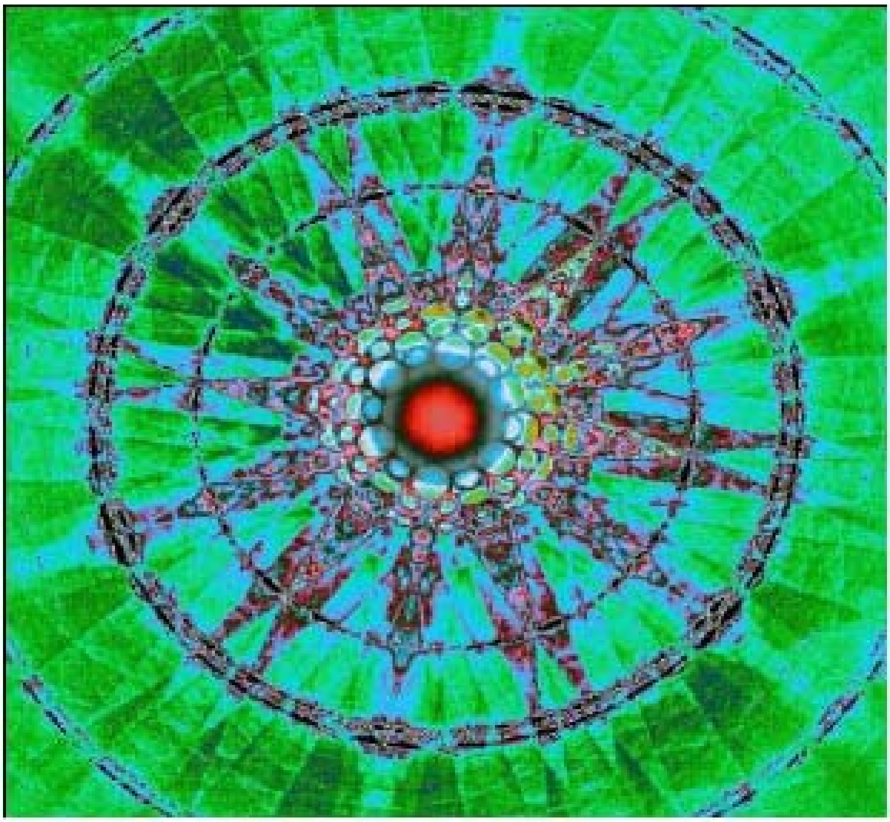
Natural Sciences Tripos Part IA

MATERIALS SCIENCE

Course A: Atomic Structure of Materials



Name............................ College.........................

Prof. Paul Midgley

Michaelmas Term 2013-14

IA

UNIVERSITY OF CAMBRIDGE
Department of Materials
Science and Metallurgy

MATERIALS SCIENCE

Course A: Atomic Structure of Materials

Paul Midgley

12 lectures

Student's Edition

(There are some (deliberate) gaps in the handout – these will be filled in during the lectures!)

Contents

Recommended Text Books

No single textbook matches this course exactly, but reading parts of the following will be helpful:

- C. Hammond, *The Basics of Crystallography and Diffraction*, III Ed, Oxford University Press, 2009

  This is also available as an e-book, see:

  http://www.msm.cam.ac.uk/library/ebooks_msm.php

- A. Putnis, *Introduction to Mineral Sciences*, Cambridge University Press, 1992
- B.D Cullity, S.R Stock, *Elements of X-Ray Diffraction*, Prentice Hall, 2001
- D. McKie, C. McKie, *Essentials of Crystallography*, Blackwell Scientific Publications, 1986
- P. Goodhew, F.J. Humphreys and R. Beanland, *Electron Microscopy and Analysis* 3rd Edition, Taylor and Francis 2001.
- D. Williams and C.B. Carter, *Transmission Electron Microscopy* Kluwer/Plenum Press, 1996 to 2004

Other books well worth looking at are:

Fundamentals of Materials Science and Engineering W.D. Callister (Wiley)

The Structure of Materials S.M. Allen and E.C. Thomas (Wiley).

Web Resources and Software

The following location provides downloadable items relating to the course (lecture handout, practicals, questions sheets, answers) as well as links to material which may be of interest:

http://www.msm.cam.ac.uk/teaching/partIA.php

To accompany IA Materials there are complementary on-line Teaching and Learning Packages within the DOITPOMS web site:

http://www.doitpoms.ac.uk/index.html

It should be available in your College computer centres and on many PCs in the Department. The pages that are of particular use for this course are:

Diffraction and Imaging
Indexing Electron Diffraction Patterns
Optical Microscopy
Reciprocal Space
Transmission Electron Microscopy
X-ray Diffraction Techniques
Atomic Scale Structure of Materials
Crystallography
Lattice Planes and Miller Indices
The Stereographic Projection

There is also a great deal of useful web-based teaching at the MATTER web site:

http://matter.org.uk/

Other Websites

Steffen Weber's homepage *http://jcrystal.com/steffenweber/*
Contains java-based applets that allow the structure of common polyhedra and crystals to be explored.

Crystallography and Minerals Arranged by Crystal Form
http://webmineral.com/crystall.shtml
A library of 'crystal forms' - the shapes adopted by natural crystals. Contains Java applets.

EPFL host a useful web site on many aspects of crystallography:

http://escher.epfl.ch/eCrystallography/

Crystal Maker

http://www.crystalmaker.com/

This is excellent software for visualizing crystal structures and for simulations of diffraction patterns. Copies to use are available on many Department PCs. The Department has a site licence.

E-mail address

Feedback on any aspect of the 1A Materials Science course may be directed to: *PartIA@msm.cam.ac.uk*

Introduction

Materials science plays a key role in almost all aspects of modern life and in the technologies and equipment we rely upon as a matter of routine. There are many examples to choose from but one that usefully illustrates this is the Apple iPhone. Almost all the components have relied upon advances in materials science and the work of materials scientists!

Consider some of the materials involved and their application:

Display. This relies upon the combination of a **liquid crystal** display and a touch screen for communication with the device. You will hear more about liquid crystals later in the year. The touch screen is made from a conductive but transparent material, indium tin oxide, a **ceramic conductor.**

ICs At the heart of the iPhone are a number of integrated circuits (ICs) built upon billions of individual transistors, all of which rely on precise control of the **semiconductor** material, silicon, to which has been added **dopant** atoms to change the silicon's electronic properties. Adding just a few dopant atoms per million silicon atoms can change the conductivity many orders of magnitude!

Interconnects Interconnects that provide the links between components are now made of copper, not aluminium, for higher speed and efficiency.

Battery The battery is a modern Li-ion battery where the atomic structure of the electrodes is carefully controlled to enable the diffusion of the Li ions.

Wireless Microwave circuits need capacitors which are **ceramic insulators** whose structure and composition is carefully controlled to optimise the capacitance.

Headphones. Most headphones use modern **magnetic** materials whose structure and composition has been developed to produce very strong permanent magnets. This is part of a transducer that turns electrical signals into sound.

With the exception of the LCD, all these materials are **solid** materials.

Classification and Terminology

Traditionally states of matter were classed into 3 ‘classical’ groups:

Gases **Liquids** **Solids**

Although gases and liquids are of course important in the understanding of materials, in Course A we will concentrate solely on **solids** and in particular on **crystalline solids**.

Nowadays these 3 traditional groups have been joined by other states of matter including for example **liquid crystals** which lie at the boundary between liquids and solids and will be discussed in other parts of the Materials course.

Solid materials can be classified into many different types and in many different ways depending on whether you want to stress, for example, their structure or their mechanical or electrical properties.

Traditionally we might talk about

Metals **Ceramics** **Polymers***

(*You will investigate the mechanical properties of a polymer in AP0)

which again are very broad descriptions and with lots of overlap, for example many ceramics are good conductors and thus in some sense could be called ‘metallic’.

We also talk about groups of materials stressing for example their electrical and magnetic properties, so we talk about

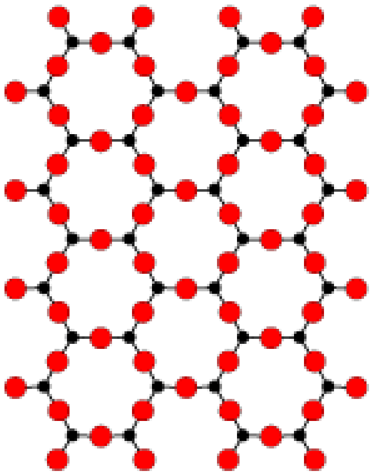
Semiconductors
Superconductors
Hard and Soft Magnetic Materials
Ferroelectric Materials

…and so on.

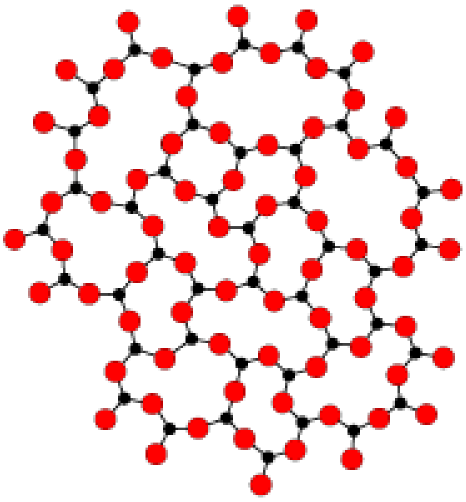
In addition we study solids that are **crystalline** (that have a crystal structure) and **non-crystalline**.

A crystalline solid is one in which the atoms are arranged in a periodic fashion – we talk about 'long-range order'.

A non-crystalline material is non-periodic it does not have long-range order but can have 'short range order' where the local arrangement of atoms (and the local bonding) is approximately the same as in a crystal.



crystalline



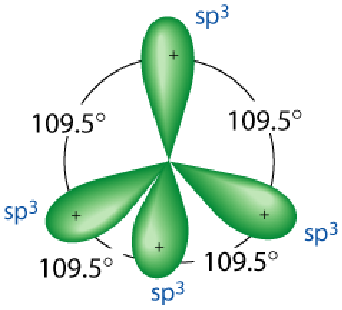
non-crystalline

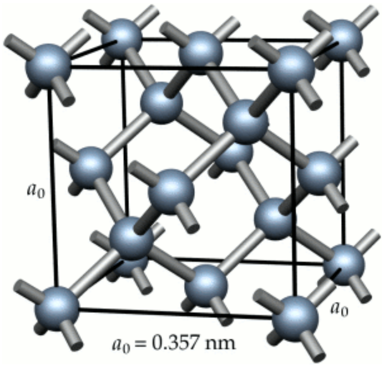
Importance of Atomic Structure

What is common to all materials is that they are composed of **atoms**.

The properties (whether mechanical, electrical, chemical etc) of all solid materials are dependent upon the relative positions of the atoms in the solid (in other words the **atomic structure** of the material) and their mutual interaction i.e. the nature of the **bonding** (whether e.g. covalent, ionic, metallic, van der Waals).

There are examples of where the atom-atom interactions is strongly reflected in the atomic structure. An example is diamond. Here the carbon-carbon interactions lead to a very directional covalent bond called a sp^3 bond which has tetrahedral symmetry – this leads to an open structure as shown below.





Of course carbon can also take the form of graphite. Here the carbon atoms are arranged in a rather different structure and graphite has very different properties to diamond!

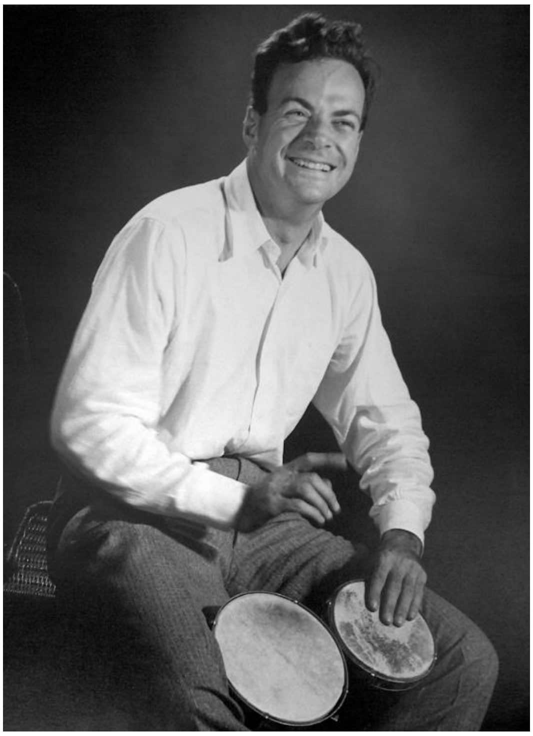
In other solid systems (for example many of the metallic elements) the atomic structure is dictated by how well we can 'pack' the atoms into 3D space – 'packing efficiency' – this leads to dense close-packed structures as we will also discuss very shortly.

So it is vital that to understand the properties of material, and to improve those properties for example by adding or removing atoms, we need to know the material's atomic structure.

As Richard Feynman said:

‘*It would be very easy to make an analysis of any complicated chemical substance; all one would have to do would be to look at it and see where the atoms are…*’

taken from ‘*There’s Plenty of Room at the Bottom*’, Richard Feynman lecture, APS meeting at Caltech, 1959



Richard Feynman

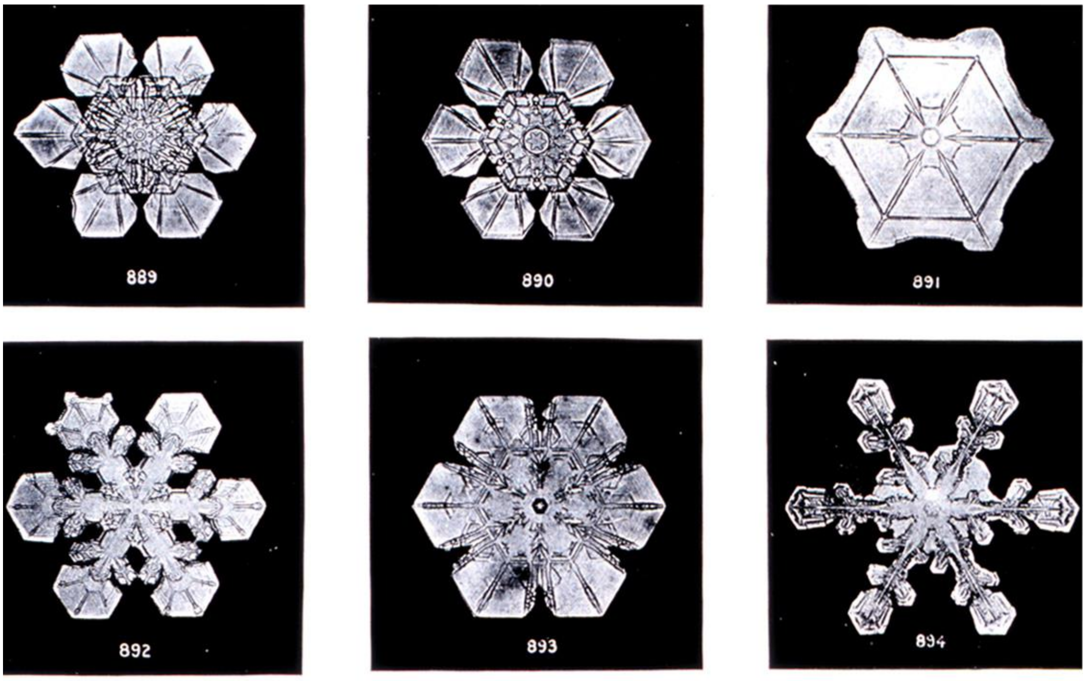
So let’s start understanding materials by understanding their atomic structure….

A. Crystals and Atomic Arrangements

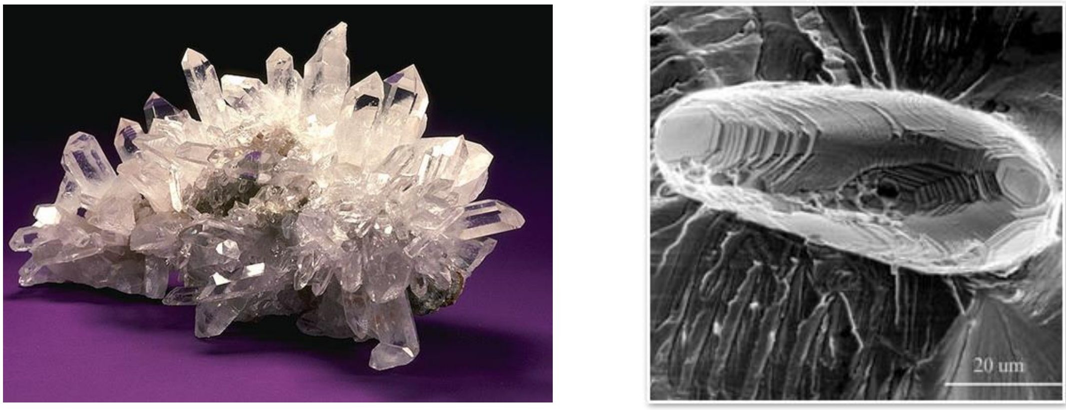
A1. Historical Introduction

There is a great deal of evidence in nature that many materials have some kind of internal order, evidence of a pattern or arrangement of underlying building blocks.

Consider the following examples:



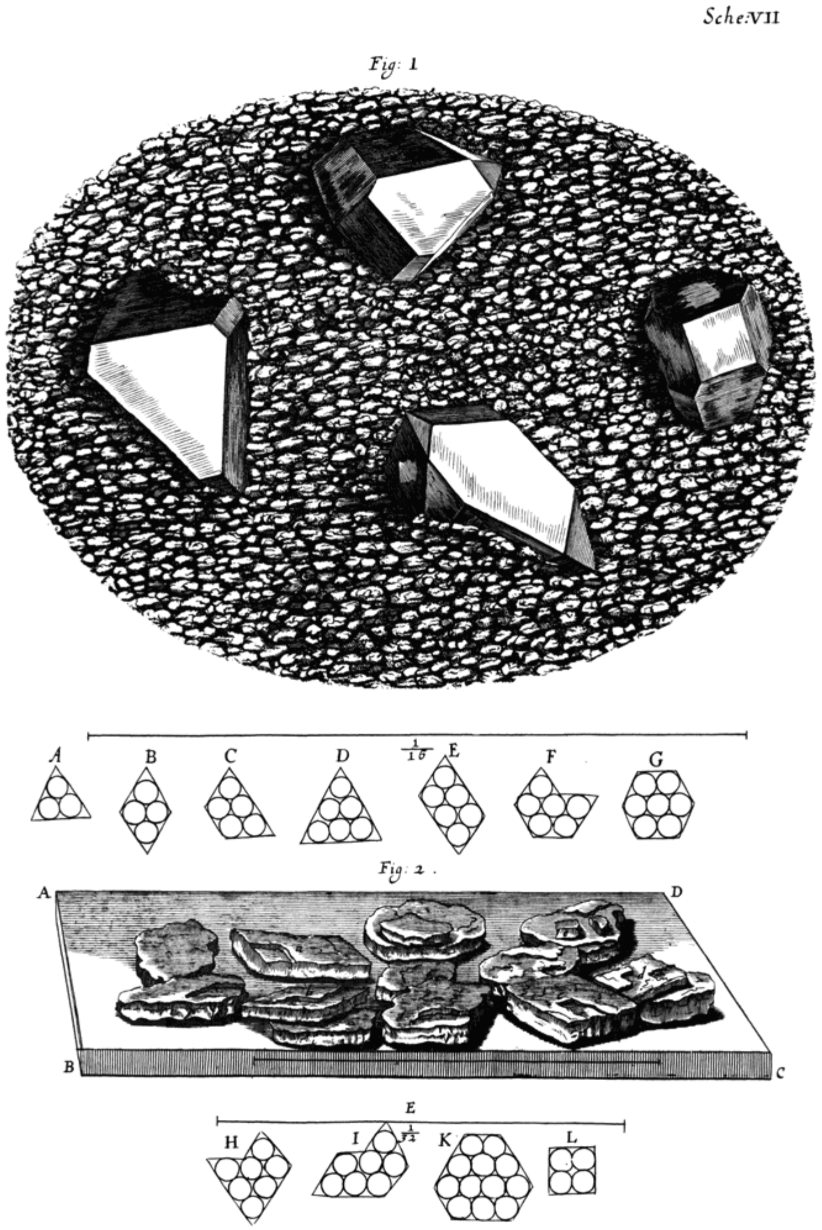
An array of micrographs showing the hexagonal symmetry of ice crystals (snowflakes)



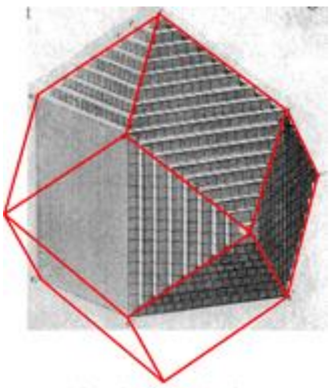
Natural quartz crystals (left) and the facetted surface of a fractured iron-aluminium single crystal (right)

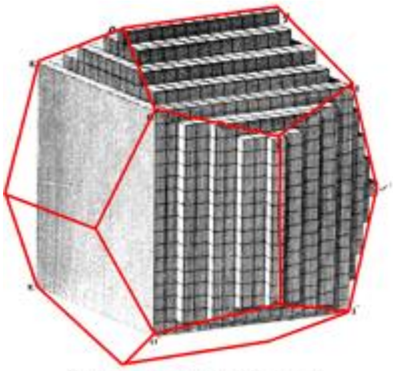
We now know that all materials are composed of atoms and it is the arrangement of the atoms that leads to the external shapes we see in the figures above.

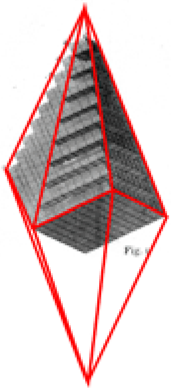
Although Kepler (1611) was the first to discuss the 6-fold symmetry of the snowflake, it was Hooke (1665) who was the first to consider the structure of ‘crystalline’ materials in his seminal book ‘*Micrographia*’ – pictures below reproduced from his book:



Haüy (1784) showed how different forms (we now say ‘habits’) of dog-tooth spar (calcite) can be described by packing together small rhombs which he called ‘molécules intégrantes’.


Rhomb-dodecahedron


Pentagon-dodecahedron


Scalenohedron

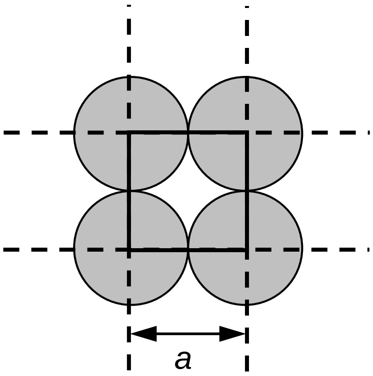
With our current knowledge we realise that Hooke’s description was in essence the packing of atoms to form a crystal and Hauy was describing the periodic array of ‘unit cells’ – more on this later…

A2. Packing Atoms in 2D

Consider again Hooke's picture. Apart from 'L', the atoms are packed in a 2D **close-packed hexagonal** arrangement. In L, the atoms are in a **square** arrangement. Note there are larger gaps (**interstices**) in the square arrangement.

The efficiency of this 2D packing is easily calculated by considering the filling of the 2D plane with circles:

Square Packing



square of side *a*

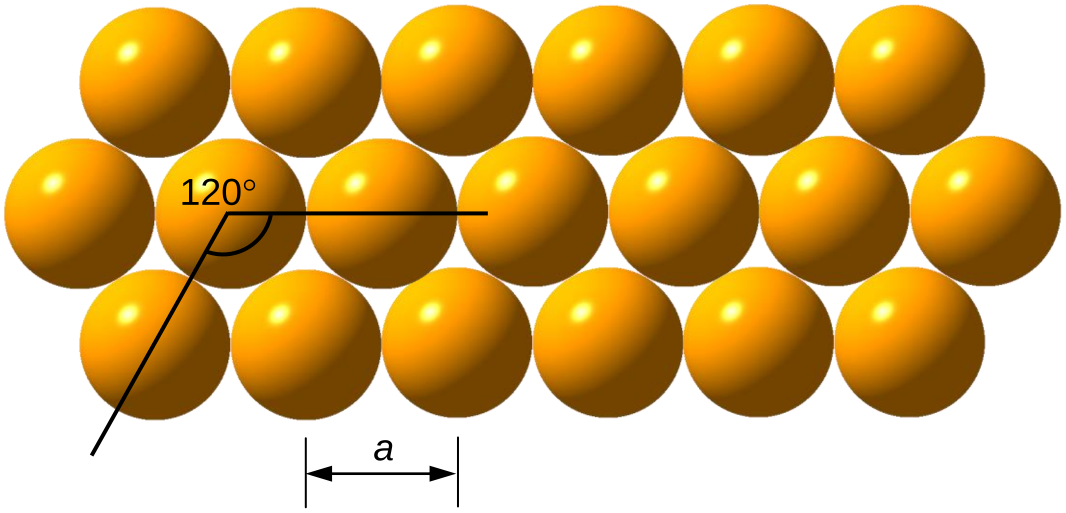
circle diameter *a*

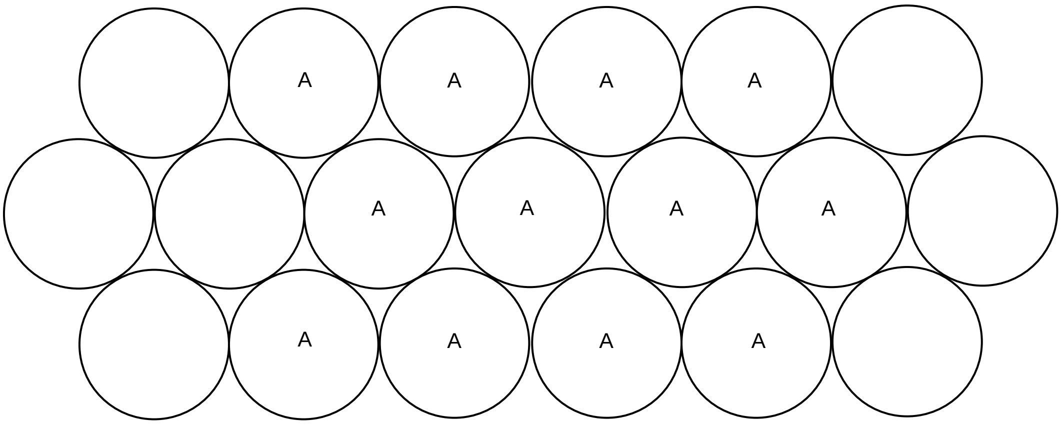
Hexagonal Packing – see question sheet.

A3. Packing Atoms in 3D

Let’s extend this picture to 3D and consider the packing of spheres (to represent atoms).

Consider again the close-packed hexagonal arrangement in one layer:



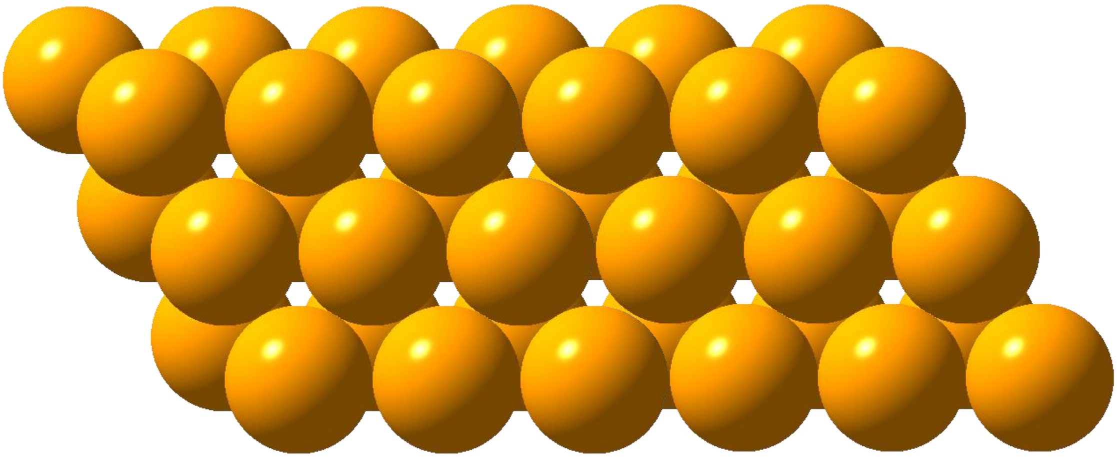


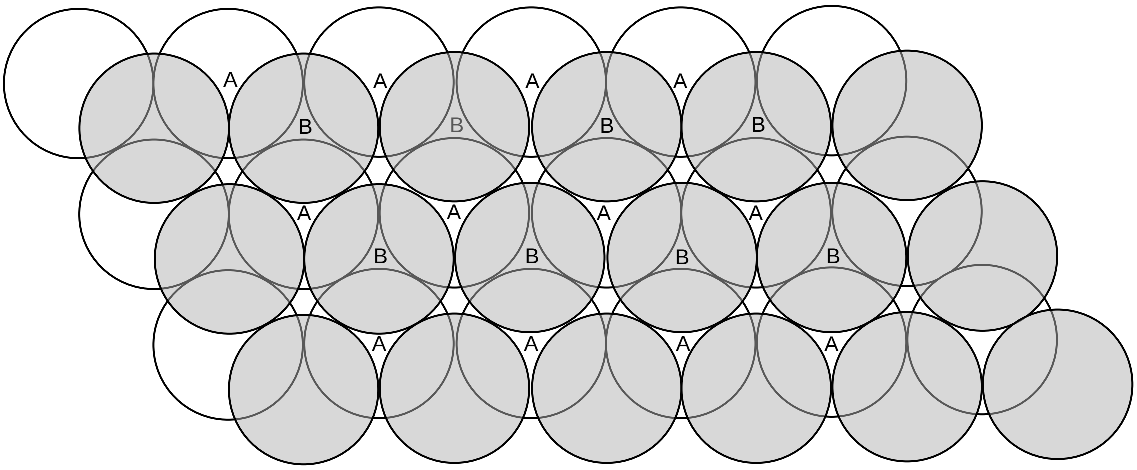
If we extend to 3D, the next layer of atoms could be placed directly above, i.e. the centre of the atoms in the next layer are also at A.

The resultant crystal structure is called the **simple hexagonal** structure. (Note what defines a crystal to be *hexagonal* we will see later).

However, no examples of elements with this structure exist in nature because the atoms can ‘slip’ into the ‘hollows’ or interstices between the atoms. This creates a more efficient packing of 3D space and is energetically more stable – for more on energy considerations, see course C.

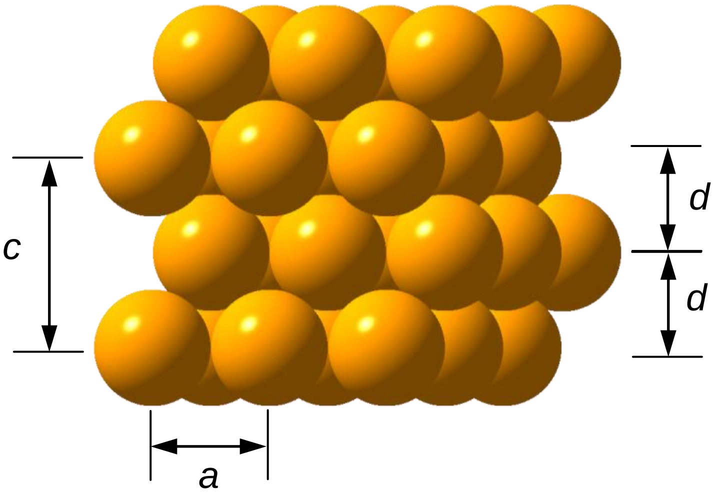
So now consider the next layer of atoms centred at the interstice B:





If the 3rd layer atoms 'slip' into the interstices of the 2nd layer then they may end up directly above the atoms of the 1st layer.

The stacking sequence is then ABAB and this is called the **hexagonal close-packed** (hcp) structure. Seen from the side:



In the ideal hcp structure, as shown, then $d = \sqrt{\frac{2}{3}}a$ (see question sheet!)

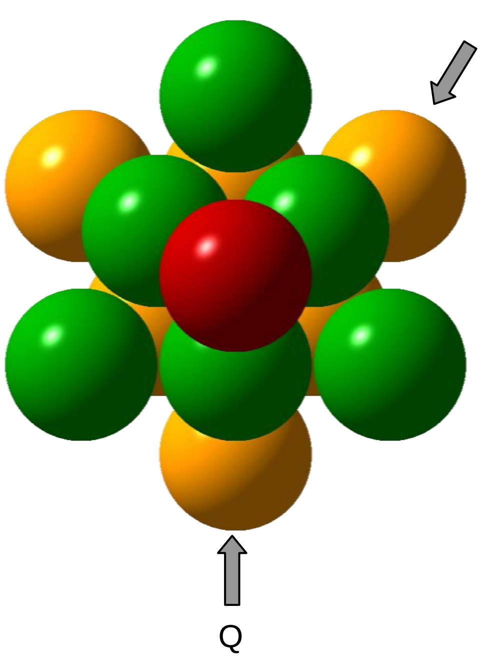
Let's define d as the spacing between the layers (or '**planes**') of atoms, then

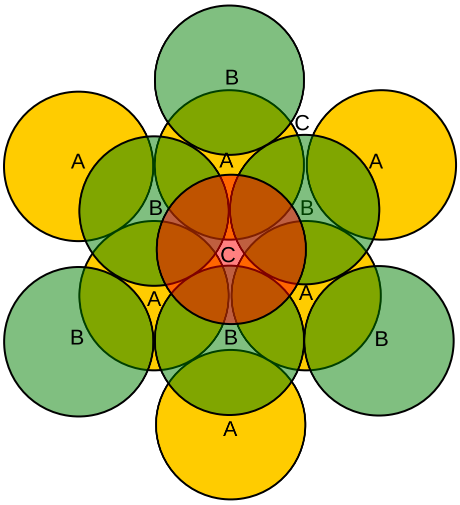
$$c = 2d = 2\sqrt{\frac{2}{3}}a = 1.633a$$

Interatomic forces in real crystals cause deviations from the ideal c/a ratio but metals such as Be, Mg and Co have hcp structures with c/a ratio close to the ideal.

Metal	***c*/*a* ratio**
Mg	1.623
Co	1.622
Be	1.567

But there is an alternative interstice in the 1st layer – let's label it as C. Atoms in the 3rd layer could be placed above C and not A.

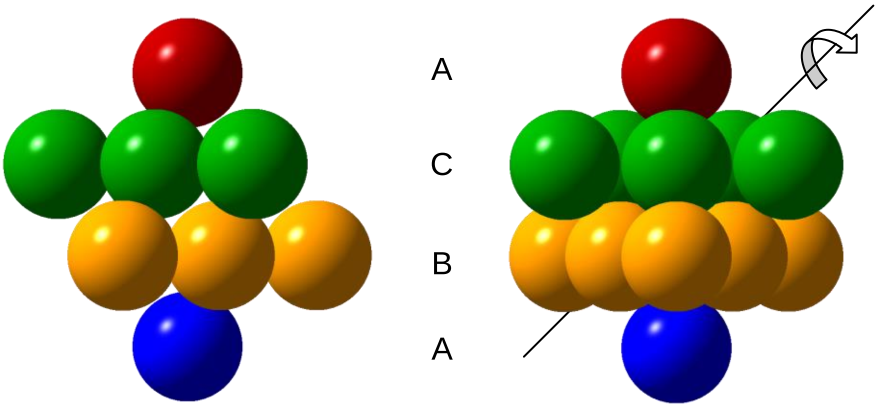




Then the sequence would be ABCABC and the resultant structure is called the **cubic close-packed (ccp)** structure. What defines a '*cubic*' crystal, we will see later.

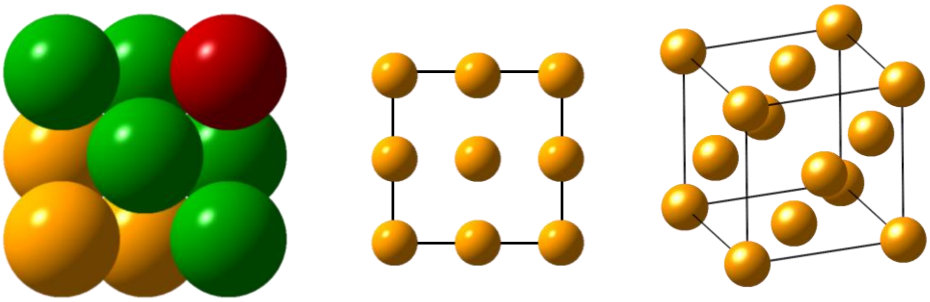
Why do we say the structure is cubic? It is because of the choice of **unit cell** and its **symmetry** – see below.

Seen from the side, looking parallel to P and Q:



direction P direction Q

If we rotate the crystal 45° about the axis as shown on the right above, then we see the following:



and the cubic symmetry of the crystal structure starts to become more obvious.

Many elements have the ccp structure including Cu, Ni and Al.

Notes:

1. Some elements have a ‘mixture’ of ccp and hcp stacking.

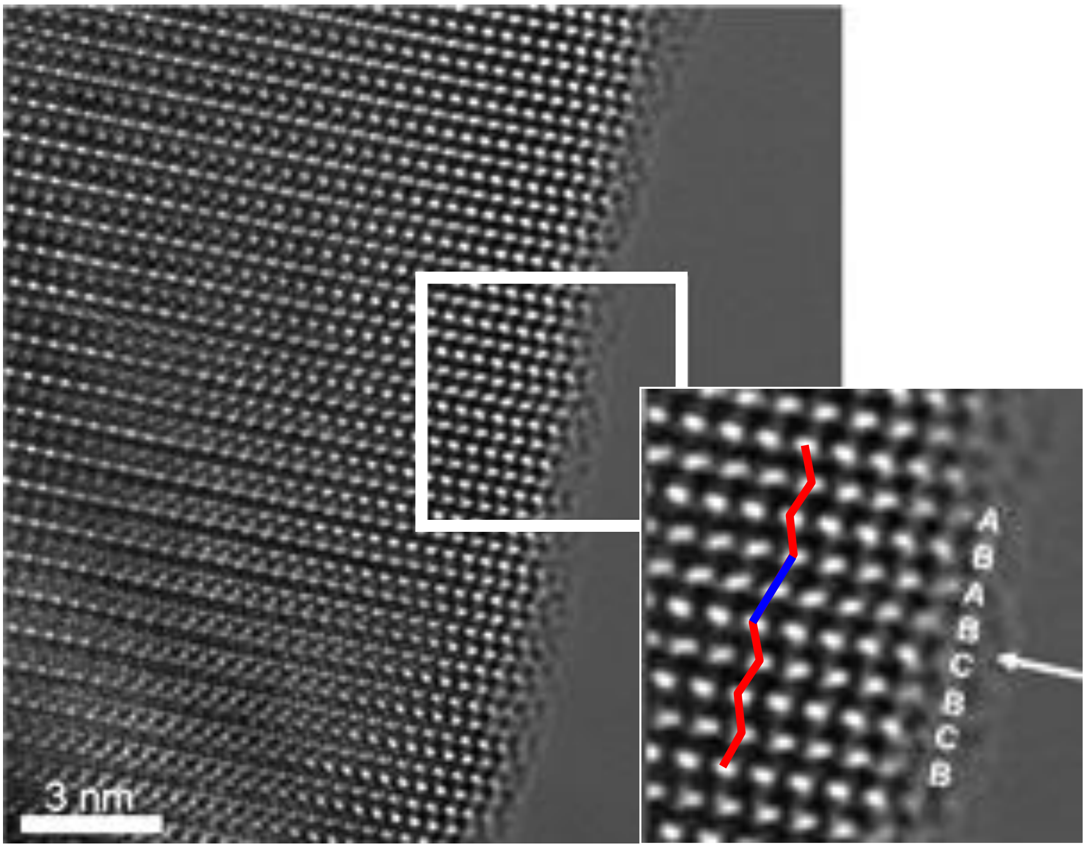
For example: Nd and Sm have ….ABACABAC….

