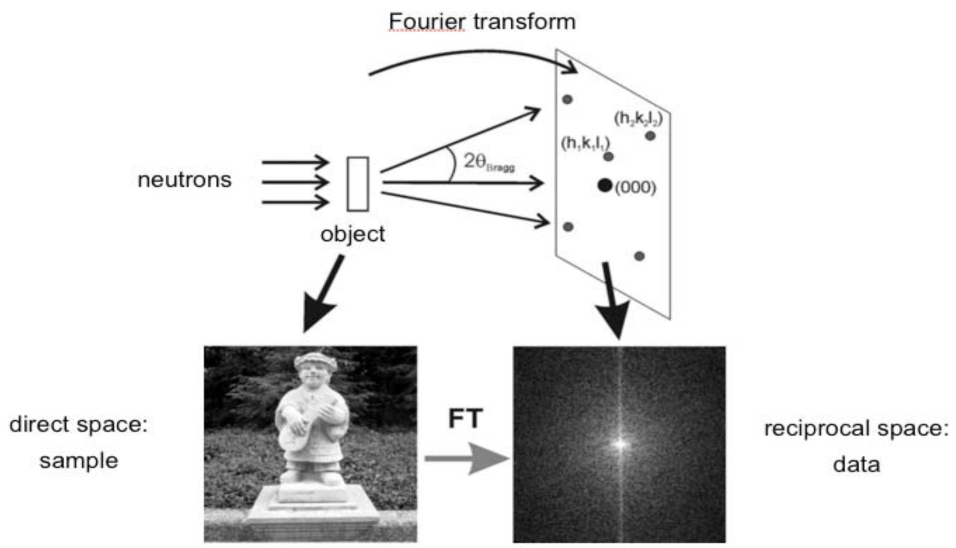
Space, reciprocal space and diffraction

Andrew S. Wills
a.s.wills@ucl.ac.uk

UCL Chemistry
The London Centre for Nanotechnology

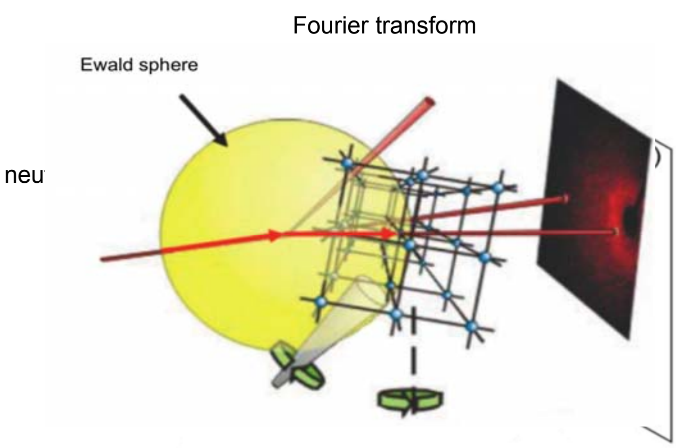
Part I – Symmetry, space and reciprocal space

Reciprocality – diffraction as a Fourier transform



3

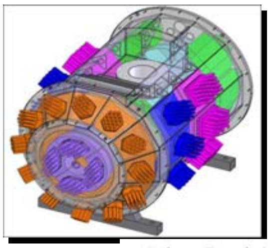
Reciprocality - overview of this section



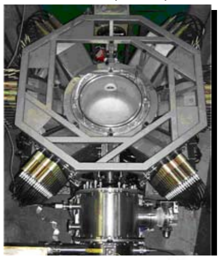
4

Thinking about experimental setups

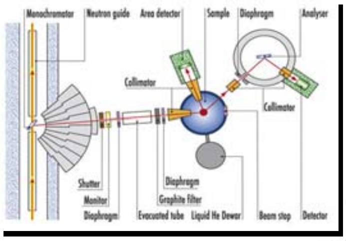
POLARIS (ISIS)



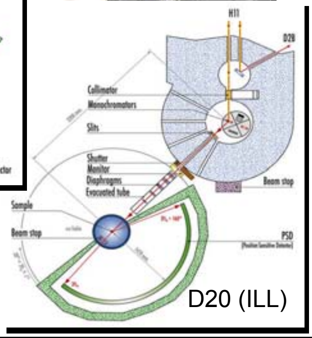
SXD (ISIS)



GEM (ISIS)



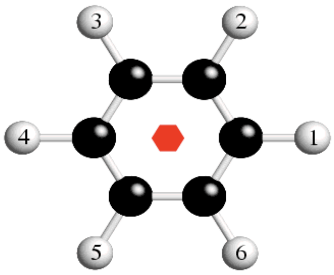
D10 (ILL)

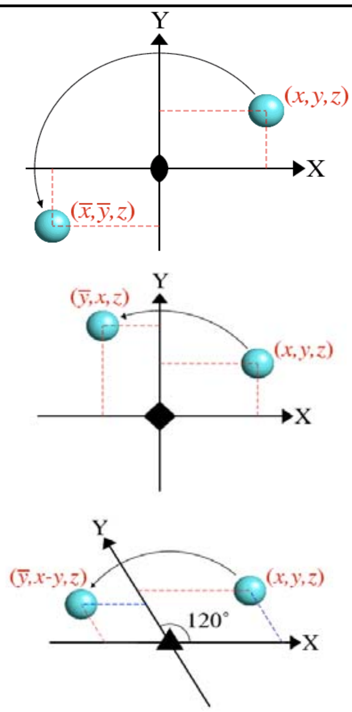


D20 (ILL)

1. Direct space - symmetries, lattices and unit cells

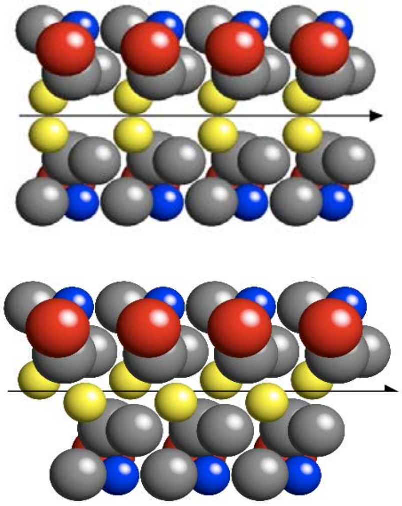
Symmetry operations - rotations





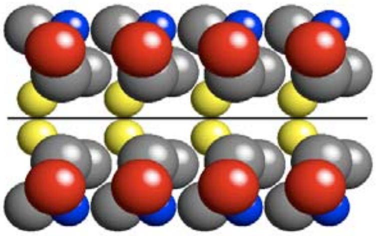
- rotation axis of order *n* is a line in space about which an object may be rotated anticlockwise by 360°/*n*

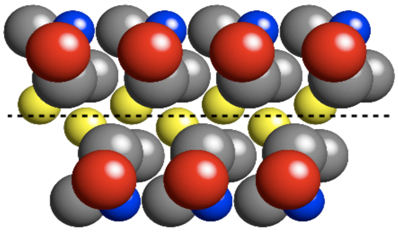
Symmetry operations - screw axes and glide planes



8

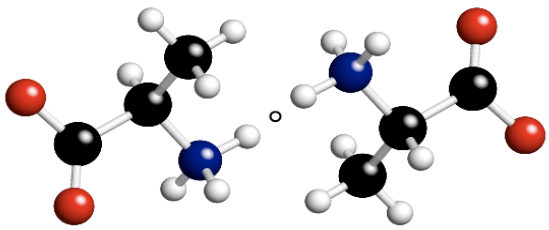
Symmetry operations - screw axes and glide planes





