Crystallography and X-ray Diffraction

Part I: crystallography
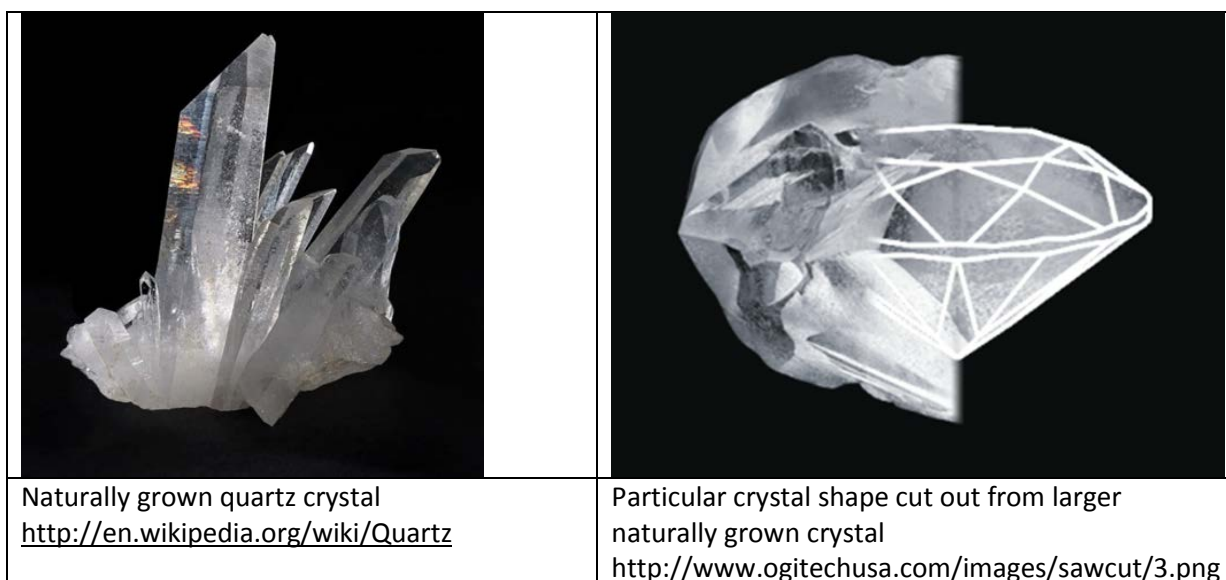
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Materials Science and Engineering
2nd year

H. Van Swygenhoven

(NXMM)

1. What is a crystalline material?

When we talk about crystals, most people will immediately think at minerals. We know them as objects with very nice outer shape. These can be found in nature i.e. they grow naturally without artificial aid as for instance the quartz crystal shown below. Quartz is silicon dioxide SiO_2 i.e one of the possible solid compounds made of silicon and oxygen. Diamond is one of the possible solid compounds made of Carbon atoms. It is also well known that we can shape crystals easily in very nice forms as is the case for diamond.

|	
Naturally grown quartz crystal http://en.wikipedia.org/wiki/Quartz	Particular crystal shape cut out from larger naturally grown crystal http://www.ogitechusa.com/images/sawcut/3.png

The beautiful shape of crystals is related to the nature of the internal order and symmetry in which atoms are arranged. For instance, the quartz crystal has grown in the form of six-sided prisms with a six-sided pyramid at the end.
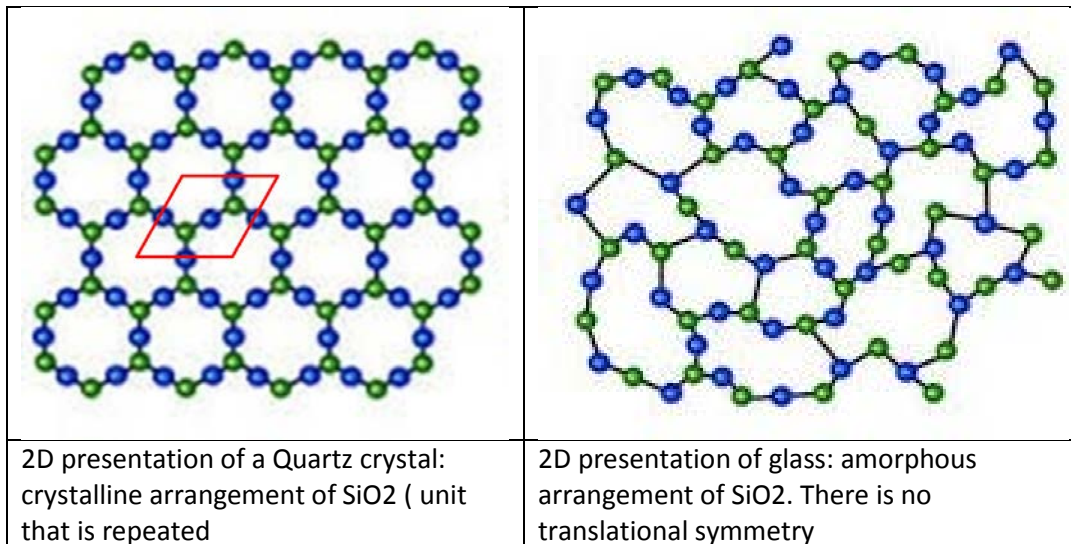
Why is it that these materials can grow (or be cut easily) in these nice shapes? This is because these crystals have translational symmetry. That brings us to the definition of a crystal

> A **crystalline material** is a material characterized by a regular arrangement of atoms or group of atoms over "large" distances, i.e. a crystal displays translational symmetry over a long range.
> In a crystal it is always possible to identify a group of atoms or molecules (can be also one atom) that repeats itself periodically on a grid in space.

In two dimensions it is easy to distinguish what is crystalline and what is not crystalline or amorphous.

Crystalline arrangement of spheres	Amorphous arrangement of spheres
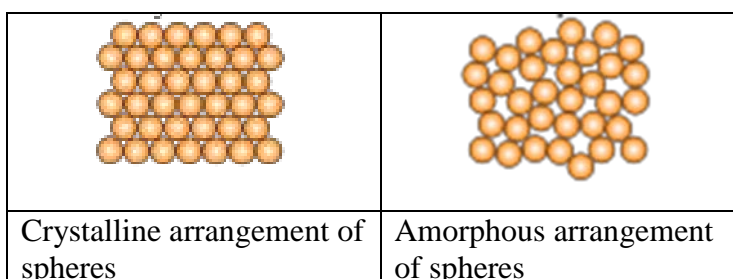
These "spheres" do not have to be atoms, they can be a group of atoms or molecules. Important is that there is translational symmetry. In crystallography the "unit" that is repeated, is called the "motif".

2D presentation of a Quartz crystal: crystalline arrangement of SiO2 (unit that is repeated	2D presentation of glass: amorphous arrangement of SiO2. There is no translational symmetry

How the translations are done together with the character of the motif determines the symmetry present in the crystal. This is easy to see in the images below. On the left, the translation gives a 4-fold rotation axis, on the right, the translation gives a 6-fold rotation axis.

|	
Translation resulting in a 4-fold rotation axis	Translation resulting in a 6-fold rotation axis
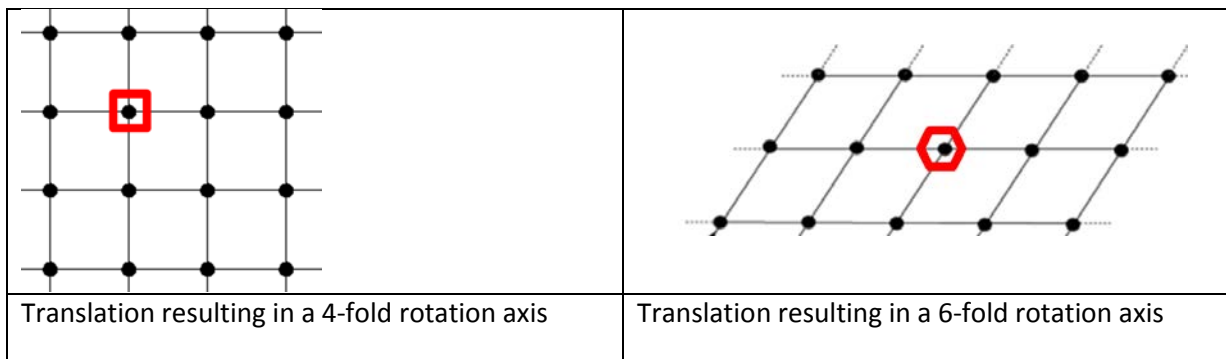
In the above sample the unit that is repeated is spherical, and does not impose particular limits to the symmetry provided by the translation. However if we do the same with a unit that is very asymmetric, the symmetry of the crystal will be different.

4-fold rotation axis is lost	6-fold rotation axis is lost
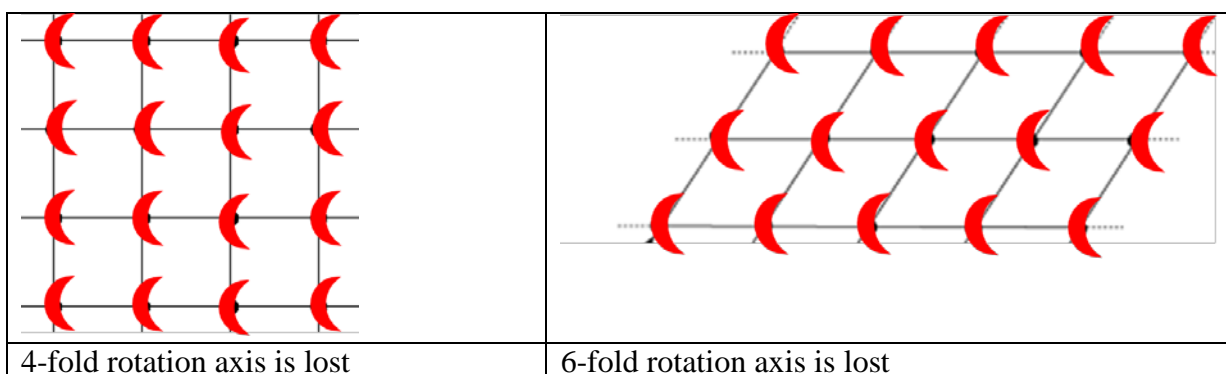
Why is symmetry important?

Symmetry plays an important role in material science. Most material properties are anisotropic which means that their properties depend upon direction or angular orientation of crystals. Examples are chemical resistance, the ability to get charged when stressed (piezoelectricity) or fracture toughness.

Take the example of cleavage. In crystals the breaking of atomic bonds can be easier in some directions than others. For example, in a crystal of sodium chloride (NaCl) cleavage can only be achieved along planes parallel to cube faces.
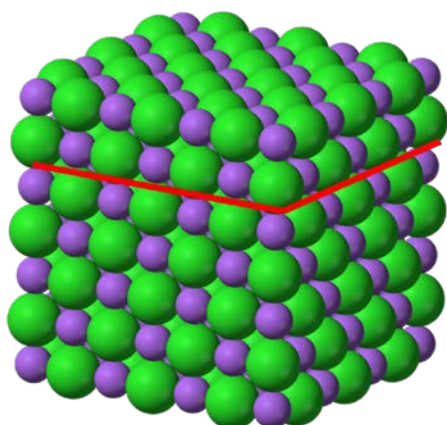

This is also the case for elastic properties. Most metals have a Young's modulus that depends on the direction of loading: the crystal is soft in some directions but hard in others. Below a picture of the surface of the modulus of elasticity reconstructed using the single crystal elastic constants of Cementite (Fe3C crystal).

Weisser et al Acta Materialia 59 (2011) 4448–
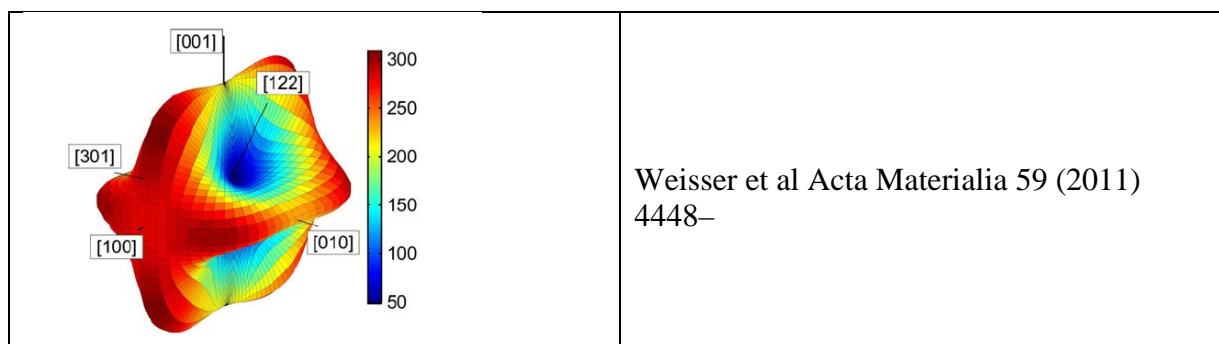
Another example of the importance of symmetry is diamond and graphite. Both materials are made of pure carbon, yet the translational symmetry is different.
Diamond is the hardest known natural mineral. It can be used as an abrasive, meanwhile the diamond self is kept polished and lustered extremely well. No known naturally occurring substance can cut or scratch a diamond, except another diamond. In diamond, a unit of four covalently bonded C atoms is repeated translationally within a cubic lattice.

In graphite the C atoms are in-plane ordered by translation with a hexagonal symmetry. These layers are stacked and the bonding between the layers is weak.
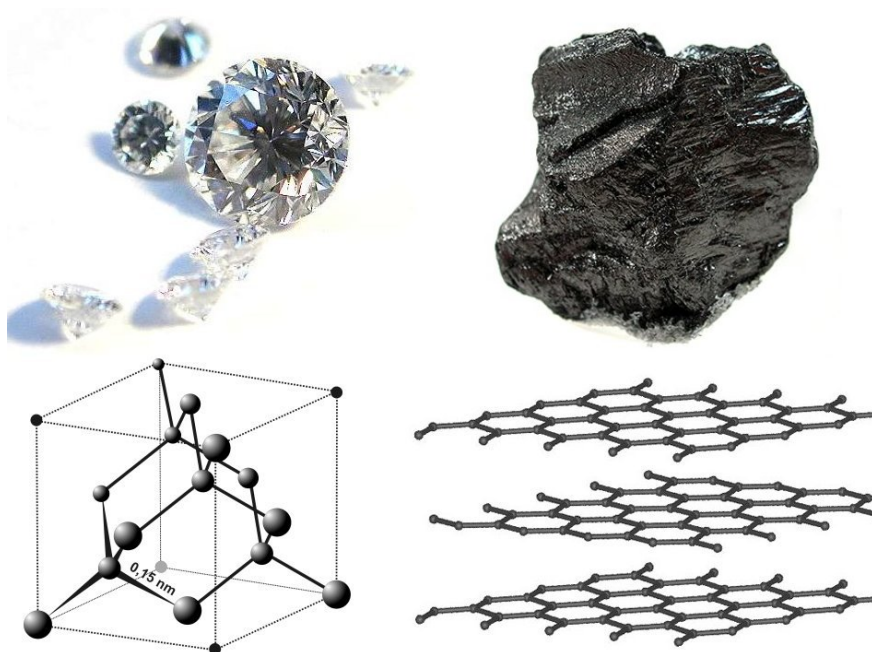
Is the outer shape unique?

With our advances observation techniques, it has been possible to show that the shape of a crystal can be already present at much smaller length scales then those of minerals as mentioned earlier. Below is a scanning electron microscopy image of GaAs wires with hexagonal shape and a length of the order of 300nm. In the same table you will find electron transmission images of MgO cubic shaped crystals supporting Au clusters.


SEM image of GaAs nanostructure revealing 6-fold symmetry Mohan et al, Nanotechnology 23 (2012) 025601	TEM image of MgO crystals supporting Ag clusters and TEM image of a Ag cluster Stancic et al, Nanoscale, 2013, 5, 2448

One can however not always rely on the outer shape of the crystal to derive symmetry. The morphology of a crystal strongly depends on how and how many building blocks are put together, as illustrated schematically below in an image taken from Hammond (fig.4.1).


Similar as the example of the sugar cubes, it is possible to make very tiny crystals with different regular shapes.
For example, Palladium is a crystalline material that can be 3-dimensional represented by the repetition of a cube. The figure below shows the yellow cube that can be repeated in 3 dimensions, a sphere represents here a Palladium atom. After stacking of the cubes, one can cut the sample along particular faces and make a shape that is not anymore a cube.
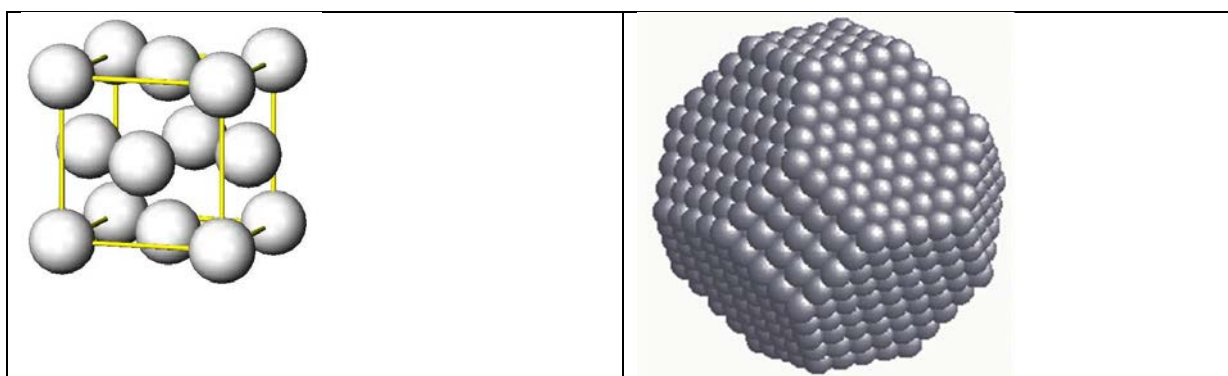

Scientist have shown that one can grow such tiny clusters directly in different shapes, as suggested below in the schematics and the transmission electron microcopy images of Pt clusters with different shapes. Which outer shape is reached in nanoclusters, depends for instance on the environment in which the clusters are grown and on the incorporated impurities. Controlling the morphology and the three-dimensional arrangement of atoms in crystalline nanoparticles is important for applications: for instance the morphology influences the catalytic properties of the cluster.

Pt nanocrystals with different shapes
Tao et al (review paper), Small 2008, 4, No. 3, 310 – 325
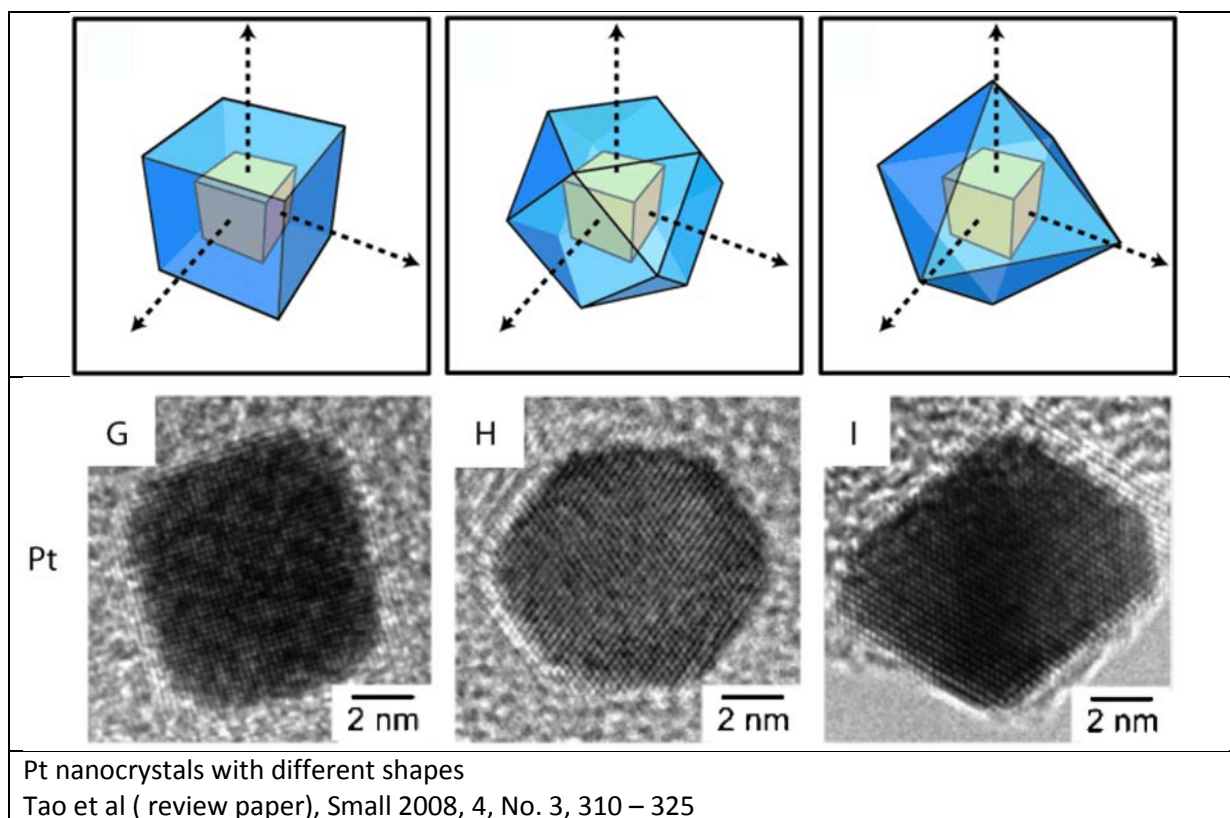
In summary, the outer shape of the crystal can be misleading for determining the symmetry of the crystal. To obtain the symmetry of a crystal one needs better characterization methods such as those based on diffraction (xray, neutron, electron..). The principles of these will be also given in this course.

*Molecular crystals and Proteins*

In early crystallography, one was always dealing with minerals, metals, pure elements in solid state etc. But as mentioned earlier, the unit that is repeated can also be a molecule. Molecules are made up of atoms linked together. However, the links between the molecules within the crystal are much weaker. Nevertheless, they can be stacked regularly as shown below for the molecular crystal cinnamide
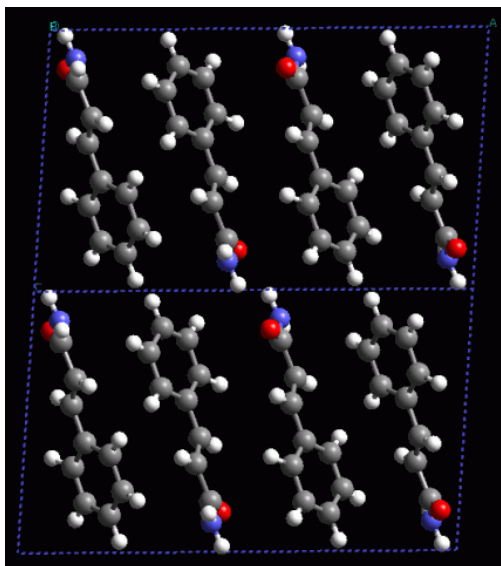
http://www.xtal.iqfr.csic.es/Cristalografia/parte_01-en.html

Crystallographers discovered that they could study biological materials, such as proteins or DNA, by making crystals of them. This extended the scope of crystallography to biology and medicine. Protein crystals are also a stacking of molecular units. In these packings there are usually many holes that are filled with water molecules (not necessarily ordered).
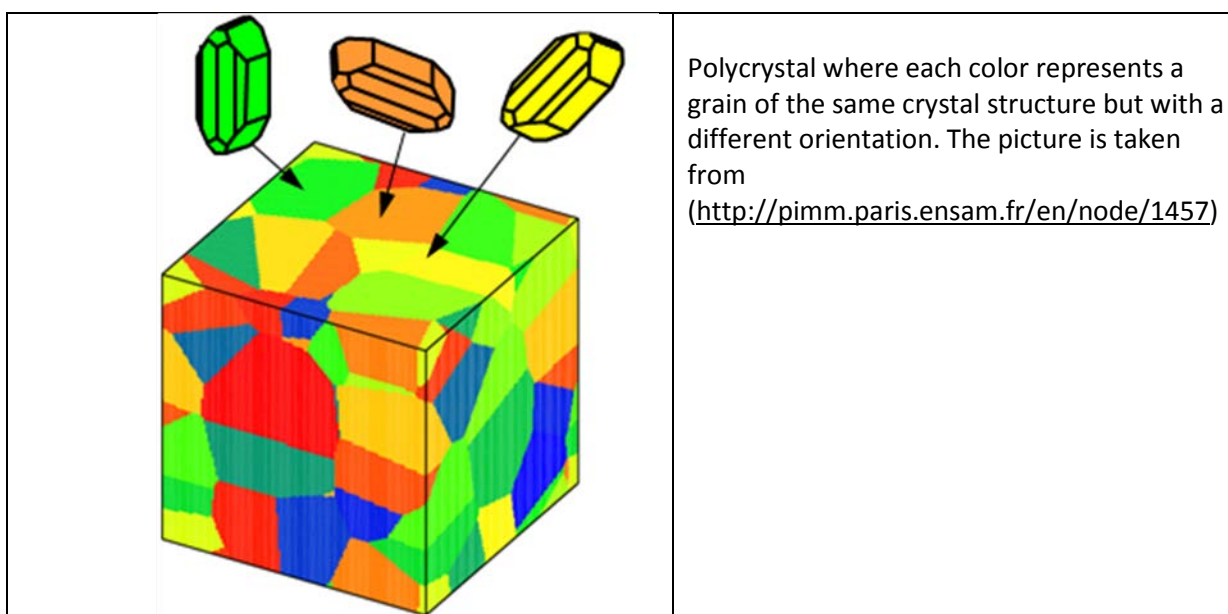
Examples are

| Crystal structure of a protein: AtHal3. | h41pkve6: crystal forming protein |
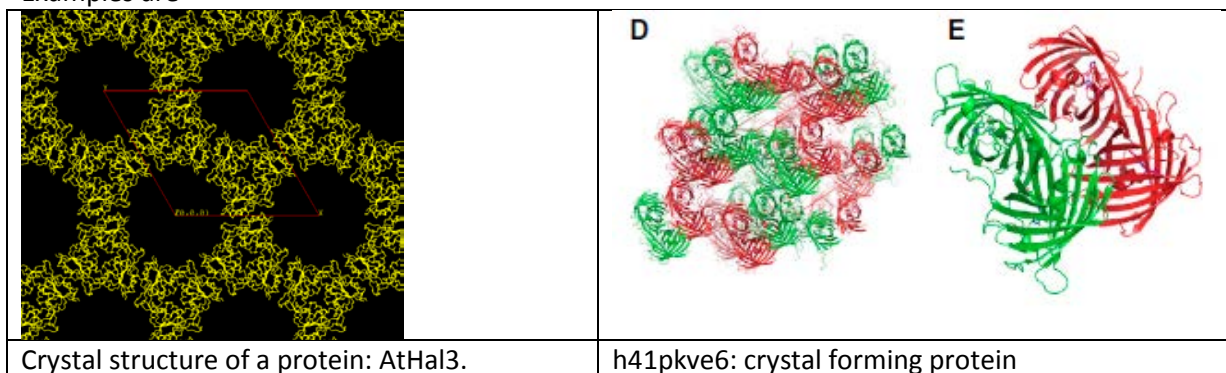
Why would you crystallize a protein? As you will see in the course, diffraction is an excellent tool to learn more about the structure and symmetries of the "repeated unit".

Polycrystalline material

Single crystals form only under special conditions and it is not so easy to grow them artificially. Most engineering materials are not single crystals, but polycrystals. As the name suggests, a polycrystalline material is an ensemble of many crystals. The individual crystallites are often referred to as grains and the junctions between these grains are called grain boundaries. This is schematically presented below. Parameters such as the size distribution of the grains, the morphology of the grains, the orientation relationships between the individual crystals are very important parameters determining the overall properties of the polycrystalline material. There are distinct diffraction methods that are designed to look at a single crystal and others to study polycrystals. Both will be discussed in this course.

Polycrystal where each color represents a grain of the same crystal structure but with a different orientation. The picture is taken from (http://pimm.paris.ensam.fr/en/node/1457)

How can we "see" the symmetry of a crystal ?

In 1895, X-rays were discovered by William Conrad Röntgen, who was awarded the first Nobel Prize in Physics in 1901. It was Max von Laue and his co-workers, however, who would discover that X-rays travelling through a crystal interacted with it and, as a result, were diffracted in particular directions, depending on the nature of the crystal. This discovery earned von Laue the Nobel Prize in Physics in 1914.
Equally important was the discovery by father and son William Henry Bragg and William Lawrence Bragg in 1913 that X-rays could be used to determine the positions of atoms within a crystal accurately and unravel its three-dimensional structure. Known as Bragg's Law, this discovery has largely contributed to the modern development of all the natural sciences because the atomic structure governs the chemical and biological properties of matter and the crystal structure most physical properties of matter. The Bragg duo was awarded the Nobel Prize in Physics in 1915.

Diffraction (and more general the interaction) of Xrays, neutrons and electrons has become the major tool to analyze the composition, structure and symmetries of crystals.

Why do we need "Crystallography"?

- The way translation is performed on a "motif" i.e. a unit made out of atoms or molecules, the crystal will have a different symmetry
- The symmetry of the crystal is not only determined by the translation induced symmetry, but also by the symmetry of the motif itself
- Symmetry plays a key role many material properties

Since there are so many ways to arrange atoms/molecules, crystallographers have developed a rigorous description of crystals and classified them according to their symmetry. To describe the crystal mathematically, crystallographers have defined the concept of a lattice. The **lattice is** an ensemble of mathematical points at specific coordinates in space constructed as such that the view from each lattice point is the same as from any other. These points are not necessary atoms, but to these points atoms or group of atoms/molecules are assigned. The lattice together with the symmetry of the crystal (which depends not only on the lattice but also on the position of the atoms) allows categorizing crystals in space groups.

If you want to read more about the history and importance of crystallography, you can read the document "Crystallography matters: international year of crystallography 2014

http://www.iycr2014.org/__data/assets/pdf_file/0010/78544/220914E.pdf

Organization of the course crystallography, part I (H. Van Swygenhoven)

First we will adopt a simpler "material science" approach before we will go to this rigorous description of crystals. We look into the different ways one can pack atoms while keeping translational symmetry in three dimensions. First we do this for stacking of atoms of the same chemical species, later we will look at other well-known crystal structures that stand as model for many other materials with more than one chemical specie.

Chapter 2: Packing of spheres (atoms)

Chapter 3: Constructing crystal structures from packing hard spheres: stacking sequences, packing densities, interstitial sites

The above chapters will help you convincing that a more rigorous approach is needed in crystallography. The coming chapters will be devoted to the mathematical description

Chapter 4: Crystal lattice and symmetry operations

Starting with the definition of the lattice, we will study the possible symmetry operations: first in 2D then in 3D. This will allows us defining 5 2-dimensional lattices. For the 3-dimensional crystals we need 7 crystal systems and 14 Bravais lattices. In this chapter we will also investigate all possible symmetries that can be combined in one point: in 2D there are 10 point symmetries, in 3D there are 32 point symmetry groups. Combining the point symmetries with the translational symmetry imposed by a lattice, allows classifying 2D objects into 17 plane groups and 3D crystals into 230 space groups.

Chapter 5: The mathematical description of the lattice

In this chapter we will describe the lattice mathematically and introduce the concept of Miller indices, used in Xray diffraction.

Chapter 6: Diffraction and interference from crystals

Now that we know how to classify crystals according to their symmetry, we will here explain the basics of Xray diffraction, used experimentally to determine the symmetries of a crystal.

