

## Class 3: Symmetry in the solid state

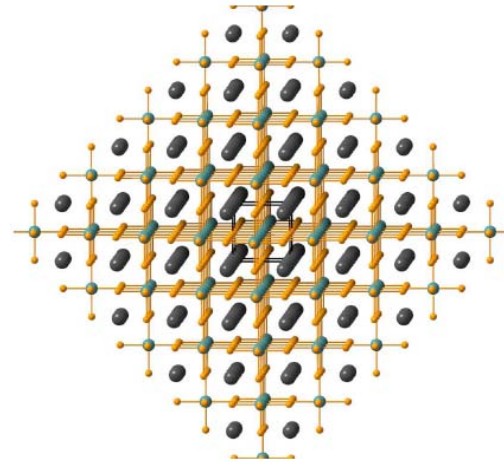
---

Lattices, unit cells, symmetry—how crystallography simplifies the depiction of structures.

Most of the materials we deal with in this course are crystalline, meaning that they are periodic at the atomic scale. The unit cell is repeated (tiled) many billions of times in every direction in order to obtain a micron sized-crystal.



The unit cell, left, and the process of *tiling*, right.



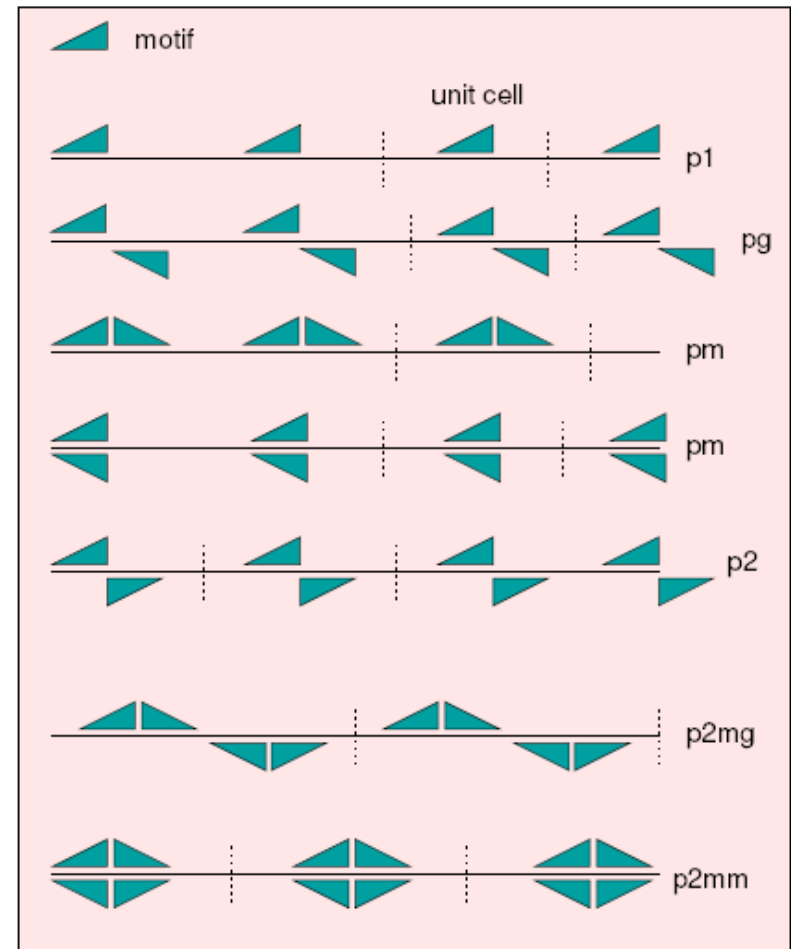
Crystallography is the science that helps understand and perhaps even rationalize the atomic-scale structure of crystalline materials. This class is a quick review. For a quick and comprehensible treatment of the subject, see C. Hammond, *The basics of crystallography and diffraction* (IUCr-Oxford). This is more than sufficient for the purpose of this course. For a more advanced treatment, see the edited book by C. Giacovazzo, *An introduction to crystallography* (IUCr-Oxford). Also look at the teaching resources on [www.iucr.org](http://www.iucr.org). Wikipedia is pretty good as well.

