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QUB XRD Course

Introduction to Crystallography

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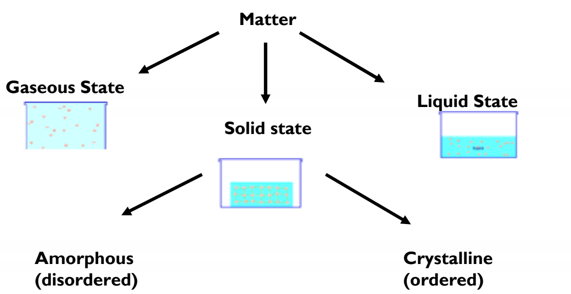
The crystalline state



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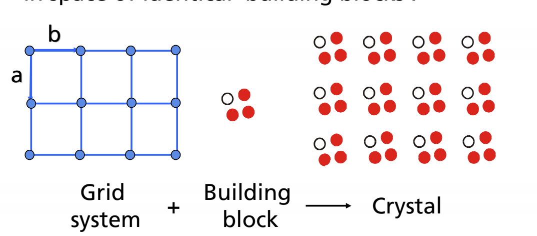
The Crystalline State

A crystal is constructed by the 'infinite' repetition in space of identical 'building blocks'.



The Crystalline State

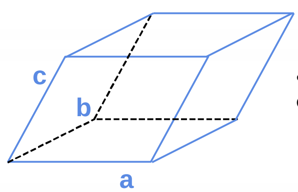
Building block → describes arrangement of groups of atoms

Grid system → describes how building block repeat in space

The lattice parameters describe the 'infinite repetition' unit. A volume element whose edges are successive grid lines.

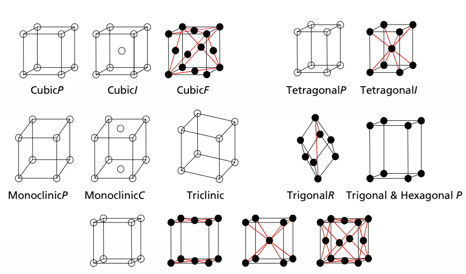
The Crystalline State

Lattice parameters



a b c - sides
α β γ - angles

The 14 Bravais Lattices



The 14 Bravais Lattices

All crystal structures must belong to one of the 14 space, or Bravais, lattices:

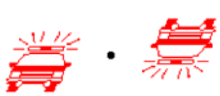
System	Number of lattices	Lattice symbols	Restrictions on conventional cell axes and angles
Triclinic	1	P	$a \neq b \neq c$ $\alpha \neq \beta \neq \alpha\beta\gamma$
Monoclinic	2	P, C	$a \neq b \neq c$ $\alpha = \gamma = 90° \neq \beta$
Orthorhombic	4	P, C, I, F	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$

The 14 Bravais Lattices

System	Number of lattices	Lattice symbols	Restrictions on conventional cell axes and angles
Tetragonal	2	P, I	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$
Cubic	3	P I or bcc F or fcc	$a = b = c$ $\alpha = \beta = \gamma = 90°$
Trigonal	1	R	$a = b = c$ $\alpha = \beta = \gamma < 120°, \neq 90°$
Hexagonal	1	P, C, I, F	$a = b \neq c$ $\alpha = \beta = 90°$ $\gamma = 120°$

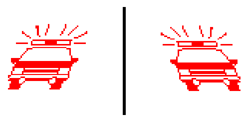
Point Groups

2 fold rotation axis

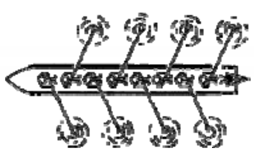


Point Groups

mirror plane



Point groups



- Each rower is related to the next by a combination of translation and reflection