Important note: **exercises will be done during the lecture. Exercises are marked in the text in grey boxes. At the end of each lecture, the answers will be provided.**

References:

Besides some web references given in the text, good reference books are
Christopher Hammond, The Basics of Crystallography and Diffraction: Third Edition
Neil W. Ashcroft, N. David Mermin, Solid State Physics

2. Packing of spheres (atoms)

Consider atoms as spheres. The densest packing of atoms in a plane has a six-fold symmetry. Around the orange atom one can stack 6 other atoms of the same size
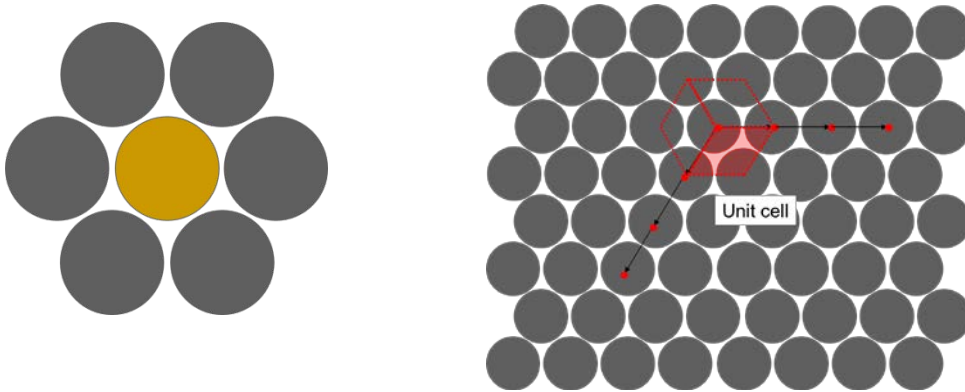

The 2D building block that when repeated in a plane reproduces the hexagonal packing has a unit cell as shown above. We call this layer A. As can be seen in the figure below, there are two types of open places which we call "interstitial" sites, the red which we call B and the blue which we call C
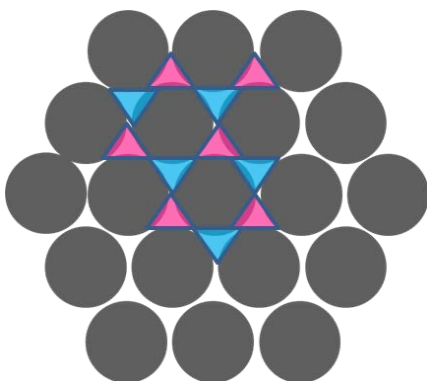
When stacking a second layer, the atoms could in principle sit on top of an atom of layer A, but this is not the most stable position or, in energy terms, this is not a lower energy configuration. Imagine we represent the atoms by points, such a A-A stacking would then correspond with a 3D unit block as shown below (left hand side). Later we will see that this is called a primitive hexagonal lattice. There are no elements in the table of Mendeleev that have this crystal structure when in mono-elemental form i.e. without the addition of other elements. This does not mean that the primitive hexagonal lattice does not exist. For instance WC (Tungsten Carbide) can occur in this form: it has then all W atoms (red) on primitive hexagonal lattice points and C atoms (grey) in interstitial positions as shown on the right hand side of the picture below
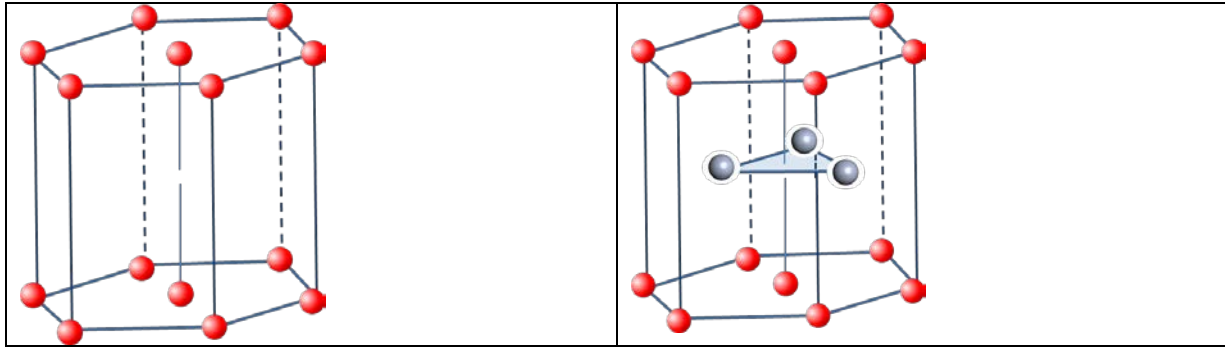
In pure mono-elemental crystals, the atoms of the second layer will always slip into one of the interstitial type sides of the A layer. Assumes the second layer covers the "B" sites
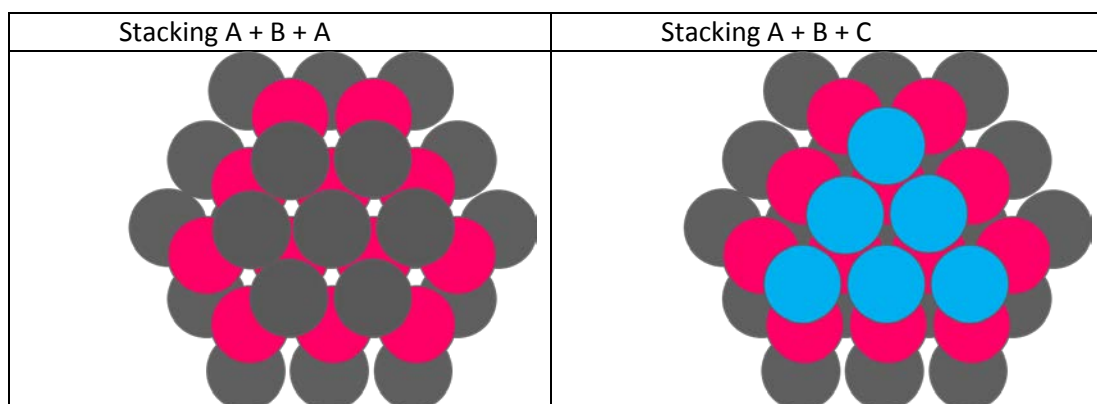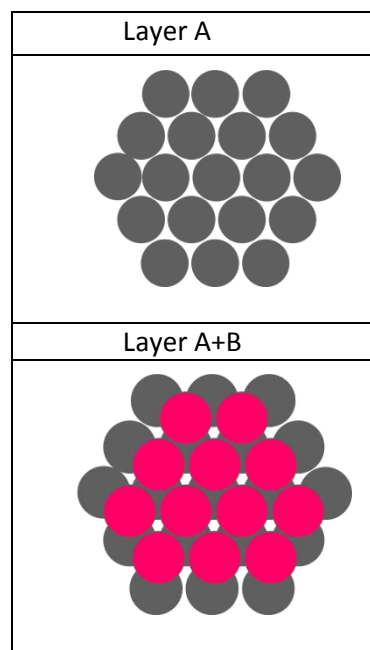
When a third layer is added, there are two possibilities: the third layer slips into the same type of interstitial sites (B) of the first layer. This is an ABAB packing. The third layer can also slip into the other type of interstitial sites i.e. "C". This is the ABCABC packing.

Lower packing factors are obtained when one does not start from a 2D hexagon but from the lower 2D square packing. Similar as in the hexagonal packing, no low energy configuration is obtained when packing two squares on top of each other. The unit block corresponding with this stacking is a primitive cubic. It is a very uncommon structure for mono-elemental crystals, nevertheless it exists: α -Polonium.

More frequently observed is when the square lattices are stacked such that alternating layers lie in the interstitial valley (shown below). This unit cell corresponds with a body-centered cube.
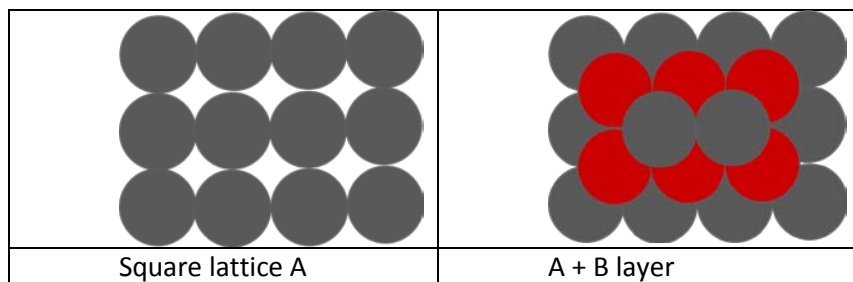
| Square lattice A | A + B layer |

3. Constructing crystal structures from packing hard spheres: stacking sequences, packing densities, interstitial sites

When one stacks atoms as previously shown, one can define a unit block and calculate for the obtained structure the packing fraction, the coordination number (number of nearest neighbors), number of atoms in a unit block and define open space i.e interstitial sites . These are important parameters that characterize the periodic structure. Open space is for instance important for alloying and impurities. Below a few examples of how the unit blocks can be determined

3.1 Crystal structure of mono-atomic crystals

Face Centered Closed packed structure: FCC (ABCABC)

The unit block for an ABC stacking corresponds to a cube with diagonal perpendicular to the triangular stacked A, B and C planes. Imagine we represent the atoms by points, as shown in the figures below. We obtain then a cube with additional points in the center of each face. Later we will see that this unit corresponds to the face centered cubic lattice.
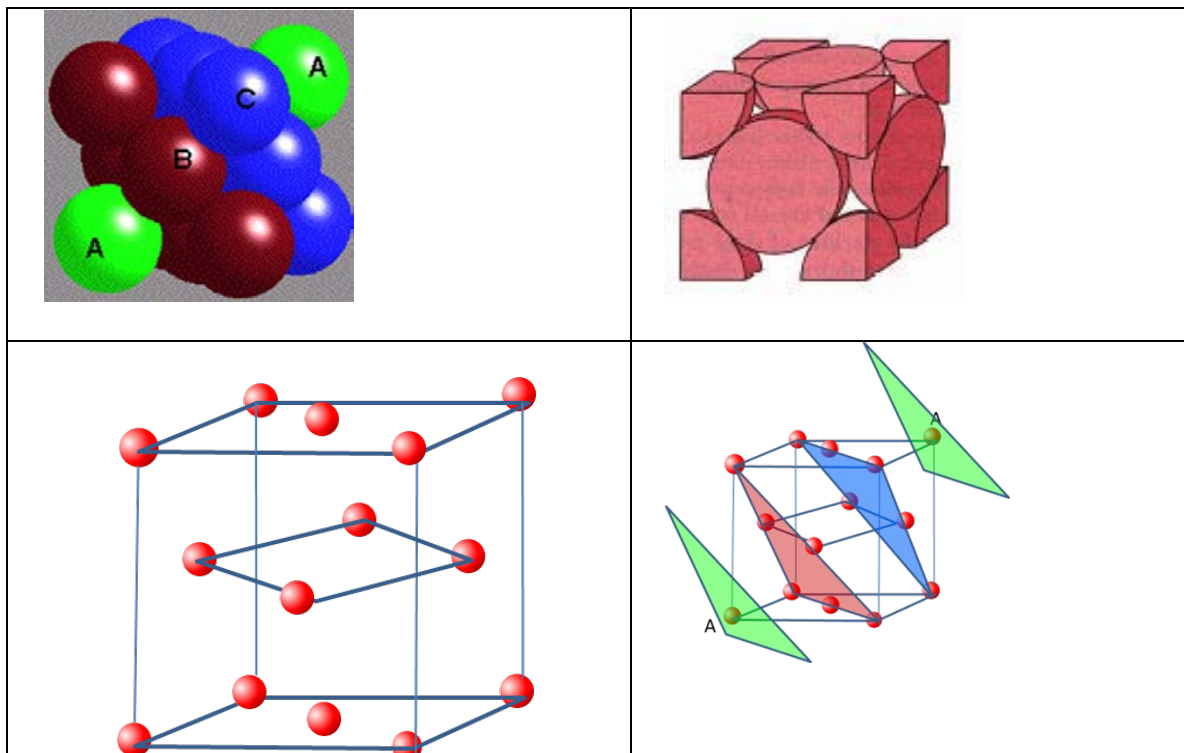
Coordination number
The coordination number = 12. Check this!

Number of atoms per unit cell

In FCC unit cell we have:
 6 face atoms shared by two cells: 6×1/2 = 3
8 corner atoms shared by eight cells: 8×1/8 =1
so the number of atoms per unit cell is 4

Packing fraction

Atomic packing factor,   APF   = fraction of volume occupied by hard spheres

$$= \text{(Sum of atomic volumes)/(Volume of cell)}.$$

To do this, we again assume the atoms as hard spheres with a radius R. At the faces of the cube, the two corner atoms and the atom in the center of the face touch each other. Hence the length of the face diagonal D = R + 2R + R = 4R.

Since $D^2 = a^2 + a^2$
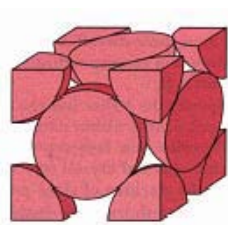
$a = 2R \sqrt{2}$

Volume of 4 hard spheres in the unit cell: $4 \times 4 \pi R^3/3$ when R is the radius of the atom. The volume of the unit cell: $a^3 = 16 R^3 \sqrt{2}$

$$APF = \frac{16}{3} \pi R^3 \Big/ 16 R^3 \sqrt{2} = \pi \Big/ 3\sqrt{2} = 0.74$$

This is the maximum possible packing factor of spheres in 3D

Interstitial sites

There are two types of interstitial open volumes in the FCC lattice: the octahedral and the tetrahedral shaped volumes. Interstitial sites are important since they are often filled up by impurities. Note that the octahedral and tetrahedral have different coordination. If another atom would sit in a tetrahedral site, the coordination would be 4, in an octahedral site it would be 6.

There are eight tetrahedral sites in the FCC unit cell (blue). They all have a corner lattice point at the top. The center of the site is of type (¼,¼,¼).

Octahedral (red): is the volume shaped by all atoms (or lattice points) in the centers of the faces of the cube. The position of the octahedral interstitial site is (½, ½, ½).
http://en.wikipedia.org/wiki/Interstitial_defect
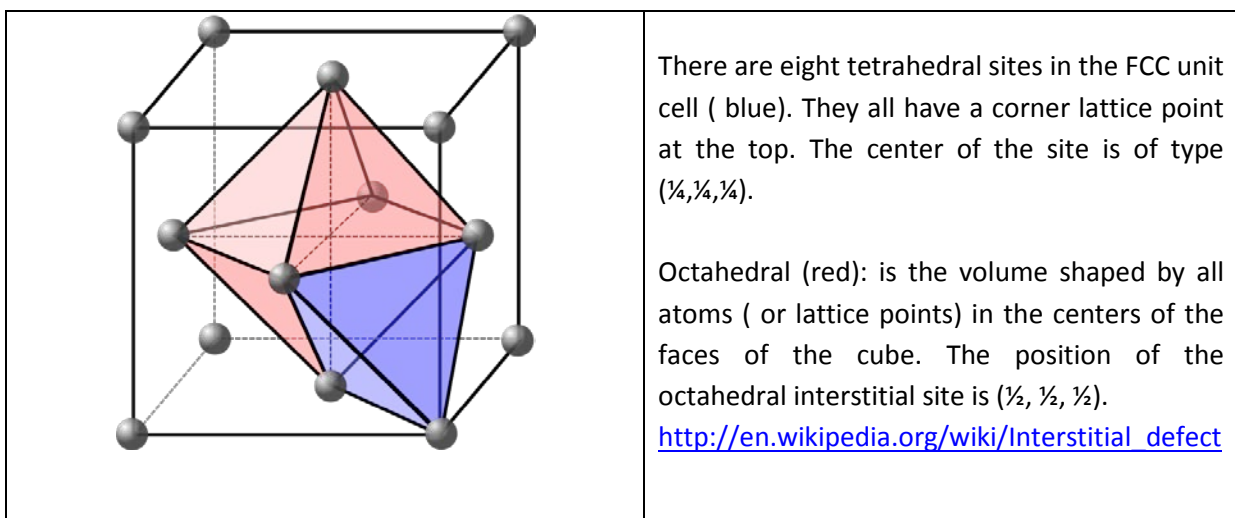
Elements with the mono-atomic FCC structure (Ashcroft-Mermin)

ELEMENT	a (Å)	ELEMENT	a (Å)	ELEMENT	a (Å)
Ar	5.26 (4.2 K)	Ir	3.84	Pt	3.92
Ag	4.09	Kr	5.72 (58 K)	δ-Pu	4.64
Al	4.05	La	5.30	Rh	3.80
Au	4.08	Ne	4.43 (4.2 K)	Sc	4.54
Ca	5.58	Ni	3.52	Sr	6.08
Ce	5.16	Pb	4.95	Th	5.08
β-Co	3.55	Pd	3.89	Xe (58 K)	6.20
Cu	3.61	Pr	5.16	Yb	5.49

Hexagonal Closed Packed structure: HCP (ABAB)

The hexagonal closed packed structure can be seen as two interpenetrating hexagonal unit blocks where one is displaced vertically by a distance ½ of their common c axis, and horizontally so that the points of one lies directly above the centers of the triangles formed by the points of the other

There is more than one way to define a unit block for this structure

- Hexagonal unit block with axis a,b,c (a=b) and 2-atoms assigned to each of the corners of the unit block: coordinates (0,0,0) and (2a/3 , a/3, c/2)
- Primitive unit cell a,b,c'
- Hexagon with three atoms in the center.

Note that this is valid for all crystal structure, i.e. there are many ways to define a unit block. That is why crystallographers have defined particular lattice types: i.e. the Bravais lattice , as we will see later.

HCP structure represented by the (green) unit block lattice with axes a,b=a,c with an extra atom inside. The structure can also be presented by the unit block a,b,c' for which a 2D projection is also shown.
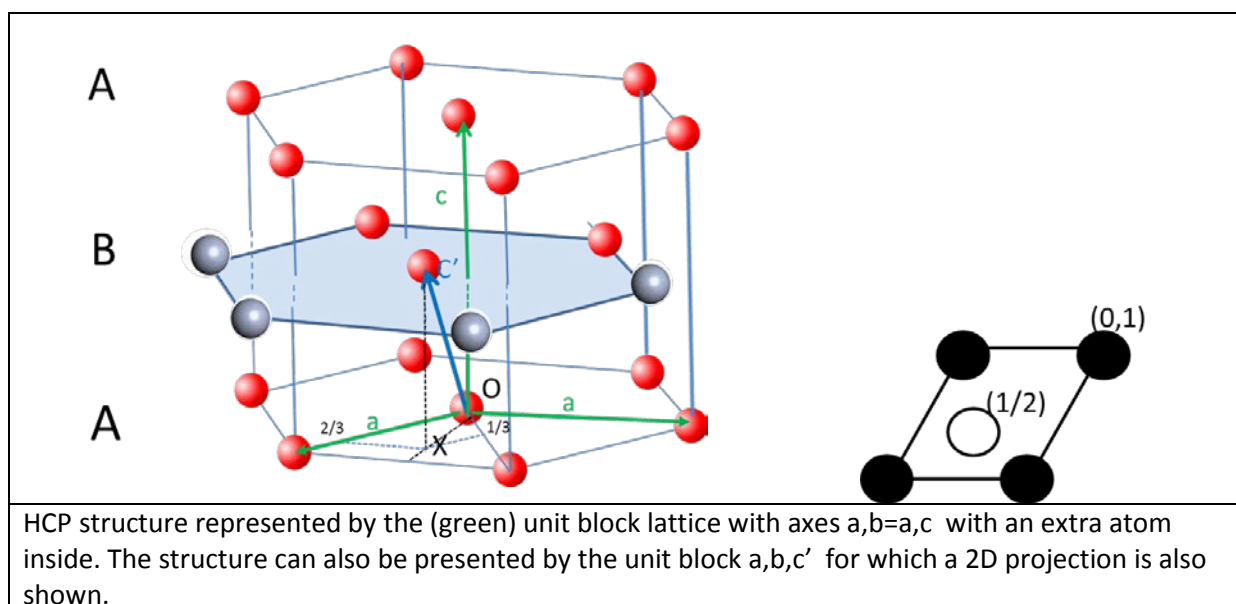
The symmetry of the closed packed lattice is independent of the c/a ratio, the packing however depends on c. The structure with the highest packing, often called the truly hexagonal closed packed structure has a ratio

$$c= \sqrt{8/3}a = 1.633a$$

Exercise 3.1
demonstrate that the highest packing is obtained for c/a = 1.63.
Hint: consider that the densest structure will be when the distance between all atoms in the primitive cell is equal i.e. c' = a=b

Not all materials that crystallize in an HCP structure have this ideal value as can be seen from the table below (Elements with a mono-atomic HCP structure).

Magnesium is nearest to the perfect ratio with 1.62 .

ELEMENT	a (Å)	c	c/a	ELEMENT	a (Å)	c	c/a
Be	2.29	3.58	1.56	Os	2.74	4.32	1.58
Cd	2.98	5.62	1.89	Pr	3.67	5.92	1.61
Ce	3.65	5.96	1.63	Re	2.76	4.46	1.62
α-Co	2.51	4.07	1.62	Ru	2.70	4.28	1.59
Dy	3.59	5.65	1.57	Sc	3.31	5.27	1.59
Er	3.56	5.59	1.57	Tb	3.60	5.69	1.58
Gd	3.64	5.78	1.59	Ti	2.95	4.69	1.59
He (2 K)	3.57	5.83	1.63	Tl	3.46	5.53	1.60
Hf	3.20	5.06	1.58	Tm	3.54	5.55	1.57
Ho	3.58	5.62	1.57	Y	3.65	5.73	1.57
La	3.75	6.07	1.62	Zn	2.66	4.95	1.86
Lu	3.50	5.55	1.59	Zr	3.23	5.15	1.59
Mg	3.21	5.21	1.62	—	—	—	
Nd	3.66	5.90	1.61	"Ideal"			1.63

Coordination number

Exercise 3.2
determine the coordination number for the truly HCP structure (c/a = 1.6233)

Number of atoms per unit cell

Exercise 3.3
determine the number of atoms in the three unit cells defined above for HCP

Packing factor:

Exercise 3.4
determine the packing factor for the truly HCP structure. Hint: take as unit cell the hexagon (the volume of a hexagon: $V = \frac{3\sqrt{3}}{2} a^2 c$)

Interstitial sides

There are six octahedral sites in a HCP cell.(green)

There are eight tetrahedral sites in the HCP unit cell.(cyan)
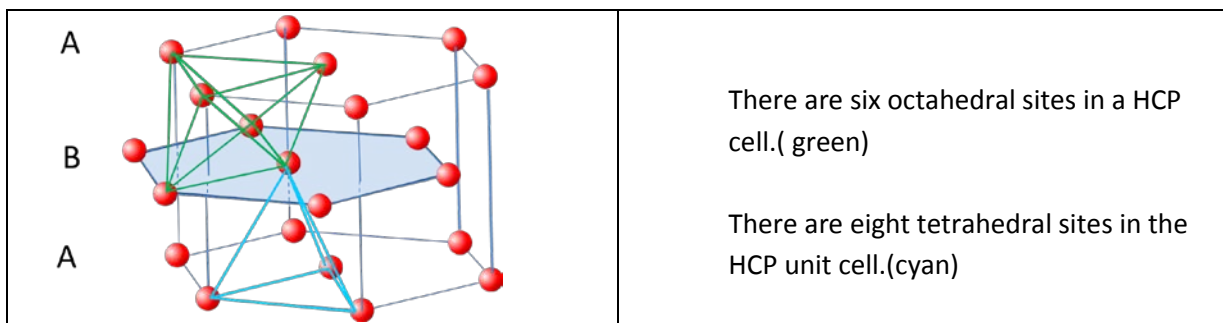
The body centered structure: BCC lattice

When packing 2D squares (lower packing factor in 2D) in three dimensional periodic structures one can of course obtain a simple cube as building block (stacking AA) but that does in mono-elemental crystals not occur. By stacking AB one obtains as building block a cube with an atom in the center. From there the name body centered structure. This structure is of course less dense packed then the FCC structure. It is a frequent occurring structure for mono-elemental crystals. The central atom has the same environment as the corner atoms since it is simply deduced from a shift of a corner point over ½ (a +b+c) as shown in the picture below. The right-hand side of the picture below shows that one can also define a different building block (green axis), which is smaller and has no extra atom inside

| Two interpenetrating cubic cells | The body centered unit cell (blue lines) and primitive cell (green) of a BCC lattice |
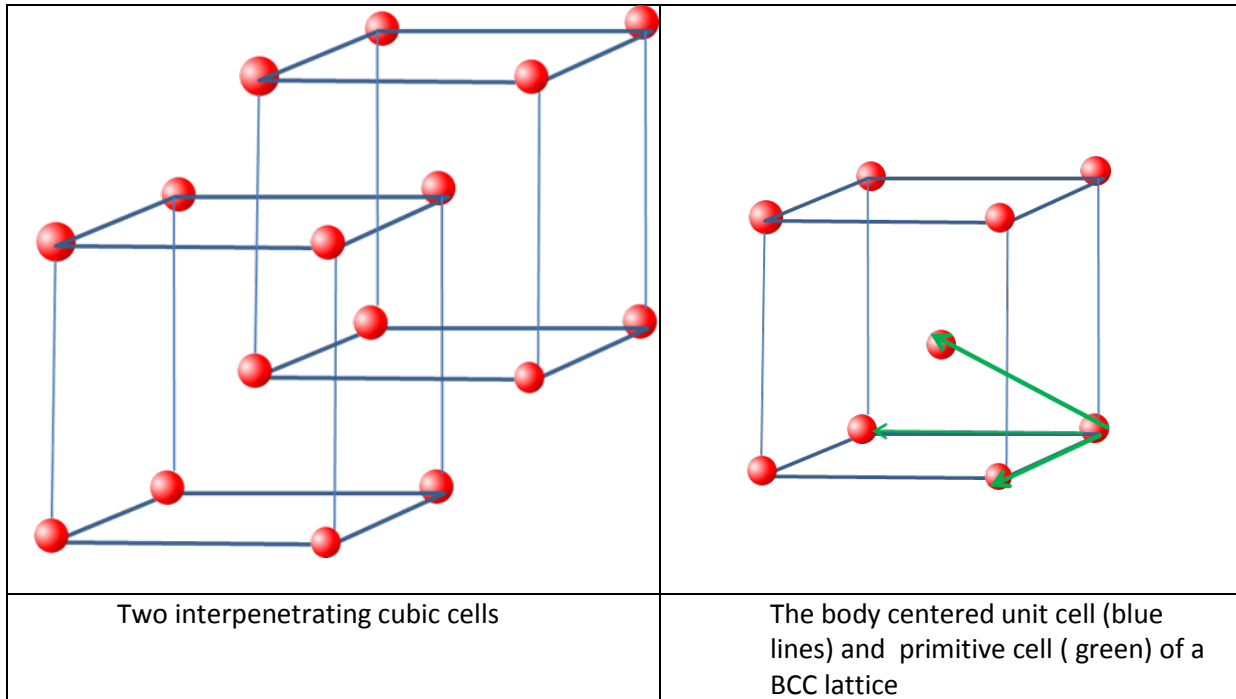
Coordination number

Exercise 3.5
determine the coordination number of the BCC structure

Number of atoms per unit cell

Exercise 3.6
determine the number of atoms for the two unit cells shown above
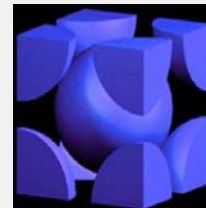
Packing fraction

Exercise 3.7
show that the packing fraction of the BCC structure APF= 0.68
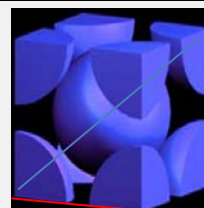
The interstitial sides of the BCC lattice

The BCC lattice has octahedral and tetrahedral interstitial free volumes.

| | | 6 octahedral sites (green)
They are centered around each of the six BCC cell faces
(e.g. coordination of the center (½,½,0))

12 tetrahedral sites (cyan)
(6x4)/2 (image middle column)
(e.g. coordination of the center (½,¼,0). |
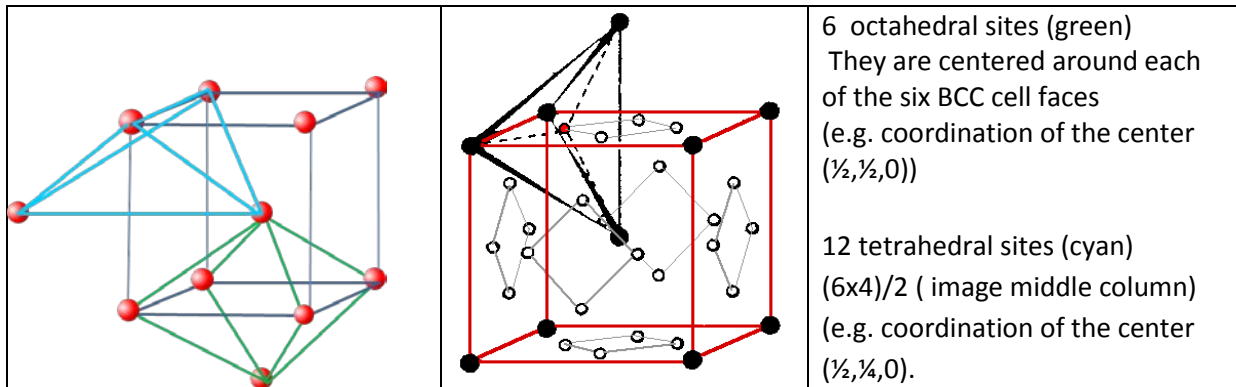
Elements with mono-atomic BCC structure

ELEMENT	a (Å)	ELEMENT	a (Å)	ELEMENT	a (Å)
Ba	5.02	Li	3.49 (78 K)	Ta	3.31
Cr	2.88	Mo	3.15	Tl	3.88
Cs	6.05 (78 K)	Na	4.23 (5 K)	V	3.02
Fe	2.87	Nb	3.30	W	3.16
K	5.23 (5 K)	Rb	5.59 (5 K)		

The diamond structure

As already mentioned, the crystal structure taken is also influenced by the atomic bonding. In the above examples we considered the atoms as being all hard spheres with the same diameter with an interaction that is isotropic or mostly isotropic.

The diamond structure is another way to pack atoms of the same species. It occurs for instance when the atom-atom bonding is a very directional covalent sp3 bond (i.e. a chemical bond that involves the sharing of electron pairs between atoms) which has a tetrahedral symmetry as shown below (www.grandinetti.org).
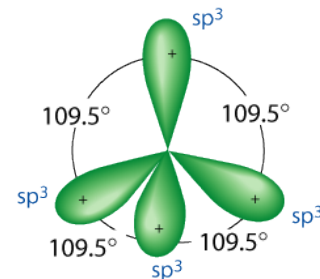
The resulting "diamond crystal structure" can be seen as an fcc-type lattice (made of Carbon atoms) but instead of only C atoms in the FCC positions, some of the tetrahedral interstitial sites are also

filled with C atoms. There is another way to look at the diamond structure: it can be considered as two interpenetrating FCC units, the second displaced by one quarter of the diagonal of the fcc lattice. Later we will see that the diamond structure can be described by an FCC lattice with a motif consisting of 2 atoms (0,0,0) and (¼, ¼, ¼).

To understand the diamond structure look at the movie on http://en.wikipedia.org/wiki/Diamond_cubic	
The diamond structure	The diamond structure showing the nearest neighbor bonds
Two interpenetrating FCC lattices shifted by (¼, ¼, ¼)	Same picture showing only the atoms in the unit block
Different views on the diamond lattice and 2D projection	

$a_0 = 0.357$ nm
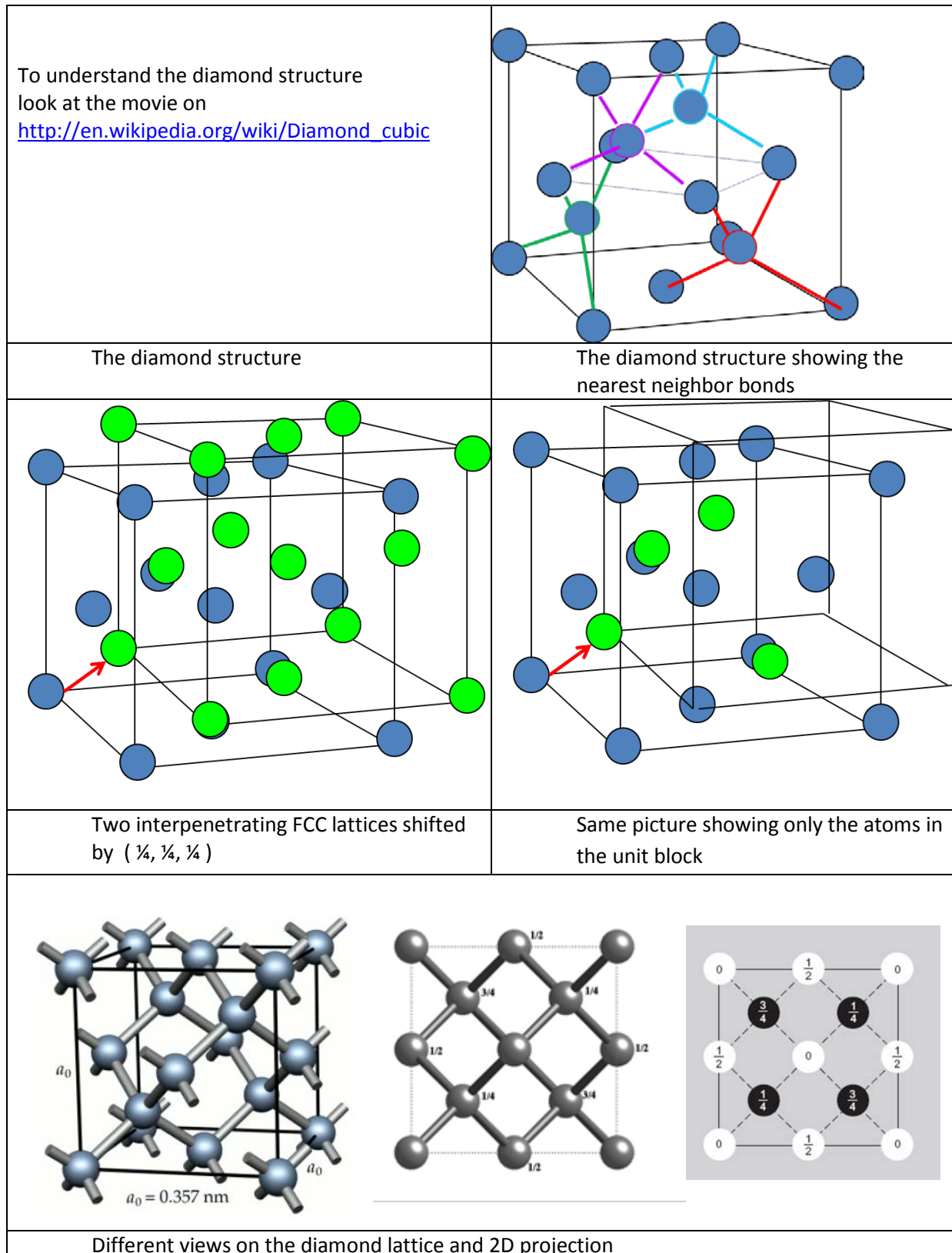
Coordination number

Exercise 3.8
determine the coordination number.

