

Materials Engineering Science
MESC. 5025

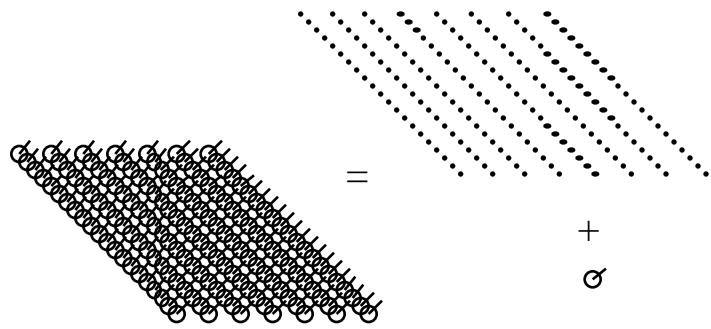
Instructor: Herve Marand

Chapter 3.
Crystal Structures, Diffraction and
Imperfections

Symmetry of Crystals, Lattices and Unit Cells

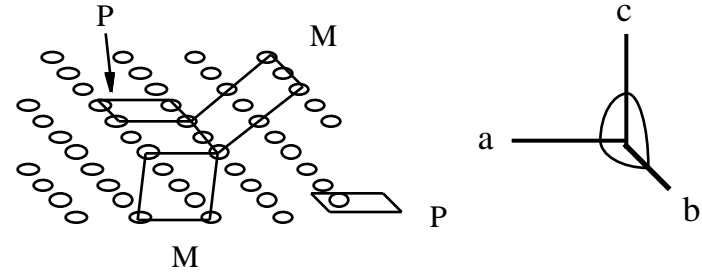
- A Crystal should be viewed as being built by the three-dimensional translational repetition of some basic structural pattern, which may comprise one or more atoms, a molecule or even a complex assembly of molecules.
- In three dimensions, an imaginary parallelepiped that contains one unit of the translationally repeating pattern is called a unit cell.
- If the repeating pattern is replaced by a point, the crystal is transformed into a lattice. A crystal lattice is then an infinite set of points that may be generated from a single point by the repetition of a set of basic translations that characterizes the lattice. Note that the crystal lattice is not the same as the structure. The lattice is the network of points on which the repeating unit or motif (content of unit cell) is laid down to yield the repeating structure of the crystal.

Crystal Lattice + Structural Motif = Crystal Structure

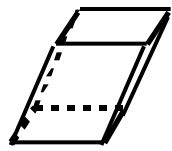


Unit Cells (Primitive or Multiple)

- Choose the unit cell whose shape displays the full symmetry of the lattice (rotational and translational) and which is the most convenient (shortest cell axes, and angles between cell axes as close as possible to 90°). In three dimensions, the unit cell axes are denoted a, b and c and the angles between them α , β and γ . α is the angle between b and c, ... etc