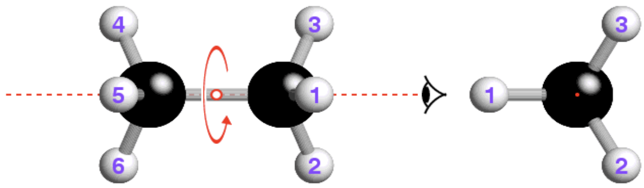
9

Symmetry operations - inversion symmetry



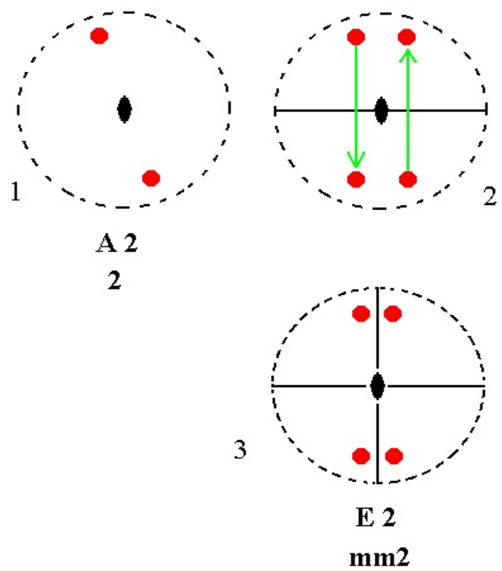
10

Symmetry operations - compound operations



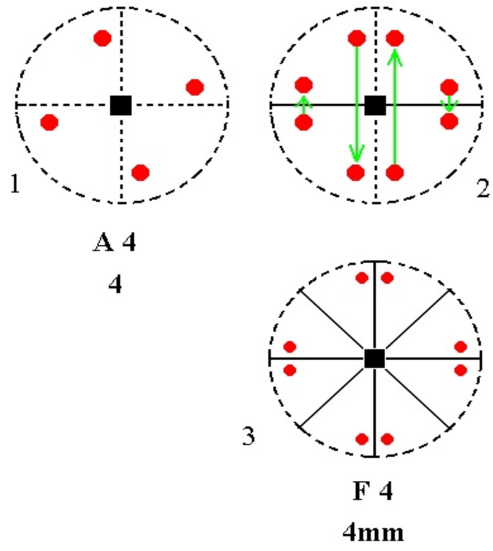
11

Symmetry operations – working together



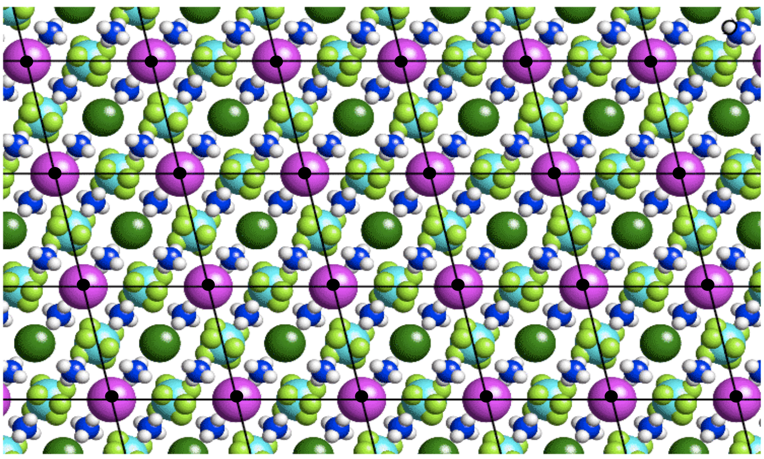
12

Symmetry operations – working together



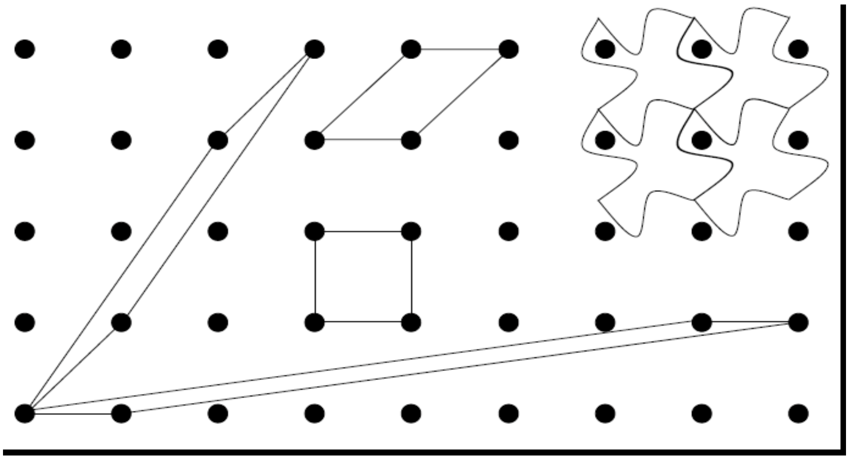
13

Crystal lattices

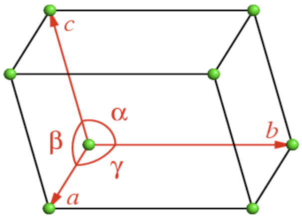


14

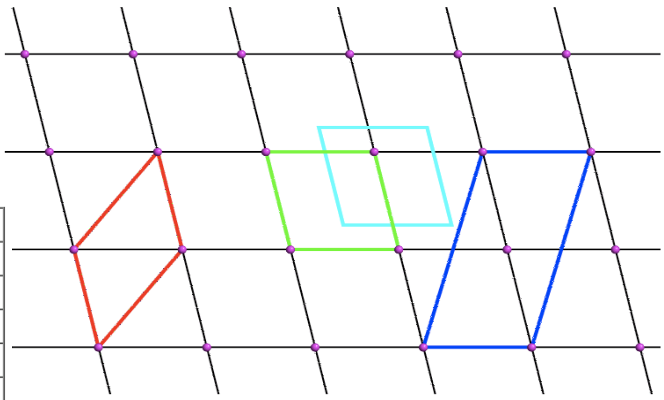
Unit cells



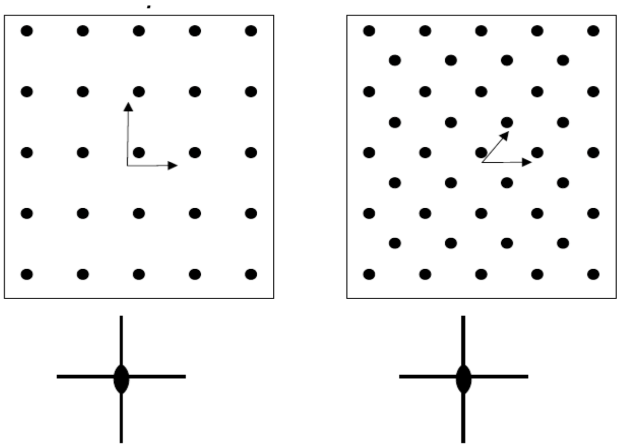
Unit cells



Centring Type	Symbol	Multiplicity
Primitive - no centring	P	1
A-face centred	A	2
B-face centred	B	2
C-face centred	C	2
All-face centred	F	4
Body centred	I	2
Rhombohedrally centred	R	3

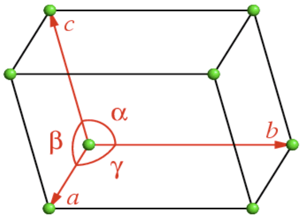


Primitive and centred



17

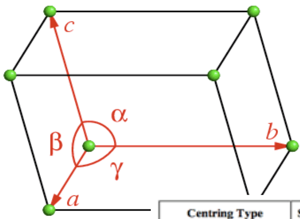
Unit cells - seven crystal systems



Crystal System	Characteristic Symmetry	Syngony	Unit-Cell Parameters	Independent Parameters
Triclinic	1× 1-fold	-1	$a \neq b \neq c$; $\alpha \neq \beta \neq \gamma$	6
Monoclinic	1× 2-fold	2/*m*	$a \neq b \neq c$; $\alpha = \gamma = 90°$; $\beta \neq 90°$	4
Orthorhombic	3× 2-fold	*mmm*	$a \neq b \neq c$; $\alpha = \beta = \gamma = 90°$	3
Tetragonal	1× 4-fold	4/*mmm*	$a = b \neq c$; $\alpha = \beta = \gamma = 90°$	2
Trigonal (see note)	1× 3-fold	6/*mmm* (P) -3*m* (R)	$a = b \neq c$; $\alpha = \beta = 90°$; $\gamma = 120°$	2
Hexagonal	1× 6-fold	6/*mmm*	$a = b \neq c$; $\alpha = \beta = 90°$; $\gamma = 120°$	2
Cubic	4× 3-fold	*m*-3*m*	$a = b = c$; $\alpha = \beta = \gamma = 90°$	1

18

Unit cells - Bravais lattices



Centring Type	Symbol	Multiplicity
Primitive - no centring	P	1
A-face centred	A	2
B-face centred	B	2
C-face centred	C	2
All-face centred	F	4
Body centred	I	2
Rhombohedrally centred	R	3

Crystal System	Characteristic Symmetry	Syngony	Unit-Cell Parameters	Independent Parameters
Triclinic	1× 1-fold	-1	$a \neq b \neq c$; $\alpha \neq \beta \neq \gamma$	6
Monoclinic	1× 2-fold	2/m	$a \neq b \neq c$; $\alpha = \gamma = 90°$; $\beta \neq 90°$	4
Orthorhombic	3× 2-fold	mmm	$a \neq b \neq c$; $\alpha = \beta = \gamma = 90°$	3
Tetragonal	1× 4-fold	4/mmm	$a = b \neq c$; $\alpha = \beta = \gamma = 90°$	2
Trigonal (see note)	1× 3-fold	6/mmm (P) -3m (R)	$a = b \neq c$; $\alpha = \beta = 90°$; $\gamma = 120°$	2
Hexagonal	1× 6-fold	6/mmm	$a = b \neq c$; $\alpha = \beta = 90°$; $\gamma = 120°$	2
Cubic	4× 3-fold	m-3m	$a = b = c$; $\alpha = \beta = \gamma = 90°$	1

No.	Crystal System	Lattice Centring	Lattice Symbol
1	Triclinic	*P*	aP
2	Monoclinic	*P*	mP
3	"	*C*	mC
4	Orthorhombic	*P*	oP
5	"	*C*	oC
6	"	*F*	oF
7	"	*I*	oI
8	Tetragonal	*P*	tP
9	"	*I*	tI
10	Trigonal	*R*	hR
11	Hexagonal & Trigonal	*P*	hP
12	Cubic	*P*	cP
13	"	*F*	cF
14	"	*I*	cI

19

Unit cells - space groups

- Combining the 14 Bravais lattices with all the consistent combinations of rotational and translational operations creates the 230 crystallographic space groups

- http://it.iucr.org/

International Tables for Crystallography

ISBN: 978-1-4020-4969-9 doi: 10.1107/97809553602060000001

This is the home page for **International Tables**, the definitive resource and reference work for crystallography. The series consists of the following volumes:

Volume A Space-group symmetry
| Contents | Sample pages | Indexes |

Volume A1 Symmetry relations between space groups
| Contents | Sample pages | Indexes |

Volume B Reciprocal space
| Contents | Sample pages | Indexes |

Volume C Mathematical, physical and chemical tables
| Contents | Sample pages | Indexes |

