Symmetry-operations, point groups, space groups and crystal structure

KJ/MV 210

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This compendium replaces chapter 5.3 and 6 in West.

Sections not part of the curriculum are enclosed in asterisks (*). It is recommended that the textbooks of West and Jastrzebski are used as supplementary reading material, with special emphasis on illustrative examples. In this compendium illustrative examples (in italics) have been chosen from close packed structures. A few symbols and synonyms are given in Norwegian as information. The compendium contains exercises which will not be explained in the classes. It is recommended to work through the exercises while reading this compendium.

Introduction.

Condensed phases may be liquids as well as solids. There are fundamental differences between liquids and solids regarding the long-range distribution of atoms. While liquids have long range disorder in a large scale, solids are mainly ordered, i.e. there is regularity in the repetition of structural fragments (atoms and/or groups of atoms) in the 3 dimensional material. Surfaces of solid materials are often somewhat differently organized than the "bulk" (i.e. the inner part of the material). The atomic (structural) arrangement near the surface will often be different from the bulk arrangement due to surface reconstruction in order to minimize the energy loss associated with complete chemical bonding in all actual directions. Liquids are disordered in bulk, but they often have an ordered surface structure.

Solids do not need to display systematic long-range order, i.e. to be crystalline. Some phases can be prepared as amorphous materials, e.g. glasses. They may be made crystallized by a suitable temperature treatment. A few phases exist which are only known in an amorphous state.

In order to simplify the description of symmetry relations in atomic arrangements (i.e. the "appearance" of a structure fragment, molecule or complex) symmetry operations are used. Symmetry-operations like mirroring and rotation are known from every-day-life. If one wishes to describe how structure fragments are repeated (translated) through a solid compound, symmetry-operations which include translation must be used in addition. Symmetry-descriptions of given isolated objects are also known from every-day-life, e.g. a lump of sugar, a dice, a wheel (with an n-fold rotation axes for n spokes equally distributed) or a pyramid (with four-fold rotation axis perpendicular to the basis plan).

This compendium does not intend to give complete introduction to the basics of symmetry descriptions of solids. That is not the objective of this part of KJ-MV 210. The text is not written in order to give the reader a perfect and full understanding of crystallography. Instead it will give a simplified picture of the field. The intension of the compendium is to provide a basic knowledge of central issues, so that the reader will be able to draw different structures based on published structural data and available references (International Tables of Crystallography). This will be very useful in later courses concerned with properties of inorganic materials. It is important to realise that there is a close connection between atomic arrangements (structure, chemical bonding) and chemical and physical properties.

The chosen examples in the compendium are related to close packing of atoms. The reader is recommended to carefully work through the examples.

The unit cell.

In the crystalline state there are rules for how structural elements are repeated through the solid. One can identify structural fragments that form the smallest repeating units; by repeating these in 3 dimensions they build the whole material. One can think of the smallest repeating unit as described inside a box. By stacking of the boxes in 3 dimensions a complete description of the structure of the solid material is obtained. Such a box is called a unit cell (enhetscelle). The box is defined by 3 vectors, $\mathbf{t_1}$, $\mathbf{t_2}$ and $\mathbf{t_3}$ [with unit cell volume $V = \mathbf{t_1} \cdot (\mathbf{t_2} \times \mathbf{t_3})$]. The vectors are not necessarily orthogonal. As a starting point there are no conditions on the 3 angles between the vectors, α, β and γ. (i.e. they are not restricted in any way, e.g. to be 90°).

When describing the structure of a solid material in the scientific literature, relevant data for the crystallographic unit cell are given. The unit cell is given by the length of the three axes, *a*, *b* and *c* (unit cell dimensions, unit cell parameters, cell edges; i.e. the lengths of the vectors $\mathbf{t_1}$, $\mathbf{t_2}$ and $\mathbf{t_3}$) and the angles α, β and γ. Definition of the angles relative to the axes ($\mathbf{t_1}$, $\mathbf{t_2}$ and $\mathbf{t_3}$ or equivalent **a**, **b** and **c**) is shown in Figure 1. In order to describe the atomic arrangement, one has in addition to defining the shape of the unit cell and also to state where the atoms are in the repeating unit cell. This is done by giving the position of the atoms as coordinates (x,y,z). The atomic coordinates are given as fractions of the unit length of the vectors. Thus position (0,0,0) is the origo of the unit cell, while the point (1,0,0) is moved $(\mathbf{t_1},\mathbf{0},\mathbf{0})$, i.e. one cell edge along the *a*-axis parallel to $\mathbf{t_1}$. An atom in the corner of the unit cell therefore has the coordinates (0,0,0), while an atom on the centre of the *a*-axis has the coordinates (1/2,0,0). As a principal rule, any given atom can be transferred to one or more atoms, of the same type and with the same surroundings, within the unit cell by symmetry operations. In order to describe all the atoms in the unit cell it is enough to give the coordinates of a certain part of the atoms along with the necessary symmetry operations.

Within a unit cell one often find several atoms of the same kind. If the surroundings of these atoms are identical, the atoms are related by symmetry operations (they are crystallographic equivalent atoms). If the surroundings are more or less different, the difference is signified by using different notations for the atoms, e.g. Cu(1) and Cu(2), where the number in brackets is just numbering of the same type of element. In such cases one would say that Cu(1) and Cu(2) are not crystallographic equivalent atoms.

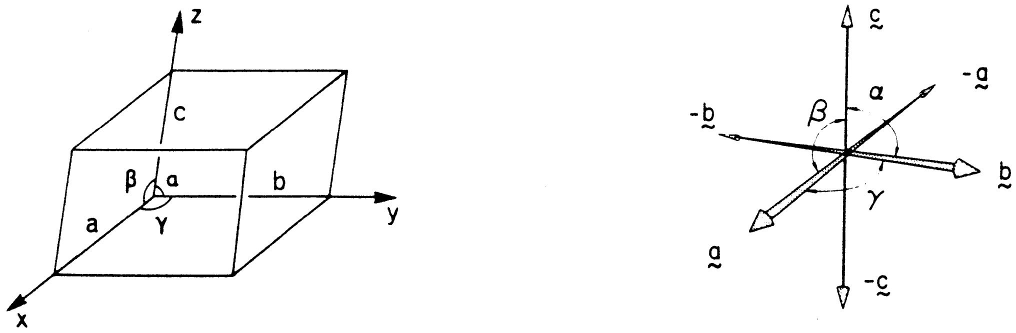
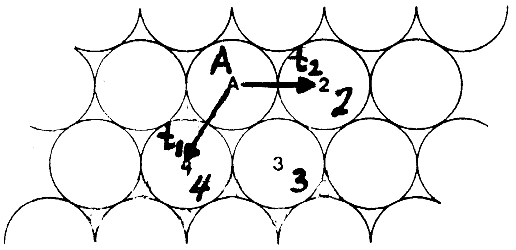
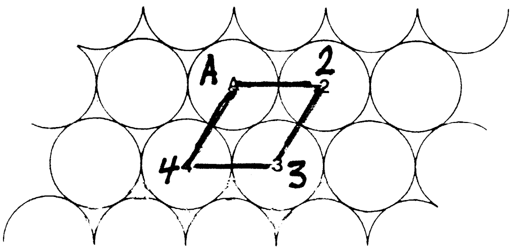


Figure 1. The definition of relations between angles and axes in unit cells. The unit cell is shown as the box on the left.

Example 1 (2-dimensional unit cell)
A number of simple structures, e.g. for metals and alloys, may be derived from close packing of spheres. Here the atoms are thought to be ideal, non compressible spheres of the same size. Before we look at such 3-dimensional structures in details, we will take a closer look at how symmetry-notation can be used to describe close packing in 2-dimensions. Then we will add different symmetry operations, still looking at the 2-dimensional model of the structure.

Consider a 2-dimensional close packing of identical spheres. The spheres are placed as close as possible (i.e. with the least possible space between them). This is shown to the left below.





Let us now define a 2-dimensional unit cell for the pattern of repeating spheres. We choose the centre of sphere A as origo. (You will get the same unit cell with any other choice of origo, but there will be less symmetry around the origo). The direction and length of the translation vectors (cell edges) must first be determined. Let $\boldsymbol{t_1}$ *be the vector from the centre of sphere A to the centre of sphere 4, and let* $\boldsymbol{t_2}$ *be the vector form the centre of sphere A to the centre of sphere 2. The unit cell is completed by translating* $\boldsymbol{t_2}$ *so that it starts in the centre of sphere 4 and* $\boldsymbol{t_1}$ *to start in the centre of sphere 2. The lengths of the vectors* $\boldsymbol{t_1}$ *and* $\boldsymbol{t_2}$ *are called a and b. It is obvious that a and b (= 2r; the radius of the sphere). The angle between* $\boldsymbol{t_1}$ *and* $\boldsymbol{t_2}$ *can easily be calculated by looking at the equilateral triangle that is formed by the centres of three adjacent spheres. The unit cell is therefore defined as* $a = b$ *and the angle* $\gamma = 120°$ *(look above to the right)*

This 2-dimensional packing of spheres is the closest possible, and such layers constitutes the 2-dimensional units that are stacked when making 3-dimensional close packed structures (notation AB... = hcp, ABC... = ccp, or more unusual and

> *complicated stacking sequence as e.g. ABAC..... An .... AA...stacking will not be close packed in 3-dimensions even though it is built from 2-dimensional close packed units).*

The values of the coordinates (x, y, z) of a point within the unit cell are all between 0 and 1 (look above). Because the unit cell is a repeating unit, any multipla of the unit vectors can be added to or subtracted from any point (x, y, z), in order to get to identical points in other unit cells. The point (x, y, z) or an atom positioned in A in figure 2, e.g. with coordinates (0.21, 0.33, 0.45) is therefore identical to the point B with the coordinates (0.21, 0.33, 1.45) through the translation (x, y, z+1); and C (-0.79, 0.33, 0.45) through the translation (x-1, y, z); and D (-0.79, 1.33, -0.55) through the translation (x-1, y+1, z-1). A, B, C and D will have identical surroundings in the unit cell and in any given atomic arrangement in a solid material. When atoms are called identical (equivalent) it means that they have absolute identical surroundings in relation to all nearby points/atoms.

> *In example 1, it is seen that the surroundings of e.g. sphere A and sphere 2 are identical. This means that the spheres with centre at the coordinates (0, 0) and (0, 1) are identical. In reality one can view the two spheres as one and the same. Sphere 2 is just sphere A translated one unit translation (the cell edge) along* $\boldsymbol{t}_2$*. All the spheres in example 1 are therefore equivalent, and the 2-dimensional packing is completely defined by giving a, b and γ together with the information that there is a sphere in origo.*

Because the unit cell is a repeating unit, a description of the symmetry and the atom coordinates is the unit cell, will describe the symmetry and structure of the solid material. This is of course only true for crystalline phases, where, as mentioned, a systematic long-range order exists. In amorphous materials there are not repeating unit cells.

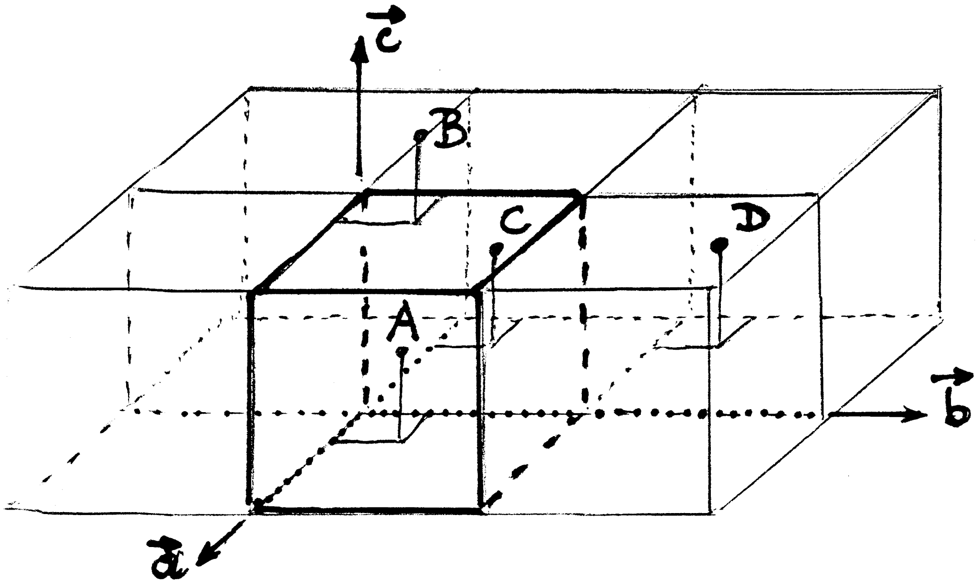


Figure 2: Same point in several unit cells.

The chemical composition of a solid material is given by the ratios between the different kind of atoms in the unit cell. If the unit cell is known, it must be possible to make a correct account of the content. One must take in to consideration that one unit is close up against other unit cells and that it shares faces, edges and corners with the surrounding unit cells. Thus, an atom in a unit cell count as 1, whereas an atom on a face counts as ½ (but this is repeated on the opposite unit cell, and together the two half atoms counts as 1); while an atom in a corner counts as 1/8 (but eight corners share a point, so that 8 · 1/8 = 1); figure 3. As an illustrated, look at Figure 3 where 8 filled symbols are drawn, two open and one hatched. There are the same number of filled, open and hatched symbols in the repeating unit (one of each).

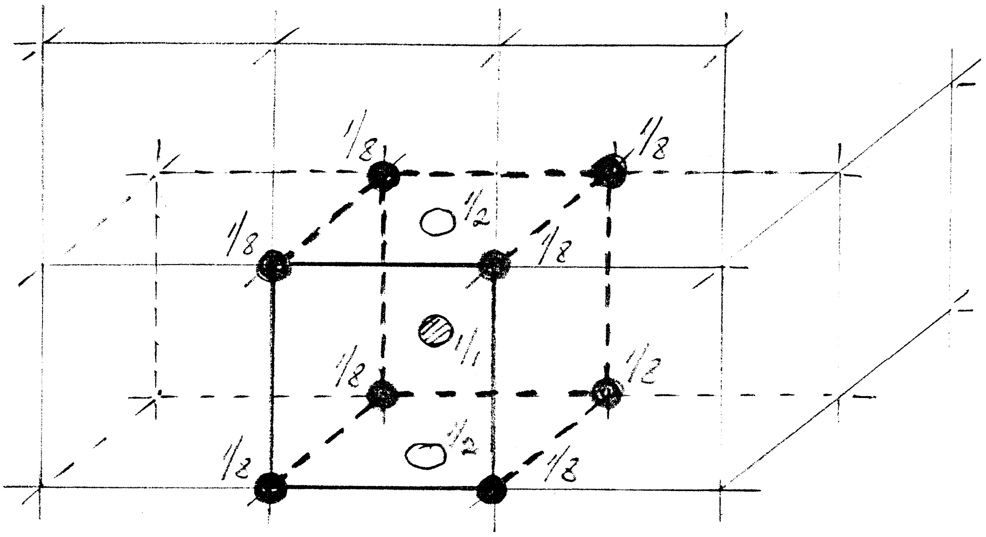


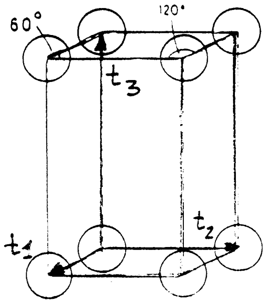
Figure 3. Atoms are placed inside the unit cell (hatched), on the faces (open) and at the corners (filled). The unit cells share faces.