Number of atoms in unit cell

Exercise 3.9
determine the number of atoms in the diamond cell

Atomic packing fraction
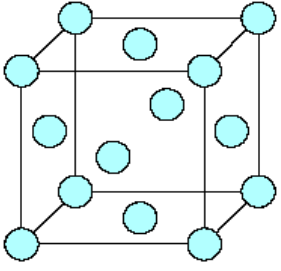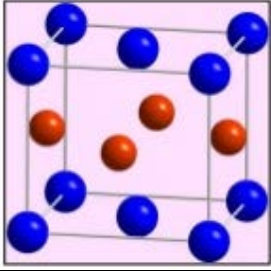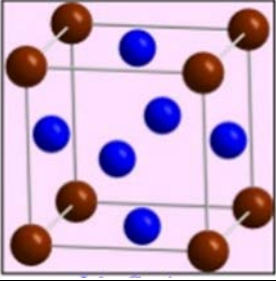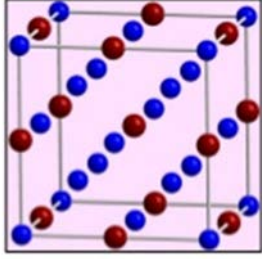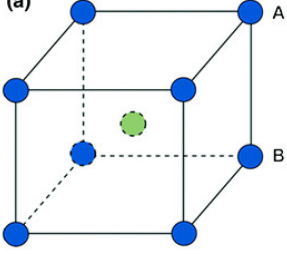
Exercise 3.10
 determine the atomic packing fraction of the diamond cell

Elements that crystallize in a diamond structure

Element	Cube side (Angstrom)
Diamond (C)	3.57
Si	5.43
Ge	5.66
α – Sn	6.49

3.3 Crystal structures of metallic alloys

Mixing several metallic elements, can give result to ordered and disordered structures, requiring different lattices. A few examples

(a) Disordered	CuAu Simple cubic, no chemical order Each light blue atoms is either Cu or Au (respecting that there are in equal amounts!)
	CuAu, CoPt, FePt, TiAl Tetragonal lattice (L1$_0$), chemically ordered (a=b ≠c) Individual elementary components are fcc, bcc or hcp, but the alloy is simple cubic
	Cu3Au, Au3Cu, Ni3Mn, Ni3Fe, Ni3Al, Pt3Fe Cubic lattice L1$_2$, chemically ordered The lattice is simple cubic with chemical ordering
	Fe3Al, Cu3Al, Fe3Si Cubic FCC lattice, chemically ordered
	NiAl, CoAl, CuZn, AuZn The lattice is simple cubic

3.2 Packing spheres of different diameter: important crystal structures of ionic solids

Ionic solids consist of positive and negative ions arranged in a manner so as to acquire minimum potential energy. Since in the ionic bond the charge distribution is only weakly disturbed, one can still consider them in a first approximation as a cation (net positive charge) and an anion (net negative charge)   with different radius. Minimum energy can be achieved by decreasing the distance between cation and anion and reducing anion-anion repulsions. The structures which these solids adopt can be described in terms of large anions/cations forming a close packed arrangement and the small cations/anions occupying one or the other type of interstitial sites. A large number of ionic solids exhibit one of these five structures which are discussed here:

Sodium chloride (NaCl)
Zinc blende (ZnS)
Wurtzite (ZnS)
Cesium chloride (CsCl)
Fluorite (CaF2)

Which crystal structure is formed depends on
- Charge balance requirement
- Relative sizes of the cations and anions.

The importance of the radius of the ions is summarized in the table below. Demonstration of the values is left as exercise.

Disposition of ions about central ion	CN	Range of cation radius ratio to anion radius		
Corners of cube	8	≥0.732		Ratio of the "radius" of the cation/anion (Cation= positive ion, anion=negative ion)
Corners of octahedron	6	≥0.414		
Corners of tetrahedron	4	≥0.225		
Corners of triangle	3	≥0.155		

CN = Coordination number

http://www.physics.uwo.ca/~lgonchar/courses/p2800/Chapter10_Ceramics_Handouts.pdf

Cesium Chloride CsCl

The lattice contains an equal amount of Cs and Cl atoms. The stacking of Cl and Cs they is BCC-type. The structure has a simple cubic building block with a motif of one Cs atom with coordinates (0,0,0) and one Cl atoms with coordinates (½, ½, ½) (or vice versa!). The coordination number for each of the atoms = 8

Unit cell of CsCl	4 unit cells showing that both elements are placed in a simple cubic structure
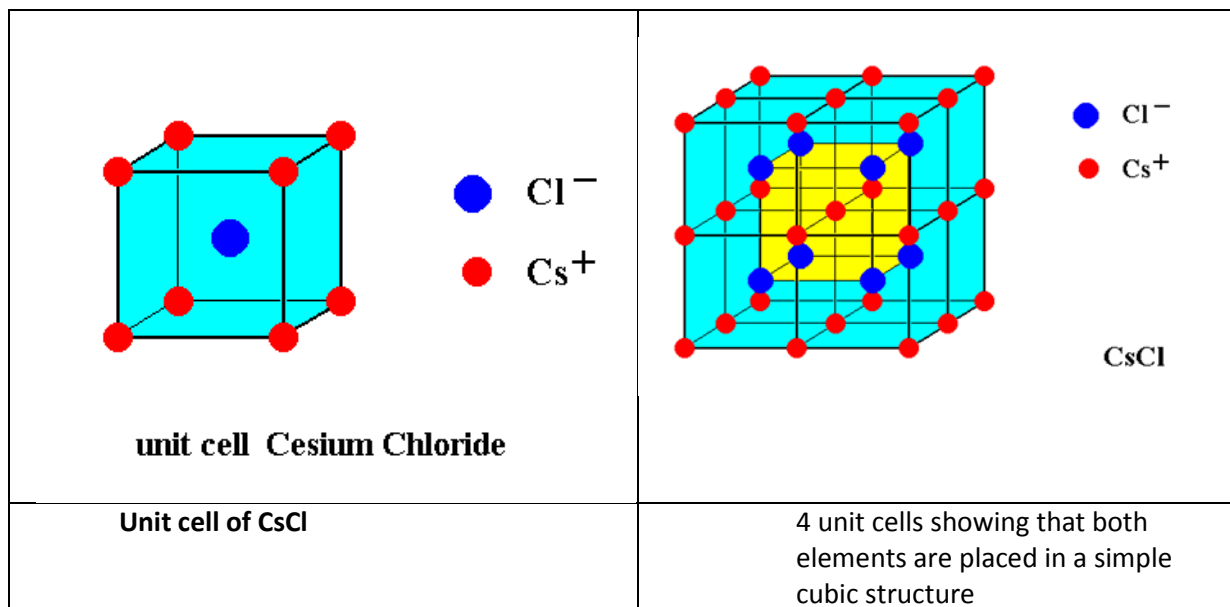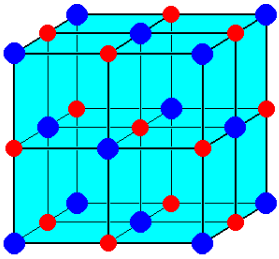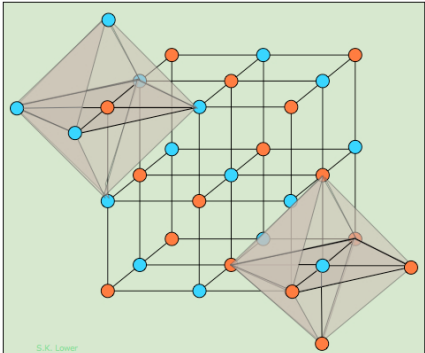
Exercise 3.11
Explain why Cs is sitting in the cubic interstitial site. The radius of Cs (+1) is ~1.67 Å and the radius of Cl (-1) is 1.81 Å .

Elements that crystallize in a CsCl structure

CRYSTAL	a (Å)	CRYSTAL	a (Å)
CsCl	4.12	TlCl	3.83
CsBr	4.29	TlBr	3.97
CsI	4.57	TlI	4.20

Sodium Chloride NaCl

NaCl consists of equal numbers of Na and Cl atoms placed at alternate points of a simple cubic unit block in such a way that each Na ion has 6 Cl atoms as nearest neighbors and vice versa. In other words, one can consider the Cl atoms at the corner of a face centered cubic lattice with the Na atoms in the octahedral sites (or vice versa) , the coordination number=6 for both of Na and Cl

	Unit cell of NaCl http://www.metafysica.nl/turing/preparation_3dim_2.html
https://www.boundless.com/image/nacl-crystal-structure/	The Cl atoms are in the octahedral sites of the Na FCC lattice (or vice versa)

Exercise 3.12

Explain why Na is sitting in the octahedral site. The radius of Cl (-1) is 1.81 Å and the radius of Na (+1) is 0.99Å.

Other binary compounds crystallizing in a NaCl structure

SOME COMPOUNDS WITH THE SODIUM CHLORIDE STRUCTURE

CRYSTAL	a (Å)	CRYSTAL	a (Å)	CRYSTAL	a (Å)
LiF	4.02	RbF	5.64	CaS	5.69
LiCl	5.13	RbCl	6.58	CaSe	5.91
LiBr	5.50	RbBr	6.85	CaTe	6.34
LiI	6.00	RbI	7.34	SrO	5.16
NaF	4.62	CsF	6.01	SrS	6.02
NaCl	5.64	AgF	4.92	SrSe	6.23
NaBr	5.97	AgCl	5.55	SrTe	6.47
NaI	6.47	AgBr	5.77	BaO	5.52
KF	5.35	MgO	4.21	BaS	6.39
KCl	6.29	MgS	5.20	BaSe	6.60
KBr	6.60	MgSe	5.45	BaTe	6.99
KI	7.07	CaO	4.81		

Zinc Blende structure ZnS

ZnS has an equal number of Zn atoms and S atoms. Zn is the cation and S the anion. One can consider that the S atoms are in an cubic face centered arrangement and the Zn atoms occupy half of the tetrahedral sites (not all because of stoichiometry 1:1). Each zinc atom is surrounded by four S atoms and in turn each S atom is also surrounded by four zinc atoms.

 If one looks careful, one can recognize that the Zn atoms form also an fcc lattice but displaced with by ¼ of the volume diagonal. In other words, cations and anions are present in equivalent positions and the coordination of zinc blende structure is described as 4:4. Another way to look at this structure: it has the same geometry as the diamond lattice but filled with Zn and S atoms instead of only C atoms.

| The Zn atoms are in tetrahedral sites |
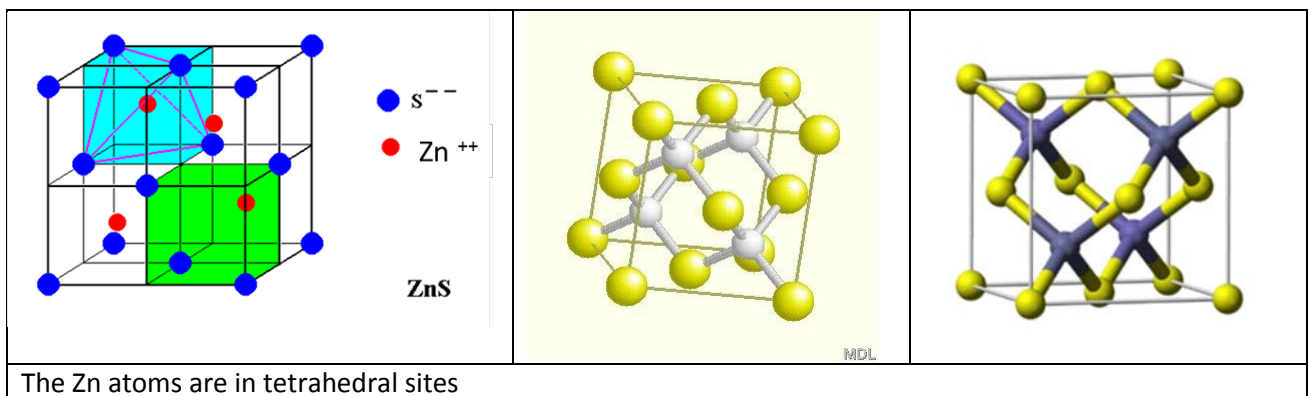
Exercise 3.13
Explain why Zn is sitting in a tetrahedral site. The ionic radius of the zinc(II) cation is 0.74 Å and that of the sulfide (2-) ion is 1.84 Å.

Other binary structures that crystallize in the Zink Blende structure

Table 7.6 *Some compounds with the zinc blende (sphalerite) structure*

	a(Å)		a(Å)		a(Å)		a(Å)		a(Å)
CuF	4.255	BeS	4.8624	β-CdS	5.818	BN	3.616	GaP	5.448
CuCl	5.416	BeSe	5.07	CdSe	6.077	BP	4.538	GaAs	5.6534
γ-CuBr	5.6905	BeTe	5.54	CdTe	6.481	BAs	4.777	GaSb	6.095
γ-CuI	6.051	β-ZnS	5.4060	HgS	5.8517	AlP	5.451	InP	5.869
γ-AgI	6.495	ZnSe	5.667	HgSe	6.085	AlAs	5.662	InAs	6.058
β-MnS, red	5.600	ZnTe	6.1026	HgTe	6.453	AlSb	6.1347	InSb	6.4782
β-MnSe	5.88	β-SiC	4.358						

Wurtzite structure ZnS

ZnS can also form in a hexagonal close packing crystal structure, keeping the coordination 4. This is shown in the picture below where the cations (Zinc) spheres and are located so that there are four sulphur anions around each zinc atom since they occupy tetrahedral sites of the hcp lattice (and vice versa). Again cations and anions are in equivalent positions.

Hexagonal image of wurtzite	Unit cell
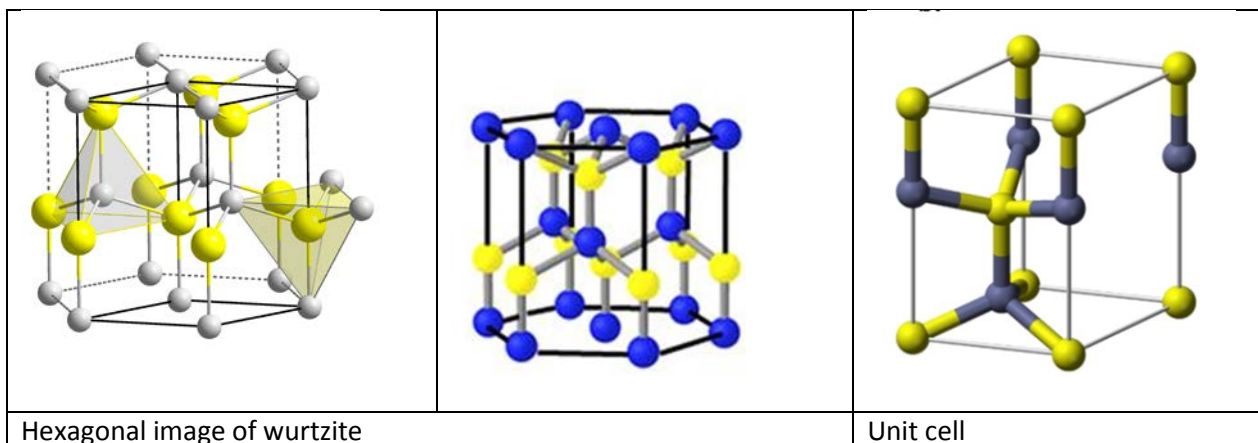
Difference between zincblende and wurtzite
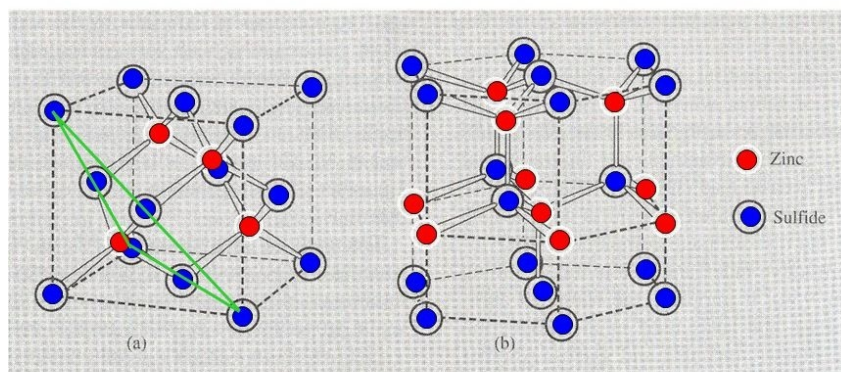
Note that in Zink Blende and Wurtzite the atoms are in a tetrahedral coordination. The difference lies in the ordering of atoms that are further away. This is shown in the picture below. Here the sequence of the most dens planes is shown. Look at the movies on http://www.chemtube3d.com/solidstate/_blende(final).htm

Zinc Blende: since it has an HCP lattice it has the typical ABC stacking	Wurtzite: since it has hexagonal lattice, it has the typical AB stacking
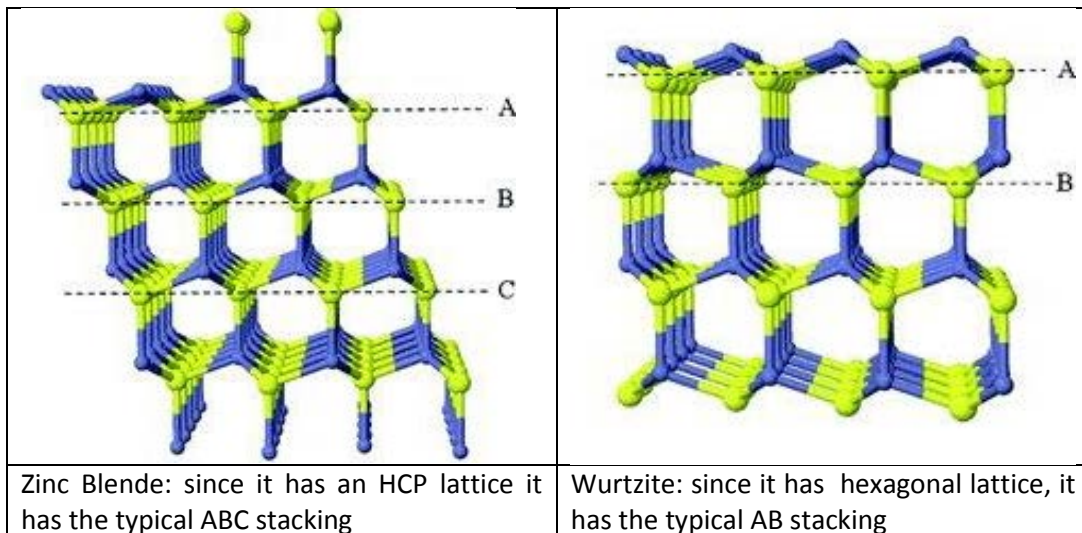
Other "Wurtzite" type crystals

Table 7.9 *Some compounds with the wurtzite structure.* (Data taken from Wyckoff, 1971, Vol. 1)

	a(Å)	c(Å)	u	c/a		a(Å)	c(Å)	u	c/a
ZnO	3.2495	5.2069	0.345	1.602	AgI	4.580	7.494		1.636
ZnS	3.811	6.234		1.636	AlN	3.111	4.978	0.385	1.600
ZnSe	3.98	6.53		1.641	GaN	3.180	5.166		1.625
ZnTe	4.27	6.99		1.637	InN	3.533	5.693		1.611
BeO	2.698	4.380	0.378	1.623	TaN	3.05	4.94		1.620
CdS	4.1348	6.7490		1.632	NH₄F	4.39	7.02	0.365	1.600
CdSe	4.30	7.02		1.633	SiC	3.076	5.048		1.641
MnS	3.976	6.432		1.618					
MnSe	4.12	6.72		1.631					

Calcium Fluroride CaF2

CaF2 has twice as much Fluor atoms as Calcium atoms. The Ca cations arrange themselves in a face centered cubic structure and the Fluor anions occupy the 8 tetrahedral interstitial sites. Therefore the coordination of Ca cation is 8 and of the F anion is 4, corresponding to the stoichiometry. The structure can however also be considered as a simple cubic structure of F anions with the Ca cations sitting in cubic (8-coordinate) holes. sits in the cubic interstitial site of the simple cubic F lattice. You will find also the opposite, sometimes called anti-Fluorite, as is the case of Na2=. Here the Na cations occupy the 8 tetrahedral sites and the O anions arrange in a face centered structure

Unit structure of CaF2 (in each sub-cube there is a F atom). Each F atoms is surrounded by 4 Ca atoms	Each Calcium ion is surrounded by eight Fluorine neighbors when the structure is imagined to be extended indefinitely.
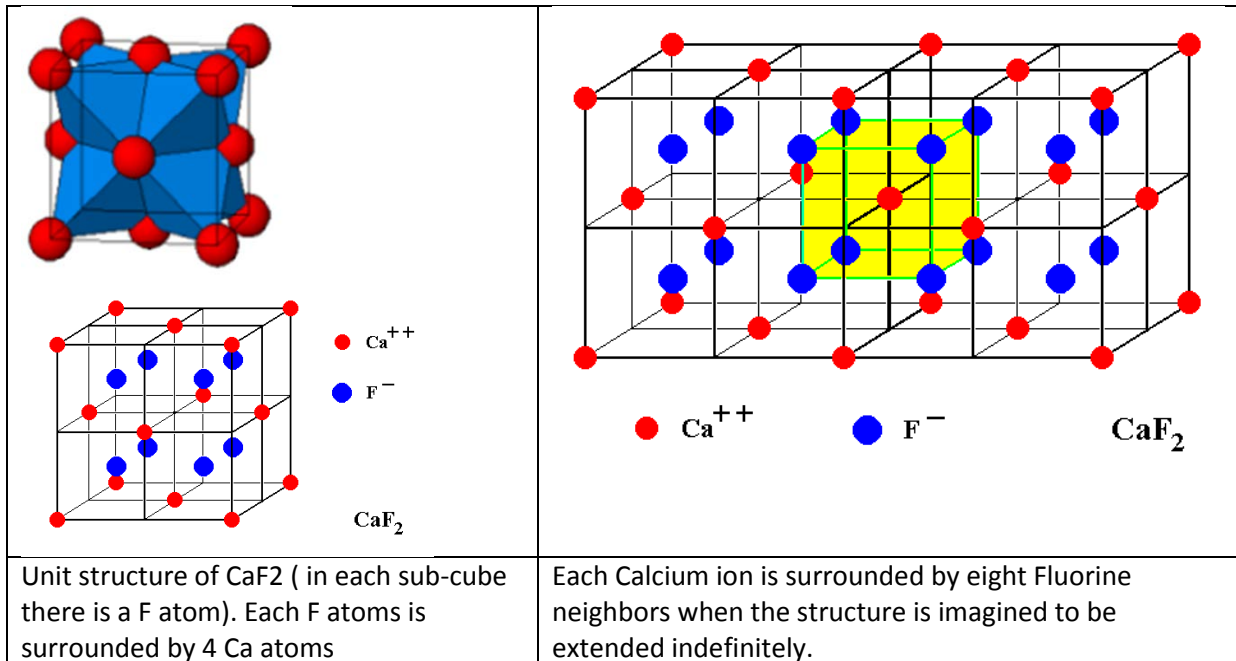
Exercise 3.14

Explain why Ca is sitting in a cubic interstitial site. The ionic radius of the Ca anion is 1.17 Å and that of the F anion is 1.26 Å.

Other crystals

Table 7.7 *Some compounds with fluorite and antifluorite structure*

Fluorite structure				Antifluorite structure			
	$a(\text{Å})$		$a(\text{Å})$		$a(\text{Å})$		$a(\text{Å})$
CaF_2	5.4626	PbO_2	5.349	Li_2O	4.6114	K_2O	6.449
SrF_2	5.800	CeO_2	5.4110	Li_2S	5.710	K_2S	7.406
$SrCl_2$	6.9767	PrO_2	5.392	Li_2Se	6.002	K_2Se	7.692
BaF_2	6.2001	ThO_2	5.600	Li_2Te	6.517	K_2Te	8.168
$BaCl_2$	7.311	PaO_2		Na_2O	5.55	Rb_2O	6.74
CdF_2	5.3895	UO_2	5.372	Na_2S	6.539	Rb_2S	7.65
HgF_2	5.5373	NpO_2	5.4334	Na_2Se	6.823		
EuF_2	5.836	PuO_2	5.386	Na_2Te	7.329		
$\beta\text{-}PbF_2$	5.940	AmO_2	5.376				
		CmO_2	5.3598				

Conclusive Note

With the above examples it is clear that
- many crystalline solids have the same crystal structure
- the same crystal can be described in several ways

We only considered some simple metals, alloys and some ionic/covalent crystals. There are however many other crystals such as for instance the perovskite structure shown below

| Perovskite structure CaTiO3 (Ca=green, O=blue, Ti=red) | Double perovskite structure $AA'_3B_4O_{12}$. |

Or molecular crystals (see http://en.wikipedia.org/wiki/Buckminsterfullerene)

| C60 molecular crystal of weakly bound C60 crystals molecules. In this example there are no atoms in the lattice points! | alkaline-metal-doped fullerenes such as Cs3C60 crystals evidencing superconductivity at 33K |
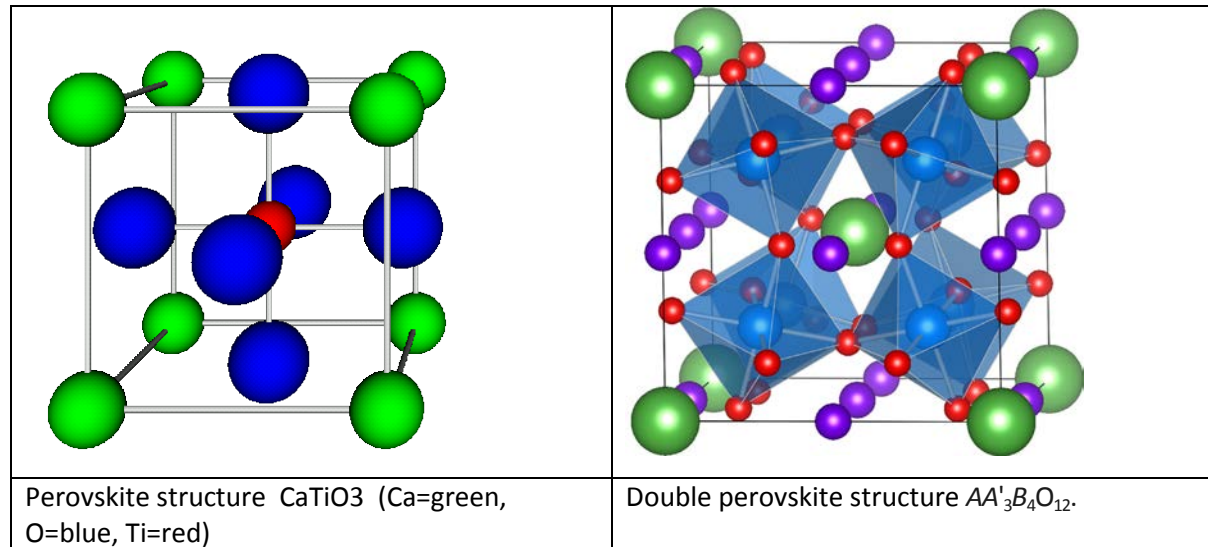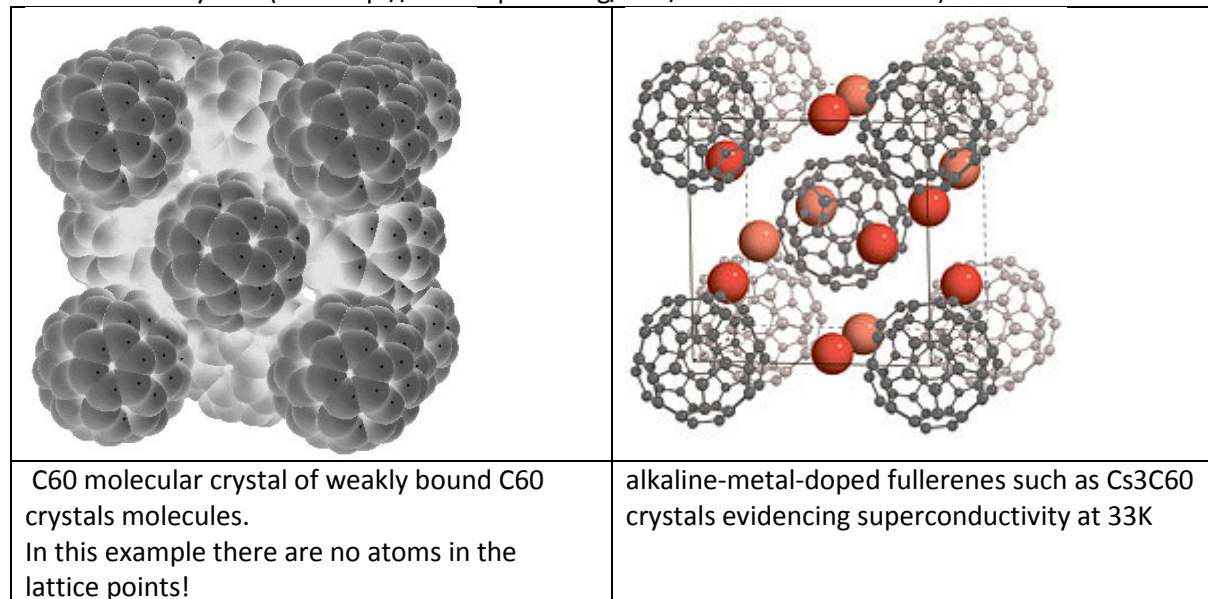
It is obvious that a rigorous mathematical description of a crystal is needed! That is what will be done in the next chapter.

Extra Exercises

3.15   Write down the coordinates of the center of all the tetrahedral and octahedral sites for the fcc and bcc structures.

3.16   Assuming that atoms are hard spheres in contact and letting r' be the radius of the interstitial site and r the radius of the solvent atom in contact, calculate the critical ratio of the radius (r'/r). i.e.

      i.   show that for the two fcc interstitial sites (r'/r) equals 0.4142 and 0.2247.

      ii.   show that for the two bcc interstitial sites octahedral and tetrahedral (r'/r) equals 0.1540 and 0.2910

3.17   Using geometrical considerations, derive the critical ratio of the radius cation/anion for the crystal structure CsCl, NaCl and ZnS. The critical radius occurs when the cations just fit into the space left by the anions so that the anions and cations just touch each other.

Show that the critical ratio corresponds to $\sqrt{3} - 1, \sqrt{2} - 1, \frac{\sqrt{6}}{2} - 1$

For imaging some of the crystal structures
http://www.dawgsdk.org/crystal/en/library/CsCl#0010

References that can be used and from which some of the pictures are taken

Christopher Hammond
The Basics of Crystallography and Diffraction: Third Edition

Neil W. Ashcroft, N. David Mermin
"Solid State Physics", 1st edition

http://www.materials.ac.uk/elearning/matter/IntroductionToPointDefects/Interstitials/introduction.html

https://www.e-education.psu.edu/matse201/node/8

http://en.wikipedia.org/wiki/Close-packing_of_equal_spheres

http://en.wikipedia.org/wiki/Hexagonal_crystal_system

http://www.tcm.phy.cam.ac.uk/~cjp20/old/lectures/topic2.pdf

http://web.nchu.edu.tw/~jillc/me/Ch03%20-%20Crystalline%20Structure%20-%20Perfection.pdf

http://www.metafysica.nl/turing/preparation_3dim_3.html

4. Crystal lattice and symmetries

4.1 Definition of a lattice

To describe the crystal mathematically, a *lattice* is defined. The **lattice is** an ensemble of mathematical points at specific coordinates in space. The view from each lattice point is the same as from any other.