Space Groups

32 crystallographic point groups

\+

14 Bravais lattices (7 crystal classes)

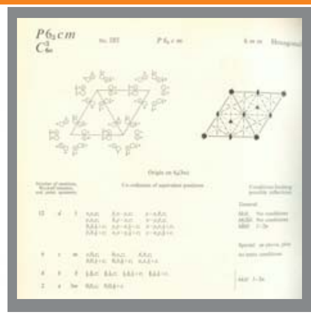
⇓

230 space groups

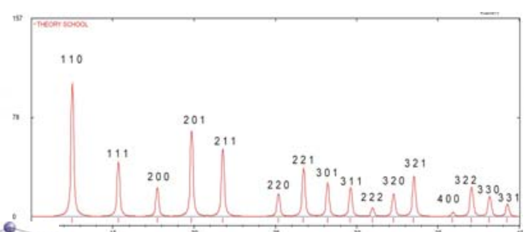
Space group

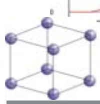
International Tables

IUCR

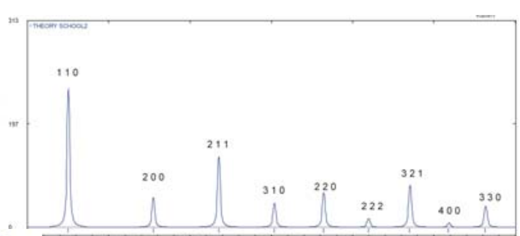


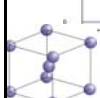
Primitive cubic





Body Centred Cubic





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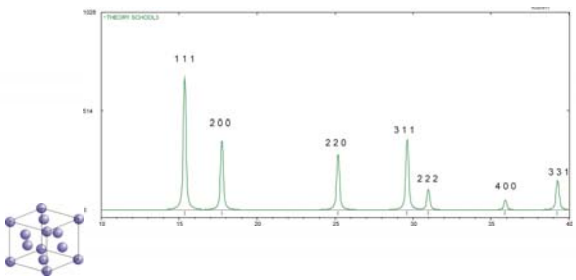
Face Centred Cubic



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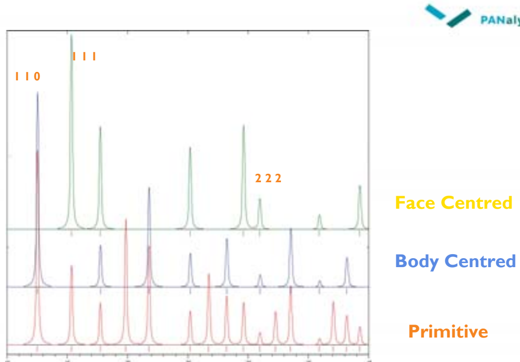

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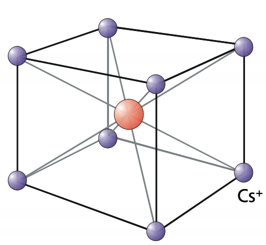
A Simple Crystal Structure

CsCl - Cesium Chloride



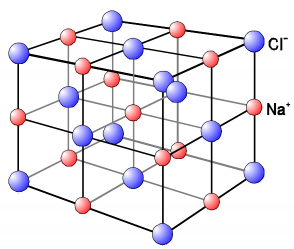
A Simple Crystal Structure

'Building block' = 1 Cs ion + 1 Cl ion
'Grid system' = primitive cube
one Cs ion at each corner site (0,0,0)
one Cl ion in the center of the cube (½, ½, ½)

Note: 8 corner sites - each corner site shared by 8 cubes.
∴ One Cs ion + one Cl ion per cube.

A (not quite so) Simple Crystal Structure

NaCl - Sodium Chloride



A (not quite so) Simple Crystal Structure

Lattice = FCC = Face Centered Cubic

	Cl	Na
FCC - atoms at	(0, 0, 0)	(½, ½, ½)
	(½, ½,0)	(0, 0, ½)
	(½,0, ½)	(0, ½, 0)
	(0, ½, ½)	(½, 0, 0)

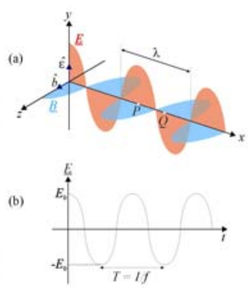
Diffraction

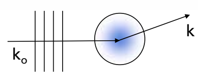
Diffraction is an 'interference' phenomenon

Waves interact with an object

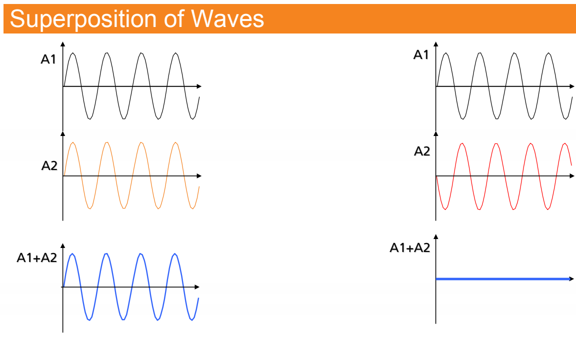
Simple example: optical diffraction

Electromagnetic Waves/ Scattering

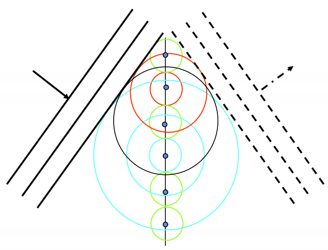




Superposition of Waves



Origin of Diffraction Phenomena



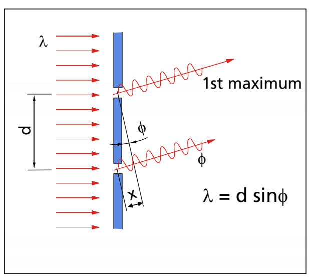
Diffraction

Light of wavelength λ incident on two slits 'd' apart:

first maximum occurs when waves from each slit are exactly in phase.