> Exercise 1
> Draw a 2-dimensional orthogonal unit cell with cell edges a = 3.80 Å and b = 3.90 Å. Place these atoms in the unit cell:
> Cu(1) in (0, 0)
> O(1) in (0, 0.5)
> O(2) in (0.5, 0)
> Calculate the distance between Cu and O and between Cu and Cu.
> Check the calculation against what you would expect based on ion/covalent bonding between cupper and oxygen.
> Such an atomic arrangement is found in 2-dimensional sections of high temperature superconductors.

Example 2 (3-dimensional unit cell; modes of illustration)
Imagine taking the 2-dimensional layer of spheres as shown in example 1 and putting it ***right above*** *the exact same layer. The spheres are positioned right on top of one another, and do not fall down the hollows in the layers. It is obvious that this is not a good utilization of the available volume and that the structure is not close packed in 3-dimensions.*

Stacking of layers is thought continued in such a way that a 3-dimensionel object is built. The unit cell of the 2-dimensional layer is exactly as seen in example 1. The repeating length in the stacking direction is given by the vector (t_3*) from the centre of sphere A to sphere A' in the next stacking layer. This vector is perpendicular to* $\boldsymbol{t_1}$ *and*

t_2 in the basal plane. The 3-dimensional unit cell is therefore $a = b \neq c$, $\alpha = \beta = 90°$ and $\gamma = 120°$. The unit cell can be drawn like this:



The structure that arises from such a stacking is said to be a simple hexagonal packing of the type ...AA... (NB not a close hexagonal packing). By using the rules for adding up the spheres/atoms will in a unit cell, one finds that the number of atoms is 8 • 1/8 = 1, i.e. the unit cell contains a formula unit of spheres/atoms; this is given as Z = 1.

Note that when one using the notation packing of spheres and looking at rigid touching spheres, this is of course a model, which does not directly describe the properties of the atoms. Atoms (e.g. the noble gases), ions (e.g. Na^+, or Cl^-) and metal atoms (e.g. Fe in metallic iron or a iron containing alloy with metallic conductivity) can to a certain degree be seen as spherical. When we draw a crystal structure, where the spheres of the packing model is replaced by atoms, for clarity they are usually drawn so small, that they do not touch one another (look at the figure above). This is done in order to make the figure easier to interpret. When illustrating how much inner volume there is in e.g. a channel in the structure (e.g. a zeolite) the atoms are drawn with a size proportional to covalent, ionic or Van der Waals radius.

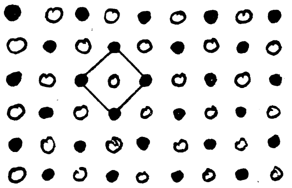
It is desirable to describe an actual crystal structure with the highest possible symmetry of the structure. For a given structure, it is quite easy to find several unit cells that all fulfil the criteria of repeatability. The crystallographic unit cell must in addition fulfil other criteria. It must:

- Display the maximal symmetry of the structure and
- At the same time be the smallest repeating unit that does this

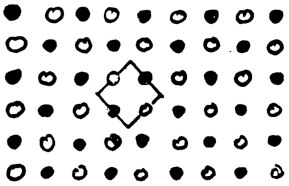
In physics (e.g. in theoretical band structure calculations) an other unit cell, the Wigner-Seitz cell, is often used. This is the smallest repeating unit, but does not show full translational symmetry. When this is used, it is in order to reduce the complexity by including the smallest possible number of atoms. The crystallographic unit cells may contain many formula units, Z (Z is of course an integer, and takes the value of 2^n3^m, e.g. 1, 2, 3, 6, etc). The Wigner-Seitz cell is the smallest repeating closed volume around origo (a lattice point). It contains only one lattice point (see space-/Bravais lattice) and shows the full rotational symmetry of the crystal system (see below). The Wigner-Seitz cell is constructed by drawing connecting lines from one lattice point to every neighbouring lattice point. Then perpendicular planes are constructed halfway between the lattice points and the surrounded volume that is defined by the planes is the Wigner-Seitz cell. This volume can have many faces.

Exercise 2:
Estimate which of the four following 2-dimensional cells fulfil the requirements of a unit cell.

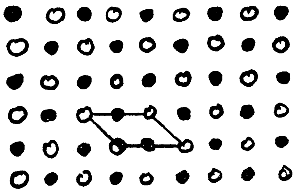
(a)



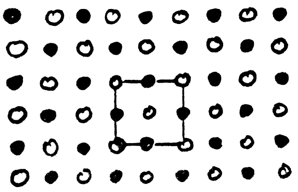
(b)



(c)



(d)



e 3:
Draw the NiAs type structure based exclusively on the basis of the following information:
a = *b* = 3.60 Å, *c* = 5.10 Å, $\alpha = \beta = 90°$, $\gamma = 120°$.
Ni(1) in (0, 0, 0)
Ni(2) in (0, 0, 0.5)
As(1) in (⅓, ⅔, ¼)
As(2) in (⅔, ⅓, ¾)
Draw sketches showing the structure seen slightly from the side and as a projection on the ab-plane.
How many formula units (Z) of NiAs are there per unit cell?
SI rules say that pm or nm should be used (in stead of Å) to give the unit cell dimensions. What is the unit cell dimensions of NiAs expressed in pm and nm?
Calculate the volume of the unit cell and the volume per formula unit.

The density of a material is often determined pycnometrically. This returns a measure of the macroscopic density. Porosity (voids, pores between grains/crystallites) and contaminants will contribute to the measured density being smaller than the theoretical value for the material if it was "perfect" and built in three dimensions from the atomic arrangement found in the unit cell. Using X-ray diffraction it is possible to obtain information about the unit cell dimensions. The so-called "X-ray density" is the density calculated from the crystallographic data for the unit cell, i.e. for a perfect material:

$$\rho = m/V = Z \cdot FW/V/N_A$$

Where FW is the formula weight, N_A is Avogadro's number, V is the unit cell volume and Z is the number of formula units in the unit cell.

In a number of materials vacancies are found on crystallographic sites, which would be occupied in a perfect case. In other cases additional atoms are situated on non-framework positions (interstitial atoms). From accurate experimental density data it may be possible to estimate the likely defect structure in strongly defect materials (as e.g. defect-generating solid solution phases, see Chapter 10 in West) if the density for different defect models can be calculated.

> Exercise 4.
> Calculate the X-ray density of NiAs. Use data for exercise 3. Would you expect the pycnometrically determined density to be larger or smaller than this?
> NiAs type phases often have significant non-stoichiometry, i.e. the phases may exist with a small or large compositional region. NiAs does not display non-stoichiometry to any significant extent, but let us assume that the phase has interstitial Ni-atoms, and can be prepared with a composition $Ni_{1.01}As$. In addition let us assume that the unit cell parameters do not change (which they in practice would). Calculate the X-ray density for $Ni_{1.01}As$ and compare it with the value calculated for NiAs.

Crystal systems

There are seven different crystal systems. They differ by having different relations between unit cell axes and angles. The relations between the length of the unit cell axes and the angles between them are given in Table 1 and simple unit cells (with one atom in each corner) are shown in Figure 4. (The notation P in Figure 4 indicate that the unit cells are primitive, i.e. they contain only one point or atom, see section on space lattice).

Table 1

Relations		Crystal system
(t1, t2, t3)		
$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Cubic
$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Tetragonal
$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Orthorhombic
$a \neq b \neq c$	$\alpha = \gamma,\ \beta \neq 90^\circ$	Monoclinic
$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	Triclinic
$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Trigonal (Rhombohedral)
$a = b \neq c$	$\alpha = \beta;\ \gamma = 120^\circ$	Hexagonal

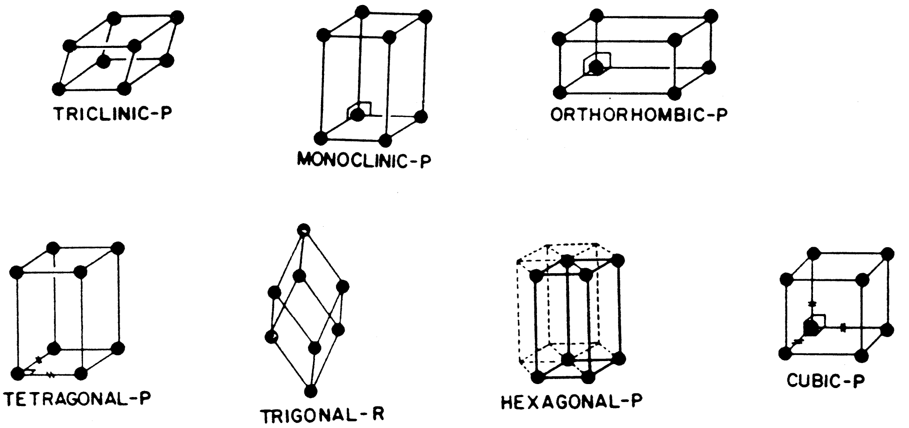


Figure 4. Schematic representation of the unit cells for the seven crystal systems (drawn with one atom in each corner of the unit cell).

Exercise 5.
Give the formula for the volume of (a) a tetragonal, (b) a monoclinic and (c) a hexagonal unit cell expressed by a, b, c, α, β and/or γ.

Crystal systems are arranged hierarchically in such a way that the higher crystal system contains at least one symmetry element that the lower system does not contain, see Figure 5. The cubic system is said to have the highest symmetry, and the triclinic the lowest. The symmetry may be seen as increasing from triclinic, via monoclinic, orthorhombic, hexagonal, tetragonal or rhombohedral to the cubic system.
Different crystallographic point groups belong to each of the seven different crystal systems (see below). The crystal systems are characterized by having certain symmetry operations. This is further detailed in the section on crystallographic point groups.

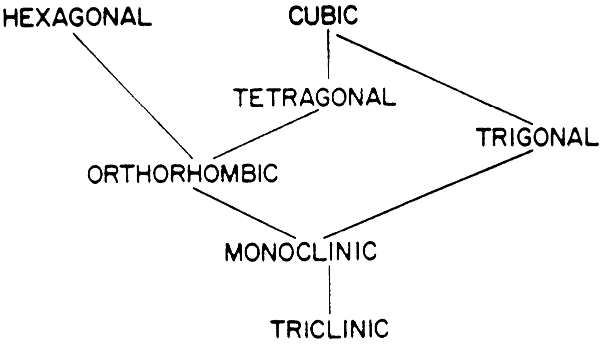
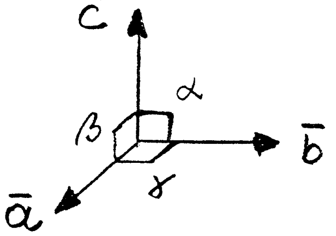
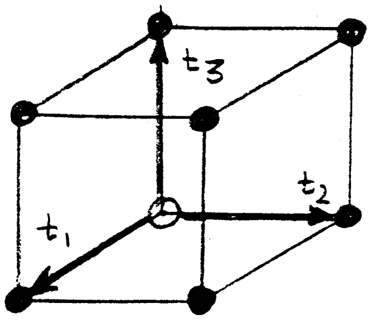


Figure 5. Hierarchy of crystal systems.

The simplest structure types (atomic arrangements) are metals and disordered alloys that crystallize with one of the close packed atomic arrangements, i.e. hexagonal (hcp, hexagonal close packing) or cubic (ccp, cubic close packing. NB! ccp is equivalent to fcc, face centred cubic). As examples could be mentioned that Mg, subgroup III (group 3) (Sc, Y, La) and subgroup IV (group 4) (Ti, Zr, Hf) have hcp structures, while Ni, Pd, Pt, Cu, Ag and Au have ccp structures. Co has both hcp and ccp phases. Hcp phases belong to the hexagonal crystal system, and ccp to the cubic. The simplest anion-cation (metal – non-metal) phases mentioned in West's book are based on close packing of anions with the cations in the small holes. For instance the NaCl-, CaF_2-, CsCl- and zinc blende structure types belong to the cubic crystal system, NiAs-type to the hexagonal crystal system, while rutile belong to the tetragonal crystal system. This means that when unit cell dimensions are tabulated for e.g. NaCl, it is sufficient to give the length of the a-axis, as the other relations ($a = b = c$, angles = 90°) are given by the cubic symmetry. For TiO_2 with the rutile structure, only the a- and c-axes are given.

Example 3 (Assignment of unit cells)
Consider the simple hexagonal unit cell, which was described in example 2. From the axes/angle-relations it is seen to satisfy the conditions for a hexagonal unit cell. Therefore the symmetry is said to be hexagonal. In much the same way a simple primitive cubic unit cell may be described by: $a = b = c$ *and* $\alpha = \beta = \gamma = 90°$. *The unit cell is shown below. The cubic unit cell (looking like a cube) has one atom in each corner. It is sufficient to specify that the unit cell is cubic and to give the length of the a-axis. When the structure is drawn as a projection on the ab- plane with the radius of the atoms* $r = a/2$, *the atoms will touch, and it will be evident that the structure is not close packed, as there are big voids between the spheres.*

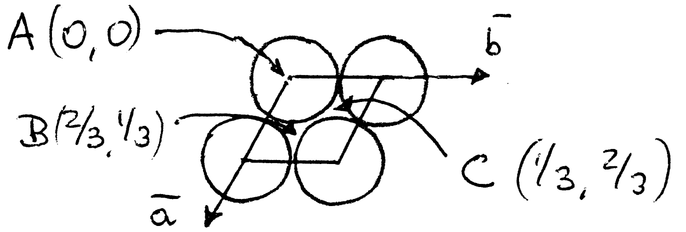




Example 4. (Close packing of spheres in three dimensions)
Again the starting point is the two-dimensional packing of spheres from example 1. Such a layer is close packed. Closer consideration reveals that the spheres touch and are placed like pearls on a string in three directions. Thus, in a close packed layer of spheres there are three close packed directions. If such layers are stacked on top of each other (along the c-axis) and systematically shifted with respect to each other in such a way that the spheres of one layer is positioned above the holes of the layer below, a three dimensional close packing of spheres is obtained.

This may be best illustrated by drawing the layers on individual transparent foils:

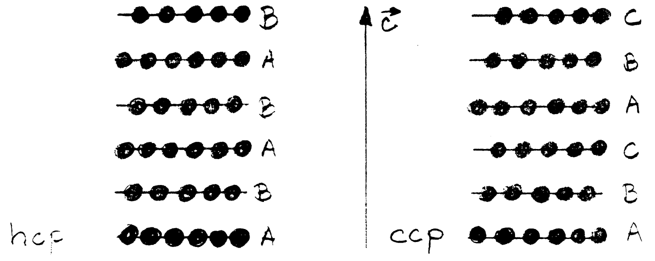
Consider one layer. On this layer you draw the two-dimensional unit cell described in example 1. The centre of atom A is the origo of the two-dimensional unit cell. We now choose this position as the origin of the three-dimensional unit cell, which we will derive from stacking of several close packed layers. The A-sphere therefore has the position (coordinate) (0,0,0). Also the spheres numbered 2, 3, and 4 in example 1 are described with this position. This is because their positions may be generated by adding to the position (0, 0, 0) multipla of the two-dimensional unit cell translations. This means that the position of all the spheres in the layer, which we now will call layer A, are given as (0+n, 0+m, 0) where n and m are integers.



Consider the four spheres in the unit cell. Between the spheres there are two indentations, between the 3 spheres A, 4 and 3, and between A, 2 and 3, respectively. We may call the positions which characterize the two indentations B and C. Consider now e.g. the triangle A,4,3 and the point B. By a bit of trigonometry the coordinates (2/3, 1/3) is found for B and (1/3, 2/3) for C. We define two new 2-dimentional sheets, named B and C, identical to the A sheet. The B sheet is placed so that there is a sphere right above the B position in the A sheet. The spheres of the B sheet have the coordinates (2/3, 1/3) relative to the chosen origo of the A sheet. In the same way the C sheet is placed so that the spheres have the coordinates (1/3, 2/3) relative to the chosen origo of sheet A.

