What constitutes crystal structure?

Crystal Structure = +

• Lattice:
  – 3-D periodic array of points in space.
  – Every lattice point has identical surroundings. This is very important!

• Unit cells represent the smallest repeating unit within a crystalline lattice.

• Each crystal/grain is built by stacking unit cells and placing objects (motifs, basis) on the lattice points.

• Basis:
  – An object or group of objects that we place on lattice points to build a crystal.
  – In crystals the objects can be single atoms or ions, groups of atoms or ions, molecules, etc…

Creation of Crystals

• Any shape, symbol, design, or object can be reproduced periodically to create a regular array that fills space.

• To fill space most efficiently, you can also apply different symmetry operations:
  – Rotation
  – Reflection
  – Inversion
  – Translation
2-D Illustration

Identical (same) environment:

Same environment and basis positions after 2 different lattice translations in ‘blue’:

Unit Cell

- Smallest portion of the lattice that contains both the basis and the symmetry elements of the lattice.

- We fill space with unit cells by translating (shifting) them parallel to the cell edges at distances equal to the lengths of the cell edges.

The groups of smiling faces represent the basis.
- They can fill an infinite plane and can be arranged in different ways on lattice.
By definition **unit cells contain all of the information that is needed to generate an infinite array or pattern.**

**Unit cells are the basic building blocks of lattices**

\[ \mathbf{R} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c} \]  
Translation (lattice) vector

\[ \mathbf{a}, \mathbf{b}, \mathbf{c}, \alpha, \beta, \gamma \]  
lattice parameters

For example, if we want to go from one corner to another across a body diagonal…….
Mathematics of Lattices  
"relationships between vectors"

Lattices are simply a large number of unit cells stacked together

Schematic representation of a lattice.  
*All lattice points are equivalent.*

3-D lattice showing position vector \( (R \text{ or } r) = \text{primitive (or lattice) vectors } a, b \text{ and } c \) with integer coefficients \( u, v \text{ and } w \)

\[
\vec{r}_{100} = 1\vec{a} + 0\vec{b} + 0\vec{c}
\]

You can define a series of lattice vectors \( \vec{r}_{uvw} \)

\[
\vec{r}_{uvw} = u\vec{a} + v\vec{b} + w\vec{c}
\]

\( \{uvw\}: \]
- \([001]\)
- \([101]\)
- \([100]\)
- \([011]\)
- \([110]\)
- \([111]\)
- \([325]=?\)

The coefficients \( u, v, w \) are integers ranging over all values corresponding to position vectors that lie within the crystal

"**IF ANY SINGLE LATTICE POINT IS SELECTED AS THE ORIGIN, THE POSITIONS OF ANY OTHER LATTICE POINT IS DEFINED ACCORDING TO THE RELATIONSHIP**":

\[
\begin{align*}
\vec{r}_{uvw} &= u\vec{a} + v\vec{b} + w\vec{c} \\
\vec{r}_{uvw} &= u\vec{a}_1 + v\vec{a}_2 + w\vec{a}_3
\end{align*}
\]

If \( a, b, c \) cell lengths are different, e.g. orthorhombic
If \( a, b, c \) cell lengths are equal, e.g. cubic

**NOTE:** You’ll see this relationship again

This concept gives a crystal periodicity, which is one of its most important characteristics.
The Four 2-D Crystal Systems (Shapes)

To fully describe a crystal structure you must characterize:

(i) the geometry of the unit cell

AND

(ii) the distribution of atoms in the unit cell and lattice.

Directions in Crystals

Directions and their multiples are identical

Ex.: [220] = 2×[110]

<table>
<thead>
<tr>
<th>Name</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Square</td>
<td>$a_1 = a_2, \alpha = 90^\circ$</td>
</tr>
<tr>
<td>Rectangular</td>
<td>$a_1 \neq a_2, \alpha = 90^\circ$</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$a_1 = a_2, \alpha = 120^\circ$</td>
</tr>
<tr>
<td>Oblique</td>
<td>$a_1 \neq a_2, \alpha \neq 120^\circ, \alpha \neq 90^\circ$</td>
</tr>
</tbody>
</table>
Objects constituting the basis can be arranged into more complex arrays using symmetry elements.

