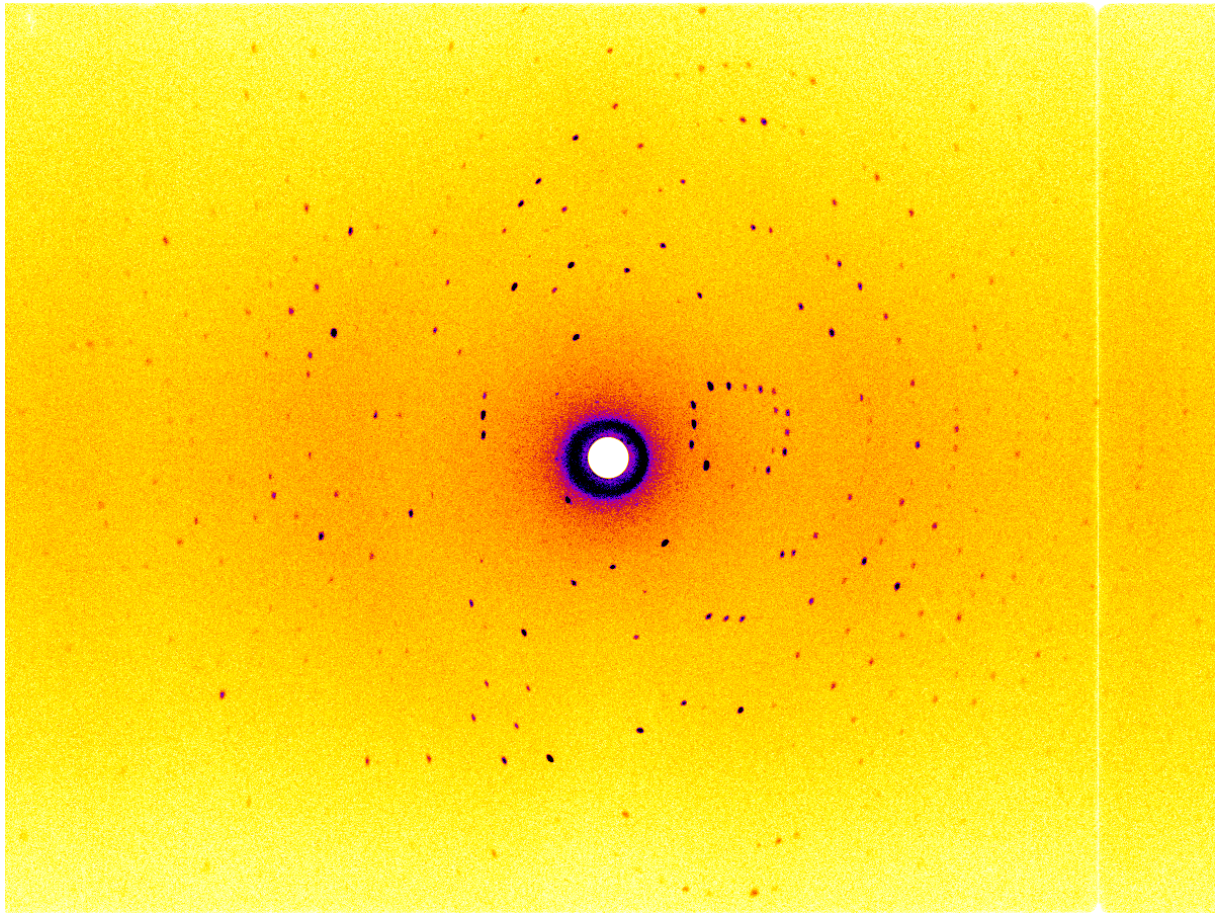
Some samples:





4.3 Diffraction: Example II – Protein Crystallography

Typical data: Rocking scan gives integrated intensity for refinement



Symmetry of crystal

↓

Width of rocking necessary to capture all inequivalent reflections

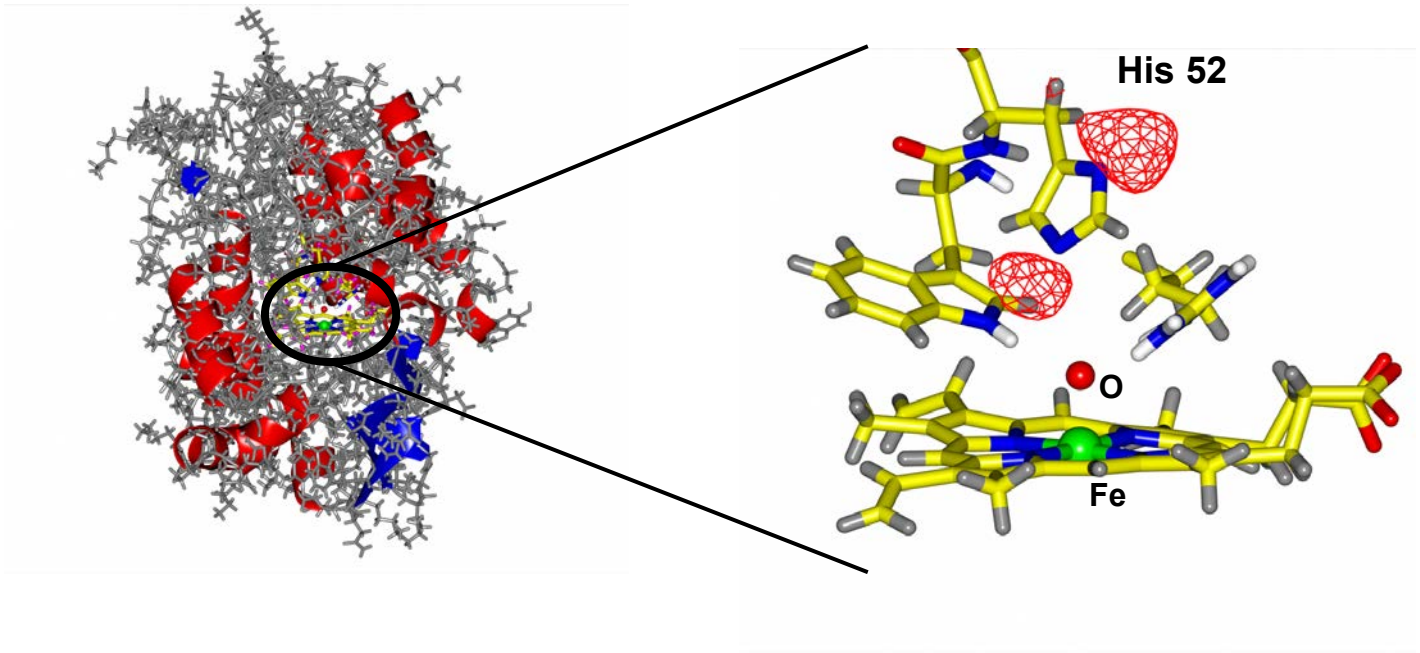
Compute the expected position of the peaks:

↓

Integrating a box around that position saves computing time

4.3 Diffraction: Example II – Protein Crystallography

Structural analysis „Intermediate state I" of the Cytochrome-c-Peroxidase at 100K
X-ray – complicated due to the reduction of the Fe! (Photolysis of H2O yields e-)



- The oxygen bound to the Fe is not protonated!
- Surprising: Amino acid HIS 52 is doubly protonated
- Reaction mechanism has to be reconsidered

Casadei et al. Science **345**, 193 (2014)

4.3 Diffraction: Example II – Protein Crystallography

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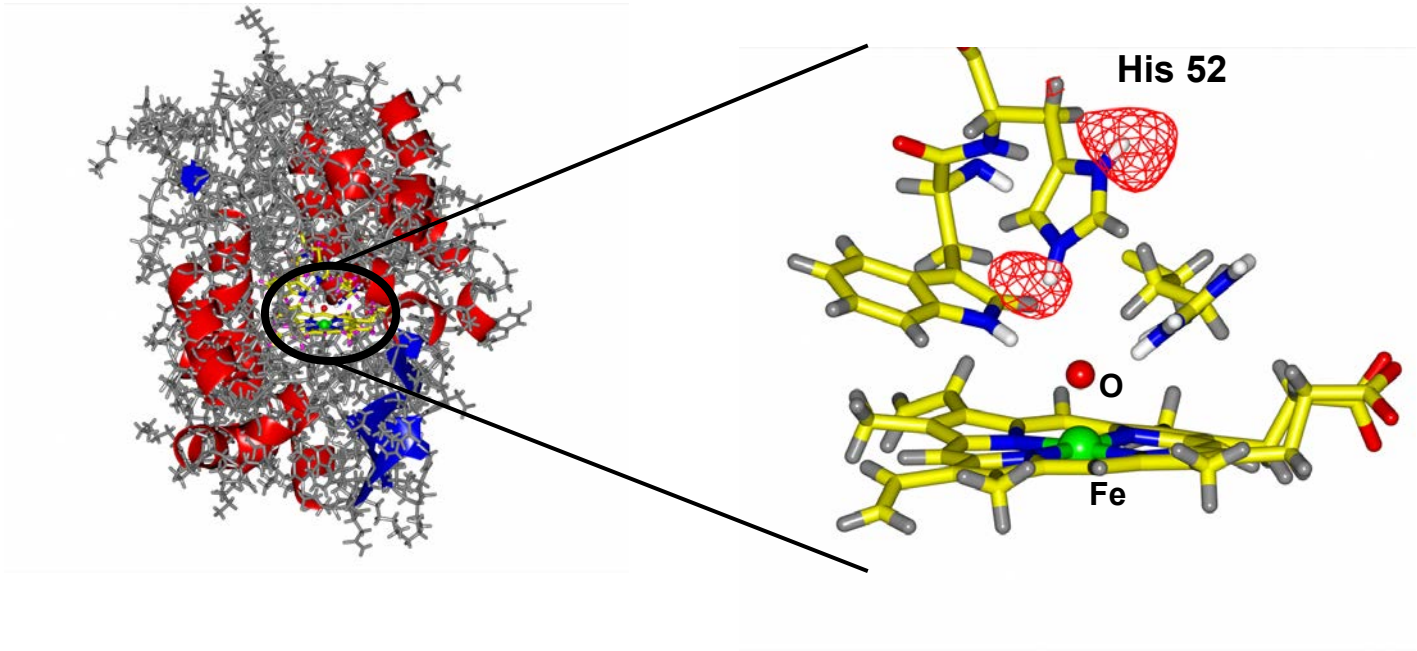

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