To reconstruct the crystal from a lattice one needs to define the *"base" or "motif"* of the crystal which are atoms or molecules in some specific arrangement unambiguously placed at every lattice point. In other words, the lattice tells you how to repeat the motif and the motif tells you what to repeat. It is important to realize that *a lattice is not a crystal, but each crystal has a lattice* even so the two words are often used synonymously in spoken language. Only in the case of elemental crystals where the motif consists of one atom sitting at each lattice point, lattice and crystal have the same meaning. This is for instance the case for pure metals such as Fe, Cu and Ti, following respectively the bcc, fcc and hcp stacking. As we have seen earlier, for instance ZnS can be described by the same lattice as Cu (fcc lattice for S) but needs a motif for the positions of the Zn atoms .

Crystal = Lattice + Motif

The lattice is a very important concept in material science. Many physical properties of crystals like elastic and plastic deformation, cleavage, electronic band structure and optical transparency are strongly governed by the lattice structure and are also described using the lattice concept. Many experimental techniques as for instance Xray, neutron and electron diffraction use for their interpretation the concept of the lattice

This section starts with the concept of the lattice which defines the translational symmetry. Then the different symmetries that can be contained in one lattice point will be introduced (point symmetries). Finally it will be shown that the combination of the motif, the translational and point symmetry allows the crystallographer to classify materials into 230 space groups.

For the ease we will explain crystallography using 2 dimensional patterns. The lattice and symmetry operations used here are those used to make the patterns in wall paper or tissues. Two dimensional lattices do however exist: a nice example is graphene (see picture below from http://en.wikipedia.org/wiki/Graphene).

Graphene and wall paper with same symmetry group
http://www.clarku.edu/~djoyce/wallpaper/groups.html
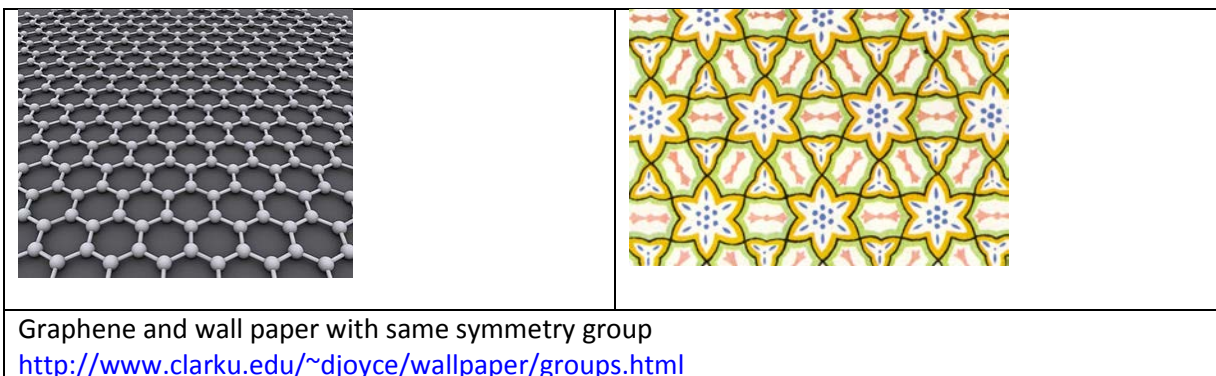
Most materials need however a 3D lattice. The classification of the 2D lattices and symmetry groups is analog to the 3D case, however much simpler. If the construction in 2D case is understood, it is easier to understand the classification of 3D crystals in 230 space groups.

4.2 The 2D lattice and symmetry operations

4.2.1 The 2D lattice

Lattice is a mathematical description of translational periodicity, and this description is usually not unique.
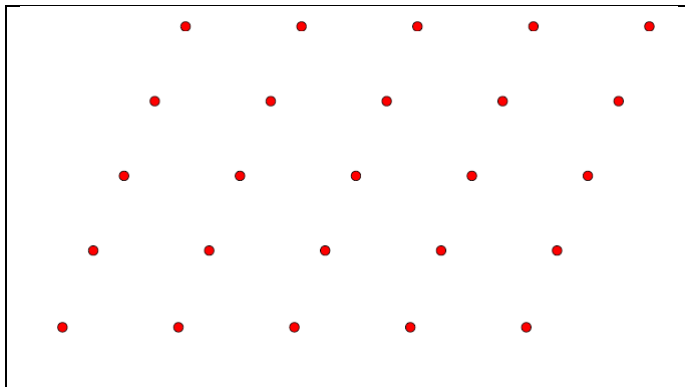
To mathematically define the translational symmetry in 2D, we need 2 vectors. The pictures below show that there are many possibilities to fully represent the translational periodicity. One can define a *unit cell*, but again the choice of the unit cell is not unique. The unit cell can be primitive i.e. the cell contains only one lattice point (pink examples) or non-primitive, when the cell contains more than one lattice point (blue example).
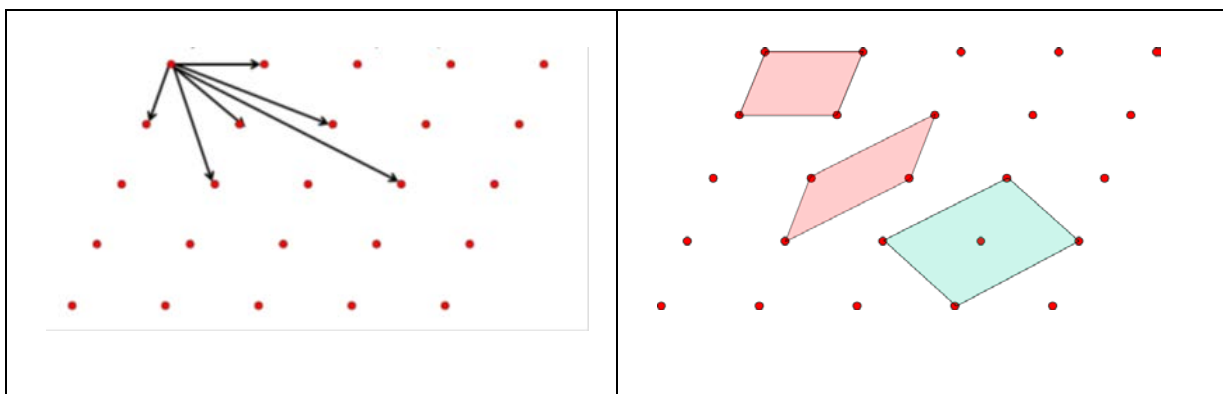
In other words, for a rigorous mathematical description of crystals, we need a common practice for defining the lattice. Criteria used are

1. Short unit vectors
2. Angles between vectors closest to 90°
3. Primitive unless the cell does not reflect the major symmetry axis of the lattice

In the 2D example from above, the lattice is called "oblique" and is by convention defined as

- The two shortest vectors, a$\neq$b
- Both angles are "closest" to 90°
- Primitive "P"
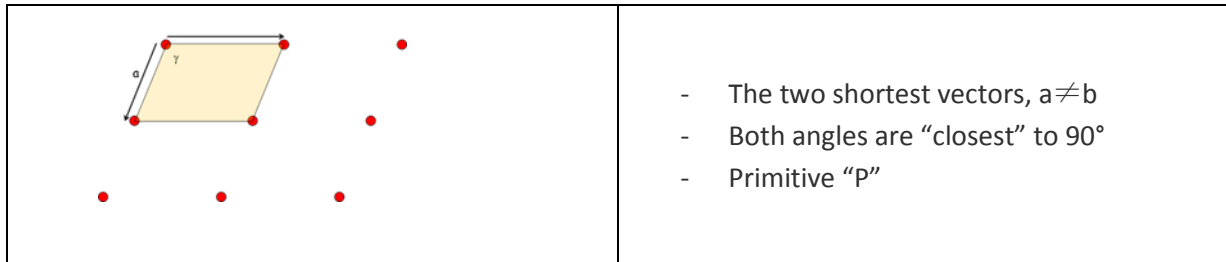
It is easy to recognize that the lattice has certain symmetries. For instance, the 2D lattice considered above has several 180° rotation axes as shown below. Such a symmetry operator is called a point symmetry because when it acts there remains at least one point unchanged

180° rotation axes of the oblique lattice
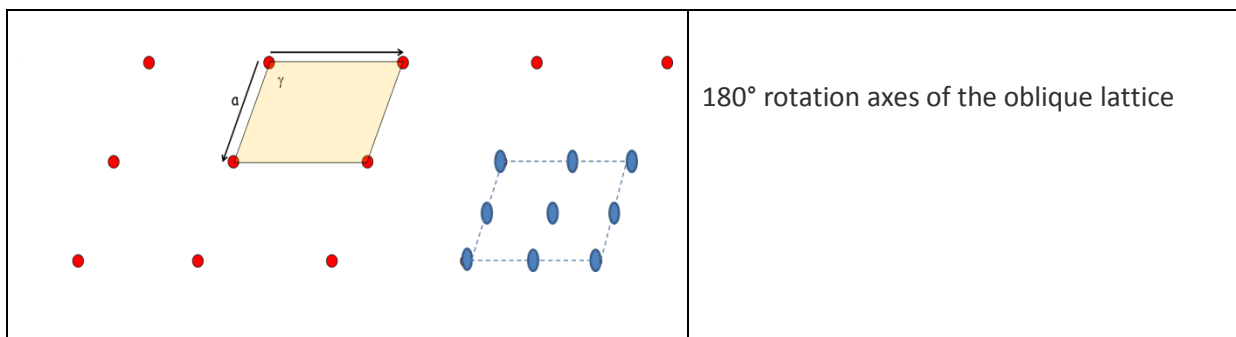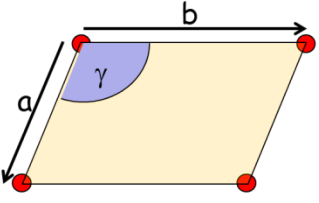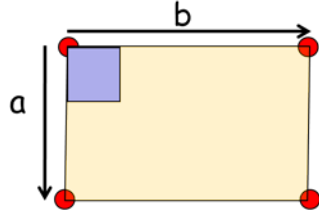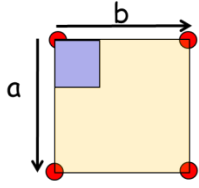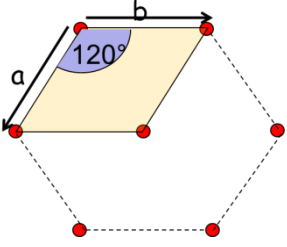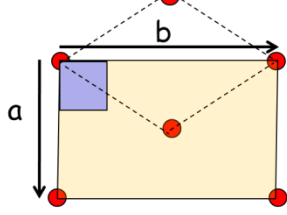
If a reflection line ("m") is present, the cell must be rectangular. This is shown for the 2D lattice below

2D lattice

a$\neq$b γ = 90

all blue lines are reflection lines
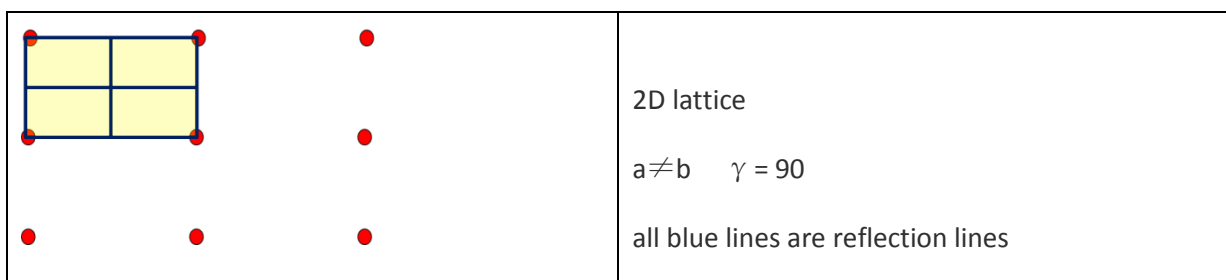
.
Presence of a 4-fold axis requires that the lattice vectors are equal in size (square lattice)

Combining translational, rotational and reflection symmetry in a plane, and using the three convention criteria listed above, has allowed to define five 2D lattice that can describe any regular 2D repeating of points in a plane: the primitive oblique lattice, the primitive rectangular lattice, the primitive square lattice, the primitive hexagonal lattice and the non-primitive rectangular lattice. The lattices are shown in the table below (red points are lattice points). In the right column the maximum symmetry a lattice point can have is provided

2D lattice		Maximal symmetry of 2D lattice
	oblique P $a \neq b$; $\gamma \neq 90, 120°$	2-fold axis
	rectangular P $a \neq b$; $\gamma = 90°$	2-fold axis with two reflection lines
	square P $a = b$; $\gamma = 90°$	4-fold axis with two reflection lines
	Hexagonal P $a = b$; $\gamma = 120°$	6-fold axis with three reflection lines
	rectangular C $a \neq b$; $\gamma = 90°$	2-fold axis with 2 reflection lines
When a primitive lattice is taken, it is called Rhombic		

What concerns the non-primitive rectangular lattice, an obvious question is why for these cases one does not choose a primitive cell with a=b. This is sometimes done (see for instance en.wikipedia.org/wiki/Wallpaper_group). The lattice however contains mirror planes and so according to convention 3, the unit cell should present the major symmetry elements of the lattice.

4.2.2 The 2D Symmetry operations

The symmetry operations in 2D that are compatible with translational symmetry are

       1-fold (no symmetry)

       2-fold (180° rotation)

       3-fold (120° rotation)

       4-fold (90° rotation)

       6-fold (60° rotation)

       Reflection line (m)

Of course rotation axis and reflection lines can be combined.
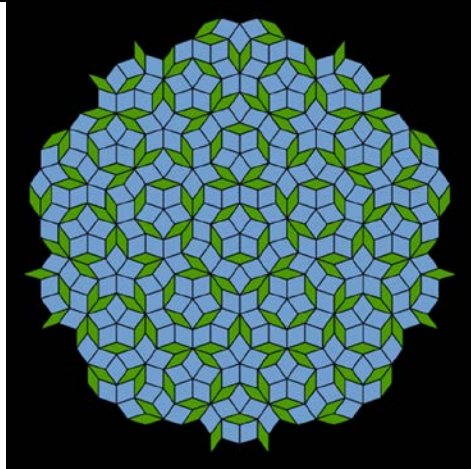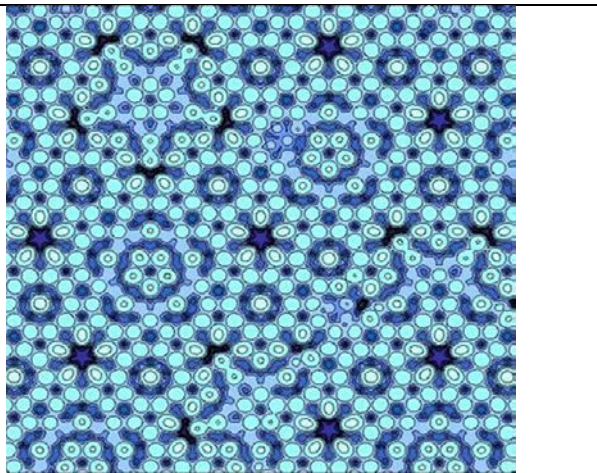
The notations used in this course are those from Hermann–Mauguin:

       1,2,3,4,6 for the rotation axis

       m for the reflection line

When symmetry operations are combined this results in notations such as

       3m: a 3-fold rotation axis lying on a reflection line

       6mm: a 6 fold axis lying on two symmetry lines

<u>Why not a 5-fold rotation axis?</u>

Penrose tilling gives a quasicrystal	Atomic model of an aluminium-palladium-manganese (Al-Pd-Mn) quasicrystal surface.
http://en.wikipedia.org/wiki/Penrose_tiling A quasiperiodic crystal (quasicrystal) is a structure that is ordered but not periodic. A quasicrystalline pattern can continuously fill all available space, but it lacks translational symmetry	http://chemvista.org/quasicrystals1.html

In the case the motif is simple and falls on the lattice point, the 2D lattices describe all possible 2D periodic structures and the lattice + motif has the same symmetry operations as the lattice. However, when the motif is more complex, the symmetry of the unit cell may change. Take the example of the square P lattice shown below. When the motif is one black spherical point, the lattice shows a 4-fold axis with two reflection lines. However when the motif consists of a black and a blue spherical point,

the translational symmetry of the lattice repeats the black and blue points on the horizontal axis. The 4-fold rotation axis reduces to a 2-fold axis and some of the mirror planes are omitted.

Square P lattice, motif: one black point

Square P lattice, motif: one black and one blue point
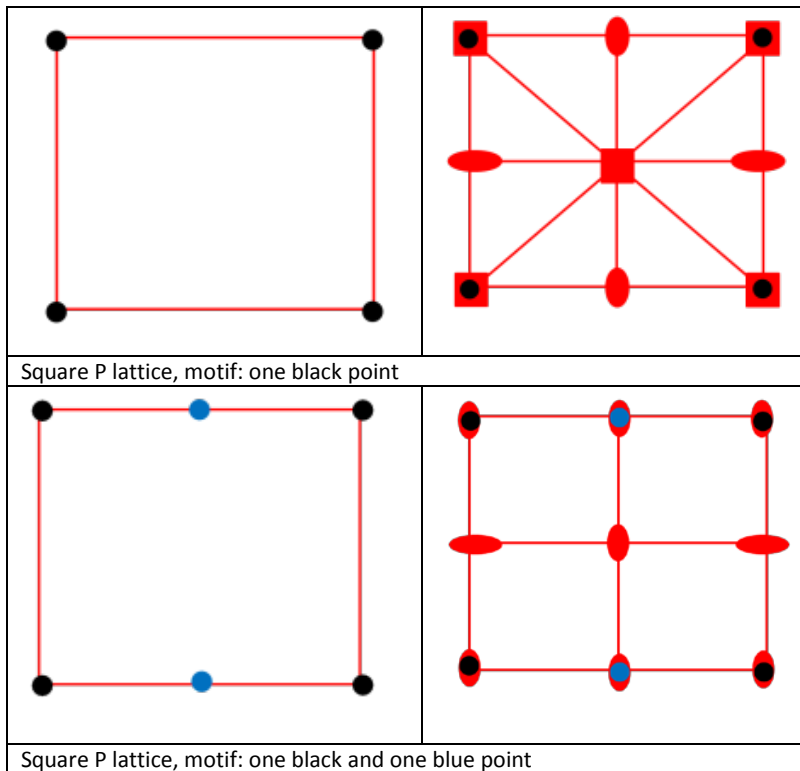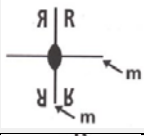
In summary, the symmetries provided on the right hand side of the table with the lattices are the maximal symmetries the lattice can have. However, as we know,

crystal = lattice + motif

This is also valid for the 2D case. Once one "decorates" a 2D lattice with a motif, the symmetry might change. To further classify 2D crystals, one has introduced the concept of 2D point groups, representing the possible symmetries operating in a point and compatible with translational symmetry. There are 10 point groups in 2D. These are illustrated in the table on the next page using a non-symmetrical motif

Exercise 4.1

Complete the table below for all 2D symmetry operations

2D Point symmetry		Symmetry elements
1	R	No symmetry
m	Я|R	One mirror line
2mm	Я|R ... m	2-fold axis and 2 mirror lines
2		2-fold axis
3		3-fold axis
3m		3-fold axis and three mirror lines
4		4-fold axis
4mm		4-fold axis and 2 mirror lines
6		6-fold axis
6mm		6-fold axis and 3 mirror lines
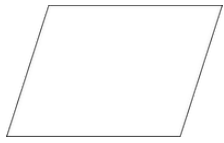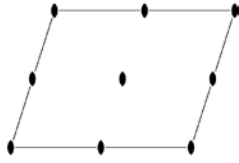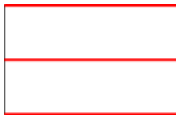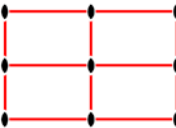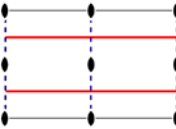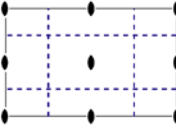
Other symmetry operators: combination with 2D translational symmetry
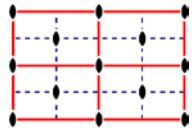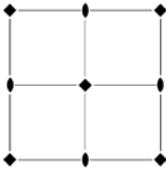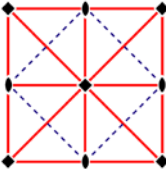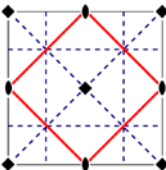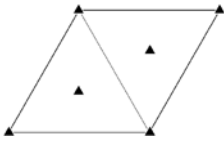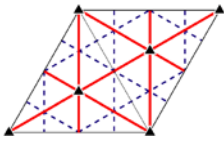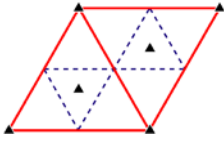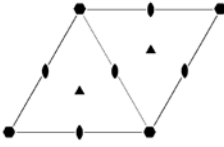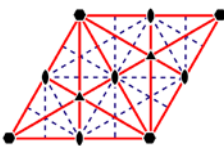
A Lattice + motif can also contain a glide line i.e. a mirror line combined with a translation vector . In the table below, the difference between a mirror line and a glide line is shown

mirror line	glide line (symbol "g" or ⅃)
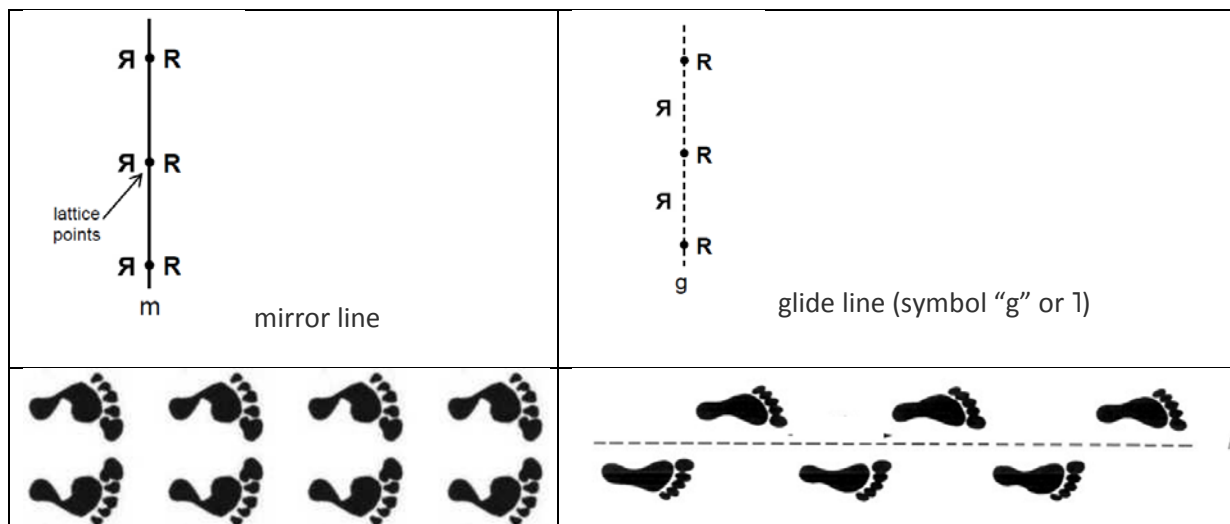
4.2.3 The 2D Plane groups

The five 2D lattices combined with the ten possible 2D point symmetries and the possibility to have a glide plane result together 17 plane groups. These are presented in the table below. As exercise, use a non-symmetric motif and perform all symmetry operations. Rotation axis are shown in black, mirror lines are red and glide lines are dashed blue; "p" stands for primitive, "c" for centered lattice For further details see https://sites.google.com/a/uw.edu/diffraction-resources/symmetry-resources/2d-symmetry-groups On this web page you can also find nice examples of wall papers.

Lattice type	Symmetry operations	Plane group
oblique		p1
oblique		p2
rectangular		pm
rectangular		pg
Rectangular C (Rhombus)		cm
rectangular		pmm (p2mm)
rectangular		pmg (p2mg)
rectangular		pgg (p2gg)

Rectangular C (Rhombus)		cmm (c2mm)
square		p4
square		p4m (p4mm)
square		p4g (p4gm)
hexagonal		p3
hexagonal		p3m
hexagonal		p31m
hexagonal		p6
Hexagonal		p6m (p6mm)

Further reading

http://users.aber.ac.uk/ruw/teach/334/groups.php

http://www.clarku.edu/~djoyce/wallpaper/seventeen.html

https://sites.google.com/a/uw.edu/diffraction-resources/symmetry-resources/2d-symmetry-groups
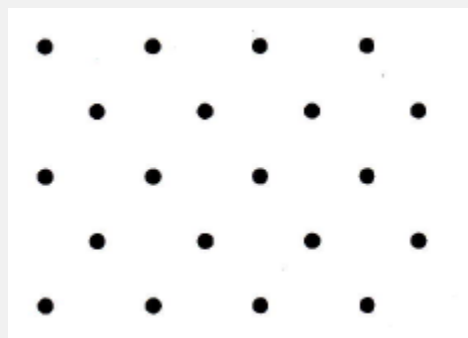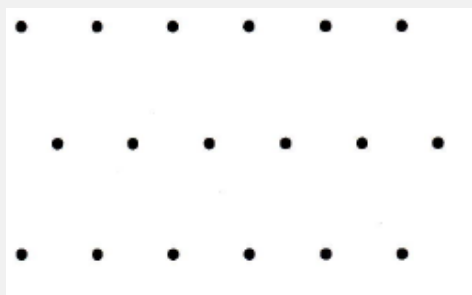
Extra Exercises

Exercise 4.2
Name the 2-dimensional lattices given below. Use the five planar lattices. Draw the primitive unit cell vectors in each case and draw a full unit cell.
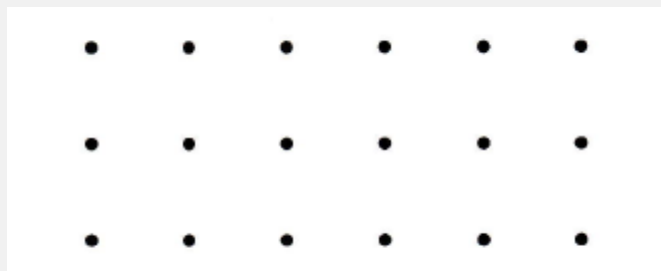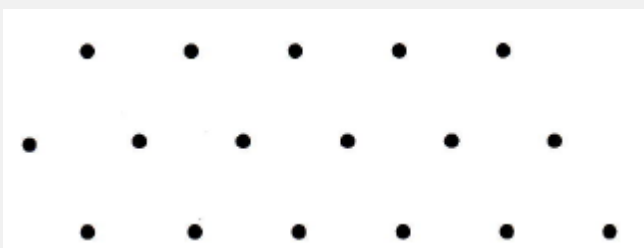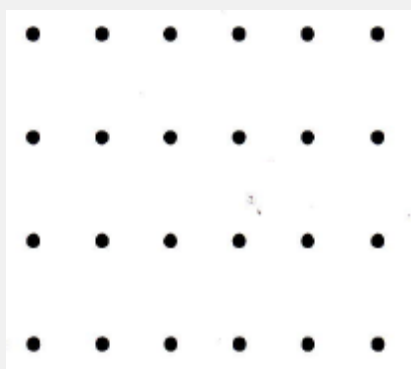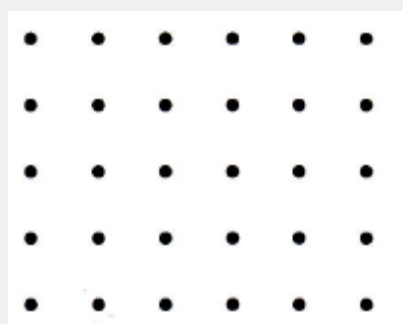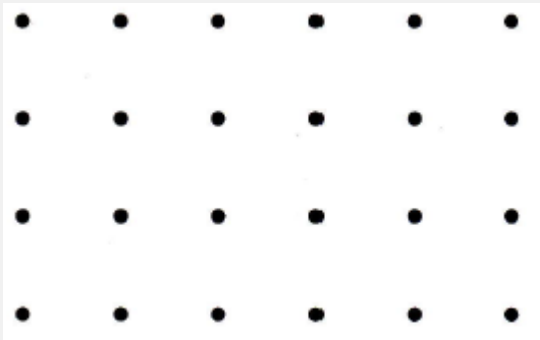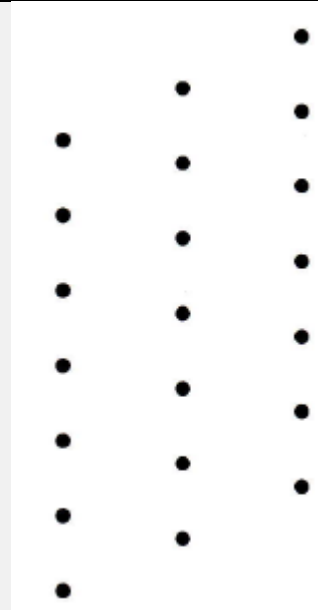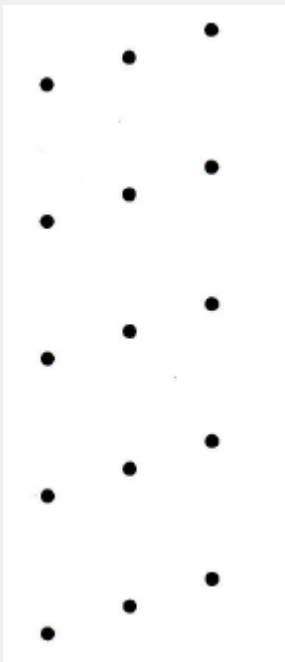
a)

b)

c)

d)

e)

f)

g)

h)

i)
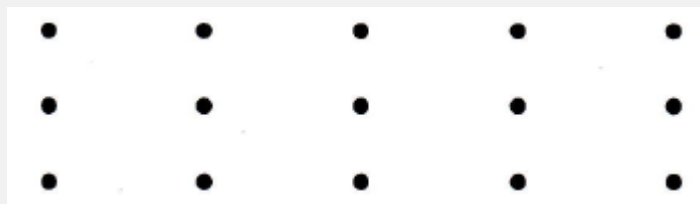
j)

Exercise 4.3

i) For the planar lattices below, indicate those pairs of vectors which are primitive (P), and those non-primitive (N)

Cell No.	Answer
1	
2	
3	
4	

ii) Calculate the number of lattice points contained within each of the unit cells given below and mark those that are primitive (P) and those non-primitive (N).

Cell No.	P or N ?	No. of points
1		
2		
3		
4		

Answers

iii) On the planar lattice below construct two different primitive unit cells (A and B) and one non-primitive unit cell (C).