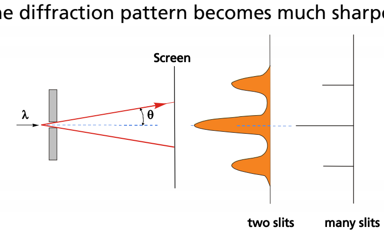
i.e. when difference in path-length is exactly = x

$$x = d \sin\phi = \lambda$$



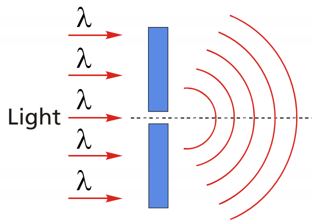
Diffraction

If, instead of two slits, we have a large number of slits then the position of the first maximum remains the same but the diffraction pattern becomes much sharper.



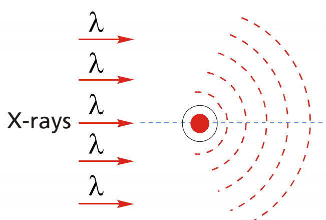
Diffraction

In this experiment each 'slit' scatters the light and becomes a point source.



Diffraction

If we replace the 'slit' by an 'atom' and the light by X-rays, then the atom scatters the X-rays and acts as a point source.



Diffraction

Placing an atom on a lattice (i.e. a crystal) gives a regular array of scatters. The (X-ray) waves scattered by these atoms can interfere in the same way as the (light) waves from the array 'scatters' in a diffraction grating.

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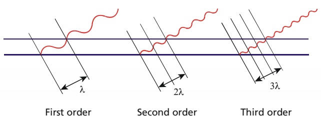
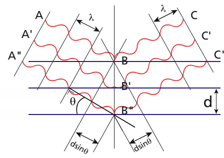
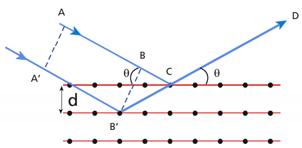
Diffraction







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

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Diffraction

The condition for all scattered waves to interfere constructively:

$\underline{\lambda} = d \sin\theta + d \sin\theta = \underline{2d \sin\theta}$ (Bragg's law)

In a 3-d crystal the atoms are arranged in 'planes'. The 'incident' and 'scattered' beam directions <u>must</u> be coplanar with the 'normal' to the plane (N).

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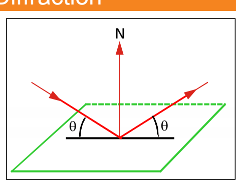
Diffraction



N <u>bisects</u> incident and reflected beams

angle of incidence = angle of reflection (symmetrical)

This is called the <u>Bragg Reflection.</u>

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

- λ is known (the wavelength of the X-ray beam)
- θ is measured (the reflection angle)
- 'd' is calculated (the spacing between the lattice planes)

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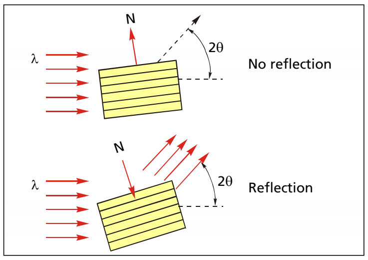
Diffraction

For a crystal the beam is reflected only when the crystal is correctly oriented.



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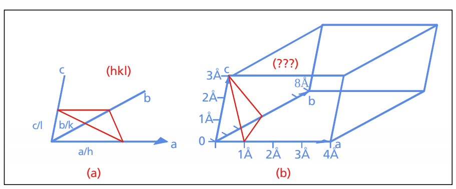
Lattice Planes and Miller Indices

The lattice is described by 3 axes: a, b, c.
Each ‘plane’ must intercept these axes.
The plane intercepts the axes at ¼a, ½b, c.