Volume D Physical properties of crystals
| Contents | Sample pages | Indexes |

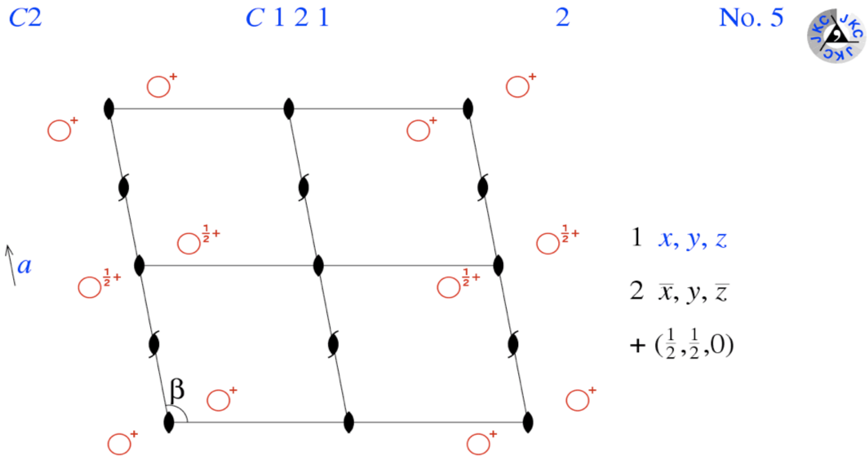
Volume E Subperiodic groups
| Contents | Sample pages | Indexes |

Volume F Crystallography of biological macromolecules
| Contents | Sample pages | Indexes |

Volume G Definition and exchange of crystallographic data
| Contents | Sample pages | Indexes |

20

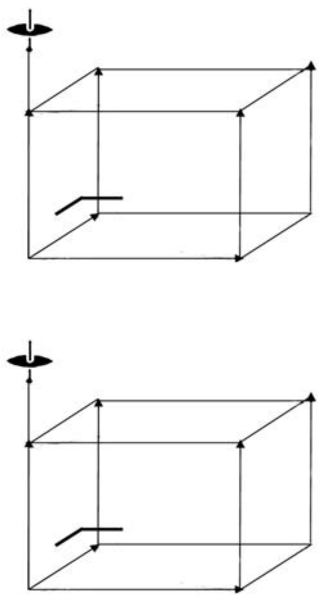
Unit cells - space groups

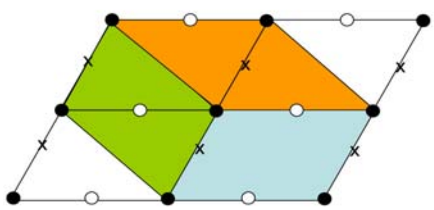


- http://img.chem.ucl.ac.uk/sgp/large/sgp.htm

21

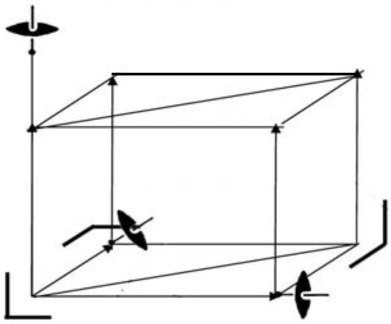
Unit cells - monoclinic





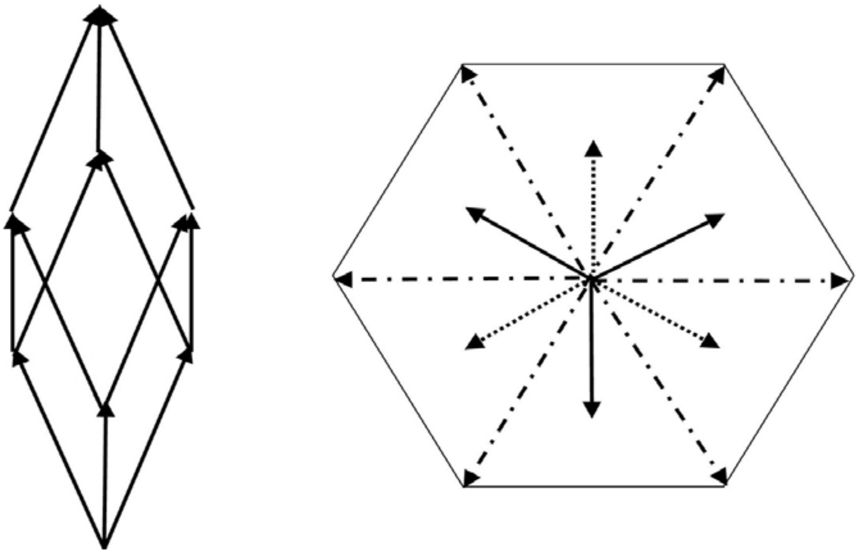
22

Unit cells - orthorhombic and tetragonal



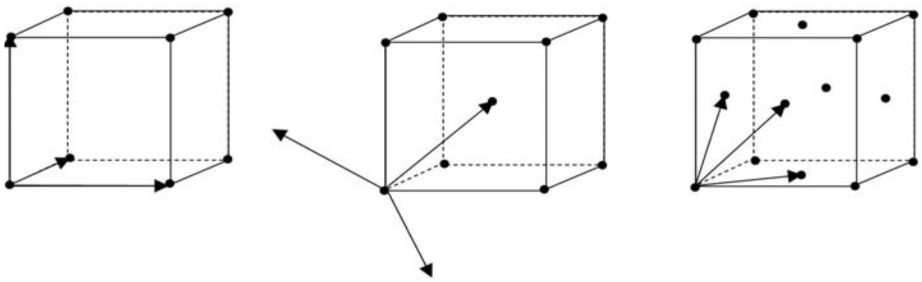
23

Unit cells - rhombohedral and hexagonal



24

Unit cells - cubic

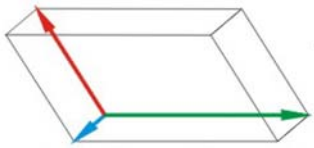


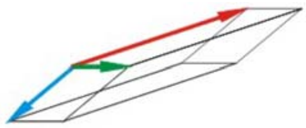
25

2. Direct space and reciprocal space

27

Direct space and reciprocal space





direct space:

sample

$$\vec{r} = x\vec{a} + y\vec{b} + z\vec{c}$$

$$\vec{r} = x\vec{a_1} + y\vec{a_2} + z\vec{a_3}$$

reciprocal space:

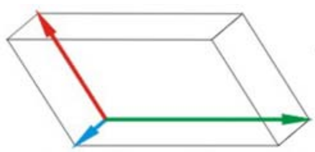
data

$$\vec{H} = h\vec{a}^* + k\vec{b}^* + k\vec{c}^*$$

$$\vec{H} = h\vec{a}_1^* + k\vec{a}_2^* + k\vec{a}_3^*$$

28

Direct space and reciprocal space



direct space:

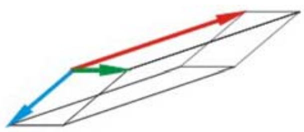
sample

$$\vec{r} = x\vec{a_1} + y\vec{a_2} + z\vec{a_3}$$

$$\vec{a}_1^* = 2\pi \frac{\vec{a_2} \times \vec{a_3}}{\vec{a_1} \cdot (\vec{a_2} \times \vec{a_3})}$$

$$\vec{a}_2^* = 2\pi \frac{\vec{a_3} \times \vec{a_1}}{\vec{a_1} \cdot (\vec{a_2} \times \vec{a_3})}$$

$$\vec{a}_3^* = 2\pi \frac{\vec{a_1} \times \vec{a_2}}{\vec{a_1} \cdot (\vec{a_2} \times \vec{a_3})}$$



reciprocal space:

data

$$\vec{H} = h\vec{a}_1^* + k\vec{a}_2^* + k\vec{a}_3^*$$

29

The utility of reciprocal space - I (Bragg diffraction)

- Reciprocal space allows an alternative expression of the Bragg equation

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

- using $\Delta\vec{k} = \vec{k}_{out} - \vec{k}_{in}$, into

$$\Delta\vec{k} = \vec{G}$$

- More specifically, the diffraction condition can be written in terms of the three Laue equations

$$\vec{a_1} \cdot \Delta\vec{k} = 2\pi h$$
$$\vec{a_2} \cdot \Delta\vec{k} = 2\pi k$$
$$\vec{a_3} \cdot \Delta\vec{k} = 2\pi l$$

30

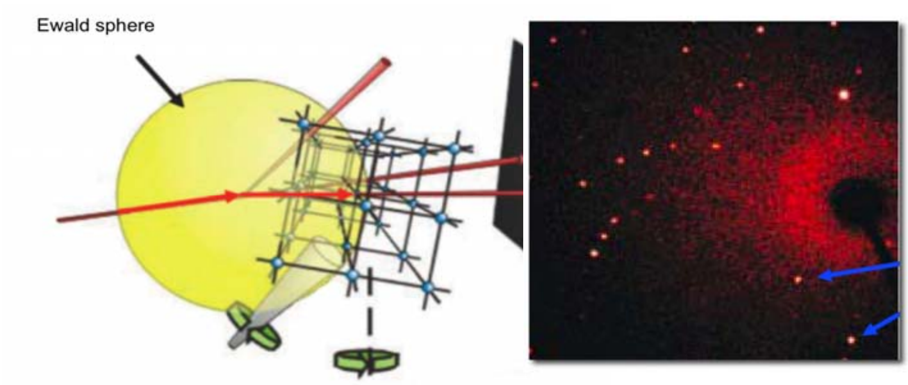
Reciprocal space and the Laue equations

$$\vec{a_1} \cdot \Delta\vec{k} = 2\pi h$$
$$\vec{a_2} \cdot \Delta\vec{k} = 2\pi k$$
$$\vec{a_3} \cdot \Delta\vec{k} = 2\pi l$$

