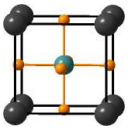
Materials 218/UCSB: Class IV Crystallography in a nutshell: Lattices, unit cells, symmetry — how crystallography simplifies the depiction of structures

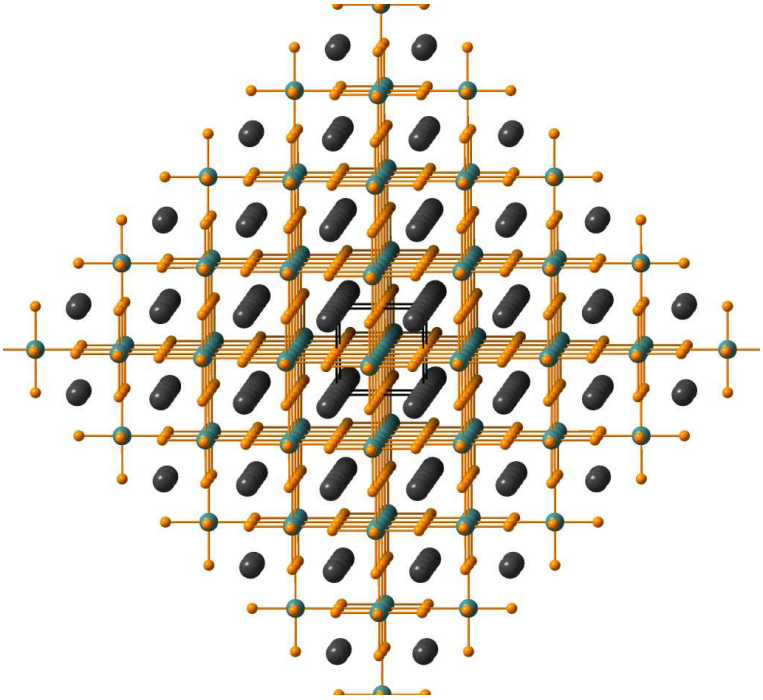
Ram Seshadri (seshadri@mrl.ucsb.edu)

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 crystal.

The unit cell:



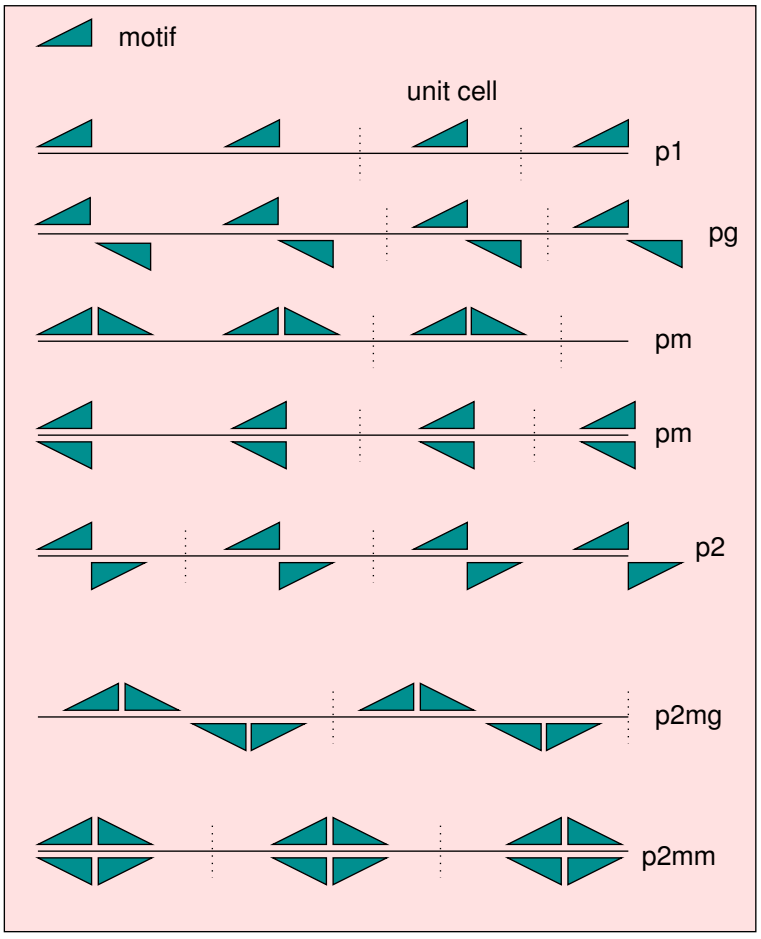
Tiled in the three directions:



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).