By adding layers on top of each other and using the indentations one obtains a 3-dimensional close packing. If the repeating sequence of layer positions is ...AB..., it is a hexagonal closest packing (hcp), if the sequence is ...ABC... it is a cubic close packing (ccp).

Any (more complicated) ordering of layers is also a close packing, if there are no layers directly above an identical layer (i.e. there is no ...AA..., ...BB... or ...CC... sequence). The simple ordering sequences are those mentioned above, ...AB... and ...ABC.... However in many cases there is very little difference in energy between different ordering sequences for real materials, and the material has many different modifications. The ordering sequences may be complicated (e.g. ...ABCACBCAB...). The different ordering variants are called polytypes. These have an identical structure in two-dimentions, but some differences in the third dimension, the ordering direction. Polytypes are known in compounds such as Co, SiC, ZnS, ABO_3 and others.

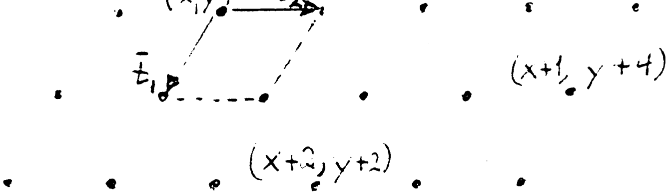


schematic – ordered stacking of sheets seen from the side (not 100 % correct displacement along the side)

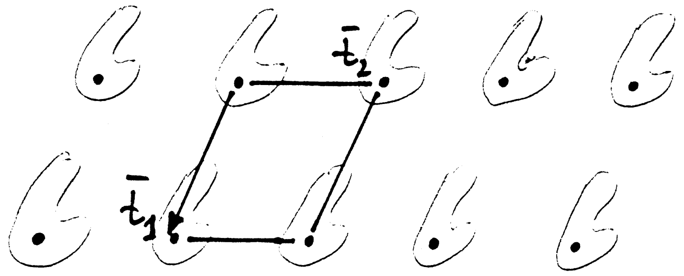
Space lattice.

The notation space lattice or lattice (rom-gitter) is a mathematical description of repeating units in solid materials. It is important to realize that a lattice is not the same as a structure. A structure is the atomic arrangement, whereas a lattice is made of mathematical points in space, and these may be translated by certain operations.

The similarity between a lattice and the unit cell is striking, especially for the primitive space lattices. The primitive space lattices contain only one point in the repeating unit, and it is placed in the corners of the unit. The different repeating units were described in "Unit cells and Crystal systems". There are 7 possibilities, and so there are 7 primitive space lattices. The relations between the translation vectors are also described above. Figure 4 was used to illustrate simple unit cells. The drawings in figure 4 may also represent the primitive space lattices with a lattice point placed in each corner. The primitive lattices are denoted with a P. The primitive rhombohedral is an exception to this rule – it is denoted with R.

> *Example 5 (primitive space lattices):*
> *Consider the primitive hexagonal space lattice. A (lattice)point (x, y, z) is transferred to equivalent points in the lattice by the translation vectors ($\mathbf{t_1}$, $\mathbf{t_2}$, $\mathbf{t_3}$). New (lattice)points have the coordinates ($x+n\mathbf{t_1}, y+m\mathbf{t_2}, z+o\mathbf{t_3}$), where n, m and o are integers. This is drawn in a 2-dimentionel projection below.*
>
> 
>
>
> *Consider the objects below. They are meant to represent a fragment of a structure. We see that the fragment is repeated in two dimensions. The repetition may be described as (new fragment) = (original fragment) + lattice translation. We choose a random point in one of the fragments, and mark similar points in the other fragments. These*

points can now be connected by translation vectors t_1 *and* t_2*, which are translation vectors of the 2-dimentional, primitive lattice.*



An absolute requirement to a space lattice is identical surroundings around every single lattice point. This is the starting point to the consideration whether there can be other space lattices than the primitive space lattices described above. It turns out, that all in all there are 14 different lattices which met the requirement. They are called Bravais lattices and are described below.

Bravais lattices.

It is relatively easy to prove that there are a total of 14 three-dimensional lattices which met the criteria of identical surroundings of the lattice points. These are called Bravais lattices, see figure 6. Seven of these are the primitive lattices described above.

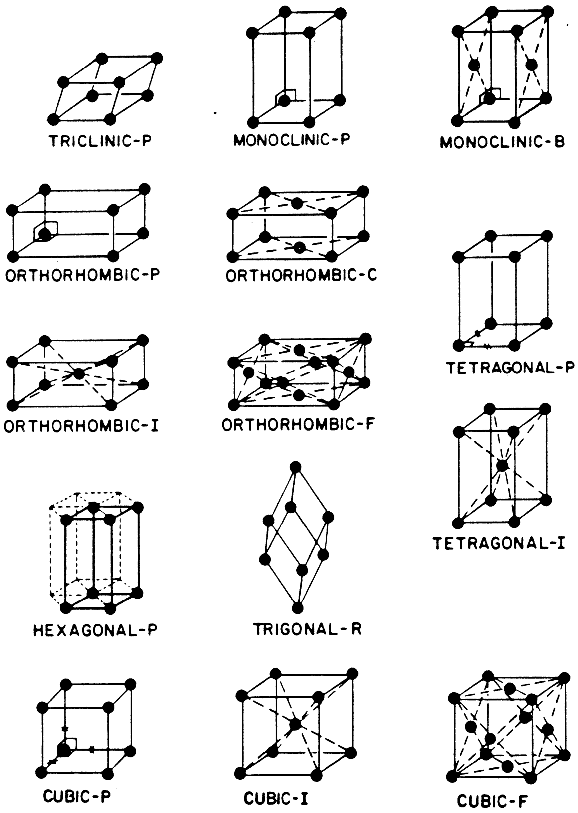


Figure 6. The 14 Bravais lattices.

The primitive Bravais lattices contain only one lattice point. The non primitive Bravais lattices contain more than one lattice point per unit cell (2 or 4), and are called centred lattices:

- Body-centred lattice (notation I for Innenzentrierung, new lattice point in **a**/2 + **b**/2 + **c**/2)
- Face-centred lattice (F, Flächenzentrierung, new lattice points **a**/2 + **b**/2 and + **a**/2 + **c**/2 and **b**/2 + **c**/2)
- Side-centred lattice (A, B or C, side centred on only some of the sides, e.g. **a**/2 + **b**/2. This is a C side centred lattice, which means that the centring are on the sides normal to the *c* direction/z axes)

The four different types of lattices are illustrated by the orthorhombic Bravais lattices in figure 6. The Bravais lattices matching the crystal systems are given in table 2.

> *Example 6 (Bravais lattices)*
> *Close packed, hcp and ccp, have a primitive hexagonal Bravais lattice and a face centred cubic Bravais lattice, respectively (see example 7). The relationship between the ccp packing and the cubic unit cell is discussed in West (see figure 7.5) but the relationship may be somewhat difficult to see. The close packed layers in the ccp structure lies perpendicular to the space diagonals in the cubic cell. The cubic unit cell has atoms placed in the corners and in the center of all the faces. If we neglect that there are atoms in the cell and replace them with mathematical points, it is clear that it is a cubic Bravais lattice with F centring. If an atom is placed at every lattice point, the face centred cubic structure is reached. This is known as fcc. This is also identical to ccp. For a fcc-metal Z = 4.*

Table 2:

Crystal system	Bravais lattice	Z
Cubic	P	1
	I	2
	F	4
Tetragonal	P	1
	I	2
Orthorhombic	P	1
	I	2
	C	2
	F	4
Monoclinic	P	1
	C	2
Triclinic	P	1
Rombohedral	R	1
Hexagonal	P	1

The centred Bravais lattices may also be represented by smaller primitive unit cells. These will however not show the highest symmetry of the system, which is a requirement for a crystallographic unit cell. See figure 7.

> Exercise 6:
> Show how the cubic F-Bravais lattice fulfils the requirements of a lattice (consider the surroundings of every lattice point).

Exercise 7:
Draw a tetragonal P lattice. Place an extra lattice point in ½, ½, 0, i.e. make a C centring of the lattice. Show that a tetragonal C lattice does not exist as such, i.e., that it is equivalent to (another) P lattice.

Brasvais lattices define the way a lattice point (ore a fragment of a structure, see example 5) is transferred to identical points (ore fragments). A crystal structure can therefore be described as

structure = lattice + basis

where the basis is made of the repeating structure fragment with a number of atoms with coordinates (x_i, y_i, z_i).

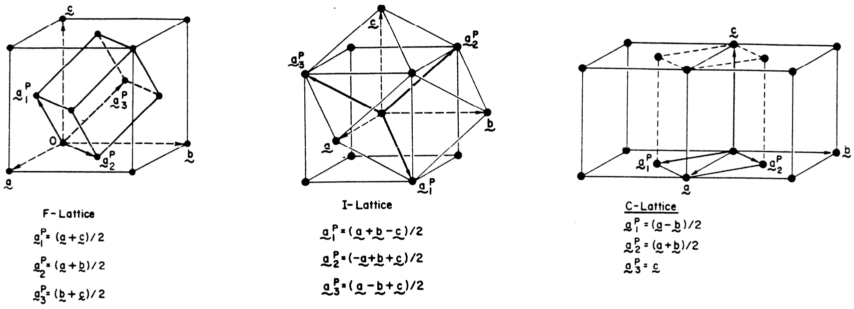


Figure 7. Relationship between primitive cells and F-, I- and C centred cells.

Some simple crystal structures are shown in Figure 8. From these it is possible to say what type of Bravais lattice the different structure types has. E.g. CsCl type structure has a Bravais lattice P-cubic, NaCl- and CaF_2 type have a F-cubic, NiAs type is P-hexagonal, whereas bcc (metal) has a I-cubic Bravais lattice. How this is seen is explained in example 7.

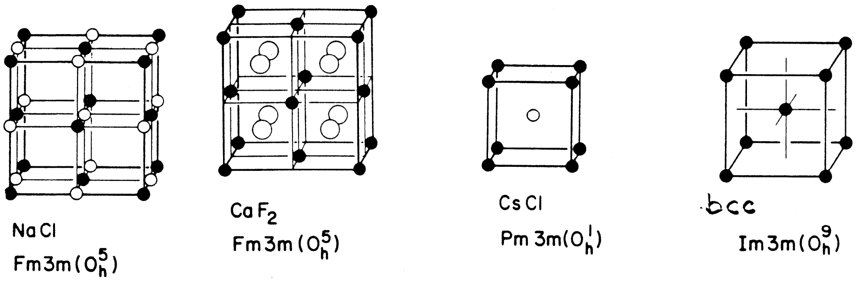


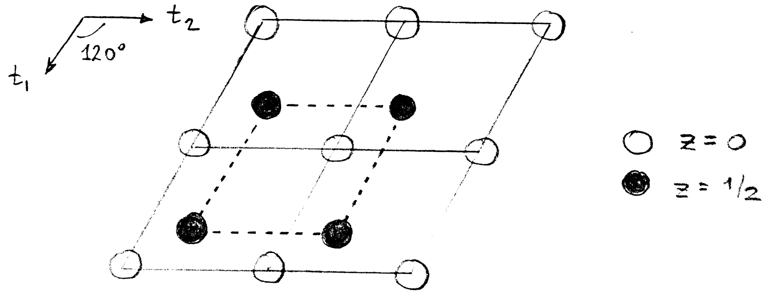
Figure 8. Schematic representation of NaCl-, CaF_2-, CsCl- and bcc type crystal structure. The symbols below the figures are space group notation.

Example 7 (Bravais lattice):
In this example we take a closer look at the CsCl type structure and hcp.

In CsCl (figure 8) the black spheres form a primitive cubic lattice (a=b=c, angles = 90°). The sphere in the centre is of another type and has nothing to do with the lattice of the black spheres. If several unit cells are drawn beside each other, it is possible to see which repeating rules that can be applied to the open spheres. You will find that the repeating unit is an identical cubic box with the same edge as the one of the black spheres. The Bravais lattice is the same, but because the spheres are different, they both are part of the basis of the structure; i.e. the CsCl type structure has a cubic P-lattice with Cs in (0, 0, 0) and Cl in (½, ½, ½). This can be seen as:

CsCl type structure = cubic P-lattice + basis [Cs in (0, 0, 0) and Cl in ((½, ½, ½)]

It is also easy to show that the hcp structure has a primitive hexagonal Bravais lattice. Look at the figure below.



The open spheres represent sheet A, the black sheet B, as in previous examples. Four unit cells (with a sphere A in origo) are marked with a full line. Consider now the 4 B-spheres. They define a unit cell as well (dotted line) which in shape and size is identical to the one defined by the A-spheres. The only difference is that the B-cells origo has been moved to (2/3, 1/3). In order to describe the hcp structure, the Bravais lattice can be said to be hexagonal primitive and basis to be two atoms in respectively (0, 0, 0) and (2/3, 1/3, 1/2); i.e.

hcp type structure = hexagonal P-lattice + basis [M in (0, 0, 0) and M in (2/3, 1/3, 1/2)]

A better description is given in example 9, where symmetry elements are considered as well.

> Exercise 8:
> Draw the structure of the anion-cation compound AB on the basis of the following information:
> The Bravais lattice is F-cubic
> Basis: A atom in (0, 0, 0) and B atom in (1/2, 0, 0)
> What is the name of this type of structure?
>
> Exercise 9:
> Ni has a cubic face centred structure, known as fcc, i.e. face centred cubic with basis: Ni in (0, 0, 0). The cell edge is 351 pm. Calculate the radius of the Ni spheres (metallic radius). Calculate the density of Ni.

Symmetry operations

In the following we will consider symmetry operations that can be used to describe isolated objects, e.g. a molecule in gas phase. The requirement of a symmetry operation is that when it operates (is used) on an atom with a set of atomic coordinates (x, y, z), an atom of the same type and with identical surroundings is created, but with the coordinates (x', y', z'). These are the symmetry elements which exist:

- Identity, that is (x, y, z) is transferred to itself (x, y, z). This symmetry element is included, because it is a requirement in the definition of a group in group theory, which is the mathematical tool used in symmetry considerations.
- Inversion, that is (x, y, z) is translated to (-x, -y, -z). If an object has this symmetry element, it is said to be centrosymmetric (det er sentrosymmetrisk).

- Rotation axis, a rotation axis is two fold, three fold etc. A n-fold axis rotate an object 360°/n.
- Mirror plane which places the object laterally reversed (mirror image) as far behind the mirror plane as it was in front. E.g. an xy-mirror plane (i.e. the xy plane is thought to be the plane of the mirror) transfers a point (x, y, z) to (x, y, -z).

Inversion symmetry and mirror planes both transfers a right handed object to a left handed object (like a mirror image; this is shown by writing a comma (,) in the circles, as shown in figure 9. The effect of these symmetry operations is schematically shown with hands in figure 9. The nomenclature (symbols) are also shown.

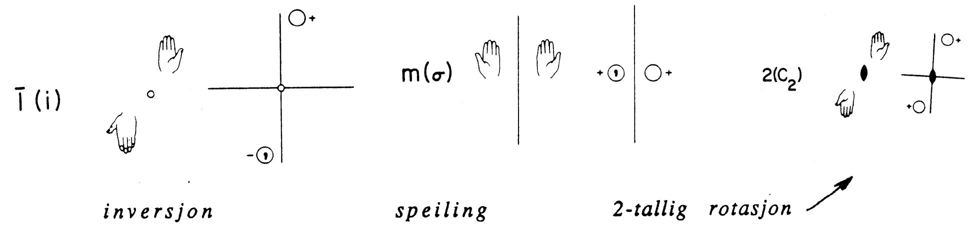


Figure 9: Inversion, reflection and two fold axes. The effect of the operations is shown with hands. The use of symbols is further described in point groups.