To fill space most efficiently, you can also apply different symmetry operations:

- Rotation
- Reflection
- Inversion
- Translation

Repeating Patterns are Defined by

- Shape of the unit cell (crystal systems)
- Symmetry within the unit cell
- Translation of the unit cell to fill space
Crystallography Basics (continued)

Crystallography

230 SPACE GROUPS (crystal structures)
   32 CRYSTAL CLASSES
   14 BRAVAIS LATTICES
   7 CRYSTAL SYSTEMS (shapes)

This means that there are
7 types/shapes of crystals in 3-D
from which we derive 14 types of lattices.

We place atoms on the lattices and apply symmetry operations,
which results in 230 possible crystal structures

THERE ARE ONLY 230 DIFFERENT CRYSTAL STRUCTURES! *

*Recently quasicrystals were discovered and do not belong to 1 of 230

All crystal structures are derived from the 7 possible crystal systems
The Seven 3-D Crystal Systems (Shapes)

- The **7 Crystal Systems** define a set of unit cell shapes that characterize all types of crystal lattices.
- There are **ONLY 7 crystal systems.**

**Unit cell:** smallest repetitive volume which contains the complete lattice pattern of a crystal.

“In 3-D, there are only 7 ways to fill space in” i.e., there are 7 common shapes for crystals!

### Crystal System, Axial Relationships, Interaxial Angles, Unit Cell Geometry

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>Axial Relationships</th>
<th>Interaxial Angles</th>
<th>Unit Cell Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>$a = b = c$</td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td><img src="image" alt="Cubic Unit Cell" /></td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$a = b \neq c$</td>
<td>$\alpha = \beta = 90^\circ, \gamma = 120^\circ$</td>
<td><img src="image" alt="Hexagonal Unit Cell" /></td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$a = b \neq c$</td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td><img src="image" alt="Tetragonal Unit Cell" /></td>
</tr>
<tr>
<td>Rhombohedral (Trigonal)</td>
<td>$a = b = c$</td>
<td>$\alpha = \beta = \gamma \neq 90^\circ$</td>
<td><img src="image" alt="Rhombohedral Unit Cell" /></td>
</tr>
</tbody>
</table>

**from your Callister Book**

- **Orthorhombic** $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$
- **Monoclinic** $a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$
- **Triclinic** $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$

These are the only 7 possible 3-D crystal systems (know them and their 6 lattice parameters)
Monoclinic - has 2-fold rotation (180°) normal to the centers of 2 unit cell edges going through the opposite sides of the cell, e.g. \{01\bar{1}\} has 2-fold symmetry denoted with *diad* shape.

Trigonal - has 3-fold rotation (120°) normal to the body diagonal, e.g. \{11\bar{1}\} has 3-fold symmetry denoted with *triangle* shape.

Cubic - has 2, 3 and 4-fold (90°) rotations, e.g. \{001\} has 4-fold symmetry denoted with *square* shape.
Cubic Crystal System Symmetry

Figure 1.13 Reference cubes showing the three major sets of planes in cubic crystals.

### Summary of the Seven 3-D Crystal Systems

There are characteristic relationships between lattice parameters for the 7 systems.

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>Axial Relationships</th>
<th>Interaxial Angles</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>$a = b = c$</td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td>Three axes at right angles, all equal.</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$a = b \neq c$</td>
<td>$\alpha = \beta = 90^\circ; \gamma = 120^\circ$</td>
<td>Two axes of equal length at $120^\circ$; third at $90^\circ$ to these.</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$a = b \neq c$</td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td>Three axes at right angles; two equal.</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>$a = b = c$</td>
<td>$\alpha = \beta = \gamma \neq 90^\circ$</td>
<td>Three axes equally inclined; not at right angles; all equal.</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$a \neq b \neq c$</td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td>Three axes at right angles; all unequal.</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$a \neq b \neq c$</td>
<td>$\alpha = \gamma = 90^\circ \neq \beta$</td>
<td>Three axes; one pair not at right angles of any lengths</td>
</tr>
<tr>
<td>Triclinic</td>
<td>$a \neq b \neq c$</td>
<td>$\alpha \neq \beta \neq \gamma \neq 90^\circ$</td>
<td>Three axes not at right angles, of any length.</td>
</tr>
</tbody>
</table>