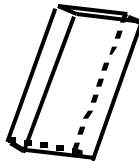


The Seven Crystal Systems



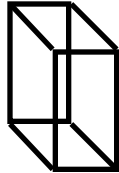
Triclinic a, b, c

, ,



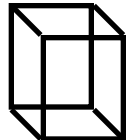
Monoclinic $a, b, c,$

$= = 90^\circ, \neq$



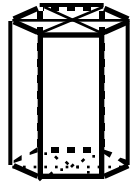
Orthorhombic

$a, b, c \neq \neq \neq 90^\circ$



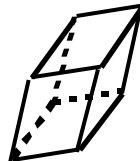
Tetragonal $a=b, c$

$= = 90^\circ$



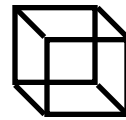
Hexagonal $a=b, c$

$= = 90^\circ, \neq 120^\circ$



Rhombohedral

$a=b=c \neq \neq \neq$



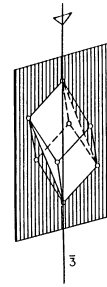
Cubic $a=b=c$

$= = 90^\circ$

Symmetry Operations

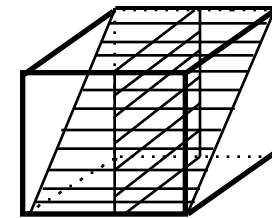
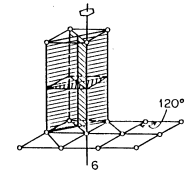
- An n-fold rotation axis, where n is any integer (1, 2, 4, 6) means that when the unit cell is rotated by $360^\circ/n$, the unit cell so-obtained is indistinguishable from the original one.
- A structure possesses a mirror plane or a plane of symmetry if there is a plane in that structure such that every part on one side of the plane is related to a part on the other side of the plane as if reflected by the plane. Such a plane is designated by the letter m.
- A combination of a two-fold rotation axis with a mirror plane normal to the axis is called an inversion. The point at the intersection of the mirror plane and the two-fold axis through which the inversion is carried out is called an inversion center or a center of symmetry. Similarly, the presence of a mirror plane and an inversion center results in the existence of a two-fold axis and the presence of a two-fold axis and an inversion center results in the existence of a mirror plane.

- A rotation axis combined with an inversion center produces a rotary inversion axis. These axes are denoted by a bar **over** the integer which describes the rotation axis.
- If we consider a point (x, y, z) :
 - the inversion operation produces $(\bar{x}, \bar{y}, \bar{z})$
 - a mirror (x, y) plane produces (x, y, \bar{z})
 - a mirror (x, z) plane produces (x, \bar{y}, z)
 - the 2-fold rotation with rotation axis z produces (\bar{x}, \bar{y}, z)
 - the 4-fold rotation with rotation axis z produces (\bar{y}, x, z)
 (\bar{x}, \bar{y}, z) (y, \bar{x}, z)
 - the 4-fold rotary inversion with rotation axis z produces (\bar{y}, x, \bar{z}) $(\bar{x}, \bar{y}, \bar{z})$ (y, \bar{x}, \bar{z})

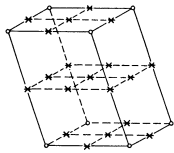


Unique mirror plane in a rhombohedral unit cell. Other planes are generated from this one by symmetry

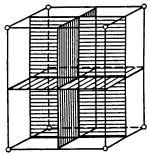
Unique mirror plane in a hexagonal unit cell. Other planes are generated from these by symmetry



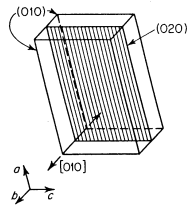
Unique mirror plane in a cubic unit cell. Other planes are generated from these by symmetry



Triclinic unit cell showing centers of symmetry at corners of unit cell and between them

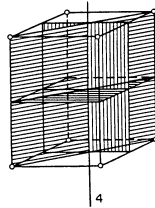


Unique mirror planes in an orthorhombic unit cell



Monoclinic unit cell showing two planes of the set (010) and one axis of the set [010]. Mirror plane (020) is also shown

Unique mirror planes in a tetragonal unit cell. Other planes present are generated from these by symmetry



Symmetry Operations and the 7 Crystal Lattices

- The inversion center is the only symmetry displayed by the triclinic lattice. It is indicated as a 1-fold rotary inversion axis, $\bar{1}$
- $2/m$ indicates a 2-fold axis with a mirror plane perpendicular to it and generates the monoclinic lattice.
- mmm indicates three mutually perpendicular mirror planes and leads to the orthorhombic lattice.
- $4/mmm$ indicates a mirror plane perpendicular to a 4-fold axis and two mirror planes parallel to the 4-fold axis and intersecting at 45° , which leads to the tetragonal lattice.
- The rhombohedral lattice has a 3-fold rotary inversion, which lies at the intersection of three mirror planes. Only one mirror plane needs to be indicated since the others are generated by the 3-fold rotary inversion. Thus $\bar{3}m$ describes the symmetry of the rhombohedral lattice.