The origin of the symmetry operations and the coordinate system are chosen so as to reveal the highest possible symmetry.

Two sets of nomenclature are used to indicate symmetry operations. Schönflies nomenclature is often used in spectroscopy, whereas Hermann-Mauguin nomenclature is used in crystallography (description of structure). The notation is different, but the operations are of course the same, see Table 3.

Table 3

Symmetry operation	Schönflies symbol	Hermann-Mauguin symbol
Identity	E or I	I
Inversion (centro symmetric)	i	$\bar{1}$
Rotation axis	C_n (n=fold)	n
Mirror plane (reflection)	σ_h, σ_v	m

σ_h and σ_v are the notation for the horizontal and the vertical mirror plane respectively (defined relative to the main rotation axis.

> Exercise 10:
> Which symmetry operations can you identify for the following objects:
> (a) H_2O (b) NH_3 (c) CO_2 (d) CH_4 (e) a d_{xy} orbital

There are also combined symmetry operations, which means that two symmetry operations are performed right after each other and thus the "intermediate state" is not considered. Rotation-inversion axes are used in crystallography [rotation-inversion axes are denoted as –n, often expressed as $\bar{n}$], i.e. a n-fold rotation is done followed by an inversion. In the

Schönflies notation rotation-inversion axes are denoted S_n. Some examples of such symmetry operations are shown in figure 10.

> Exercise 11:
> The tetrahedron belongs to the group of objects with a symmetry in the cubic system. Compare the 4-fold rotation axes in a cube and in a tetrehedra.

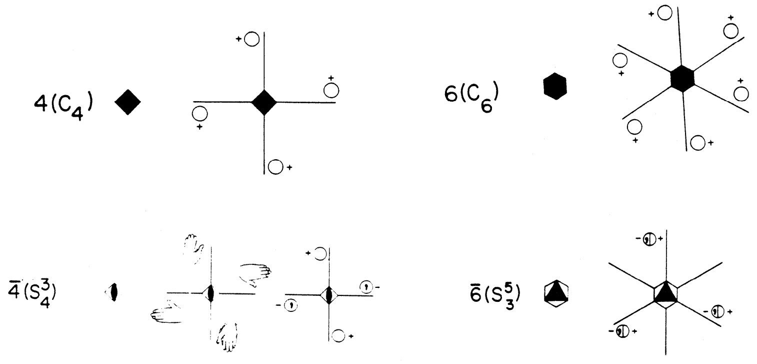
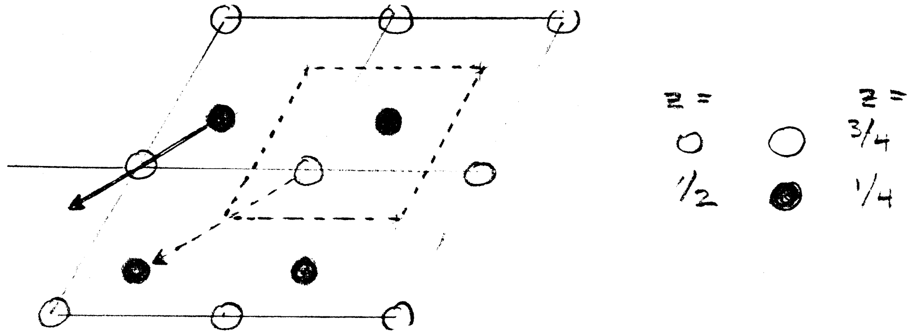


Figure 10: Symmetry operations 4, 6, $\bar{4}$ & $\bar{6}$.

Example 8 (Rotation axes, crystal system)
Let us consider hcp close packing. Let us first consider a 2-dimensional A sheet, and choose origo to be in the centre of a chosen sphere. We can now evaluate the n-fold rotation axis perpendicular to the close packed sheet. By a rotation of 60° the picture is identical, i.e. we have a 360°/60° = 6-fold rotation axis.
This is characteristic for the hexagonal crystal system, cf. Table 5. If we construct an ...AB... packing, we see that the 6-fold axes is not preserved, but in each sheet there are points with a 6-fold symmetry. This is discussed further in the paragraph on glide planes and screw axes.

Example 9 (Choise of origo, center of symmetry):
We consider at a projection of the hcp structure onto the ab plane:



Let us evaluate if this unit cell has an inversion center, i.e. it is centro symmetric. In this case all atomic coordinates, were given relative to the centre of symmetry placed in origo, must be transferred to identical coordinates for atoms by the inversion operation

$$(x_i, y_i, z_i) \rightarrow (-x_i, -y_i, -z_i)$$

If the origin chosen at the centre of an A-atom (open symbol, solid unit cell) we see that there are no centro symmetric surrounding A. For atom B with coordinates (2/3, 1/3, 1/2) there are no identical B- or A-atoms (A and B are identical atoms/spheres) *with coordinates (1/3, 2/3, 1/2) = (-2/3, -1/3, -1/2) = (-2/3 +1, -1/3 +1, -1/2+1); see solid arrow. The apparent lack of centro symmetry is actually due to the fact that we have chosen the wrong point as the centre of symmetry.*

Let us choose the point (1/3, 2/3, 1/4) as origo, which is assumed to be a centre of symmetry. First the coordinates in sheet A and B must be transformed to (0 -1/3, 0 -2/3, 0 -1/4) = (2/3, 1/3, 3/4) and (2/3 – 1/3, 1/3 – 2/3, 1/2 – 1/4) = (1/3, 2/3, 1/4), respectively. It is now easy to see that a centre of symmetry relates sheet A and sheet B, cf. the dotted arrow. The hcp structure is therefore centro symmetric. The unit cell with a center of symmetry in origo is dotted. A closer look at the figure reveals that there are more points, which are center of symmetry than (0, 0, 0).

Point groups.

A point group is described by a characteristic assembly of symmetry operations. A certain number of symmetry operations with defined geometrical relations among themselves can be found for any given object. The object is said to have symmetry described by the given point group. Different objects which have different symmetry will therefore be described with different point groups. All symmetry elements present refer to a common point, the origo.

*A point group must fulfil the mathematical requirements of a group:

- The product of two operations is another operation in the group
- The identity element (I) is present
- The existence of an inverse operator $RR^{-1} = 1$
- Associative multiplication of operations*

The point groups have different notation in Schönflies and Hermann-Mauguin nomenclature. In Schönflies nomenclature there are point groups such as C_{nv}, C_{nh}, D_{nh}, T_d, O_h etc, where n is the highest number of rotation axes present and v is the vertical mirror plane, which is only mentioned if there are no horizontal mirror planes (h). If there are two-fold axes perpendicular to the highest rotation axes, the point group is D_{nh}. T is a tetrahedral and O is an octahedral point group (cubic crystal system).

In the Hermann-Mauguin nomenclature similar information is given. The highest rotation axis is given first. E.g. a point group with only a two-fold rotation axes is denotated 2. C_{2h} (Schönflies) is notated 2/m, where the slash indicate that the mirror plane is perpendicular to the two-fold axis.

In the following only the Hermann-Mauguin nomenclature is used. The two types of nomenclature are compared for a number of point groups in Table 4.

Table 4.

Hermann-Mauguin nomenclature:

1	2	3	4	6	222	32	422	622	23	432
$\bar{1}$	2/m	$\bar{3}$	4/m	6/m	mmm	$\bar{3}$m	4/mmm	6/mmm	m3	m3m

Schönflies nomenclature:

C_1	C_2	C_3	C_4	C_6	D_2	D_3	D_4	D_6	T	O
C_i	C_{2h}	S_6	C_{4h}	C_{6h}	D_{2h}	D_{3d}	D_{4h}	D_{6h}	T_h	O_h

Example 10 (point symmetry):
Consider a small section of the close packing in twomensions in example 1 by choosing one sphere and the surrounding six. First we define the directions by letting the a- and b-axes be in the basal plane as shown in example 1. We let the c-axis be perpendicular to the ab-plane. The relations between the axes are those required in the hexagonal crystal system. We observe a 6-fold rotation axis runs through the central sphere and parallel to the c-axis. The basal plane is a mirror plane. Therefore the Hermann-Mauguin symbol must be 6/m. The full symbol is larger because all information on the symmetry relations along the axes in the basal plane must be given as well. This is described in the second part of the example below.

Exercise 12.
Give the Schönflies and Hermann-Mauguin symbols for point groups with the following symmetry elements: (a) a four-fold rotation axis (b) identity and an inversion axis (c) a four-fold rotation axis and a mirror plane perpendicular to the rotation axis.

Exercise 13:
Which symmetry elements can you identify in the point groups: (a) –1 (b) 3 (c) 6/m (d) –4/m

For isolated objects there is no limit on the "n"-fold of a rotation axis. Therefore one can imagine an infinite number of point groups, but only a few of these are found frequently in real objects. A five-fold rotation axis exists e.g. in an isolated flat C_5H_5 molecule. Global five-fold symmetry cannot appear in ordered, three-dimensional crystalline phases. On the other hand it is possible to observe units with a local five-fold symmetry in solid materials, even though it is not possible to fit 5-fold symmetry into a repeating lattice (see below).

The point group symbol tells which symmetry elements are essential to the point group (these may create other symmetry elements by being used on each other). Consider e.g. the point group 2/m. The symbol reveals that there is a two-fold rotation axis and a horizontal mirror plane. Because these elements are both present, the inversion element is automatically present too, figure 11. Thus, 2/m is a centro symmetrical point group. All in all the point group 2/m contain the symmetry operations. Identity, two-fold rotation axis, horizontal mirror plane and inversion.

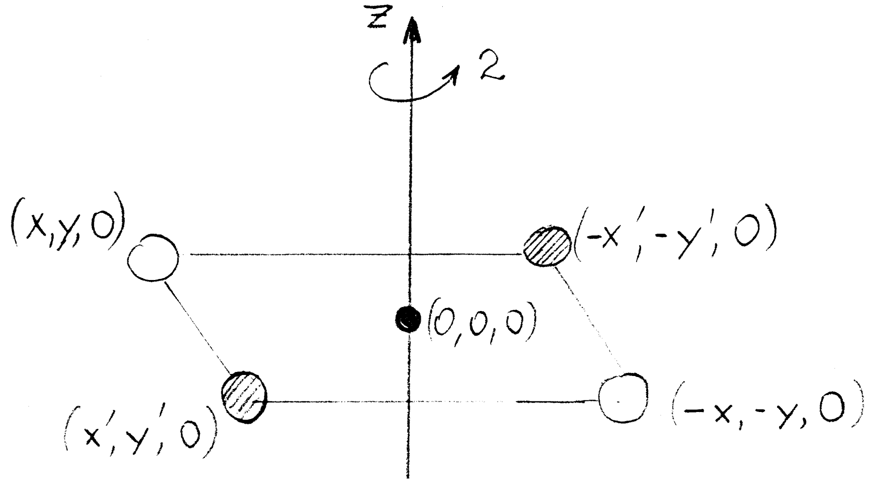


Figure 11. Structure fragment with point symmetry 2/m.

Those point groups which contain an inversion element are considered centro symmetrical. Certain properties in a material depend on the symmetry, e.g. the existence of electric dipoles, optic activity, pyro- and piezo-electricity. The last two are discussed in chapter 15 in West (not part of the curriculum).

> Exercise 14:
> Explain why a molecule with a permanent electric dipole (i.e. the molecule has a dipole moment) cannot be centro symmetric. Can a material built by hcp-packing display permanent polarization (i.e. have a total sum of dipole moments that is not zero)?

So far we have limited the description to cases with one rotation axis and one mirror plane (vertical or horizontal). If the description is extended to include also symmetry relations in orthogonal directions, the result is a number of new point groups. One can e.g. imagine a point group with three two-fold rotation axes, in the directions x, y and z in a cartesian coordinate system. This point group is called 222 (orthorhombic system) where all the symbols (the 2's) describe the symmetry relations in the orthogonal directions.

The combined point group symbols e.g. mm2 are interpreted following certain rules. For example the first symbol for orthorhombic and tetragonal point groups describes the symmetry along the z-axis (which is thereby chosen to have the highest rotation axis in the tetragonal crystal system), the next symbol describes the relations in a perpendicular direction (e.g. the y-axis) and in the orthorhombic system the last symbol describes the relations in the third direction, whereas in the tetragonal system it describes the symmetry in the [110] direction. More specialized rules for symbol, 2 and 3 must be used for trigonal, hexagonal and cubic point groups.

> *Example 10 (point symmetry, continued):*
> *In the hexagonal crystal system the first part of the combined point group symbol describes the symmetry conditions along the c-axis, the next the conditions along the a- and b-axes, and the third the conditions along a direction perpendicular to the a- and b-axes. If we look at the isolated object (1+6 spheres) we see that the a-axis is a two-fold rotation axis with a perpendicular mirror plane, i.e. with the symbol 2/m. We also note that perpendicular to the a-axis there is another two-fold rotation axis with a perpendicular mirror plane. The correct point group symbol is therefore 6/m2/m2/m.*

> Exercise 15:
> Consider the flat molecule trans-dichloro-ethen $C_2H_2Cl_2$. Draw the molecule in the xy-plane (let the z-direction be the direction with the two-fold axis). Identify the symmetry operations I, C_2^z, σ_h^{xy} and i (in Schönflies nomenclature). What are these called in Hermann-Mauguin nomenclature? Explain why the point group symbol is C_{2h} (Schönflies). How would you describe the point group with crystallographic nomenclature? Show that the assembly of symmetry elements fulfils the requirements of a group.

The point groups are classified under the different crystal systems. For a given crystal system certain characteristic symmetry elements can be identified, see Table 5. Note that the cubic crystal system is not characterized by the presence of four-fold axes, but by the existence of four three-fold axes.

Table 5:
Characteristic symmetry of different crystal systems:

Triclinic	-
Monoclinic	2 || **y**
Orthorhombic	2 || **x**, 2 || **y**, 2 || **z**
Trigonal	3 || [111]
Hexagonal	6 || **z**
Tetragonal	4 || **z**
Cubic	four times 3 || <111>

Example 11 (point group symbol):
The point group belonging to the hcp-packed structure is 6/m 2/m 2/m. From the symbol it is possible to say something about which crystal system the point group belongs to. 6/m means that the group has a six-fold rotation axis with a perpendicular mirror plane. A six-fold rotation axis is characteristic of the hexagonal crystal system, cf. table 5. Note that the highest rotation axis is always chosen to be parallel to the z-axis (Table 5). In the symbol of the point group, the symmetry along the highest rotation axis is mentioned first.

Exercise 16:
What can you read from the point group symbol: (a) 4/mmm (b) –42m?

Representation of point groups.

Visualization of symmetry relations is important in order to show which symmetry operations are present and at the same time show their relative position. This can be done by stereograms or by other kinds of projections. The different symmetry elements are assigned different symbols when they are represented in stereograms or in figures of symmetry elements of a space group (see below). The symbols are given in table 6 (the symbols have previously been used in the figure on symmetry operations).

Table 6:

Symmetry element	H-M symbol	graphic symbol
Rotation axes	1	nothing
(n-fold)	2	⬮
	3	▲
	4	◆
	5	⬟
	6	⬢
Inversion axes	-1	nothing
	-2 (≡m)	—
	-3	◬
	-4	◈
	-6	⬡
Mirror plane	m	—

Stereographic projections are used to represent the symmetry relations of a point group. These projections are made the following way (cf. figure 12):

(i) The crystal (object) is imagined surrounded by a sphere
(ii) The object is projected down on a xy-equatorial plane
(iii)The projection point at the xy-plane of a point on the object is found by drawing a connection line between the point and the opposite pole (notation + and – respectively) of the sphere. The point is at the interception between the line and the xy-plane
(iv)If the point lies in the + side of the sphere, it is drawn as •, if it in the – part, it is drawn as ◦.