Exercise 4.4

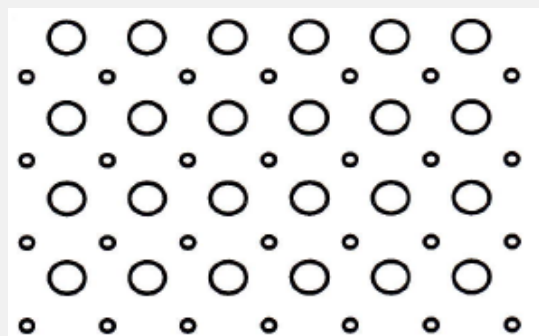Name the lattices of the structures given below and draw the unit cell that illustrates the symmetry of the lattice. Identify the motif in each case and identify the number of atoms in the motif

a)
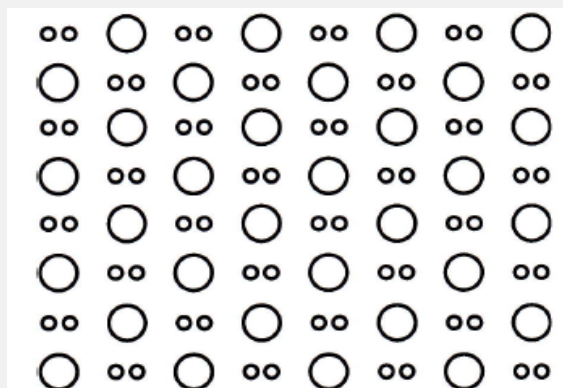
b)
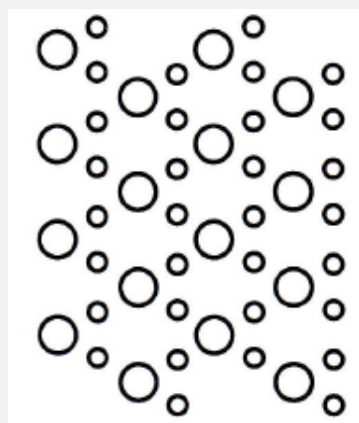
c)
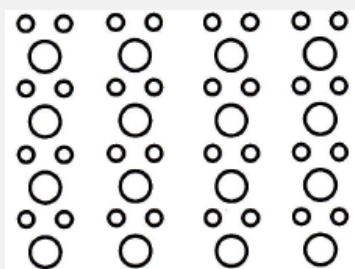
d)
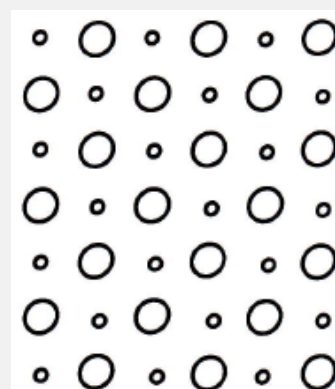
e)
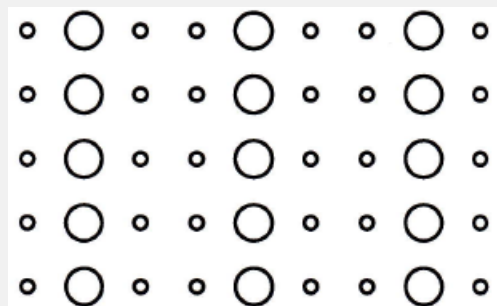
f)
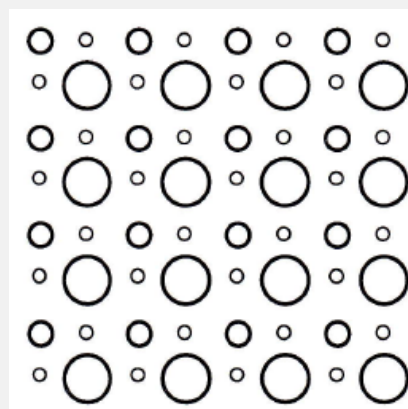
g)
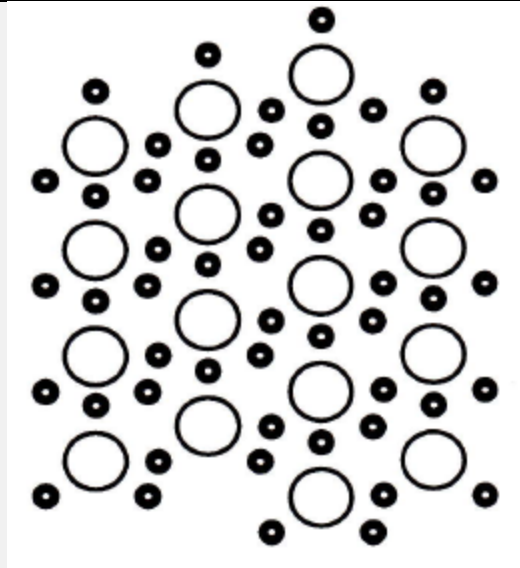
i)

Exercise 4.5

Show that Graphene and the two wallpapers below belong to the same plane group symmetry p6mm. To demonstrate this, use the unit cell below (upper left hand side) on which all symmetry operations are indicated. Demonstrate the presence of the rotation axis, glide planes, mirror planes

http://en.wikipedia.org/wiki/Wallpaper_group

p6m

http://www.jameshedberg.com/

4.3. The 3D lattice and symmetry operations

4.3.1 The 3D Bravais lattice
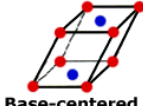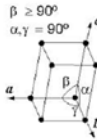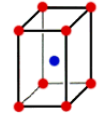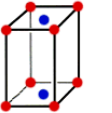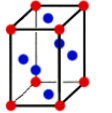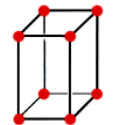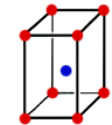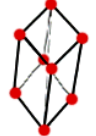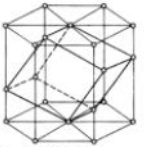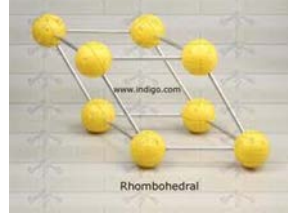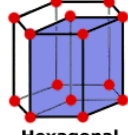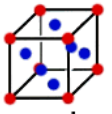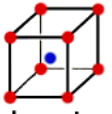
The number of ways points can be arranged regularly in 3D space such that stacking the unit cells fills the space is also limited**. Bravais showed in 1848 that all possible arrangements can be presented by 14 lattices.** His work was to a great extend based on the work of Frankenheim who showed in 1845 that the number of lattices was limited, he claimed however there were 15.

The 14 Bravais lattices can be classified according to a set of defining symmetry elements which any crystal within that system mus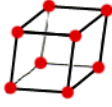t possess as a minimum requirement. This allowed classifying the 14 Bravais lattices into 7-systems(cubic, tetragonal, orthorhombic, trigonal, hexagonal, monoclinic and triclinic). The geometry of the cells are specified by the length of their axis (a,b,c) and the angle between them: α between **b** and **c**, β between **a** and **c**, γ between **a** and **b**. A right hand axes is used by convention (see picture below)

	3D lattice using a right hand axis
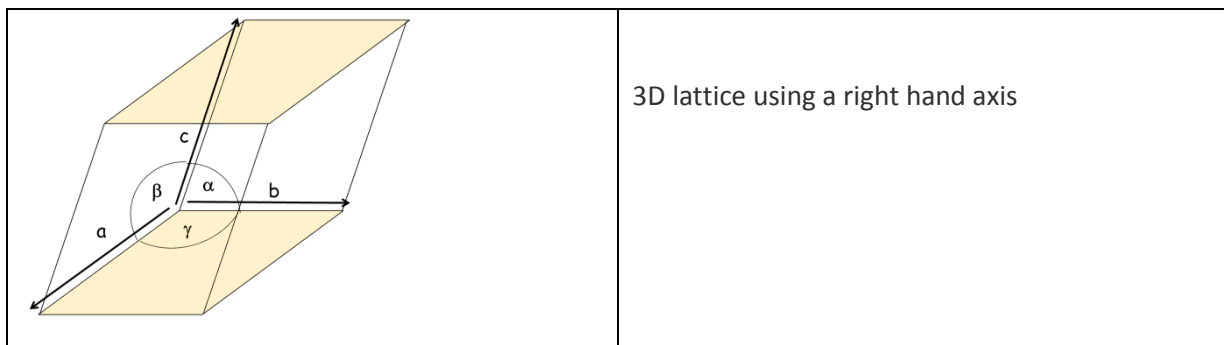
 The seven crystal systems are listed below and shown in a table together with the symmetry element that defines the shape of the crystal system

- The *triclinic* system: one primitive Bravais lattice (P).
- The *monoclinic* system: a primitive (P) and a base-centered (C) Bravais lattice. (the nomenclature C comes from the fact that the lattice point lies in the plane defined by a and b vectors).
- The *orthorhombic* system: 4 Bravais lattice unit cells; the primitive-P, and three non-primitive unit cells: the face centered-F, the body centered-I and the side centered-C
- The *tetragonal* system: a primitive P and a body-centered I Bravais lattices
- The *rhombohedral* system: one primitive Bravais lattice
- The *hexagonal* system: a primitive P lattice
- The *cubic* crystal system: 3 Bravais lattice unit cells; the primitive-P, and two non-primitive unit cells: face centered -F and body centered-I

Crystal system	The 14 Bravais lattices	Defining symmetry
Triclinic **a≠ b ≠ c** **α≠β≠γ≠90°**	Triclinic	1-fold axis
Monoclinic **a ≠ b ≠ c ;** α = γ = 90°; β ≠ 90	Simple Monoclinic Base-centered monoclinic $\beta \geq 90°$ $\alpha, \gamma = 90°$	2-fold axis
Orthorhombic **a≠ b ≠ c** **α=β=γ=90°**	Simple orthorhombic Body-centered orthorhombic Base-centered orthorhombic Face-centered orthorhombic	3 x 2 fold axis
Tetragonal **a= b ≠ c** **α=β=γ=90°**	Simple tetragonal Body-centered tetragonal	4-fold axis
Rhombohedral (trigonal) **a= b = c** **α=β=γ≠90°**	Rhombohedral P Trigonal R Rhombohedral	3-fold axis
Hexagonal **a= b ≠ c** **α=β=90, γ=120°**	Hexagonal	6-fold axis
Cubic **a= b = c** **α=β=γ=90°**	Simple cubic Face-centered cubic Body-centered cubic	4 x 3-fold axis

Note that also here the choice of the unit cell is not unique. We have seen in the section on stacking sequences of hard spheres that one can take for instance instead of a body centered cubic lattice also a primitive lattice. Analytically all lattice points can be described by a linear combination of the primitive lattice vectors or by the bcc unit cell. The shape of the primitive cell does however not reflect the highest symmetry of the cube i.e. the 90° rotation axis, which is a convention for Bravais lattices.

4.3.2 The 3D point symmetry operators

In 3D there are more symmetry operators than in 2D

Rotation axis
1-fold (no symmetry)
2-fold (180° rotation)
3-fold (120° rotation)
4-fold (90° rotation)
6-fold (60° rotation)

Reflection or mirror plane
This is the equivalent of a mirror line in 2D . Graphically the mirror plane is shown by a full line (see table below).

the inversion center and the roto-inversion axis.
These symmetry operators are easiest to visualize when using a projection on the plane of the paper (see below) The inversion center will project a point that lies above the plane (black circle) into a point that lies below the plane (open circle)
A roto-inversion axis is a rotation followed by an inversion center. The roto-inversion axis is graphically shown by the same symbol as the rotation axis but with a open circle in the center
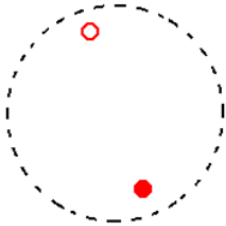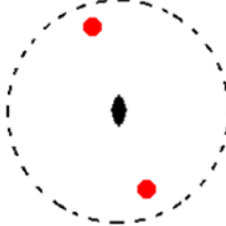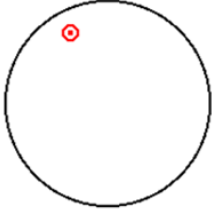
Examples:
Take a point that lies above the surface of the paper plane.
The picture below shows the operation of an inversion center on a red point, a 2-fold axis and a 2-fold roto-inversion axis, which is noted as $\overline{2}$.
The inversion center turns the full red point (above the plane) into an open red circle (point below the plane) through reflection at the central point of the circle.
The 2-fold axis rotates the full red point over 180° (also lying above the plane).
The 2-fold roto-inversion axis rotates the point above the plane (red circle) over 180° around the rotation axis and then the symmetry center acts, bringing the point back to its original position but this time below the plane (open circle). Note that the action of a 2-fold roto-inversion axis is the same as a mirror plane m (that is also why the circle is shown as a full line) .
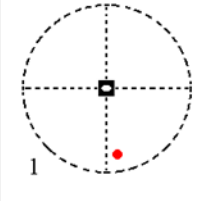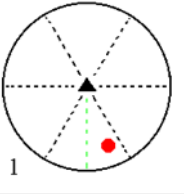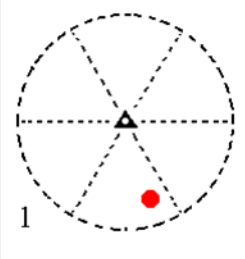
Inversion center	2-fold roto-axis (2)	2-fold roto-inversion axis= Mirror plane ($\bar{2}$=m)

Exercise 4.6

Show the operation of a 4-fold, 6-fold and 3-fold roto-inversion axis and demonstrate that 6-fold roto-inversion axis = 3 fold roto-axis + mirror plane m perpendicular to the 3-roto axis. That is why there is no special symbol for a 6-fold roto-inversion axis.

4-fold roto-inversion axis	**6-fold roto-inversion axis = 3 fold roto-axis + mirror plane m**

3-fold roto-inversion-axis

4.3.3 The 32 3D symmetry point groups

Similar as the 2D case, 3D lattices are regular arrays of "points" in space. A real crystal has atoms associated with these points i.e. there is motif

Crystal = lattice + motif

Examples:
Ni (and also Al, Cu, Pd..) has a face centered cubic (fcc) Bravais lattice with as motif one Ni atom at each lattice point. The Ni crystal has therefore the highest point symmetry that a fcc Bravais lattice can have. The diamond lattice is also face centered cubic (see section packing) but the motif consists of two carbon atoms, one at position (000) and the other at (1/4, ¼, ¼). It is easy to see that the diamond crystal has less symmetry then the Ni crystal, the reason being motif
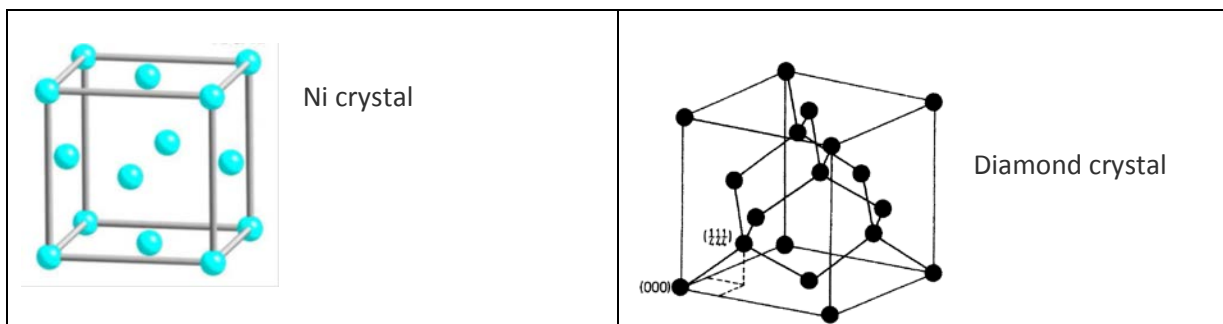
A point symmetric operation is an operation that leaves at least one point of a crystal fixed. A set of symmetry operations in a crystal (rotation, mirror plane, center of symmetry, rotary inversion) forms a point group symmetry. It does not consider translation but since it describes the symmetry of a crystal (and not just symmetry), the point groups are combinations of 3D symmetry elements passing through a point and compatible with translational symmetry. That is why a 5-fold rotation is not included since it is not self-consistent with translational symmetry (but it exists i.e. the quasicrystal)

Crystallographers have found that all symmetry operations that can exist in a point of a lattice can combine in 32 possible crystallographic point groups. These are listed in the table for the 7 crystal systems.

Nomenclature
- m is used in preference to $\bar{2}$
- mirror plane normal to symmetry axis, X/m with X=2,3,4 or 6
- where there are two distinct sets of mirrors parallel to ~~a~~symmetry axes mm is used
- Up to three symbols or combination of symbols are used to describe the
  point group and not more: for instance 3m, 23, 432 and 6/mmm The order is important

Crystal system	No center of symmetry	Center of symmetry	Min symmetry
Triclinic **a≠ b ≠ c** **α≠β≠γ≠90°**	1	$\bar{1}$	None
Monoclinic **a≠ b ≠ c** **α≠β≠γ≠90°**	2, m	2/m	1 diad or inversion diad (=mirror plane)
Orthorhombic **a≠ b ≠ c** **α=β=γ=90°**	222, 2mm	mmm	3 diads equally inclined at 90°
Tetragonal **a= b ≠ c** **α=β=γ=90°**	4, $\bar{4}$, 422, 4mm, $\bar{4}$2m	4/m, 4/mmm	1 tetrad or inversion tetrad
Rhombohedral **(trigonal)** **a= b = c** **α=β=γ≠90°**	3, 32, 3m	$\bar{3}$, $\bar{3}m$	1 triad or inversion triad (= triad + center of symmetry)
Hexagonal **a= b ≠ c** **α=β=90, γ=1200°**	6, $\bar{6}$, 622, 6mm, $\bar{6}$m2	6/m, 6/mmm	1 hexad or inversion hexad(= traid +mirror plane perpendicular)
Cubic **a= b = c** **α=β=γ=90°**	23, 432, $\bar{4}$3m	m3, m3m	4 triads equally inclined at 109.47°

Note that the point group symmetry of a crystal system is independent of whether the Bravais lattice is primitive or not. For instance all cubic lattices can have the same point group symmetry. This has important consequences: it is not possible to derive from the observed point symmetry of a crystal, whether the underlying Bravais lattice is primitive or not.

Coming back on our two examples, it is clear that Ni belongs to the symmetry point group that has the highest symmetry corresponding to a cubic Bravais lattice i.e m3m. Diamond on the other hand belongs to a lower symmetry point group of the cubic Bravais lattice, i.e. m3

Translational symmetry elements in 3D

As mentioned earlier, the point groups do not take into account the possible translational symmetries.
In 3D there are two extra types of translational symmetry elements (in 2D it was the glide line)

- The *glide plane.* They are usually symbolized by a,b,c according to which plane of the unit cell they are parallel. There is also the n glide, which is a glide along the half of a diagonal of a face, and the d glide, which is a fourth of the way along either a face or space diagonal of the unit cell
- The *screw axis*: a combination of a rotation and a translation that leaves the crystal unchanged. It is usually indicated by the rotation symbol with a lower index that specifies the translation as a portion of the lattice vector parallel to the rotation axis. Below the **example of a 2_1 screw axis**, it is a 180° (twofold) rotation followed by a translation of 1/2 of the lattice vector.
The 3_1 axis is also shown: a 120° (threefold) rotation followed by a translation of 1/3 of the lattice vector. The 3_2 axis is a 120° (threefold) rotation followed by a translation of 2/3 of the lattice vector.
-
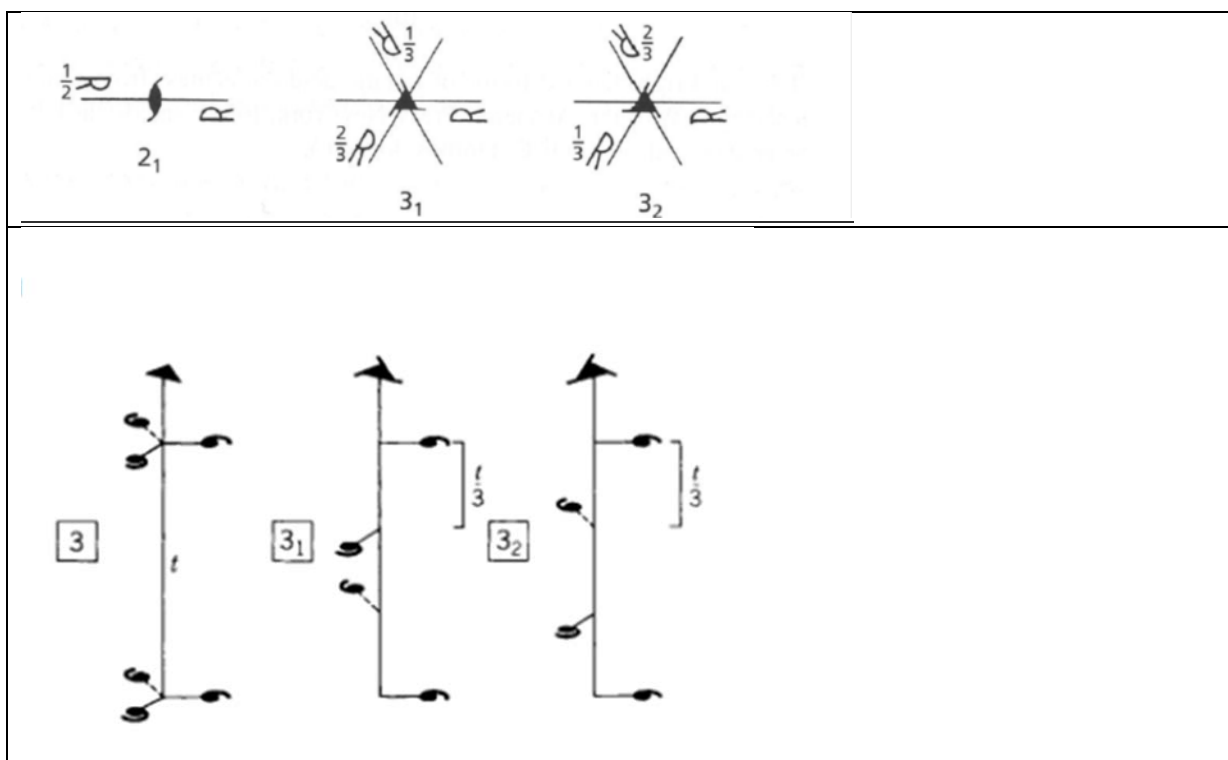
The possible screw axes are 2_1, 3_1, 3_2 ,4_1, 4_2, 4_3 ,6_1, 6_2, 6_3 ,6_4, 6_5 . Note that 3_1 and 3_2 are different and are not each other mirror image, they are called enantiomorphous

---

Exercise 4.7
Show the projection along the axis of a 4_1, 4_2, 4_3 screw axis using the asymmetric motif R

Exercise 4.8
Show the projection along the axis of a 6_1, 6_2, 6_3 ,6_4, 6_5 screw axis using the asymmetric motif R

3D view of all screw axes (http://ictwiki.iitk.ernet.in/wiki/index.php/Unit-1:_Introduction_to_Crystallography)

4.3.4 The 230 Space groups

Finally, when combining all 14 Bravais lattices with the 32 point symmetry groups and the extra translational symmetry elements, it can be demonstrated that there are 230 possible 3D patterns or space groups.
We will here not further elaborate on these space groups. What has to be understood is how they are constructed. The list and details can be found on the web
http://en.wikipedia.org/wiki/Crystallographic_point_group
http://en.wikipedia.org/wiki/Space_group

a stereographic projection of all space groups can be found on
http://img.chem.ucl.ac.uk/sgp/mainmenu.htm

Extra Exercises

4.9   To image space groups, often the stereographic projection is used: the stereographic projection is a particular mapping that projects a sphere onto a plane (see principle below). You will learn more details in the second part of the course. Here we need only the basics in order to be able to "read" the projections of the space groups.
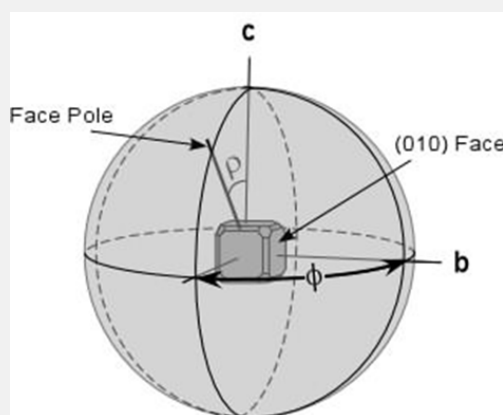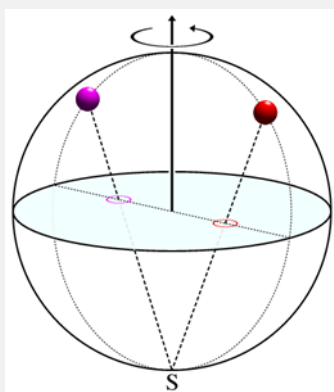
Show where in the stereographic circle the 3-fold rotation axes of a cube are lying

4.10   Show the highest symmetry elements that one can have in one point of the orthorombic, tetragonal, cubic and hexagonal system. Make also the 2D stereographic projection

4.11   Compare motif, lattice and point symmetry operations for Cu, Fe, NaCl, CsCl, CaF2

4.12   The hexagonal crystal system has only one Bravais lattice but can host 7 point symmetry groups
(6, $\bar{6}$, 622, 6mm, $\bar{6}$m2, 6/m, 6/mmm) Draw using the 2D visualization the symmetries for the 7 point groups

---

4.13 All hexagonal space groups that are compatible with the point group 6 can be derived from considering 6 and the possible screw axes. How many space groups can you find besides P6? Draw the hexagonal lattice with the symmetries corresponding to P6 and those to $P6_1$, $P6_2$, $P6_3$, $P6_4$, $P6_5$, $P\bar{6}$, P6/m . What is the difference? Use symbols

Where "+" or "-" means lying above or below the plane, the "comma" indicates a change of handedness, the last symbol means that all possibilities are present
http://img.chem.ucl.ac.uk/sgp/mainmenu.htm

4.14 The orthorhombic Crystal system contains 4 Bravais lattices P (primitive), I (body centered), A (or B,C one face centered) and F (face centered. The lattice is compatible with 3 point symmetry groups 222, 2mm and mmm. All space groups corresponding with the primitive lattice are obtained by combining the lattice with the point symmetry groups, including the possibility to replace
- a rotation axis by a screw axis
- a mirror plane "m" by a glide plane "a,b,c , n or d" (n= half of body or face diagonal, "d" fourth of the way along either a face or space diagonal of the unit cell)
Below all space groups that can be derived for the orthorhombic P lattice. The number corresponds with the number of the space group.

16. *P 2 2 2*   17. *P 2 2 2₁*   18. *P 2₁ 2₁ 2*   19. *P 2₁ 2₁ 2₁*   20. *C 2 2 2₁*

21. *C 2 2 2*   22. *F 2 2 2*   23. *I 2 2 2*   24. *I 2₁ 2₁ 2₁*   25. *P m m 2*

26. *P m c 2₁*   27. *P c c 2*   28. *P m a 2*   29. *P c a 2₁*   30. *P n c 2*

31. *P m n 2₁*   32. *P b a 2*   33. *P n a 2₁*   34. *P n n 2*   35. *C m m 2*

36. *C m c 2₁*   37. *C c c 2*   38. *A m m 2*   39. *A b m 2*   40. *A m a 2*

41. *A b a 2*   42. *F m m 2*   43. *F d d 2*   44. *I m m 2*   45. *I b a 2*

46. *I m a 2*   47. *P m m m*   48. *P n n n*   49. *P c c m*   50. *P b a n*

51. *P m m a*   52. *P n n a*   53. *P m n a*   54. *P c c a*   55. *P b a m*

56. *P c c n*   57. *P b c m*   58. *P n n m*   59. *P m m n*   60. *P b c n*

61. *P b c a*   62. *P n m a*   63. *C m c m*   64. *C m c a*   65. *C m m m*

66. *C c c m*   67. *C m m a*   68. *C c c a*   69. *F m m m*   70. *F d d d*

71. *I m m m*   72. *I b a m*   73. *I b c a*   74. *I m m a*

a) Draw in 2D the orthorhombic P lattice (projection along c axis> and show all additional symmetry operations of the space group   **P222, P222₁, Pmm2, Pcc2, Pba2, Pmmm.**

b) Draw also **C222** , **I222, F222,**

c)   Look at **Cmm2, Ima2, Fmm2** and verify if you can understand the symmetries

Use symbols above and others as defined on
http://img.chem.ucl.ac.uk/sgp/mainmenu.htm

4.15   The tetragonal crystal system has two Bravais lattices (P and I) and can host 7 symmetry point groups (4, $\bar{4}$, 422, 4mm, $\bar{4}$2m, 4/m, 4/mmm). Using 2D visualization and the same symbols, draw the tetragonal lattice and show all symmetry operations for P4, P4$_1$,P4$_2$ P$\bar{4}$, P4/m, P422.

4.16   Understand the difference in space group between
Cu: Fm$\bar{3}$m (nr 225), CsCl: Pm$\bar{3}$m (nr 221), Fe: Im$\bar{3}$m (nr 229)
Use the images and symbols used on
http://img.chem.ucl.ac.uk/sgp/mainmenu.htm

$Fm\bar{3}m$	$F\,4/m\,\bar{3}\,2/m$	$m\bar{3}m$	No. 225

1 x, y, z	25 $\bar{x}, \bar{y}, \bar{z}$
2 $x, \bar{y}, \bar{z}$	26 $\bar{x}, y, z$
3 $\bar{x}, y, \bar{z}$	27 $x, \bar{y}, z$
4 $\bar{x}, \bar{y}, z$	28 $x, y, \bar{z}$
5 z, x, y	29 $\bar{z}, \bar{x}, \bar{y}$
6 $\bar{z}, \bar{x}, y$	30 $z, x, \bar{y}$
7 $z, \bar{x}, \bar{y}$	31 $\bar{z}, x, y$
8 $\bar{z}, x, \bar{y}$	32 $z, \bar{x}, y$
9 y, z, x	33 $\bar{y}, \bar{z}, \bar{x}$
10 $\bar{y}, z, \bar{x}$	34 $y, \bar{z}, x$
11 $\bar{y}, \bar{z}, x$	35 $y, z, \bar{x}$
12 $y, \bar{z}, \bar{x}$	36 $\bar{y}, z, x$
13 $x, \bar{z}, y$	37 $\bar{x}, z, \bar{y}$
14 $x, z, \bar{y}$	38 $\bar{x}, \bar{z}, y$
15 $\bar{x}, \bar{z}, \bar{y}$	39 x, z, y
16 $\bar{x}, z, y$	40 $x, \bar{z}, \bar{y}$
17 $z, y, \bar{x}$	41 $\bar{z}, \bar{y}, x$
18 $\bar{z}, y, x$	42 $z, \bar{y}, \bar{x}$
19 $\bar{z}, \bar{y}, \bar{x}$	43 z, y, x
20 $z, \bar{y}, x$	44 $\bar{z}, y, \bar{x}$
21 $\bar{y}, x, z$	45 $y, \bar{x}, \bar{z}$
22 $y, \bar{x}, z$	46 $\bar{y}, x, \bar{z}$
23 $\bar{y}, \bar{x}, \bar{z}$	47 y, x, z
24 $y, x, \bar{z}$	48 $\bar{y}, \bar{x}, z$

$+ (0,\tfrac{1}{2},\tfrac{1}{2}), (\tfrac{1}{2},0,\tfrac{1}{2}), (\tfrac{1}{2},\tfrac{1}{2},0)$

$Pm\bar{3}m$ $P\,4/m\,\bar{3}\,2/m$ $m\bar{3}m$ No. 221

1 x, y, z	25 $\bar{x}, \bar{y}, \bar{z}$
2 $x, \bar{y}, \bar{z}$	26 $\bar{x}, y, z$
3 $\bar{x}, y, \bar{z}$	27 $x, \bar{y}, z$
4 $\bar{x}, \bar{y}, z$	28 $x, y, \bar{z}$
5 z, x, y	29 $\bar{z}, \bar{x}, \bar{y}$
6 $\bar{z}, \bar{x}, y$	30 $z, x, \bar{y}$
7 $z, \bar{x}, \bar{y}$	31 $\bar{z}, x, y$
8 $\bar{z}, x, \bar{y}$	32 $z, \bar{x}, y$
9 y, z, x	33 $\bar{y}, \bar{z}, \bar{x}$
10 $\bar{y}, z, \bar{x}$	34 $y, \bar{z}, x$
11 $\bar{y}, \bar{z}, x$	35 $y, z, \bar{x}$
12 $y, \bar{z}, \bar{x}$	36 $\bar{y}, z, x$
13 $x, \bar{z}, y$	37 $\bar{x}, z, \bar{y}$
14 $x, z, \bar{y}$	38 $\bar{x}, \bar{z}, y$
15 $\bar{x}, \bar{z}, \bar{y}$	39 x, z, y
16 $\bar{x}, z, y$	40 $x, \bar{z}, \bar{y}$
17 $z, y, \bar{x}$	41 $\bar{z}, \bar{y}, x$
18 $\bar{z}, y, x$	42 $z, \bar{y}, \bar{x}$
19 $\bar{z}, \bar{y}, \bar{x}$	43 z, y, x
20 $z, \bar{y}, x$	44 $\bar{z}, y, \bar{x}$
21 $\bar{y}, x, z$	45 $y, \bar{x}, \bar{z}$
22 $y, \bar{x}, z$	46 $\bar{y}, x, \bar{z}$
23 $\bar{y}, \bar{x}, \bar{z}$	47 y, x, z
24 $y, x, \bar{z}$	48 $\bar{y}, \bar{x}, z$

$Im\bar{3}m$ $I\,4/m\,\bar{3}\,2/m$ $m\bar{3}m$ No. 229

1 x, y, z	25 $\bar{x}, \bar{y}, \bar{z}$
2 $x, \bar{y}, \bar{z}$	26 $\bar{x}, y, z$
3 $\bar{x}, y, \bar{z}$	27 $x, \bar{y}, z$
4 $\bar{x}, \bar{y}, z$	28 $x, y, \bar{z}$
5 z, x, y	29 $\bar{z}, \bar{x}, \bar{y}$
6 $\bar{z}, \bar{x}, y$	30 $z, x, \bar{y}$
7 $z, \bar{x}, \bar{y}$	31 $\bar{z}, x, y$
8 $\bar{z}, x, \bar{y}$	32 $z, \bar{x}, y$
9 y, z, x	33 $\bar{y}, \bar{z}, \bar{x}$
10 $\bar{y}, z, \bar{x}$	34 $y, \bar{z}, x$
11 $\bar{y}, \bar{z}, x$	35 $y, z, \bar{x}$
12 $y, \bar{z}, \bar{x}$	36 $\bar{y}, z, x$
13 $x, \bar{z}, y$	37 $\bar{x}, z, \bar{y}$
14 $x, z, \bar{y}$	38 $\bar{x}, \bar{z}, y$
15 $\bar{x}, \bar{z}, \bar{y}$	39 x, z, y
16 $\bar{x}, z, y$	40 $x, \bar{z}, \bar{y}$
17 $z, y, \bar{x}$	41 $\bar{z}, \bar{y}, x$
18 $\bar{z}, y, x$	42 $z, \bar{y}, \bar{x}$
19 $\bar{z}, \bar{y}, \bar{x}$	43 z, y, x
20 $z, \bar{y}, x$	44 $\bar{z}, y, \bar{x}$
21 $\bar{y}, x, z$	45 $y, \bar{x}, \bar{z}$
22 $y, \bar{x}, z$	46 $\bar{y}, x, \bar{z}$
23 $\bar{y}, \bar{x}, \bar{z}$	47 y, x, z
24 $y, x, \bar{z}$	48 $\bar{y}, \bar{x}, z$

$+ \left(\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}\right)$

4.17   Compare the symmetry point operations in Cu ($m\bar{3}m$) and Zinc Blende, ZnS, ($\bar{4}3m$) and understand the different space groups
Cu: $Fm\bar{3}m$ (nr 225), ZnS: $F\bar{4}3m$ (nr 216)

4.18	Compare the symmetry point operations of two hexagonal systems: Zn (6/mmm) and Wurtzite, ZnS, (6mm) and understand the different space groups Zn: **P63/mmc (nr 194)**, ZnS: : P6$_3$mc (nr 186)
4.19	Diamond has a FCC lattice and belongs to the space group Fd$\overline{3}$m space group, point symmetry group. Determine the screw axis and glide planes in the diamond structure.
4.20	Why has Zinc Blende not a glide plane, although atoms are sitting in similar positions?