2. It is also possible to have ‘mistakes’ in the stacking sequence – known as **stacking faults**.

For example for hcp:

$$\ldots.\mathrm{ABABABABA}\overbrace{\mathrm{B}\underset{\substack{\uparrow\\ \text{fault}}}{\mathrm{C}}}^{\text{‘ccp’}}\mathrm{BCBCBCBCBC}\ldots.$$

Stacking faults can be seen directly in the transmission electron microscope:

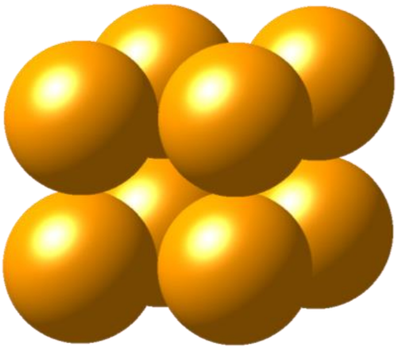


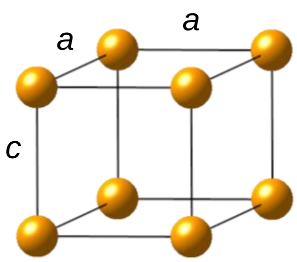
High-resolution electron microscope image showing the location of a stacking fault in a core-multishell ZnS nanowire

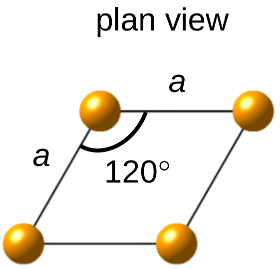
A4. Unit Cells of the hcp and ccp Structures

We need to find a way to represent the hcp and ccp structures with fewest number of atoms that still show the essential structure and symmetry – these are the **unit cells.**

Simple Hexagonal



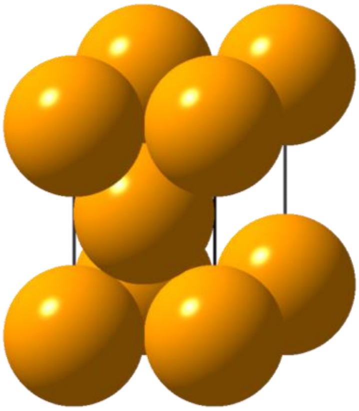


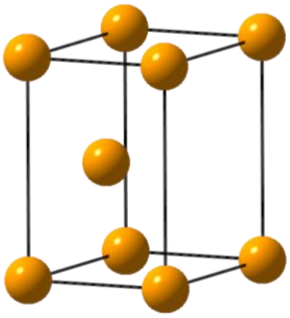


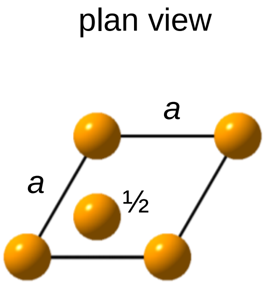
ideal c/a =1

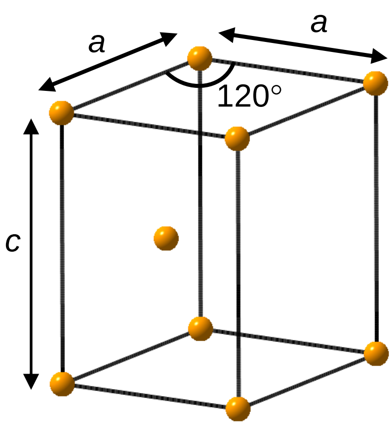
Unit Cell Angles = 90°, 120°

Hexagonal Close-Packed (hcp)



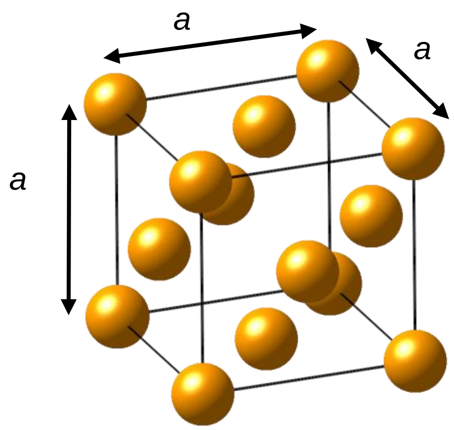






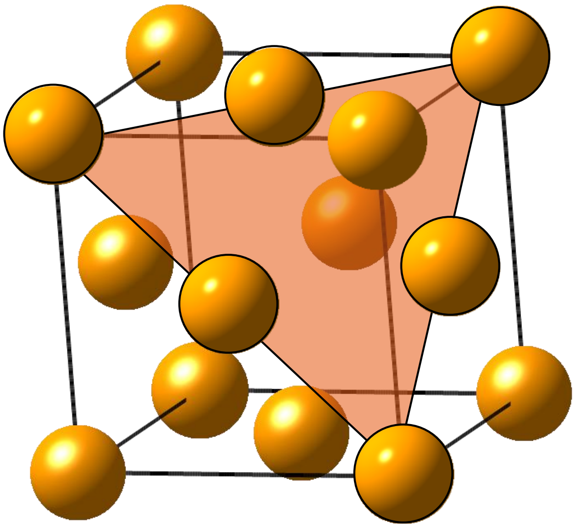
Unit Cell Angles = 90°, 120°

Cubic Close-Packed (ccp)



Unit Cell Angles = 90°

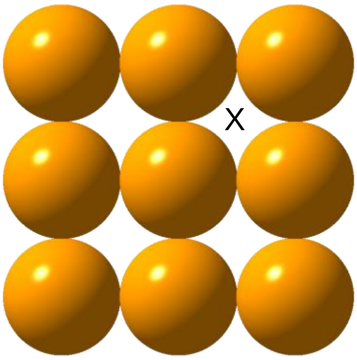
Packing Efficiency of ccp and hcp structures:



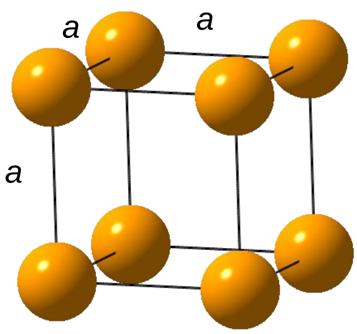
Assume atoms are touching in the close-packed plane (orange triangle), along the diagonal of the faces of the unit cell (the ‘face diagonal’):

A5. Square Layers of Atoms

Consider a single layer of atoms arranged in a square lattice:

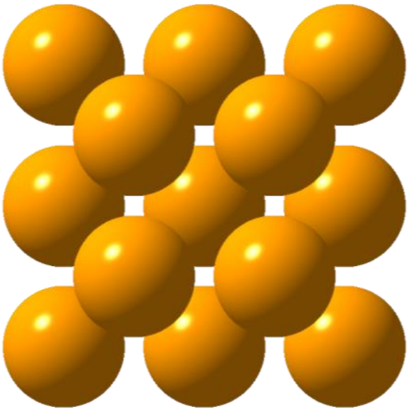


The next layer could be placed directly on top. This then forms the **simple cubic** structure. An example is α-polonium.

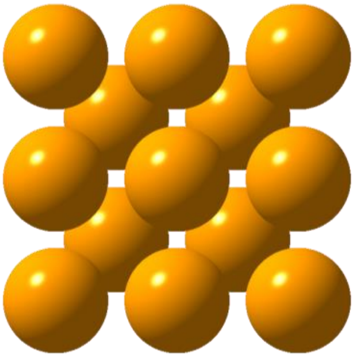


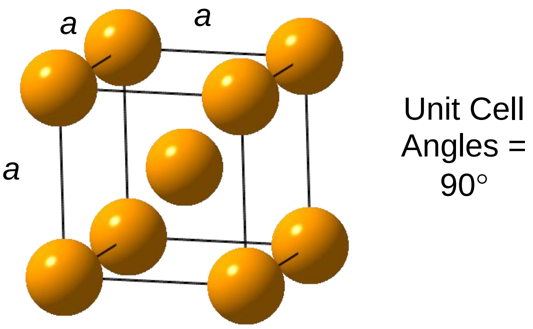
Unit Cell Angles = 90°

Or the next layer could ‘slip’ into the interstices, such as the one marked ‘X’ above.



The 3rd layer can then placed above the 1st layer:

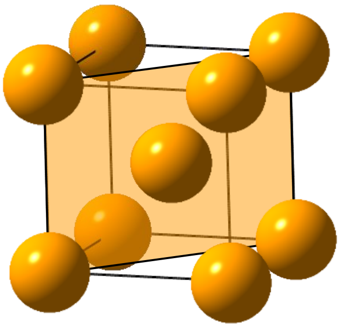


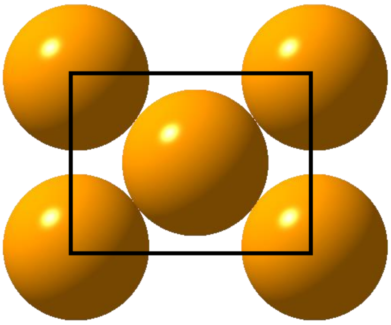


Here if we consider the unit cell as shown then the atoms of the 2nd layer are in the centre of the cube – we call this structure **body-centred cubic** (bcc).

Many metals take this structure, e.g. Cr, Mo, Ti (high temperature form), Fe (low temperature form).

In the bcc structure the atoms are most closely packed in the diagonal plane with atoms touching only along the body diagonal.





Packing Efficiency of bcc – see question sheet!

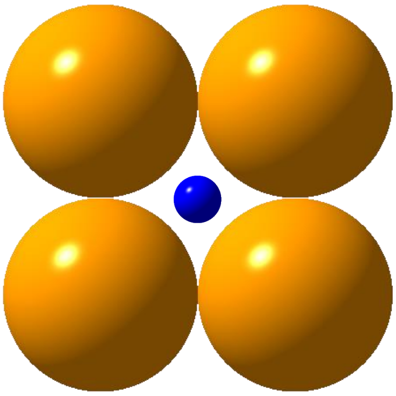
A6. Interstitial Structures

We’ve considered the packing of one size of atom (sphere) but we can also use these ideas to describe the structure of compounds with two or more elements.

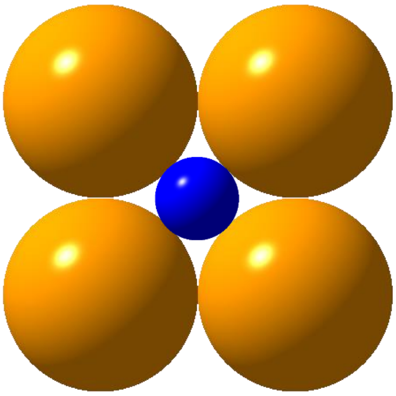
This is especially useful for compounds with dissimilar atoms sizes where ‘small’ atoms or ions (often **cations)** fit into the interstices between ‘large’ atoms or ions (often **anions)**. As we will see there are a number of possible interstices to choose – which one would the atom, or ion, fit best? Need to invoke:

Goldschmidt’s Packing principle:

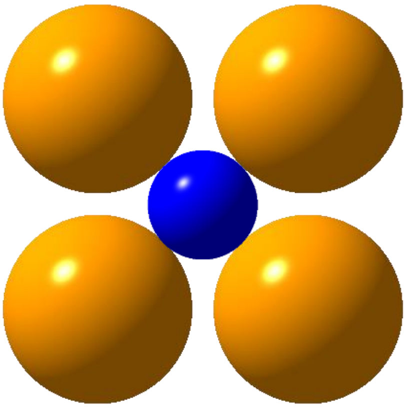
The number of anions surrounding a cation tends to be as large as possible, subject to the condition that all anions touch the cation.



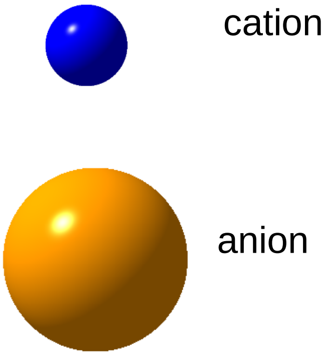
unstable



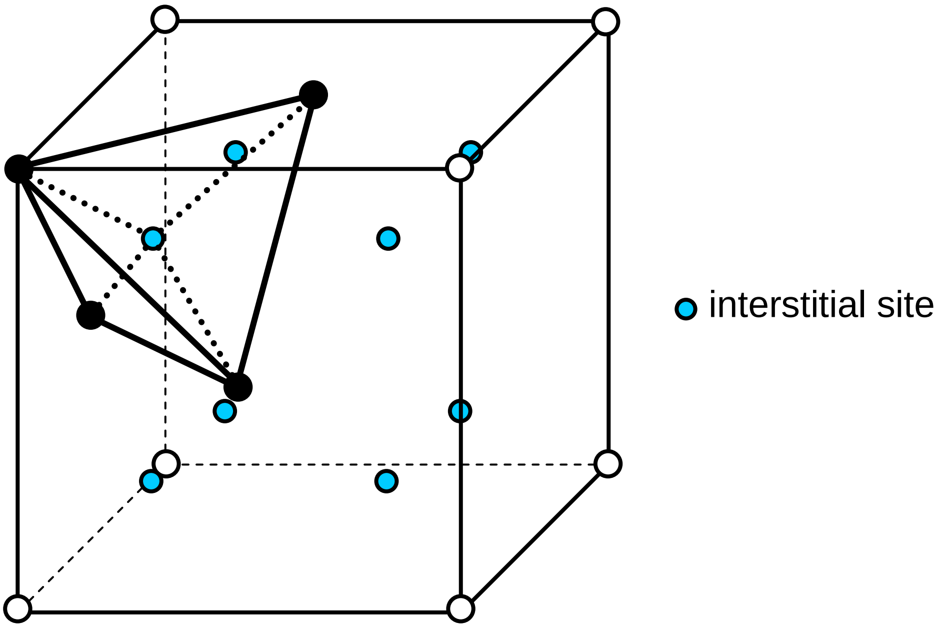
‘ideal’

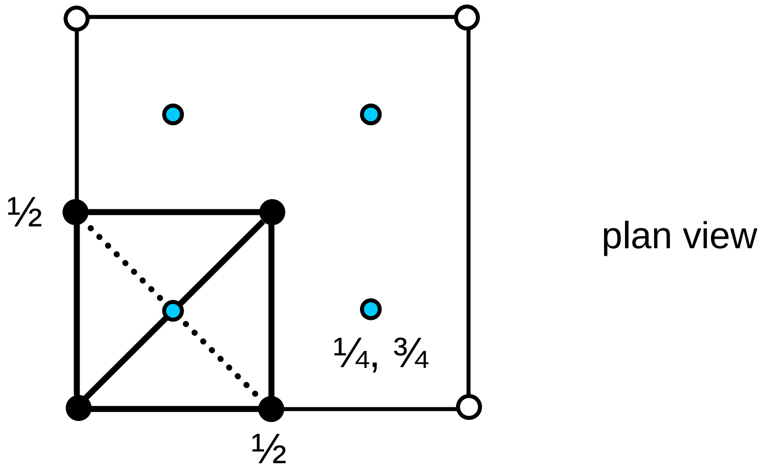


stable



Consider again the ccp structure (for clarity only some atoms are shown):





It is possible to place an atom at an interstitial site (coloured blue) which is at the centre of the tetrahedron formed by the 4 (black) atoms shown. The 4 atoms surround or **co-ordinate** the smaller interstitial atom at a **tetrahedral interstice**.

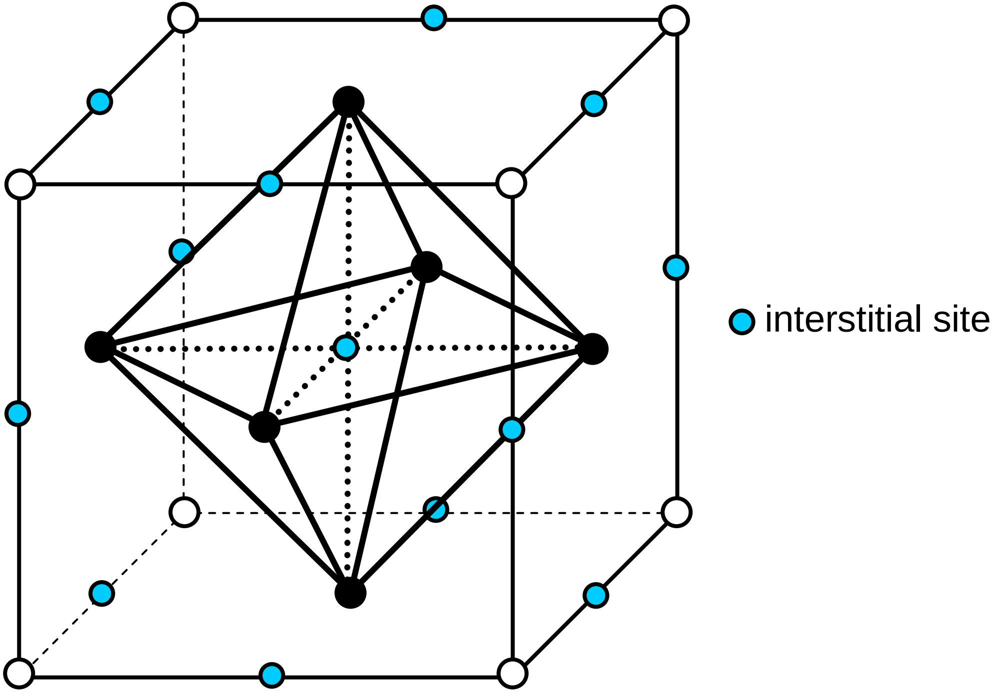
What size of atom can be accommodated in the tetrahedral interstice? The limiting case, according to Goldschmidt's Principle (the geometrically 'ideal' size) would be when the large atoms and the interstitial atom all just touch. Therefore it depends on the ratio of the size of the two atoms:

Consider large atoms (call them A atoms) have radius r_A and interstitial atoms have radius r_X .

For ccp structures, the A atoms touch along the face diagonal.

For the ideal case, atoms A and X touch along the body diagonal:

Consider another possible interstitial site:



Here an interstitial atom can be placed at the centre of an octahedron of 6 atoms, hence the name **octahedral interstice** and the interstitial atom is 6-fold co-ordinated.

The space available in the octahedral interstitial site is larger and so can accommodate an atom of larger radius. What is the ‘ideal’ radius ratio? See question sheet!

<u>*Note*</u>: Of course the interstitial spaces available in *hcp* are the same as *ccp* – the two structures differ only by a stacking sequence.

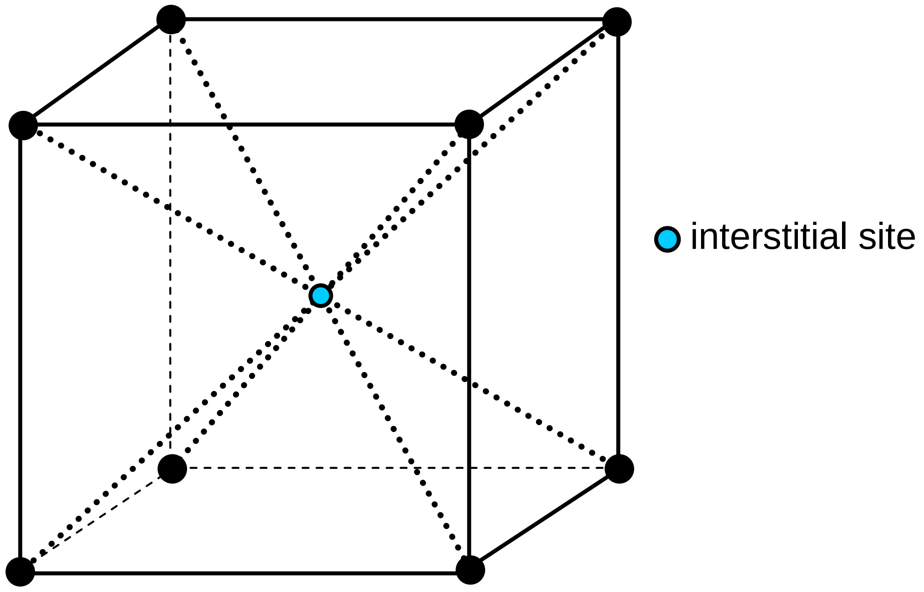
The table below gives the relation between radius ratio and co-ordination number:

Radius ratio r_x / r_A	**Coordination number**	**Type**
<0.155	2	Linear
0.155-0.225	3	Triangular
0.225-0.414	4	Tetrahedral
0.414-0.732	6	Octahedral
0.732-1.000	8	Cubic
1.000	12	Cuboctahedral (Close packed)

So for example if a radius ratio was calculated to be, say 0.5 then the interstitial atom would be accomodated in an octahedral site. However, if the ratio decreased to say 0.4 the atom would be in a tetrahdral site.

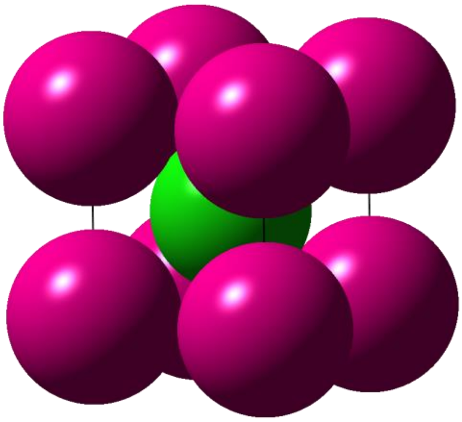
Notice how the co-ordination number increases as the cation and anion radii become similar.

Consider now the simple cubic structure:



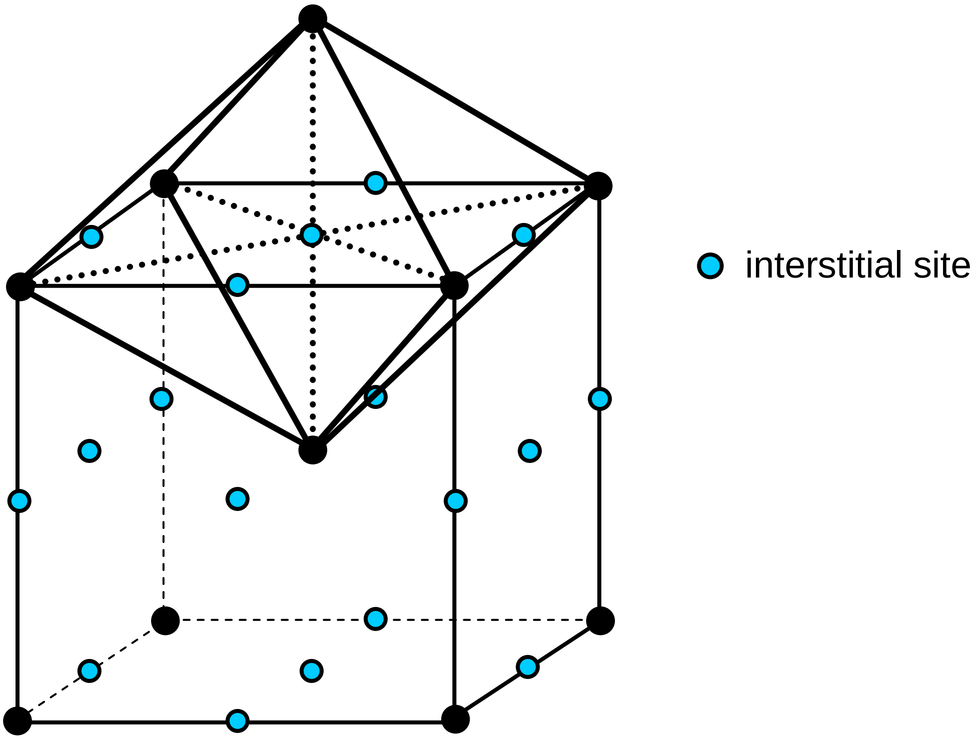
The interstitial atom is placed at the centre of the cube surrounded by 8 atoms and the site is called the **cubic interstitial site**.

An example of this is CsCl with a smaller Cs^+ ion (green) surrounded by larger Cl^- ions (purple).

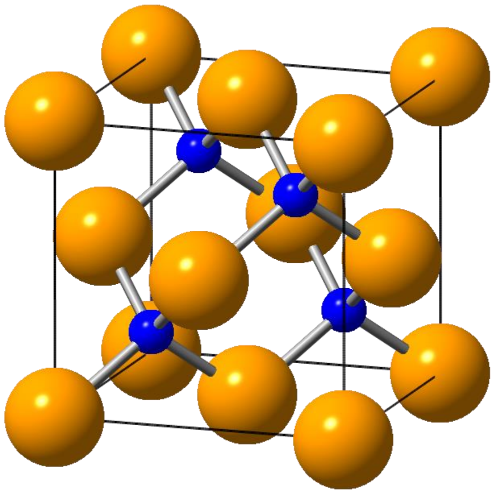


Similar interstitial sites are present in bcc crystals but these are ‘distorted’ octahedral and tetrahedral interstices in that some A atoms will be closer to the interstitial atom than others in the octahedron / tetrahedron. In terms of calculating how well the interstitial atom will fit, it is of course the distance to the <u>nearest</u> A atom that matters!

In the figure below, as an example, we show the ‘distorted’ octahedral sites in bcc.



Other examples of interstitial compounds are metal hydrides, borides and nitrides. In these cases the ‘large’ atoms are the metal atoms:

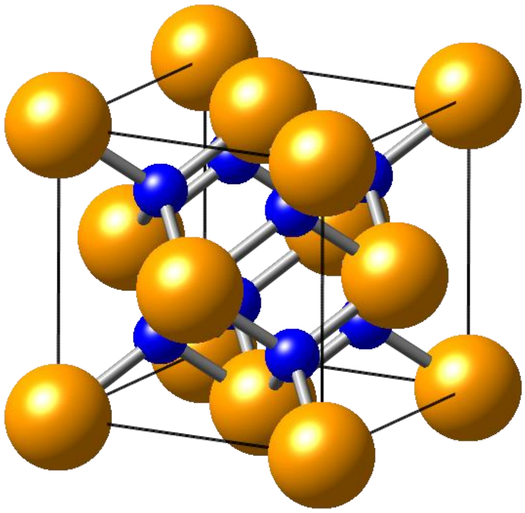


TiH

Ti ccp structure
H occupy half the
tetrahedral interstices

4-fold co-ordination of Ti around H
4-fold co-ordination of H around Ti

(isomorphous with ZnS)

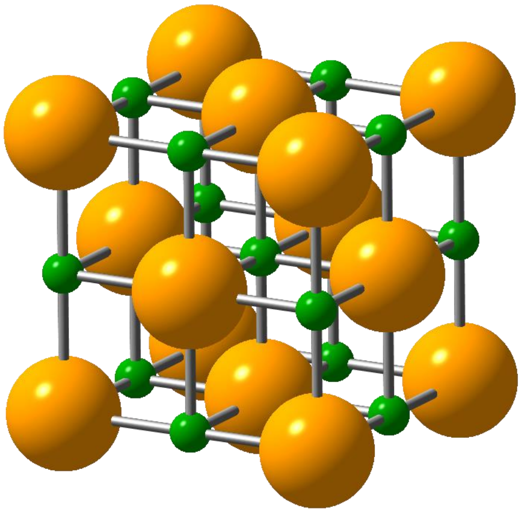


TiH_2

Ti ccp structure
H occupy ALL tetrahedral interstices

4-fold co-ordination of Ti around H
8-fold co-ordination of H around Ti.

(isomorphous with CaF_2)



TiN

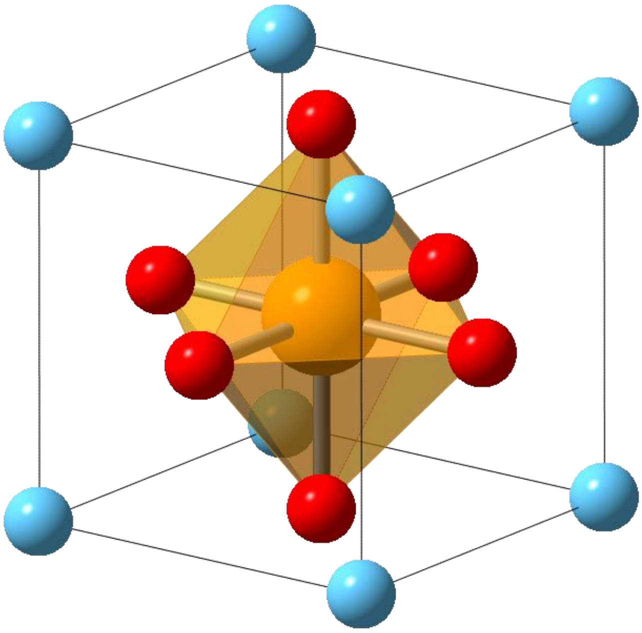
Ti ccp structure
N in octahedral interstices

6-fold co-ordination of Ti around N
6-fold co-ordination of N around Ti.

(isomorphous with NaCl)

Representing Crystal Bonding with Co-ordination Polyhedra:

Crystal structures can be represented using ball and stick models or with co-ordination polyhedra. Here we use $BaTiO_3$ as an example of both:

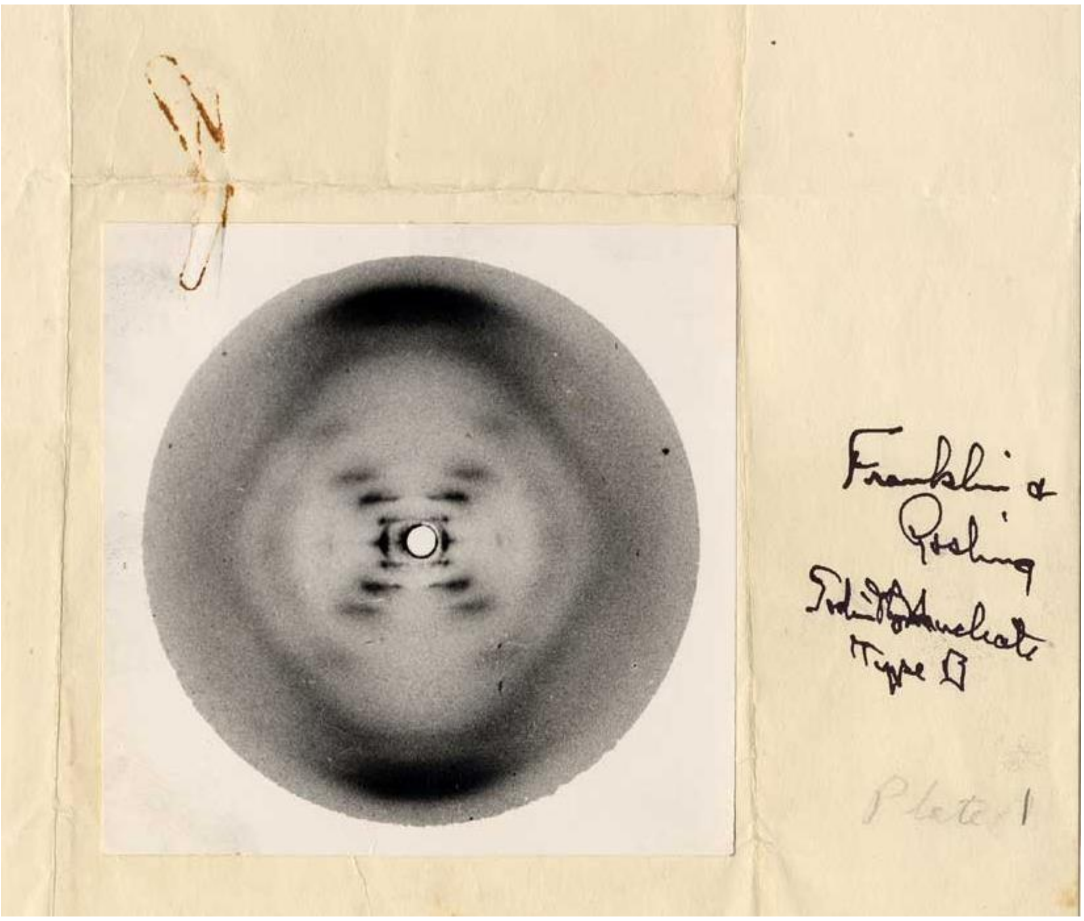


B. 2D Patterns, Lattices and Symmetry

In section A we took a pragmatic approach to building up the structure of simple crystalline materials using the close packing of atoms.

To explore more complicated structures, and to describe the structures of crystals in a more systematic and rigorous way, we need to adopt a different approach.

By having a more rigorous framework to describe crystals we'll be able to interpret experimental diffraction patterns and determine crystal structures, just as Crick and Watson did in 1953!



The famous 'Photo 51': X-ray diffraction pattern of sodium salt of DNA. B configuration. This pattern will be studied further in Question Sheet 3!

No. 4356 April 25, 1953 NATURE 737

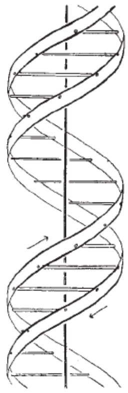
MOLECULAR STRUCTURE OF NUCLEIC ACIDS

A Structure for Deoxyribose Nucleic Acid

We wish to suggest a structure for the salt of deoxyribose nucleic acid (D.N.A.). This structure has novel features which are of considerable biological interest.

A structure for nucleic acid has already been proposed by Pauling and Corey[1]. They kindly made their manuscript available to us in advance of publication. Their model consists of three intertwined chains, with the phosphates near the fibre axis, and the bases on the outside. In our opinion, this structure is unsatisfactory for two reasons: (1) We believe that the material which gives the X-ray diagrams is the salt, not the free acid. Without the acidic hydrogen atoms it is not clear what forces would hold the structure together, especially as the negatively charged phosphates near the axis will repel each other. (2) Some of the van der Waals distances appear to be too small.

Another three-chain structure has also been suggested by Fraser (in the press). In his model the phosphates are on the outside and the bases on the inside, linked together by hydrogen bonds. This structure as described is rather ill-defined, and for this reason we shall not comment on it.



This figure is purely diagrammatic. The two ribbons symbolize the two phosphate—sugar chains, and the horizontal rods the pairs of bases holding the chains together. The vertical line marks the fibre axis

We wish to put forward a radically different structure for the salt of deoxyribose nucleic acid. This structure has two helical chains each coiled round the same axis (see diagram). We have made the usual chemical assumptions, namely, that each chain consists of phosphate diester groups joining β-D-deoxyribofuranose residues with 3′,5′ linkages. The two chains (but not their bases) are related by a dyad perpendicular to the fibre axis. Both chains follow right-handed helices, but owing to the dyad the sequences of the atoms in the two chains run in opposite directions. Each chain loosely resembles Furberg's[2] model No. 1; that is, the bases are on the inside of the helix and the phosphates on the outside. The configuration of the sugar and the atoms near it is close to Furberg's 'standard configuration', the sugar being roughly perpendicular to the attached base. There is a residue on each chain every 3·4 A. in the z-direction. We have assumed an angle of 36° between adjacent residues in the same chain, so that the structure repeats after 10 residues on each chain, that is, after 34 A. The distance of a phosphorus atom from the fibre axis is 10 A. As the phosphates are on the outside, cations have easy access to them.

The structure is an open one, and its water content is rather high. At lower water contents we would expect the bases to tilt so that the structure could become more compact.

The novel feature of the structure is the manner in which the two chains are held together by the purine and pyrimidine bases. The planes of the bases are perpendicular to the fibre axis. They are joined together in pairs, a single base from one chain being hydrogen-bonded to a single base from the other chain, so that the two lie side by side with identical z-co-ordinates. One of the pair must be a purine and the other a pyrimidine for bonding to occur. The hydrogen bonds are made as follows: purine position 1 to pyrimidine position 1; purine position 6 to pyrimidine position 6.

If it is assumed that the bases only occur in the structure in the most plausible tautomeric forms (that is, with the keto rather than the enol configurations) it is found that only specific pairs of bases can bond together. These pairs are: adenine (purine) with thymine (pyrimidine), and guanine (purine) with cytosine (pyrimidine).

In other words, if an adenine forms one member of a pair, on either chain, then on these assumptions the other member must be thymine; similarly for guanine and cytosine. The sequence of bases on a single chain does not appear to be restricted in any way. However, if only specific pairs of bases can be formed, it follows that if the sequence of bases on one chain is given, then the sequence on the other chain is automatically determined.

It has been found experimentally[3,4] that the ratio of the amounts of adenine to thymine, and the ratio of guanine to cytosine, are always very close to unity for deoxyribose nucleic acid.

It is probably impossible to build this structure with a ribose sugar in place of the deoxyribose, as the extra oxygen atom would make too close a van der Waals contact.

The previously published X-ray data[5,6] on deoxyribose nucleic acid are insufficient for a rigorous test of our structure. So far as we can tell, it is roughly compatible with the experimental data, but it must be regarded as unproved until it has been checked against more exact results. Some of these are given in the following communications. We were not aware of the details of the results presented there when we devised our structure, which rests mainly though not entirely on published experimental data and stereochemical arguments.

It has not escaped our notice that the specific pairing we have postulated immediately suggests a possible copying mechanism for the genetic material.

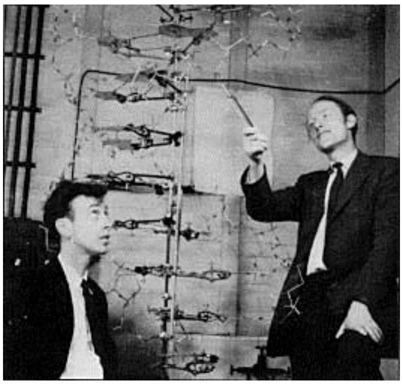
Full details of the structure, including the conditions assumed in building it, together with a set of co-ordinates for the atoms, will be published elsewhere.

We are much indebted to Dr. Jerry Donohue for constant advice and criticism, especially on interatomic distances. We have also been stimulated by a knowledge of the general nature of the unpublished experimental results and ideas of Dr. M. H. F. Wilkins, Dr. R. E. Franklin and their co-workers at King's College, London. One of us (J. D. W.) has been aided by a fellowship from the National Foundation for Infantile Paralysis.

J. D. Watson
F. H. C. Crick

Medical Research Council Unit for the
Study of the Molecular Structure of
Biological Systems,
Cavendish Laboratory, Cambridge.

April 2.



[1] Pauling, L., and Corey, R. B., *Nature*, **171**, 346 (1953); *Proc. U.S. Nat. Acad. Sci.*, **39**, 84 (1953).

[2] Furberg, S., *Acta Chem. Scand.*, **6**, 634 (1952).

[3] Chargaff, E., for references see Zamenhof, S., Brawerman, G., and Chargaff, E., *Biochim. et Biophys. Acta*, **9**, 402 (1952).

[4] Wyatt, G. R., *J. Gen. Physiol.*, **36**, 201 (1952).

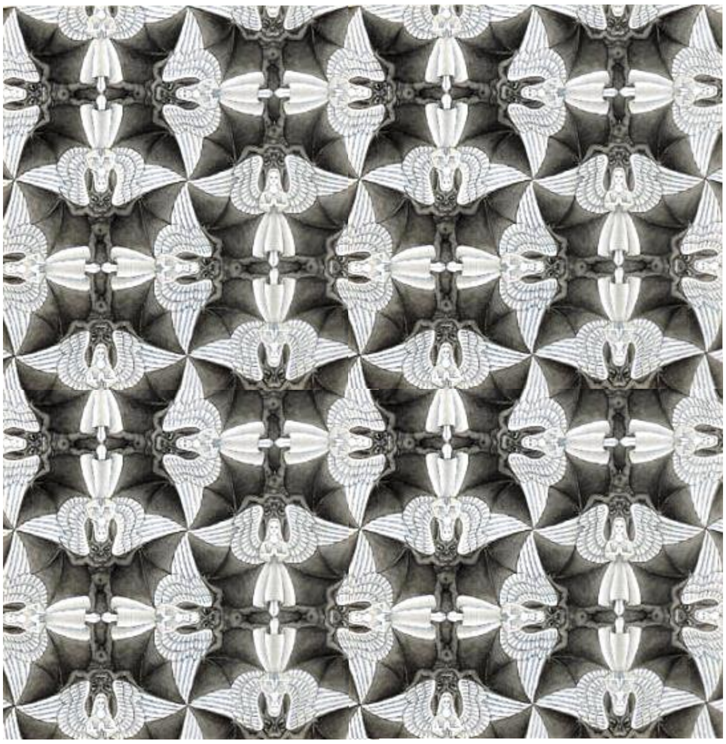
[5] Astbury, W. T., Symp. Soc. Exp. Biol. 1, Nucleic Acid, 66 (Camb. Univ. Press, 1947).

[6] Wilkins, M. H. F., and Randall, J. T., *Biochim. et Biophys. Acta*, **10**, 192 (1953).

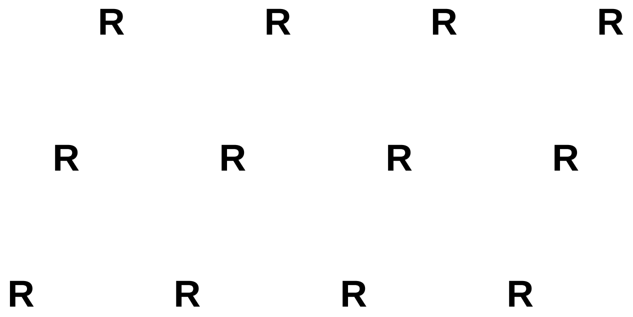
B1. 2D Patterns and Lattices

We start in 2D and consider 2D patterns and lattices. Examples of such patterns can be found for example on the tiled walls of the Alhambra Palace in Granada:

The artist M.C. Escher was instrumental in bringing the geometry of 2D tiling to a wider audience (see also Question Sheet 2!):



Consider a regular 2D pattern composed of the letter ‘**R**’ repeated indefinitely.