- for a Bragg reflection, $\Delta\vec{k}$ must lie on a cone about the direction of $\vec{a_1}$
- for a Bragg reflection, $\Delta\vec{k}$ must lie on a cone about the direction of $\vec{a_2}$
- for a Bragg reflection, $\Delta\vec{k}$ must lie on a cone about the direction of $\vec{a_3}$

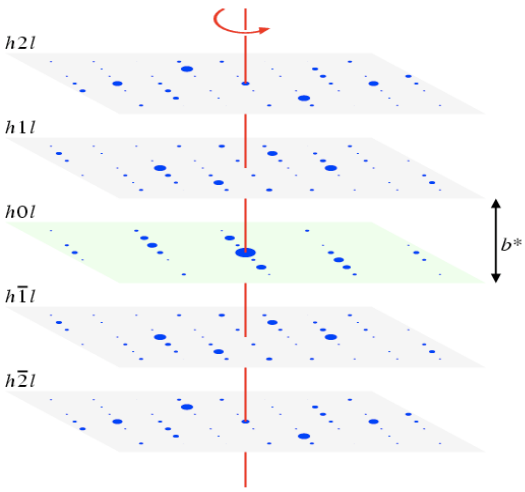
31

Reciprocal space and diffraction



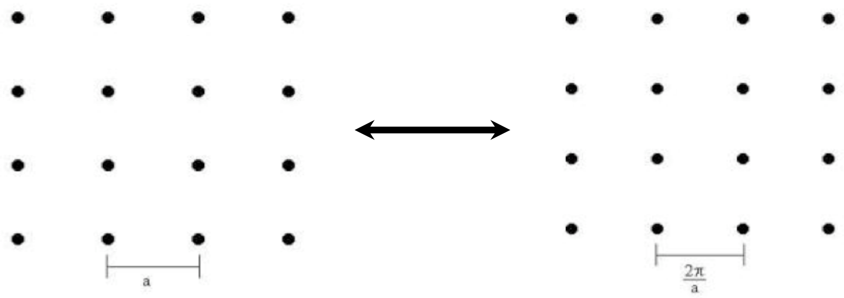
32

Diffraction patterns in 3D space



33

Reciprocal space examples- a 2D lattice



direct space:
sample

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

reciprocal space:
data

34

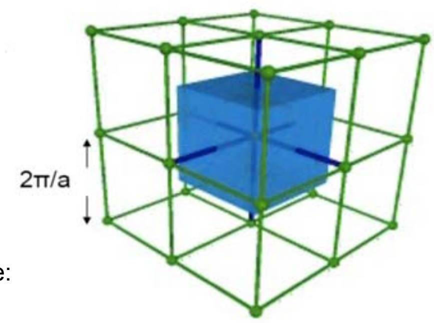
Reciprocal space example - a primitive cubic lattice

- The primitive translation vectors of any simple cubic lattice are:

$$\vec{a_1} = \vec{a_2} = \vec{a_3} = \vec{a}$$

- Using the definition of the reciprocal lattice vectors

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

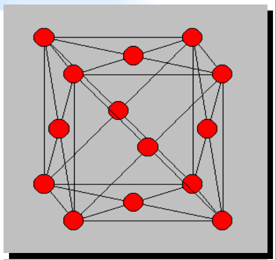


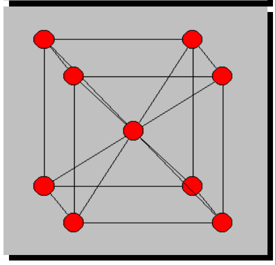
- The reciprocal lattice vectors are therefore:

$$\vec{a}_1^* = \frac{2\pi}{\vec{a}}, \quad \vec{a}_2^* = \frac{2\pi}{\vec{a}}, \quad \vec{a}_3^* = \frac{2\pi}{\vec{a}}$$

35

Reciprocal space example - a face centred cubic lattice





- A face centred cublic lattice with cubic lattice constant *a* has primitive lattice vectors given by:

$$\vec{a_1} = \frac{\vec{a}}{2} + \frac{\vec{b}}{2},\ \vec{a_2} = \frac{\vec{b}}{2} + \frac{\vec{c}}{2},\ \vec{a_3} = \frac{\vec{a}}{2} + \frac{\vec{c}}{2},$$

$$\vec{a_1} = \frac{1}{2}\left(\vec{a} + \vec{b}\right),\ \vec{a_2} = \frac{1}{2}\left(\vec{b} + \vec{c}\right),\ \vec{a_3} = \frac{1}{2}\left(\vec{a} + \vec{c}\right)$$

$$\vec{a_1} = \frac{a}{2}\left(\hat{a} + \hat{b}\right),\ \vec{a_2} = \frac{a}{2}\left(\hat{b} + \hat{c}\right),\ \vec{a_3} = \frac{a}{2}\left(\hat{a} + \hat{c}\right)$$

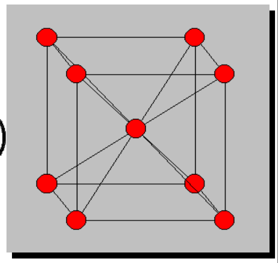
- The primitive translation vectors in reciprocal space will then be given by:

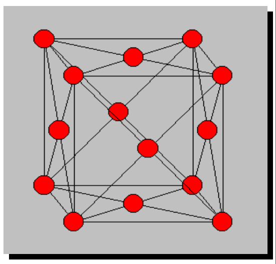
$$\vec{a_1^*} = \frac{2\pi}{a}\left(\hat{a} + \hat{b} - \hat{c}\right),\ \vec{a_2^*} = \frac{2\pi}{a}\left(\hat{b} + \hat{c} - \hat{a}\right),\ \vec{a_3^*} = \frac{2\pi}{a}\left(\hat{c} + \hat{a} - \hat{b}\right)$$

- Which is a body centred cubic lattice

36

Reciprocal space example - a body centred cubic lattice





- A body centred cublic lattice with cubic lattice constant *a* has primitive lattice vectors given by:

$$\vec{a_1} = \frac{a}{2}\left(\hat{a} + \hat{b} - \hat{c}\right),\ \vec{a_2} = \frac{a}{2}\left(-\hat{a} + \hat{b} + \hat{c}\right),\ \vec{a_3} = \frac{a}{2}\left(\hat{a} - \hat{b} + \hat{c}\right)$$

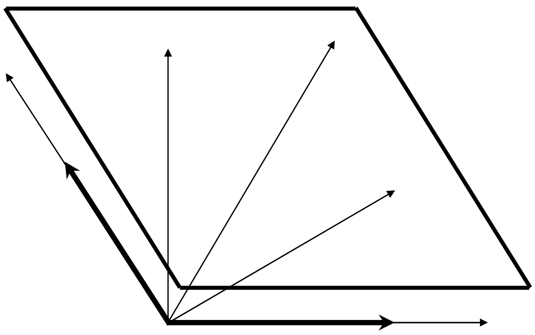
- The primitive translation vectors in reciprocal space will then be given by:

$$\vec{a_1^*} = \frac{2\pi}{a}\left(\hat{a} + \hat{b}\right),\ \vec{a_2^*} = \frac{2\pi}{a}\left(\hat{b} + \hat{c}\right),\ \vec{a_3^*} = \frac{2\pi}{a}\left(\hat{c} + \hat{a}\right)$$

- Which is a face centred cubic lattice

37

Reciprocal space reminder- a 2D hexagonal lattice



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

38

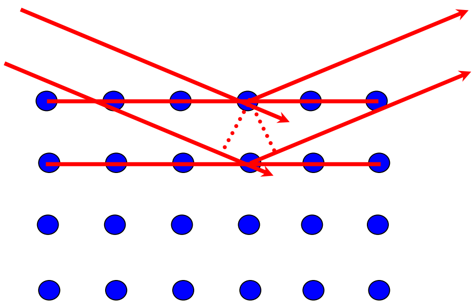
Part 2 – Theory of diffraction and data analysis

39

3. Diffraction - in direct and reciprocal space

40

Diffraction in direct space - Bragg's law

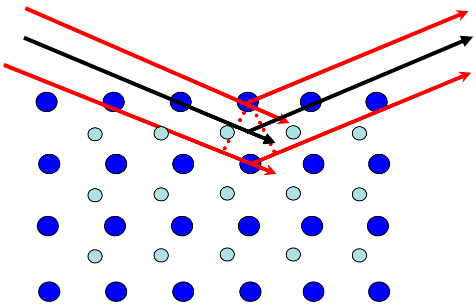


- Constructive interference when

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

41

Diffraction in direct space - Bragg's law



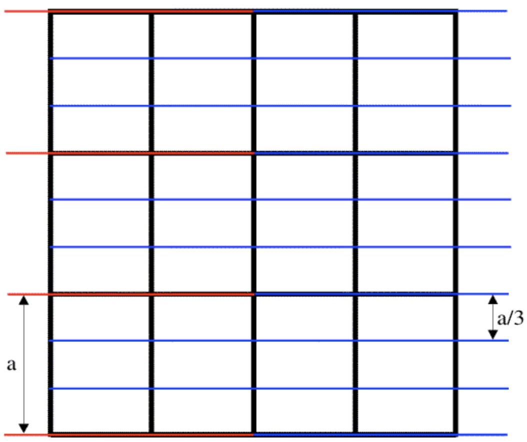
- Constructive interference when

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

- Destructive, otherwise...