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Lattice Planes

To find the Miller Indices:

- *Find intercepts on a, b, c axes* ¼ ½ 1
- *Take reciprocals* 4 2 1

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- *(hkl) = (421)*
- *All lattice planes can be indexed in the same way.*

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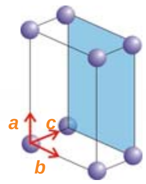
Miller Indices



The plane is parallel to the *a* axis
it crosses a at ∞

The plane is parallel to the *b* axis
it crosses b at ∞

The plane crosses c at 1

The Miller Indices of this plane is (0 0 1)

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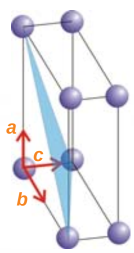
Miller Indices



The plane crosses a at 1

The plane crosses b at 1

The plane crosses c at 1

The Miller Indices of this plane is (1 1 1)

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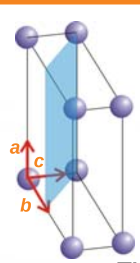
Miller Indices



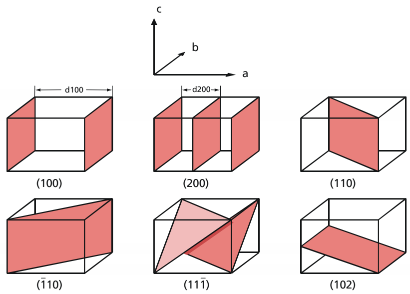
The plane crosses a at ∞

The plane crosses b at ½

The plane crosses c at 1

The Miller Indices of this plane is (0 2 1)

Lattice Planes



Lattice Planes

Real crystal structure CsCl a = 4.11Å, λ=1.54

Calculate: $d_{(hkl)}$ and θ_{hkl} for the following (hkl)

hkl	d	θ	2θ
100			
110			
111			
200			

Lattice Planes

Real crystal structure CsCl a = 4.11Å, λ = 1.54

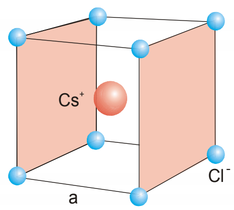
Calculate: $d_{(hkl)}$ and θ_{hkl} for the following (hkl)

hkl	d	θ	2θ
100	4.11	10.798	21.596
110	2.91	15.343	30.686
111	2.37	18.935	37.870
200	2.06	22.006	44.012

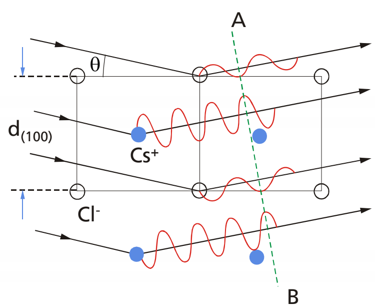
Intensities

What influences the <u>intensities</u> of Bragg reflections?

Example: CsCl



Wavefronts



Wavefronts

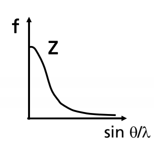
The diagram shows the (100) planes scattering in phase.

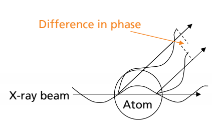
- *The reflecting power of atoms (normally called the atomic scattering factor) is related to the number of electrons in the atom.*

  ∴ Cs^+ = 54 electrons

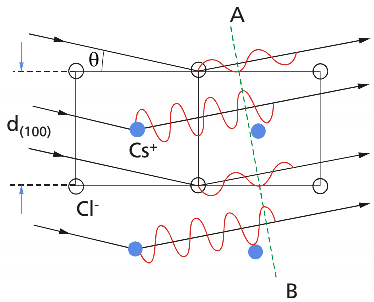
  Cl^- = 18 electrons

  ∴ the reflected beam from Cs^+ atoms has an amplitude 3x larger than the beam from Cl^- atoms





Wavefronts



Wavefronts

Look at the wave front A - B of the reflected beam

- *Beams from Cl^- atoms (on planes d_{100} apart) are in phase.*
- *Beams from Cs^+ atoms (also on planes d_{100} apart) are in phase.*

But, since Cs^+ planes are exactly half-way between Cl^- planes, beams from Cs^+ and Cl^- planes are exactly out of phase.

Wavefronts

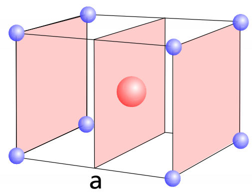
$\therefore$ Amplitude of diffracted beam $\propto$ A(54 - 18)
= A(36)

$\therefore$ Intensity = $I_{100} \propto$ A2 $(36)^2$ = $1296A^2$
(A is some constant)

$\therefore$ Weak reflection

Reflection

The (200) planes



Reflection

This time all atoms scatter in-phase.