- $6/mmm$ for the hexagonal lattice is the counterpart of $4/mmm$ for the tetragonal lattice. The c -axis is the 6-fold axis and has a mirror plane perpendicular to it. Parallel to the 6-fold axis are two mutually perpendicular planes that intersect along the c -axis.
- Each body diagonal in the cube is a 3-fold axis. One of these, along with a plane of symmetry parallel to that axis and a second plane of symmetry are sufficient to describe the symmetry of the cubic lattice.
- The 7 simple lattices have one lattice point at each corner of the unit cell. Thus there is one lattice point per unit cell ($8 \times 1/8$). These lattices are called primitive and are designated by the letter P ($P \bar{1}$, $P 2/m$, $P mmm$, $P 4/mmm$, $R \bar{3}m$, $P 6/mmm$, $Pm\bar{3}m$)
- In his study of lattices, Bravais discovered some lattices that were more complex (nonprimitive) but that still conformed to the symmetry of one of the seven crystal systems.

The Seven Crystal Systems

- These seven crystal systems are defined by the minimum symmetry of the unit cell and define the possible shapes of the crystal lattice. They should be viewed as seven different coordinate systems, in which the atomic positions are easily reported.

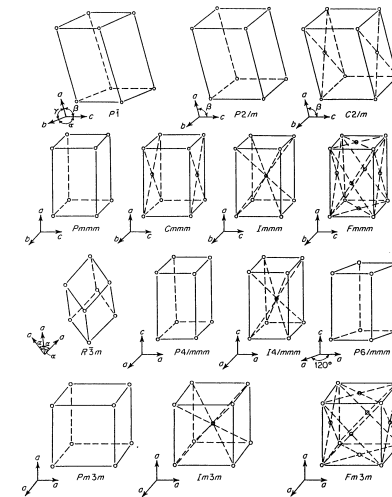
Minimum Point Group Symmetry of a Crystal	
Triclinic	No n -fold axes
Monoclinic	2-fold axis parallel to b
Orthorhombic	3 mutually perpendicular 2-fold axes
Tetragonal	4-fold axis parallel to c
Rhombohedral	3-fold axis parallel to a+b+c
Hexagonal	6-fold axis parallel to c
Cubic	3-fold axes along the cube diagonals

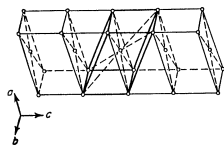
- What is the use of these symmetry operations ? Properties....

14 Bravais Lattices

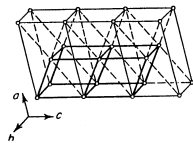
- The seven lattice shapes give rise to a total of 14 distinct lattices.
P: primitive; F: there is a lattice point at the center of each face (face centered); A, B, C: only that pair of faces has a lattice point at their center; I: the center of the cell has a lattice point (body centered)
- Triclinic P
- Monoclinic P C
- Orthorhombic P C F I
- Tetragonal P I
- Hexagonal P
- Rhombohedral P
- Cubic P F I

14 Bravais Lattices

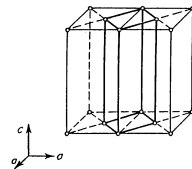




Choice of C or I unit cells
in monoclinic lattices



Relationship between
monoclinic B and P
lattices



Relationship between
tetragonal C and P lattices

Point Groups

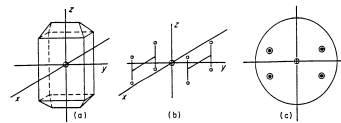
- If we define a solid crystal in terms of its faces, one can see that the faces are related to each other by the same types of symmetry operations as found in lattices (rotation axes, mirrors, center of symmetry, rotary inversions). Therefore, crystals can be classified in terms of the group of symmetry operations relating their faces. Each of these point groups corresponds to a unique combination of crystallographic symmetry elements.
- There are 32 point groups which can be divided among the seven crystal classes. The lattice which is characteristic of each class always has the highest symmetry possible within the class and defines the most symmetrical point group which can be accommodated in the lattice. When crystals form, their faces always conform to the symmetry of one of the 32 point groups.