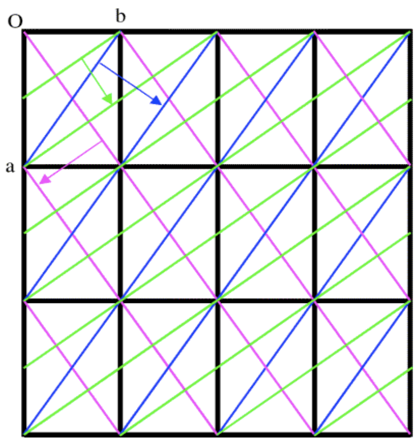
42

Diffraction planes and Miller indices



43

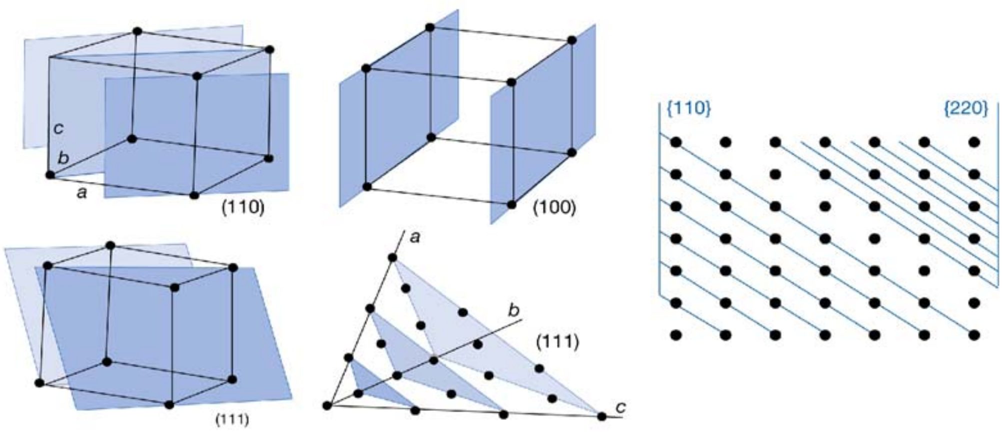
Diffraction planes and Miller indices



- The d-spacing of a set of planes is the distance between them

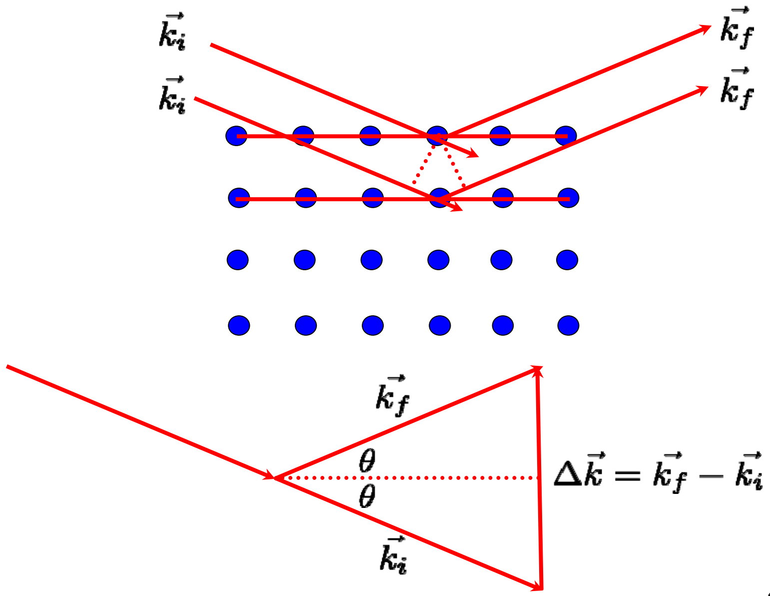
44

Diffraction planes and Miller indices



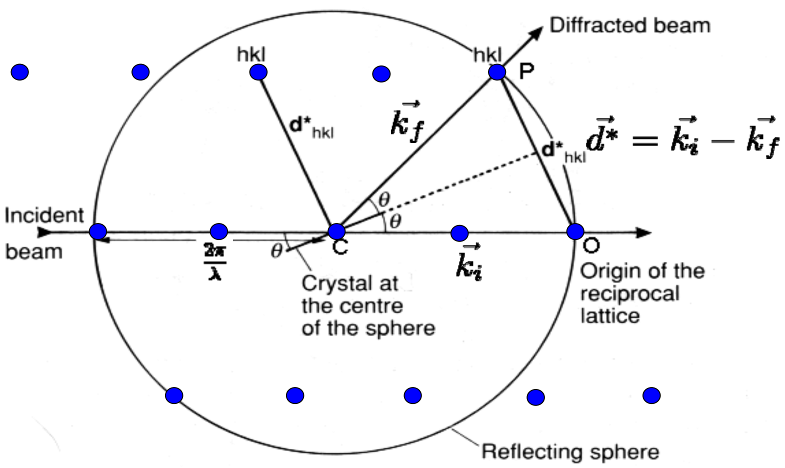
46

Diffraction - an alternative view on Bragg's law



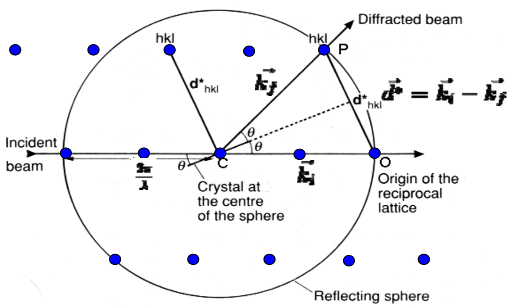
47

Diffraction in reciprocal space-Ewald's construction



48

Diffraction - Ewald's construction



Consider a wave incident on a crystal.

•The crystal is represented by its reciprocal lattice, with origin at O.

•Chose a reciprocal lattice point according to the orientation of the specimen with respect to the incident beam. (Define that as the origin O.)

•The incident wave is represented by a reciprocal vector $\boldsymbol{k}_i$.

•Draw the incident wave vector, $\boldsymbol{k}_i$, ending at O.

•Construct a sphere (circle) with radius 2π/λ (*i.e.* |$\boldsymbol{k}$|), with its centre at the start of $\boldsymbol{k}_i$ that passes through O.

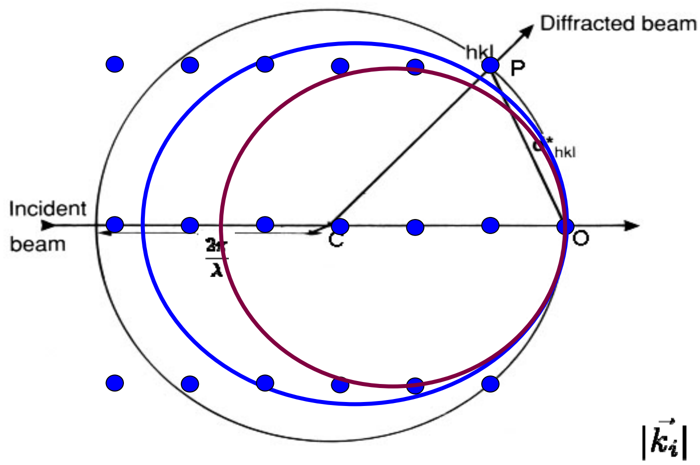
•Draw a vector from the start of $\boldsymbol{k}_i$ to any reciprocal lattice point on the edge of the circle. This is $\boldsymbol{k}_f$.

•Wherever a reciprocal lattice point touches the circle, Bragg's Law is obeyed and a diffracted beam will occur.

- $\boldsymbol{k}_i$ represents the incident beam
- $\boldsymbol{k}_f$ represents the diffracted beamthe angle between them is 2θ

49

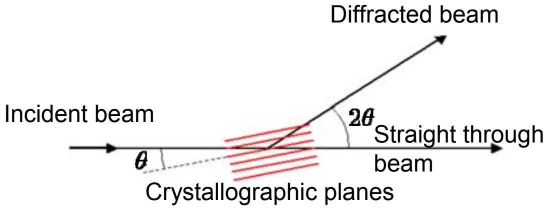
Diffraction - Ewald's construction

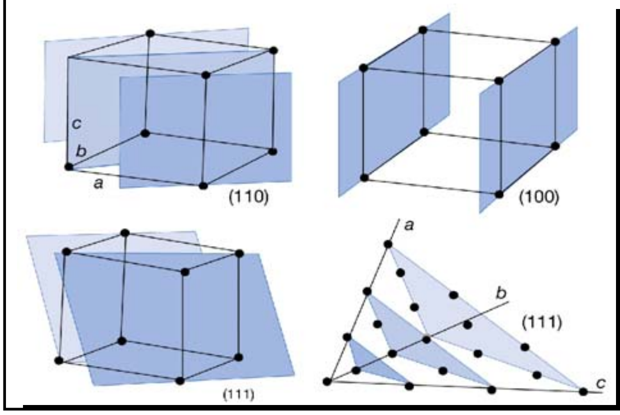


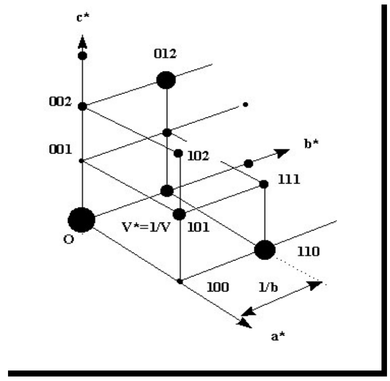
$$|\vec{k_i}| = |\vec{k_f}|$$
$$\Delta\vec{k} = \vec{G}$$