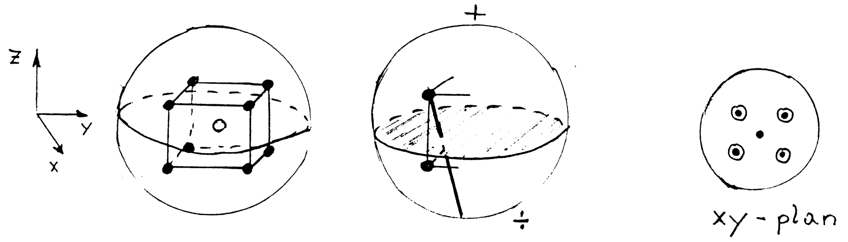


Figure 12. Principle of the stereographic projection.

It is easy to identify the symmetry elements from the distribution of points in a stereogram. On the other hand, if one draws one point in a stereogram and use the different symmetry operations in the point group on this, one will obstain a picture of how and how many times the point is repeated in the sphere/stereogram. Stereograms are used to indicate points, symmetry elements or crystal planes. Points are shown as open or closed symbols, and symmetry elements are shown by thick lines or symbols as shown in table 6.

A circle limits the stereograms, representing the intersection of the xy-plane with the sphere. Help lines are drawn as thin lines, e.g. marking the x- and y-direction. The z-axis, which is always chosen as the highest rotation axe, is perpendicular to the projection plane. Symmetry elements are drawn using the graphical symbols shown above. Vertical mirror planes are drawn as thick straight lines (according to the rules of how a projection is done), whereas a horizontal mirror plane is drawn as a thick line around the circle periphery in order to indicate that the xy-plane is a mirror plane. Stereograms for the point groups 2/m (monoclinic) and mmm (orthorhombic) are shown as examples in figure 13.

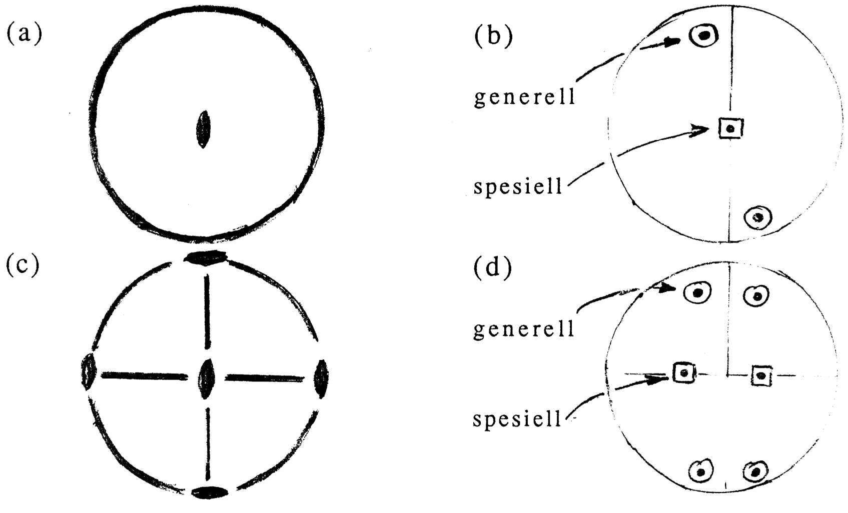
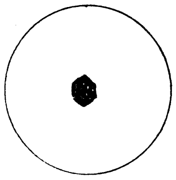
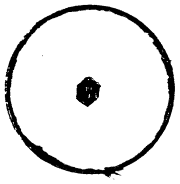


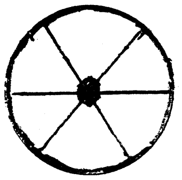
Figure 13. Stereogram for the point groups 2/m, (a) symmetry elements (b) the effect of the symmetry elements on general and special positions; and similar for mmm in (c) and (d).

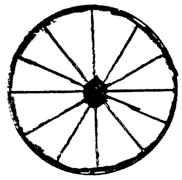
A general point is a point not situated on a symmetry element. Such a point is repeated the maximum number of times when operated on by all symmetry operations in the point group. The number of repetitions (including the identity operation) is characterise of the general position in the given point group. If the point is repeated 8 times, the position is said to be 8-fold. If the point is lying on one or more symmetry elements, these operations will transform the point onto itself. This means that the number of formed equivalent points is lower than it was the case for the general position. Points on symmetry elements are called special points (positions).

Example 12 (stereograms; symmetry elements):
If we are constructing a stereographic projection of the point group 6/mmm (relevant in hcp packing), we must first know the rules for the second (i.e. m) and the third symbol (also m). The second symbol inform of symmetry relations along the a- and b-axis in the hexagonal group, while the third symbol indicate the symmetry relations perpendicular to the a- and b-axes. We must to show the symmetry elements in a stereogram. The z-axis with the six-fold symmetry is chosen to be perpendicular to the projection plane. It is symbolised by a ⬢. Perpendicular to this is a mirror plane (therefore the symbol 6/m), i.e. the projection plane must be a mirror plane, which is indicated by a thick line around the projection circle. We indicate a vertical mirror plane along the a-axis by a thick straight line. Because this mirror plane is vertical, the six-fold symmetry will recreate the mirror plane total of 6 times. These mirror planes are also drawn as thick lines. Finally the mirror planes (and the equivalent mirror planes) perpendicular to the a-axis are drawn as thick lines, and the 6-fold symmetry repeats it 6 times.





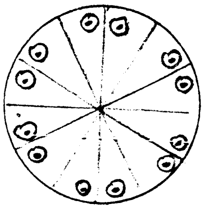


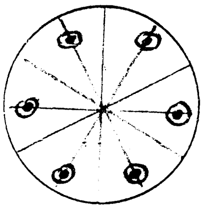


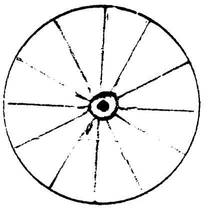
We can evaluate whether there are more symmetry elements than those specifically drawn in the figures above. It is for instance possible to identify 2-fold rotation axes along the a- and b-axis and perpendicular to these. This means that both symbols no. 2 and 3 in the point group symbol could be given as 2/m, so the whole symbol is 6/m 2/m 2/m. The last symbol is known as the full symbol of the point group. It is however unnecessary to give the full symbol, because the "new" symmetry operations (the two-fold axes) do not give any new equivalent positions, apart from those already made. The symbol 6/mmm identify all the essential symmetry elements of the point group.

Example 13 (Stereograms, points):
We consider the stereogram for the point group 6/mmm (see last Figure in the sequence above, example 12). We shall now look at how symmetry operations transform points. On a separate stereogram we place a general point (x,y,z). With a general point we understand a point that is not lying on any of the symmetry elements drawn in the stereogram in example 12. This is done at random, but the point is placed close to the periphery in order to make the figure easier to read. We can now operate using the actual symmetry elements in order to see how many times and where the general position is repeated – a total of 24 times (see below, to the left). Now we can make a specific choice to position the point on one of the vertical mirror planes

(see below, in the center). This mirror plane will not recreate the point anywhere else. The point represent a special position and is repeated 12 times by the symmetry elements of the system. If we imagine a point on the six-fold axis [in (0, 0, z), below to the right] none of the vertical mirror planes will recreate the point in a new position, and neither will the six-fold axis. The horizontal mirror plane will, on the other hand, recreate it (if it is not placed in the origo; $z \neq 0$). This is a two-fold position. We see that the point group is centro symmetrical (for the point x,y,z there is an equivalent point $-x,-y,-z$). The three described points are said to be 24-, 12- and 2-fold, respectively







Exercise 17:
Draw stereograms of the following point groups, and insert the symmetry elements: (a) 2 (b) m (c) 2/m 2/m 2/m (d) m m 2. Can any of the point groups be written in a simpler way, i.e. with a shorter symbol made of only the essential symmetry elements?

Exercise 18:
Place a general point (x,y,z) in a sphere and show the point in a stereographic projection. Operate on the point with the symmetry operations of each of the point groups in Exercise 17. Count how many times the general point is repeated in each case. What is the n-fold of the general positions of each of the four point groups?

Exercise 19:
Consider dichloromethane, CH_2Cl_2. Place the C-atom in origo and identify the symmetry elements. Draw the symmetry elements in a stereographic projection. State the point group symbol. Consider a general point. How many times is the general point repeated? Place points to represent the positions of C, H and Cl.

Exercise 20:
Use example 13 as a starting point. Identify a point in the stereogram of the point group 6/mmm that represent a 6-fold position.

Crystallographic point groups.

By crystallographic point groups we understand a selection of point groups that have symmetry elements that can all operate on a (infinite, 3-dimensional) lattice. This requirement is only fulfilled by 32 point groups.

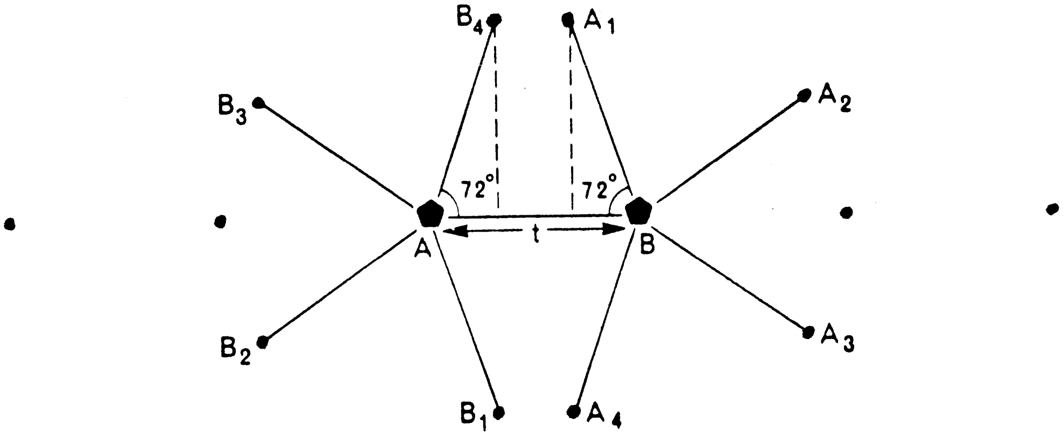


Figure 14. A representation of lattice points A and B. 5-fold rotation axes pass through the points A and B perpendicular to the paper.

We will take a closer look at these limitations and evaluate which rotation axes are possible for a lattice. Consider figure 14. The points A and B are two lattice points. According to the definition of a lattice, the points must have identical surroundings. We then evaluate this statement for different rotation axes that are thought to be perpendicular to the plane and pass through the points in such a way, that B recreate A and vice versa, as shown in figure 14 (the new points are numbered A_1, A_2 etc). The distance between two lattice points must be a multiple of the distance t between A and B (e.g. the distance B_4A_1; general A'B'). This means:

$$A'B' = AB - AB'\cos\delta - A'B\cos\delta = t(1 - 2\cos\delta) = mt, \text{ where m is an integer}$$

Because $-1 \leq \cos\delta < 1$, $(1 - m) = 2\cos\delta$ must be -2, -1, 0, 1 or 2, i.e. $\delta = \pi, \pm 2/3\pi, \pm 1/2\pi, \pm 1/3\pi$ or 0, so that the rotation axes has a fold $n = 2\pi/\delta$ equal to 2, 3, 4 or 6. Five-fold or higher than six-fold rotation axes are therefore not possible in a lattice. This, however, does not mean that it is impossible to find structure fragments with a five- or seven-fold symmetry, which is repeated by lattice/symmetry operations (this context also include quasi crystals).

There are 32 crystallographic point groups, divided into seven crystal systems (Table 7):

Table 7:

crystal system	crystallographic point group
triclinic	1, -1
monoclinic	2, m, 2/m
orthorhombic	222, mm2, mmm
tetragonal	4, -4, 4/m, 422, 4mm, -42m, 4/mmm
trigonal	3, -3, 32, 3m, -3m
hexagonal	6, -6, 6/m, 622, 6mm, -6m2, 6/mmm
cubic	23, m3, 432, -43m, m3m

Of these 11 are centro symmetric while 21 are non-centro symmetric. [*Systematic extinction, in the diffraction patterns (see crystallography and diffraction) are not depending on whether there is centro symmetry or not. If this is taken into account, one can only differentiate between 11 of the original 32 point groups. These 11 groups are known as Laue groups.*]

Glide planes and screw axes

In addition to the symmetry operations described for point groups, there are special symmetry operations for a solid material formed by pairing certain symmetry operations (rotation and mirroring) with translation. Two new symmetry elements appear, glide planes and screw axes.

A screw axis have the notation n_m where n is the rotation axis "fold" and m/n is the translation given as a fraction of the unit translation parallel to the rotation axis. There are e.g. 2_1, 4_1 and 6_3 screw axes. Figure 15 shows schematically how a 2_1 axis (parallel to the a-axis in the plane of the paper) operate on an object. If the object is e.g. a coin, the operation with the 2_1 axis means that tail (T, figure 15) is transferred to head (H, figure 15) and at the same time the coin is moved *a*/2 (1/2 unit vector) along **a**.

There are several types of glide planes; axial, diagonal and diamond type. Axial glide planes involve mirroring combined with a translation ½ along an axis. The axial glide planes are called a, b or c. Figure 15b shows a glide plane. The mirror plane consist of the xz-plane and the translation is done along **a**. In a similar example with a coin the tail side will remain tail after the operation, but it will appear as a mirror image (right – left hand operation).

Diagonal glide planes have the notation n, and diamond glide planes have the notation d.

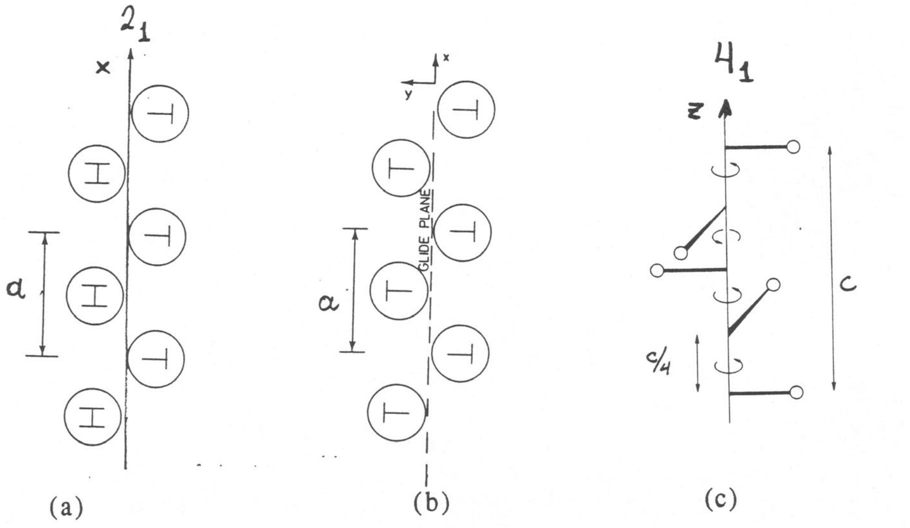


Figure 15. The effect of (a) 2_1 screw axis and (b) a-glide plane on a coin, whereas (c) is a 4_1 screw axis. The sides of the coin are marked by T and H, respectively.

In projections where symmetry elements are shown, glide planes are drawn either as dotted lines (different types of dots have different meaning) or their presence is marked separately by angled arrows. Screw axes are shown with the same symbols as rotation axes, but the symbol have "wings" in the corners (different number of wings e.g. for 4_1, 4_2 and 4_3 axes), see chosen examples in Figure 16.