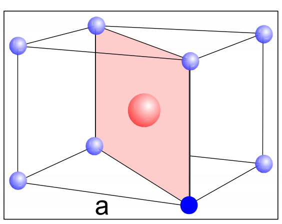
∴ Amplitude of diffracted beam $\propto$ A (54 + 18) = A72

Intensity of diffracted beam $I_{(200)} \propto A^2 \times 72^2 = 5184A^2$

∴ Strong reflection

Reflection

The (110) planes



Cs^+ and Cl^- ions all lie in the (110) planes

∴ Cs^+ and Cl^- scatter in phase

Reflection

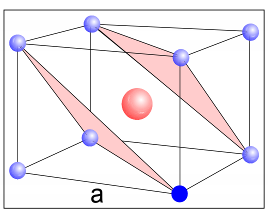
$$\therefore d_{(110)} = \frac{a}{\sqrt{2}} = \frac{4.11}{\sqrt{2}} = 2.91\text{Å} \qquad \therefore \theta_{110} = 15.34^{\circ}$$

$$I_{(110)} \propto A^2(54+18)^2 = 5184A^2$$

$\therefore$ Strong reflection

Reflection

Now look the (111) planes



Cl^- ions lie in (111) planes and are d(111) apart

$\therefore$ Cl^- ions scatter in phase

Cs^+ ions lie mid-way between Cl^- planes

$\therefore$ Cs^+ ions scatter out of phase

Reflection

$$d_{(111)} = \frac{a}{\sqrt{3}} = \frac{4.11}{\sqrt{3}} = 2.373\text{Å} \qquad \therefore \theta_{(111)} = 18.94^{\circ}$$

$$I_{(111)} \propto A^2(54-18)^2 = 1296A^2$$

$\therefore$ Weak reflection

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Reflection

The (222) reflection <u>must be strong</u>:

$I(222) = A^2(54+18)^2 = 5184A^2$

$d(222) = 1.187Å$ $\theta(222) = 40.44°$

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Reflection

To summarize:

hkl	*d*	*2θ*	*I*
100	*4.11 Å*	*21.6°*	*weak*
110	*2.91 Å*	*30.69°*	*strong*
111	*2.373 Å*	*37.87°*	*weak*
200	*2.055 Å*	*44.01°*	*strong*

from lattice → Crystal structure ← from 'building block'

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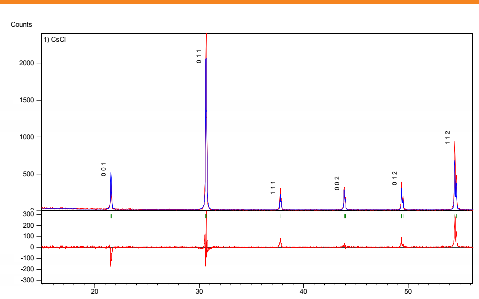
CsCl



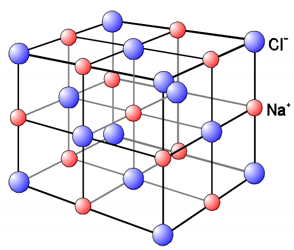
Form Factor

The ‘form factor’ reduces intensities of higher angle Bragg reflections:

- *Temperature factor*
- *Lorentz-polarization factor*
- *Instrumental factors*
- *Sample factors*

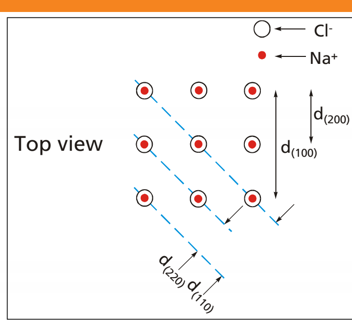
A (not quite so) Simple Crystal Structure

NaCl - Sodium Chloride



Reflection

NaCl (FCC)



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Reflection

- (100) absent completely
- (200) strong
- (110) absent completely
- (220) strong

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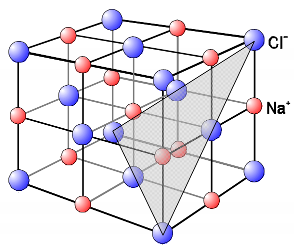
Reflection

The (111) planes



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Reflection

Cl^- atoms lie in (111) planes
Na^+ atoms lie in between } ∴ Scatter out of phase
$I \propto A^2(18-8)^2 = 100A^2$

<u>∴ = (111) is quite weak</u>

Cl^- atoms lie in (222) planes
Na^+ atoms lie in (222) planes } ∴ Scatter in phase
$I \propto A^2\,(18+8)^2 = 262A^2$

<u>∴ = (222) is quite strong</u>

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Summary

The diffraction pattern is like a finger print of the crystal structure:

➔ d values reflect the unit cell parameters ('grid')

➔ intensities reflect the atoms/molecules ('building blocks')