- The crystal is built up by tiling the unit cell
- The contents of the unit cell are atoms and molecules
- The use of symmetry elements simplifies the description of the contents of the unit cell. Symmetry is usually **not** employed to describe relations between species in different unit cells.

## Class 3: Symmetry in the solid state

### Symmetry in 1D

- In 1 D, there are 7 line groups - the crystallography of frieze patterns. **Frieze:** *n* "A band of painted or sculptured decoration." More interestingly, "that member in the entablature of an order which comes between the architrave and cornice. Also in extended sense."
- These line groups possess three different kinds of symmetry elements, the mirrors *m*, the two-fold rotations *2*, and the glides *g*. They act on the motif to copy it within the unit cell.
- The dotted vertical lines mark the outlines of the unit cells.



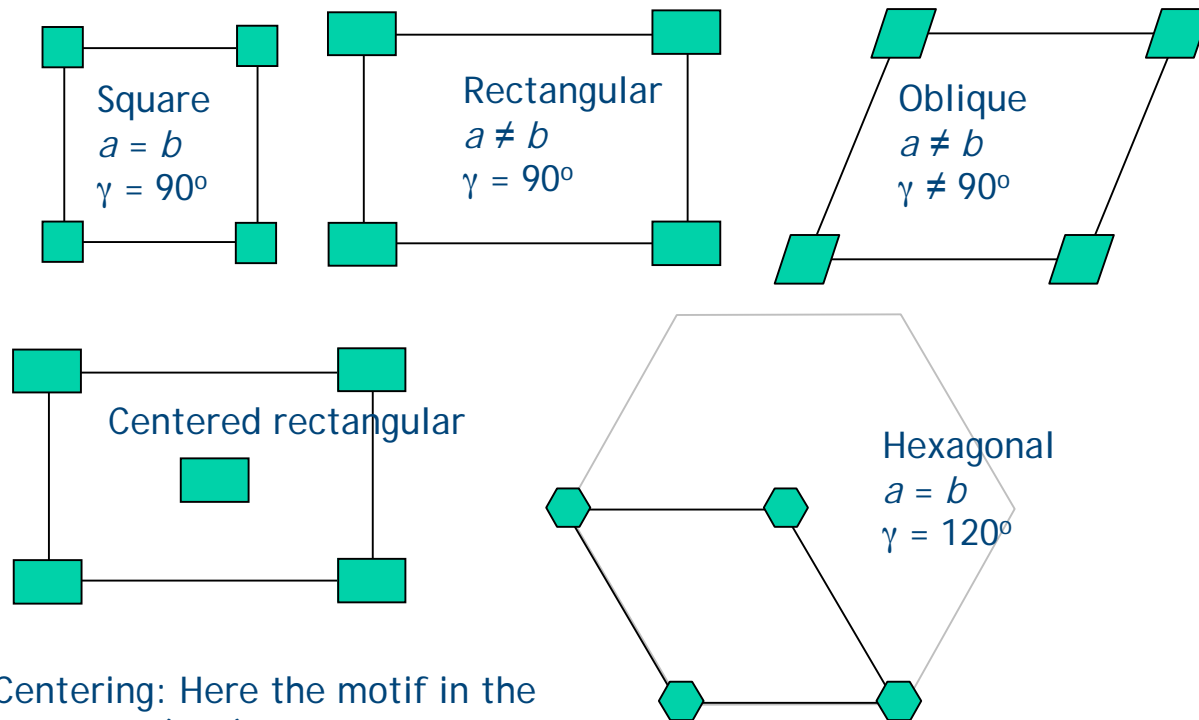
## Class 3: Symmetry in the solid state

---

### Symmetry in 2D

In going from 1D to 2D (where there are now seventeen plane groups) only one new concept is added - that of centering.