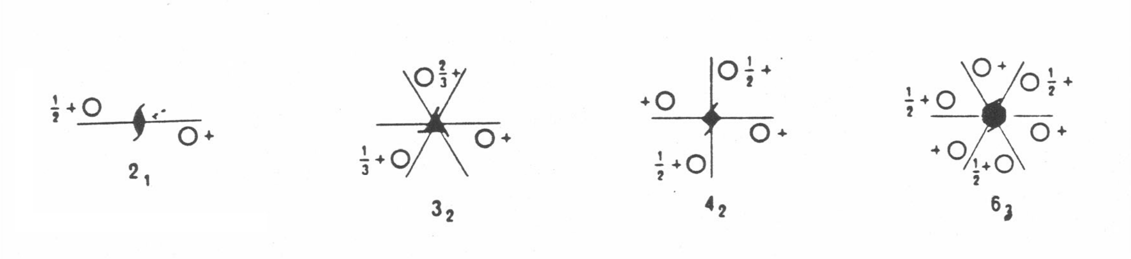
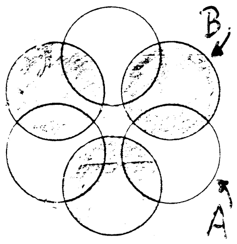


Figure 16: Examples of screw axis operations; projection perpendicular to the axes.

Example 14 (screw axes)
We consider again hcp. In example 8 it was shown that a close packed layer have a 6-fold rotation axis, which is not maintained if we stack several layers on top of each other in a close packing. In example 9 origo was defined in such a way that hcp was centro symmetrical. We choose this description as a basis for the following considerations, i.e. A-spheres are in the position (2/3, 1/3, 3/4) and B-spheres in (1/3, 2/3 1/4). A section of hcp consisting of six spheres (3 A and 3 B) is shown below.



*We let a rotation axis run perpendicular to the paper plane through origo (marked by x). We see that the axis is a three-fold rotation axe. The question is now whether the rotation can be continued with translation. Let us test the possibilities of a six-fold screw axe, i.e. a 6_m axe. When operating a 6_m axe, first a rotation of 60° is done followed by a translation in the direction of the axis (z-axis) i.e. m/6 units in fractional coordinates. In the ...AB... packing the next A layer has a z-value that is 1 higher than the original A-layer (i.e. one unit translation along **c**). The B-layer is in between the two A-layers (which are chosen to have z = 0 and z = 1), and is therefore given z = 1/2. From the figure it is seen that with an A-sphere as the starting point, a 60° rotation will give a B-sphere if the rotation is combined with a translation ½ along **c**. This means that a 6_3 screw axis is present. The situation is schematically shown in Figure 16 for 6_3 axes.*

***Mathematical description and nomenclature**

The orientation of x-, y- and z-axes in the coordinate system used in the description of the unit cells crystal system is following the right hand rule.

A symmetry operator, R, operates on a point **r** (see Figure 17) so that

$$\mathbf{r'} = \mathrm{R}\,\mathbf{r}$$

where R is a 3 x 3 matrix, i.e.

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

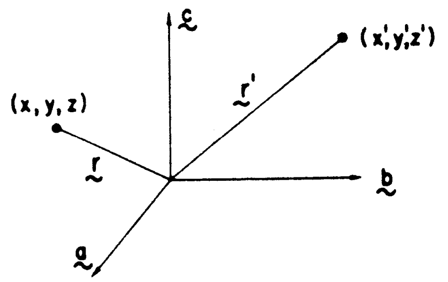


Figure 17: A point in space before and after a symmetry operation.

Symmetry operations in a three-dimensional lattice can be described more generally by a Seitz operator which include both a rotation and a translation part.

$$(\mathrm{R} \mid \mathbf{t}) = \mathrm{R}\mathbf{r} + \mathbf{t}$$

For the identity operator, I, all $a_{ij} = 0$ and $a_{ii} = 1$, and there is no translation. As Seitz operator the identity operator is written an (1 | 0). To describe a lattice, which is centred or only consist of unit translations, the Seitz operator (1 | $\mathbf{t}_n$) is used, where $\mathbf{t}_n = t_1\mathbf{a} + t_2\mathbf{b} + t_3\mathbf{c}$ and **a**, **b** and **c** are primitive translation vectors.

A rotation axis is defined as n [uvw] depending on the direction within the reference system (n fold, uvw give the direction). A two-fold rotation axis parallel to the z-axis is called 2[001].

$$(2[001] \mid 0)\ (x, y, z) \quad = \quad \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \quad = \quad \begin{bmatrix} -x \\ -y \\ z \end{bmatrix}$$

The inversion operator is described as

$$(-1 \mid 0)\ (x, y, z) = (-x, -y, -z)$$

A mirror plane (m) is defined by the direction as normal to the mirror plane. For instance a xy mirror plane is denoted m[010], and is described by:

$$(m[010] \mid 0)\ (x, y, z) = (x, -y, z)$$

By help of the mathematical formulas one can easily derive what happens when operating two different (or Identical) operators right after one another:

$$(m[001] \mid 0)(2[001] \mid 0) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = (-1 \mid 0)$$

From this we see that 2/m corresponds to inversion symmetry (-1 or $\bar{1}$).

A *b* glide plane with a yz mirror plane is described as

$$(m[100] \mid (0, 1/2, 0))\mathbf{r} = m[100]\mathbf{r} + (0, 1/2, 0)$$

and transfer the point (x, y, z) onto (-x, 1/2+y, z).*

Exercise 21:
Show how a 4_1 screw axis parallel to the z-axis influences the coordinates x, y, z.

Exercise 22:
Write the Seitz operator and describe with matrixes how a 3_2 screw axis parallel to the z-axis operate.

Space groups.

The combination of the 32 crystallographic point groups and the 14 Bravais lattices (which are again combinations of different crystal systems and non-centred or centred lattices) give rise to 230 different space groups (romgrupper).

A given crystal structure and a given structure type, will be described within a given space group, i.e. the Bravais lattice is defined together with the point symmetry. When structural data for a structure / compound are given in the literature the space group symbol, unit cell dimensions and coordinates (x, y, z) for the atoms are given.

Of the 230 space groups, 73 arise from combinations of Bravais lattices and the crystallographic point groups without any extra symmetry operations such as screw axes and glide planes being involved. These space groups are called symmorphic space groups. There are therefore 157 not-symmorphic space groups, and these must be described through one or more operators of the type

$$(R \mid \mathbf{t})\mathbf{r} = R\mathbf{r} + \mathbf{t} \text{ where } \mathbf{t} \neq 0.$$

The space groups are referred to by a so called space group symbol Xefg, where X gives the Bravais lattice (P, F, I or A, B, C). efg is the characteristic symbol for the crystallographic point group, but symbols of symmetry operations combined with translation, i.e. screw axes or glide planes, can be given instead of normal symbols of rotation axes and mirror planes. The not-symmorph space groups are characterised by their symbol contain e.g. a, b, c, n, 2_1, 3_2, 4_2......

In the triclinic crystal system there are only P-lattices, i.e. primitive Bravais lattices. This means that only Pefg space groups are found. In the triclinic system only a very few symmetry elements can be present. When more or higher symmetry elements than identity and inversion are present, the symmetry will be higher, i.e. there will be restrictions on angles or axes. In the triclinic system there are therefore only two possibilities; presence of only the identity element, and the identity together with inversion symmetry. The only two space groups in the triclinic system are P1 and P-1.

In the monoclinic system both mirror planes and two-fold rotation axes can be present, c.f. the monoclinic point groups 2, m and 2/m. The Bravais lattice may be primitive or side centred. This give rise to a total of 13 monoclinic space groups. In the orthorhombic system there are 59 space groups. We will not go further into detail regarding space groups here.

From the space group one can generally find the type of Bravais lattice (first letter in the symbol) and the crystallographic point group. To obtain the latter, one must exchange the symbols of the symmetry elements that involve translation with the symbols for elements without translation in the efg-symbol. Accordingly mirror plane symbols such as a, b, c, n and d must be replaced by m; screw axis symbols such as 2_1, 3_2, 6_1 are replaced by 2, 3 and 6, respectively.

> *Example 15 (Crystallographic point group belonging to space groups):*
> *hcp, bcc and fcc structures are described by the space groups* $P6_3/mmc$*, Im3m and Fm3m, respectively. From the space group symbols we can establish that hcp has a primitive Bravais lattice (P), bcc has a body centred (I) and fcc has a face centred lattice (F). It can also be established that they have the crystallographic point groups 6/mmm, m3m and m3m, respectively.*
>
> *Example 16 (Point symmetry):*
> *In the close packed structures hcp and fcc there are voids that may potentially be filled by (small) atoms. This is the basis for discussion of other structure types, e.g. NaCl and NiAs type structures, using the sphere packing model as a starting point. Consider an A- and a B-layer. Between these there are many voids – e.g. in the xy-positions we already have given for the sheet of type C. These holes are octahedral holes. Consider such a hole (use the figure in example 14). The octahedral hole is characterised by having 6 closest A- and B-spheres at the same distance and with a spatial distribution so that the symmetry relations of an octahedral point group is fulfilled (i.e. the actual symmetry relations are present). The local symmetry of the hole is octahedral. The corresponding applies for tetrahedral holes.*

>> Exercise 23:
>> Show that if a two-fold axis is present, the system cannot be triclinic. Show the same for a mirror plane.
>>
>> Exercise 24:
>> Consider a monoclinic system. Assume that a two-fold rotation axis is present and that there is also a mirror plane. How should the mirror plane be oriented relative to the two-fold axis in order to maintain the monoclinic symmetry?
>>
>> Exercise 25:
>> Which of the following space groups are symmorphic: (a) $P2_1/m$ (b) Pnma (c) $P6_3/mmc$ (d) I4/mmm ?
>> Based on example 14, determine whether hcp is described by a symmorphic or a non-symmorphic space group. For (a) – (d) give the corresponding crystallographic point group.
>>
>> Exercise 26:
>> To which crystal system belong the following space groups: (a) P2 (b) Pmm2 (c) Pnma (d) R3 (e) Fm3m (f) I4/mmm (g) $P6_3mc$?
>>
>> Exercise 27:
>> Which of the following space groups are centro symmetrical: (a) P2/m (b) Pmmm (c) P1 (d) $P2_1/c$ (e) P222 ?

International tables for crystallography.

“International tables for crystallography” is a composite work with information on the 230 space groups. The work is extensively used as a tool in the description of crystal structures. As a representative example, tabulated data are listed for the space group Pnma in the Appendix and it is discussed in the following.

The top line in the table section
Pnma D_2^{16} *mmm Orthorhombic*
tell that the space group is Pnma, it belongs to the crystallographic point group with the Schönflies symbol D_{2h} (numbered variants) and mmm in the Hermann-Maugin nomenclature. The crystal system is orthorhombic.

Next line
No. 62 $P2_1/n\ 2_1/m\ 2_1/a$ *Patterson symmetry Pmmm*
gives the number of the space group (numbered from 1 to 230 with increasing symmetry from triclinic to cubic), the full space group symbol (screw axes (2_1) perpendicular to the glide- and mirror planes are given in addition to the short symbol nma; i.e. the full space group symbol is shown). The last point shows the symmetry of a special map used in solving crystal structures from diffraction data.

Origin at -1 *on* 12_11
Tells whether the origo is placed relative to the symmetry elements. Origo is here on a center of symmetry. Generally origo is chosen to display the centro symmetry in centro symmetrical space groups.

Asymmetric unit $0 \leq x \leq 1/2;\ 0 \leq y \leq 1/4;\ 0 \leq z \leq 1$
give the smallest unit that will recreate the full picture of the structure in the unit cell when repeated using the symmetry operations of the space group. In this case the asymmetric unit is 1/8 of the unit cell.

Symmetry operators
List the symmetry operations (according to earlier stated nomenclature) and give their position within the unit cell.

The second page of the table for the space group is more important for the use of the tables as a tool to describe a given structure.

Positions
Multiplicity, Wyckoff letter, Site symmetry, Coordinates
Multiplicity describe how many times a given position is repeated by using all symmetry operations in the space group. The maximum number characterise the general position (i.e. a point that is not situated on any symmetry element). The general position is 8-fold in Pnma (the same as in the crystallographic point group) and there are three different special positions, all 4-fold. “Wyckoff letter” is a continuance alphabetic notation, which begins with “the most special position”. “Site symmetry” tell the point symmetry of the given (general or special) point. Coordinates gives the transformed coordinates of (x, y, z) after different symmetry operations have been operated. There are as many sets as the multiplicity of the position.

Reflection conditions
gives extinction conditions of the Bragg reflections, hkl, when the atoms are placed in the given Wyckoff positions (see Crystallography and diffraction).

Structural data

One main point for this compendium is to communicate enough knowledge to make it possible to use crystallographic data in literature to get a structural description. Often one may want to describe coordination polyhedra with bond distances and angles. Another aspect is to try to correlate structural and physical properties of materials.

Structure data for manganese monophosphide, MnP, as they are found in literature is given in table 8. The section from International Tables for Crystallography for the actual space group Pnma is shown in the Appendix and discussed above. Table 8 contains only the information that is strictly needed.

Table 8.

Compound: *MnP*
Space group: *Pnma*
Unit cell: *a = 525.5 pm, b = 318.0 pm, c = 590.5 pm*
Atom coordinates: *Mn in 4(c)* *x = 0.0050, z = 0.1885*
P in 4(c) *x = 0.1850, z = 0.5670.*

On the basis of these data and by using the International Tables for Crystallographic the structure is unambiguously described.

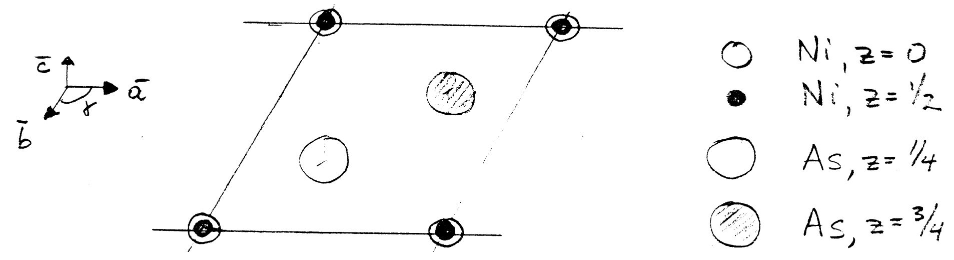
If the symbols for glide planes (n and a) are replaced by m for mirror plane in the space group symbol, one can from the symbol Pmmm identify a primitive lattice with a crystallographic point group (mmm) characteristic of the orthorhombic crystal system. As a consequence no angles need to be defined for the unit cell (all are 90°).

In order to be able to draw the structure of MnP one must use the information from "International Tables for Crystallography". One must know how the 4(c) positions are transformed. Note that it is not necessary to give the value of y in the listed structural data (Table 8) because 4(c) is a special position with y fixed in ¼ or ¾ (the position lies on a symmetry element that cannot be moved freely within the unit cell). On the contrary x and z are free parameters that can take any value between 0 and 1. The given values of x and z for MnP are determined from experimental diffraction data.

A sketch of a given structure is often made as a projection on a chosen (crystallographic) plane. Often the shortest possible projection axis is chosen in order to get the least possible number of overlapping atoms in the projection. For MnP one would make the projection on the **ac**-plane, because the b-axis is by far the shortest. Atoms of different kinds are drawn as different symbols (size, shape) and hatching is often used to illustrate different heights above the projection plane (the value of the third coordinate is often entered next to the symbols for the atoms). Computer programs are made in order to make better structural drawings. This makes it possible to obtain pictures while turning the structures, which makes it easier to discover details concerning coordination and bonding.