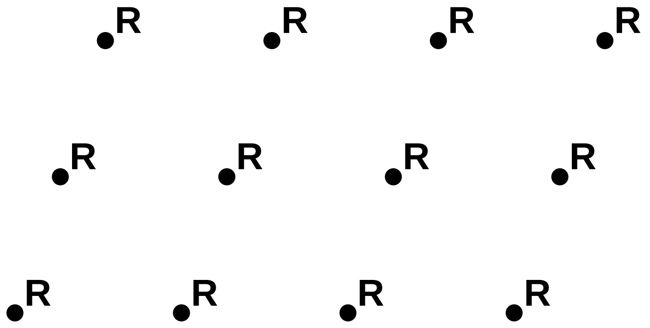


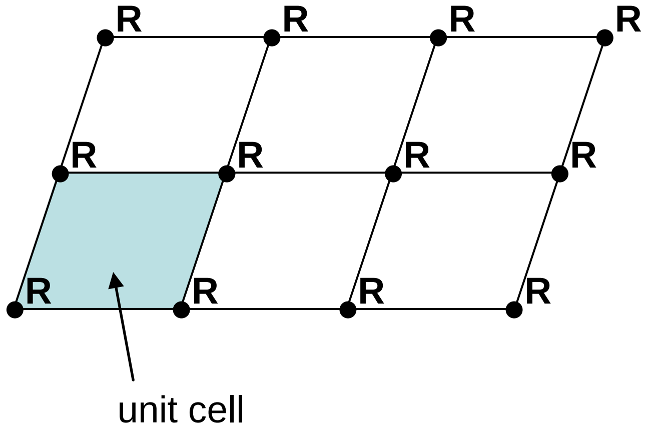
The repeating ‘unit of pattern’ is called the **motif**. In a crystal, the motif is composed of atoms.

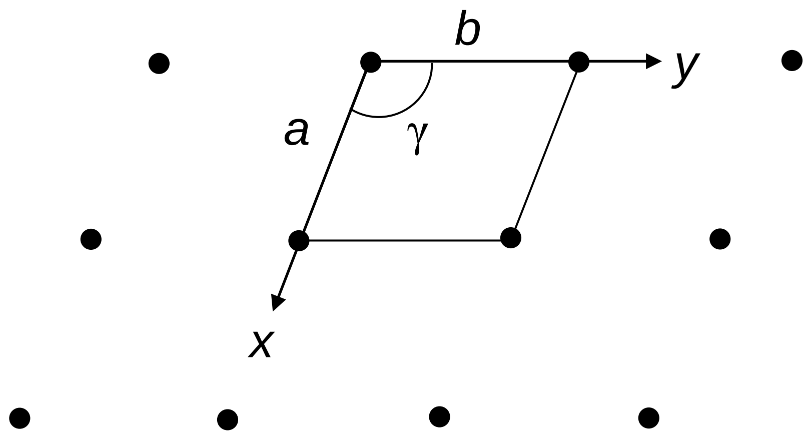
The motifs can be considered to be situated at or near the intersections of an (imaginary) grid.

The grid is called the **lattice** and the intersections are called **lattice points**.

Sometimes, it is said that ‘**structure = lattice + motif**’. What this really means is that all crystal structures can be built up by placing a motif of atoms at every lattice point.

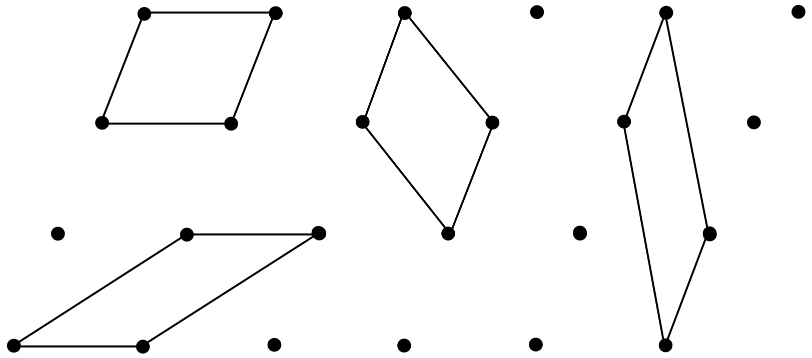






The lattice in 2D is completely specified by a statement of the repeat lengths *a* and *b* parallel to its *x*-axis and *y*-axis and its interaxial angle γ.

In principle, there are an infinite number of ways of drawing the lattice but convention is to choose a lattice to give a unit cell with angles closest to 90°.



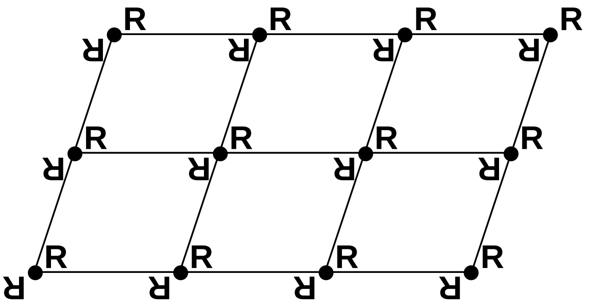
Each motif is identical and for an infinitely extended pattern, the environment (i.e. the spatial distribution of the surrounding motifs and their orientation) around each motif is identical. Leads to….

Definition of a Lattice

A lattice is an infinite array of points repeated periodically throughout space. The view from each lattice point is the same as from any other.

B2. Symmetry Elements

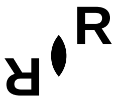
Consider:



Here the unit cell and lattice is as before but now the motif is

Clearly there's an internal **rotational symmetry** in the motif. A rotation of 180° (2-fold) about an axis through the lattice point marked.

The 2-fold rotation axis is called a **DIAD** and is represented by ⬮. Thus:

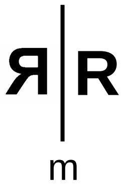


Notice that additional diads are now generated in the 2D structure, at the mid-points between neighbouring lattice points and at the centre of the unit cell.

Other rotation axes are possible:

3-fold: **TRIAD**	4-fold: **TETRAD**	6-fold: **HEXAD**
▲	◆	⬢

In addition to rotational symmetry, it is also possible to have **mirror symmetry** as part of the motif:

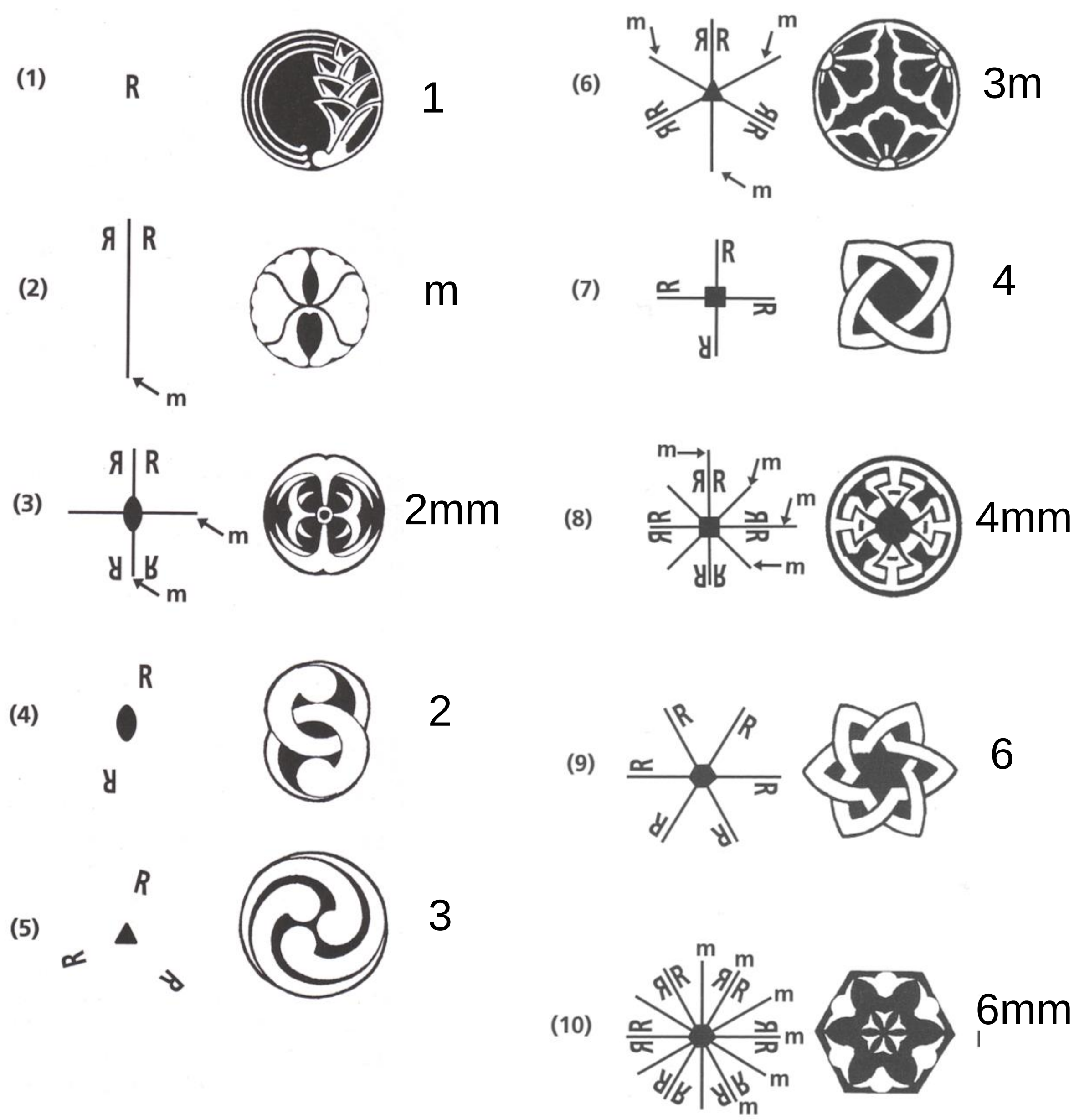


Or a combination of rotation axes and mirrors. This leads to the 10 **2D crystallographic** or **plane point groups**.

Definitions

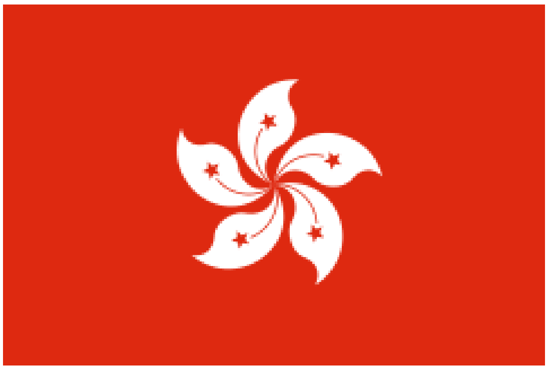
The symmetry elements (or operators) of a finite body must pass through a point, taken as the centre of the body: such a **group** (or combination) of symmetry elements is known as a **point group**.

The 10 **2D crystallographic** or **plane point groups** are illustrated below (taken from Hammond's book):

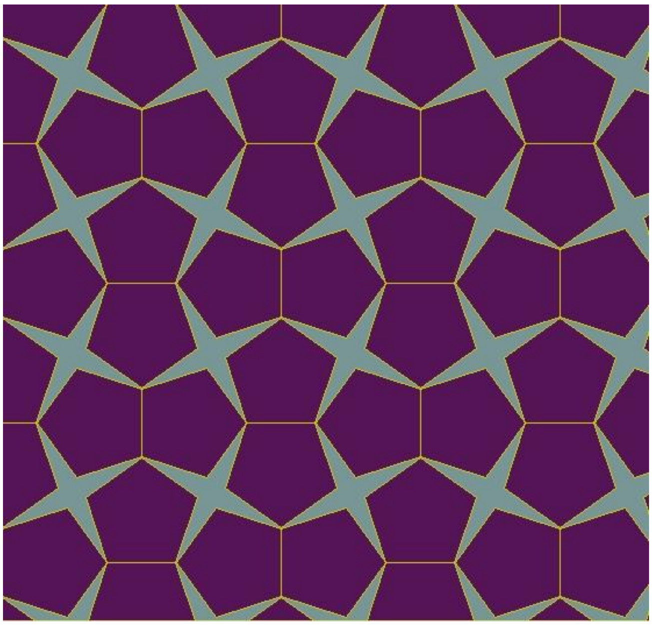


Aside:

Why not point groups with 5-fold rotation axes, or 7-fold, etc? Definitely possible to have for example 5-fold point group! For example the motif on the flag of Hong Kong:



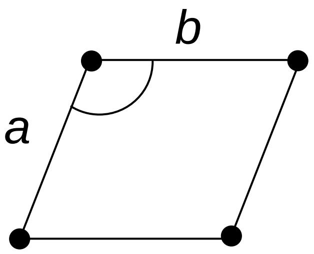
However, only these 10 point groups can occur in regular repeating 2D patterns. Patterns with 5-fold symmetry are non-repeating, non-periodic.



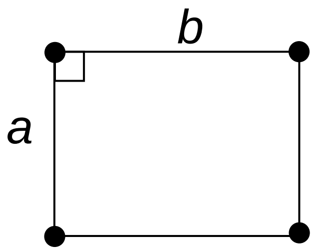
If you try to fit pentagons together you get gaps! The overall pattern does not have 5-fold symmetry.

B3. 2D Lattices

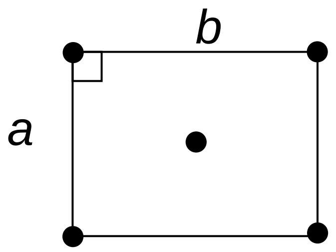
The need for periodic tiling of the 2D surface limits the number of possible 2D lattices to just 5:



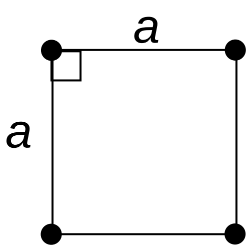
oblique *p*



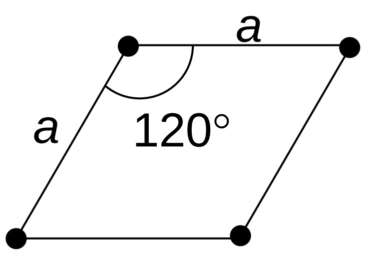
rectangular *p*



rectangular *c*



square *p*

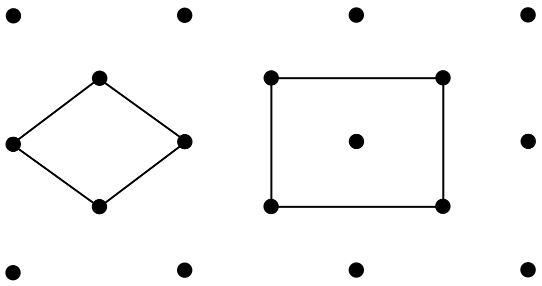


hexagonal *p*

p -'**primitive**' 2D lattice – only <u>one</u> lattice point per unit cell

c -'**centred**' 2D lattice – <u>two</u> lattice points per unit cell

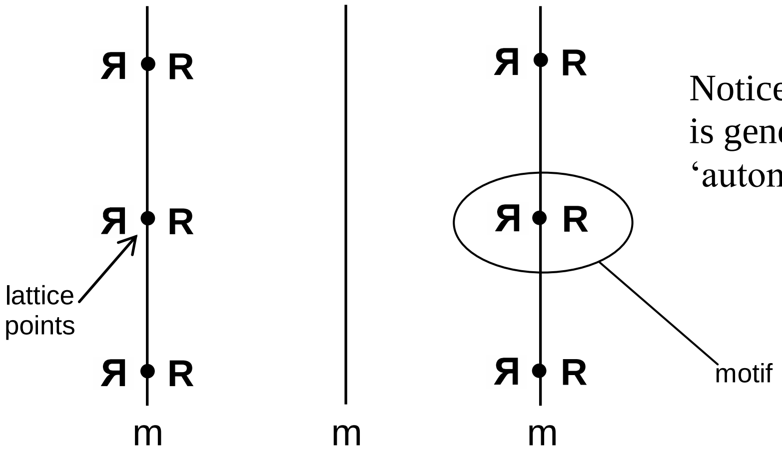
Why not just choose a primitive cell for rectangular *c*?



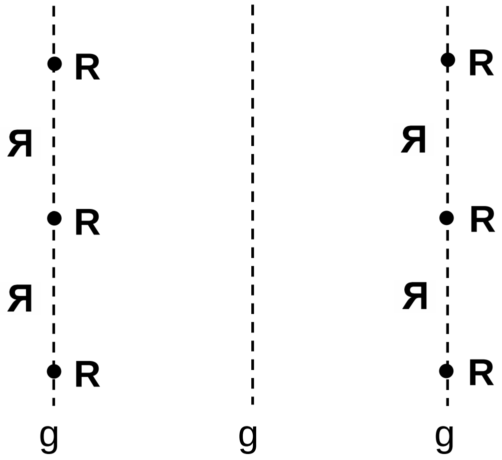
Indeed we can! But it does not reflect the full symmetry of the lattice – we choose a larger unit cell and a centred lattice because the axes joining the sides are at 90°.

We are almost ready to combine the motif and the lattice but we first need to consider one further symmetry element called a **glide line** in 2D (**glide plane** in 3D).

Consider a rectangular *p* lattice:

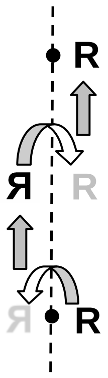


Notice an extra mirror is generated ‘automatically’.



Glide Lines
An extra glide line also generated

The Action of a Glide:
glide ≡ reflect about line/plane and translate by ½ lattice spacing



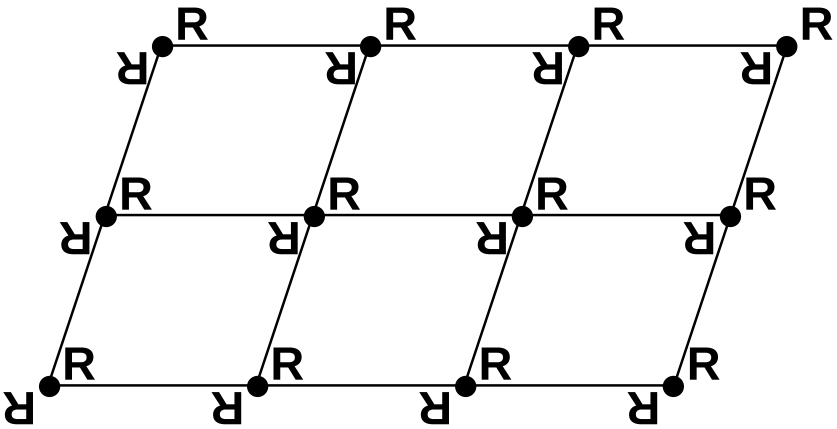
‘Macroscopic’ example of a glide line (footprints on a beach at St Kitts!):

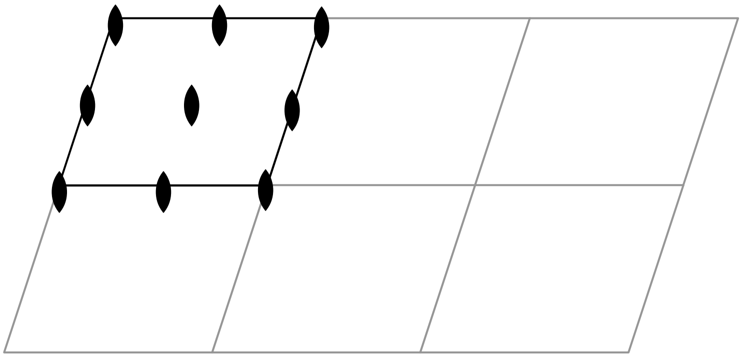
B4. The 2D Plane Groups

So we can now put together the 5 possible 2D lattices with the 10 possible crystallographic 2D point groups to give all the possible 2D **plane groups** – there are 17 in total.

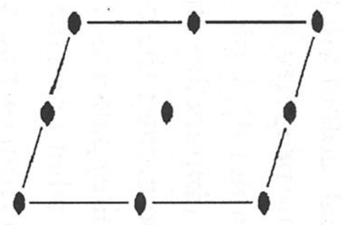
These are shown in Appendix 1.

Consider just one example here. We saw from before:





From Appendix 1:



*p*2

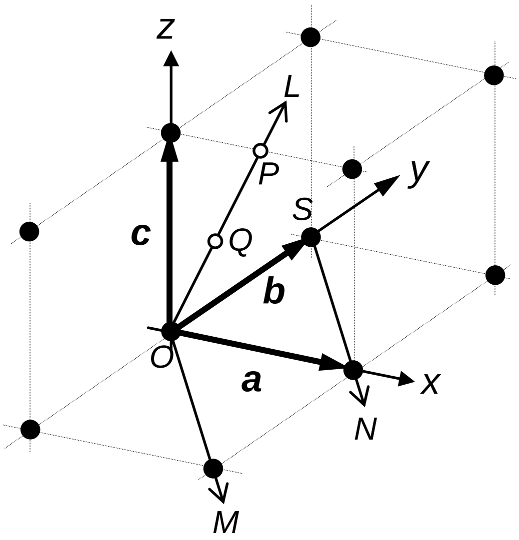
Some symmetry elements (glides, diads) are generated automatically. For example extra glide lines in *p*4*mm*, extra diads in *p*2.

C. Describing Crystals

Before we continue with our analysis of crystallographic symmetry in 3D, we need to explore a convenient system to describe directions and planes in crystals.

C1. Indexing Lattice Directions (Zone Axes)

Consider a general 3D lattice with lattice points and unit cell as shown:



The unit cell has unit cell edge vectors sometimes called **basis vectors**: **a**, **b**, **c** (which are not necessarily orthogonal or equal).

We want to write the direction OL using convenient nomenclature or **index**.

(i) Co-ordinates of P are ½,0,1
(ii) Express as a ratio of whole numbers (multiply by 2 in this case) and put in square brackets, i.e. [102]
(iii) Thus [102] is the direction symbol for OL.

Consider now SN, shift origin to S (or consider OM which is parallel to SN) and proceed as before to find SN = $\left[1\bar{1}0\right]$ which we say as ‘one bar-one oh’.

Directions can be written in terms of the basis vectors:

$$\mathbf{r}_{102} = 1\mathbf{a} + 0\mathbf{b} + 2\mathbf{c}$$

Thus in general for a direction [*uvw*]:

$$\mathbf{r}_{uvw} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$$

Notes

a, **b**, **c** are thus [100], [010] and [001].

When using crystallographic axes, we often talk about the **a**, **b**, **c** axes rather than x, y, z axes.

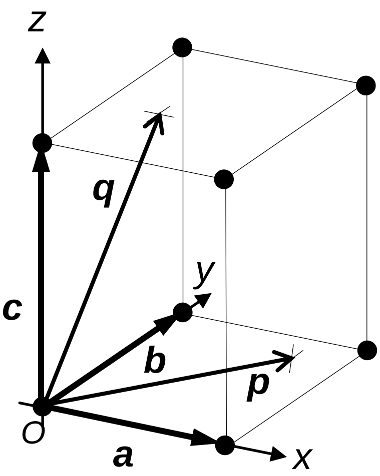
C2. Angles Between Lattice Vectors (Interzonal Angles)

The angle between two vectors **p** and **q** is given by the dot, or scalar, product:

$$\mathbf{p}.\mathbf{q} = pq\cos\theta \qquad \text{where } p = |\mathbf{p}| \text{ and } q = |\mathbf{q}|$$

$$\text{Therefore } \theta = \cos^{-1}\left(\frac{\mathbf{p}.\mathbf{q}}{pq}\right)$$

Consider a unit cell with $a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$



$$\mathbf{p} = [u_1\, v_1\, w_1] \qquad \mathbf{q} = [u_2\, v_2\, w_2]$$

Consider general vector [*uvw*], we can write:

$$[uvw] = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$$

$$= ua\mathbf{i} + vb\mathbf{j} + wc\mathbf{k}$$

where $a = |\mathbf{a}|$, $b = |\mathbf{b}|$ and $c = |\mathbf{c}|$

i = unit vector in direction **a**
j = unit vector in direction **b**
k = unit vector in direction **c**

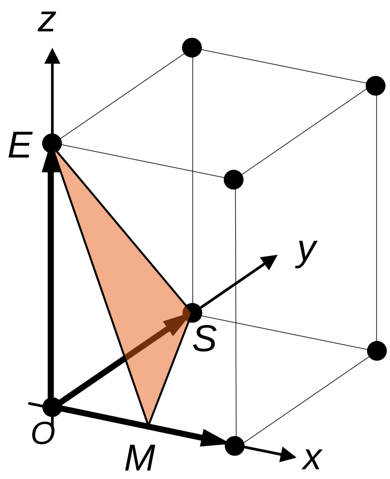
Therefore
$$\cos\theta = \frac{u_1u_2a^2 + v_1v_2b^2 + w_1w_2c^2}{\sqrt{u_1^2a^2 + v_1^2b^2 + w_1^2c^2}\sqrt{u_2^2a^2 + v_2^2b^2 + w_2^2c^2}}$$

C3. Indexing Lattice Planes – Miller Indices

A **lattice plane** is a plane which passes through any three lattice points which are not in a straight line.

A set of parallel lattice planes is characterised by its **Miller indices** (*hkl*).

Consider again a general 3D lattice:



The routine for indexing the plane EMS is as follows:

(i) write down the intercepts of the plane on the axes of the unit cell or unit cell vectors **a**, **b**, **c**.

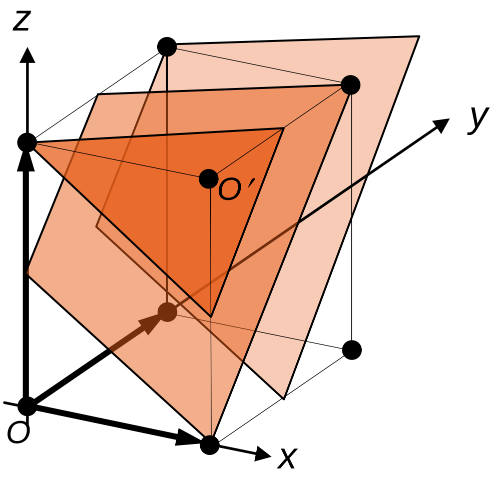
i.e. ½**a**, 1**b**, 1**c**

expressed as fractions of the cell edge length this is ½, 1, 1

(ii) Take the reciprocal of these fractions and put the whole numbers into round brackets:

This gives (211) - this is the Miller index of plane EMS

Now consider the following set of planes:



What's the index of this set of planes?

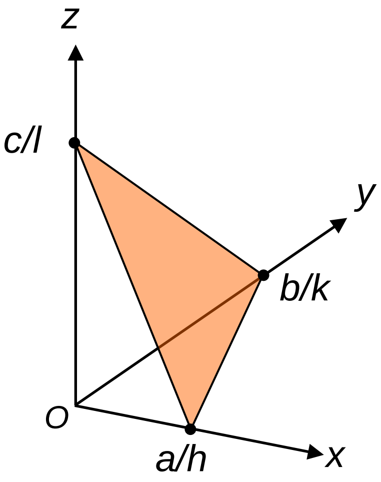
Easiest way to tackle this is to move the origin to a different lattice point – always allowed to do this! Let's move the origin to O′ keeping the direction of the axes the same.

Intercepts (relative to O′) for the first plane seen in the series are at:

-1, ½, -½

Therefore the plane is $\left(\bar{1}2\bar{2}\right)$

In general a plane (*hkl*) will intercept the x-axis at *a*/*h*, the y-axis at *b*/*k* and the z-axis at *c*/*l*



But remember there are a set of parallel planes (*hkl*), so the first plane intercepts the x-axis at *a*/*h*, the second at 2*a*/*h*, the third at 3*a*/*h*, and so on. Remember also that the origin can be moved and so (*hkl*) is equivalent to ($\bar{h}\bar{k}\bar{l}$).

C4. Miller Indices and Lattice Directions in Cubic Crystals

The positive and negative directions of the crystal axes vectors

$$\pm\mathbf{a}, \pm\mathbf{b}, \pm\mathbf{c}$$

can be expressed as

$$[100], [\bar{1}00], [010], [0\bar{1}0], [001], [00\bar{1}]$$

In a cubic crystal the axes are crystallographically equivalent and interchangeable and may be expressed collectively as <100>, implying all 6 variants of 1,0,0.

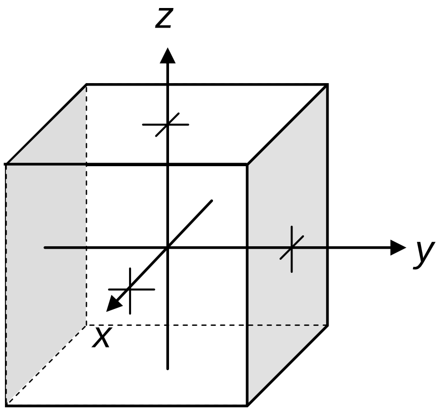
In fact we can do this for any direction in the cubic system, so for a general direction <*uvw*> there are 48 (24 pairs) variants. For example consider for yourself <123>.

A similar concept can be applied to Miller indices of crystal planes. The 6 faces of a cube (with the origin at the centre) are:

$$(100), (\bar{1}00), (010), (0\bar{1}0), (001), (00\bar{1})$$

These are expressed collectively as {100}. Such a group of planes is sometimes known as a **form**.

shaded planes are (010), $(0\bar{1}0)$.



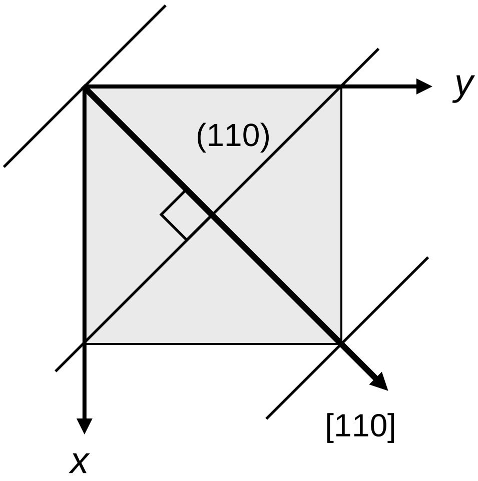
For a general plane {*hkl*} in the cubic system, there are 48 (24 pairs) variants. This number is sometimes known as the **multiplicity** and given the symbol m_{hkl}. It is an important quantity when interpreting the intensities of powder x-ray diffraction patterns – see later.

So for example the multiplicity of the {100} planes is 6, for the {111} planes, it is 8, and so on.

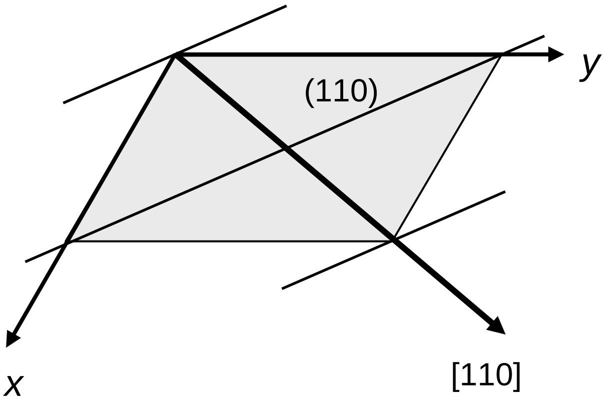
For a cubic system, the directions are perpendicular to planes with the same numerical indices. For example

[110] is perpendicular to (110);
[123] is perpendicular to (123).

But this is not true in general! See below:



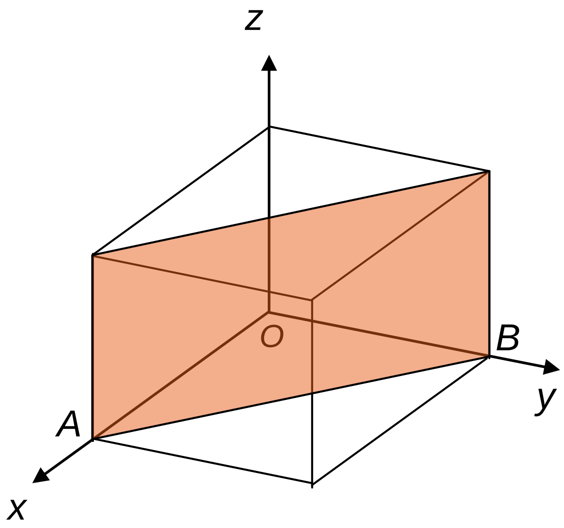
CUBIC



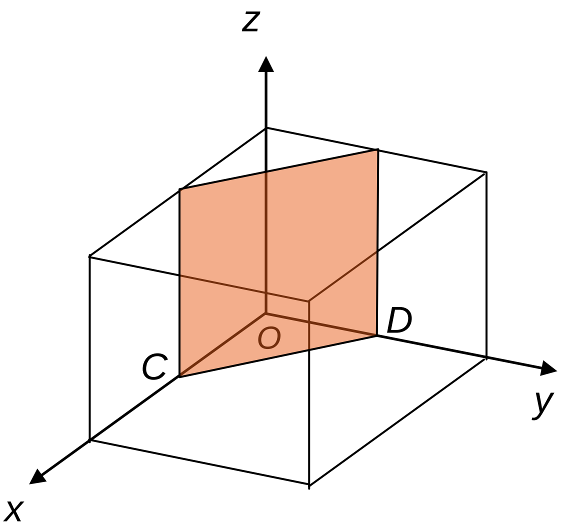
NON-CUBIC

C5. Interplanar Spacings

Consider the following planes:

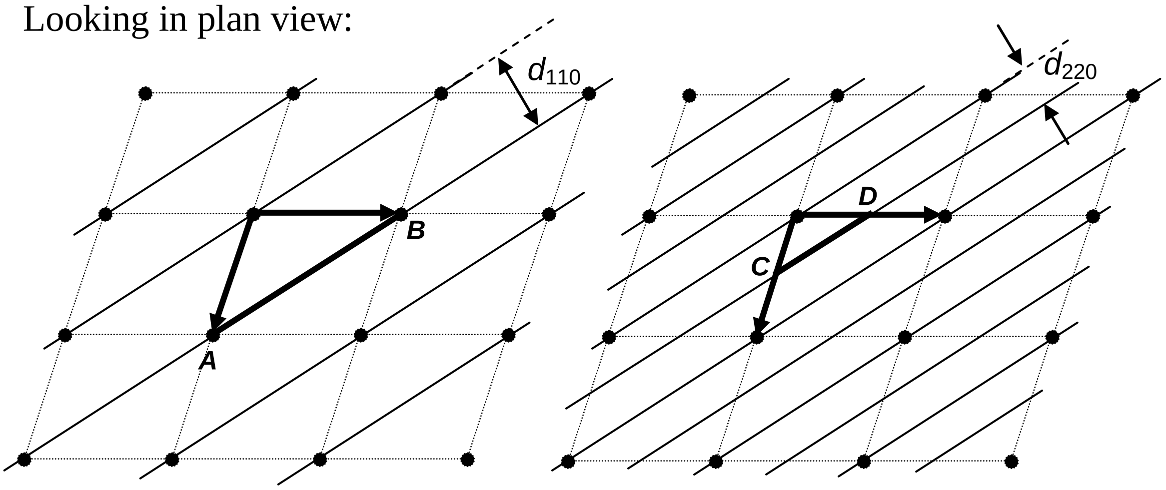


(110)

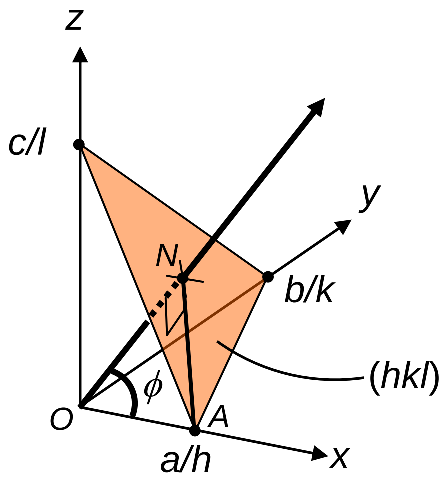


(220)

Looking in plan view:



In general, consider a plane (*hkl*):



There is of course a parallel plane (not shown) passing through the origin, O, and so the interplanar spacing is given by the length of the normal to the (*hkl*) plane, ON.

Angle AON = ϕ (angle between normal and x-axis)

Define: θ as the angle between ON and the y-axis
ψ as the angle between ON and the z-axis

Therefore by comparing to above, we can write:

$$\cos\beta = \left(\frac{k}{b}\right)d_{hkl} \quad \text{and} \quad \cos\gamma = \left(\frac{l}{c}\right)d_{hkl}$$

For <u>orthogonal axes,</u> using Pythagoras' theorem,

$$\cos^2\phi + \cos^2\theta + \cos^2\psi = 1$$

we can write that $\left(\frac{h}{a}\right)^2 d_{hkl}^2 + \left(\frac{k}{b}\right)^2 d_{hkl}^2 + \left(\frac{l}{c}\right)^2 d_{hkl}^2 = 1$

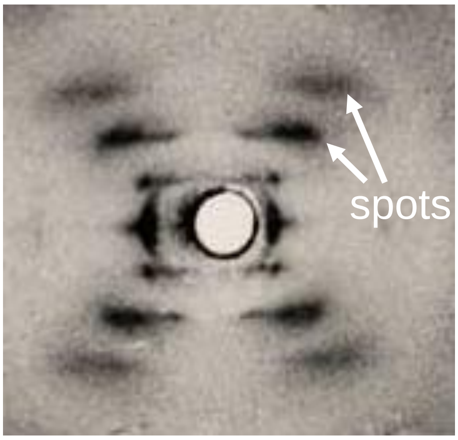
and $\therefore \quad \frac{1}{d_{hkl}^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2$

For <u>cubic crystals</u>, $a = b = c$

and $\therefore \quad \frac{1}{d_{hkl}} = \frac{\sqrt{h^2+k^2+l^2}}{a}$ or $d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$.

Measuring Interplanar Spacings with X-Rays

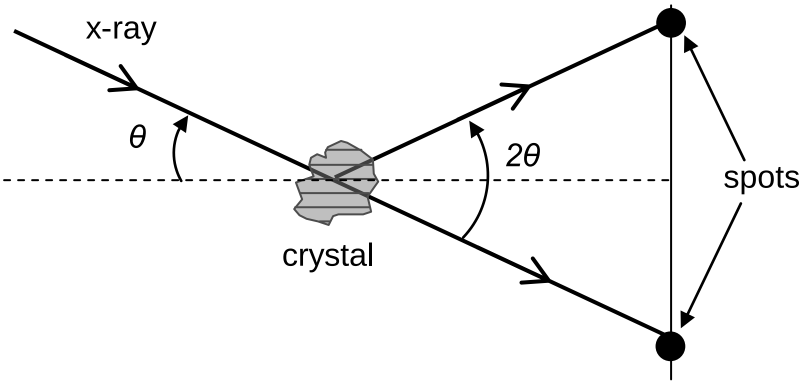
Recall the x-ray photograph of DNA shown on AH33 (central part reproduced below):



The x-ray diffraction pattern shows a series of spots (or 'reflections') whose spacing depends upon the interplanar distances, d, in the DNA crystal; the relationship is given by **Bragg's Law** (known also as the 'Bragg equation'):

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

where λ is the x-ray wavelength and θ is known as the **Bragg angle**, as shown below



You need Bragg's Law for practical AP2. The derivation of Bragg's Law will be given later – see AH76.

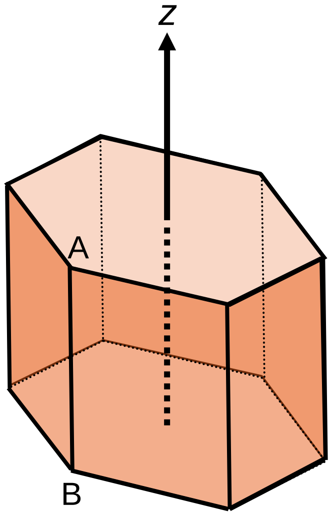
C6. Weiss Zone Law

We said before that a lattice direction is sometimes called a **zone axis**. Why? What's a **zone**?

A **zone** maybe defined as a 'set of faces or planes in a crystal whose intersections are all parallel'.

The common direction of the intersections is called the **zone axis**.

An illustration of this:

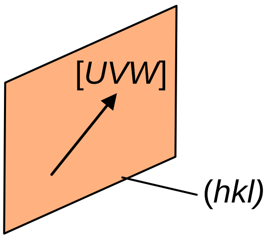


All intersections of planes (e.g. AB) are parallel to the z-axis. Thus the planes belong to a zone whose zone axis is parallel to z.

The Weiss Zone Law

If a lattice vector $\mathbf{r}_{UVW}$**,** or simply $[UVW]$, is contained in a plane of the set (hkl), there is a relationship that links the lattice vector to the lattice planes:

$$hU + kV + lW = 0$$



Note: Proof of the Weiss Zone Law given in Appendix 4.