50

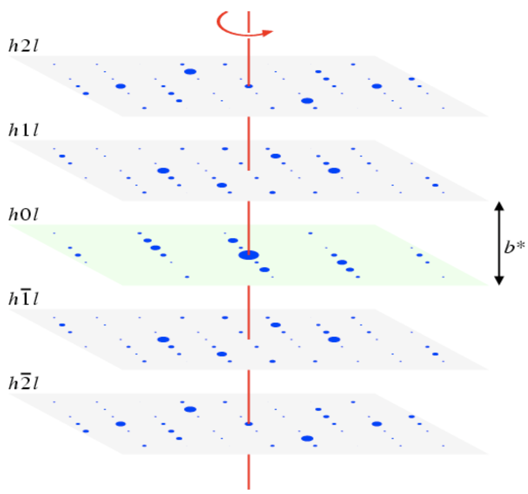
Diffraction - Bragg versus Ewald







Diffraction in 3D - Bragg and Ewald

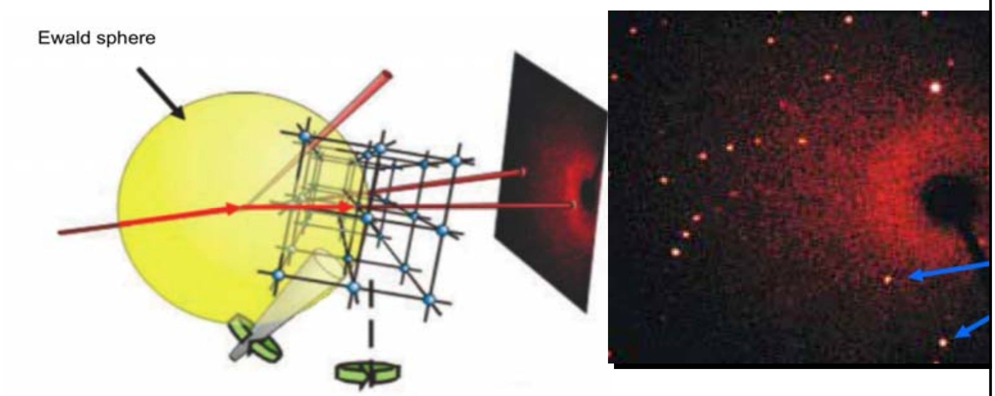


4. Diffraction - Ewald spheres and instruments

53

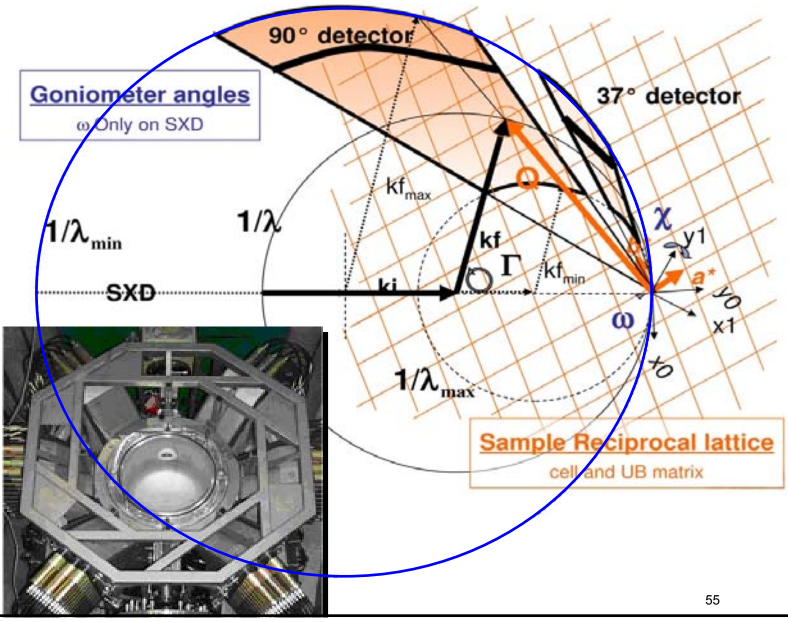
Single crystal diffraction experiments

- Bragg diffraction occurs when $\Delta\vec{k} = \vec{G}$
- There will be intensity at some 2θ angle, and Φ angle in reciprocal space

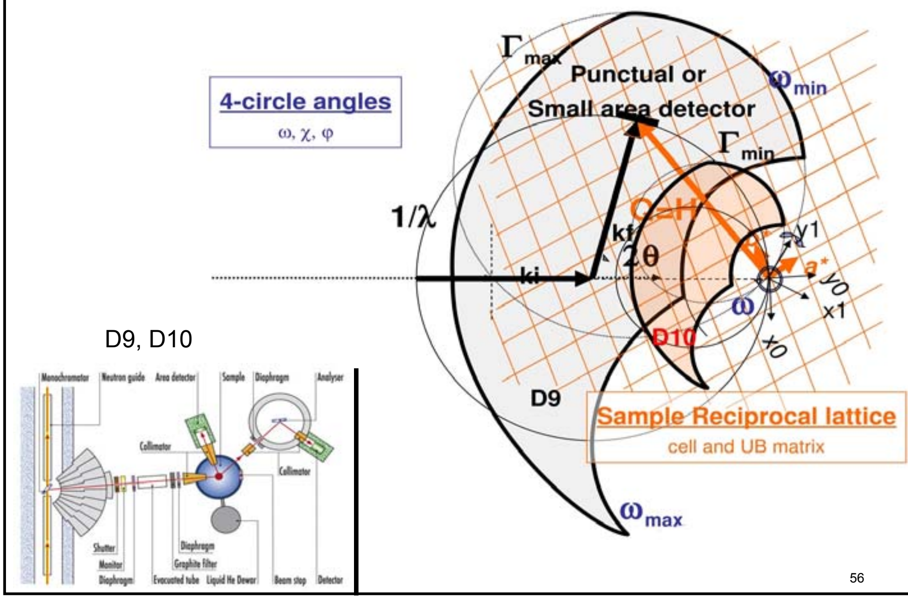


54

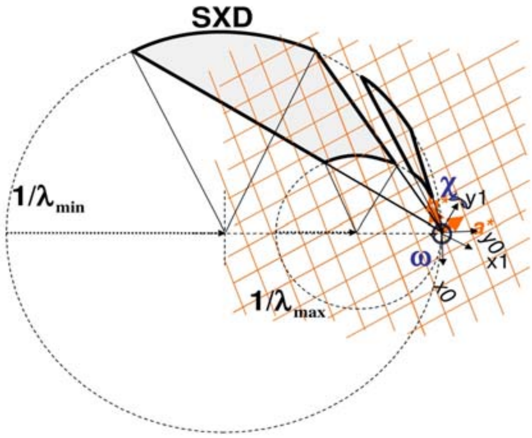
Diffraction - TOF Single crystal Laue diffraction



Diffraction - Constant wavelength single crystal diffraction

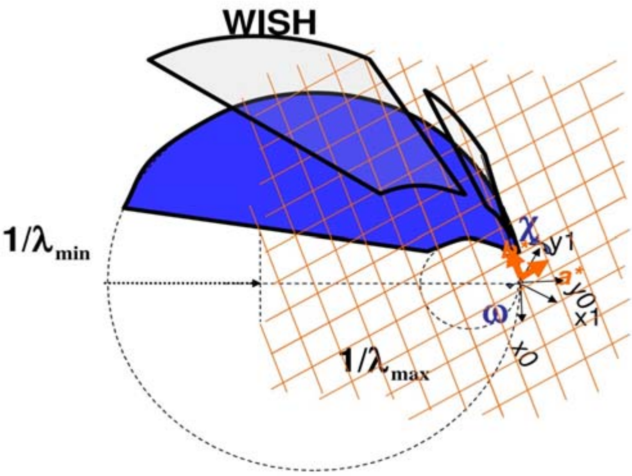


Diffraction - TOF Single crystal diffraction



57

Diffraction - TOF Single crystal diffraction

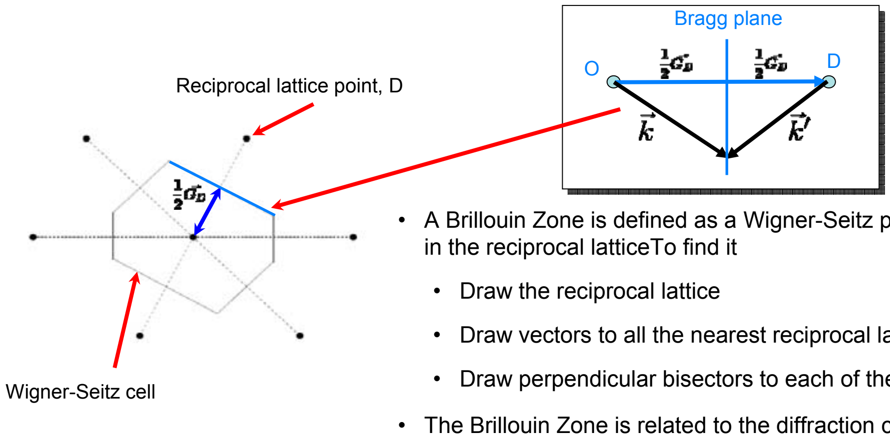


58

5. Reciprocal space is more then diffraction...

59

Brillouin zones

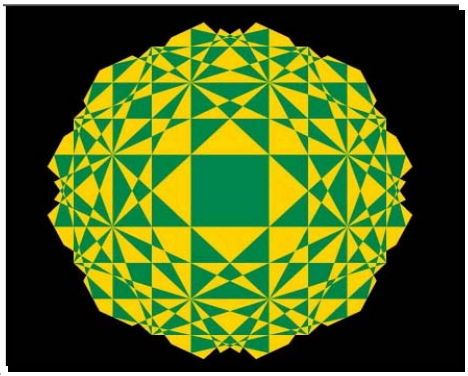


- A Brillouin Zone is defined as a Wigner-Seitz primitive cell in the reciprocal latticeTo find it
  - Draw the reciprocal lattice
  - Draw vectors to all the nearest reciprocal lattice points
  - Draw perpendicular bisectors to each of these
- The Brillouin Zone is related to the diffraction condition
  - Vectors from the origin to the perpendicular bisectors of any reciprocal lattice point satisfy the Bragg condition and are called 'Bragg planes'