Crystallographic Space Groups

	Triclinic	Monoclinic/ Orthorhombic	Trigonal	Tetragonal	Hexagonal	Cubic
n	1	2	3	4	6	23
$**$		$2_1/m$	3_2	4_2	6_2	$2_3+2/m\bar{3}$
\bar{n}	$1/m + \bar{2}$	$2/m$	$3/m + \bar{3}$	$4/m$	$6/m$	$2/m\bar{3} + m\bar{3}$
nm	$1/m + \bar{2}$	$2/m + m\bar{2}$	$3m$	$4m + 4/m\bar{m}$	$6m + 6/m\bar{m}$	$2m\bar{3} + \bar{4}3m$
$\bar{n}m$	$\bar{1}m + 2/m$	$\bar{2}m + 2/m$	$\bar{3}m$	$\bar{4}m + \bar{4}2/m$	$\bar{6}m + \bar{6}2/m$	$\bar{4}3m$
$n2$	$12 + 2$	$22 + 222$	32	$42 + 422$	$62 + 622$	$422 + 43$
$n/m\bar{n}$	$1/m\bar{n} + 2/m$	$2/m\bar{n} + m\bar{n}$	$3/m\bar{n} + \bar{6}m$	$4/m\bar{n} + 4/m\bar{n}m$	$6/m\bar{n} + 6/m\bar{n}m$	$4/m\bar{3}m + m\bar{3}m$

•• Centrosymmetric

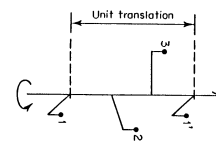
Plane Representation of the 32 Point Groups



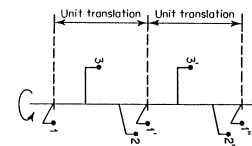
a) Crystal of Symmetry mmm , b) set of points related by symmetry mmm , c) plane representation of symmetry mmm

- All lattice points are equivalent by translational symmetry, all lattices (except the triclinic) have at least one mirror plane and various kinds of n -fold rotational axes, all lattices have centers of inversion. However, motifs arranged on these lattices need not have the same symmetry elements as the lattice.
- When one considers the number of symmetry elements that are compatible with the 14 different Bravais lattices, then we find that there are 230 distinct combinations of symmetry elements. One says there are 230 different crystallographic space groups.
- A simpler approach to defining space groups is to consider that the translation in a lattice introduces two new kinds of symmetry operations: screw axes and glide planes. When these two symmetry operations are combined with these discussed earlier, they lead to the 230 space groups.

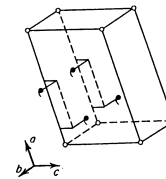
- A screw axis results from the combination of a rotation axis and a translation parallel to the rotation axis. The direction of a screw axis is generally along a unit cell edge and the translation must be an subintegral fraction of the unit cell dimension in that direction. They are denoted n_m where n is associated with the n -fold rotation and m is associated with the translation by the fraction m/n of the unit cell length in that direction. Note that for instance 3_1 and 3_2 are related in the same way as right and left-handed screws (enantiomorphs).
- The combination of a mirror plane and a translation parallel to the reflecting plane produces a glide plane. The translation in such a plane is along an edge or a face diagonal of the unit cell. A glide plane is designated by a , b , c if the translation is by $a/2$, $b/2$, or $c/2$ and by n if the translation is $(a+b)/2$, $(a+c)/2$ or $(b+c)/2$. There is an additional glide plane, the diamond glide plane denoted, d . It can only occur in face- or body-centered unit cells and is characterized by $(a+b)/4$, $(b+c)/4$, or $(a+c)/4$.