In general we may wish to find the direction vector [UVW] which is common to the planes ($h_1k_1l_1$) and ($h_2k_2l_2$). We need to solve 2 simultaneous equations:

$$h_1U + k_1V + l_1W = 0$$

$$h_2U + k_2V + l_2W = 0$$

Solutions are:

$$U = k_1l_2 - l_1k_2$$

$$V = l_1h_2 - l_2h_1$$

$$W = h_1k_2 - h_2k_1$$

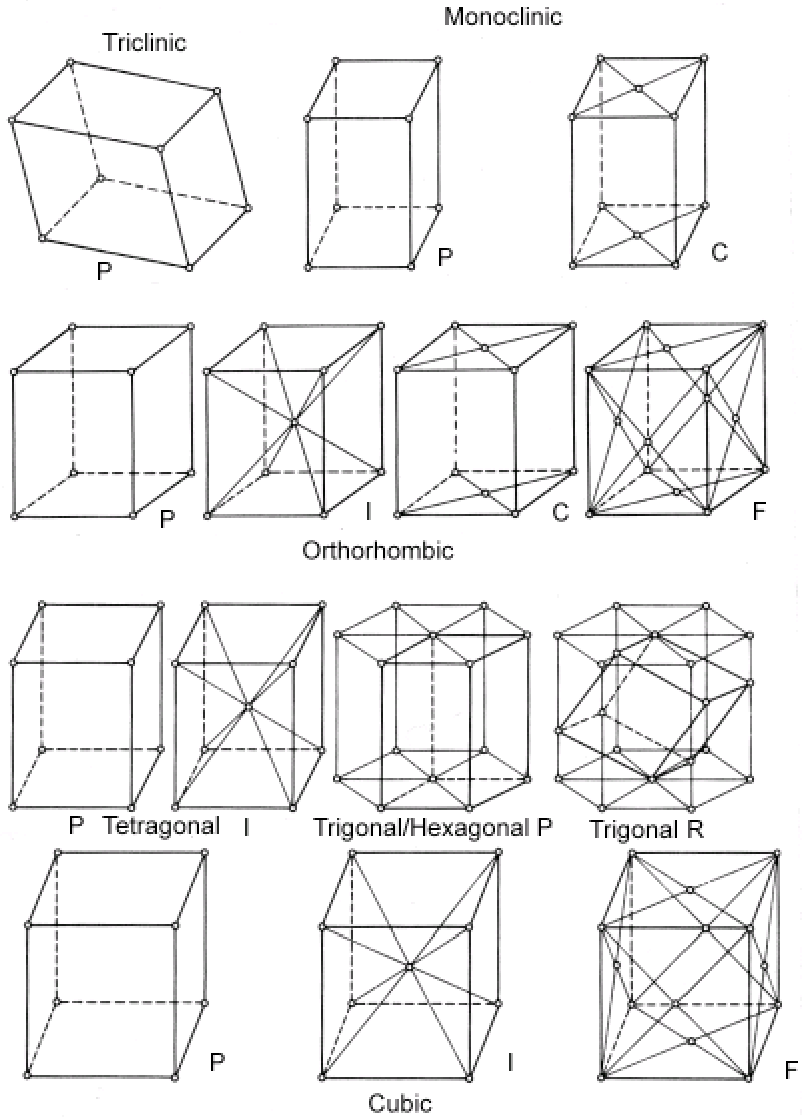
D. Lattices and Crystal Systems in 3D

We can now continue with our exploration of crystals in 3D armed with a method to describe directions and planes.

Recall that we had 5 possible lattices in 2D. Taking one of those lattices and stacking 'layers' on top of each other it is possible to build up all the possible 3D lattices.

Doing this we find that there are 14 crystallographically distinct 3D space lattices, called **Bravais lattices**.

The unit cells of the Bravais lattices are shown below, grouped into the 7 distinct **crystal systems** (or **crystal classes**).



Note we have **primitive** (P), **body-centred** (I), **face-centred** (F) and **base-centred** (C) lattices. There is also a **rhombohedral** (R) lattice.

Crystal System	Defining Symmetry (rotation or inversion)	Conventional Unit Cell	Conventional Lattice Types
Cubic	4 triads	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	**P, I, F**
Hexagonal	1 hexad	$a = b \neq c$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	**P**
Trigonal	1 triad	$a = b \neq c$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	**P, R**
Tetragonal	1 tetrad	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	**P, I**
Orthorhombic	3 diads	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	**P, C, I, F**
Monoclinic	1 diad	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ, \beta \geq 90^\circ$	**P, C**
Triclinic	**-**	$\boldsymbol{a \neq b \neq c}$ $\boldsymbol{\alpha \neq \beta \neq \gamma}$	**P**

The different shapes and sizes of these cells may be described in terms of three cell edge lengths a, b, c or lattice vectors **a**, **b**, **c**, and the angles between them α, β, γ.

Note, by convention: α is the angle between **b** and **c**

β is the angle between **a** and **c**

γ is the angle between **a** and **b**

But what defines something as being say‘cubic’, or ‘tetragonal’. It is not the shape of the unit cell but the symmetry of the crystal.

For a crystal to belong to a particular system it must have a characteristic (minimum) symmetry. For example

<u>Cubic</u>	four 3-fold axes (triads) parallel to the <111> axes
<u>Tetragonal</u>	one 4-fold axis (tetrad) parallel to the c-axis, the [001] axis.

Of course the empty lattice can have a higher symmetry than the crystal – it depends on the position of atoms in the motif. For example there are cubic crystals without 4-fold symmetry but whose unit cell has orthogonal sides of equal length (i.e. a cube).

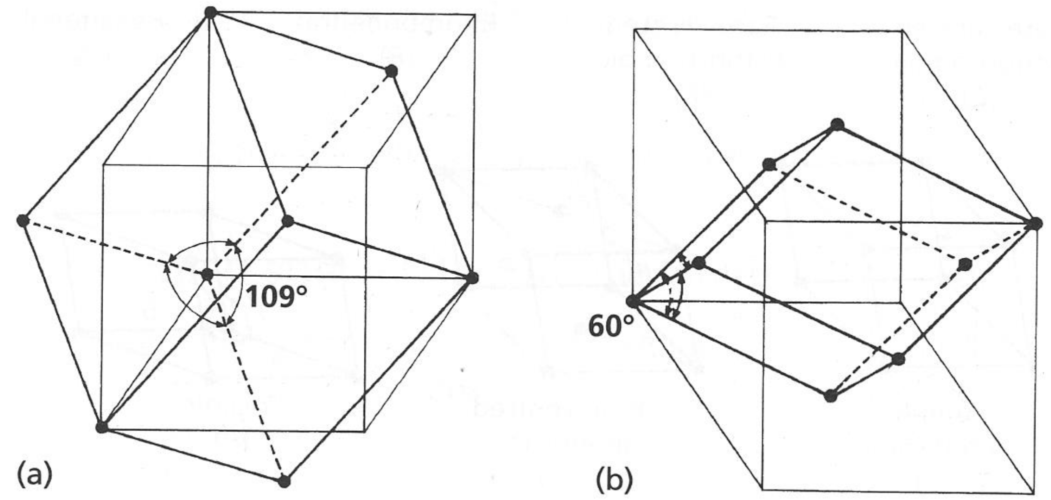
Centred Lattices

We saw in 2D the possibility of a centred lattice. In 3D there are also centred lattices as well as the primitive lattice (*P*):

P lattice	primitive lattice	1 lattice points / unit cell
I lattice	body-centred lattice	2 lattice points / unit cell
F lattice	face-centred lattice	4 lattice points / unit cell
C lattice	base-centred lattice	2 lattice points / unit cell

(The last is called a *C*-centred lattice because the extra lattice point is in the **a**-**b** face. It is possible to have *A*-centred and *B*-centred lattices but these are non-conventional.)

We can always construct a primitive cell from the centred lattice. For example consider below (a) the cubic *I* and (b) cubic *F* lattices:



However, as in 2D, these 3D primitive cells are not often used because:

(i) The inter-axial angles are not the convenient 90°(i.e. they are not orthogonal)

(ii) They do not reveal very clearly the cubic symmetry of the cubic *I* or cubic *F* lattice.

Close Packed Structures Revisited

The ccp structure has a cubic *F* lattice with one atom in the motif at 0,0,0.

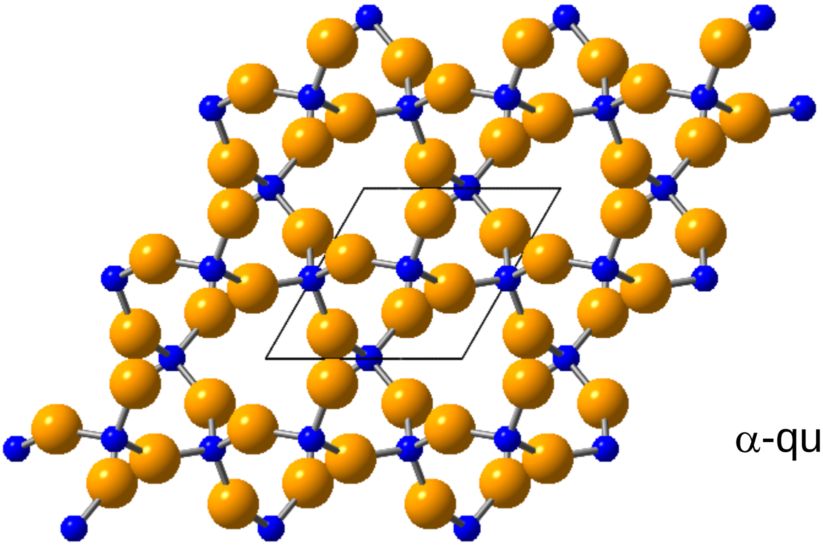
The bcc structure has a cubic *I* lattice with one atom in the motif at 0,0,0.

The hcp structure has a hexagonal *P* lattice with two atoms in the motif at 0,0,0 and $^{2}/_{3}$, $^{1}/_{3}$, $^{1}/_{2}$.

Trigonal System

Some crystals with a hexagonal lattice (e.g. quartz) do not show hexagonal symmetry (i.e. they do not have 6-fold rotational symmetry) but have only 3-fold symmetry. As such, these crystals must be assigned to the **trigonal system**.

Hence the trigonal system includes crystals with both hexagonal and rhombohedral Bravais lattices.



α-quartz (SiO_2)

E. Crystal Symmetry in 3D

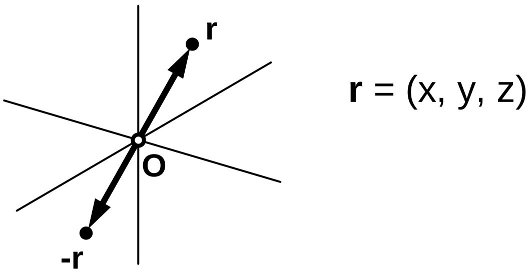
In 2D we found that by combining symmetry elements we could determine 10 distinct crystallographic point groups.

In 3D we find that there are 32 distinct crystallographic point groups. However to describe these we need to discuss two other symmetry elements that exist only in 3D (not in 2D).

E1. Centres of Symmtery and Roto-Inversion Axes

If a crystal possesses a **centre of symmetry**, then any line passing through the centre of the crystal connects equivalent faces, or atoms, or molecules.

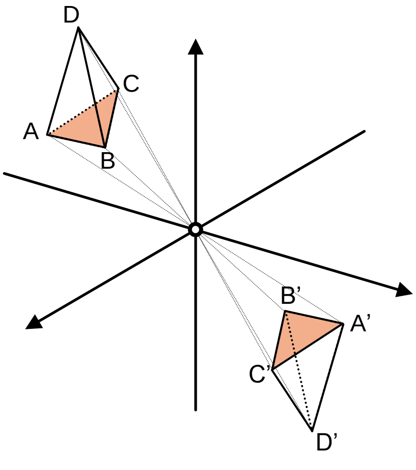
In other words, if an atom is located in the crystal at (x, y, z) then the same atom must be located at (-x, -y, -z).



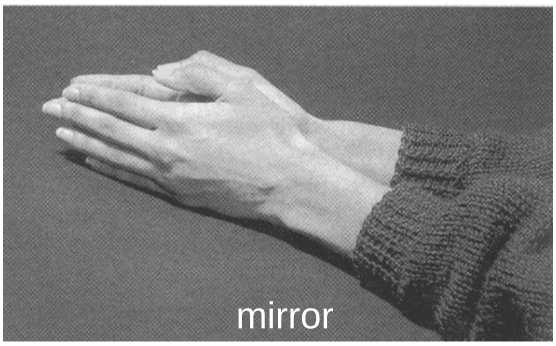
The origin O is called a **centre of symmetry** (or **inversion centre**) and a crystal possessing a centre of symmetry is said to be **centrosymmetric**.

If a crystal does not posess a centre of symmetry, then it is said to be **non-centrosymmetric.**

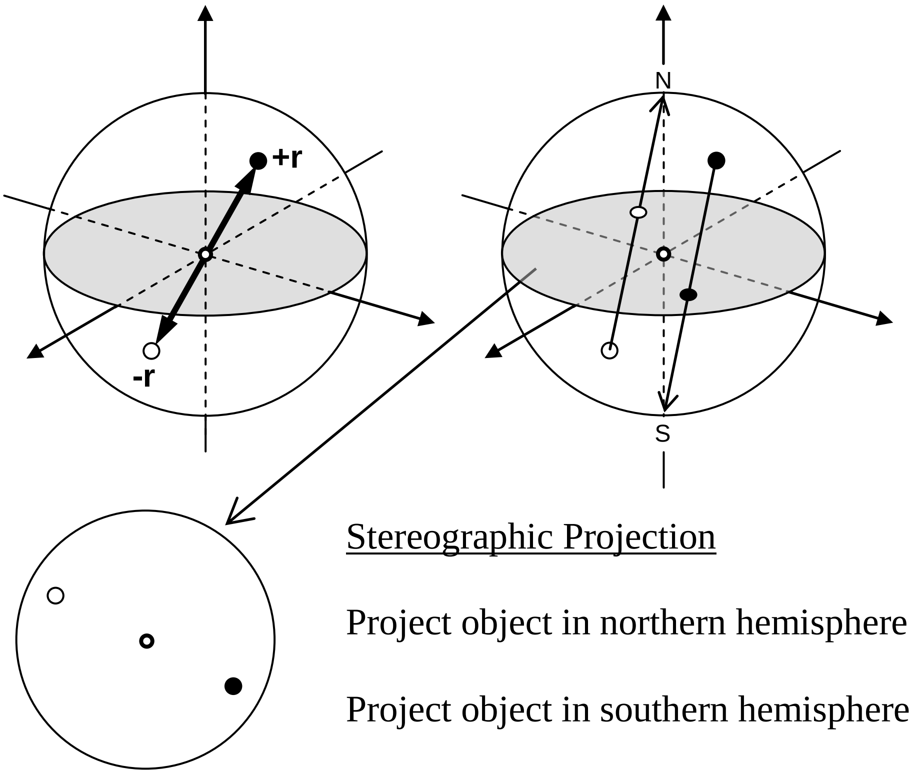
Consider how a centre of symmetry operates on a more complex object:



An everyday example of a centre of symmetry (inversion centre) is seen in the figure below (c.f. with the mirror):



Consider again the previous figure, we can imagine the atoms at ± **r** sitting on the surface of a sphere of radius *r* and the centre of symmetry then being at the centre of the sphere.



Stereographic Projection

Project object in northern hemisphere as ●

Project object in southern hemisphere as ○

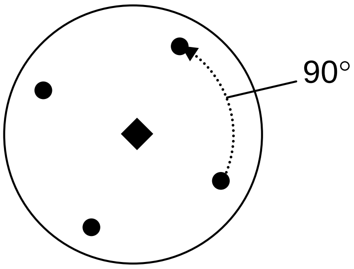
Thus the stereographic projection shown above represents a centre of symmetry (inversion centre).

It is given the symbol $\bar{1}$ and is marked on the stereographic projection as a small circle ○

NOTE: In this course we use the stereographic projection only as a pictorial device. However, it can be used quantitatively, for interest only see: *http://www.doitpoms.ac.uk/tlplib/stereographic/index.php*

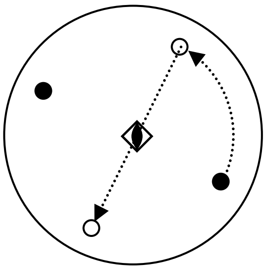
Can we combine centres of symmetry with rotation axes? Yes! They are called **roto-inversion axes**.

For example using our stereographic projection we can first represent a 4-fold axis (with the rotation axis pointing up):



Now combine this 4-fold rotation axis with an inversion centre to produce a 4-fold roto-inversion axis. This is given the symbol $\bar{4}$ and the operation is:

- (i) rotate by 90° (i.e. 360°/4)
- (ii) invert through the centre



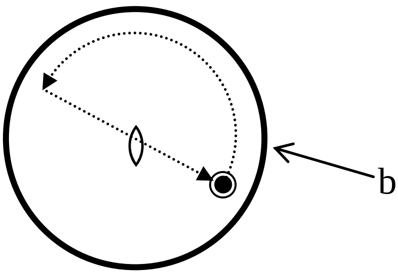
Notice that contained within the $\bar{4}$ symmetry element is a 2-fold rotation axis.

Hence the symbol is ◈ showing the ‘automatic’ presence of ⬮.

As before the roto-inversion axis is pointing up.

We can also have $\bar{3}$ and $\bar{6}$ symmetry axes.

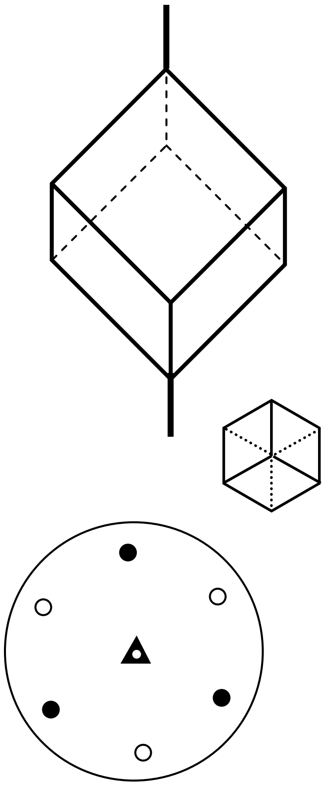
What about $\bar{2}$? It is a horizontal mirror! Therefore $\bar{2} \equiv \mathrm{m}$.



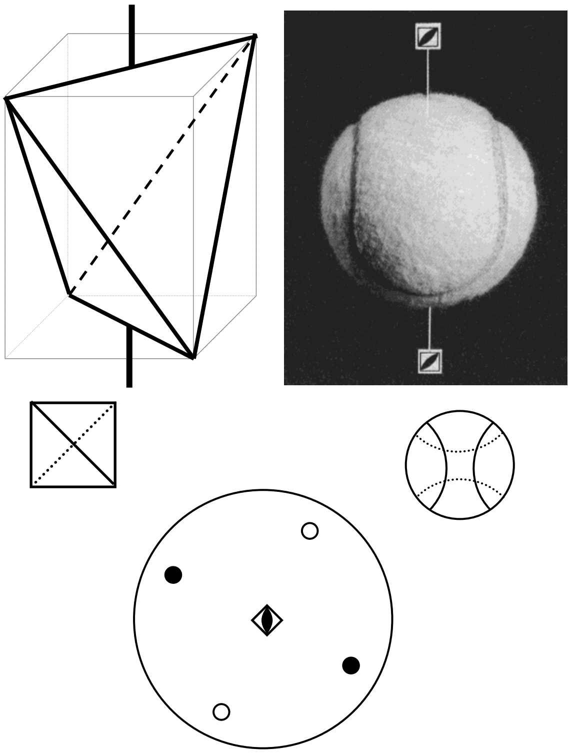
bold to indicate a horizontal mirror

So actually we can say also that a centre of symmetry is also a roto-inversion axis $\bar{1}$ where the operation is to rotate by 360°/1 and invert through the centre.

Examples of roto-inversion axes



$\bar{3}$



$\bar{4}$

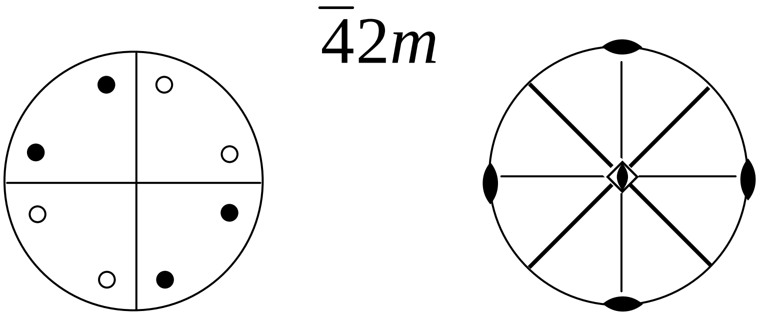
E2. Crystallographic Point Groups

(Note: This section is for background only – non-examinable.)

Just as we did in 2D, we can combine symmetry elements to establish all the possible crystallographic point groups.

In Appendix 2, we list all the 32 possible crystallographic point groups showing the international symbol and a representative stereographic projection.

As an example consider the tetragonal point group $\bar{4}2m$:



‘$\bar{4}$’ indicates a $\bar{4}$ roto-inversion axis parallel to the tetragonal *c*-axis shown pointing up from the page.

‘2’ indicates a 2-fold axis (diad) perpendicular to the $\bar{4}$ axis (i.e. parallel to both the *a*-axis and *b*-axis.

‘*m*’ indicates mirrors at 45° to the 2-fold axis, i.e. mirror planes whose normals are parallel to [110] and [$\bar{1}$10].

Note. The mirrors are generated automatically from the $\bar{4}$ and 2 symmetry operations.

E3. Crystal Symmetry and Properties

The symmetry of a crystal is of paramount importance in understanding physical properties.

In general, the arrangement of atoms within a crystal means that the crystal properties vary with direction, i.e. they are **anisotropic**.

(i) Electrical Conductvity

A simple and well-known example is the electrical conductivity of graphite, which has a highly layered crystal structure, whose conductivity in the hexagonal basal plane is much higher than that perpendicular to the planes.

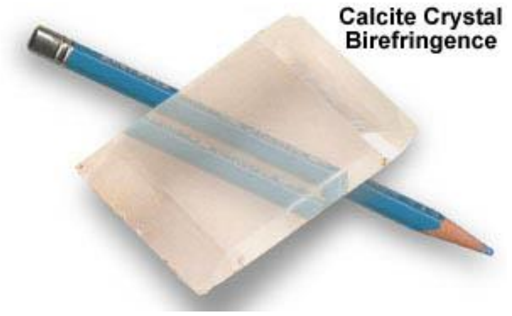
(ii) Pyroelectricity and Ferroelectricity

Some crystals have an internal **polarization** brough about by the arrangement of positive and negative ions, forming an **electric dipole**. The total polarization per unit volume of the crystal is the sum of all these internal electric dipoles. However, the dipole must lie along a **unique direction** (not repeated by a symmetry element) and there are only 10 point groups with this property (knows as the 10 **polar point group**s).

Of course the polar point groups cannot have a centre of symmetry (they are all non-centrosymmetric) as this would cancel out the dipole.

(iii) Optical Properties

For example, the refractive index is symmetry-dependent: tetragonal, hexagonal and trigonal crystals are characterized by 2 refractive indices and leads to the phenomenon of **birefringence** (e.g. as seen in calcite).



(iv) Enantiomorphism (Chirality)

Many molecules are **chiral** (they can be right-handed or left-handed), e.g. DNA in nature (the B-form) is always right-handed. When crystallized these molecular crystals have chiral symmetry. Aspargine occurs in two enantiomorphous forms, one tastes bitter, the other sweet!

Optical activity of a crystal is where the vibrational direction of light rotates such that it propagates through the crystal in a helical manner either to the right (dextro-rotatory) or the left (laevo-rotatory) – this phenomenon occurs only in crystals that are enantiomorphous.

E4. Translational Symmetry Elements

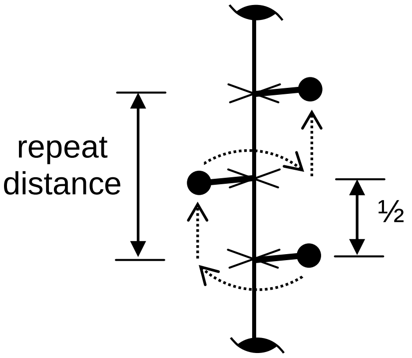
In 2D we introduced glide lines as translational symmetry elements, in 3D these become **glide planes** but act in the same way.

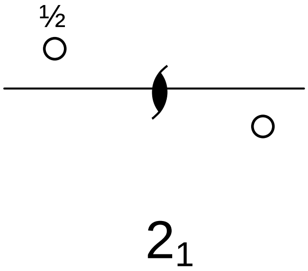
Glide planes are symbolized as *a*, *b* or *c* glides depending on whether the translation is parallel to the *x*, *y* or *z* axis.

(*Note*. **Non-examinable**: There are also *n* ('diagonal') and *d* ('diamond') glides involving translations along more than one axis.)

Screw axes are combinations of rotations and translations and are represented by the general symbol R_n where R represents the rotation and n represents the number of translations for one complete rotation of a helix.

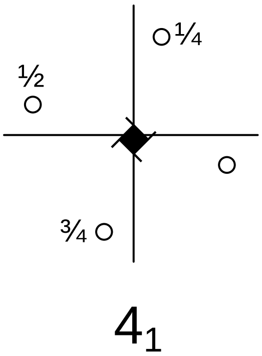
For example, the 2_1 screw axis is a rotation of 180° followed by a translation of ½ of the repeat distance.



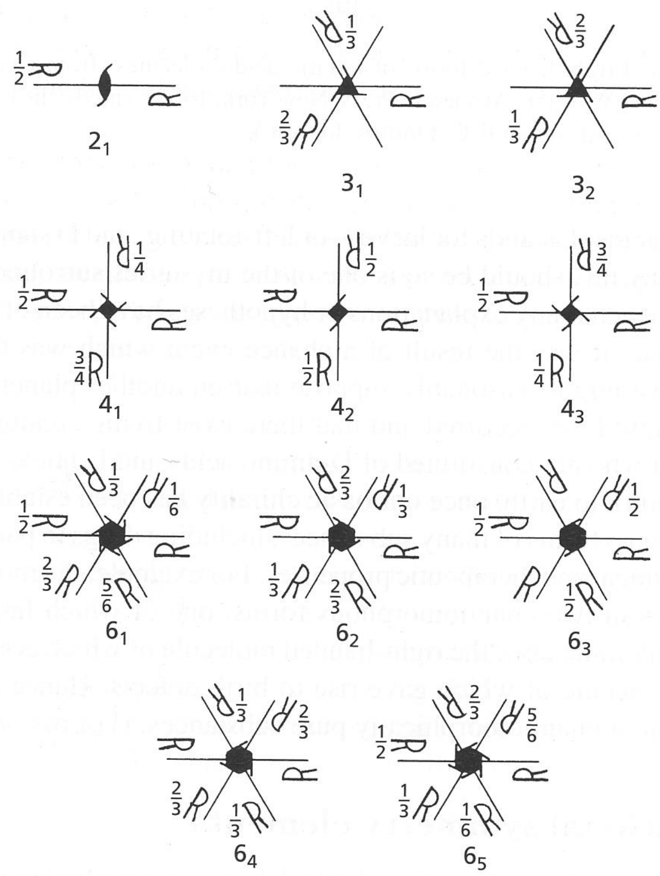


Note the horizontal line is simply a guide to the eye, representing an axis, and is not representing a mirror.

Another example is the 4_1 screw axis:

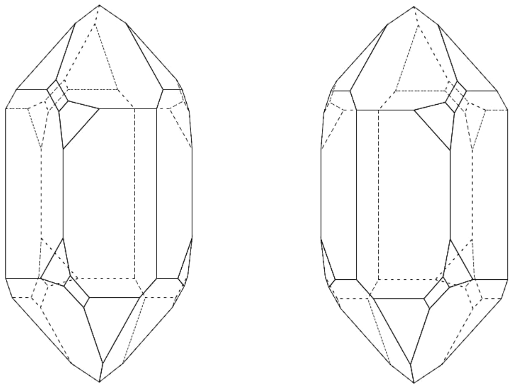


The complete set of possible screw axes is shown in the figure below (fractions indicate height up the screw axis as a fraction of the repeat distance).



<u>Example</u> α-quartz (enantiomorphous)

SiO_2 units are arranged along the *c*-axis in either a 3_1 or 3_2 screw orientation. This gives rise to optical activity.



left-handed 3_2 right-handed 3_1

E5. Space Groups

Finally, by combining the 14 Bravais lattices with the 32 point groups and translational symmetry elements, it can be shown that there are 230 possible 3D patterns or **space groups**.

A full description of the space groups would take too long (outside the scope of this lecture course!) but the space groups are tabulated in all their glory in the *International Tables for Crystallography, Volume A*.

F. Introduction to Diffraction

How do we discover the internal arrangements of atoms in a crystal?

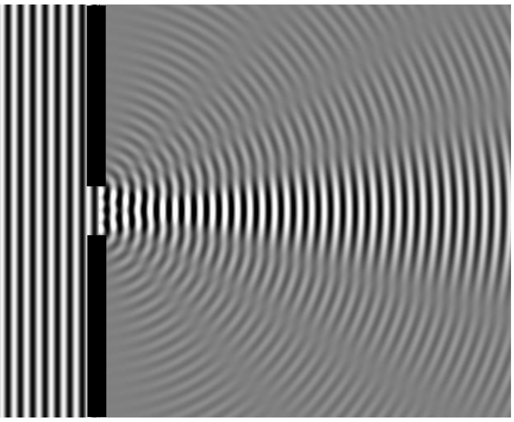
Some crystals, especially minerals, give clues as to their internal symmetry through their external shape, or crystal **habit**.

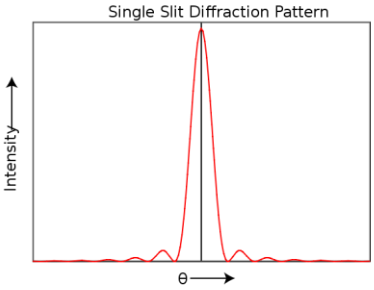
However, to really determine the atomic arrangement we need a ‘probe’ that penetrates the crystal and interacts with the atoms. X-rays, neutrons and electrons are all used to probe the atomic arrangement of crystals. The incoming radiation is scattered from the atoms and interferes constructively only at special scattering angles, and these angles can be related back to the lattice planes of the crystal.

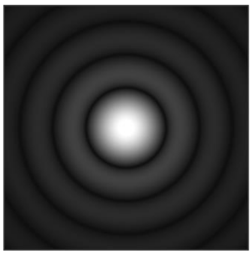
F1. Interference and Diffraction

To explore this further, let’s start by reviewing some basic ideas of diffraction and interference.

Consider a wave with uniform planar wavefront impinging on a single slit in an otherwise impenetrable barrier:

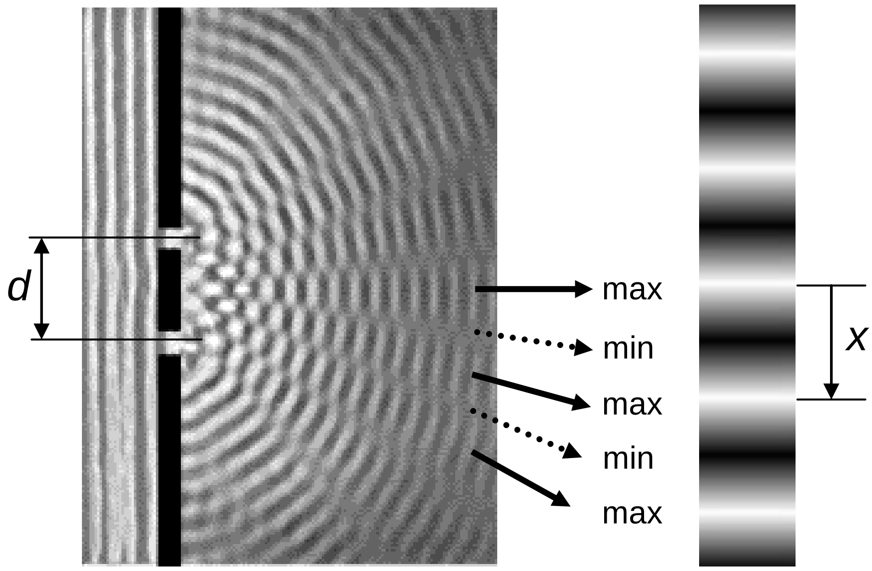






The slit acts as a secondary source producing a circular (spherical in 3D) wavefront.

If we have two slits:

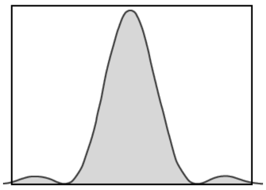


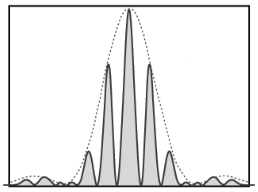
We now have 2 spherical wavefronts which will interfere to produce an **interference pattern** at some detector a distance from the slits.

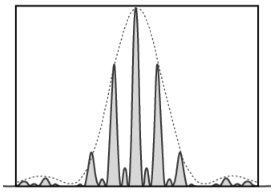
The interference will be a series of intensity maxima and minima - e.g. a series of bright and dark fringes if light is used. The fringes tend to fade in intensity as you go away from the central maximum because the interference pattern is modulated by the diffraction from each slit.

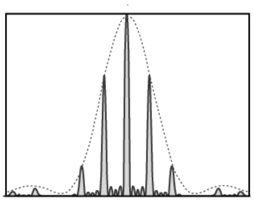
This is Thomas Young’s famous experiment of 1803 to explain the wave theory of light. Importantly, Young found that the spacing between a maximum on the detector and the centre of the pattern, *x* was proportional to the reciprocal of the separation between the slits, *d* – see AP8.

If we add a 3rd and then more slits, tending towards an infinite number of slits, the maxima become very sharp, tending towards delta functions:

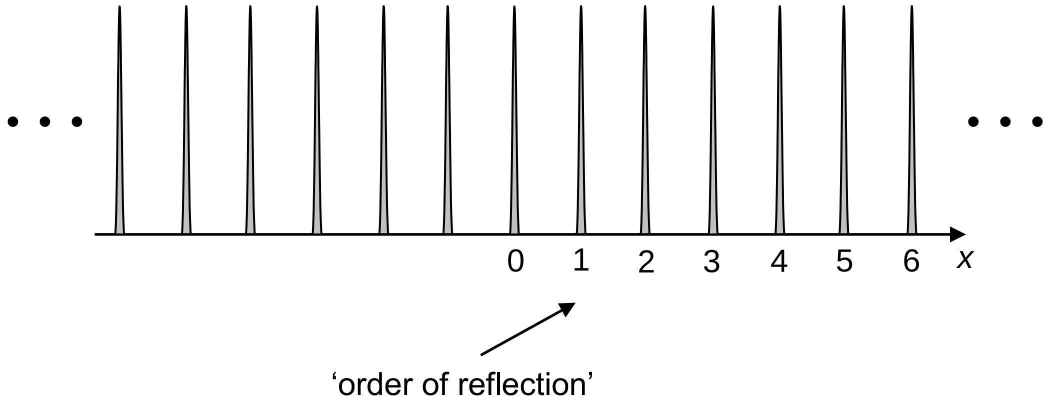

1 slit


2 slits


3 slits


5 slits

For very fine slit widths the envelope function becomes much broader and so for a series of slits (tending towards an infinite number) which are very narrow in width (tending to zero) then the diffraction pattern becomes:

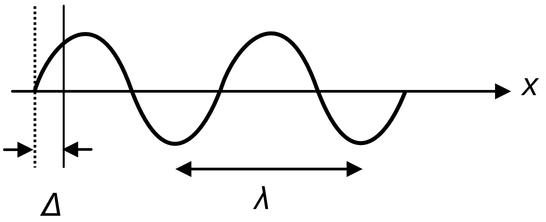


Essentially we have **destructive interference** (zero intensity) everywhere EXCEPT at special positions on the detector, corresponding to special scattering angles, where we get maximum constructive interference (i.e where the wavefronts match identically and the **path difference**, $\Delta = n\lambda$.

Quick reminder about interference:

λ is the wavelength

Δ is the path difference

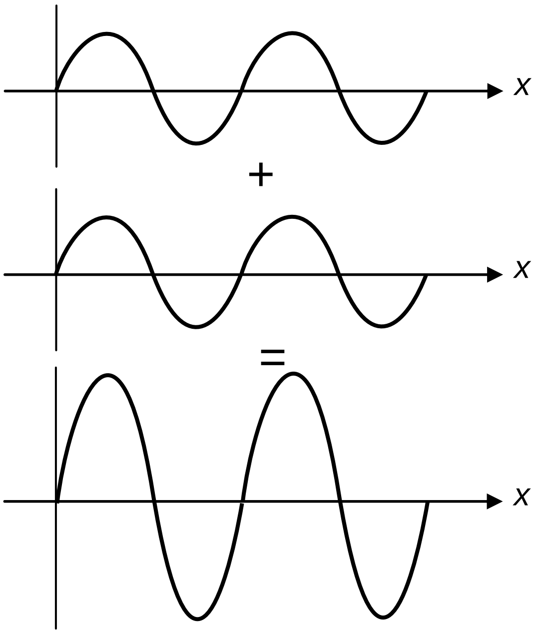


Consider adding two waves with the same amplitude and frequency/wavelength but different phases. In general you will get partial constructive/destructive interference, but there are two special cases:

Case 1

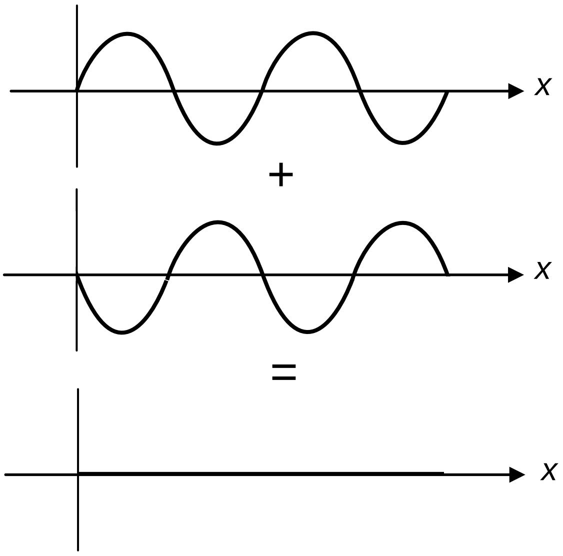
$\Delta = n\lambda$

n is a integer



Case 2

$\Delta = (n+½)\lambda$

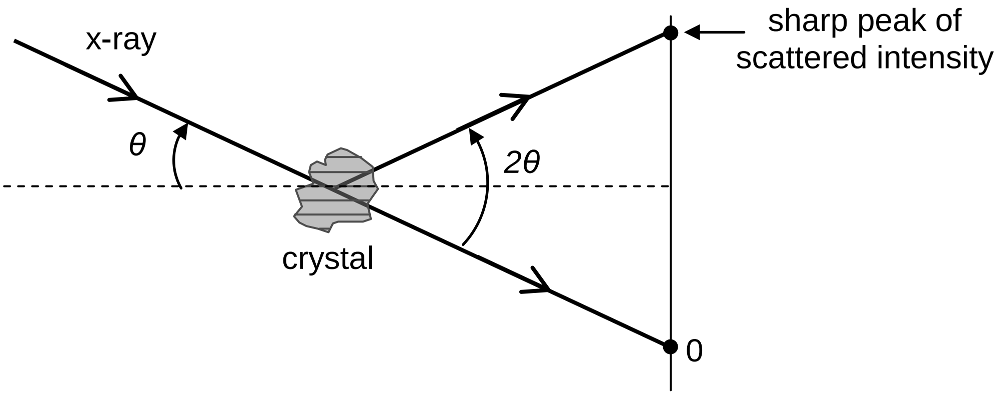


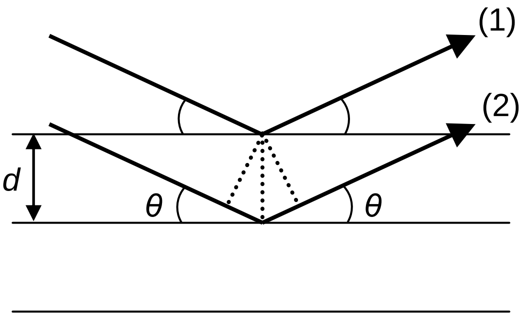
F2. Bragg's Law

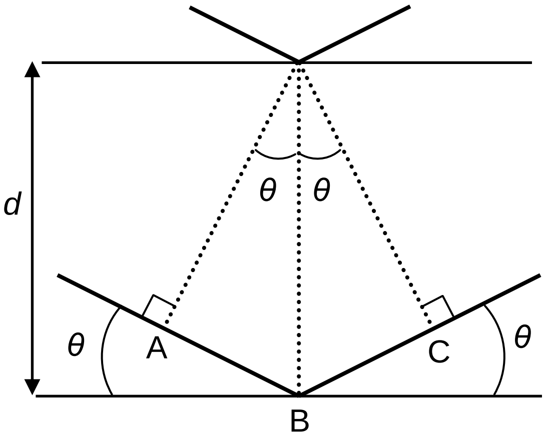
We can now make the analogy between an infinite array of slits and our crystal lattice composed of an infinite array of lattice planes.

The spacing between the slits is analogous to the spacing between crystal planes.

Consider the scattering of x-rays from a series of lattice planes. (Geometry for x-ray diffraction explained further in AP5 and section H.)