Calculation of interatomic distances and angles is necessary to get an overview of how the different atoms are bonded. Coordination and bonding distances are for instance different for different oxidation states for the same d-element (e.g. Cr^{III} is octahedral while Cr^{VI} is tetrahedral. Because the ionic radius $r(Cr^{III}) > r(Cr^{VI})$ the Cr-O distances depend on the oxidation state of chromium). For ionic anion-cation compounds short distances between the anions and cations are expected, where as there are longer distances (due to repulsive interactions) between cation and cation (and anion and anion). Metallic bonding is characterised by short metal-metal bonds. Physical properties (such as electric and magnetic properties, ionic transport etc) are closely related to the atomic arrangement. One must therefore be able to calculate distances and angles from listed crystallographic data.

Example 17 (Projection of structure):
Given the following data for the compound NiAs: $a = 360$ *pm,* $c = 510$ *pm, space group* $P6_3/mmc$ *with Ni in 2(a) and As in 2(c) positions. A copy of the relevant page from "International Tables for Crystallography" is given in the appendix.*
From the space group symbol it is seen that the Bravais lattice is primitive, and that the corresponding point group is 6/mmm (found by replacing symbols that involve translations with the corresponding symbols for operations without translations). The presence of a 6-fold axis means that the crystal system is hexagonal. The mirror plane perpendicular to the rotation axis (6/m) implies centro symmetry. As the unit cell has a 120° angle, it is natural to let the angle lie in the projection plane, i.e. we chose the ***ab****-plane as the projection plane, see the Figure below. If the axes are drawn to correct scale, it is possible to measure distances within the projection plane and to use Pythagoras to calculate interatomic distances.*



Example 18 (Interatomic distances):
We can calculate interatomic distances for NiAs and use this to describe the structure. If one draw several unit cells of NiAs (i.e. expands the figure in two dimensions) it is easily seen that the Ni atom is surrounded by 6 As atoms, and that the six atoms are distributed as an octahedral coordination polyhedron. The NiAs type structure is described as a hcp of As atoms, where all the octahedral voids are filled by Ni atoms. If you remove all the Ni atoms from the figure, you will recognize the hcp pattern for the As atoms.
The longest space diagonal has the length

$$l = \sqrt{a2 + a2\ \ 2aacos120^{o}} = a\sqrt{3}$$

The bond length d(Ni-As) is therefore

$$d(Ni\text{-}As) = \sqrt{((av3)/3)2 + (c/4)2}\ ] = 243.8\ pm.$$

The six Ni-As distances are identical.
The distance between the Ni atoms along the c-axis (the projection axe) are very short:

$$d(Ni\text{-}Ni) = c/2 = 255\ pm,$$

This clearly indicate, metallic bonding between the Ni atoms. According to this NiAs show metallic conductivity.

Exercise 28:
Draw a projection of the MnP type structure onto the *ac*-plane (use the data given above). How many formula units are there per unit cell? What is the crystallographic density of MnP? What kind of coordination polyhedron does Mn and P have? What is the average Mn – P bond distance for the six shortest (bonding) distances? What kind of bonding do you think exist between Mn and Mn based on calculations of distance and comparison of bond distances in pure Mn metal?

Exercise 29:
Use the MnP type structure as starting point. Let the unit cell dimensions be $a = 525.0$ pm, $b = 318.0$ pm and $c = 318.0 \bullet \sqrt{3}$ pm. Move the atoms so that Mn has the coordinate (0, 1/4, 1/4) and P (1/4, 1/4, 7/12), then use the symmetry operations. Consider then a projection onto the ***bc***-plane. Can you now identify a different symmetry than orthorhombic? Where is the 6_3 screw axis? Can you indicate a hexagonal unit cell? What is this structure type called?

Crystallographic planes and directions.

The unit cell vectors **a**, **b** and **c** for the unit cell define an internal coordinate system, which only in the case of cubic symmetry is Cartesian and have equal length of the vectors along the three directions. For solid materials of lower symmetry the axes *a*, *b* and *c* are often very different, e.g. one of the axes may be many times longer than the second longest axis. Not all crystal systems have orthogonal axes. For the monoclinic system the angle $\beta \neq 90^o$. For the hexagonal system $\gamma = 120^o$, see figure 4.

Crystallographic planes and directions are given relative to the coordinate system which is defined in the unit cell.

The crystallographic planes are <u>not</u> derived from the crystal structure itself, i.e. from the particular pattern of atoms or chemical bonds. On the contrary, planes and directions are defined from the unit cell / lattice.

For a given crystallographic plane or direction one can identify the distribution of atoms. For a layered structure the layers (with strong bonds between the atoms) are often stacked (via weak bonds) along a well defined crystallographic direction (often an axis in the unit cell). This applies e.g. to hcp close packing, where the ordering sequence ABABAB... follows the hexagonal c-axe, see figure 18, and the close packed layers are in the *ab*-plane. Mechanical properties (dislocations) for metals are closely related to planes and directions where there is close packing. The lubricating properties of graphite and MoS_2 are due to weak van der Waal forces between 2-dimensional layers bound together by strong bonds.

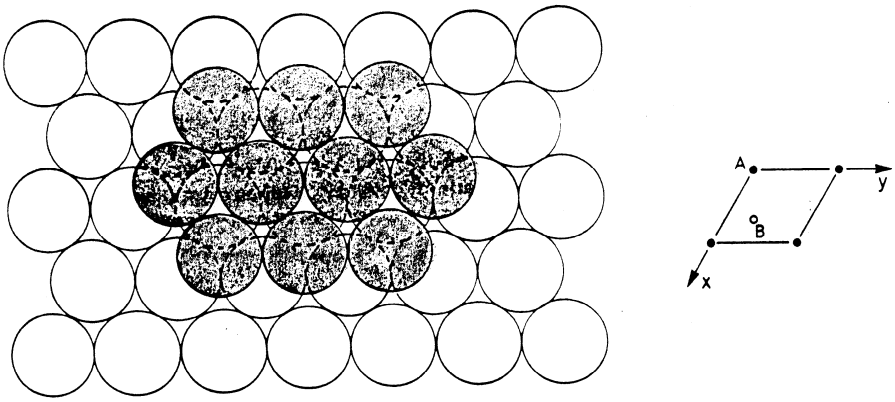


Figure 18: Hexagonal close packing. Open spheres A-layer, filled spheres B-layer. Projection on the *ab*-plane.

A plane that cuts through the x-, y- and z-axes (parallel to the *a*-, *b*- and *c*-axes for the unit cell) can generally be described through

$$x/u + y/v + z/w = 1$$

where u, v and w represent the values of where the plane intersect the three axes. Every crystallographic plane is identified of the so called Miller indices (hkl). The Miller indices are given by

$$h = 1/u,\ k = 1/v \text{ and } l = 1/w$$

Miller indices are integers (i.e. if necessary fractions are multiplied to integers for h, k and l). A plane that intersect the a-axis in a/2, the b-axis in b and the c-axis in c/4 has $u = 1/2$, $v = 1$ and $w = 1/4$, so that $h = 2$, $k = 1$ and $l = 4$. The Miller indices are therefore (214). In the same way one can from the Miller indices easily draw the particular planes for a given structure / unit cell / lattice. A plane (hkl) intersect the unit axes in 1/h, 1/j and 1/l. Some examples of crystallographic planes are shown in figure 19.

The intersection points between a plane and the axes may have positive or negative values. I.e. h, k and l can be positive, 0 or negative. Negative values for Miller indices are shown by a line above of the number, e.g. (10-1) is often written as (101). Note that a value of 0 in the Miller indices means that the plane is parallel to the actual axis, e.g. the (hk0) plane is parallel to the c-axis, Figure 19. *If one considers the ***ab***-plane for a hexagonal crystal it may be relevant to define a fourth axis (the third within the ***ab***-plane) if an 120° angle to the *a*- and *b*-axes. This results in an extra Miller index (see below) with the notation i, but because the requirement $h + k + i = 0$ always applies, it is not necessary to state i.*

This way of describing is used for crystallographic planes within the unit cell and for describing outer surfaces of a macroscopic crystal (e.g. in mineralogy). The outer crystal planes are mostly parallel to certain crystallographic planes. This means that the crystal growth has been in certain preferred directions. Some materials are formed as needles (e.g. asbestos), others as plates (mica), something which often can be understood by considering the crystal structure. Diamonds are cut in such a way that the outer surface are parallel to certain crystal planes (brilliants).

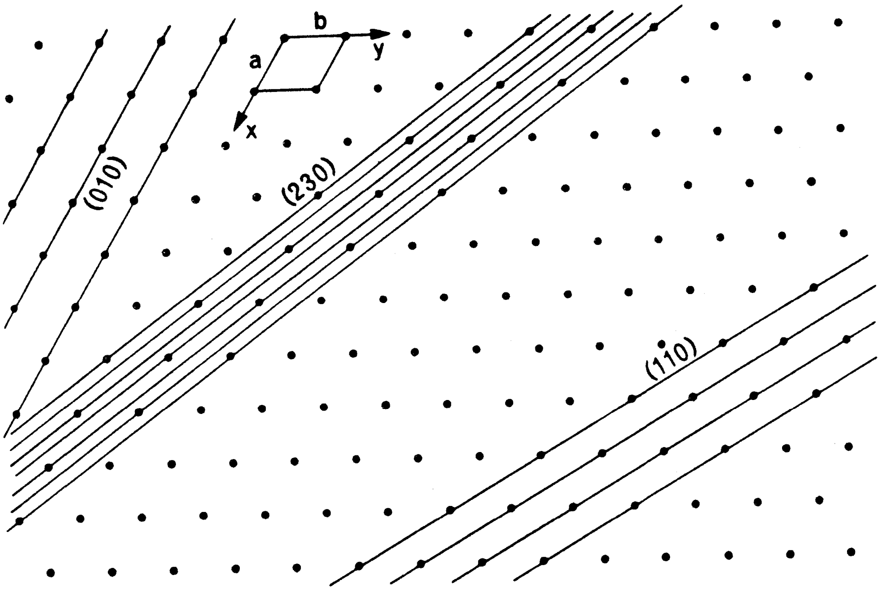


Figure 19. Projection of lattice points in a hexagonal primitive lattice onto the *ab*-plane. Different crystallographic planes parallel to the z-axis are shown.

Indices for the faces of a hypothetical crystal are shown in figure 20. These are also given as (hkl). Note that (100) is parallel to the y- and z-axes and intersect the x-axis of a positive value of x, and that $(\bar{1}00)$ is also parallel to the y- and z-axes but intersect the x-axis of a negative value.

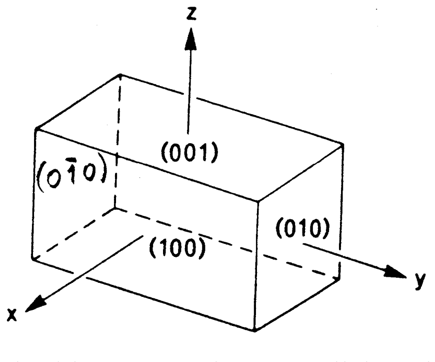


Figure 20: Hypothetic crystal with outer surfaces parallel to the faces of the corresponding crystallographic unit cell.

Directions within a crystal are easiest defined from origo. Directions are given in square brackets. The direction [100] is parallel to the a-axis, while [001] is parallel to the c-axis. $[00\bar{1}]$ is also parallel to the c-axis but points towards smaller values of the z-coordinates (in negative direction). Generally, directional indices are vector components of the directions concerning the unit cell axes. The direction [111] can be defined as the line through origo and the point translated from origo by the unit translations $1\mathbf{t}_1$, $1\mathbf{t}_2$, $1\mathbf{t}_3$ (generally for [uvw]; the direction from origo through the point $u\mathbf{t}_1$, $v\mathbf{t}_2$, $w\mathbf{t}_3$), see figure 21.

Planes are always given in brackets; i.e. as (hkl). If one wishes to indicate all sets of equivalent planes it is given as {hkl}. Directions are given is square brackets [uvw]. If one wishes to give all equivalent directions, e.g. all [111] directions within a cubic crystal, it is indicated by <hkl>.

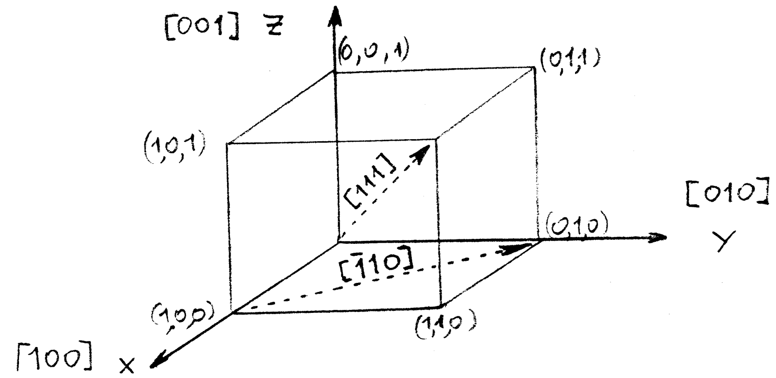
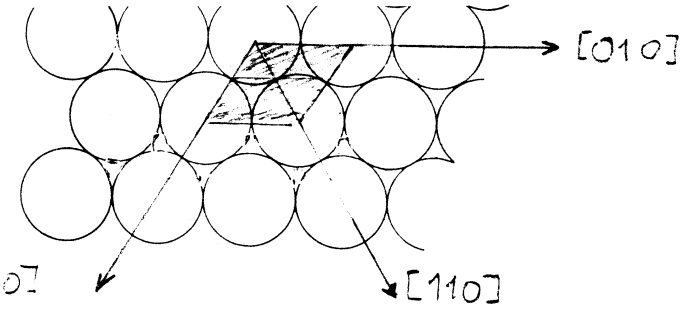


Figure 21. Statement of crystallographic directions [uvw]. Coordinates for some points are given in brackets (must not be confused with statement of planes).

Example 19:
Again we consider the most common metal structures, hcp, bcc and fcc. Mechanical properties of metals are related to the number of close packed directions and planes. We first consider a close packed plane, like those found in hcp and fcc materials.



In such a layer (hexagonal unit cell indicated; compare examples 1 – 3) there are directions where the atoms (spheres) lie like pearls on a string, i.e. as close as possible. There are three such close packed directions, along the a-axis [100], along the b-axis [010] and along the c-axis [001], respectively. Every close packed layer has three close packed directions.

In the hcp structure the basal plane is made of this close packed layer, i.e. it lies in the ab-plane perpendicular to the hexagonal axis. This means that the c-axis is normal to the close packed layer. The close packed layer can be given as (001). The hcp structure has only one close packed layer.

In the fcc unit cell the relation to the close packed layer is somewhat more complicated (compare West figure 7.5.). The close packed layers normally lie on the space diagonal for the cubic face centred unit cell. I.e. such a plane can be given with the Miller indices (111). In the cubic unit cell four space diagonals can be drawn. There are close packed layers perpendicular to all these. All these equivalent layers are given as {111}. The fcc structure has four close packed layers.

Thus, last we consider the bcc structure. This is not a close packed structure and does not contain any close packed layers. If we consider the unit cell with atoms in (0, 0, 0) and in (1/2, 1/2, 1/2), we see that the central atom can be thought to touch all atoms in the corners of the cube. This means that the atoms lie like pearls on a string along the space diagonals. As in the fcc structure, bcc has 4 close packed directions, i.e. <111>, but it does not have any close packed planes.

Exercise 30:
Identify the planes with the Miller indices (100), (110) and (111) for the NaCl type structure (unit cell parameter a = 450 pm). How many Na and Cl atoms are there per unit area in the three planes?

Exercise 31:
Consider NaCl again (exercise 30). Calculate the distance between closest laying planes with Miller indices (100), (110) and (111). Make similar calculations for the planes (100), (200) and (400).

Exercise 32:
Show that the intra plane distance d_{hkl} in a cubic crystal (with the unit cell parameter a) is generally given by (see Jastrsebski)
$d = a/(h^2 + k^2 + l^2)^{1/2}$
How will this equation look like for (a) a tetragonal and (b) an orthorhombic crystal.