- There are 5 kinds of cells in 2D –the plane lattices:



Centering: Here the motif in the corner at (0, 0) is automatically taken also to  $(\frac{1}{2}, \frac{1}{2})$

# Class 3: Symmetry in the solid state

## Symmetry in 2D

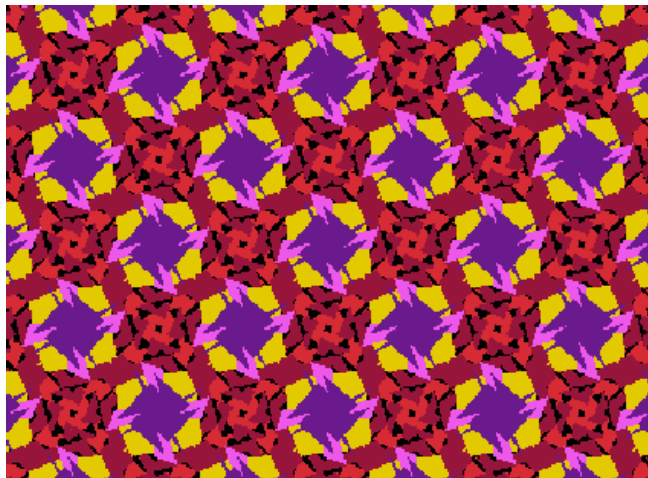
The 17 plane groups. See the additional handouts for further descriptions. Hammond described a flow chart that can be used for determining the specific plane group associated with a pattern.

See also:

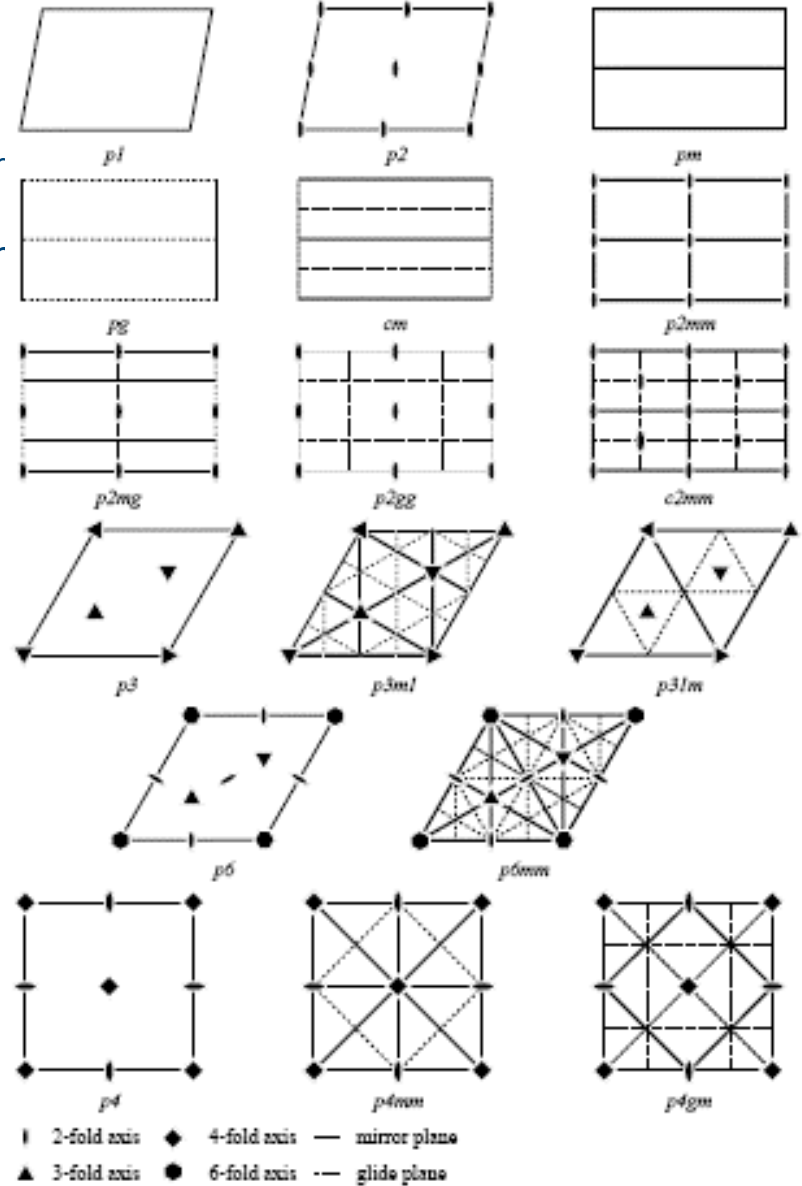
<http://www.clarku.edu/~djoyce/wallpaper/seventeen.html>