We will see a sharp peak (maximum constructive interference) at a special scattering angle, 2θ which must arise only because the path difference between waves (1) and (2) is equal to $n\lambda$.

Consider the geometry:

$$\text{path difference, p.d.} = n\lambda = AB + BC$$

$$AB = BC = d \sin \theta$$

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

This leads to **Bragg's Law**:

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

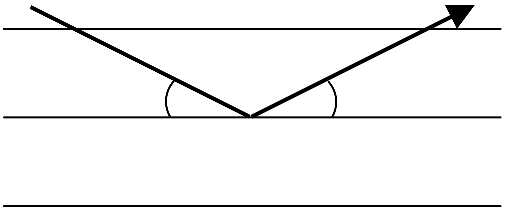
Note: θ is known as the **Bragg angle** and is sometimes given the symbol θ_B.

Where's n ?! It's 'hidden' in d.

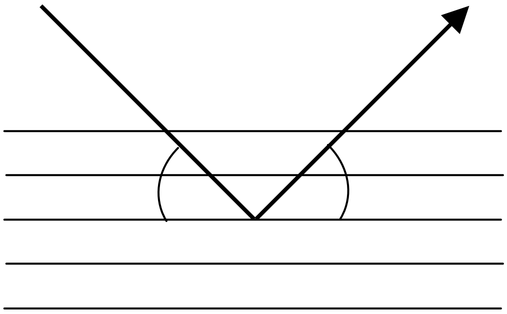
1st order reflection $d = d_{100}$

2nd order reflection $d = d_{200} = \frac{d_{100}}{2}$

nth order reflection $d = d_{n00} = \frac{d_{100}}{n}$



(100) planes

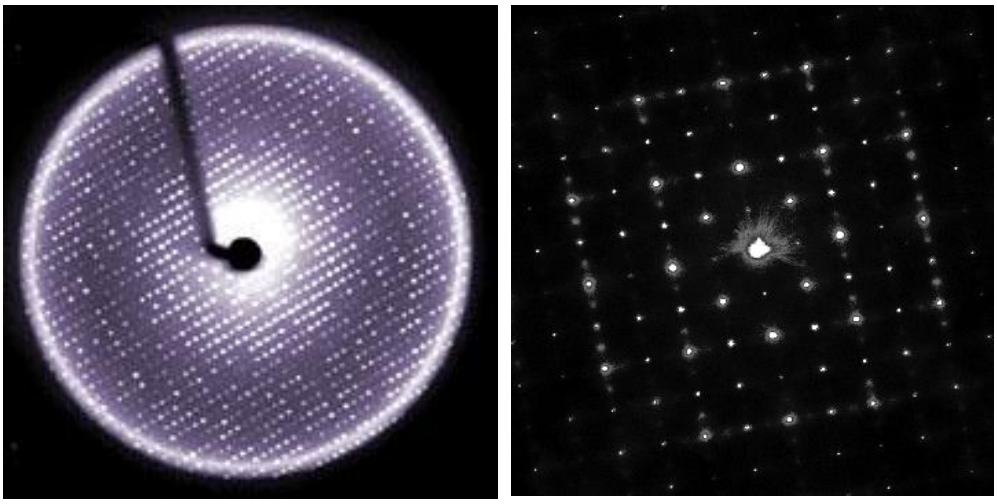


(200) planes

Thus in a diffraction experiment (see for example practical AP2, AP3), by knowing the wavelength of radiation and measuring the Bragg angle, the crystal planar spacing can be found.

For a real (3D) crystal, the lattice is a 3D array and so we need to consider scattering from not just a 1D array of slits or a single array of lattice planes but a 2D or 3D array of lattice planes.

The same analysis (Bragg's Law) can be used and we will see an array of maxima, e.g. an array of intense spots on a 2D detector. For example, the x-ray (left)and electron diffraction (right) patterns in the figure below:



We see a ‘lattice’ of Bragg ‘reflections’ whose spacing is determined by the reciprocal of the crystal lattice spacing.

If a reflection has arisen from a plane (*hkl*) then the reflection is known as the *hkl* reflection.

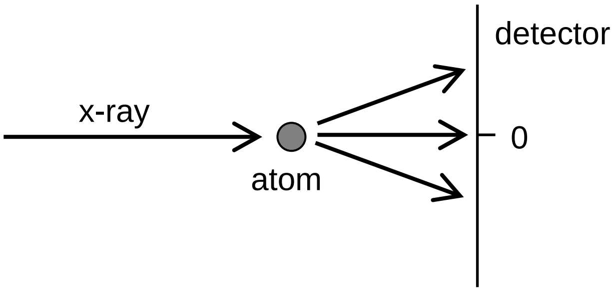
The lattice of reflections corresponds directly to the crystal’s **reciprocal lattice** – see later.

F3. The Intensities of Bragg Reflections

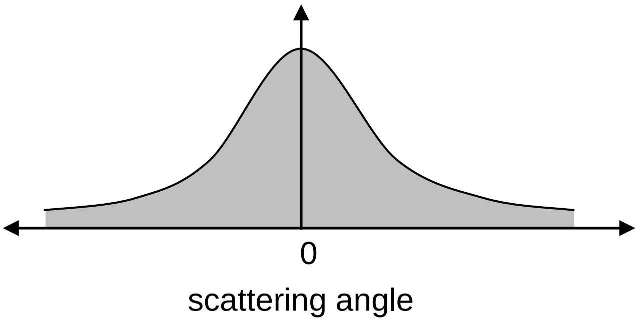
Using Bragg's Law (and the Ewald sphere construction – see later) we can understand the spacing of the reflections in a diffraction pattern – but what about the intensities of each reflection which, as we saw in the diffraction patterns above, can vary dramatically from one reflection to another.

To understand that variation we need to consider how waves scatter from the arrangement of atoms in a crystal.

First consider how waves e.g. x-rays, scatter from a single atom:



If we look at the amplitude of scattering on the detector we would see:



This scattering amplitude, known as the x-ray **atomic form factor** (or **atomic scattering factor**), and given the symbol f is conventionally plotted as a function of both angle, θ and wavelength, λ.

Qualitatively this is similar to the trace seen for diffraction from a single slit, see for example at the bottom of page 72.

We can define the atomic form factor as:

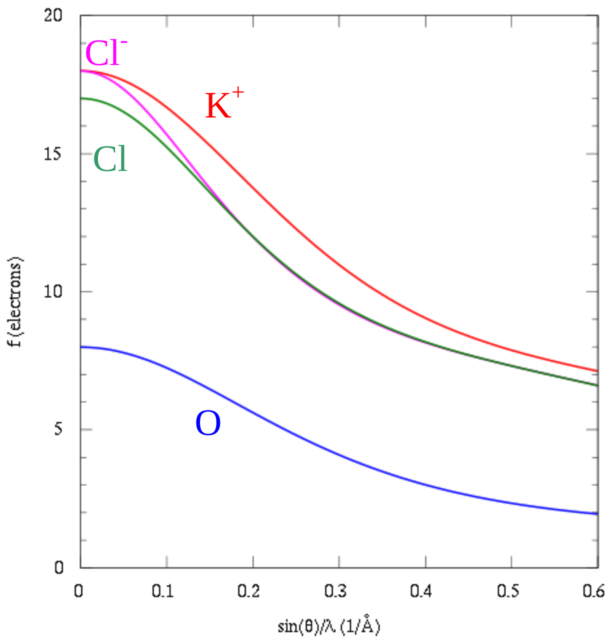
$$f = \text{atomic form factor} = \frac{\text{amplitude of scattering by atom}}{\text{amplitude of scattering by a single electron}}$$

X-rays scatter almost exclusively from the atomic electrons and so *f* is primarily the contribution of all the electrons in the atom. For an atom of **atomic number** *Z*, there are *Z* electrons.

At zero scattering angle, all these *Z* electrons scatter in phase and so $f = Z$.

As the scattering angle increases, there is only partial constructive interference and *f* falls below the value of *Z*.

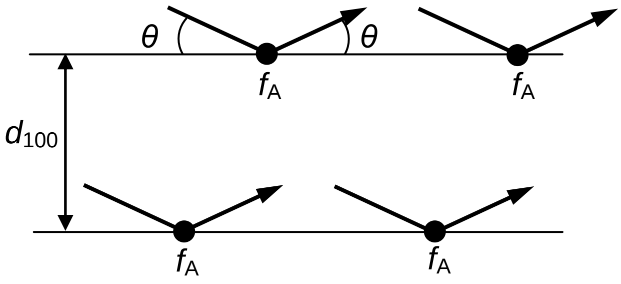
Below is a figure plotting *f* as a function of $\sin\theta/\lambda$:

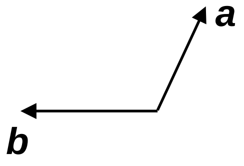


Calculated X-ray atomic form factors:
oxygen (blue)
chlorine (green)
Cl^- (magenta)
K^+ (red).

If we now consider scattering from two atoms, do we simply add their individual form factors? Not quite. We have to consider their relative positions – just like in the 2-slit experiment before.

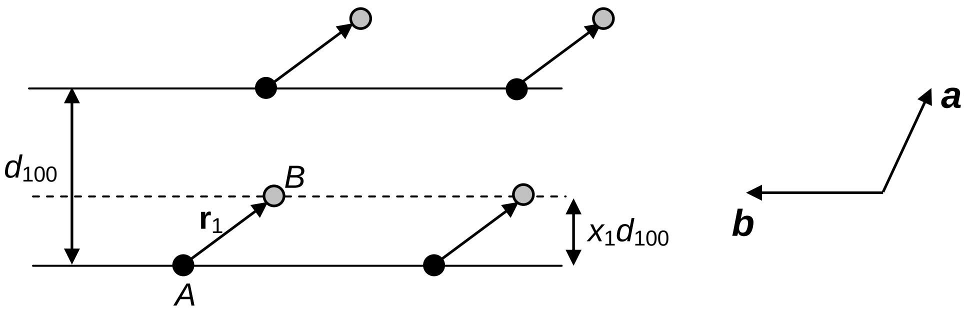
Consider a part of a crystal lattice with atoms A situated at the lattice points. These atoms have atomic form factors f_A.





If x-rays are incident on the crystal at the Bragg angle θ for the (100) planes then we know that all the waves scattered from each atom A will be in phase (because each atom A is at a lattice point), we will get constructive interference and we will detect a corresponding diffracted spot in a diffraction pattern.

Let's now add a second atom B, with scattering factor factor f_B, to the motif:



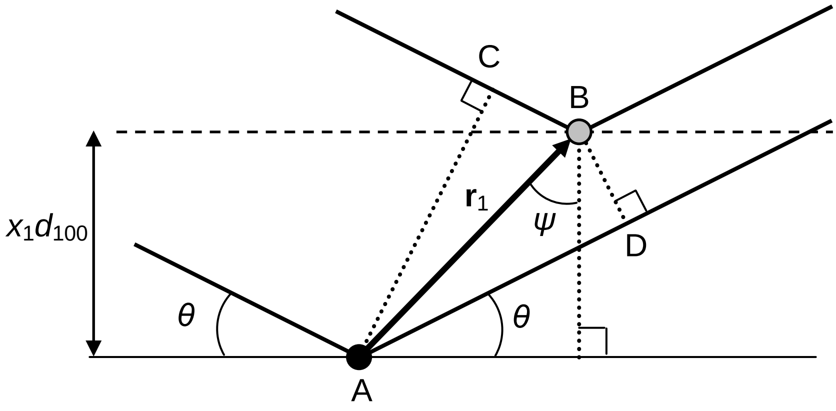
The position vector $\mathbf{r}_1$ links atoms A and B and can be written in general as:

$$\mathbf{r}_1 = x_1\mathbf{a} + y_1\mathbf{b} + z_1\mathbf{c}$$

where x_1, y_1 and z_1 are fractions of the cell edge length.

How will the addition of this atom B affect the scattering? Need to consider the path difference between waves scattered by A and by B.

Consider:



We need to determine, for scattering from (100) lattice planes, what is the path difference between waves scattered from A and from B.

We can show (exercise for the student!) that:

$$\text{path difference, p.d.} = \text{AD-BC} = 2\text{AB} \cos\psi \sin\theta$$

$$\text{but AB} \cos\psi = x_1 d_{100}$$

$$\text{and} \therefore \text{p.d.} = 2x_1 d_{100} \sin\theta$$

$$\text{but Bragg's Law is } \lambda = 2d \sin\theta$$

$$\therefore \text{p.d.} = x_1\lambda$$

$$\text{phase difference} = \frac{2\pi}{\lambda} \times \text{path difference}$$

$$= 2\pi x_1$$

In this case, θ is the Bragg angle for d_{100}. For a more general case of (h00) planes, then:

$$x_1 d_{100} \rightarrow x_1 h d_{h00}$$

$$\text{phase difference} = 2\pi h x_1$$

If another atom was added with co-ordinates x_2, y_2, z_2 then this would give rise to a phase difference of $2\pi h x_2$, etc.

Similar analysis can be done for the other two dimensions so that in general for scattering from planes (hkl) each atom at position x_n, y_n, z_n leads to a phase difference of:

$$\phi_n = 2\pi(hx_n + ky_n + lz_n)$$

Note: ϕ_n is a phase angle.

So how do we add waves of different amplitude and phase? We can use an **amplitude-phase diagram** (!) sometimes called a ‘vector-phase ‘diagram.

Let's consider again atoms A and B in our motif. If these are the only atoms in our unit cell then we simply need to add the contributions from A and B to know the scattering from the whole crystal (as each unit cell is identical).

Atom A is at the origin, so:

$$(x, y, z) = (0, 0, 0) \text{ and } \phi_A = 0$$

Atom B is at position x_1, y_1, z_1 and so

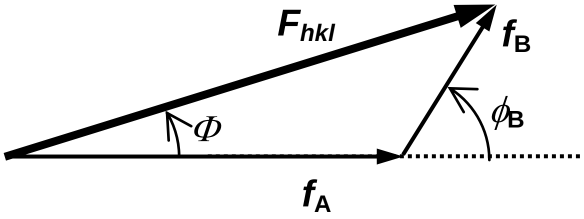
$$\phi_B = 2\pi(hx_1 + ky_1 + lz_1)$$

Amplitude of scattering from A = f_A

Amplitude of scattering from B = f_B

We can use this information to draw an amplitude-phase diagram.

Let's assume that $f_A > f_B$

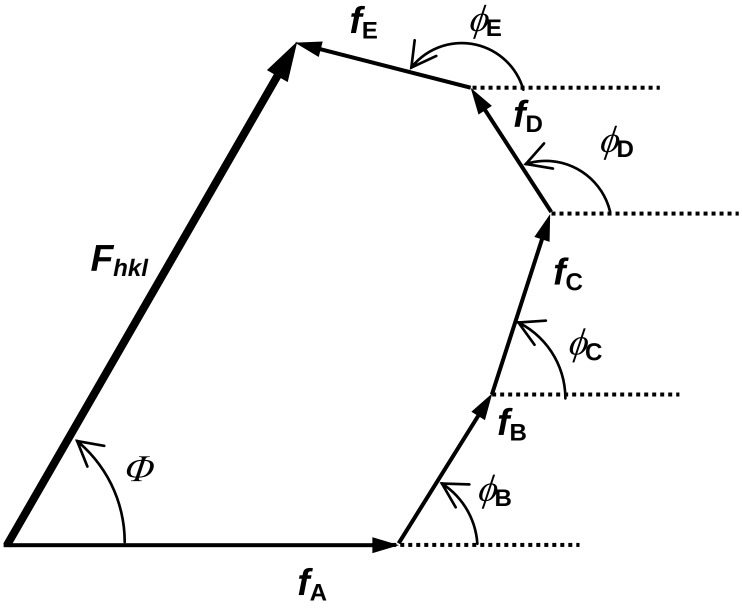


The resultant vector on this diagram F_{hkl} is known as the **structure factor** and is the sum of all the atomic form factors f_n taking into account the relative phase factors ϕ_n.

So if we had for example 5 atoms in the unit cell:

A, B, C, D, E with scattering amplitude f_A, f_B, f_C, f_D, f_E, phase angle ϕ_A, ϕ_B, ϕ_C, ϕ_D, ϕ_E

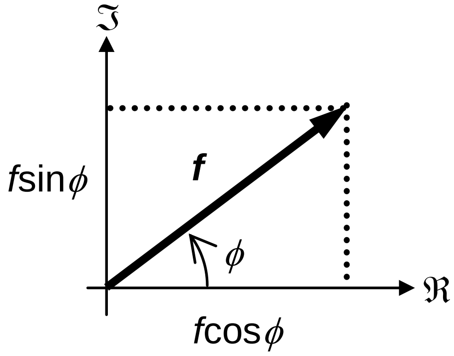
Let's put atom A at the origin as before, so that $\phi_A = 0$:



Note the phase angles, ϕ_n are all measured with respect to the origin (horizontal line).

The length or modulus of the vector F_{hkl} represents the resultant amplitude of the scattered beam and the angle Φ is the resultant phase angle.

Such diagrams are equivalent to **Argand diagrams** when the structure factor $\boldsymbol{F}_{hkl}$ is represented by a complex number. Consider a vector **f**:



The axis marked with the curly R ($\Re$) is known as the **real axis** and with a curly I ($\Im$) is the **imaginary axis**.

Thus we can write:

$$\boldsymbol{f} = f(\cos\phi + i\sin\phi)$$

but $$e^{i\phi} = \cos\phi + i\sin\phi$$

$$\therefore \ \boldsymbol{f} = fe^{i\phi}$$

and so the structure factor can be written as:

$$\boldsymbol{F}_{hkl} = \sum_{n=1}^{N} f_n \left\{\cos 2\pi\left(hx_n + ky_n + lz_n\right) + i\sin 2\pi\left(hx_n + ky_n + lz_n\right)\right\}$$

or $$\boldsymbol{F}_{hkl} = \sum_{n=1}^{N} f_n \exp 2\pi i\left(hx_n + ky_n + lz_n\right)$$

The diffracted intensities I_{hkl} are proportional to $|\boldsymbol{F}_{hkl}|^2 = \boldsymbol{F}_{hkl}.\boldsymbol{F}_{hkl}{}^*$

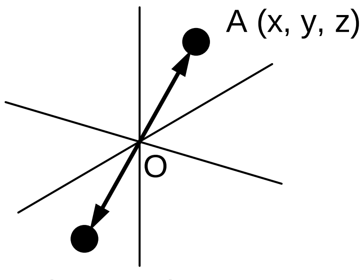
$$\left|\boldsymbol{F}_{hkl}\right|^2 = \boldsymbol{F}_{hkl}.\boldsymbol{F}_{hkl}{}^* = F_{hkl}e^{i\phi}.F_{hkl}e^{-i\phi} = F_{hkl}^2 e^{i(\phi-\phi)} = F^2$$

Therefore:

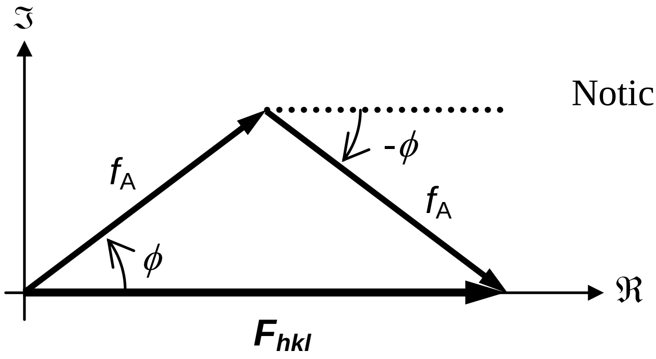
$$\left|\boldsymbol{F}_{hkl}\right|^2 = \left\{\sum_{n=1}^{N} f_n \cos 2\pi\left(hx_n + ky_n + lz_n\right)\right\}^2 + \left\{\sum_{n=1}^{N} f_n \sin 2\pi\left(hx_n + ky_n + lz_n\right)\right\}^2$$

Centre of Symmetry

Consider again our 2-atom motif but now make atom B the same as atom A. if we also move the origin to be mid-way between the two atoms then the origin is lying at a centre of symmetry.

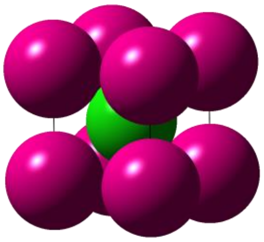


Now we have an atom at (x, y, z) and an identical atom at ($-x$, $-y$, $-z$).



Notice that $\boldsymbol{F}_{\text{hkl}}$ is real.

Example of CsCl



P lattice with motif:

Cl (0,0,0)
Cs (½, ½, ½)

$$\boldsymbol{F}_{hkl} = f_{Cl} \exp 2\pi \boldsymbol{i}(0) + f_{Cs} \exp 2\pi \boldsymbol{i}\left(h\,{}^1\!/_2 + k\,{}^1\!/_2 + l\,{}^1\!/_2\right)$$

$$\boldsymbol{F}_{hkl} = f_{Cl} + f_{Cs} \exp i\pi(h+k+l)$$

Thus for $h + k + l$ = even $\exp i\pi(h+k+l) = 1$

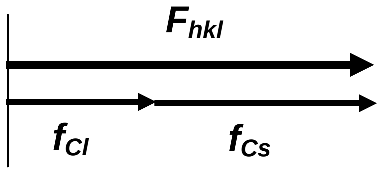
for $h + k + l$ = odd $\exp i\pi(h+k+l) = -1$

Thus for $h + k + l$ = even $\boldsymbol{F}_{hkl} = f_{Cl} + f_{Cs}$

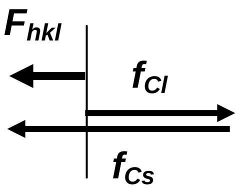
for $h + k + l$ = odd $\boldsymbol{F}_{hkl} = f_{Cl} - f_{Cs}$

In terms of an Argand diagram:

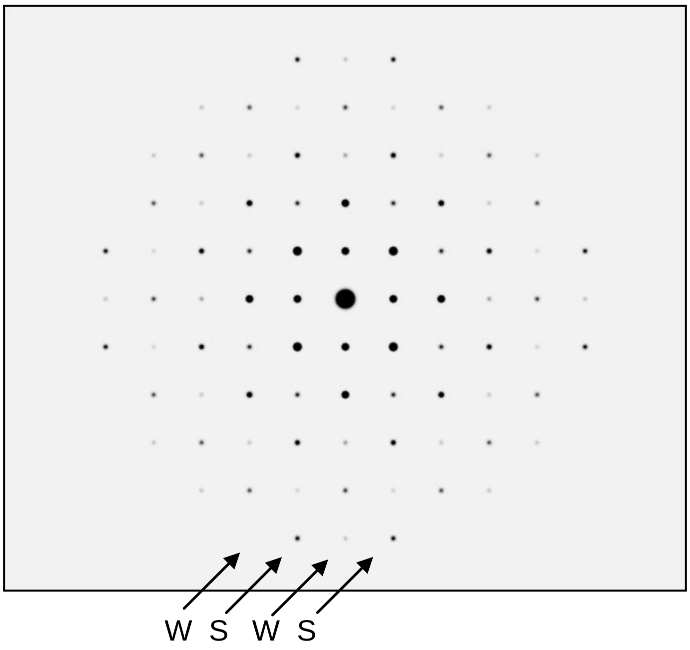
h + *k* + *l* = even



h + *k* + *l* = odd



Thus in a diffraction pattern we would expect to see alternating strong (S) and weak (W) reflections:



Electron diffraction pattern of CsCl parallel to the <100> zone axis

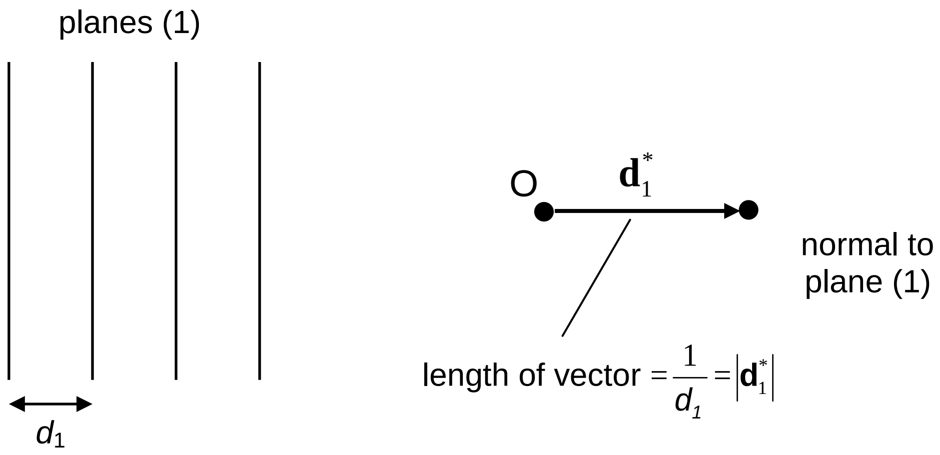
G. The Reciprocal Lattice

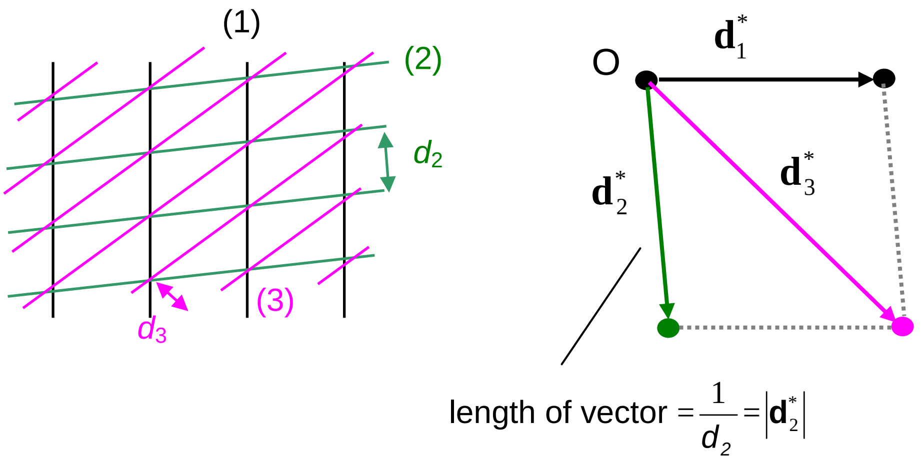
The concept of the **reciprocal lattice** is a very simple one yet is remarkably powerful in helping to interpret the scattering seen in diffraction patterns.

The reciprocal lattice can be defined in a purely mathematical approach which though elegant and rigorous does not perhaps emphasize the connection between the **reciprocal lattice vectors** and the crystal planes – this is what we will do here.

We saw before that in the diffraction from a series of slits (grating) we recorded a series of spots whose spacing was proportional to the reciprocal of the slit spacing. An analogy was made with planar spacings in a crystal.

Consider again a series of crystal planes:



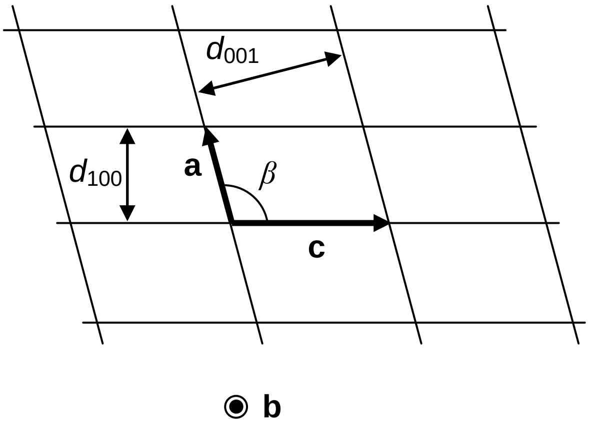


A third set of planes (3) can be constructed automatically from the first two sets, and in reciprocal space this means that $\mathbf{d}_3^*$ is a vector sum of $\mathbf{d}_1^*$ and $\mathbf{d}_2^*$, i.e.

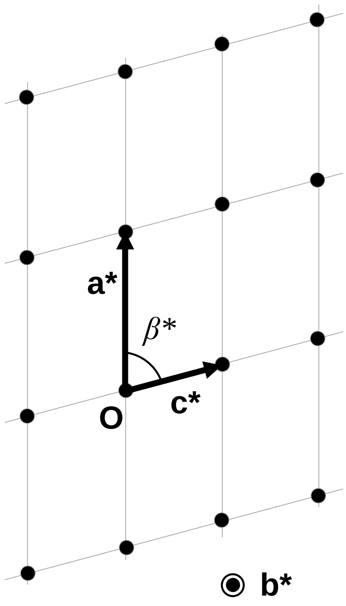
$$\mathbf{d}_3^* = \mathbf{d}_1^* + \mathbf{d}_2^*$$

We can continue and construct an infinite reciprocal lattice composed of **reciprocal lattice vectors**.

Consider a primitive monoclinic lattice viewed parallel to [010]:



Real Space



Reciprocal Space

Note:

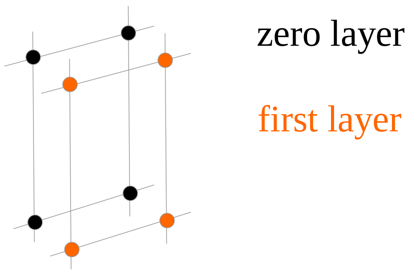
$$\mathbf{a}^* = \mathbf{d}_{100}^* \qquad \left|\mathbf{a}^*\right| = \frac{1}{d_{100}} \qquad\qquad \mathbf{c}^* = \mathbf{d}_{001}^* \qquad \left|\mathbf{c}^*\right| = \frac{1}{d_{001}}$$

$\mathbf{a}^*$ and $\mathbf{c}^*$ are in general <u>not</u> parallel to **a** and **c**.

β^* is the complement of β (i.e. $\beta^* = 180° - \beta$)

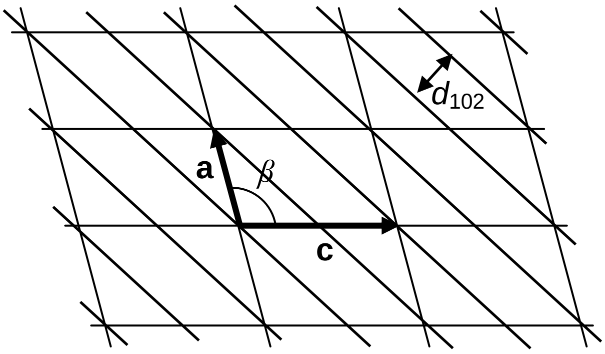
For this monoclinic cell, the 3rd axis **b** of the unit cell is pointing up perpendicular to the page and therefore $\mathbf{b}^*$ is perpendicular to both $\mathbf{a}^*$ and $\mathbf{c}^*$ and in this case the next layer of the reciprocal lattice will lie directly above the layer containing the origin, O, known as the zero layer.

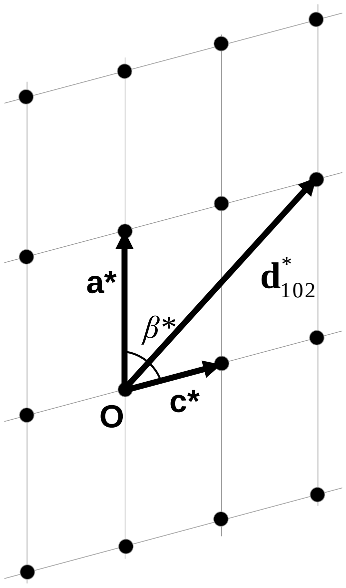
Note: For the most general case, a triclinic crystal, that first layer up would be displaced. Looking in reciprocal space in the same direction as before:



Any reciprocal lattice vector $\mathbf{d}^*$ can be written in terms of the 3 reciprocal lattice vectors $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$.

For example, consider the planes (102):





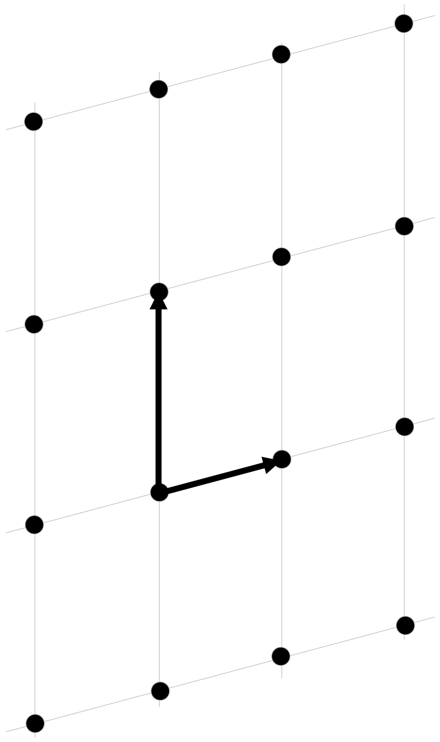
We can write:

$$\mathbf{d}^*_{102} = 1\mathbf{a}^* + 0\mathbf{b}^* + 2\mathbf{c}^* = \mathbf{a}^* + 2\mathbf{c}^*$$

or in general,

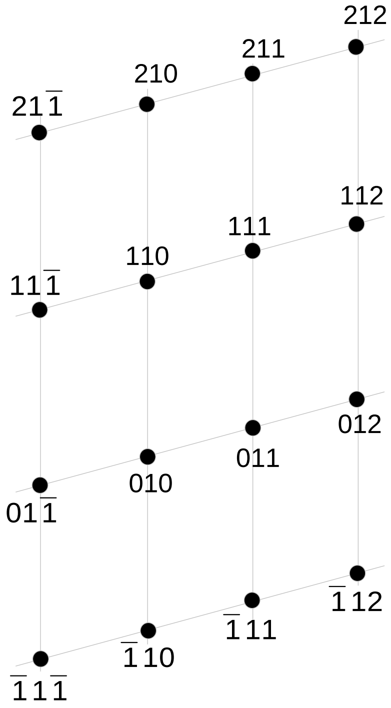
$$\mathbf{d}^*_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$

The reciprocal lattice points are indexed *hkl* with no brackets:



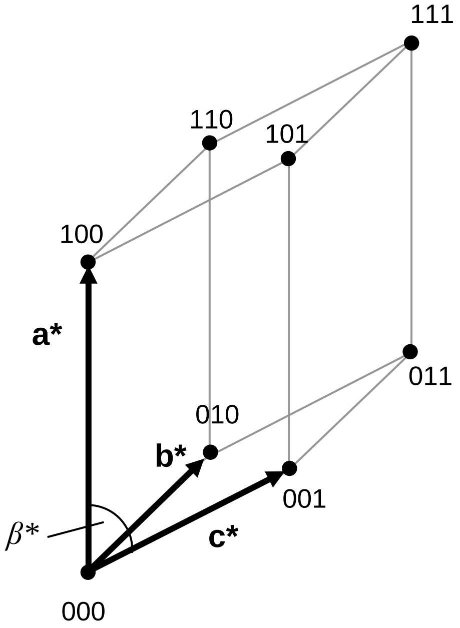
*h*0*l* section

In the case of this monoclinic cell, directly above this section, or zero layer, at a height equal to $\left|\mathbf{d}_{100}^{*}\right| = \left|\mathbf{b}^{*}\right|$, is the *h*1*l* section, or first layer:



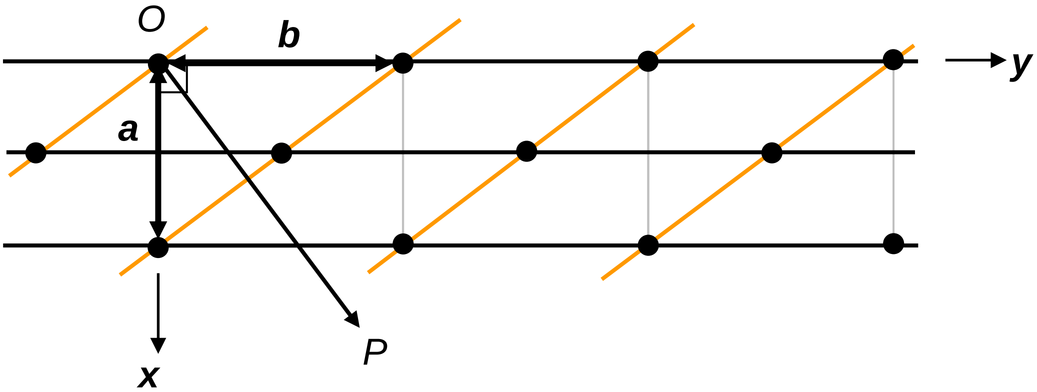
*h*1*l* section

We can draw in perspective the primitive monoclinic reciprocal lattice unit cell as:



Primitive real space lattices	→	primitive reciprocal space lattices.
Centred real space lattices	→	centred reciprocal space lattices.

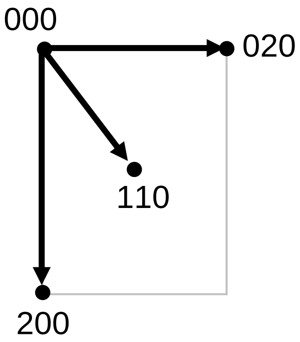
Consider an orthorhombic *C* lattice looking down the *c*-axis:

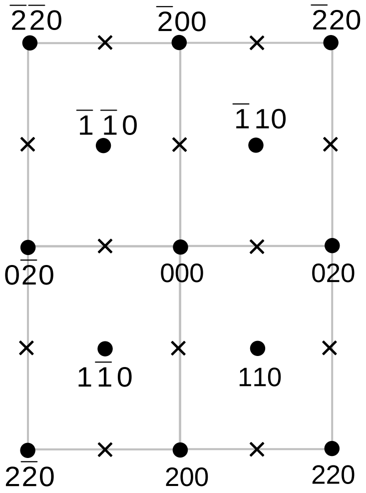


Consider the lattice planes perpendicular to the *x*-axis. Moving in the *x*-direction from the origin the first set of lattice planes encountered is not the (100) but the (200) and so the first reciprocal lattice vector in the *x*-direction must be $\mathbf{d}^*_{200}$ and not $\mathbf{d}^*_{100}$.

Likewise in the *y*-direction, the (020) planes are encountered first and so the first reciprocal lattice vector in the *y*-direction must be $\mathbf{d}^*_{020}$.

Moving in the direction *P* perpendicular to the (110) planes, the first plane encountered is the (110) plane and so in this direction the first reciprocal lattice vector is $\mathbf{d}^*_{110}$. Thus:



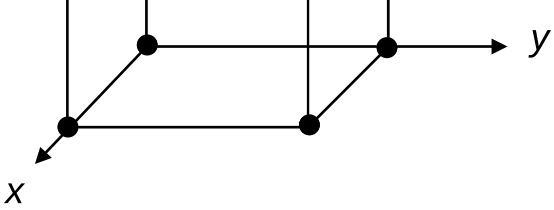


Thus for such a *C*-centred lattice, a mesh of reciprocal lattice points are absent (marked above with a ×) and only those with $h + k = 2n$ (*n* integer) are allowed.

Remember the absent reciprocal lattice points are absent because of our choice of a non-primitive real space lattice.

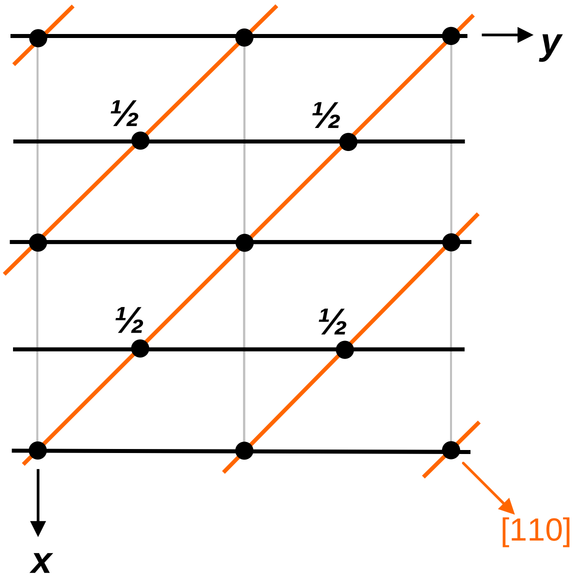
Let's look at the important case of cubic crystals.

Consider an *I*-centred cubic real space lattice:



Again, we will have absent reciprocal lattice points because of our choice of non-primitive real space lattice:

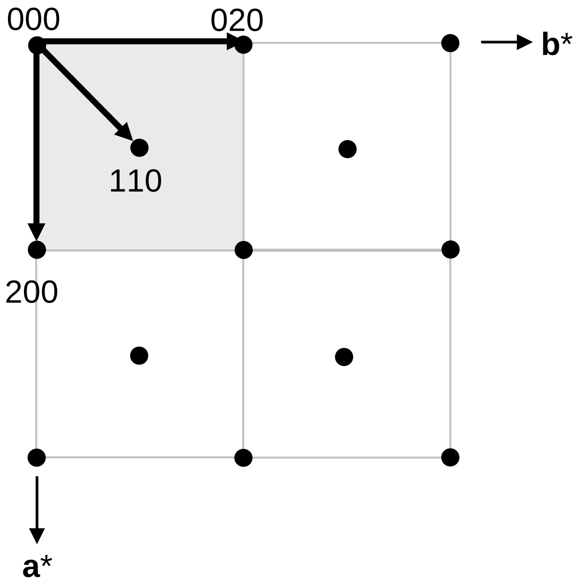
Look in projection down the *z*-axis in real space:



In the *x*-direction, we have a similar situation to that of the *C*-centred orthorhombic cell and so in reciprocal space, the 100, 300, etc reciprocal lattice points will be absent.