5. The mathematical description of a lattice

5.1 The unit cell

To define the geometry of the unit cell in 3 dimensions we choose a right-handed set of crystallographic axes, x, y, and z, which point along the edges of the unit cell. The origin of our coordinate system coincides with one of the lattice points.

The length of the unit cell along the x, y, and z direction are defined as a, b, and c. The angles between the crystallographic axes are defined by:

α = the angle between b and c

β = the angle between a and c

γ = the angle between a and b
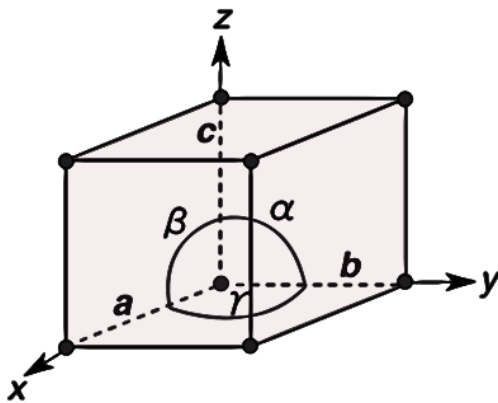
a, b, c, α, β, γ are collectively known as the lattice parameters (often also called 'unit cell parameters', or just 'cell parameters').

Lattice points

They are given by the coordinates in the coordinate system. For instance

5.2 Lattice direction

Lattice direction

A lattice vector is a vector joining any two lattice points. Any lattice vector can be written as a linear combination of the unit cell vectors a, b, and c. The direction is the vector **t** passing though the origin of the lattice

t= u**a** + v**b**+ w**c**

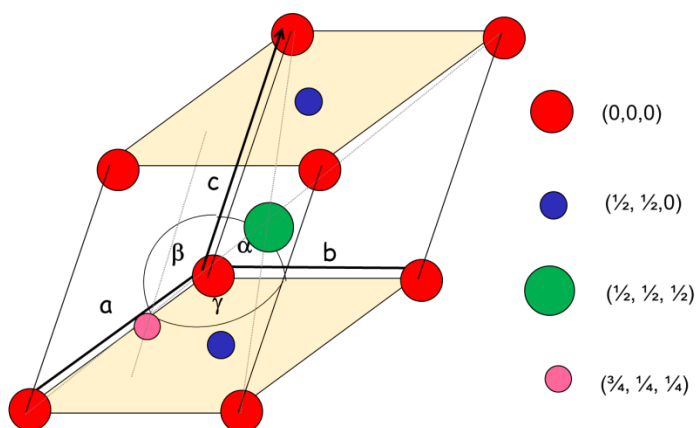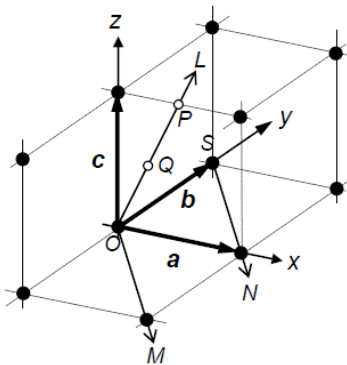where u,v and w are the coordinates of a point (any point) in this direction when a,b and c are the unit vectors resp. along the x,y,z axis. Note that the vectors are either written bold or have a bar i.e. $\vec{a}, \vec{b}, \vec{c}$

The direction is written in the form   [UVW] where U,V,W are integers.

Example:

Direction OP

Coordinates point P:	½, 0,1	vector OP = ½ **a** + **c**	or [1/2 0 1]
Coordinates point Q:	½ ,0, ½	vector OQ = ¼ **a** + ½ **c**	or [1/4 0 ½]

Both vectors define the direction OP=OQ=OL. Directions are expressed with whole numbers i.e the [102] direction

Direction SN
consider OM which is parallel to SN
Coordinates OM: 1, -1,0
Vector OM= **a − b**
Direction SN and OM: [1$\bar{1}$0]   Note: when the number is negative, a bar is added above the number

⇨ direction of the basics lattice vectors a,b,c are resp. [100], [010] and [001]

A family of directions

Due to the symmetry of crystal systems, different directions can be equivalent.
e.g. For cubic crystals, the directions [1 0 0], [-1 0 0], [0 1 0], [0 -1 0], [0 0 1], [0 0 -1] are all

equivalent by symmetry. There is a special notation for directions of the same form: <100>, which in this case means the family made of the three basis axis **a,b,c**

Similarly, there are 8 equivalent <111> directions in a cubic system , as shown below. The number of equivalent directions is called the multiplicity of the direction.
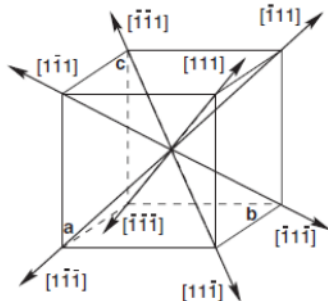
Angles between directions

Angle between two directions is given by the scalar product of two vectors of the resp. directions
t$_1$.t$_2$= t$_1$.t$_2$ cosϑ where t$_1$ and t$_2$ are the length of the lattice vectors **t$_1$** and **t$_2$** , ϑ is the angle between two vectors

Or in the notation of the directions
The angle between the directions [u$_1$ v$_1$ w$_1$] and [u$_2$ v$_2$ w$_2$] is

$$\cos \vartheta = \frac{u_1 u_2 + v_1 v_2 + w_1 w_2}{\sqrt{u_1{}^2 + v_1{}^2 + w_1{}^2} \cdot \sqrt{u_2{}^2 + v_2{}^2 + w_2{}^2}}$$

5.3 Lattice planes

A lattice plane is a plane passing through at least three lattice points. Because of the translational symmetry of the Bravais lattice, a lattice plane contains an infinite number of lattice points which form a 2D Bravais lattice. Below a picture of two types of lattice planes in a simple cubic Bravais lattice. As exercise, draw the 2D lattice of both type of planes. (taken from Ashcroft-Mermin fig 5.3)
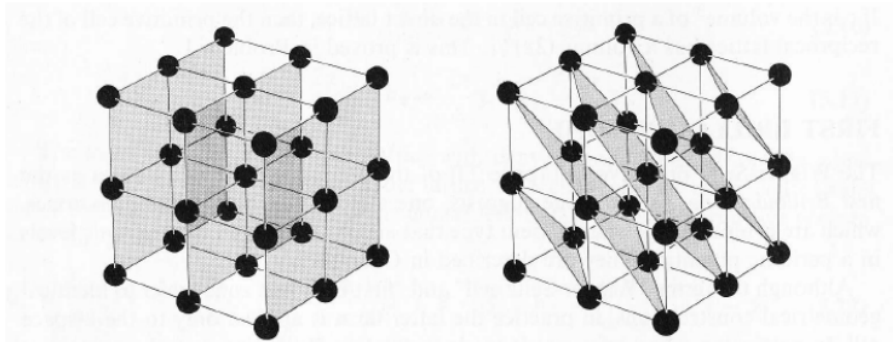
A family of lattice planes is a set of parallel equally spaced lattice planes which together contain all the points of the Bravais lattice. Such families play an important role in X-ray diffraction as we will see later.). In the example above all planes on the left hand side picture belong to one family, all planes on the right hand side to another family

Notation of family of planes in crystals

The general equation of a plane is of the form

px + qy + rz=1

and any other plane parallel to this can be written as px + qy + rz=c
The value of p,q,r,c are found by filling into the equation the coordinates of points lying on the plane

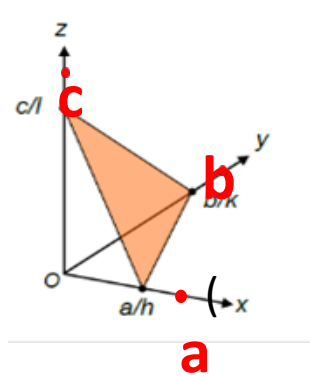In crystallography one expresses the coordinates as a fraction of the unit vector along the axis x,y,z.

$$\rightarrow \frac{h}{a}x + \frac{k}{b}y + \frac{l}{c}z = 1$$

A lattice plane family is characterized by its Miller indices (hkl)
The Miller indices are integers with no common factors. Negative indices are indicated with horizontal bars, as in directions.

Any other plane from the same family can be written as

$$\frac{h}{a}x + \frac{k}{b}y + \frac{l}{c}z = C$$

where C is a constant. The value of C is determined by the coordinates of a point in the plane.
C = zero is the plane through the origin of the unit cell

In practice,
To determine the Miller indices of a family of planes one takes the plane which is nearest to the origin but does not go through the origin. The Miller indices of the family are proportional to the *inverse* of the intercepts of that plane with the unit cell (in the basis of the lattice vectors). If a plane is parallel with a unit vector, the intersection is at infinity and the Miller index will be zero. If the plane intersects the unit cell in the origin, the plane has to be shifted away from the origin to the find the Miller indices.

Notation used:
Miller indices of a family of planes: (hkl)

It becomes clear when looking at an example

OM= a
OS=b
OE=c   Plane EMS // plane E'M'S'
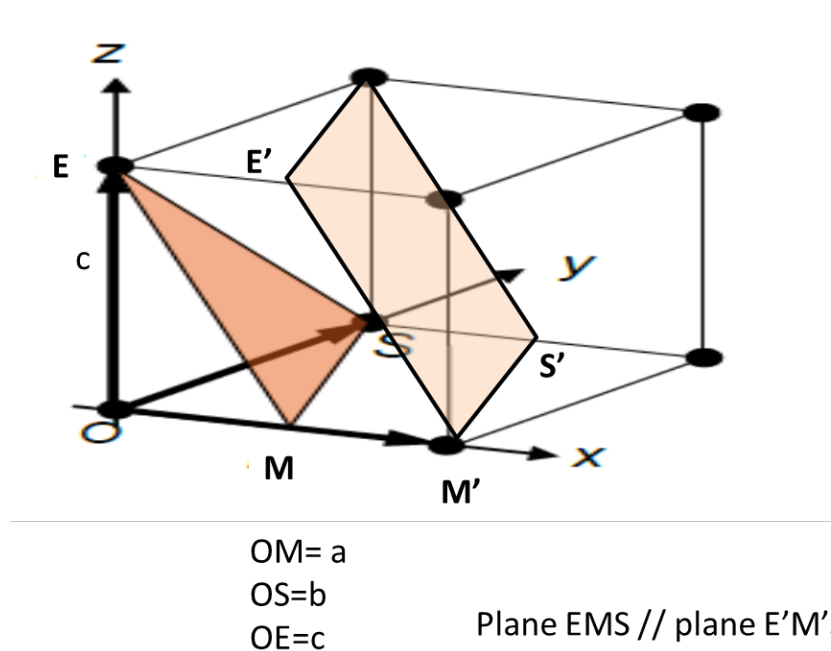
The planes EMS and E'M'S' belong to the same family of the Bravais lattice determined by the unit cell with unit vectors **a,b,c** along the x,y,z axis

The intersects of plane EMS: ½, 1, 1,
Inverse of the intercepts: 2,1,1, so the   Miller index of this family is (211)

The same Miller indices would have been obtained by considering E'M'S'
Intersects: 1,2,2
Inverse of intersects: 1, ½,½
which expressed as whole numbers give the same Miller indices (211)

Multiplicity of a plane

Miller indices of the set of all planes that are equivalent by symmetry of the lattice: {hkℓ} . The number of equivalent planes is called the multiplicity of the (hkl) plane. This is strongly dependent on the symmetry i.e. on the crystal system.

For instance in a cubic crystal system the (110) and (011) planes belong to the same {110} set of planes. However in a tetragonal system the (110) and (011) are not equivalent and belong to different sets {110} and {011}.

Exercise 5.1

Show that in the tetragonal system the (110) and (011) planes are not equivalent

Exercises 5.2

For the following structures, define:

        a.   The crystal system
        b.   The indices of the directions

(remember to use a right hand axes)
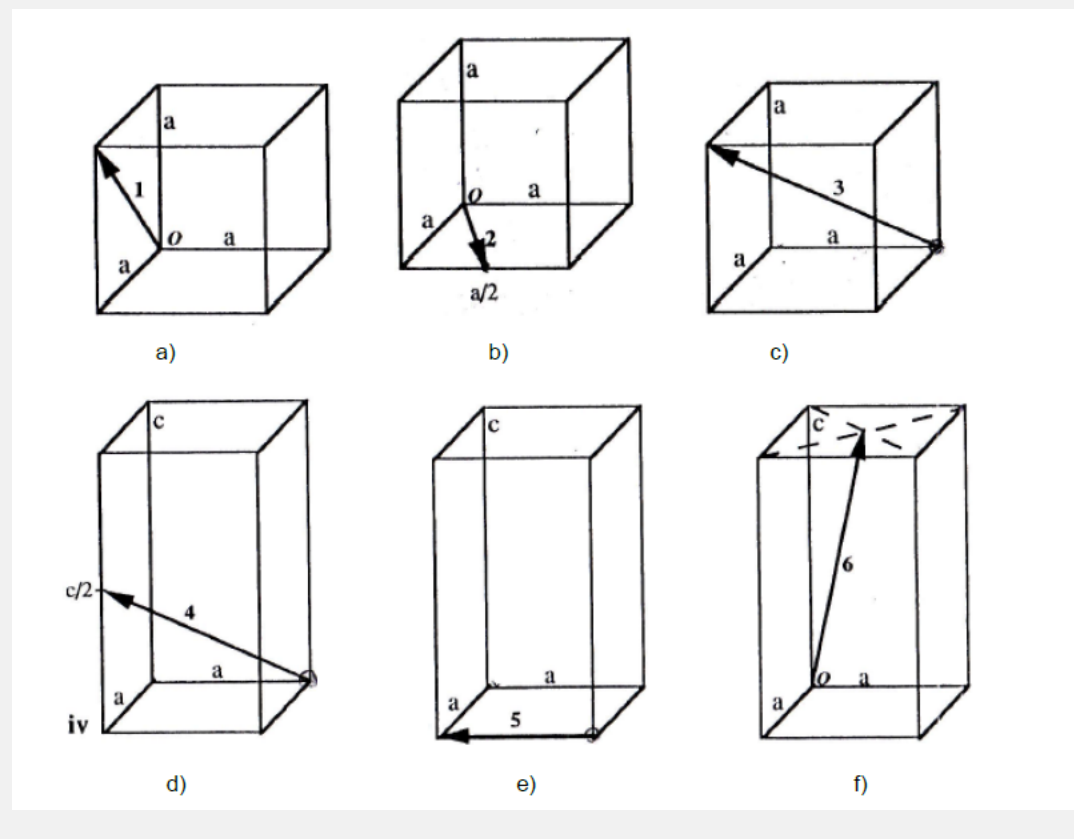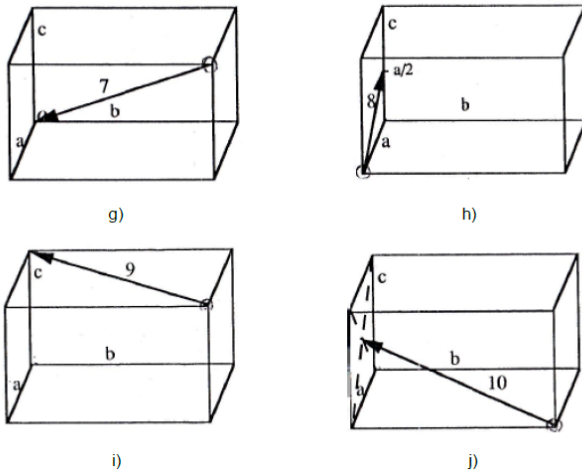
Exercise 5.3

Draw cells showing the [121] direction in each of the following latticies:

       i) cubic
       ii) tetragonal where a = l, c = Z
       iii) orthorhombic where a = 1, b = 2. c = 3

Exercise 5.4

For the following stuctures, what is
       -    the Bravais lattice
       -    the Miller Indices of the shaded plane
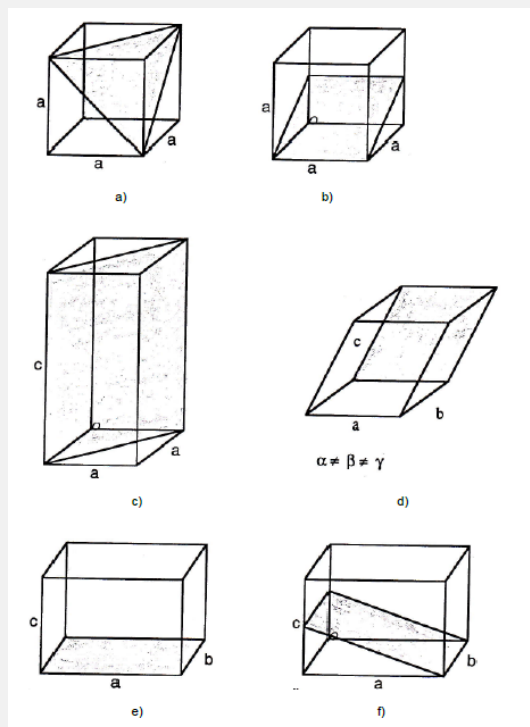
Exercise 5.5

Draw unit cells showing the planes given. Draw a total of 10 unit cells, one for each plane:

Cubic: (111), (013), (1$\bar{1}$1), (101)

Orthorhombic; (001), (123), (010)

Tetragonal: (011), (122), (112)
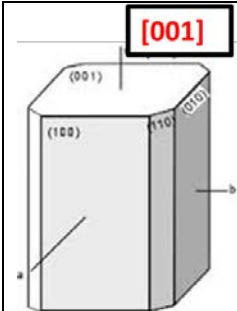
Exercise 5.6

For the cubic system, write out all the families (sets) of planes included in each of the following:

{112}, {110}, {400}, {321},

5.4 Intersections of planes, zone axis

A zone is defined as "a set of planes in a crystal whose intersections are parallel". The common direction of the intersections is called the zone axis. Therefore one often has to calculate the intersection of two planes

For instance the [001] direction is the zone axis of the {100} and {110} family of planes.

The calculation of the zone axis is very important during electron diffraction microscopy and Laue diffraction

How to calculate a zone axis?

Assume there are two crystal planes ($h_1 k_1 l_1$) and ($h_2 k_2 l_2$) which are not parallel to each other. The intersection of these two planes is a line. What is the direction of the lines? Assume the direction of the line is [$u\,v\,w$]. The two planes, when translated to the origin of the unit cell are

$$\begin{cases} \dfrac{h_1}{a}x + \dfrac{k_1}{b}y + \dfrac{l_1}{c}z = 0 \\ \dfrac{h_2}{a}x + \dfrac{k_2}{b}y + \dfrac{l_2}{c}z = 0 \end{cases}$$

The intersection is the ensemble of points lying on both planes. Mathematically this is a problem of three variables, two equations so only the ratios of the variables can be determined..

After some math (divide the equations by one parameter) one can show that the ratios fulfill

$$x:y:z = a \begin{vmatrix} k_1 & l_1 \\ k_2 & l_2 \end{vmatrix} : b \begin{vmatrix} l_1 & h_1 \\ l_2 & h_2 \end{vmatrix} : c \begin{vmatrix} h_1 & k_1 \\ h_2 & k_2 \end{vmatrix}$$

Of course one can additionally require the intersection line is shifted trough the origin. The base vector [uvw] is then defined as

$$\begin{bmatrix} \dfrac{x}{a} & \dfrac{y}{b} & \dfrac{z}{c} \end{bmatrix} = \begin{bmatrix} u & v & w \end{bmatrix} = \begin{bmatrix} \begin{vmatrix} k_1 & l_1 \\ k_2 & l_2 \end{vmatrix} & \begin{vmatrix} l_1 & h_1 \\ l_2 & h_2 \end{vmatrix} & \begin{vmatrix} h_1 & k_1 \\ h_2 & k_2 \end{vmatrix} \end{bmatrix}$$

Or

$u=(k_1 l_2 - k_2 l_1)$, $v=(l_1 h_2 - l_2 h_1)$ and $w=(h_1 k_2 - k_1 h_2)$

It is not necessary to know the above derivation for the exam. However you must know the trick to calculate the zone axis

Trick to calculate the zone axis

2- Miller indices of the two faces have to be known, $(h_1 \, k_1 \, l_1)$ and $(h_2 \, k_2 \, l_2)$
3- The indices of each face are written twice.
4- Using cross multiplication of determination law.

:Example: The indices of the two faces are (011) and (111), find the zone axis [uvw].

    0 1 1 0 1 1

    1 1 1 1 1 1

  u = 1x1 – 1x1 =0
  v = 1x1 – 0x1 =1
  w = 0x1 – 1x1 =-1

So the zone axis direction [uvw]= $[01\bar{1}]$

Zone axis and "Weiss zone law"

Weiss Zone Law: A zone axis [u v w] is parallel to a family of lattice planes of Miller indices (hkl) if:

uh + vk + wl = 0

This is a way to check whether an axis is the zone axis of a family of planes

Prove:
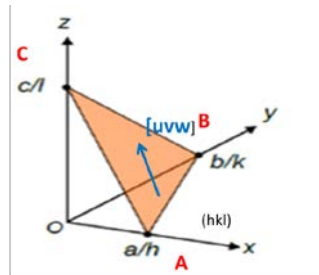
Any lattice vector [uvw] in a plane (hkl) can be formed by a linear combination of two other lattice vectors
I.e. for instance of the vectors AB $[\overline{1/h}$ 1/k   0] and AC $[\overline{1/h}$ 0   1/l]

In other words, if [uvw] lies in the plane (hkl) then
[uvw] =λ $[\overline{1/h},$ 1/k 0] + μ$[\overline{1/h}$ 0 1/l]

Or   u= -1/h(λ+μ)   v=λ/k   w=μ/l

By substituting λ and μ in the equation for u one becomes   hu + kv+lw=0

Examples for the use of Weiss law: do $[11\bar{1}]$ and $[1\bar{1}1]$ lie in (101)?
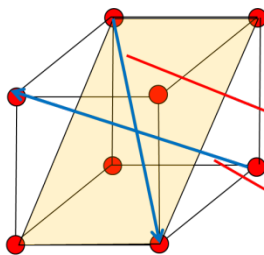
Example: does $[11\bar{1}]$ lie in (101):

(1 × 1) + (1 × 0) + (1 × -1) = 0

But for $[1\bar{1}1]$:

(1 × 1) + (-1 × 0) + (1 × 1) = 2

Examples of directions and Miller indices for planes in the cubic system

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

$\langle 100 \rangle$

$[110], [1\bar{1}0], [\bar{1}10], [\bar{1}\bar{1}0]$
$[011], [0\bar{1}1], [01\bar{1}], [0\bar{1}\bar{1}]$
$[101], [\bar{1}01], [10\bar{1}], [\bar{1}0\bar{1}],$

$\langle 110 \rangle$

$[111], [\bar{1}\bar{1}\bar{1}]$
$[\bar{1}11], [1\bar{1}\bar{1}]$
$[1\bar{1}1], [\bar{1}1\bar{1}]$
$[11\bar{1}], [\bar{1}\bar{1}1]$

$\langle 111 \rangle$

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

$\{100\}$

$(110), (1\bar{1}0), (\bar{1}10), (\bar{1}\bar{1}0)$
$(011), (0\bar{1}1), (01\bar{1}), (0\bar{1}\bar{1})$
$(101), (\bar{1}01), (10\bar{1}), (\bar{1}0\bar{1}),$

$\{110\}$

$(111), (\bar{1}\bar{1}\bar{1})$
$(\bar{1}11), (1\bar{1}\bar{1})$
$(1\bar{1}1), (\bar{1}1\bar{1})$
$(11\bar{1}), (\bar{1}\bar{1}1)$

$\{111\}$

Important note :

in the cubic system the (hkl) plane and the vector [hkl] are normal to one another but this characteristic is unique to the cubic crystal system and does not apply to crystal systems of lower symmetry. This has important consequences when anal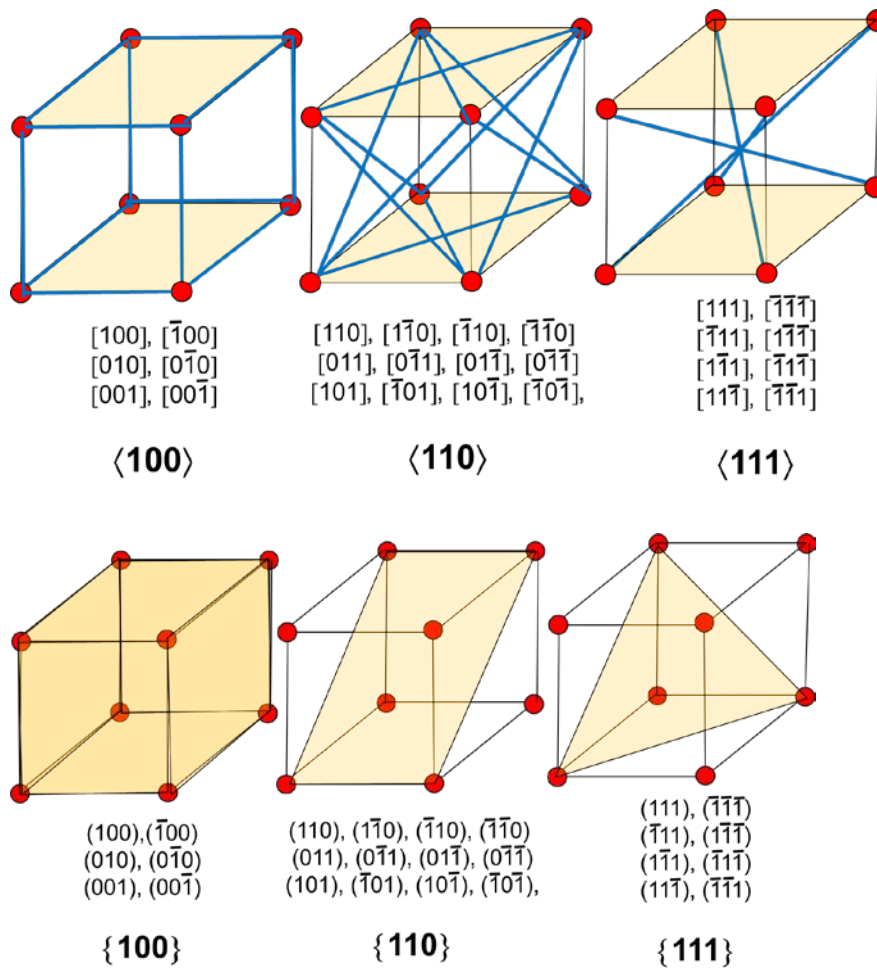yzing diffraction patterns, we will come back to that later. As an exercise, verify that the [011] direction is not perpendicular to the (011) plane in the tetragonal system.

Exercises 5.7

Answer the following :

        a. Does $[\bar{3}21]$ lie parallel to (111)?

        b. Does [110] lie parallel to $(0\bar{1}0)$?

        c. Does [210] lie parallel to (110) ?

        d. Does [111] lie parallel to $(01\bar{1})$?

        e. Does $[\bar{3}11]$ lie parallel to (1-12) ?

Exercises 5.8

What are the directions of intersections for the following pairs of planes?

        f.   (110) and ($1\bar{1}1$)

        g. (010) and ($0\bar{1}0$)

        h. (111) and ($1\bar{2}2$)

        i.   ($0\bar{1}0$) and ($01\bar{1}$)

        j.   (012) and (001)

Exercises 5.9

Find the planes in which the following pairs of directions lie.

        k. [$2\bar{1}1$] and [$1\bar{1}1$]

        l.   [100] and [$1\bar{1}\,\bar{1}$]

        m. [$20\bar{1}$] and [$1\bar{2}0$]

        n. [102] and [$3\bar{1}1$]

        o. [010] and [$4\bar{1}1$]

5.5 Miller indices for trigonal and hexagonal Bravais lattices: Miller-Bravais symbols

The above Miller indices and derived rules are valid for all Bravais lattices. They are however not very convenient for trigonal (or rhombohedral) and hexagonal systems. Consider the picture below
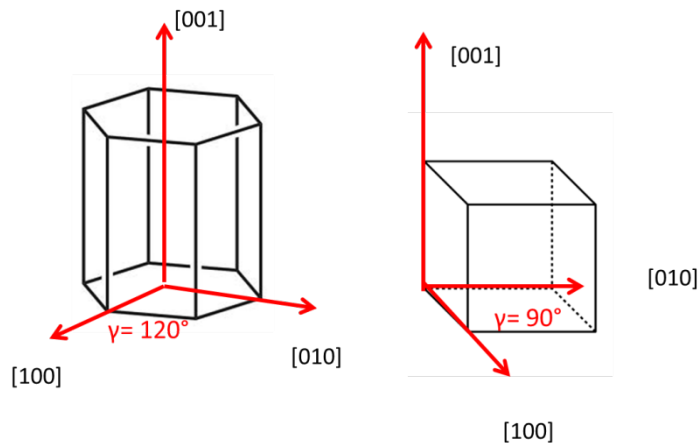
We have seen in the previous section that, for a cubic system, we can list all the members of a family {*hkl*} by writing down all the permutations of the three numbers *h*, *k*, and *l* and their negatives.

 If the symmetry of the system is lower than cubic, then the members of a family are still given by permutations, but not all permutations belong to the same family. This was shown for instance in the tetragonal system for {110} and {011}. In the rhombohedral system we have {100} = {*(100), (-100), (010), (0-10), (001), (00-1)*} as a family set of equivalent planes. In the orthorhombic system {100} = {*(100), (-100)*} contains just two type of planes. The only exception to this rule of index permutations is the *hexagonal crystal system*.
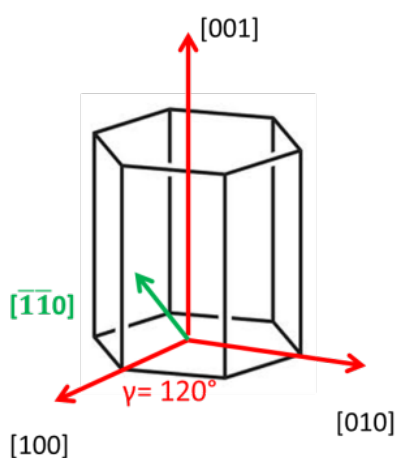

In the hexagonal system one does not obtain equivalent planes by permutation of the numbers

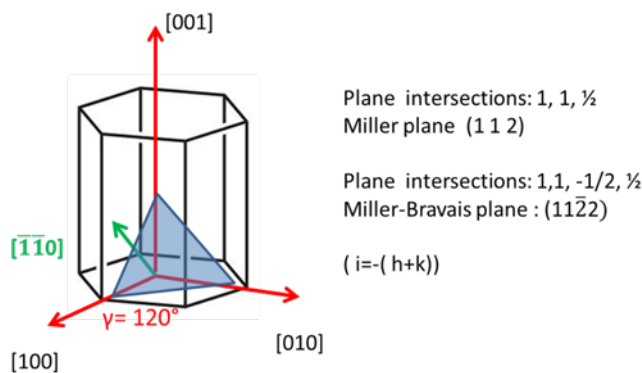Here we would have in the Miller notation for instance {100}$_{hexagonal}$ = (100), (010) and (-110)

To overcome this problem, often a fourth axis is used in the hexagonal system: i.e. an . The index on this axis is called "i"

The Miller-Bravais indices for a plane are now
(hkil) where i= -(h+k)

This notation has the advantage that the planes of the zone belonging to the z-axis can be obtained by permutation
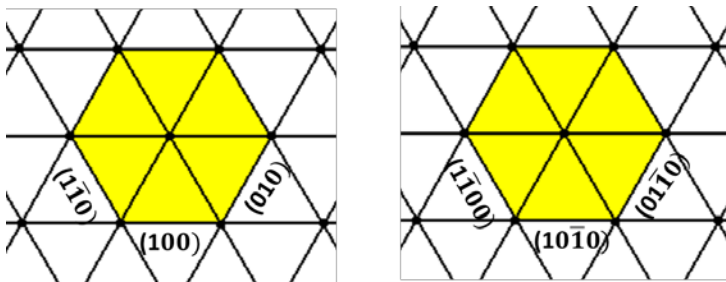
In this way, the meaning of the four Miller-Bravais indices of a plane is the same as the three Miller indices i.e. the inverse of the intersection of the plane with the four axes

Plane intersections: 1, 1, ½
Miller plane (1 1 2)

Plane intersections: 1,1, -1/2, ½
Miller-Bravais plane : (11$\bar{2}$2)

(i=-(h+k))

The notation for zone axis has then also a 4-digit index, however determining these vectors i.e. the components of a vector using four base vectors in a 3D space is not straight forward. Essentially, the components of the vector [UVTW] are adapted so that the condition T= -(U + V) is fulfilled.