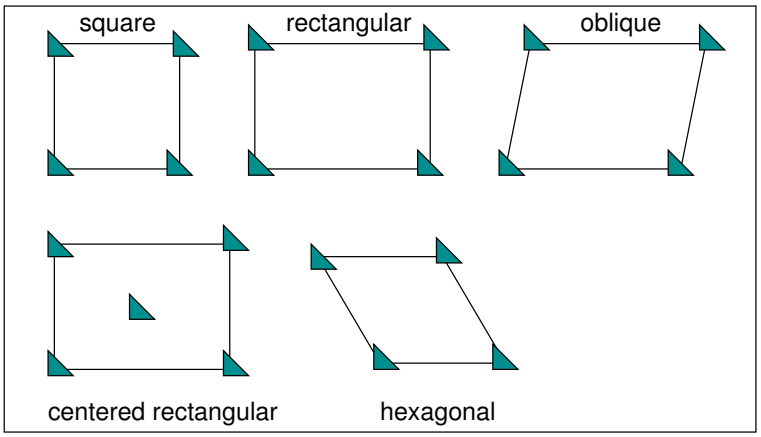
- The crystal is built up by tiling the unit cell
- The contents of the unit cell are atoms and molecules
- The use of *symmetry elements* simplifies the description of the contents of the unit cell

- 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.



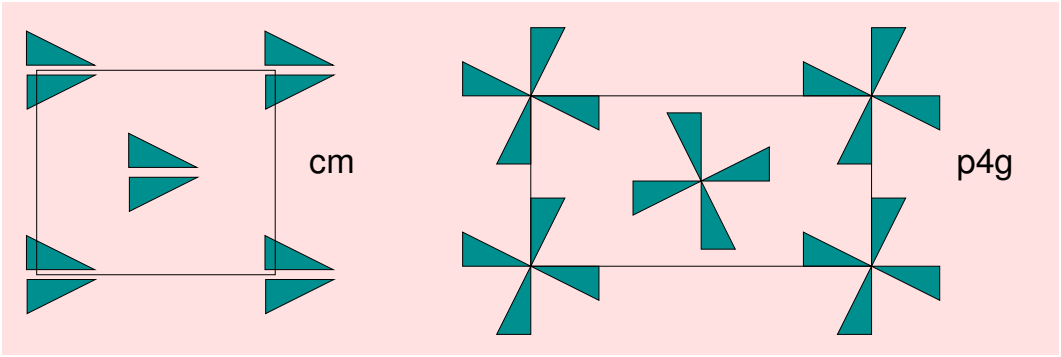
The doted vertical lines mark the outlines of the unit cells.

- 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:

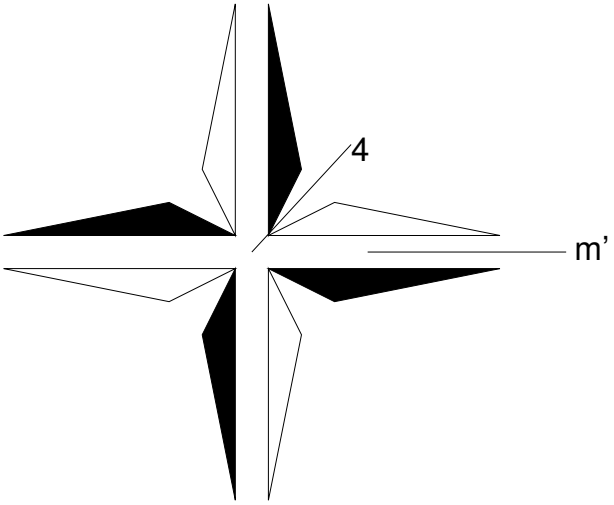


- There are 17 plane groups, obtained by combining all the possible symmetry operations in 2D. The operations are: 2, 3 and 4-fold rotations, mirrors m, glides g, centering c.

  Examples of plane groups:



- Sometimes, it is useful to add another element of symmetry. For example, two-color symmetry (indicated by a prime) switches black to white and *vice-versa*. These are called Shubnikov groups.