The cubic symmetry means that this must be true in the *y* and *z* directions also.

In the [110] direction, the first set of planes encountered is the (110) so that $\mathbf{d}^*_{110}$ is allowed in reciprocal space. So we find in reciprocal space:



Thus we have a ‘face-centred’ reciprocal lattice in this section and this is repeated in the other sections to give a **face-centred cubic reciprocal lattice**.

For a face-centred *F* lattice in real space we find a body-centred *I* lattice in reciprocal space.

(This reciprocal relationship is true also for *F* and *I* lattices in other crystal systems.)

We can construct a table illustrating which reciprocal lattice points are absent or not depending on the lattice chosen:

Lattice Type	**Condition for Presence**
P	none
I	$h + k + l = 2n$
C	$h + k = 2n$
F	*h, k, l* **all odd** or **all even**

Note: The presence of symmetry elements such as glide planes, screw axes may also lead to ‘missing’ reflections in reciprocal space.

H. The Geometry of X-ray Diffraction

H1. The Ewald Sphere

We found by analysis of scattering using a real space model that:

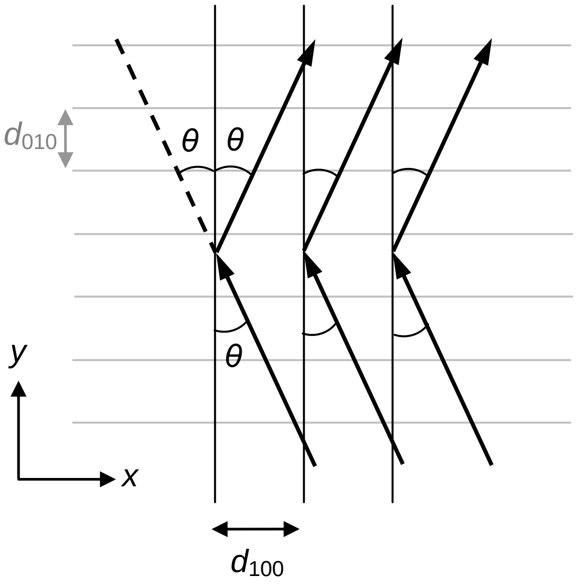
$$\lambda = 2d \sin\theta \qquad \text{Bragg's Law}$$

Now that we have knowledge of reciprocal space can we describe Bragg's Law in reciprocal space?

[Note that we can write:

$$\frac{1}{2d} = \frac{\sin\theta}{\lambda} \quad \text{or} \quad \frac{1}{2}d^* = \frac{1}{\lambda}\sin\theta \quad]$$

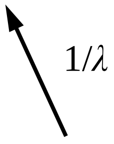
Consider:



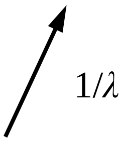
Consider radiation to be x-rays of wavelength λ.

We can represent the x-rays in reciprocal space by a wavevector whose length is equal to $\frac{1}{\lambda}$

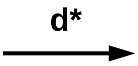
Incoming wavevector:



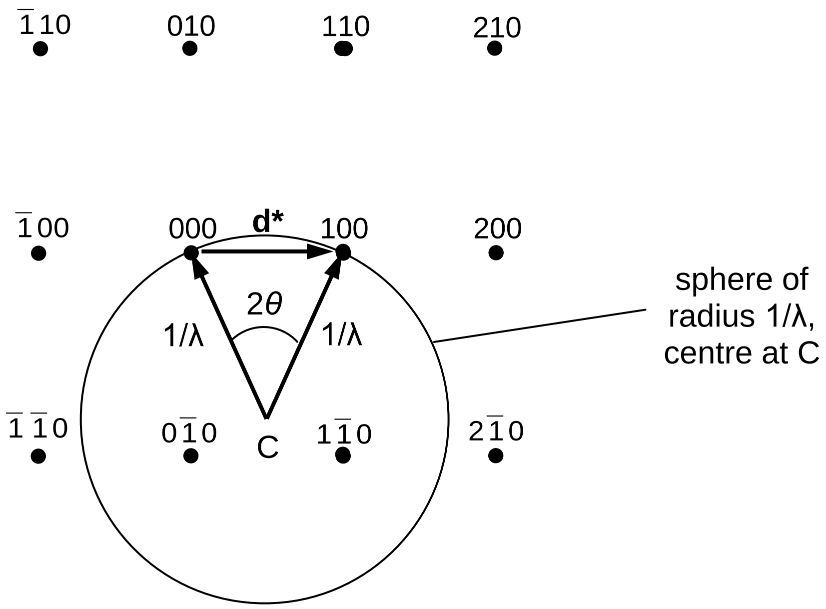
Outgoing wavevector:



Reciprocal lattice vector for the (100) planes as shown:



We can put this all together on our reciprocal lattice for this crystal:



The angle between the incoming and outgoing wavevectors = 2θ

Thus from the diagram, simple trigonometry gives:

$$\frac{1}{2}d^* = \frac{1}{\lambda}\sin\theta$$

Of course $d^* = \dfrac{1}{d}$ $\therefore \dfrac{1}{2d} = \dfrac{\sin\theta}{\lambda}$ $\therefore \lambda = 2d\sin\theta$

The wavectors are often given the symbol **k** for the incoming wave and **k′** for the outgoing wave and so:

$$\mathbf{k'} - \mathbf{k} = \mathbf{d^*}$$

This is simply Bragg's Law expressed in reciprocal space and we would say that the 100 reflection is at the 'Bragg condition'. No other reflection satisfies the condition and so no other planes will scatter radiation to give constructive interference.

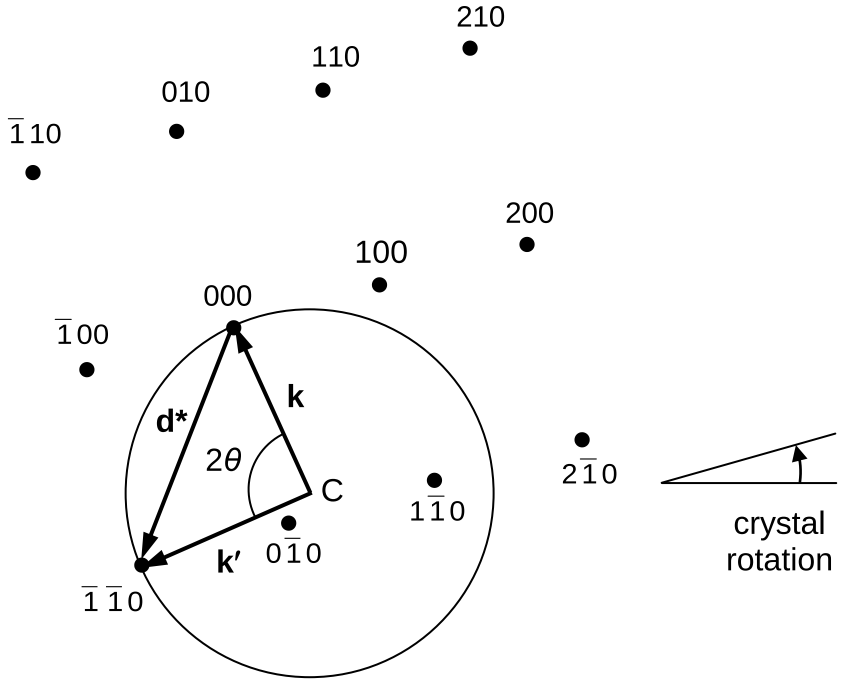
The wavevectors **k** and **k′** lie on a circle (sphere in 3D) of radius 1/λ, called the Ewald sphere.

For the Bragg condition to be satisfied for a reflection *hkl* the Ewald sphere must pass exactly through the reflection *hkl.*

The Ewald sphere always passes through the origin of reciprocal space.

This construction is extremely useful in understanding which reflections we will detect in a diffraction experiment.

For example if we keep the incoming radiation fixed, and rotate the crystal, we will eventually find an angle where the Ewald sphere will intercept another reciprocal lattice point and thus we will detect that reflection in our diffraction experiment:



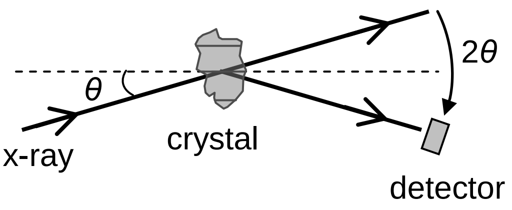
In this mode, we will therefore only see one reflection at a time.

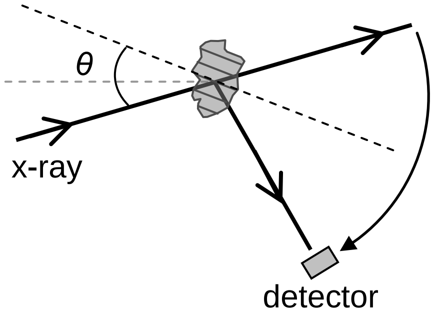
If the detector is ‘left on’ continuously and we rotate the crystal then we will detect more and more reflections within the geometry of the Ewald sphere – this is the basis of the **oscillation**, **rotation** and **precession** methods of single crystal x-ray diffraction – these are known as **fixed λ varying θ** methods.

H2. Single Crystal X-ray Diffractometry

We rotate the crystal about a defined axis and monitor the diffracted x-rays in a ring around the axis. Only planes whose normals are perpendicular to the rotation axis will be detected.

Consider:

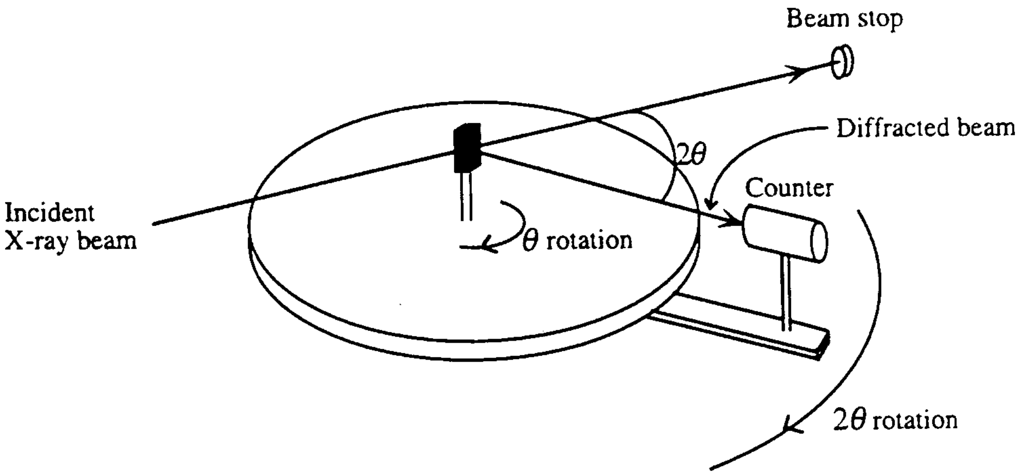




Remember that crystal planes with smaller interplanar distances have larger Bragg angles, θ.

2-Circle Diffractometer

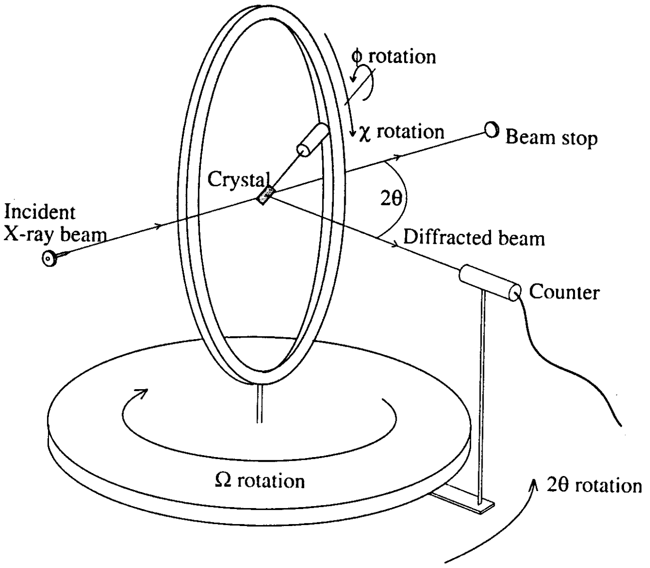
This is the type of diffractometer used in AP2 and AP3 and is explained in more detail in those practicals.



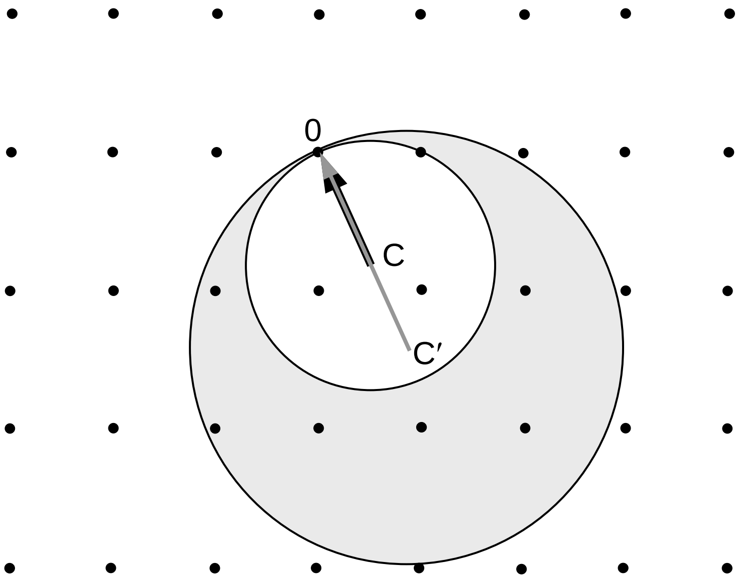
4 –circle Diffractometer

The crystal can now be rotated about 3 different axes: ϕ, χ, Ω. The detector moves around 2θ.

Positions and intensities of all reflections can be recorded.



If we use ‘white radiation’ with a range of wavelengths (indicated by the shaded portion below) then many reflections will be recorded at once with reciprocal lattice points being intercepted by Ewald spheres of different radius (1/λ) – see example in Question Sheet 4.

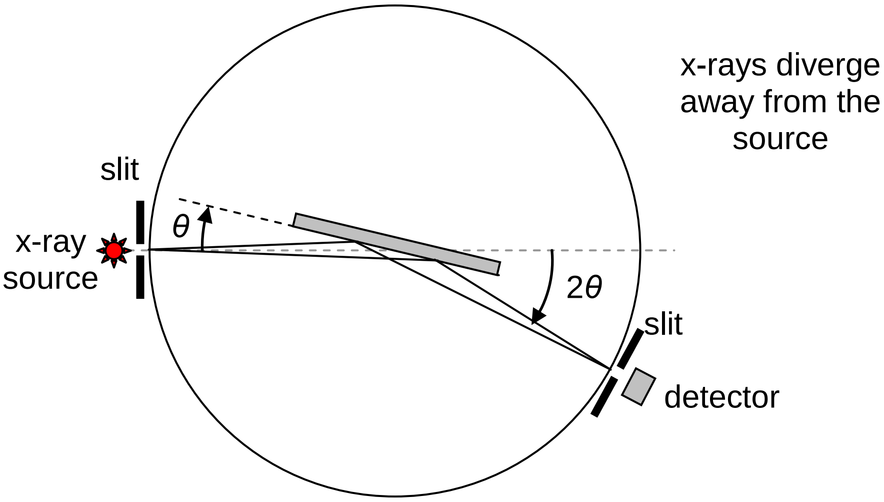


This technique is called the **Laue** technique and recorded patterns are known as **Laue patterns**. This is a **fixed *θ* varying *λ*** method.

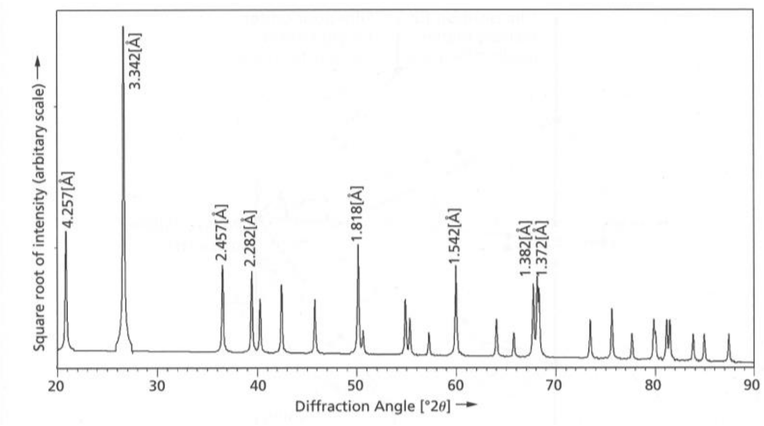
H3. X-ray Powder Diffractometry

Many samples cannot be grown in single crystal form with sufficient size for single crystal x-ray diffraction. Instead, we can examine the sample in powder form. If the powder is finely ground such that individual crystallites are likely to be found at all orientations then powder x-ray diffractometry can be applied. (Note: if some orientations are preferred this is known as 'texture' and the powder diffraction requires a different analysis.)

In modern diffractometers the powder is pressed into a thin uniform layer onto a substrate and mounted in a θ - 2θ 2-circle diffractometer; this is sensitive only to the interplanar spacing d_{hkl} and not the orientation of the plane.



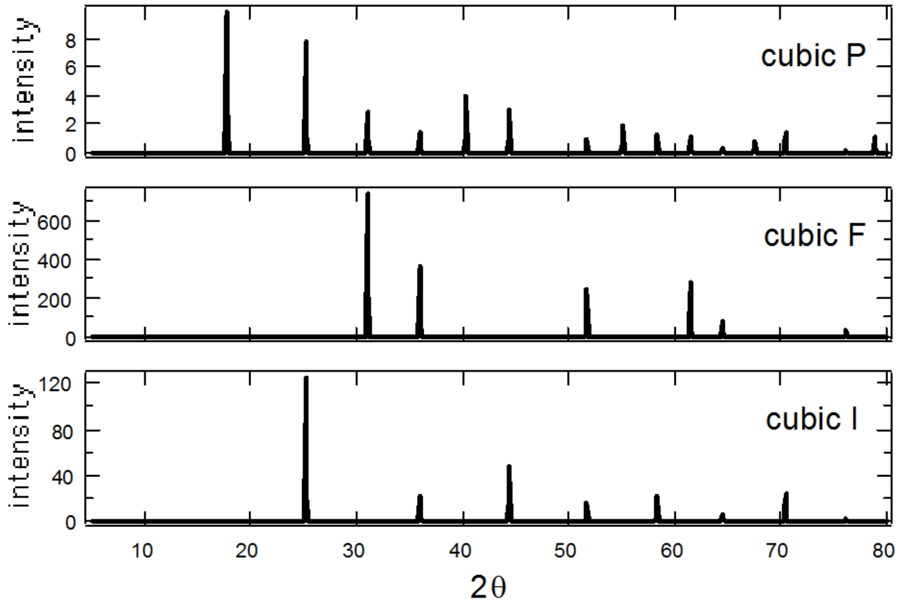
The use of slits at the source and detector plus the use of this so-called 'Bragg-Brentano' geometry ensures that the angular resolution of the diffractometer trace is high. An example from SiO_2 is shown below:



The diffracted intensity of a peak in a powder x-ray diffraction trace is proportional to $m_{hkl}\boldsymbol{F}_{hkl}\cdot\boldsymbol{F}_{hkl}^{*}$ where m_{hkl} is the **multiplicity** and takes into account the symmetry equivalence of $\{hkl\}$ planes.

Note. Depending on the diffractometer used, there may be additional geometric factors that change the relative intensities of the peaks.

X-ray powder diffraction of cubic crystals (see also AP3)



For cubic crystals $d_{hkl} = \dfrac{a}{\sqrt{h^2+k^2+l^2}} = \dfrac{a}{\sqrt{N}}$

Bragg's Law: $\lambda = 2d_{hkl} \sin\theta$ and therefore $\sin^2\theta = \dfrac{\lambda^2}{4a^2}N$

Permitted values of $N = h^2 + k^2 + l^2$:

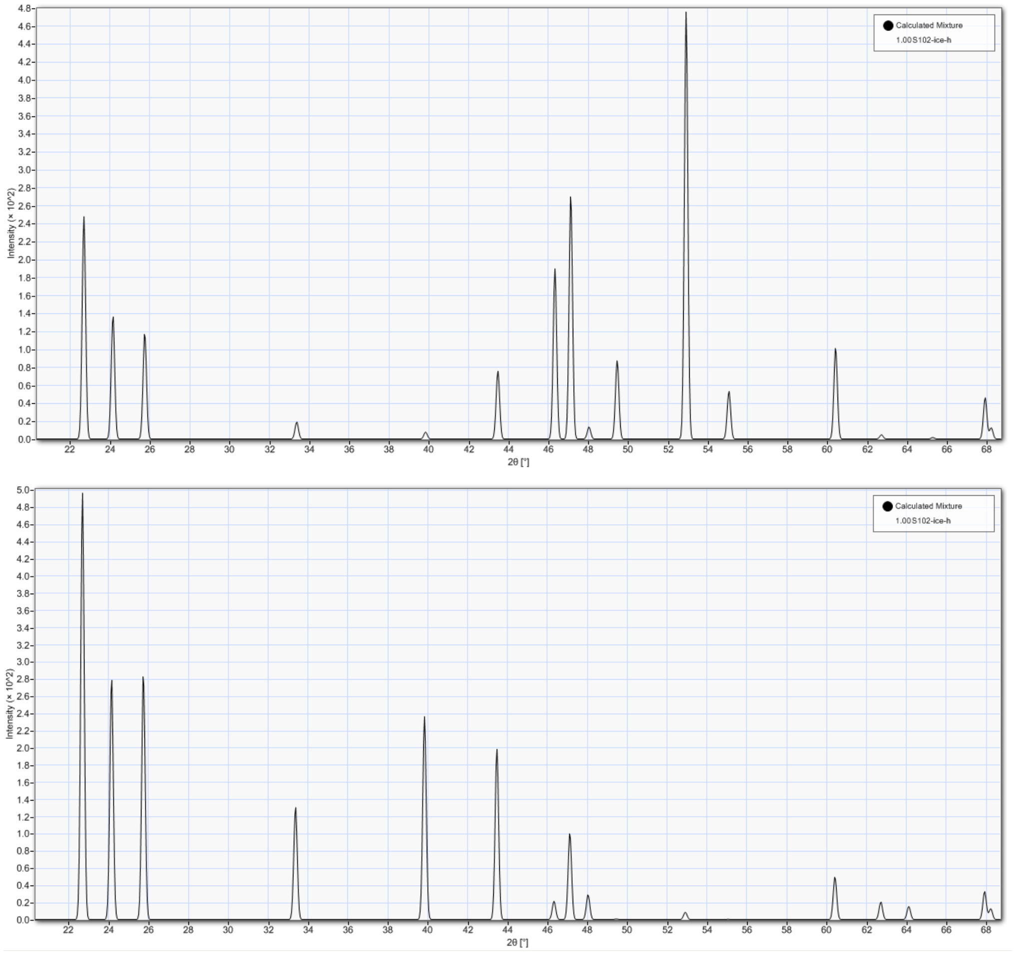
hkl	P	I	F	*hkl*	P	I	F
100	1	-	-	400	16	16	16
110	2	2	-	410, 322	17	-	-
111	3	-	3	330, 411	18	18	-
200	4	4	4	331	19	-	19
210	5	-	-	420	20	20	20
211	6	6	-	421	21	-	-
-	-	-	-	332	22	22	-
220	8	8	8	-	-	-	-
300,221	9	-	-	422	24	24	24
310	10	10	-	500, 430	25	-	-
311	11	-	11	510, 431	26	26	-
222	12	12	12	333, 511	27	-	27
320	13	-	-	-	-	-	-
321	14	14	-	520, 432	29	-	-
-	-	-	-	521	30	30	-

H4. Neutron Diffraction – non-examinable!

Neutrons can be used in a similar way to x-rays to investigate single crystals and powder samples.

The scattering factors (known as **scattering lengths**) are different to those for x-rays because for non-magnetic atoms, the neutron scatters only from the atomic nucleus and so the scattering lengths are independent of scattering angle.

The relationship between scattering length and atomic species is more complicated. A great advantage of neutron diffraction is that light elements (e.g. hydrogen and oxygen) have relatively large scattering amplitudes relative to heavy metal atoms, allowing their location to be determined more easily than with x-ray diffraction.



Simulated powder patterns for hexagonal ice:
(top) neutron diffraction; (bottom) x-ray diffraction

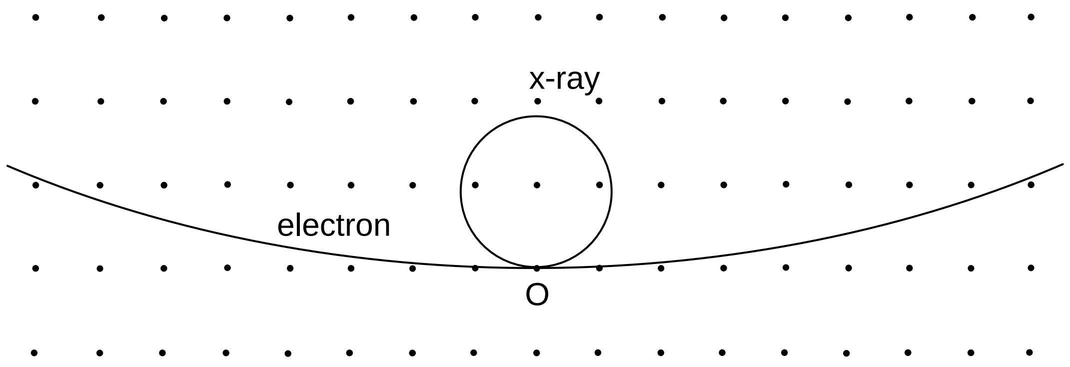
I. Electron Microscopy and Diffraction

I1. Electron Diffraction

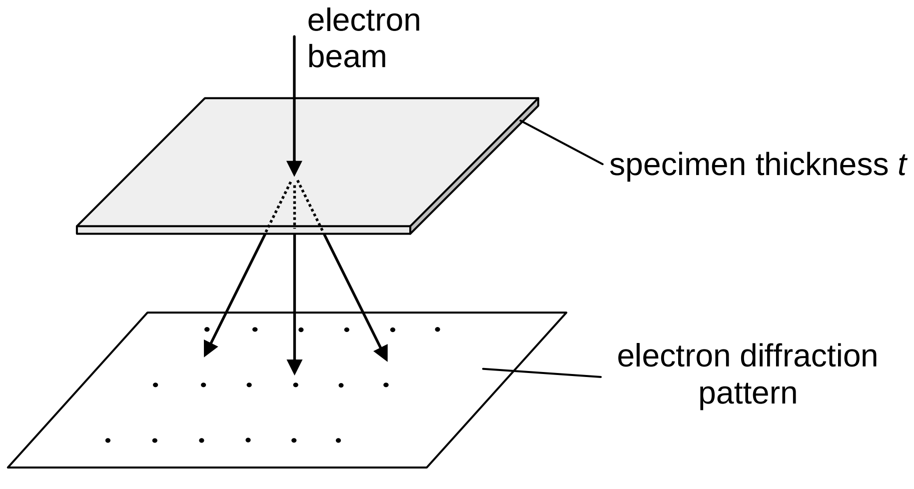
To understand the scattering of electrons from a crystal, and thus to interpret electron diffraction patterns, we can invoke the Ewald sphere construction and use Bragg's Law just as we did to understand x-ray diffraction.

There are however two key differences:

(i) for most electron diffraction experiments the energy of the electron beam (typically 200-300keV) is normally far higher than that of a typical x-ray beam (e.g. 8keV) and so the wavelength of radiation is much smaller. This means that the Ewald sphere radius (=1/λ) is much larger for electron diffraction. (N.B. 1 eV = 1.6×10^{-19} J)



(ii) the crystals studied by electron diffraction (and electron microscopy) are normally in the form of a thin film, perhaps a few millimeters in the plane of the film but only a few 10's nm normal to the film plane, i.e. parallel to the incoming beam.

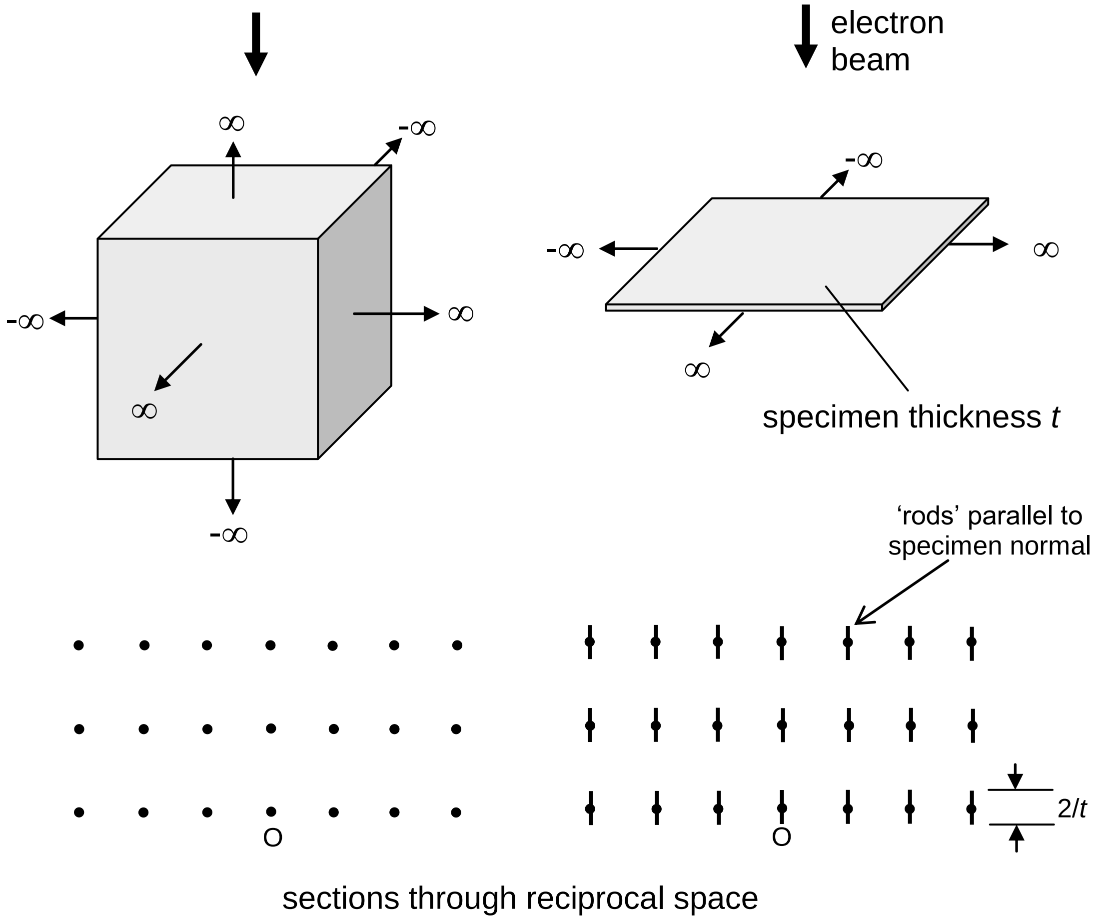


The sample has to be thin in the direction parallel to the incoming beam because electrons, being charged particles, interact very strongly with the atoms in the crystal. If the crystal is too thick the electrons are scattered many times (dynamical scattering), scattered to very high angles (even scattered back towards the electron source), will lose energy and not be transmitted into the diffraction pattern.

Having such a thin film in one direction means that, effectively, the reciprocal lattice points are no longer simply ‘points’, but are broadened out into ‘rods’ in the direction of the specimen normal.

The strict condition for constructive interference we saw for an infinite array of slits (or atoms) is relaxed and in an electron diffraction experiment we see intensity in a diffracted beam even if it is not exactly at the Bragg condition.

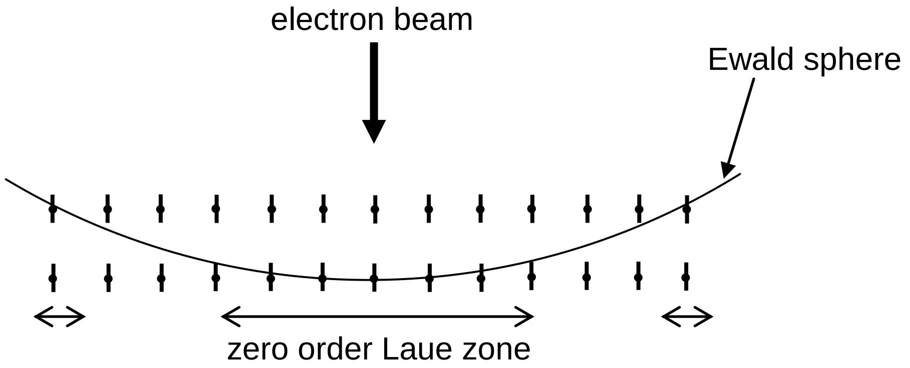
The size of the rod in reciprocal space is proportional to the reciprocal of the specimen thickness, *t*. To a good approximation, the length of the ‘reciprocal lattice rod’, is equal to 2/*t*, i.e. ±1/*t* above and below the reciprocal lattice point.

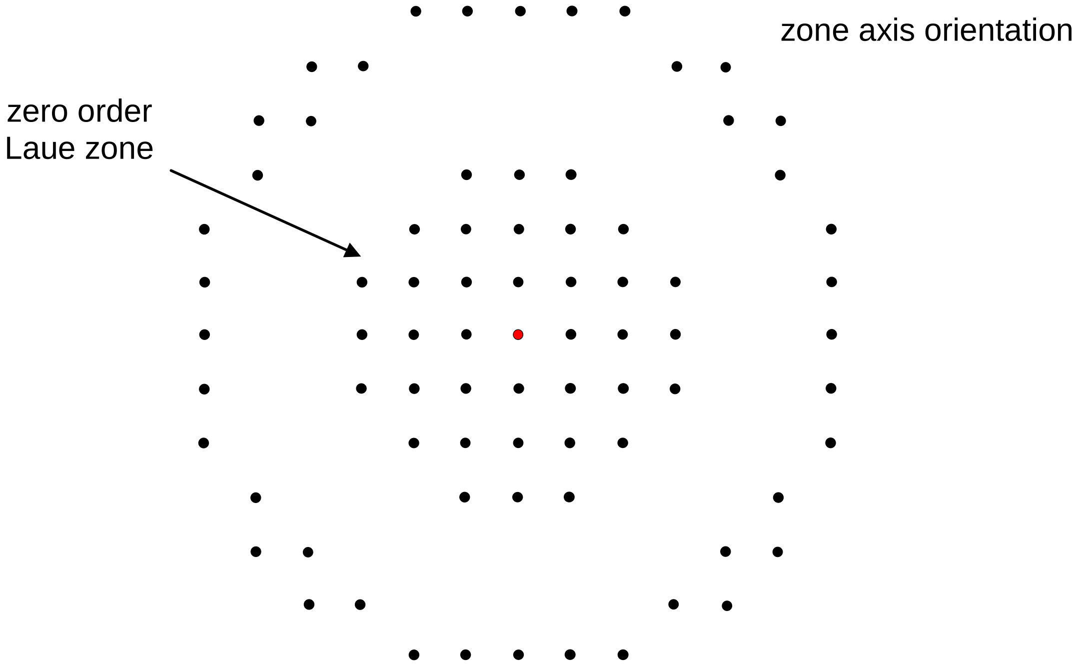


sections through reciprocal space

In fact the ‘rod’ shape is similar to that seen from diffraction from a single slit of width *t*.

With such a flat Ewald sphere in an electron diffraction experiment, many reflections will be seen in a single diffraction pattern of fixed orientation and fixed (single) wavelength.



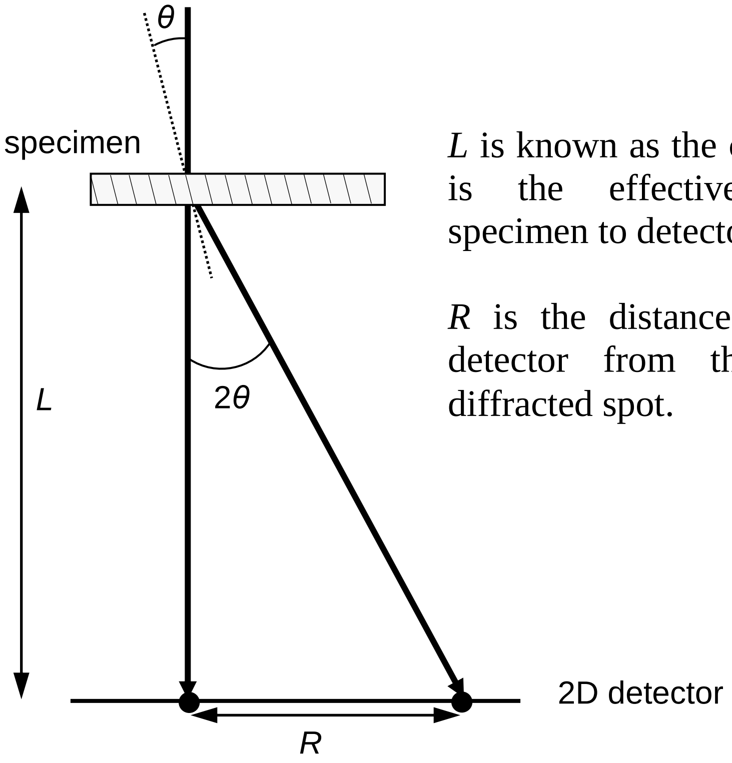


A zone axis electron diffraction pattern can be considered in terms of layers or **Laue zones** of reciprocal space, perpendicular to the zone axis:

Zero Order Laue Zone (ZOLZ)
First Order Laue Zone (FOLZ)
etc.

Electron diffraction patterns can be interpreted very simply as sections of reciprocal space. They are recorded on 2D detectors, for example a CCD camera.

It is relatively straightforward to determine planar spacings:



L is known as the **camera length** and is the effective distance from specimen to detector.

R is the distance measured on the detector from the origin to the diffracted spot.

From the diagram: $\tan 2\theta = \frac{R}{L}$

For electron diffraction with very small wavelengths this means that Bragg angles are also very small (typically <1°). Thus:

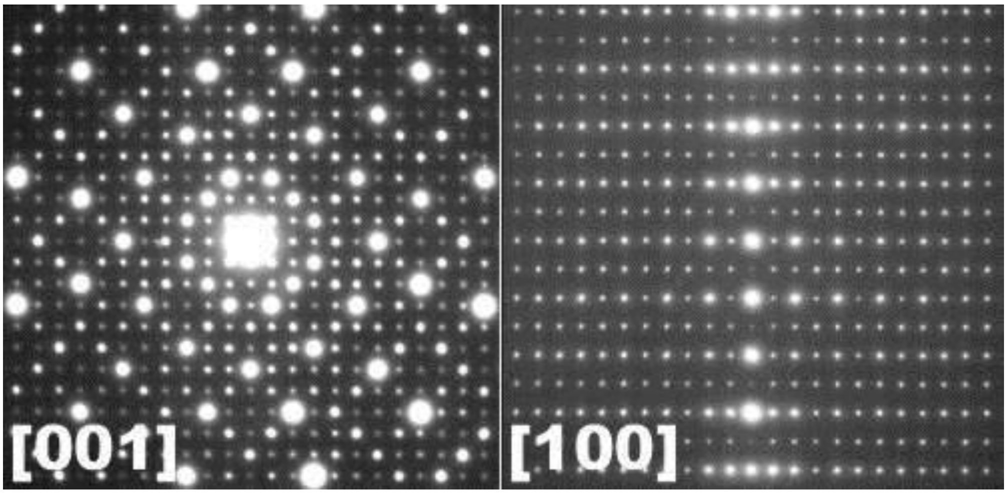
$$\tan 2\theta \approx 2\theta \quad \text{and} \quad \sin\theta \approx \theta$$

Therefore Bragg's law can be written as: $\lambda = 2d\theta$ or $2\theta = \frac{\lambda}{d}$ and

$$\therefore 2\theta = \frac{R}{L} = \frac{\lambda}{d} \qquad \text{and} \qquad d_{hkl} = \frac{\lambda L}{R}$$

The quantity λL is sometimes known as the **camera constant**.

There are many applications of electron diffraction in materials science. In the example below, diffraction patterns from mutually perpendicular directions of a complex alloy $Ta_{97}Te_{60}$ allow the lattice parameters to be measured.