For a number of different “wallpapers”

For example, the group  $p4$  below.



The 17 Plane Patterns

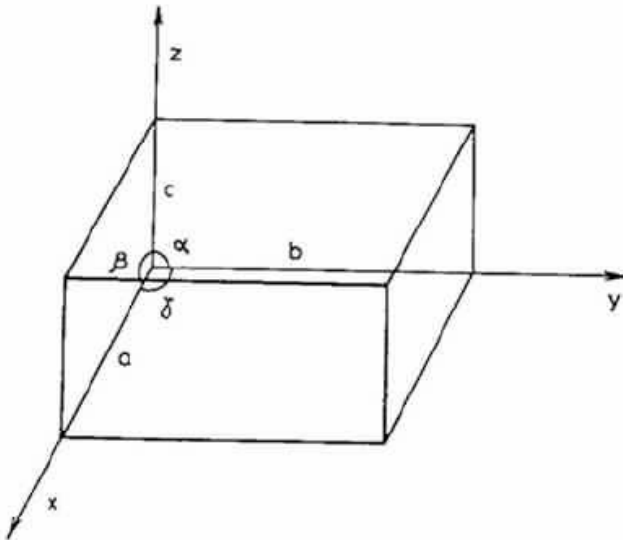


## Class 3: Symmetry in the solid state

**3 Dimensions:** 7 crystal systems (the different shapes of unit cells, all of which are parallelepipeds), 14 Bravais lattices (the crystal systems and the different kinds of centering), the 32 point groups, and the 230 space groups.

A new symmetry type: Screw axes are added on going to 3D: Please see the hardcopy handout

The 7 crystal systems and the 14 Bravais lattices:



### 7 crystal systems

System	Characteristic symmetry	Unit cell shape	Lattice types
Triclinic	None	$a \neq b \neq c$ * $\alpha \neq \beta \neq \gamma \neq 90^\circ$	<i>P</i>
Monoclinic	One two-fold axis (2 or $\bar{2} = m$ )	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$	<i>P, C</i> (or <i>A</i> )
Orthorhombic	Three mutually perpendicular two-fold axes	$a \neq b \neq c$ $\alpha = \beta = \gamma \neq 90^\circ$	<i>P, C,</i> (or <i>A</i> or <i>B</i> )
Tetragonal	One four-fold axis	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	<i>P, I</i>
Trigonal	One three-fold-axis	$a = b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	<i>P, R</i>
Hexagonal	One six-fold axis	$a = b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	<i>P</i>
Cubic	Four three-fold axes (along body diagonals of a cube)	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	<i>P, I, F</i>

≠ Not necessarily equal to.