Crystallography and diffraction.

The systematic repeating lattice in a solid material, and hence the resulting repeating pattern of atoms will, when the material is irradiated by neutrons, X-ray phonons or electrons with a wavelength of the same size as the interatomic distances, give rise to characteristic diffraction patterns. The diffraction pattern from e.g. a powder material, is often given in form of d-values for the so called Bragg reflections. The reason for the observed reflection with the d-value d_{hkl} is interference from the crystal planes (hkl). These planes have a reciprocal plane distance d_{hkl}. In addition to the d-value the measured intensity is given for the observed reflection.

Powder diffraction gives in a fast and practical way information on Bragg reflections with a d-value d_{hkl} and intensity I_{hkl}. The set of d_{hkl} and I_{hkl} constitute a characteristic fingerprint for a given compound. Collecting diffraction data is a very central in characterisation of synthesis products, materials, minerals, corrosion products etc. Such characteristic sets of d_{hkl} and I_{hkl} for inorganic and organic compounds are assembled in databases.

Crystallographic planes are related to diffraction angle and wavelength for the radiation used through Braggs law

$$2\, d_{hkl} \sin \theta = \lambda$$

where d_{hkl} is the distance between planes. In diffraction experiments the diffracted intensity is measured as a function of diffraction angle θ. This gives a set of d_{hkl} and I_{hkl}. Note, that reflections from planes with the largest plane distance will be observed with the lowest θ. For monoclinic phases d_{hkl} will be different from d_{-hkl}, see figure 22. This mean that more reflections are observed in the diffraction diagram. For $\beta = 90^\circ$ d_{hkl} is equal to d_{-hkl}.

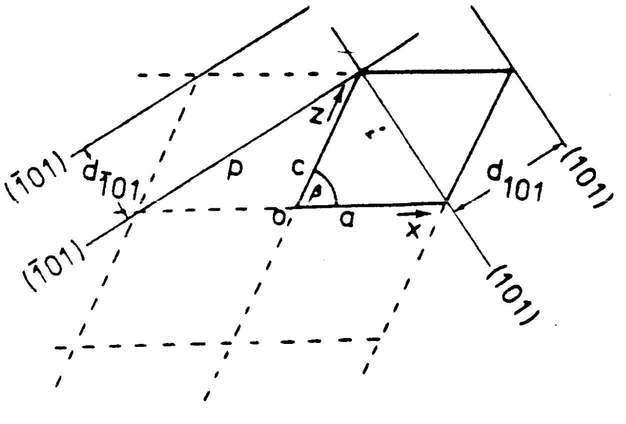


Figure 22. Negative and positive Miller indices for crystallographic planes.

When special symmetry operations are present, the closest lying plane (with the same hkl) reflects with the opposite phase and the combined intensity will be zero, i.e. $I_{hkl} = 0$. Such cases are called systematic extinction. From the observed reflections (or lack of observed reflections) possible extinction rules can be identified, which is a great help in determination of the space group. It is often a requirement for single crystal diffraction data that one can get enough data from different planes to make a reliable identification of the extinction rules. In powder diffraction data there will often be an overlap of reflections that are too close in d-value to be separated in the measured data (depends on instrument, beam and quality of the sample).

Systematic extinction exist because of centring of the Bravais lattices, compare Table 9. The conditions mentioned must be fulfilled for $I_{hkl} \neq 0$; i.e. in order to observe the Bragg reflections.

Table 9.

I centring	*hkl: h+k+l=2n (i.e. 0 or an even number)*
F centring	*hkl: h+k=2n; h+l=2n; k+l=2n; i.e. h,k and l are all either even or odd*
C centring	*hkl; h+k=2n*

From the information in Table 9, it is seen that if only (111), (200), (220), (311), (222), (400), (331) etc are observed for a cubic lattice, the lattice must be F-centred. If only (110), (200), (211), (220), (222), (321), (400), (330), (420) etc. are observed, the lattice is I-centred. If the reflections 100 and 110 are observed for a cubic phase, the lattice must be primitive.

Screw axes and glide planes (because they involve translations) also give rise to systematically extinctions (but this will not be considered here).

Powder X-ray diffraction, as described above, are central in characterisation of solids / inorganic compounds. One can e.g. determine purity (0.5 – 2w%), identify pollution phases, determine symmetry and the unit cell parameters, and by more sophisticated experiments, determine the crystal structure.

Often conventional X-ray from an X-ray tube and an x-ray generator is used for such experiments. Different types of radiation can be used, e.g. monochromatic Cr, Cu or Mo-radiation (this is discussed thoroughly in KJ/MV 213). The choice of radiation depends on what one wishes to study. Some elements emit considerable fluorescence (give more background; i.e. reduce the signal to noise ratio) when they are being exposed to a certain wavelength. In some experiments it is desirable to get good angular resolution (in θ), in other experiments it is desirable to collect information on a many Bragg reflections as possible (position d_{hkl} and intensity I_{hkl}).

As an example we consider a powder sample of a cubic phase with unit cell dimension a = 600 pm. If the material is studied using both $CrK\alpha_1$ radiation with λ = 228.98 pm and $MoK\alpha_1$ radiation with λ = 71.09 pm, one can give the following estimate of how many reflections can be observed if the maximum available experimental scattering angle is $\theta_{max} = 45^o$:

$$2d \sin\theta = \lambda \text{ and}$$

$$d = a/(h^2+k^2+l^2)^{1/2} \text{ (only applies for cubic symmetry)}$$

so that

$$(h^2+k^2+l^2)_{max} = 4a^2\sin^2\theta_{max}/\lambda^2 = 72/\lambda^2$$

For the two types of radiation the number of reflections is calculated as:
$CrK\alpha_1$: $(h^2+k^2+l^2)_{max} = 13.7$, i.e. $(h^2+k^2+l^2)_{max} = 13$ (integer)
$MoK\alpha_1$: $(h^2+k^2+l^2)_{max} = 142.5$, i.e. $(h^2+k^2+l^2)_{max} = 142$ (integer),
i.e. for a primitive (P) cubic lattice there will be maximum of 12 (note that it is not possible to have a plane so that $h^2+k^2+l^2 = 7$) and around one hundred reflections to be observed in the two cases, respectively.

> *Example 20:*
> *We consider which reflections we may expect to observe from a fcc metal with unit cell parameter a = 400 pm. Because the Bravais lattice is F-centred, only reflections in agreement with the systematic extinction rules can be observed. I.e. reflections where h, k and l are not all odd or all even will have zero intensity (compare Table 9). We therefore expect to observe the reflections (111), (200), (220), (311), (222), (400), (331), (420), etc. These are observed in the powder diffraction diagram for d-values given by* $d_{hkl} = (400\text{ pm}/(h^2+k^2+l^2)^{1/2}$, *so that e.g.* $d_{200} = 200$ *pm and* $d_{311} = 110.9$ *pm. In the scattering angle* θ, *this corresponds to* 45.3^o *and* 88.0^o *,respectively, if monochromatic* $CuK\alpha_1$ *radiation is been used with* $\lambda = 154.06$ *pm.*
>
> > Exercise 33.
> > Give the first five reflections which are expected to be observed in a powder diffraction diagram of NiAs with a = 360 pm and c = 510 pm, space group $P6_3/mmc$. The rule which applies for a hexagonal crystal structure is:
> > $1/d^2_{hkl} = [(h^2+k^2+hk)/3a^2 + l^2/4c^2]$

Defects and crystallography

Defects are categorised depending on whether they are isolated one-, two- or three-dimensional. Some comments will be made concerning isolated defects (point defects) and condensed defects in form of defect clusters.

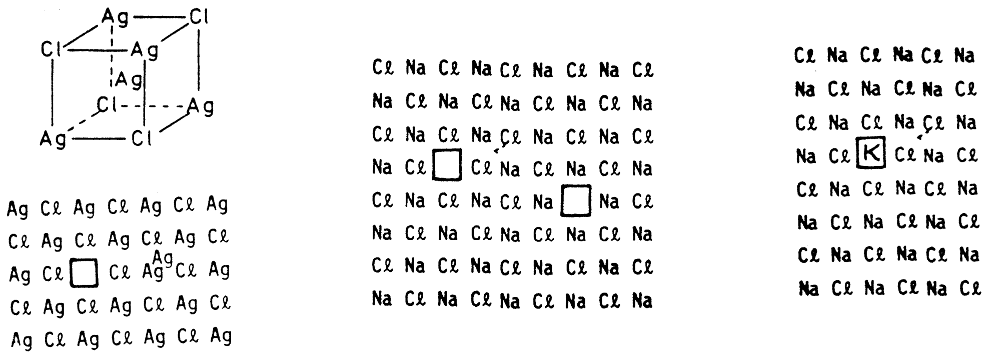
The ideal crystal structure is a natural reference system in which all atomic positions are completely filled. These positions are defined from symmetry operations in the unit cell and the repeating pattern of unit cells (the lattice). In the perfect case all atomic positions for all types of atoms in a compound are 100 % filled.

It should be noted that from this definition there are compounds which are never perfect – i.e. the compounds exist only because of the presence of a significant number of defects (the presence of non-stoichiometry). Some ion conducting materials belong to this category. Other compounds have measurable but very small deviations from ideal behaviour. The formation of defect in a material costs enthalpy but increase the entropy. This means that the defect concentration in a material increases with temperature.

Isolated defects (see chapter 9 in West and figure 23) are found e.g. as:

- vacancies
- wrong distribution of atoms on atomic positions belonging to the structure
- extra (interstitial) atoms in positions other than usual in the structure.

All these types of defects influenceson the distribution of atoms on the different possible crystallographic positions. They have nothing to do with the lattice, which is only a mathematical description of the repetition of lattice points. In order to describe an interstitial defect situation, one must add extra atom positions in the structure description and allow a small statistic distribution of atoms on these positions. When giving a chemical formula for a defect material this must be done in agreement with crystallographic realities. NiO can be prepared with a molar ratio of Ni/O < 1. The phase must be described as $Ni_{1-x}O$ and not NiO_{1+y} because there is a formation of vacant Ni positions in normal octahedral positions in the NaCl type structure. The situation in wüstite, $Fe_{1-x}O$ is described in details in West. In wüstite the defect concentration is high so that defects can interact and form defect clusters (minimizing energy). Vacancies are found on octahedral positions and in addition some tetrahedral positions are the filled by Fe^{3+}. The formation of vacancies and filling of tetrahedral positions are spatially confined, i.e. they are located close to each other.



(a) (b) (c)

Figure 23: Schematic representation of (a) vacancy on Ag-positions in AgCl (NaCl type structure) with simultaneous interstitial Ag in a vacant tetrahedral position (Frenkel defect), (b) vacancies in both cation and anion positions (Schottky defect) and (c) K substitution on the cation position.

Measurements of pycnometric density and comparison with the X-ray density calculated from the measured unit cell dimensions and different presumed defect models may, when defect concentrations are large, show which type of defect situation exists (vacancies versus interstitial).

> Exercise 34:
> Frenkel defects in NaCl type compounds, e.g. AgCl, are related to vacancies in normal Ag positions at the same time as Ag are located in interstitial positions. To be more explicit; Ag is situated in a tetrahedral position in a close packed

arrangement of Cl-anions. Give the coordinates for the two positions which are effected by a Frenkel defect (i.e. the normal Ag-position and the tetrahedral position).

Unit cell and solid solution

When complete solid solubility between two phases exists, one has a so called mixed phase / solid-solution phase (see Chapter 10 in West). If the two end members have the same structure type (the structures must be closely related in order to get a complete solubility) then the crystal system, Bravais lattice and space group will remain unchanged regardless of the composition of the solid solution phase. One would expect certain small changes for the unit cell dimensions and atomic coordinates since the atoms which subsidise each other have somewhat different size.

In the ideal case Vegard's law is followed, i.e. the unit cell dimensions varies linearly with the ratio of the composition of the values of the end members. Different types of deviation from ideal behaviour may be observed; negative, positive (both symmetric deviance) or asymmetrically deviation. Positive deviation (on the volume-composition-curve) may be taken as an indication of additional repulsive interaction, something which may indicate that a splitting of the two phases and limited solubility range in the studied system could exist at lower temperatures. A positive deviation is found for $(Al_{1-x}Cr_x)_2O_3$, as indicated in the variations in the unit cell parameters in Figure 24. The data for $(Al_{1-x}Cr_x)_2O_3$ represent samples prepared at high temperature which are not in thermodynamic equilibrium at room temperature. If $(Al_{1-x}Cr_x)_2O_3$ is prepared at a lower temperature a splitting into two phases is obeserved.

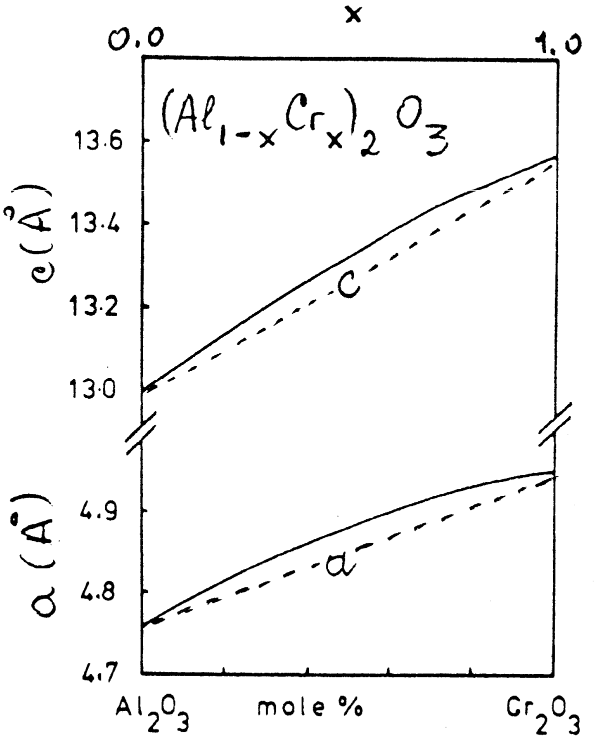


Figure 24: Variation of the unit cell parameters *a* and *c* for the solid solution phase $(Al_{1-x}Cr_x)_2O_3$ $0.0 \leq x \leq 1$. Positive deviation from Vegard's law is observed.

Solid-solubility between two phases AB and AC may be related to the “anion” or the “cation” part of the structure. A better description is to say that the solubility is tied to the metal or the non-metal part of the structure. To more precisely state the nature of the solubility, this must be shown as a representative chemical formula for the mixed structure. An example of this is the solid solution phase between Al_2O_3 and Cr_2O_3 (see Figure 23). Al and Cr substitute for each other on metal positions in the structure, i.e. the mixed phase is described by the formula $(Al_{1-x}Cr_x)_2O_3$. For the limited solubility phase between NaCl and $MnCl_2$ vacancies (أ) are created on metal positions when the cations are substituted, in order to maintain an overall neutral charge. The mixed phase is best described as $Na_{1-x}Mn_x$أ$_x$Cl. Alternatively the overall charge could be preserved by introducing interstitial chloride ions, and the phase would in this case be described as $Na_{1-x}Mn_xCl_{1+x}$ with $0.0 \leq x \leq x_{max}$. Experimentally it has been shown that the first description is correct.

One often find descriptions which refer to a “metal sublattice”, a “cation sublatice” etc. From these descriptions one might think, that there are different lattices for different atoms/kinds of atoms in a solid. This is completely wrong, and the concept is misleading. Whereas the lattice is the mathematical repeating network of lattice points, is it the basis that contain information about the metal (cations) and non-metal (anions). The concept “sublattice” may be conveniently used if one is completely aware of the fact that is has nothing to do with the lattice in a crystallographic context.