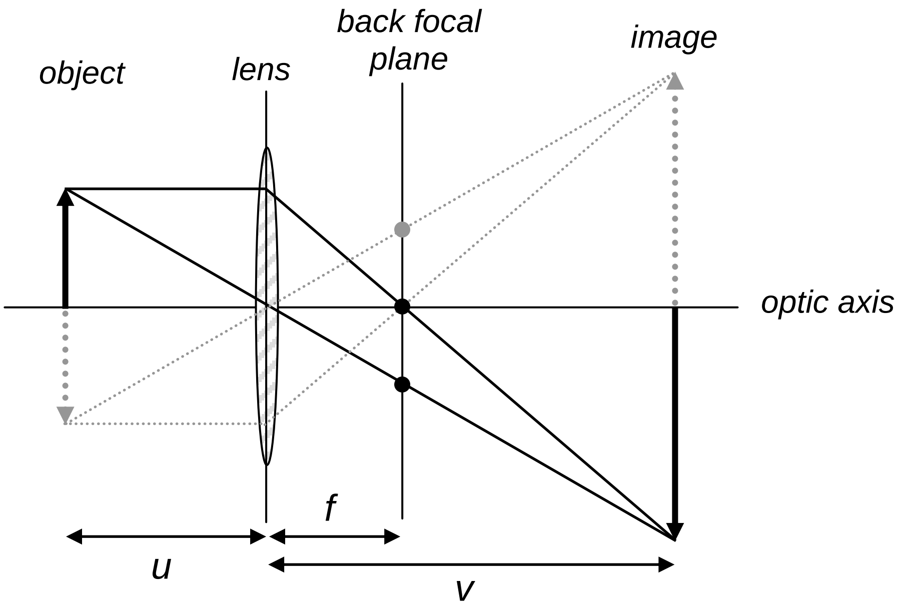


I2. Microscopy and Image Formation

The great advantage of electrons over x-rays is that an electron-optical lens can be placed behind the specimen and an **image** of the specimen can be formed.

We can use simple ray optics developed for light microscopy to understand electron microscopy images. Electro-magnetic lenses can be considered as if they were convex lenses.

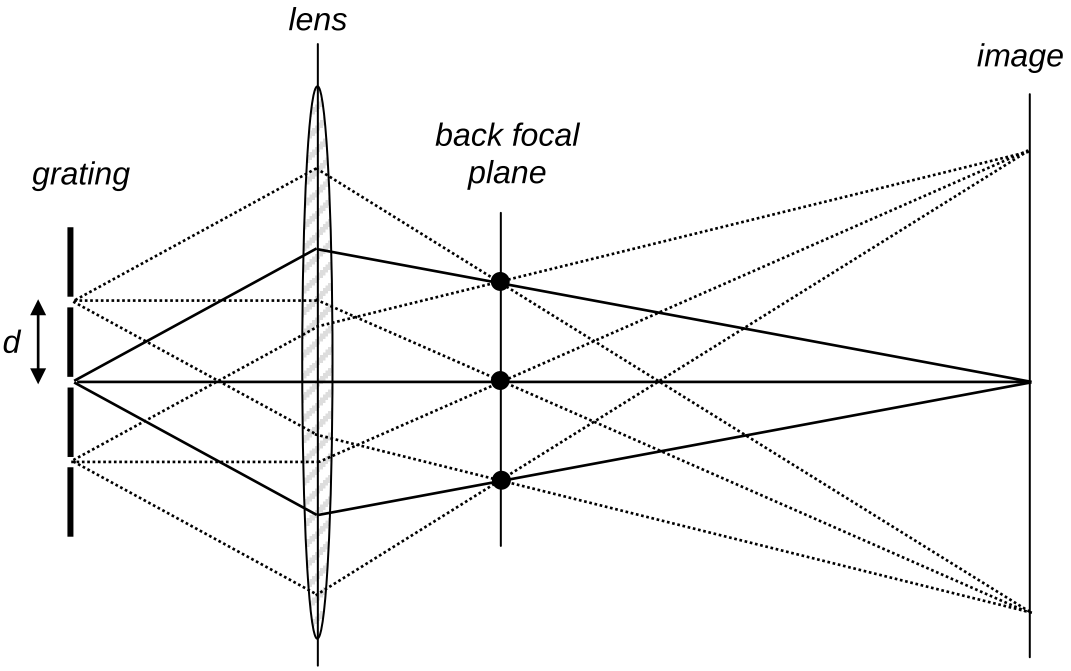
First let's remind ourselves about the action of a convex lens:



This shows a simple construction to indicate the position of the image and its magnification, $M = v / u$.

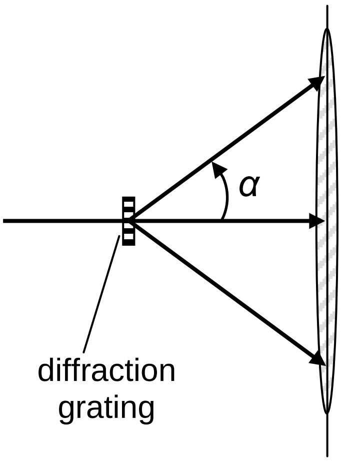
It also indicates the focal length of the lens, *f*, and the plane containing *f* is known as the **back focal plane** of the lens.

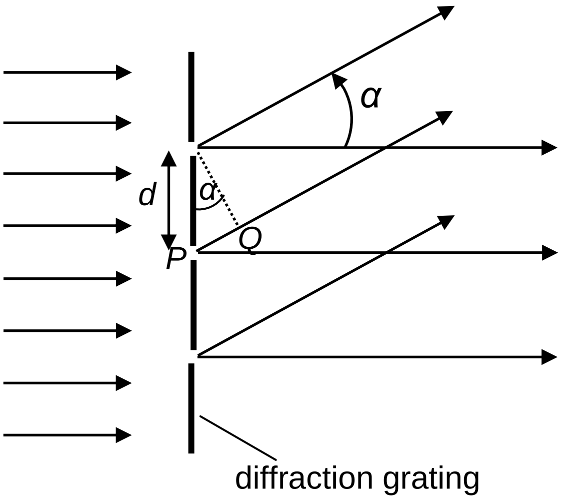
Now consider again an array of slits, or a 'grating', that we now wish to image using a lens:



What determines the resolution of the image?

Abbe's theorem states that to resolve a diffraction grating with slit separation *d* then at least two beams (typically the direct beam and the first order diffracted beam) should enter the lens. The image is effectively formed by the interference of the diffracted beams and the direct beam at the image plane. Let's simplify the diagram:





If α is the scattering angle for the 1st order diffracted beam, then the path difference PQ must be equal to the wavelength λ (for constructive interference).

$$\therefore \text{ p.d.} = PQ = \lambda = d\sin\alpha$$

$$\therefore d = \frac{\lambda}{\sin\alpha}$$

In fact the requirement to achieve *d* is 'over-fulfilled' in the diagram above because the lens is collecting light scattered to an angle *α* below as well as above the optic axis. This means that, in this geometry, the resolution is improved by a factor of 2, so $d \rightarrow d/2$ and therefore:

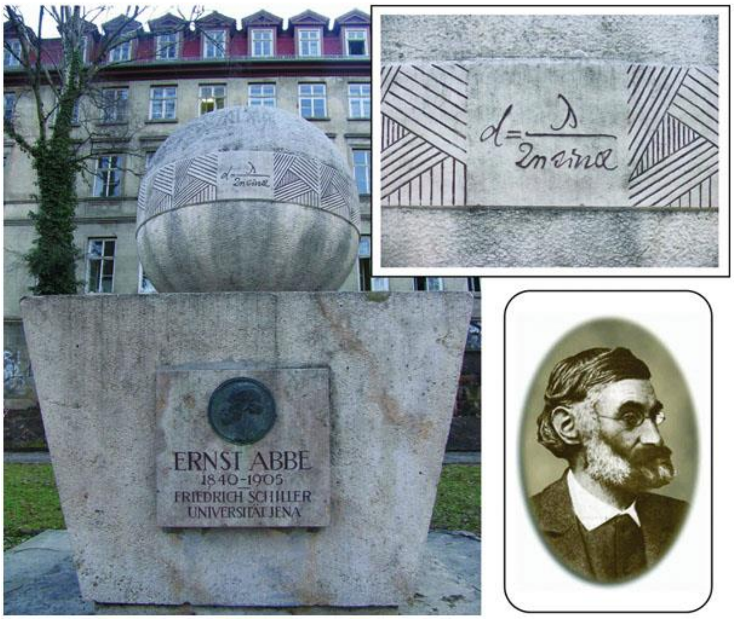
$$d = \frac{\lambda}{2\sin\alpha}$$

So therefore if we use radiation with wavelength *λ*, and collect diffracted rays over an angle ±*α*, we will be able to resolve distances *d* in the image, i.e. the **limit of resolution** is *d*.

If we wish to improve the image resolution further then the object has to be illuminated with radiation of smaller wavelength or have a lens which can collect rays scattered to higher angles.

Note: For optical microscopy, by filling the space between the object and the lens with oil of refractive index *n* it is possible to improve the resolution:

$$d = \frac{\lambda}{2n\sin\alpha}$$



The quantity $n \sin \alpha$ is called the **numerical aperture**, NA, of the lens.

Thus ‘high resolution’ optical microscopes work with the object and lens almost touching to maximize α.

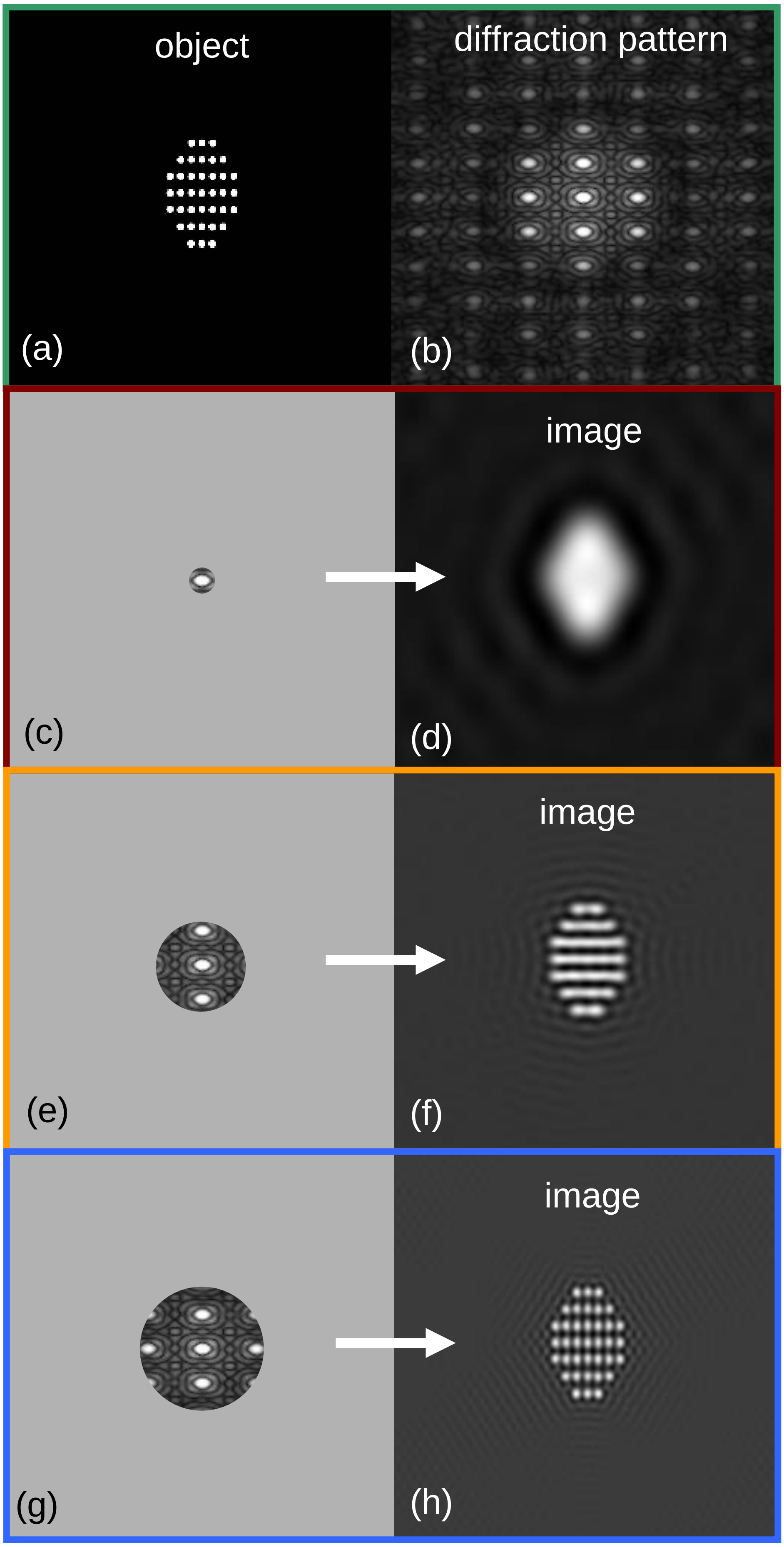
Illustration of Abbe’s Theorem

In the figure overleaf, an object has been simulated which is a series of discs arranged in a rectangular array limited within a diamond ‘envelope’ – see (a). The diffraction pattern (b) shows an array of reciprocal lattice points as expected.

(c) If an aperture is placed to allow only the central spot through then the image formed (d) is a simple diamond shape with a lack of detail – there is no information about the periodicity of the array.

(e) If the aperture is made larger to allow the first order diffracted spots through in the vertical direction then the periodicity is seen in that direction in the image (f).

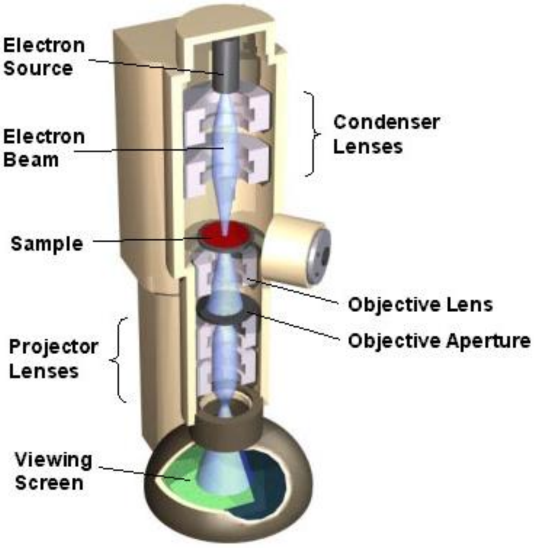
If the aperture is enlarged further to include the first order diffracted spots in the horizontal direction (g) then the array is seen in both directions (h).


object
diffraction pattern
(a)
(b)
image
(c)
(d)
image
(e)
(f)
image
(g)
(h)

I3. Electron Microscopy

Although a large aperture increases the limit of resolution, to improve resolution further though, we need to reduce the wavelength and for that we need then to use high energy electrons:

Electron Energy	30keV	100keV	300keV	1MeV
Electron Wavelength (Å)	0.0698	0.037	0.0197	0.0087

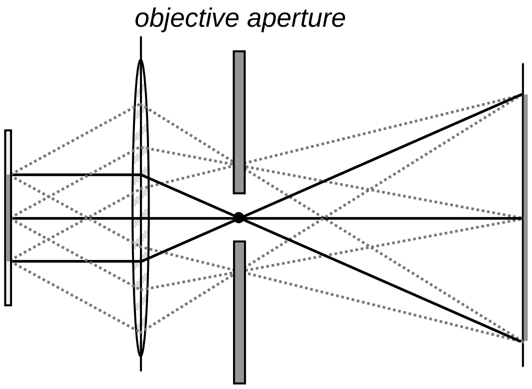


Thus for electron microscopes we might expect a limit of resolution of only a few pm. However the severe aberrations of electro-magnetic lenses limits the usable range of angles α and the NA is typically ~0.01 (c.f. NA ~1 for high quality optical lenses) and so the limit of resolution for electron microscope lenses is ~0.1nm.

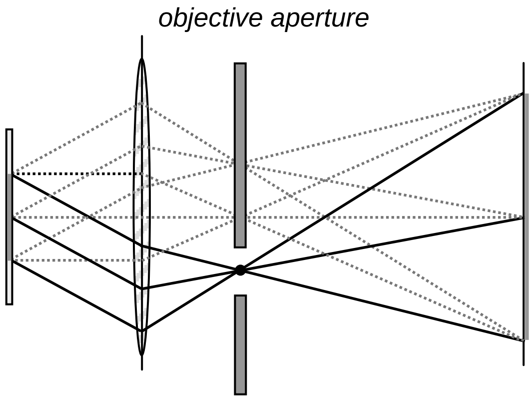
However this resolution enables the imaging of atomic structures directly, such as seen in a figure later.

Imaging in the electron microscope can be performed in variety of ways by using an aperture in the back-focal plane of the imaging lens.

For example by placing an aperture around the direct beam only, you form a bright-field (BF) image. If an aperture is placed around a diffracted beam only, a dark-field (DF) image is formed – see also AP4.

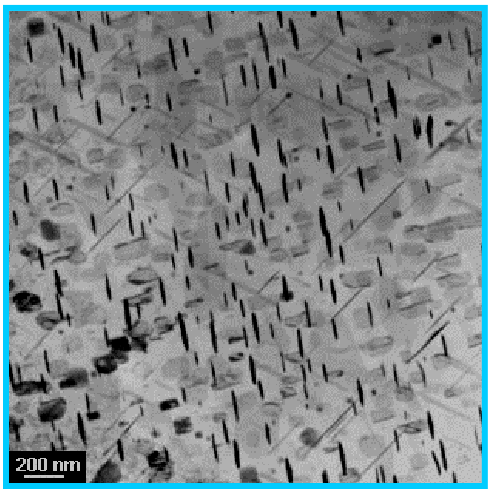


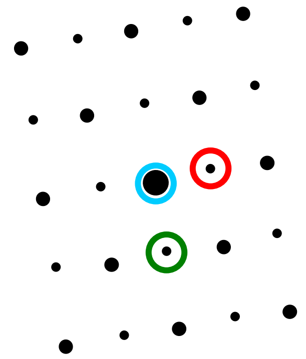
bright field (BF) imaging



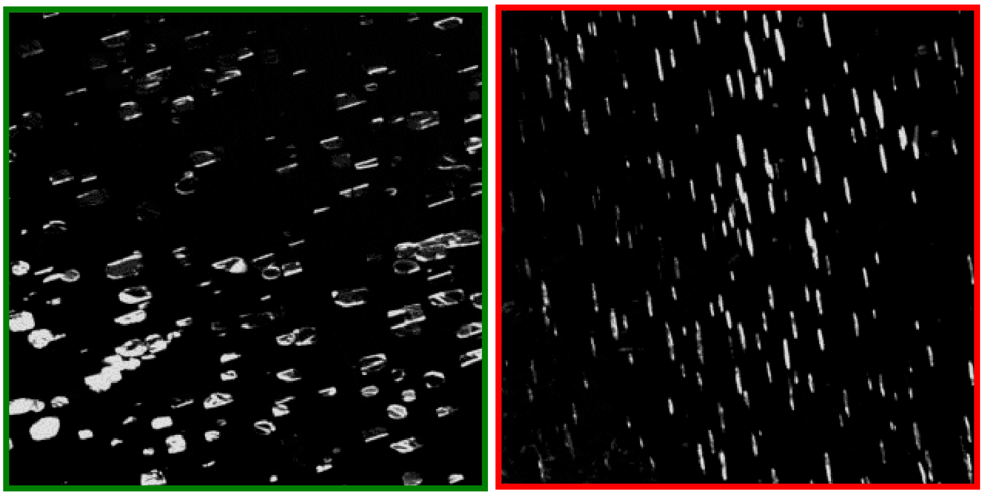
dark field (DF) imaging

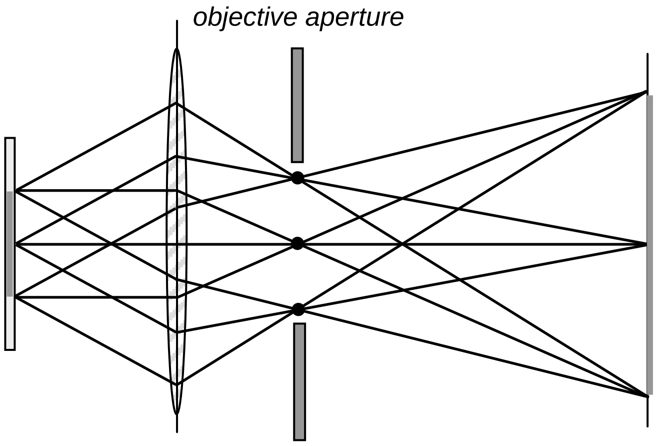
This is illustrated in the example below – taken from an aluminum alloy containing precipitates that give rise to extra weak reflections in the diffraction pattern because the precipitates have a different structure to the aluminium-rich matrix.



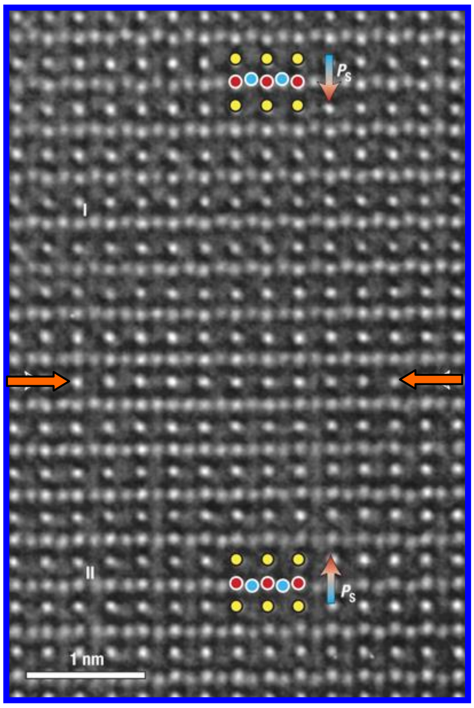


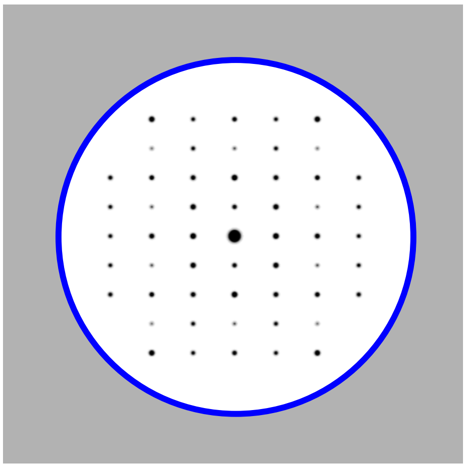
Schematic pattern: weak spots arise only from the precipitates





If the aperture is large and placed around many beams you form a high resolution ‘**lattice image**’.





This shows ferroelectric PZT near a boundary (orange arrows) which separates crystal with polarization pointing down from crystal with polarization pointing up. If you look carefully you’ll see the slight zig-zag in the structure caused by the oxygen displacements change as the boundary is crossed.

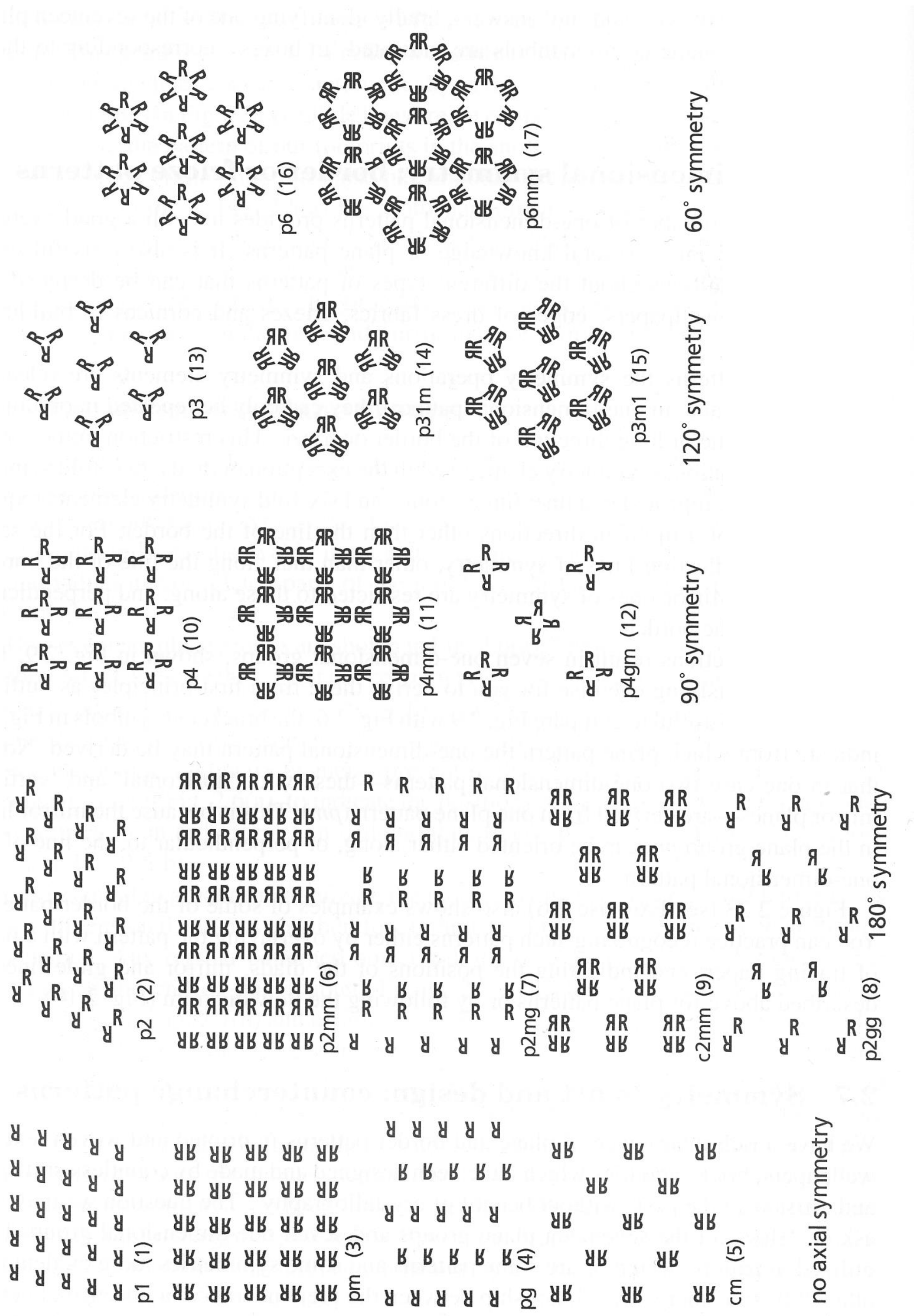
We end with another Feynman quote from the same lecture in 1959:

‘…the electron microscope is one hundred times too poor. I put this out as a challenge: Is there no way to make the electron microscope more powerful?’

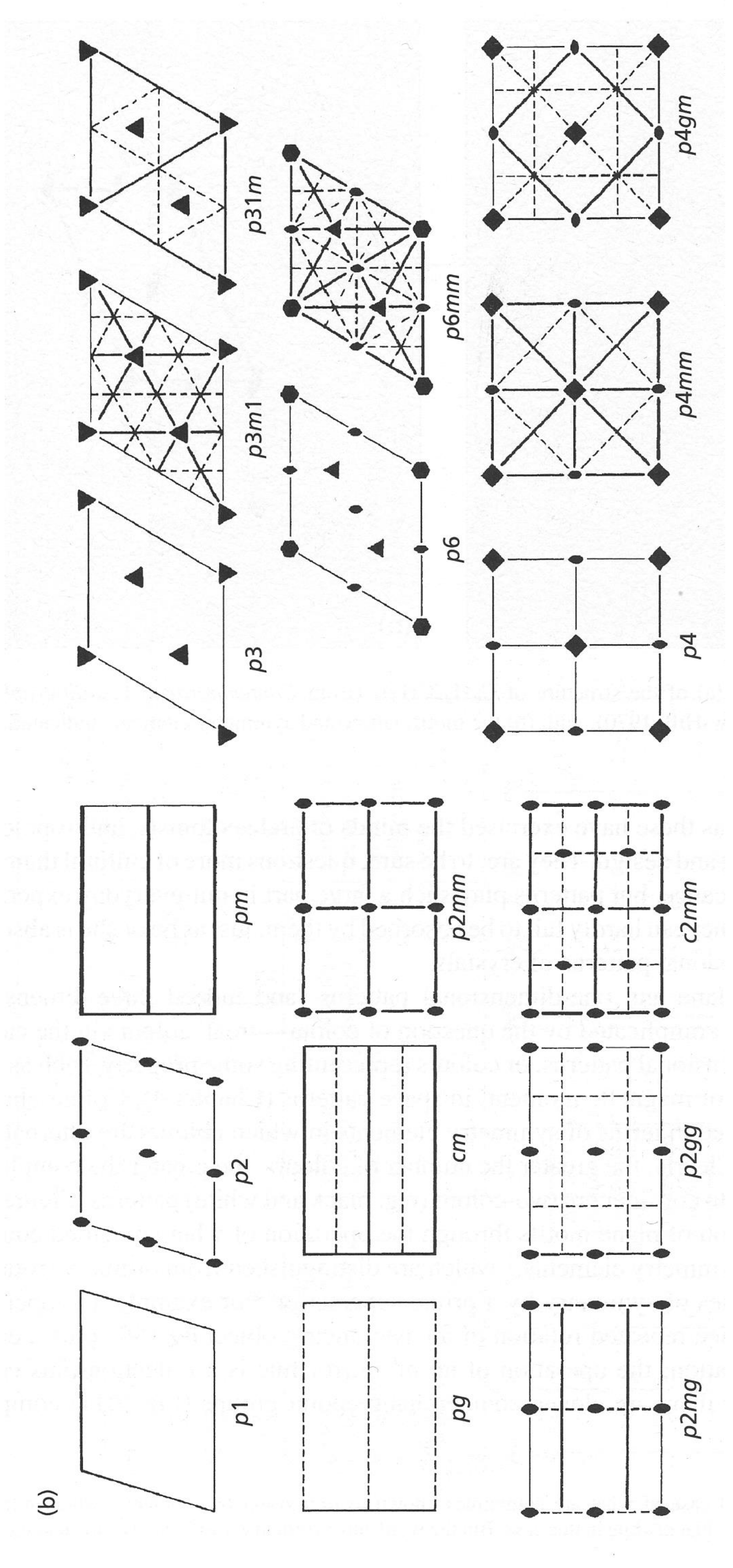
…from the image above, we can say that we are almost there!

Appendix 1. The 2D Plane Groups

17 2D Plane Groups

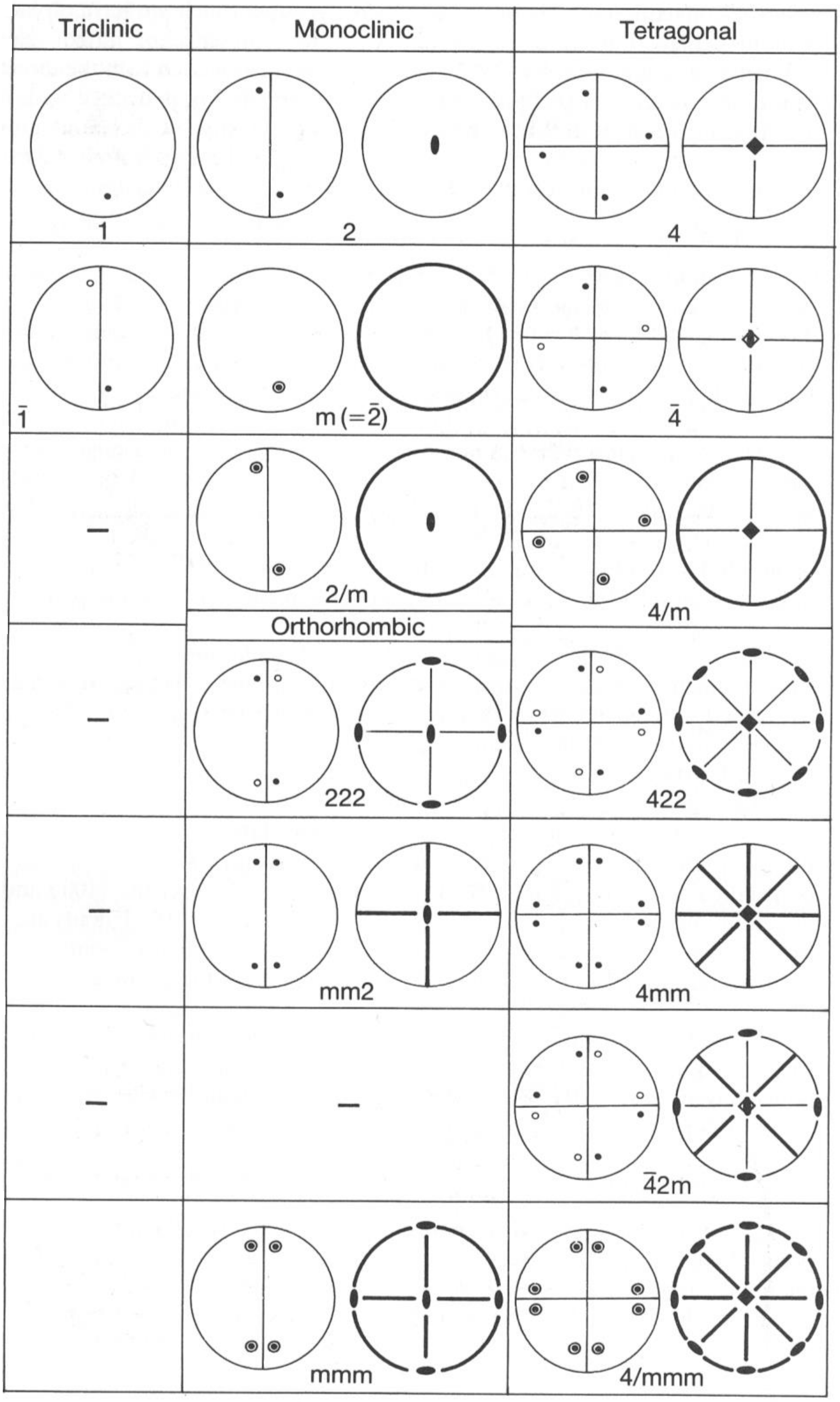


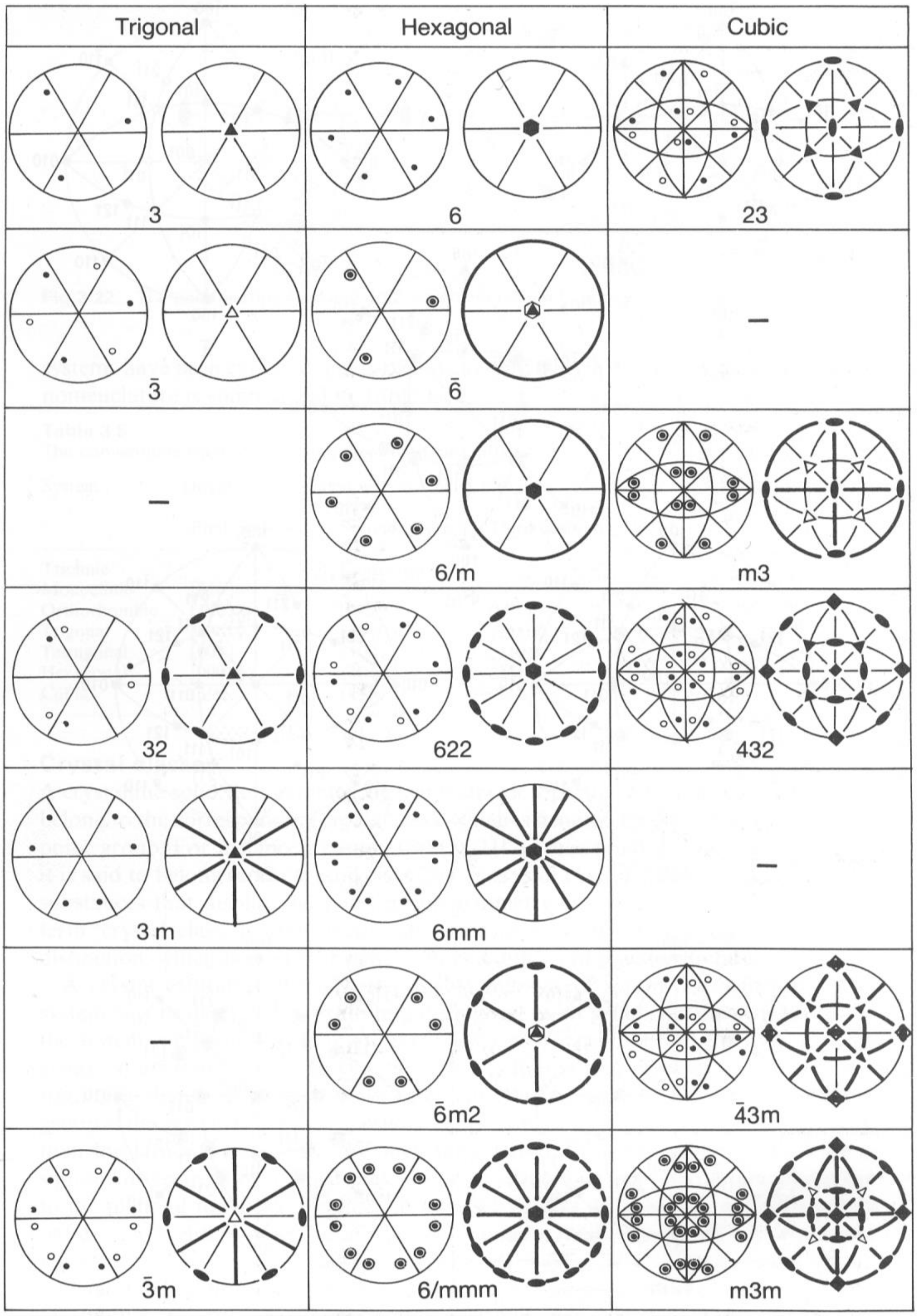
17 2D Plane Groups (showing symmetry elements)



Appendix 2. The 32 Point Groups

(taken from McKie and McKie)




Trigonal
Hexagonal
Cubic
3
6
23
3̄
6̄
—
—
6/m
m3
32
622
432
3m
6mm
—
—
6̄m2
4̄3m
3̄m
6/mmm
m3m

Appendix 3. Complex Numbers

For those not yet familiar with complex numbers, here's a very brief introduction.

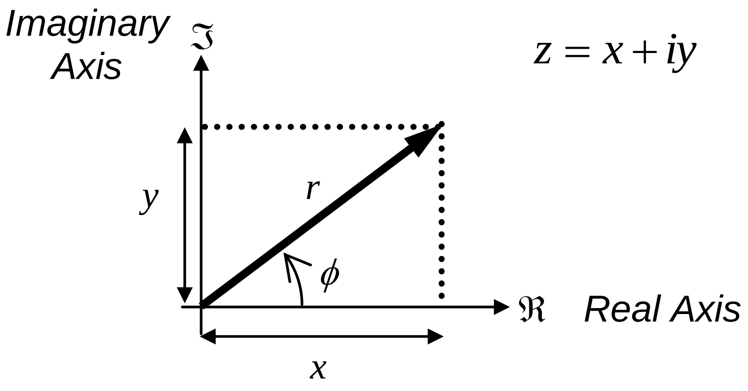
Complex numbers have a **real** and **imaginary** component.

We can write a complex number as $z = x + iy$

where x and y are real numbers and i is $\sqrt{-1}$.

x is known as the real part of the complex number and iy is the imaginary part.

We can represent a complex number on an **Argand diagram** where the real part is plotted on the horizontal axis and the imaginary part on the vertical axis:



The complex number can be considered like a vector and thus the 'length' or **modulus** of the complex number = $r = \sqrt{x^2 + y^2}$

If ϕ is the angle as shown then we can write

$$z = r\cos\phi + ir\sin\phi = r(\cos\phi + i\sin\phi)$$

By using Euler's formula $e^{i\phi} = \cos\phi + i\sin\phi$ we can write:

$$z = re^{i\phi}$$

Adding complex numbers is rather like adding vectors. It is simply a matter of adding the real parts and adding the imaginary parts separately. Thus, for example:

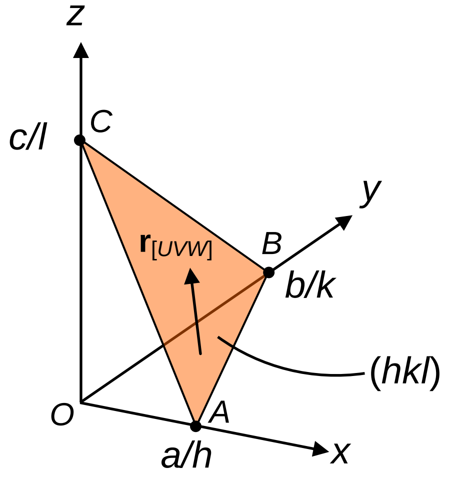
$$(A + iB) + (C + iD) = (A + C) + i(B + D)$$

The **complex conjugate** of a complex number, symbol z^*, is one which has the same modulus but negative angle, ϕ, i.e.

$$z^* = r\cos\phi - ir\sin\phi = r(\cos\phi - i\sin\phi) = re^{-i\phi}$$

Note that $z \cdot z^* = re^{i\phi} \cdot re^{-i\phi} = r^2$

Appendix 4. Proof of Weiss Zone Law



Any lattice vector $\mathbf{r}_{UVW}$ lying in the plane (*hkl*) can be formed as a combination of two vectors ***AB*** and ***AC*****:**

$$\mathbf{r}_{UVW} = U\mathbf{a} + V\mathbf{b} + W\mathbf{c} = \lambda \boldsymbol{AB} + \mu \boldsymbol{AC}$$

We can write the two vectors in the plane (*hkl*) as

$$\boldsymbol{AB} = \frac{1}{k}\mathbf{b} - \frac{1}{h}\mathbf{a} \qquad \text{and} \qquad \boldsymbol{AC} = \frac{1}{l}\mathbf{c} - \frac{1}{h}\mathbf{a}$$

Thus:

$$U\mathbf{a} + V\mathbf{b} + W\mathbf{c} = -\frac{\lambda + \mu}{h}\mathbf{a} + \frac{\lambda}{k}\mathbf{b} + \frac{\mu}{l}\mathbf{c}$$

Comparing left and right hand sides of the equation, it follows that

$$hU = -(\lambda + \mu)$$

$$kV = \lambda$$

$$lW = \mu$$

And therefore $hU + kV + lW = 0$

Glossary of Terms

Alloy: A metallic substance that is composed of two or more elements.