Screw Axis 3_1



Screw Axis 3_2



Glide plane a

Symbols for Symmetry Elements

Symmetry	Symbol	Designation if parallel to plane of projection	Designation if perpendicular to plane of projection
Center	I	○	○
2-fold axis	2	↔	●
3-fold axis	3	—	▲
4-fold axis	4	—	■
6-fold axis	6	—	●
2-fold screw axis	2 ₁	↔	⌘
3-fold screw axis	3 ₁	—	⌘
3-fold screw axis	3 ₂	—	⌘
4-fold screw axis	4 ₁	—	⌘
4-fold screw axis	4 ₂	—	⌘
4-fold screw axis	4 ₃	—	⌘
6-fold screw axis	6 ₁	—	⌘
6-fold screw axis	6 ₂	—	⌘
6-fold screw axis	6 ₃	—	⌘
6-fold screw axis	6 ₄	—	⌘
6-fold screw axis	6 ₅	—	⌘
Mirror	<i>m</i>	∟	—
<i>a</i> glide plane	<i>a</i>	↘	----
<i>b</i> glide plane	<i>b</i>	↙	----
<i>c</i> glide plane	<i>c</i>	—
<i>n</i> glide plane	<i>n</i>	↖
<i>d</i> glide plane	<i>d</i>	↗	→....

- For example, $Pbcn$ corresponds to a space group for which we have a primitive unit cell related to the mmm point group but containing three glide planes instead of three simple mirrors.
- A complete list of space groups is provided in the International Tables for X-ray Crystallography (vol 1., N.F. Henry, K. Lonsdale, eds., Kynoch Press, Birmingham, England, 1952, pp 543-553).
- In most structures, some groups of atoms or ions in each unit cell are related to others in the same unit cell by some symmetry operation other than translation. The smallest part of the crystal structure from which the complete structure may be obtained from the space group symmetry operations (including translations) is called the asymmetric unit.

Miller Indices

- A system of notations called Miller indices provides a concise, unambiguous numerical label for all crystal planes.
- $x/A + y/B + z/C = 1$ is the equation of the plane PQR. For this plane, we note that $x=A$ when $y=z=0$, similarly, $y=B$ when $x=z=0$ and, $z=C$ when $x=y=0$

The plane PQR is delineated by the intercepts Aa, Bb, Cc. The equation of the plane is also given by: $BCx + ACy + ABz = ABC$

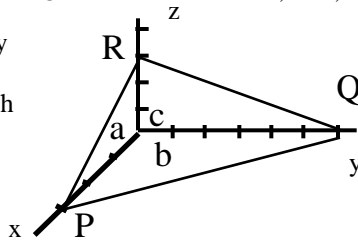
$$A=3 ; B=6; C=3$$

$$h=18 ; k=9; l=18$$

$$h=2 ; k=1; l=2$$

The Miller indices are given by the lowest values of hkl which preserve their ratio and are such that:

$$\begin{array}{l} h \quad BC \\ k \quad AC \text{ same constant} \\ l \quad AB \text{ for the three.} \end{array}$$



- Planes are then written as (h k l) with parentheses. In this case, one refers to the specific plane that intersects the x-axis at $1/h$, the y-axis at $1/k$ and the z-axis at $1/l$. When the Miller indices are enclosed by braces, e.g. {100}, they denote all planes of the form (100) viz. (100), (010), (001), ($\bar{1}$ 00), (0 $\bar{1}$ 0), (00 $\bar{1}$), where the bar **over** the numeral indicates a negative intercept. Note that a Miller index of 0 indicates that the plane is parallel to the corresponding axis (i.e. it intercepts the axis at infinity, $1/\text{infinity} = 0$)
- Crystallographic directions are indicated by bracket, i.e. [uvw]. The complete set of equivalent directions is denoted <uvw>. Note here that u, v, w are the coordinates of the vector which defines the direction of interest. uvw are not Miller indices !!!

- Note that for the hexagonal unit cell (six-fold symmetry), four coordinate axes are used (x, y, u, z). $x, y,$ and u lie in the same plane and are inclined at 120° from each other, while the z -axis is perpendicular to this plane and is the six-fold rotation symmetry axis. There are therefore four Miller indices for any lattice plane in a hexagonal crystal structure ($hkil$) with the necessary condition ($i=-(h+k)$)