In practice the procedure is to determine the zone axis [uvw] and then transform according to

U = (2u-v)/3
V = (2v-u)/3
T = -(u+v)/3 = -(U+V)
W=w

The reserves transformation is easier
u=(U-T)
v=(V-T)
w=W

When using the Miller-Bravais symbols, the zone law axis becomes
hU+kW+iT+lW=0

Exercises 5.10

Draw hexagonal lattices showing the following planes. Draw a new lattice for each plane:

(0001)

$(1\bar{1}00)$

$(10\bar{1}0)$

$(10\bar{1}1)$

Exercises 5.11

Index the directions shown below using four index notation.
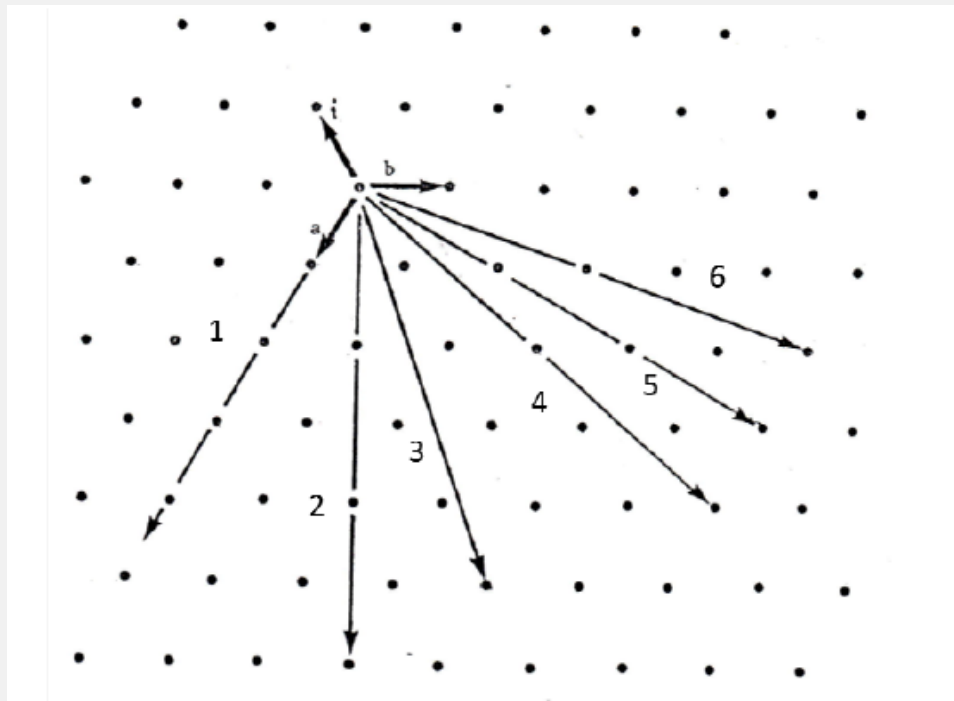
Extra exercizes

5.12 Determine the indices for the directions shown in the following cubic unit cell
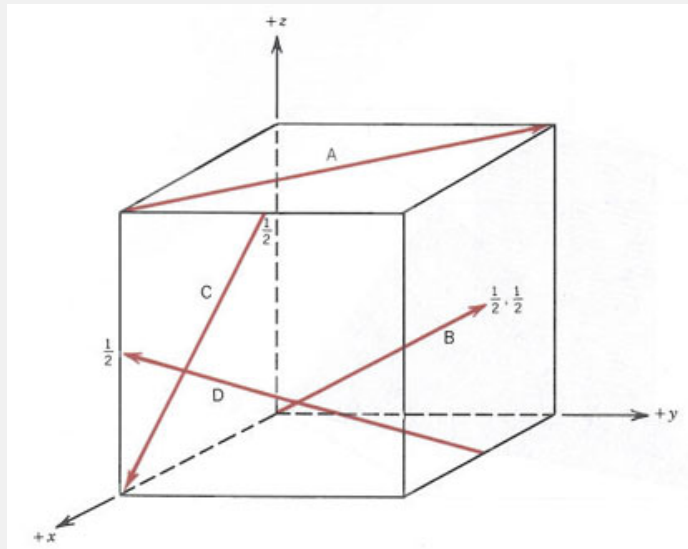
5. 13 Sketch within a cubic unit cell the following planes

a) (1 0 -1)
b) (2 -1 1)
c) (0 1 2)
d) (3 -1 3)
e) (-1 1 -1)
f) (-2 1 2)
g) (3 -1 2)
h) (3 0 1)

5.14 Determine the Miller indices for the planes shown in the following unit cell:
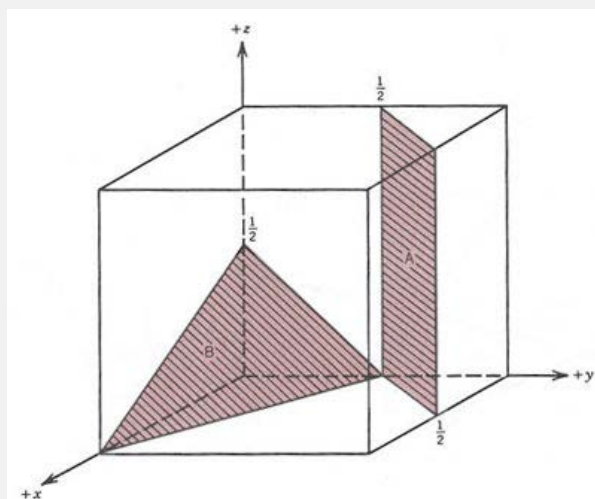
5.15   Within a cubic unit cell, sketch the following directions

a) [1 0 1]
b) [2 1 1]
c) [1 0 -2]
d) [3 -1 3]
e) [-1 1 -1]
f) [-2 1 2]
g) [3 -1 2]
h) [3 0 1]

6 Diffraction and interference from crystals

Till now we have learned that crystals have periodic lattices and can exhibit a variety of symmetries. In this section we are going to discuss methods allowing the detection of the crystal symmetry and lattices. For that we are going to use a "probe" i.e. a radiation that is scattered by an atom. Then we will use well-known interference and diffraction laws to show that the angles of constructive interference can be related to the distance between lattice planes

In what follows, the basics of diffraction and interference are summarized. We start by refreshing the concepts of interference and diffraction and elaborate the conditions for light falling onto a grating with gaps that are parallel lines. Then we will discuss diffraction of waves from a crystal lattice. Later on we will briefly discuss the possible radiation probes (Xrays, neutrons and electrons).

6.1 General aspects of diffraction and interference
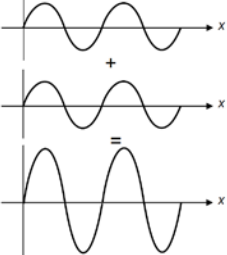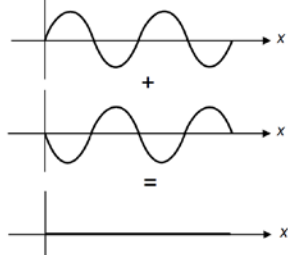
Interference

When two or more propagating waves of same type are incident on the same point, they will interfere and the total displacement at that point is equal to the vector sum of the displacements of the individual waves: this is called the superposition principle. After they have passed they return to their original forms. This is true for all waves, i.e. if they have the same frequency, amplitude or phase

At the point they meet, the two waves will combine to give a resultant wave whose amplitude (or intensity) may be greater or less than the original two waves. If a crest of a wave meets a crest of another wave of the same frequency at the same point, then the magnitude of the displacement is the sum of the individual magnitudes – this is constructive interference. If a crest of one wave meets a trough of another wave then the magnitude of the displacements is equal to the difference in the individual magnitudes – this is known as destructive interference. If the waves are coherent i.e. they have a constant phase relationship between each other, they will interfere to produce a fixed pattern.

Interference (and also diffraction) are easiest to visualize with mechanical waves although similar phenomena occur with electromagnetic waves (Note: an electromagnetic wave can propagate trough vacuum, i.e. it does not need a medium to transmit its energy; a mechanical wave requires a medium to transport its energy)

Below an illustration of interference for a one-dimensional transverse mechanical wave (imagine a wave traveling along a rope)

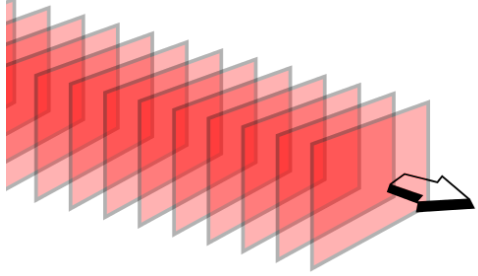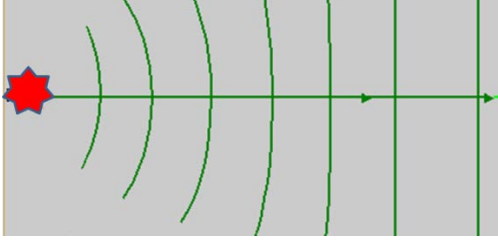| Constructive interference: two waves with the same wavelength and a phase difference of nλ (n = integer)	Destructive interference: : two waves with the same wavelength and a phase difference of (n+1/2)λ (n = integer)

A nice way to demonstrate interference patterns is with water waves (this are surface waves, for more info see http://www.physicsclassroom.com/class/waves/u10l1c.cfm) . The waves are here coming from a point source and if they have a constant phase relationship, they will create the well known interference patterns on the surface http://people.rit.edu/andpph/exhibit-splashes.html
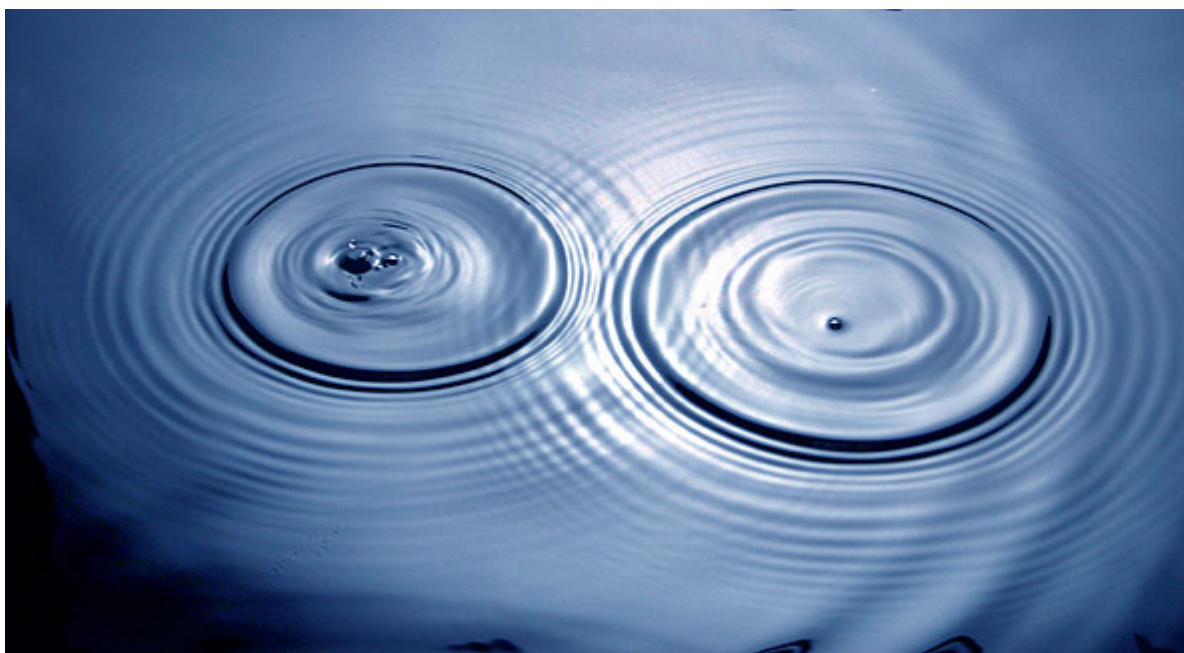
Weather ones sees at a point a crest will depend on the phase difference of the waves arriving in the point. This phase difference depends on the difference in path the wave has to travel
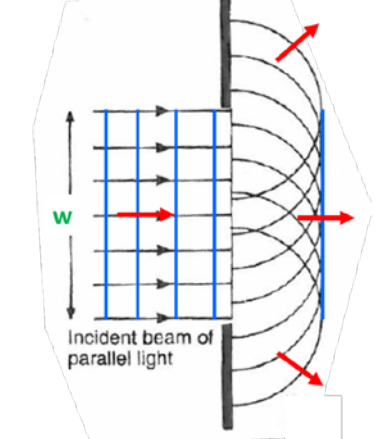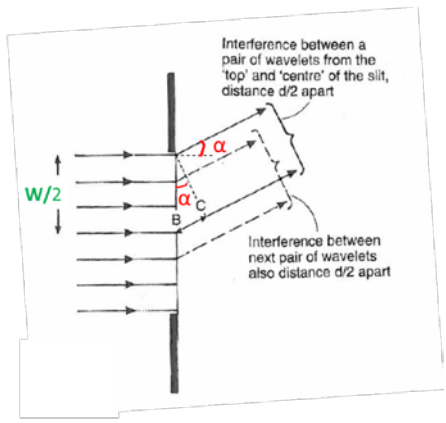
The waves we will deal with here in this course are 3 dimensional electromagnetic waves. For such waves threads are radiating out in all directions. Connecting points of constant phase makes a spherical surface (a bit like the layers of an onion). Such a wave is called a spherical wave. A long way from a coherent source, the curve of the wave fronts (the surfaces of constant phase) becomes flat surfaces (plane surfaces) in the case of three-dimensional waves. That is what we call a plane wave and that is what we will work with in this chapter.

3D representation of plane wave front http://upload.wikimedia.org/wikipedia/commons/thumb/2/20/Plane_wave_wavefronts_3D.svg/330px-Plane_wave_wavefronts_3D.svg.png	2D representation of a plane wave front: The picture illustrates that far away from a 3D source, the wave can be taken as a plane wave

Because of ease of presentation, in what follows we will always talk about plane waves and present them in 2D sections.

Diffraction at a single slit

Diffraction is the bending of a wave around objects and results in the spreading of wave after passing through a gap. To understand diffraction, one often uses the Huygens' Principle which says that each point in a wave front may be regarded as a new source of secondary wavelets (pictured by the small circles). Note that Huygens principle (1680) has no physical meaning and is only valid for elastic or mechanical waves. If coherent light with a planar wave front (surface connecting the crests) impinges on a gap (front parallel to the gap) , diffraction from various places in a gap will lead to path differences and will make an interference pattern. That is why interference is often associated with diffraction – since it is responsible for the diffraction pattern!(Hammond fig. 7.8)

Schematic (2D) presentation of Huygens principle applied on a gap (line with opening width w): the Huygens wavelets are shown behind the gap, the wave fronts before and after are represented by the blue lines	Interference of Huygens wavelets: for certain directions of α there will be destructive interference

The picture on the right hand side assumes that we look at distances far away from the gap so that the Huygens wavelets can be considered as planar waves.

In the forward direction, the waves will constructively interfere. At increasing angles away from direct beam direction, the waves will start to interfere destructively. The first destructive interference can be obtained as follows: imagine dividing the width of the gap in two parts. When the path difference between the upper wavelet and the central one equals λ/2, destructive interference will occur for these two wavelets and for each of the other wavelets, another wavelet with a λ/2 path difference can be found. The path difference can be written as

BC= λ/2= (w/2) sinα

where α= angle between the viewing direction and the direction of the incoming wave

This is not the only direction where destructive interference will be obtained. The second destructive interference will be obtained by doing the same reasoning but with the wavelet from the top and the wavelet from a quarter of the gap. It is easy to show that destructive interference will be obtained when looking at angles for which

Sinα= λ/w, 2λ/w, 3λ/w, …

The angle at which the first min is observed in a diffraction pattern, depends on the ratio between the wavelength and the width of the gap. (http://hyperphysics.phy-astr.gsu.edu/hbase/phyopt/sinslitd.html)
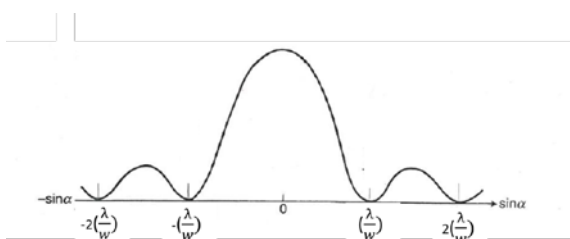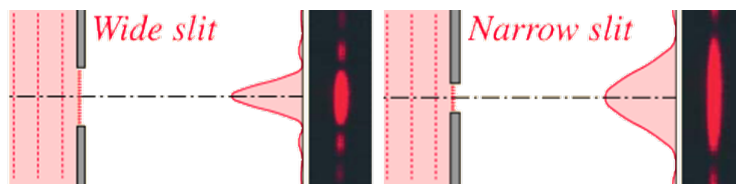
Depending on the dimensions of the width w, a typical diffraction patterns will have one central high intense peak with lower intensity peaks on each side

 If the width of the gap is large compared with the wavelength, the wavefront in the forward direction will be hardly disturbed, as is shown below. To benefit from constructive and destructive interference effects in diffraction, the width of the gap must be of the order of the wavelength or lower.
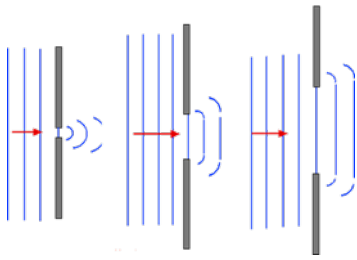
Diffraction from a grating

In 1803, Thomas Young showed in a two-slit experiment that the distance between the maximum of a detector and the center of the pattern was proportional to the reciprocal of the distance between the slits. This is easily demonstrated by assuming each slit as a single course emitting a single wavelet and calculating the conditions for constructive and destructive interference by using the path difference. The picture below illustrates this (Hammond fig. 7.5)
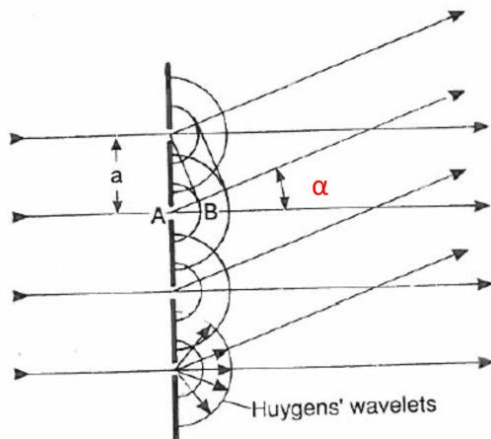
The conditions for constructive interference are very similar as for diffraction at one gap, but here the path difference is a function of the distance a between the openings in the diffraction grating

$a\sin\vartheta = n\lambda$ where n is an integer

Note that such an interference pattern will need a wavelength that is of the order of the distance between the slits.

This is however only valid if each slit is so narrow that it can be considered as just one Huygens wavelet. This is practically not the case and therefore the diffraction pattern will depend on the width of a slit (w) and on the distance between the slits (a). There are analytically and graphical ways by means of amplitude and phase diagrams to sum up the contributions of each wavelet. This is however beyond the scope of this course.

Summary interference and diffraction from grating

The important aspects of interference and diffraction from a grating made of multiple slits of width w and separation are:

1. To have constructive interference among slits
   $$n\lambda \le a \text{ (distance between slits)}.$$
   This means that we need a wavelength of the order of the distance between the width. If the wavelength is much smaller, the maxima will be very close to the forward direction i.e. the interference fringes will be very close to each other

2. When the width w of the slit is only slightly larger than λ smaller and w<a, the envelope function becomes broader and the first min induced by the width of the slit might not be visible. The pattern will look like
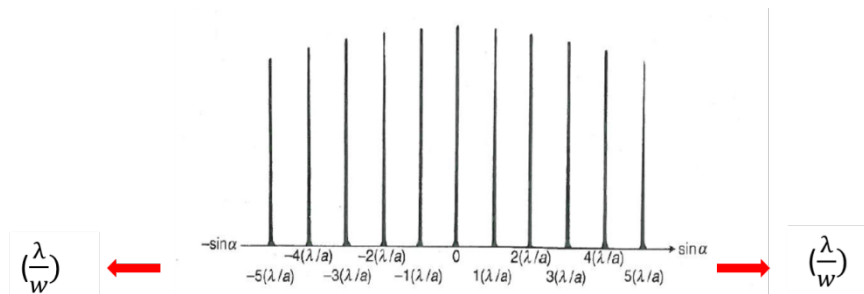
When w is larger than λ but still w<a, the diffraction pattern will look like
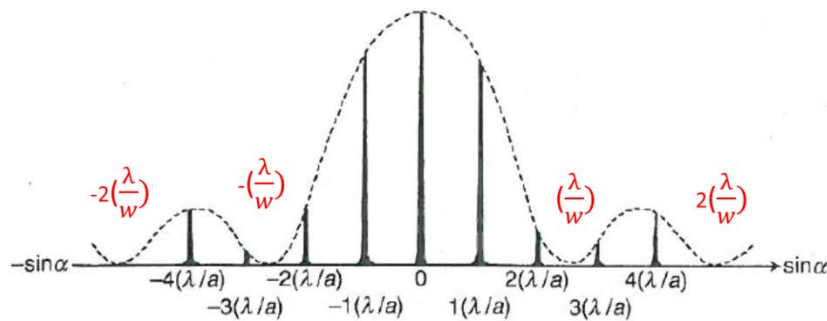
3. The diffraction angles are invariant under scaling; that is, they depend only on the ratio of the wavelength to the size (w) of the diffracting object
4. While diffraction occurs whenever propagating waves encounter slits, its effects are generally most pronounced for waves whose wavelength is roughly similar to the dimensions of the diffracting objects
5. When multiple slits are present, the spacing between a maximum on the detector and the center of the pattern is proportional to the reciprocal of the separation between the slits

The pictures below show the diffraction patterns for a planar diffracting grating consisting of circular openings, illustrating the same trends for this 2D grating (Hammond fig. 7.3)
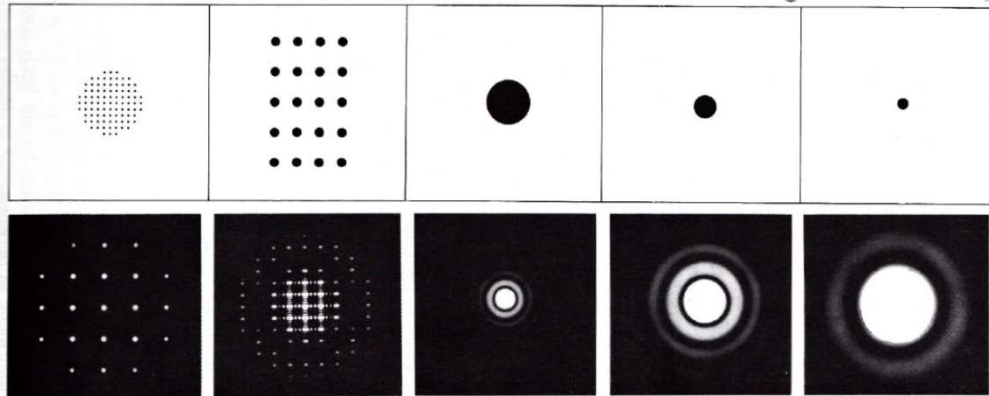
6.2 Diffraction from crystals: the lattice plane view

Classical diffraction theory at a series of line slits (2D aperture grating) can be extended to diffraction at a 3D crystal lattice. That is in principle the contribution of Max von Laue and William Lawrence and William Henry Bragg (father and son). In 1912 Von Laue had the idea to send a beam of X-rays through a copper sulfate crystal and showed that there were diffraction spots surrounding the central spot of the primary beam. Around the same time, crystallographers were becoming convinced of the lattice-like construction of crystals. Paul Ewald revealed that the spacing between lattice points was possibly a suitable distance to create interference of X-rays

If one derives it from an analogy with the slits, the distance between the atoms is the grating distance and the size of the atoms is the width of the slit. Of course in such a simple comparison, one assumes that atoms are sitting solely at lattice points (which is as we know not always the case!) and one also assumes that the interaction of the wave can be compared to light going through a slit.

From what we learned in the previous section, visible light will not be a good probe since the wavelength is 400nm-700nm, which is much bigger than the distance between the atoms, typically of the order of a few 10^{-10}m. For instance,
- the lattice parameter of the element Ni is 3.6 10^{-10}m,
- the size of an atom is about 1.4 10^{-10}m.
⇨ This means that w<a, so one can have constructive interference.

Which radiation?
Xrays, neutrons and electrons can be used, the wavelength are shown below.

	Energy	wavelength
Neutrons	1 – 5 meV (cold)	9 - 4 A
	25 – 50 meV (thermal)	1.8 – 1.3 A
Xrays	100keV	0.12 A (hard Xrays)
	40 keV	0.31 A
	5 keV	2.48 A (soft Xrays)
Electrons	200 keV	0.025 A

Xrays and electrons fulfill the conditions for the relations between a, w and λ, the diffraction patterns will however differ i.e. the relation between λ and ϑ will differ. For instance, when one uses hard xrays, the angle at which one will see constructive interference will be smaller than when using soft xrays. Cold neutrons have a too large wavelength for diffraction from Ni crystals.

Within a year of the discovery that X-rays diffract at crystals, father and son Bragg, have exploited the phenomenon to solve the first crystal structure and determined the rule governing a diffraction:

The interference will be constructive when

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

where d is the spacing between diffracting planes, θ is the incident angle, n is any integer, and λ is the wavelength of the beam (right).

The picture below shows that the Bragg law is simply the criteria that the path difference (AB + BC) where AB=BC=dsinϑ is an integer of the wavelength λ.
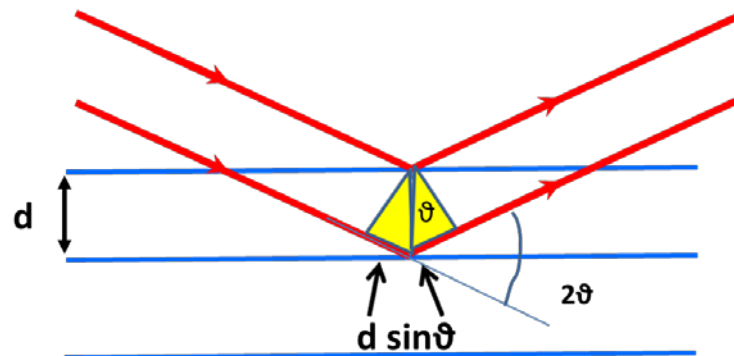
The discoveries of von Laue and Bragg gave birth to two new sciences, X-ray crystallography and X-ray spectroscopy, and two Nobel Prizes in physics: Max von Laue "for his discovery of the diffraction of X-rays by crystals" in 1914 and to Bragg and his father, Sir William Henry Bragg, "for their services in the analysis of crystal structure by means of X-rays" in 1915. William was then 25 years old!

Max von Laue
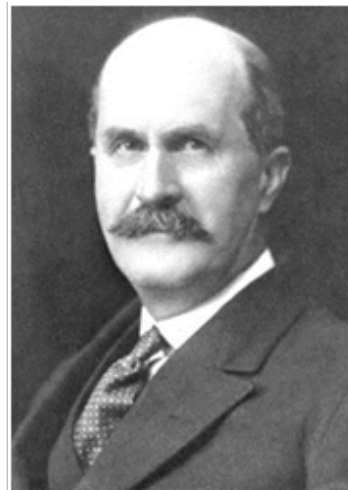
William Lawrence Bragg
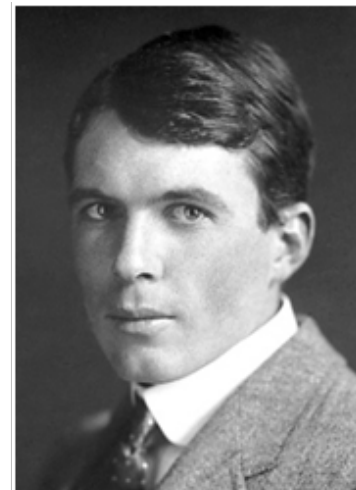
William Henry Bragg

Max von Laue made already in 1912 the analogy between grating interference and diffraction at crystals but he took the 3D crystal as an ensemble of rows of atoms. His theory did not become immediately popular because it was rather complex. Father (W.H. Bragg) and son (W.L.) Bragg explained these patterns as layers of planes of atoms which behave as reflecting planes. This is not really correct in physical sense since planes of atoms do not reflect Xrays (lattice planes are an geometrical construction and not real) but the electrons in the atom interact with the Xrays.

Bragg law defines on a purely geometrical basis for which angles constructive interference <u>can</u> occur

More general pictures related Bragg's law are

Or

Green angle= π/2 -ψ
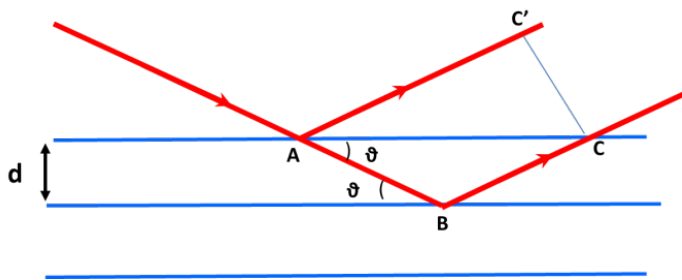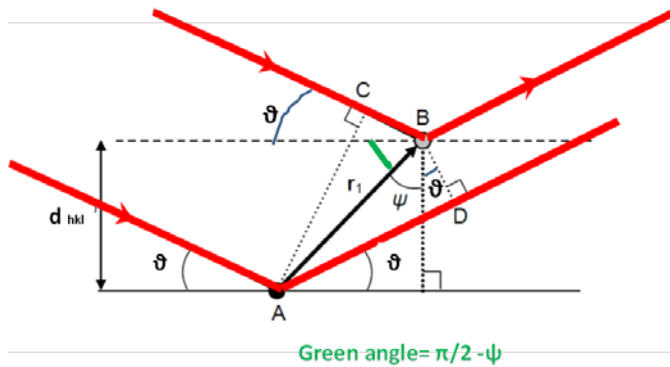
In both cases, the path difference between the two red reflected rays should be an entire number of λ for constructive interference

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Exercise 6.1

Show that in both cases there will be constructive interference when Bragg equation is fulfilled

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One can find in internet many different schematics to explain Bragg law. Often pictures with atoms on the planes are shown such (as those below).

From these pictures one gets the impression that for fulfilling Bragg's law the atoms need to be in special positions in a plane. This is not correct, Bragg's law only refers to the distance to the planes.

http://en.wikipedia.org/wiki/Bragg's_law
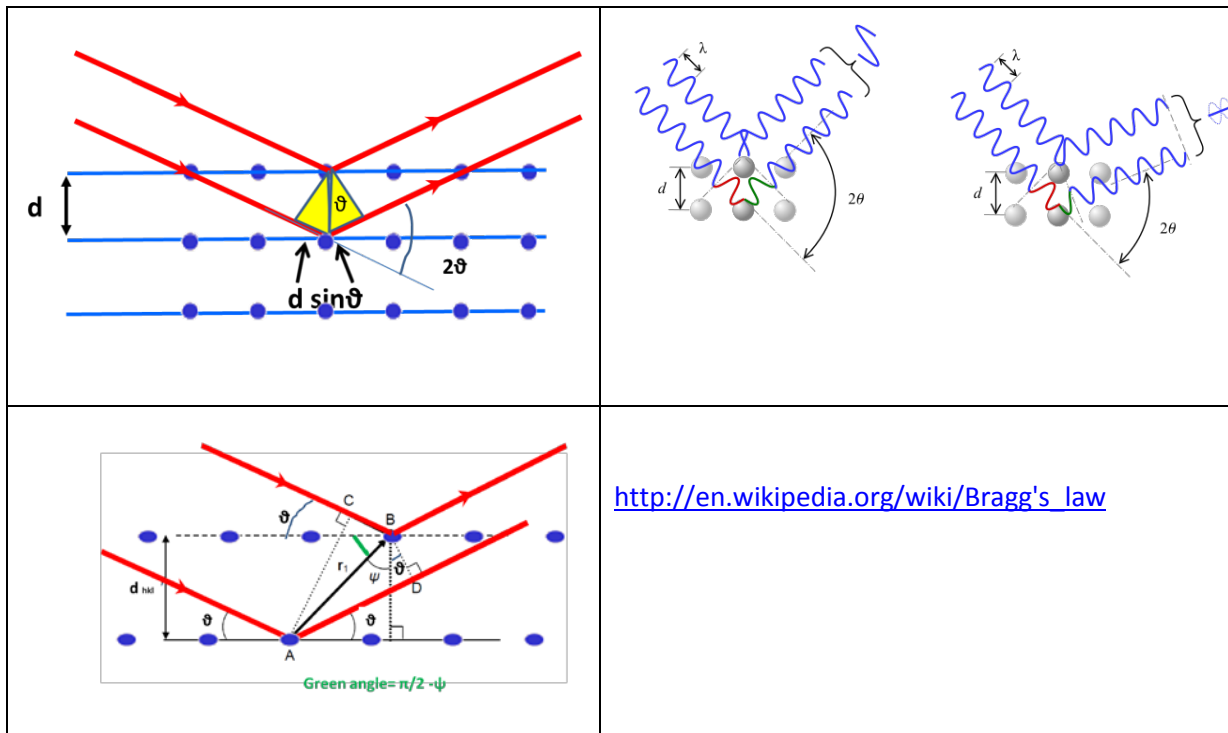
These images reflect however better that Xrays interact with the electrons in the atom which will be discussed in the next section. The derivations of Bragg's law done in exercise 6.1 show however clearly that the law is valid independent where atoms are placed.