Amorphous: Irregular; having no discernible order or shape. In the context of solids, the molecules are randomly arranged, as in glass, rather than periodically arranged, as in a crystalline material. A non-crystalline structure.

Anisotropic: Having properties that vary according to the direction of measurement.

Atomic form factor: The amplitude of radiation scattered by a single atom. It varies with atomic number and with the angle of scattering**.**

Atomic scattering factor: Same as *atomic form factor*

Birefringence: The difference in refractive index between two permitted vibration directions.

Body-centred unit cell: A non-primitive unit cell that is described with a lattice point at the centre of each unit cell.

Bragg equation: The basic diffraction equation which relates interplanar spacings to the angle through which beams of radiation are diffracted, for a given wavelength of radiation.

Bravais lattice: Classification of lattices based on symmetry, allowing for all possible lattices consistent with a given symmetry. There are 14 Bravais lattices.

Centre of symmetry: A point though which an object can be inverted (i.e. all x, y, z are transformed to $-x$, $-y$, $-z$) to bring the object into coincidence with itself.

Centrosymmetric: Possessing a centre of symmetry.

Ceramic: A compound of metallic and nonmetallic elements, in which the interatomic bonding is predominantly ionic.

Close packed structure: A structure in which the atoms are packed closely together. For structures made of only one atom type, the common close-packed structures are *cubic close-packed* and *hexagonal close-packed*.

Constructive interference: The combination of rays which are in phase and give an intense beam.

Coordination number: The number of atoms forming a polyhedron around a central atom in a structure.

Coordination polyhedron: The polyhedron (commonly a tetrahedron or octahedron) that can be constructed around a cation with the centres of the surrounding anions forming the vertices

Constructive interference: The combination of rays which are in phase and give an intense beam.

Conventional unit cell: A unit cell that is oriented in a specific way with respect to the symmetry elements of the crystal. The conventional cell may or may not be primitive.

Critical radius ratio: The ratio of cation radius to anion radius for the condition where the surrounding anions are touching each other as well as the central cation.

Crossed polars: Two sheets of polaroid (polariser and analyser) oriented at 90° to each other between which a sample is placed for optical examination.

Crystal: A solid form of matter showing translational periodicity in three dimensions in its atomic arrangement.

Crystal structure: The arrangement of atoms in a single crystal.

Crystal system: Classification based on the symmetry of the lattice. There are 7 crystal systems.

d_{hkl}: The spacing between lattice planes (*hkl*)

Destructive interference: The combination of rays which are out of phase, giving zero intensity.

Diffraction pattern: The distribution of intensity of radiation scattered by an object.

Diffractometer: An instrument used for recording intensities of diffracted X-rays as a function of diffraction angle and sample orientation. There are many different types of diffractometers.

Disordered materials: In general this term is used to refer to materials that lack the three-dimensional long-range periodicity of a crystalline substance (e.g. liquids, glasses, polymers, liquid crystals).

Face-centred unit cell: A non-primitive unit cell that is described with a lattice point at the centre of each face of the unit cell.

Ferroelectric material: One that produces domains of spontaneous polarization whose polar axis can be reversed in an electric field directed opposite to the total dipole moment of the lattice.

Fractional coordinates: Set of coordinates x, y , z that define the position of an atom in a unit cell in terms of fractions of the unit cell lengths

Glass: A solid form of matter formed by cooling a liquid sufficiently fast to avoid crystallisation. The arrangement of atoms in a glass does not exhibit periodicity, but on a short length-scale the bonding may resemble that found in a crystal.

Glide Plane: a glide plane is symmetry operation describing how a reflection in a plane, followed by a translation parallel with that plane, may leave the crystal unchanged.

Ionic bond: A primary bond arising from the electrostatic attraction between two oppositely charged ions.

Inversion centre: Same as *centre of symmetry*.

Isotropic: Having properties that are the same regardless of the direction of measurement. In the isotropic state, all directions are indistinguishable from each other. See also anisotropic.

Lattice: An infinite array of points repeated periodically throughout space. The view from each lattice point is the same as from any other.

Lattice parameters: The set of lengths of the edges of the unit cell, a, b and c, and the angles between the unit cell axes, α, β, and γ.

Lattice plane: One of a set of parallel planes containing two non-parallel intersecting lattice vectors, defined by the Miller indices (hkl).

Lattice type: Same as *Bravais lattice*.

Lattice vector: The vector between two lattice points, defined by the symbol [UVW]=U$\boldsymbol{a}$+V$\boldsymbol{b}$+W$\boldsymbol{c}$.

Liquid crystal: A thermodynamic stable phase characterized by anisotropy of properties without the existence of a three-dimensional crystal lattice, generally lying in the temperature range between the solid and isotropic liquid phase, hence the term mesophase.

Long-range order: Order between particles correlated over large distances in a solid.

Miller indices: A set of parallel, equally-spaced lattice planes is specified by the Miller indices (hkl) with reference to the unit cell, where h, k and l are integers. The first plane out from the origin makes intercepts of length a/h, b/k and c/l along the three unit cell axes. If one of the indices is zero, the planes are parallel to the associated axis.

Microstructure The arrangement of *phases* and other structural features that make up a solid material.

Mirror plane: A plane through which reflection of an object brings it back into coincidence with itself.

Motif: The element of a structure associated with any lattice point

Multiplicity: The number of equivalent lattice planes which are related by symmetry; important for understanding the intensities of X-ray powder diffraction patterns.

Non-crystalline: The solid state wherein there is no long-range atomic order. Sometimes the terms amorphous, glassy and vitreous are used synonymously.

Non-primitive unit cell: A unit cell that encompasses more than one lattice point. Lattice points will be found at the corners of the unit cell, and also in positions such as the centre of the unit cell or in the centres of some or all of the faces of the unit cell.

Packing efficiency: The ratio of the volume contained within the atoms in a crystal structure to the volume of the crystal. Put another way, it is the fraction of the volume of the crystal that is contained within the constituent atoms.

Perovskite: Family of ABX_3 compounds which commonly show displacive phase transitions by octahedral tilts or atomic displacements.

Phase: a physically distinct form of a given material, when the material can exist as different phases under different conditions of temperature or pressure. Also used to refer to a homogeneous portion of a system that has uniform physical and chemical characteristics

Phase angle: The phase difference between radiation scattered from an atom at the origin of a unit cell and from an atom at a general position within the unit cell.

Polarisation: The property of electromagnetic waves, such as light, that describes the direction of the transverse electric field.

Polarised light: Light that has passed through a sheet of polaroid and has a transverse electric field that vibrates in one direction only.

Polymorphism: The existence of a single compound as two or more phase with different crystal structures stable under different conditions.

Primitive unit cell: A unit cell that encompasses only one lattice point, i.e. a unit cell where the lattice points are only found at the corners of the unit cell.

Radius ratio: The ratio of the radii of the cations and anions in a simple ionic structure, which is sometimes useful as a measure of the relative stabilities of different structures possible for a given material.

Rotation axis: The axis, of order n, about which rotation by a given fraction $1/n$ of a complete rotation brings an object back into coincidence with itself.

Screw Axis: a screw axis is a symmetry operation describing how a combination of rotation about an axis and a translation parallel to that axis leaves a crystal unchanged.

Structure factor: The amplitude of radiation scattered by all atoms in a unit cell. It depends on (a) the fractional co-ordinates, x, y, z, of atoms in a unit cell and (b) diffraction geometry, as specified by the planes (*hkl*) from which the diffracted beams are said to be reflected

Systematic absences: Diffracted beams from a crystal which have strictly zero intensity, due to repeating units of structure which scatter exactly out of phase with each other. They are most easily summarised in terms of lattice type.

Short-range order: Order which implies strong correlations between the positions of atoms in a glass over distances of a few Å.

Translational order: A condition when molecules have some arrangement in space. Crystals have three degrees of translational order (each molecule is fixed in space with an x, y, and z coordinate) and liquids have no translational order.

Unit cell: Any parallelepiped in a lattice having lattice points at all corners.

Unit cell parameters: see *lattice parameters*

Glossary of symbols

a	A unit cell edge length
$\mathbf{a}$	Vector along the a unit cell edge
b	A unit cell edge length
$\mathbf{b}$	Vector along the b unit cell edge
c	A unit cell edge length
$\mathbf{c}$	Vector along the c unit cell edge
d	Interplanar spacing
f	Atomic scattering factor
F_{hkl}	Structure factor
h	One of the Miller indices
I	Symbol to denote a body-centred unit cell
F	Symbol to denote a face-centred unit cell
I_{hkl}	Intensity of diffracted beam from (hkl) planes
k	One of the Miller indices
ℓ	One of the Miller indices
m	Multiplicity of lattice planes
N	Integer (= $h^2+k^2+l^2$ for cubic system)
P	Symbol to denote a primitive unit cell
U	One of the components of a lattice vector
V	One of the components of a lattice vector
W	One of the components of a lattice vector
α	A unit cell interaxial angle
β	A unit cell interaxial angle
γ	A unit cell interaxial angle
ϕ	Phase angle
λ	Wavelength
θ	Angle (sometimes Bragg Angle)

Question Sheet 1

1. Look at the DOITPOMS *Crystallography* package:

   http://www.doitpoms.ac.uk/tlplib/crystallography3/index.php

   Work through the section on *'Close Packing and Packing Efficiency'* before starting the rest of this question sheet.

2. Determine the packing efficiency of a 2D hexagonal array of solid circles.

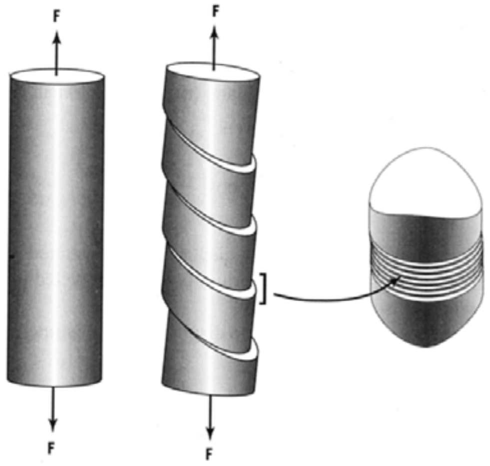
3. Determine the packing efficiency of a b.c.c. structure.

4. Using a hard sphere model, determine the ideal radius ratio for an atom to fit into an octahedral interstice in a c.c.p. structure.

5. Repeat the calculation for question 4 for the octahedral interstice in a b.c.c. crystal. *Hint*: consider carefully which is the nearest atom.

6. For the ideal h.c.p. structure, show that the layer spacing, d, as defined in lectures, is equal to $\sqrt{2/3}a$.

7. In the deformation of c.c.p. and b.c.c. metals, **slip** (planar shearing, see figure below) generally occurs on the close-packed or 'closest-packed' planes and in close-packed directions. Each combination of slip plane and direction is called a **slip system**. How many slip systems are there in these metals?



8. Iron is known to be able to crystallise with three different structures: α-Fe is body centred cubic, γ-Fe is cubic close-packed and ε-Fe is hexagonal close-packed. Lattice parameters quoted in the scientific literature for these three polymorphs of Fe are a = 2.87 Å (bcc), a = 3.67 Å (ccp) and a = 2.50 Å, c = 4.02 Å (hcp).

a) Sketch a plan view of one unit cell of each structure, as viewed down the crystallographic *z*-axis.

b) Calculate the number of Fe atoms in each unit cell and the volume of each unit cell. Hence calculate the density of each polymorph of iron. (Look up values of Avogadro's number and the atomic mass of Fe in the Data Book).

Question Sheet 2

1. Look at the DOITPOMS *Crystallography* package:

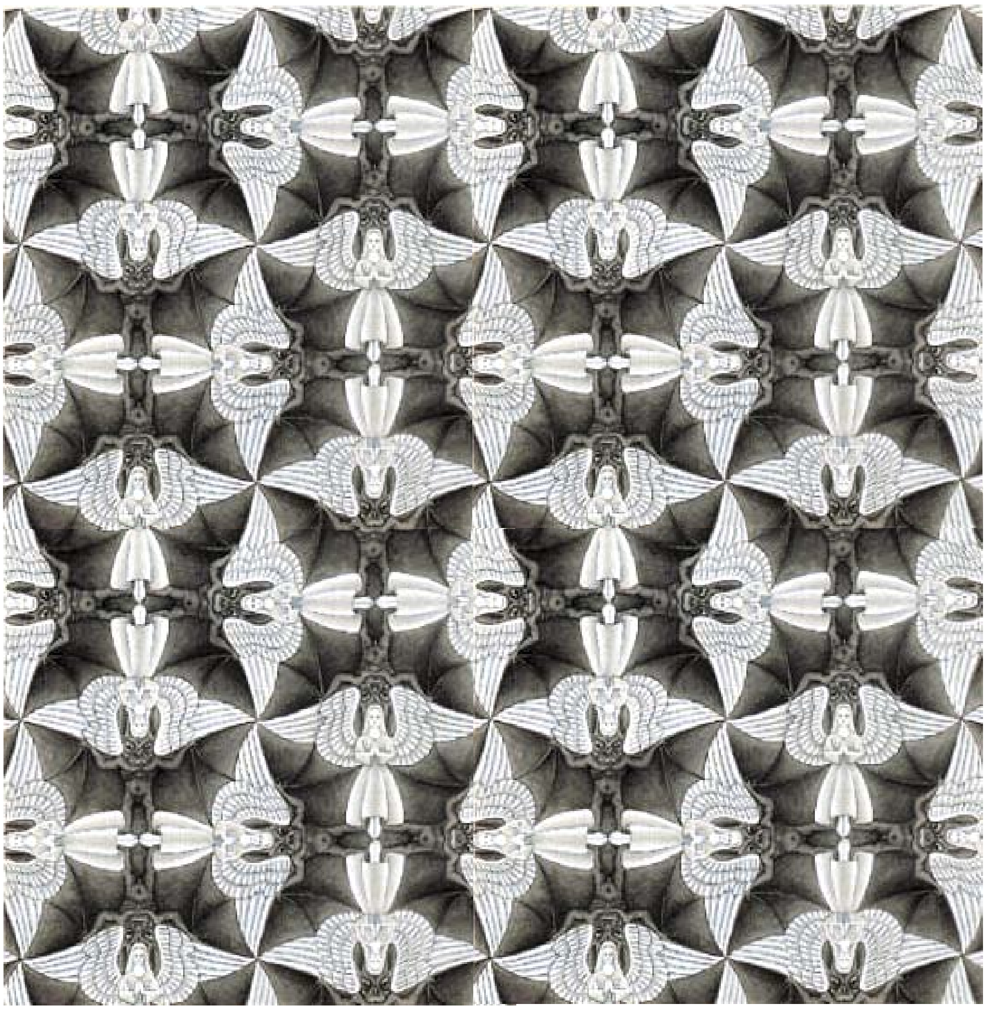
   http://www.doitpoms.ac.uk/tlplib/crystallography3/index.php

   Work through the section on **'***Symmetry'*, '*Lattices'*, '*Unit Cell*' '*Lattice Geometry'*,

   There is also a separate TLP on '*Lattice Planes and Miller Indices*' which should be considered:

   http://www.doitpoms.ac.uk/tlplib/miller_indices/index.php

2. Consider the Escher pattern below known as 'Angels and Devils':



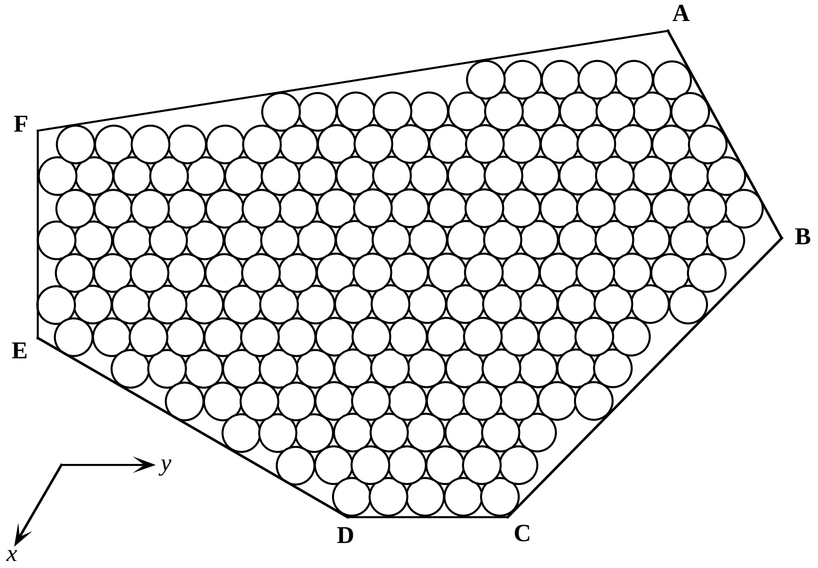
   Look carefully at the pattern. The pattern has a number of symmetry elements, namely 4-fold rotations (tetrads), 2-fold rotations (diads), mirrors and glide lines.

   (a) Indicate the position of the symmetry elements on the 'greyed' version (printed separately at the end of the question sheet) and draw on a possible unit cell.

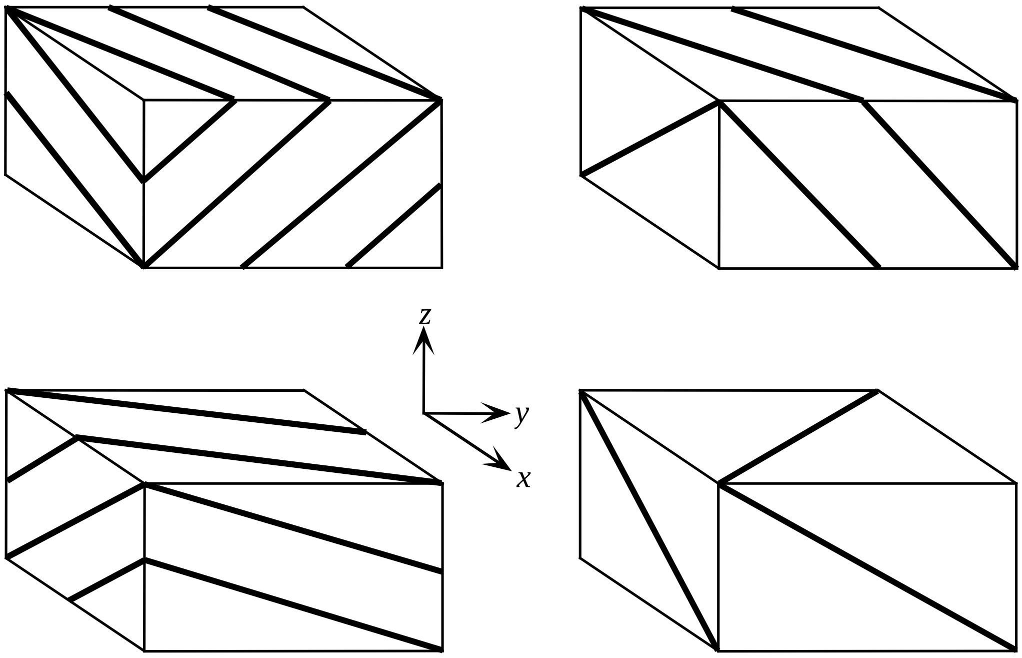
   (b) By comparing the arrangement of symmetry elements on your annotated pattern with the 17 possible plane groups given in your handout, determine to which plane group the Escher pattern belongs.

3. (a) The lines **AB**, **BC**, **CD**, **DE**, **EF** and **FA** bound the fragment of a close-packed plane of spherical atoms shown below. Use the given axes to index the lines as lattice vectors [*UV*0].

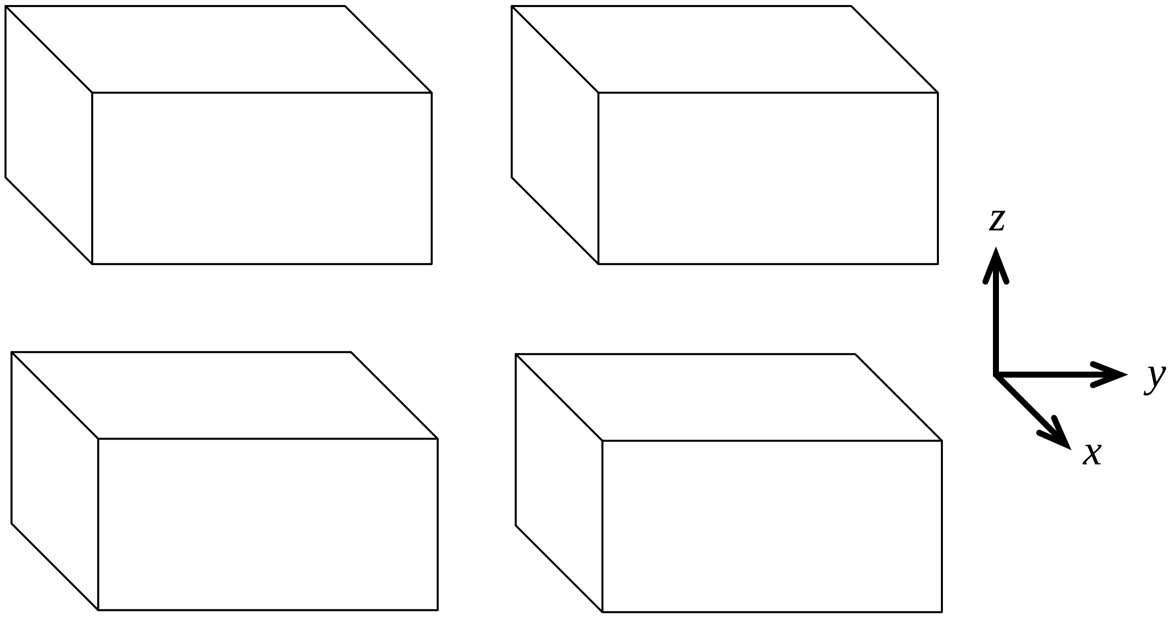
(b) Using the same reference axes, and taking the origin inside the fragment, index the lines as planes (*hk*0) cutting through the plane of the diagram.



4. Index the planes shown intersecting the surfaces of the following unit cells:



5. Sketch, on the surfaces of the following unit cells, the intersections of the lattice planes (213), $(1\bar{2}2)$, $(20\bar{1})$ and (020), respectively.



6. Cementite (Fe_3C) is found in many different steels. It has an orthorhombic structure with lattice parameters a = 4.52 Å, b = 5.08 Å, c = 6.74 Å.

   (a) Determine the interplanar spacing, *d*, for the following planes: (101), (001), (111) and (202).

   (b) Determine the angles α, β, γ between the normal to the (111) plane and the three crystal axes.

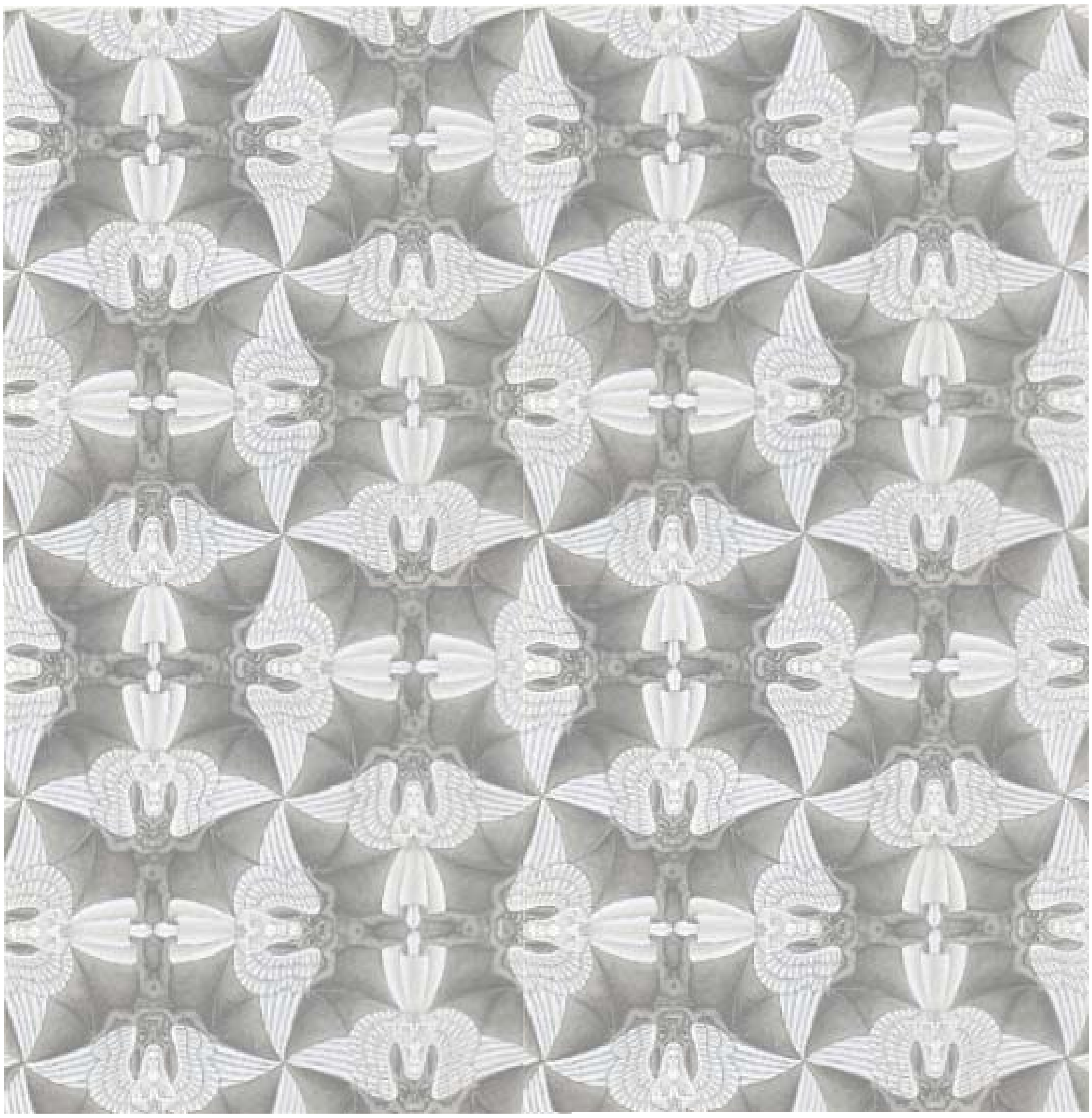
7. (a) Which of the following directions, if any, lie parallel to the plane (115) ?

   [110], [732], $[3\bar{1}0]$, $[23\bar{1}]$.

   (b) Which of the following planes, if any, lie parallel to the direction $[1\bar{1}\bar{1}]$?

   (113), (321), $(14\bar{2})$, $(1\bar{1}1)$.

Hand the annotated version of this pattern to your supervisor with the rest of your answers.



Question Sheet 3

1. Look at the DOITPOMS *Crystallography* package:

   http://www.doitpoms.ac.uk/tlplib/crystallography3/index.php

   Work through the section on *'Crystal Systems'* before starting the rest of this question sheet.

2. Ag_2O is cubic with the following atomic positions in the unit cell:

   Ag: ¼ ¼ ¾ ¾ ¾ ¾ ¾ ¼ ¼ ¼ ¾ ¼
   O: 0 0 0 ½ ½ ½

   (a) Draw a plan of a block of 2 x 2 unit cells viewed parallel to [001] and mark the heights of the atoms on your plan.

   (b) Describe the shape of the co-ordination polyhedra of oxygen around silver and silver around oxygen.

   (c) What is the lattice type?

   (d) How many formula units of Ag_2O are there in the motif?

3. The Bragg angles (θ) corresponding to the (100) and (001) planes from an hexagonal crystal, measured using Cu $K\alpha$ radiation ($\lambda = 1.542$ Å) were found to be 8.68° and 6.82°, respectively. Calculate the lattice parameters.

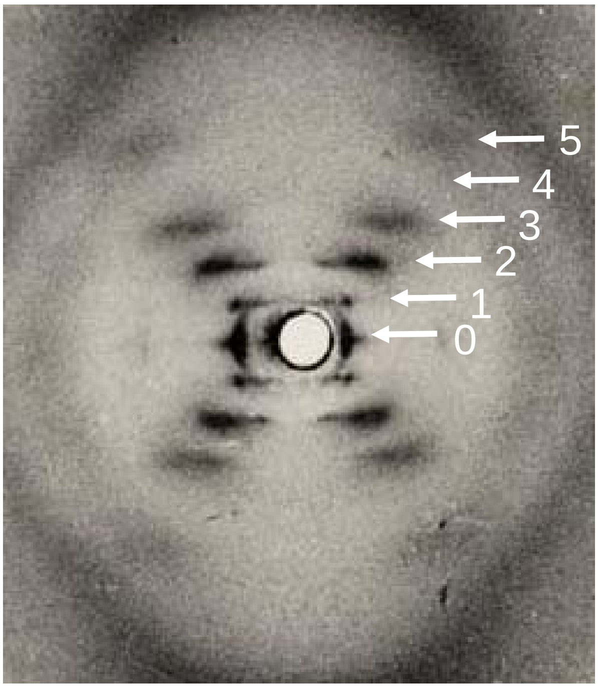
4. X-ray diffraction data were collected from a natural sample of galena, PbS. The material was found to be cubic, with four formula units per unit cell. The first eight lines in an X-ray powder diffraction trace corresponded to the following reflections: 111, 200, 220, 311, 222, 400, 331, 420. The ratio of the intensities for the 420 and 331 reflections, $I_{420} : I_{331}$, was measured as 1.7 : 1.

   Use these observations to determine whether galena has a structure similar to caesium chloride, sodium chloride or zinc sulphide (zinc blende). [Atomic form factors at diffraction angles comparable with those of the 420 and 331 reflections are: $f_{\mathrm{Pb}} = 46.4$, $f_{\mathrm{S}} = 6.8$.]

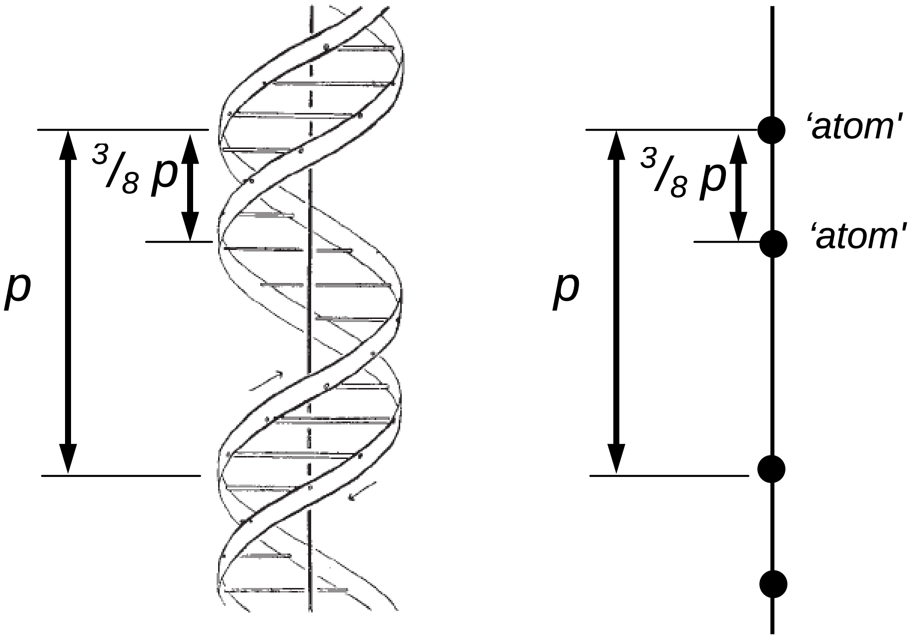
   Hint: Consider possible absent reflections and determine expressions for the structure factors for each of the possible structures using information in the Data Book.

   [*Note*: the zinc blende structure is also known as the *sphalerite* structure.]

5. The figure below is a magnified version of the centre of the famous Photo 51 x-ray micrograph from which Crick and Watson determined the structure of DNA. If you look closely, the x-ray photograph is composed of a 'X' of scattered intensity which is broken up into horizontal layers (arrowed).



Importantly, the 4th 'layer line' is missing, i.e. it has zero intensity and the first 3 lines have the pattern: **weak**, **strong**, **strong**. DNA is composed of two helices running in opposite direction of equal wavelength or pitch, *p*, but with an offset of 3/8 of the pitch (see below left). We can simplify this into a one-dimensional schematic (below right):



Consider DNA as a 1-D crystal with a lattice of length p and a motif of 2 identical 'atoms' (approximating the two DNA strands) with 'atomic' form factor f separated by 3/8 p (as shown on the figure above on the right)

(a) Write down a general expression for the structure factor $\boldsymbol{F}_h$ where h is the order of the layer line, i.e. the reflection, h.

(b) Draw amplitude-phase diagrams showing the individual contributions from the two 'atoms' and the resultant $\boldsymbol{F}_h$ ($h = 1, 2, 3, 4$).

(c) Determine the scattered intensity I_h for $h = 1, 2, 3, 4$ and confirm the pattern: weak, strong, strong, zero.

Question Sheet 4

1. Look at the DOITPOMS *X-ray Diffraction* package:

   http://www.doitpoms.ac.uk/tlplib/xray-diffraction/index.php

   Work through the package before starting the rest of this question sheet.

2. Iron (b.c.c. a = 2.866Å) is irradiated with Cu $K\alpha$ x-rays (λ = 1.542Å). Find the indices {*hkl*}of planes which give rise to x-ray reflections.

3. Barium titanate ($BaTiO_3$) undergoes a phase transition at around 120° C from a cubic phase (above 120° C) to a tetragonal phase (below 120° C). Figure 1 (see end of the question sheet) shows two x-ray diffractometer traces for $BaTiO_3$ at 150° C and at 20° C. The wavelength of the x-rays used is λ = 1.5405Å.

   (a) By considering the indexing of the peaks, determine the lattice types of the two structural states of barium titanate. Why are there more reflections in the low temperature trace?

   (b) What are the multiplicities for planes of the form {220} in the cubic system and {220}, {022} of the tetragonal system? Explain the splitting of the line at close to 66° 2θ in the tetragonal diffraction pattern.

   (c) Use the 2θ values for the lines close to 66° 2θ to calculate the lattice parameters of the cubic and tetragonal forms.

4. Sketch the 2D reciprocal lattice section containing ***a**** and ***b**** for a cubic crystal with (a) a *P* lattice, (b) an *F* lattice, and (c) an *I* lattice.

   At temperatures above 400° C crystals of Cu_3Au have a disordered distribution of Cu and Au atoms on the sites of a c.c.p. array with a statistically cubic *F* lattice. Holding the crystals at 280° C causes ordering of the Cu and Au atoms, and the lattice type changes to *P*. How might you recognise the onset of ordering in a thin specimen of Cu_3Au held in a heating stage of an electron microscope (electron beam parallel to [001]) if the sample temperature was gradually reduced from above 400° C?

5. During an x-ray investigation of indium (tetragonal cell, a = 3.25Å, c = 4.95Å, I lattice), a single crystal was held in a fixed position relative to the x-ray beam or slowly rotated in the beam. Draw to scale the ***a**** - ***c**** section of the reciprocal lattice of indium and use the Ewald sphere construction to predict the indices of reflections of the type $h0l$ which could be recorded in the following experiments:

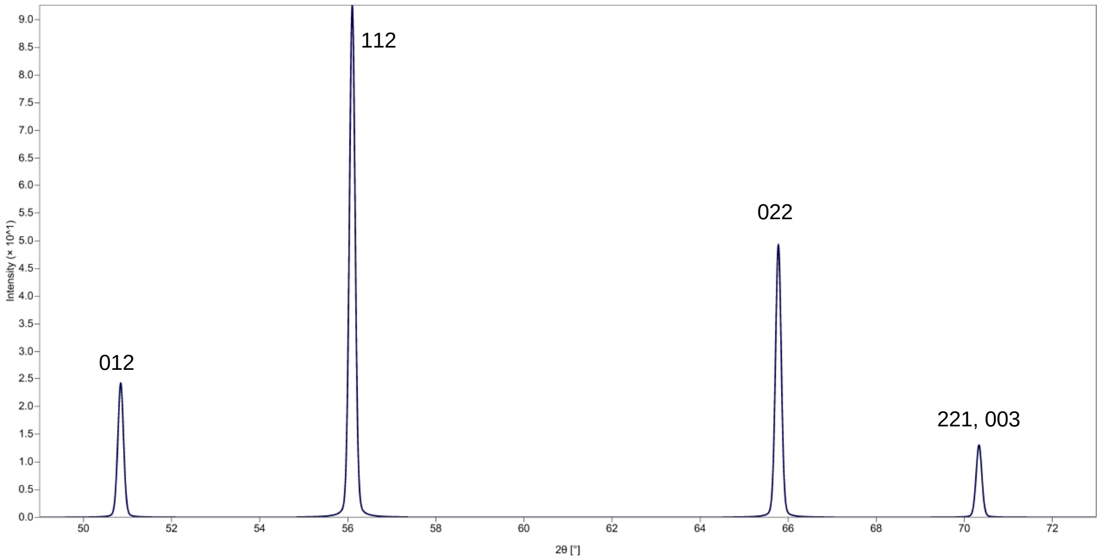
(a) The crystal is held stationary with its $[\bar{1}00]$ direction parallel to an incoming beam (i.e. with the [100] direction pointing towards the x-ray source) of Co Kα x-rays (λ = 1.789Å).

(b) The crystal is then rotated slowly through 25° about its [010] axis, followed by a slow rotation through 50° in the opposite direction (i.e. $[\bar{1}00]$ reaches limits of ±25° from the direction of the x-ray beam).

(c) The crystal is held in its original position, described in (a), but white radiation (wavelength range 1.0 – 2.0 Å) is used instead of Co Kα radiation.

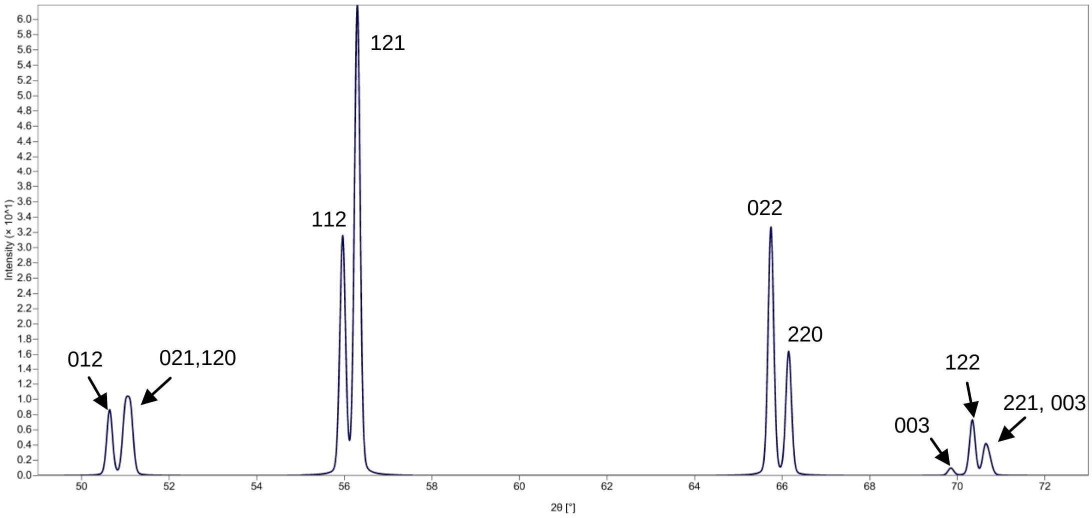
Figure 1. X-ray diffractometer traces for question 3.

(1) $BaTiO_3$ at 150°C



The 022 line is at $2\theta = 65.7789°$

(2) $BaTiO_3$ at 20°C



The 022 line is at $2\theta = 65.7453°$

The 220 line is at $2\theta = 66.1506°$