60

Higher order Brillouin zones - e.g. 2D square lattice

- 1st Brillouin zone
  - Form perpendicular bisectors (Bragg planes) to nearest reciprocal lattice points. The volume that has no Bragg planes between it and the origin defines the BZ
- 2nd Brillouin zone
  - Volume of reciprocal space in which a point has one Bragg plane between it and the origin
- 3rd Brillouon zone
  - Volume of reciprocal space in which a point has two Bragg planes between it and the origin
- 4rd Brillouon zone, *etc*...
- Higher Brillouin zones exist, and are important in the theory of electronic levels in a periodic potential
- All Brillouin zones have the same volume



61

1st Brillouin zone - primitive cubic lattice

- The primitive translation vectors of any simple cubic lattice are:

$$\vec{a_1} = \vec{a_2} = \vec{a_3} = \vec{a}$$

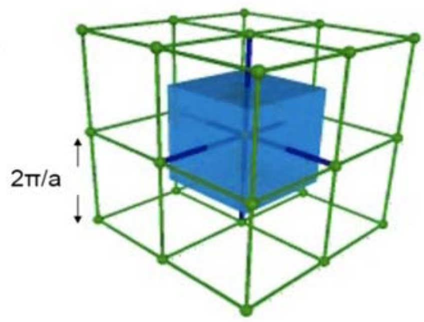
- The reciprocal lattice vectors are therefore:

$$\vec{a_1^*} = \frac{2\pi}{\vec{a}},\ \vec{a_2^*} = \frac{2\pi}{\vec{a}},\ \vec{a_3^*} = \frac{2\pi}{\vec{a}}$$

- The boundaries of the 1st Brillouin zone are the planes normal to the six reciprocal lattice vectors:

$$\pm\vec{a_1^*}, \pm\vec{a_2^*}, \pm\vec{a_3^*}$$

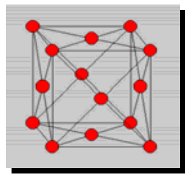
- The length of each side is 2π/*a*



Reciprocal space example - a FCC lattice

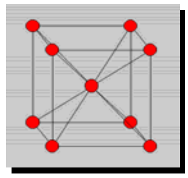
- A face centred cublic lattice with cubic lattice constant *a* has primitive lattice vectors given by:

$$\vec{a_1} = \frac{a}{2}\left(\hat{a}+\hat{b}\right),\ \vec{a_2} = \frac{a}{2}\left(\hat{b}+\hat{c}\right),\ \vec{a_3} = \frac{a}{2}\left(\hat{a}+\hat{c}\right)$$

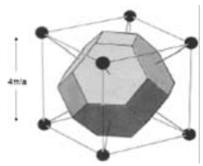


- The primitive translation vectors in reciprocal space form a body centred cubic lattice

$$\vec{a_1^*} = \frac{2\pi}{a}\left(\hat{a}+\hat{b}-\hat{c}\right),\ \vec{a_2^*} = \frac{2\pi}{a}\left(\hat{b}+\hat{c}-\hat{a}\right),\ \vec{a_3^*} = \frac{2\pi}{a}\left(\hat{c}+\hat{a}-\hat{b}\right)$$



- The 1st Brillouin zone of the FCC cubic lattice has 14 sides
  - The volume of this cell in reciprocal space is $4(2\pi/a)^3$

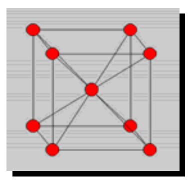


63

Reciprocal space example - a BCC cubic lattice

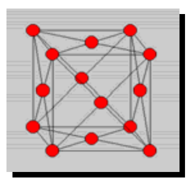
- A body centred cublic lattice with cubic lattice constant *a* has primitive lattice vectors given by:

$$\vec{a_1} = \frac{a}{2}\left(\hat{a}+\hat{b}-\hat{c}\right),\ \vec{a_2} = \frac{a}{2}\left(-\hat{a}+\hat{b}+\hat{c}\right),\ \vec{a_3} = \frac{a}{2}\left(\hat{a}-\hat{b}+\hat{c}\right)$$

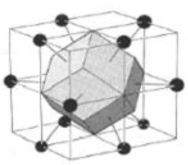


- The primitive translation vectors in reciprocal space forms a face centred cubic lattice

$$\vec{a_1^*} = \frac{2\pi}{a}\left(\hat{a}+\hat{b}\right),\ \vec{a_2^*} = \frac{2\pi}{a}\left(\hat{b}+\hat{c}\right),\ \vec{a_3^*} = \frac{2\pi}{a}\left(\hat{c}+\hat{a}\right)$$



- The 1st Brillouin zone has 12 sides (rhombic dodecahedron)The volume of this cell in reciprocal space is $2(2\pi/a)^3$



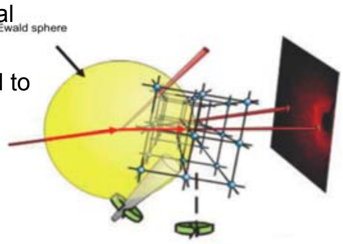
64

6. Diffraction and experiments

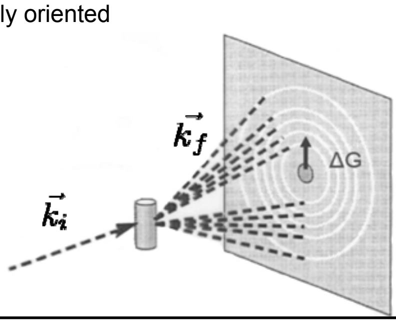
65

Diffraction - powders are lots of single cystals

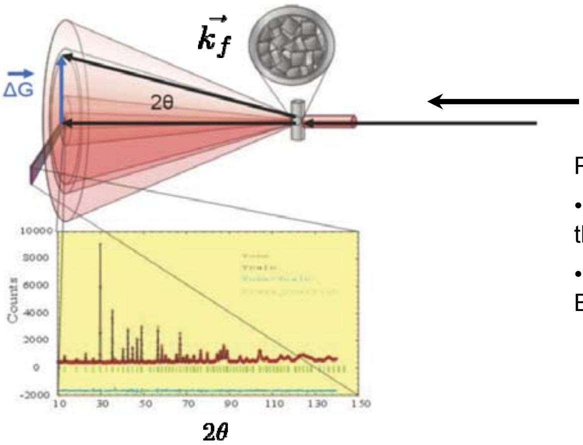
- For single crystals, Bragg peaks occur as spots in reciprocal space.
  - Peaks occur at reciprocal space vectors that correspond to reciprocal lattice vector
  - i.e. $\vec{k} = \Delta G$



- Powders can be considered as a collection of randomly oriented crystallites
  - ΔG occurs on a cone
  - Consider Ewald circle rotated about $\vec{k_i}$



Powder Diffraction



Powders

•Data are typically taken as a slice through the scattering cones

•Intensity peaks occur when Bragg's law is satisfied

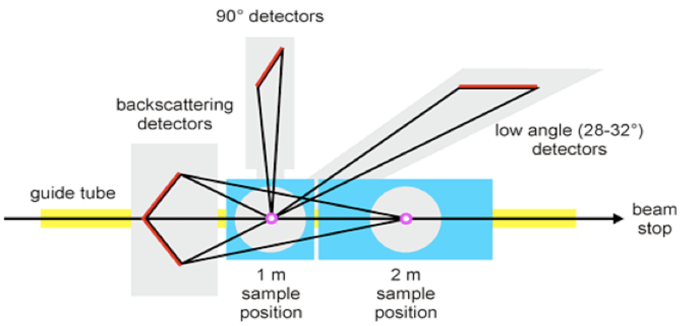
$$n\lambda = 2d\ \sin\ \theta$$

67

Powder Diffraction - time of flight

- Calculate the relative uncertainty in the d-spacing:

$$(\delta d/d)^2 = (\delta t/t)^2 + (\delta L/L)^2 + (\cot\theta\ \delta\theta)^2$$

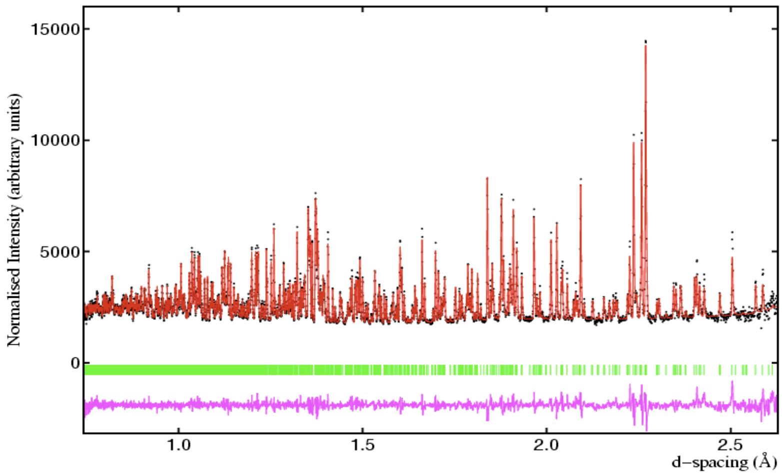


- high d-spacing resolution may be achieved by
  - (a) using a long flight path, *L*, which also increases the TOF, *t*
  - (b) by positioning the detectors at high scattering angle, 2θ.