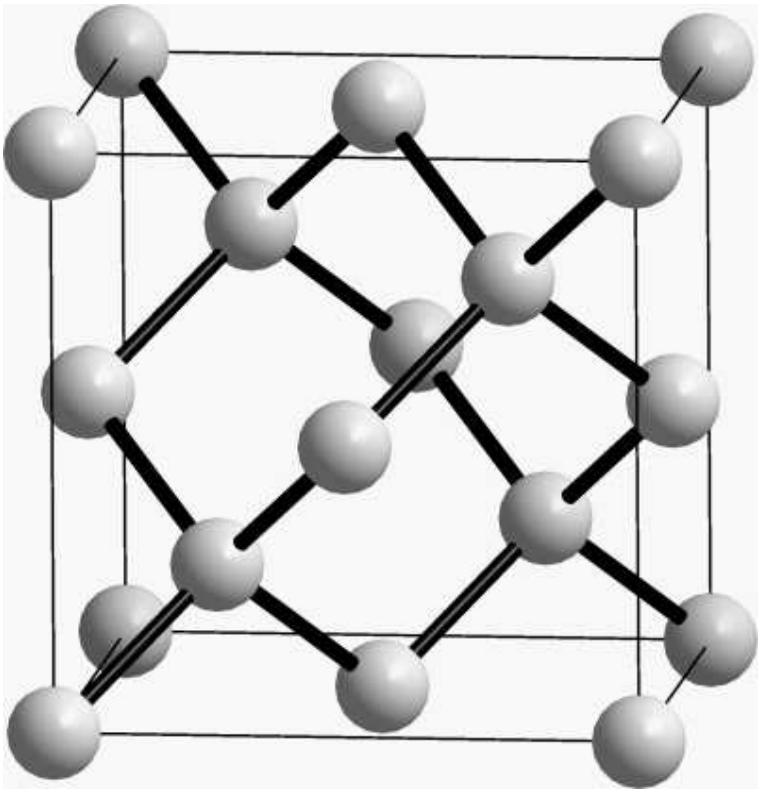
Shubnikov groups are useful when properties such as spin need to be overlaid over the normal crystallographic symmetry.

- What about 3D ?

  "We shall have mercifully little to say about the 230 space groups ..." N. W. Ashcroft and N. D. Mermin, Solid State Physics.

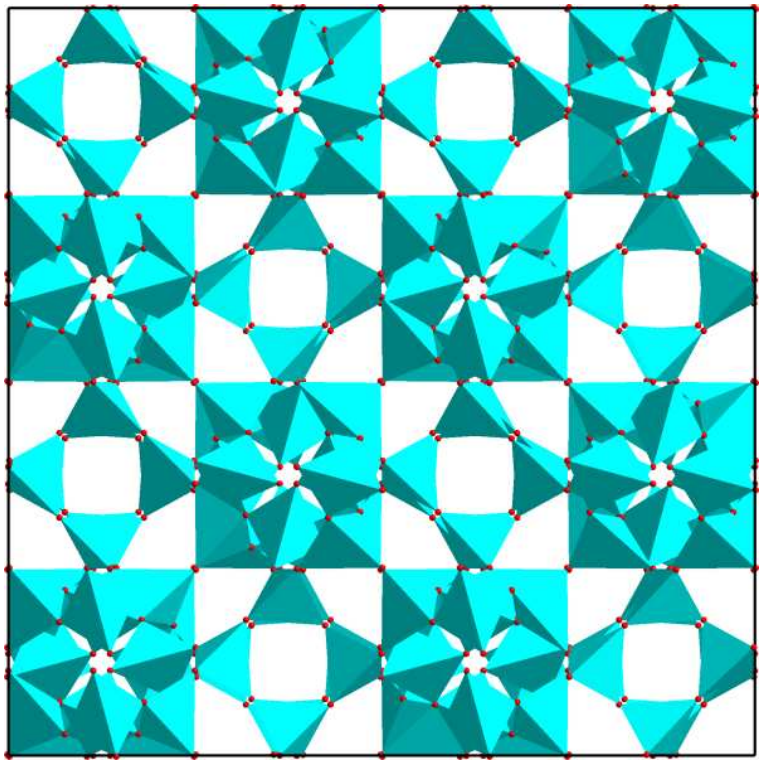
- There are 14 lattices in 3D – the *Bravais* lattices
- The only new elements of symmetry on going from 2D to 3D are the *screw axes*. See the handout for an illustration of what these are.
- Crystallography simplifies the description of crystal structures
  - The diamond structure: Cubic close-packing of C atoms, with C occupying some of the tetrahedral interstices.
    Space Group $Fd\bar{3}m$ (227); $a = 3.56$ Å.

Atom	Wyckoff letter	Site symmetry	x	y	z
C	$8a$	$\bar{4}3m$	0	0	0



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

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 Si-O framework of the zeolite Faujasite. The tetrahedra have Si at the center. Approximately 640 atom positions are required to make this drawing.

– Tetragonal, ferroelectric $PbTiO_3$ at room temperature:
Space Group $P4mm$ (99); $a = 3.904$ Å $c = 4.152$ Å.

Atom	Wyckoff letter	Site symmetry	x	y	z
Pb	1a	4mm	0	0	0.116
Ti	1b	4mm	1/2	1/2	0.572
O1	2c	2mm	0	1/2	1/2
O2	1b	4mm	1/2	1/2	0