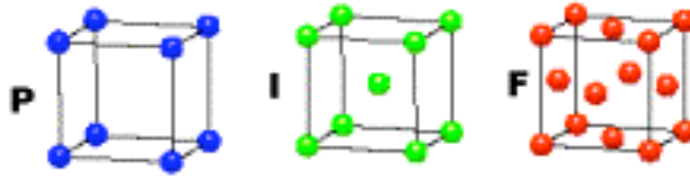
\* That is, no restrictions.

# Class 3: Symmetry in the solid state

## CUBIC

$$a = b = c$$

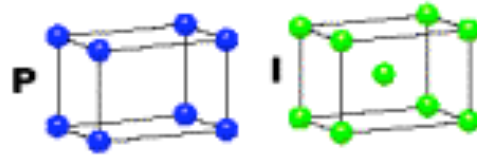
$$\alpha = \beta = \gamma = 90^\circ$$



## TETRAGONAL

$$a = b \neq c$$

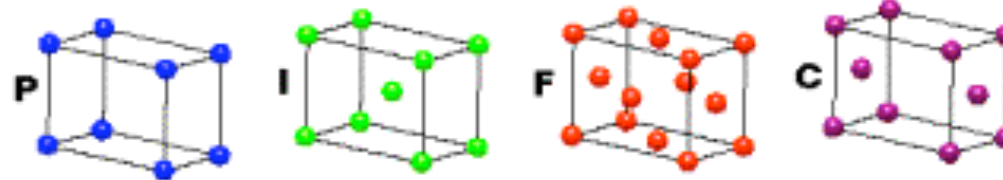
$$\alpha = \beta = \gamma = 90^\circ$$



## ORTHORHOMBIC

$$a \neq b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$

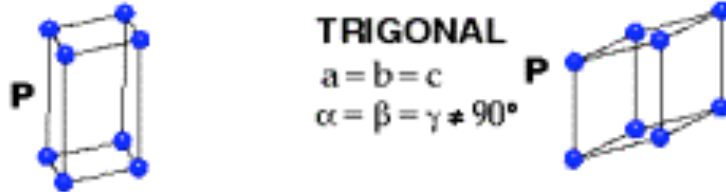


## HEXAGONAL

$$a = b \neq c$$

$$\alpha = \beta = 90^\circ$$

$$\gamma = 120^\circ$$



## TRIGONAL

$$a = b = c$$

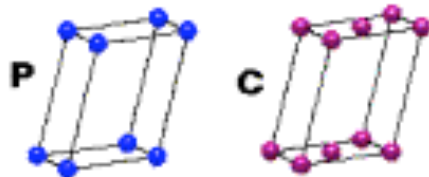
$$\alpha = \beta = \gamma \neq 90^\circ$$

## MONOCLINIC

$$a \neq b \neq c$$

$$\alpha = \gamma = 90^\circ$$

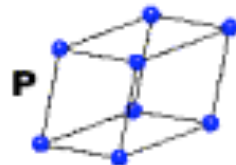
$$\beta \neq 120^\circ$$



## TRICLINIC

$$a \neq b \neq c$$

$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$



### 4 Types of Unit Cell

P = Primitive

I = Body-Centred

F = Face-Centred

C = Side-Centred

+

7 Crystal Classes

→ 14 Bravais Lattices

## Class 3: Symmetry in the solid state

---

Why do we need symmetry: The example of the the siliceous zeolite faujasite:

The zeolitic Si-O framework of this material is described by five atoms. Space Group  $Fd-3m$  (227);  $a = 24.56 \text{ \AA}$ .

Atom	Wyckoff letter	Site symmetry	$x$	$y$	$z$
Si	192i	1	0.0364	0.1272	0.3029
O1	192i	1	0	0.3864	0.6136
O2	96g	m	0.0012	0.0012	0.1447
O3	96g	m	0.0684	0.0684	0.3126
O4	96g	m	0.3257	0.3257	0.0288

The information provided above allows the unit cell of faujasite (right,  $\text{SiO}_4$  tetrahedra of show) to be portrayed. 640 atoms were used for the depiction.