68

Powder Diffraction - time of flight

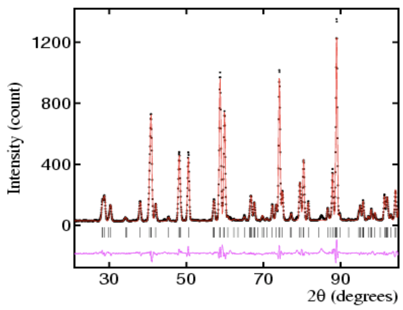
- TOF Data Collection

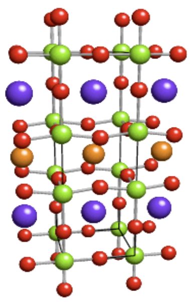


69

Powder Diffraction - Rietveld refinement

- In 1969 Rietveld wrote a revolutionary paper in which he discarded the conventional approach of analysing a powder diffraction pattern in terms of diffraction peaks, and instead analysed the whole pattern simultaneously in which many relevant factors were taken into account regardless of whether they involved the atomic structure of the specimen.
- This helped to overcome one of the principal problems in powder diffraction (overlapping peaks).





70

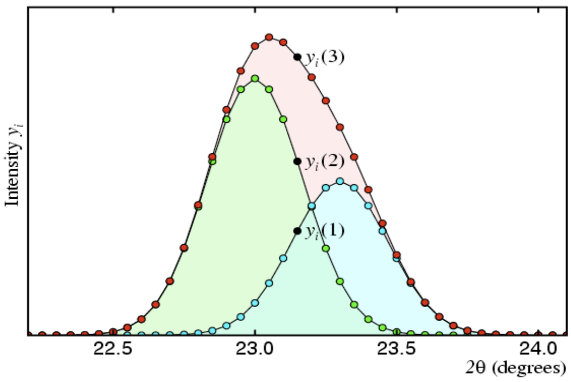
Powder Diffraction - Rietveld refinement

Dr. Rietveld at the neutron powder diffractometer at the High Flux Reactor of the Energy Reseach Foundation ECN in Petten, The Netherlands. (1987)

71

Powder Diffraction - Rietveld refinement

- *"The method of using the total integrated intensities of the separate groups of overlapping peaks in the least-squares refinement of structures, leads to the loss of all the information contained in the often detailed profile of these composite peaks. By the use of these profile intensities instead of the integrated quantities in the refinement procedure, however, this difficulty is overcome and it allows the extraction of the maximum amount of information contained in the powder diagram."* H. M. Rietveld



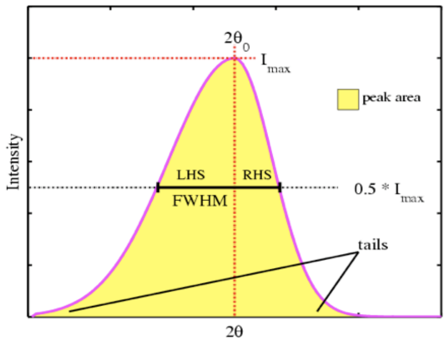
- Minimise the difference between the calculated pattern and the data
- Do not try to extract intensities of overlapping peaks

72

Powder Diffraction - peak profiles

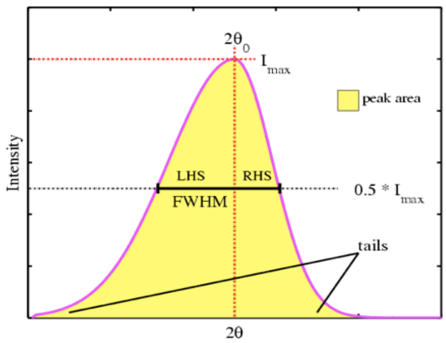
$$F_{hkl} = \sum_{n=1}^{N} b_n \exp\{2\pi i(hx + ky + lz)\} \exp\{-W_n\}$$

$$I_{hkl} \propto F_{hkl}^2$$



- Gaussian
- Lorentzian
- Pearson VII
  - Lorentzian raised to a power of *m*
- pseudo-voight
  - G convoluted with L
- split functions
- non-analytical functions
  - analytical functions

Powder Diffraction - peak profiles



(a) Instrumental Contributions

•the source of radiation (neutrons) has a finite physical size (i.e. is not a perfectly sharp spot or line)

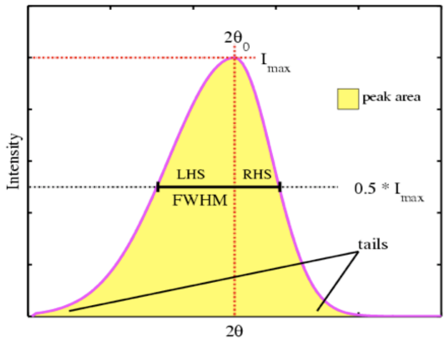
•the radiation is not perfectly monochromatic, but rather consists of a small range, δλ, of wavelengths around the mean, λ

•the active diffracting volume within the sample is finite and therefore diffraction occurs away from the true centre of the diffractometer

•axial divergence of the incident/diffracted beams

•the configuration of defining slits used in the diffractometerany misalignment of the diffractometer

Powder Diffraction - peak profiles



(b) Sample Contributions

•crystallite/diffracting domain size

•crystal lattice distortion (micro-strain) due to dislocations and concentration gradients

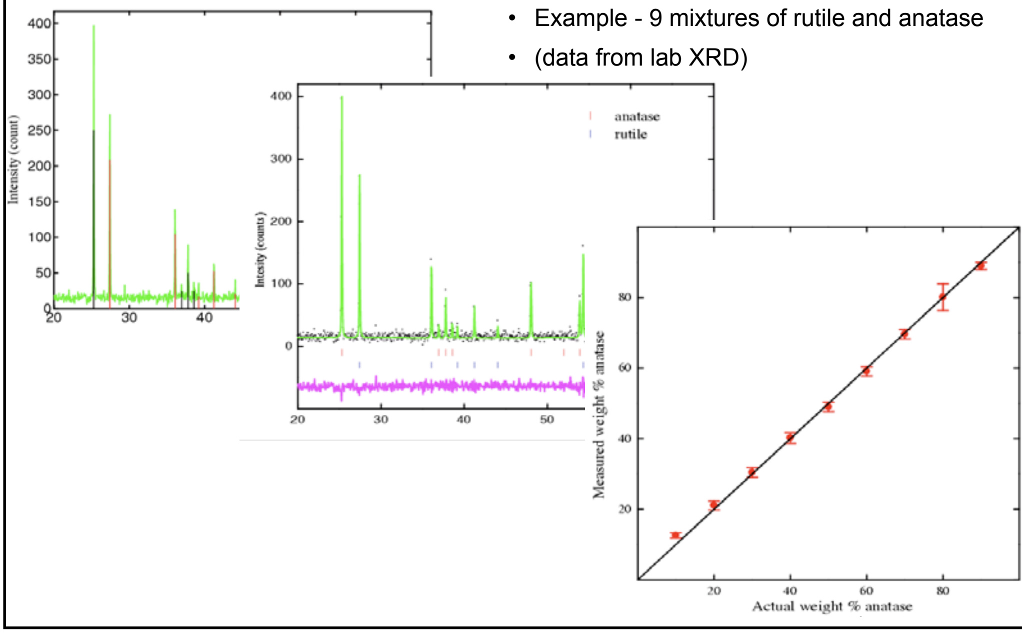
•structural “errors" such as stacking faults, twin faults

•concentration gradients in non-stoichiometric compounds

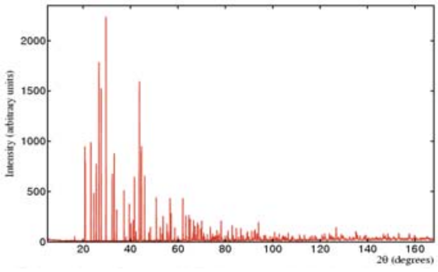
75

Powder Diffraction - whole pattern quantitative analysis

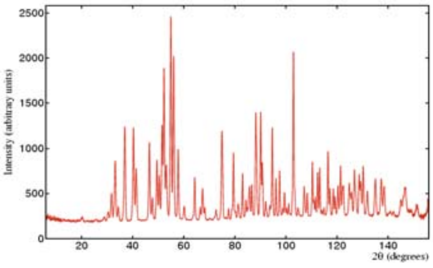
- Example - 9 mixtures of rutile and anatase
- (data from lab XRD)



Powder Diffraction - X-rays and neutrons



- laboratory data set of the mineral anglesite, $PbSO_4$, collected with Cu $K_{\alpha 1}$ radiation in Bragg-Brentano geometry
- $f(2\theta) = Z$ for $2\theta = 0°$



- same material collected on a constant wavelength medium-resolution powder diffractometer (D1A at the ILL, Grenoble) with a neutron wavelength equal to 1.909 Å
- *b* values are a property of the nucleus and do not vary in the systematic way

77

Acknowledgements

•These lectures drew on material provided by:

- Chris Wiebe (Manitoba, Canada)
- Paolo Radaelli (Oxford)
- Laurent Chapon (ISIS, ILL)
- Charles L. B. Macdonald (Windsor, Canada)
- Jeremy Cockroft (UCL)
http://pd.chem.ucl.ac.uk/pdnn/pdindex.htm#symm1

78