Is this not contradictive??
It is important to understand that Bragg's law gives the geometrical condition for constructive interference. This condition depends solely on the spacing between the planes which needs irrespective of where the atoms are sitting in that plane. HOWEVER, when Bragg's law is fulfilled, that does not mean that the interference peak will be always there! The intensity can be zero!

Exercise 6.2

Consider the situation below: Bragg law is fulfilled for the planes with interplanar distance d (full lines). Imagine the motif of that crystal lattice has two atoms, one atom sitting at the lattice points and one atom sitting in between on the dashed line, both atoms having the same chemical character. In spite that Bragg is fulfilled for d and λ at the angle ϑ, the intensity will be zero. Why??
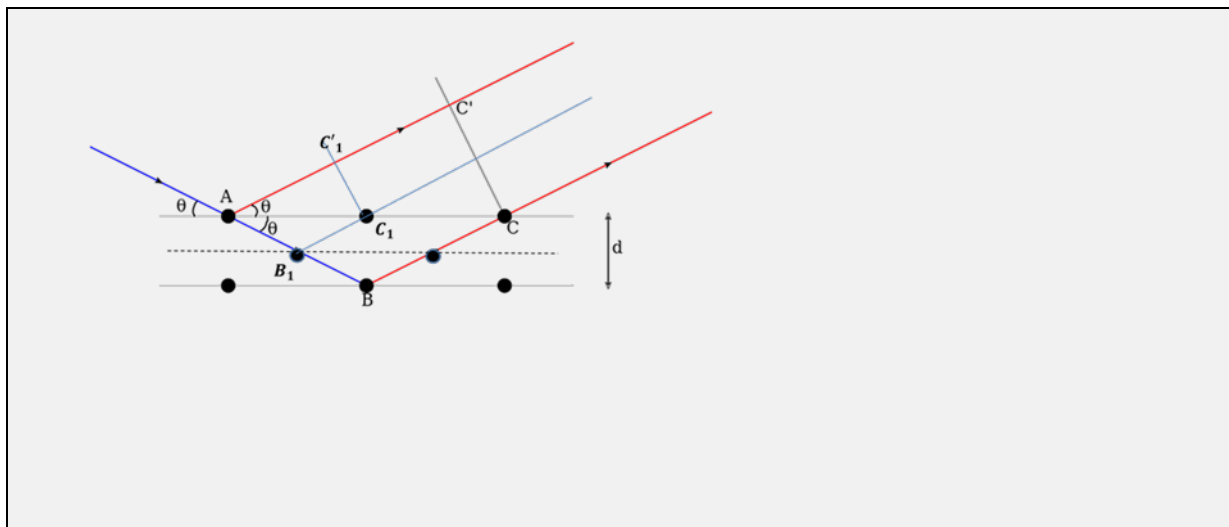
In other words, if one describes crystals with Bravais lattices + motif, one will use Bragg's law to determine where reflections can ocuur, but will have to take into account the extinctions occuring due to th enon-primitive chgaracter of the lattice and/or the motif. This part will be discussed in more detail later in the section of the structure factor.

Important notes

1) Even if only one λ is used (monochromatic Xray beam), more than one lattice plane might reflect. This will occur under a different angle ϑ' and correspond with a different distance d' between the lattice planes.
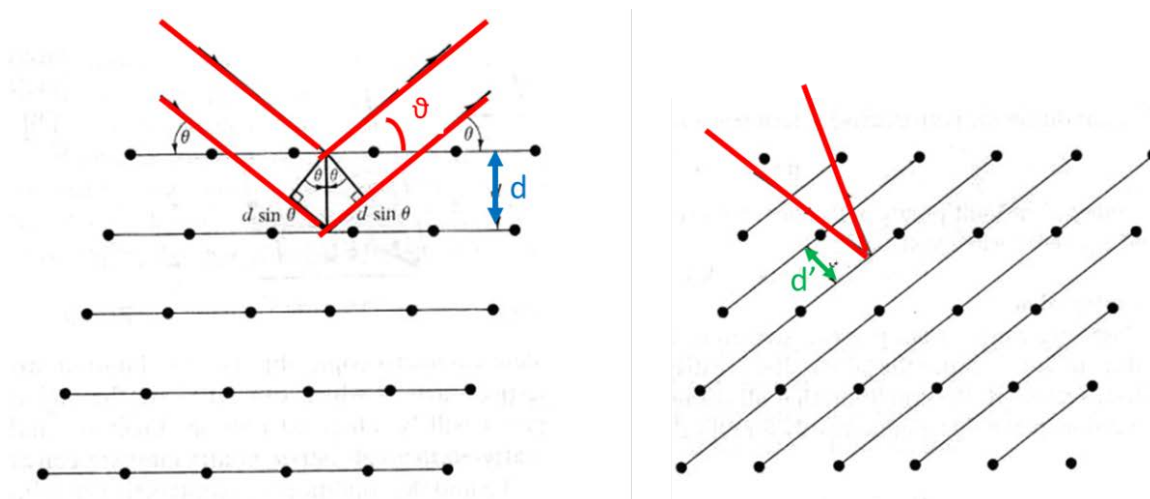
If the xray beam is polychromatic (contains many wavelengths) usually more reflections can be obtained simultaneously. This will be treated later when discussing the different diffraction methods.

2) What is the meaning of the order n in the Bragg equation?.
   The first order is when n=1

   $2d\sin\vartheta=\lambda$

   The second order when n=2

   $2d\sin\vartheta=2\lambda$ which can be also written as $2(d/2)\sin\vartheta'=\lambda$

   In other words, the second order can be always seen as a reflection under a different angle of lattice planes half way, schematically presented in 2D below (first row pictures).

| Diffraction from (100) planes | Diffraction from (200) planes |
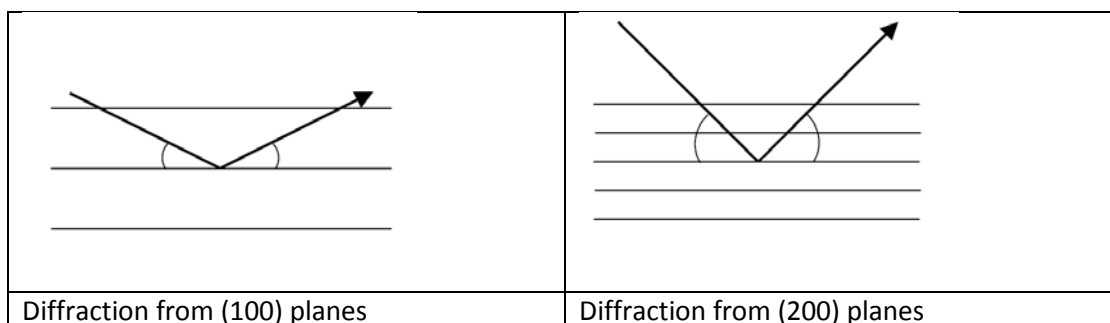
In summary

The most important conclusions of the Bragg equation is that it demonstrates that the diffraction pattern has a unique relation with the distance between lattice planes i.e. the sinus of the angle at which constructive interference <u>can</u> take place is inverse proportional to the distance between the lattice planes. Bragg's law applies independent of the position of the atoms in the lattice plane, and it is solely the spacing between the planes that has to be considered. We will see later that for non-primitive lattices some of the possible Bragg reflections become extinct and that a motif can induce additional changes in intensities of the diffracted beams.

The unique relation with the inverse of the distance between the lattice planes is the motivation to introduce the reciprocal lattice (done in chapter 7)

Extra exercise 6.3

Calculate the angles at which there will be reflections for the following sets of planes in KCl which is cubic with a = 6.27 Å and CuKα radiation, λ = 1.54 Å.
(001)
(110)
(111)

What is the difference when using a smaller wavelength i.e. xrays with higher energy?

6.3   Diffraction from crystals: the structure factor

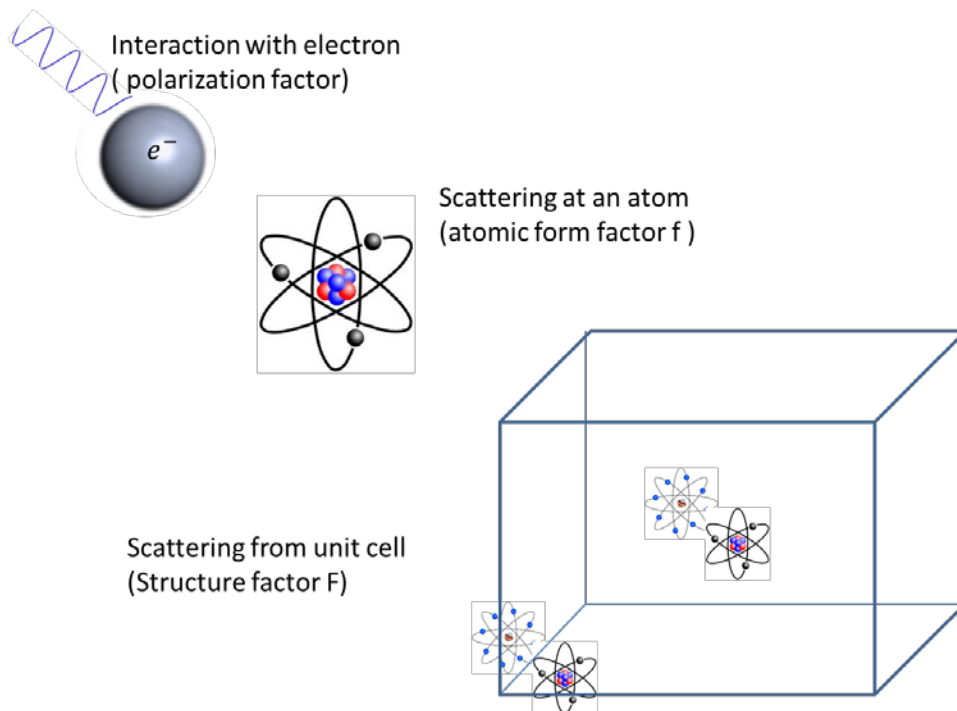The crystal can be seen as a 3-D array of lattice points to which a motif is assigned. Bragg's law gives the geometrical condition for obtaining constructive interference when radiation with a wavelength of the order of the distance between the crystal planes falls in on the crystal.

It was already mentioned that it is physically not correct to say that the impinging waves interact with lattice planes or that all lattice planes diffract similar. There are several mechanisms for interaction of Xray photons with matter. Bragg diffraction of X-rays is primarily due to the scattering of X-ray from electrons bound to the atoms of the crystal structure i.e. Thompson scattering, also called elastic or coherent scattering.

The incident photon interacts with an electron in the outer-shell by causing it to vibrate momentarily at the same frequency as the incoming photon. The vibration causes the electron to radiate energy in the form of another x-ray photon with the same frequency and energy as in the incident photon, but the direction of the incident x-ray photon is altered.

Then of course one has to take into account that there might be several outer shell atoms and several atoms in the lattice. In other words, this means that we need to follow the following chain in order to know what the scattering power is of a crystal: scattering from an electron, scattering from an atom and scattering from the unit cell, as schematically presented below

Interaction with electron
(polarization factor)

e^-

Scattering at an atom
(atomic form factor f)

Scattering from unit cell
(Structure factor F)

In other words, to calculate the amplitude of the scattered wave coming from a unit cell, one has to sum over the atoms in the cell (positions relative to the origin of the unit cell) and to sum over all the positions of the electrons relative to the center of the atom

The polarization factor

It can be schematically presented as follows: when an electromagnetic wave falls in on an electron (charged particle) the electron will start oscillating with the same wavelength as the incoming wave and there will be a defined phase relationship, i.e. the radiation is coherent.

Let's picture this for the simplified case of a planar wave traveling in the z direction. Assume the wave is linear polarized in the direction x. This wave will cause the electron oscillate in the x direction and create a dipolar field. The electromagnetic radiation emitted by the oscillating electron will then not be spherical. The field in the xz plane is shown in the *figure (Neutrons and Synchrotron Radiation in Engineering Materials Science, 2008, editors Walter Reimers, Anke Rita Pyzalla, Andreas K. Schreyer, Helmut Clemens; Online ISBN: 9783527621927)*
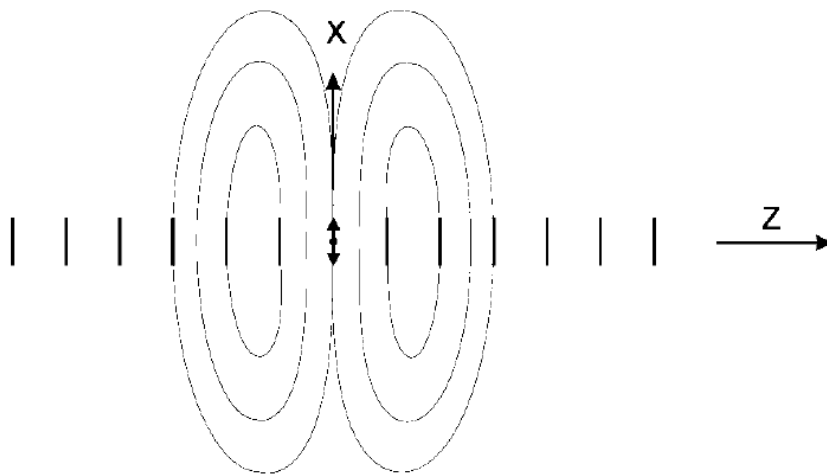
Although the incidental radiation has a particular direction, the scattered radiation will occur in all directions but the intensity will depend on the direction of the incoming beam

Expressed in terms of the angle 2ϑ between the incoming beam and the scattered direction, the intensity will in certain approximations (free electron) be proportional to

$$\left(\frac{e^2}{c^2 m_e}\right)^2 (1 + cos^2 2\vartheta)$$

The factor $1/m_e{}^2$ shows why the electrons are the only effective scatteres in the atom. The same type of radiation would be possible with any charged particle of the atom but for instance the proton (lightest nucleus in case of Hydrogen) has a mass that is 1837 times higher

Important to realize here is that the scattered intensity from a charged particle depends on the angle between the incoming beam and the scattered intensity and that the maximum intensity is scattered in the forward direction.
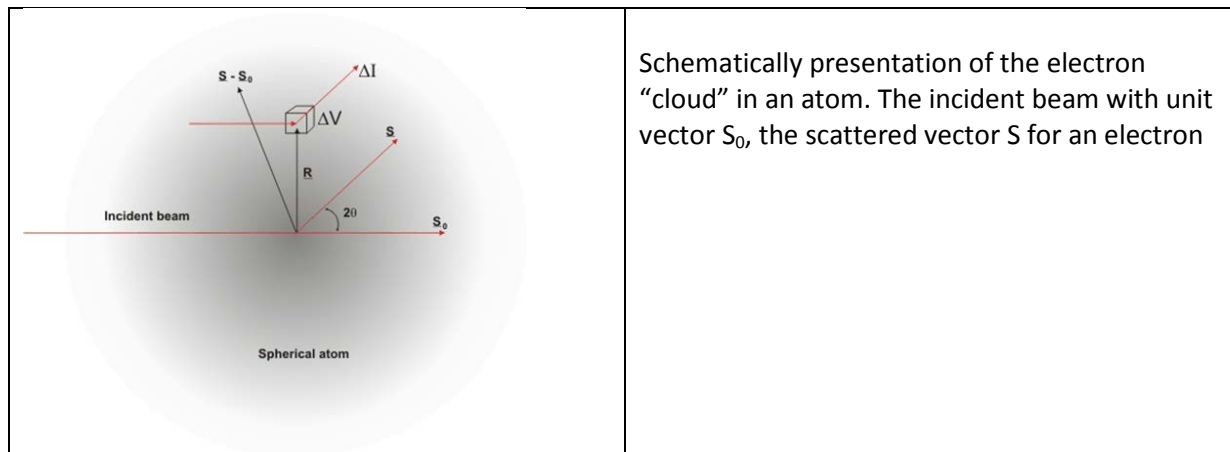
The atomic scattering factor

The atomic scattering factor (or form factor) is defined as

Atomic scattering factor $\quad f=\dfrac{amplitude\ scattered\ by\ one\ atom}{amplitude\ scattered\ by\ a\ single\ electron}$

It is beyond the purpose of this course to derive the formula, but it is important to understand the origin and know the influence on the overall scattered intensity by the crystal. On the web you can find the picture below which illustrates well the influence of the electron distribution (http://www.xtal.iqfr.csic.es/Cristalografia/parte_05-en.html)

Schematically presentation of the electron "cloud" in an atom. The incident beam with unit vector S_0, the scattered vector S for an electron

An atom with Z electrons (its atomic number) can be expected to scatter Z times. The distances between the electrons of an atom are of the order of the X-rays wavelength (dimension of the atom 10^{-10}m), and therefore destructive interferences can occur among the scattered waves. This will affect of course only partially the wave scattered by the electrons, since electrons are sitting in a cloud and do not have these regular positions as atoms in a lattice. Since Thompson scattering has the highest intensity in the forward direction there will be also a dependence on the angle between the incident radiation and the direction where we measure the scattering.

The orbital electrons in an atom move very fast (of the order of 10^{-18} sec for an orbital) and therefore an impinging wave sees only an average electron cloud which is characterized by an electron density of charge $\rho(r')$.

If this distribution is considered spherically symmetric, its influence on the scattering will predominantly depend on the distance to the nucleus. The atomic scattering factor can be described as (r is the position of the electron in the atoms)

$f(k) = 4\pi \int_0^\infty r^2\, \rho(r)\, \dfrac{\sin(k-k_0).r}{(k-k_0).r}$ $\quad$ where $k\text{-}k_0 = (s\text{-}s_0)/\lambda$

Note that $4\pi\int r^2\rho(r)dr$ is equal to the total number of electrons Z in the atom. Hence the atomic form factor is equal to Z when θ=0 (forward direction) , and less then Z for all other angles of scattering. Important is however to realize that the form factor depends via $(s\text{-}s_0)$ on $\sin\vartheta/\lambda$.

The dependence of the atomic scattering factor of Z is an important aspect of Xray scattering since it makes light elements "invisible".

Below a few diagrams showing the dependence of the atomic scattering factor on $\sin\vartheta/\lambda$
Lower intensities are observed for higher diffraction angles.

Atomic scattering factors for several ions with the same number of electrons. One can observe that the O^{--} has a more diffuse electronic cloud than Si^{4+} and shows a faster decay.	Atomic scattering factors calculated for atoms and ions with different numbers of electrons. Hydrogen (only one electron) scatters very little as compared with other elements.
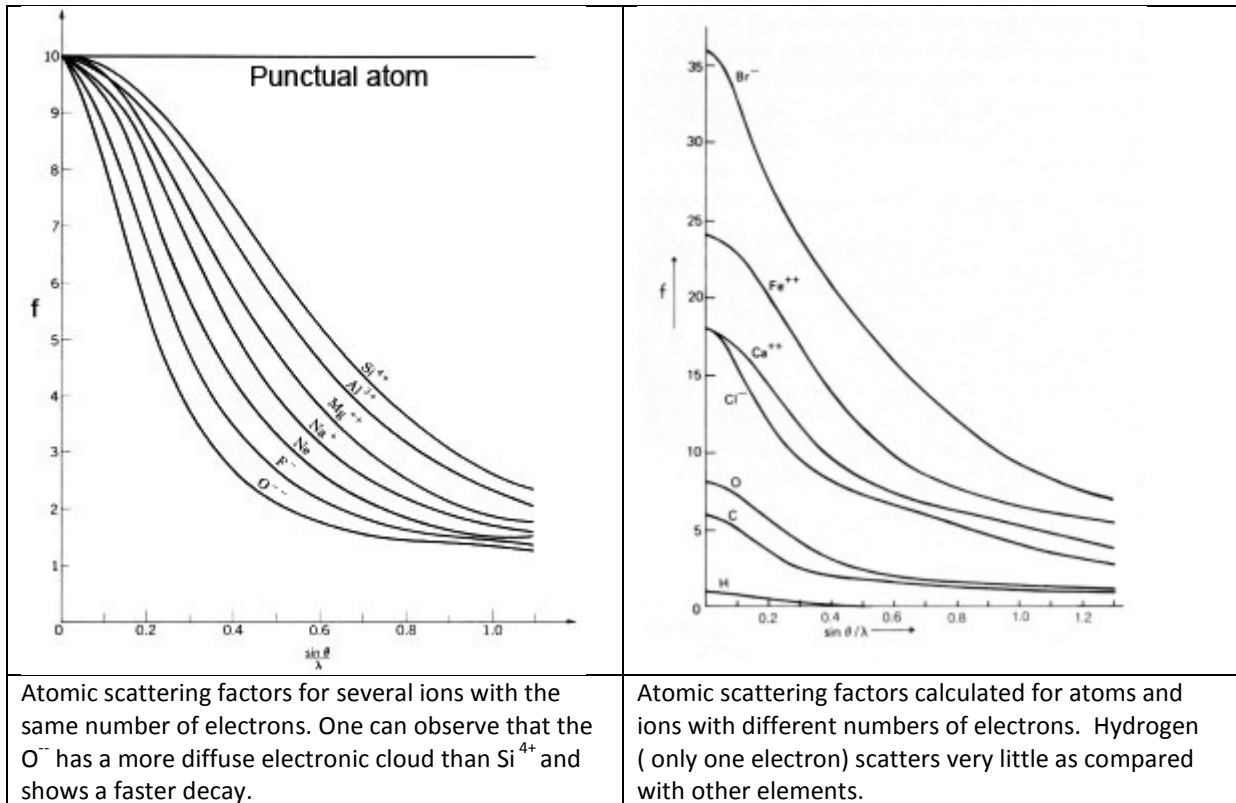
The Structure factor

Now that we know how an atom scatters, let us investigate how the arrangement of the atoms in the unit cell can influence the scattered intensity. A unit cell has a motif and this can be one atom at a lattice point but it can be also a cluster of atoms related to a lattice point
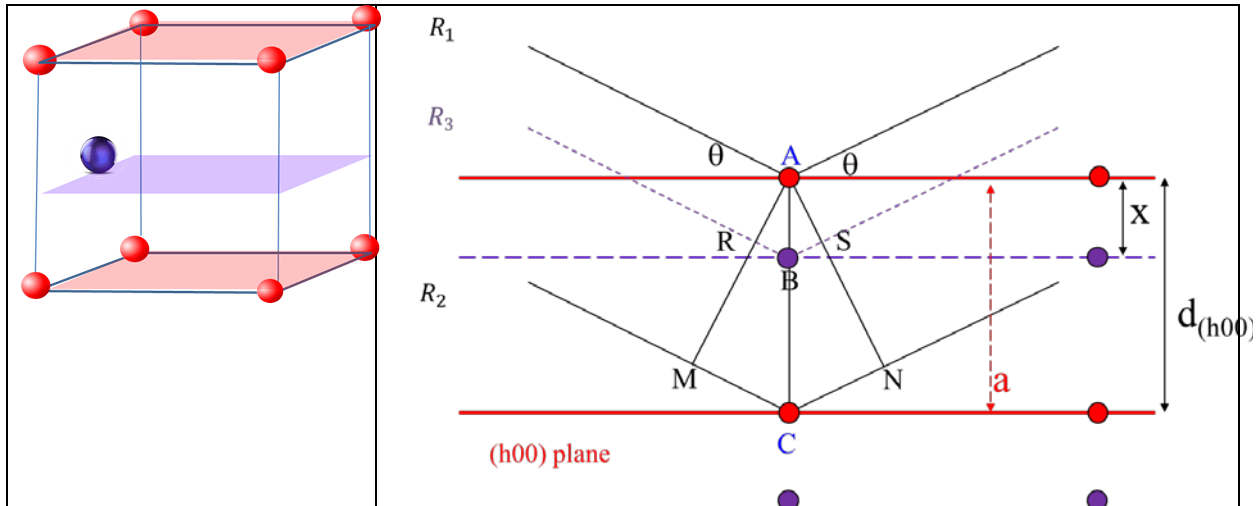
Imagine a simple cubic unit cell with a motif with one (red) atom at a lattice point and one (blue) atom in one of the faces at a position x from the top face. The atoms are different chemical species. The red planes are those that fulfill the Bragg equation. The purple plane is parallel to the Bragg planes but does not fulfill the Bragg equation.

The path difference between the rays (R1 and R2) impinging on the (h00) Bragg planes. If we directly compare with the lattice drawn in the picture above, this is the (100) plane but to keep it more general we take the (h00) plane. The distance between the (h00) planes is then noted as d_{h00} and has the length a/h where a is the lattice parameter.

MCN= 2AC sinϑ = 2 d_{h00} sinϑ = λ as expected since Bragg is fulfilled

The path difference between R1 and R3 (from the blue plane) is

RBS= 2ABsinϑ

AC is the distance between the lattice planes (h00) with length $d_{h00} = $ a/h

Taking the ratio's $\dfrac{AB}{AC} = \dfrac{x}{\frac{a}{h}}$

and implementing AB as a function of AC in the equation of RBS

RBS= $\dfrac{x}{\frac{a}{h}}$ 2AC sinϑ

And since 2ACsinϑ= λ finally result in a path difference

$$RBS = h\frac{x}{a}\lambda$$

This will result in a phase difference of the wave and so a reduction in intensity. Note that for an atom sitting halfway (distance x/a=1/2) there will be maximal reduction in intensity. In case of two similar atoms, this will result in extinction. This means that even when the geometrical Bragg condition for diffraction is fulfilled, the intensity can be strongly reduced or even extinct.

General expression for the structure factor

$$F(hkl) = \sum_0^N f_n e^{i2\pi(hx_n+ky_n+lz_n)}$$

where f_n is the atomic form factor of atom n, and (x_n, y_n, z_n) are the coordinates of atom n expressed in the lattice. N is the total number of atoms in the unit cell

the term $2\pi(hx_n + ky_n + lz_n)$ is the phase angle φ

The intensity is proportional to the square of the structure factor, I ~ (F(hkl). F^*(hkl)) which equals to $F(hkl)^2$ when the structure factor is real (see examples). There will be extinctions when the structure factor is zero. F does not give us absolute values of intensities, but one can use ratios of intensities of different reflections to get information on the motif. That is what crystallographers do.
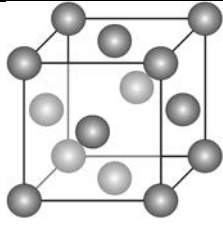
6.4 Diffraction from Bravais lattices: systematic absences

The structure factor for non-primitive Bravais lattices show systematic extinctions, Below the example foe an face centered cubic lattice, the others are left as an exercise. To calculate the structure factor, we assume only one chemical specie and atoms that are sitting at the lattice point.

For the calculations, remind that $e^{i\pi n}$ = 1 when n is an even integer
$\qquad\qquad\qquad\qquad\qquad$ = -1 when n is an odd integer

And that even + even = even, odd + odd = even, even + odd = odd

Face centered cubic lattice with one atomic specie

	The number of atoms in the Bravais unit cell is 4 Positions of equivalent atoms (0,0,0) (½, ½, 0), (½, 0, ½), (0, ½, ½) $$F = f\left[e^{i[2\pi(0)]} + e^{i[2\pi(\frac{h+k}{2})]} + e^{i[2\pi(\frac{k+l}{2})]} + e^{i[2\pi(\frac{l+h}{2})]} \right]$$ $$= f[1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}]$$
	hkl all even or odd: F=4f e.g. *(111), (200), (220), (333), (420)* hkl mixed: F=0 e.g. . *(100), (211); (210), (032), (033)*

Exercises 6.4

Define for which hkl values extinction or maximal constructive interference occurs in

- I- body centered orthorhombic lattice with one atomic specie
- C-centered orthorhombic lattice with one atomic specie
- A centered orthorhombic lattice
- B centered orthorhombic lattice
- P primitive lattice

Exercises 6.5

Determine the 8 Bragg reflections of Cu (FCC lattice with a=3.615) with the smallest ϑ value and determine the angle ϑ when λ= 1.54184 Angstrom. Will all these reflections have the same intensity?

Exercise 6.6

Define for the two Ni-Al alloys for which (hkl) planes one has maximal intensity and for which minimal intensity

- NiAl: an alloys with a primitive cubic Bravais lattice with positions Al (0,0,0) , Ni (½, ½, ½)

- Ni3Al: an alloy with a primitive cubic Bravais lattice with positions Al (0,0,0) , Ni (½, ½, 0)

Which reflections are present in Ni3Al that would have been extinct in pure Ni

Exercise 6.7

Write the structure factor for NaCl. What is the effect on the Bragg reflections?
Compare the intensity of the (111) and the (200) reflection with those of Cu

Exercise 6.8

Write the structure factor for zincblende ZnS (take S atom placed at the origin of the unit cell)
Evaluate the intensities of the (111), (200), and (220) reflections assuming that atomic scattering factors are proportional to atomic number
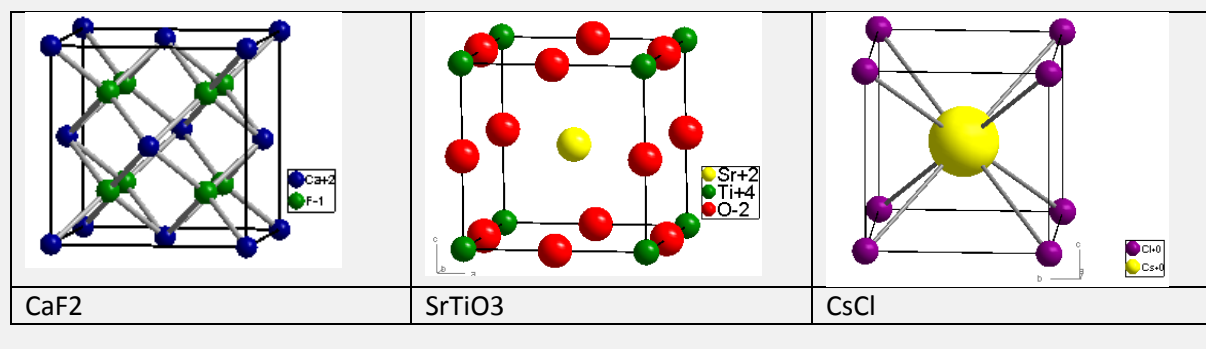
Exercise 6.9

Write the structure factor for Ti (HCP Bravais lattice) and discuss intensities

Exercise 6.10

Write the structure factor for Diamond and discuss intensities

Exercise 6.11

Identify the Bravais lattice of CaF2, SrTiO3 (perovskite) and CsCl and write down the coordination of the atoms necessary to describe the crystal. Make a 2D plot of the structure
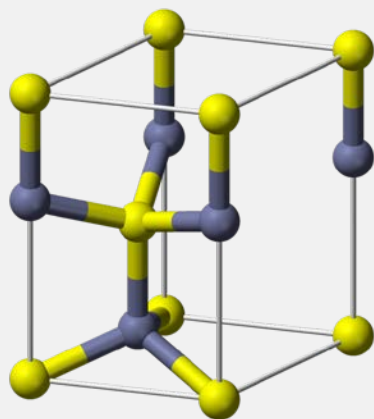

| CaF2 | SrTiO3 | CsCl |

Exercise 6.12

Write the structure factor for CaF2

Exercise 6.13 (not for exam)

Write the structure factor for Wurzite (HCP Bravais lattice) using the unit cell below

Exercise 6.14

Demonstrate that also a screw axes can cause systematic extinctions. Take as example the 2_1 screw axis parallel to b. This will have the effect of replicating each atom j, originally at (x_j, y_j, z_j), at $(-x_j, 1/2 +y_j, -z_j)$. Calculate the structure factor and determine conditions for extinction