ORDER IN ATOMIC ARRANGEMENTS

- No order (*e.g.*, monatomic gases)
  - No regular spatial relationship between atoms

- Short-range order (*e.g.*, inorganic glasses, noncrystalline polymers, molecular liquids)
  - Nearest neighbors may have fixed orientations and separations

- Long-range order (crystals)
  - Identical structural units repeating continuously in three dimensions over hundreds of atomic spacings — ***periodicity***

Q: How many atoms in a tiny crystal, 1 μm × 1 μm × 1 μm?

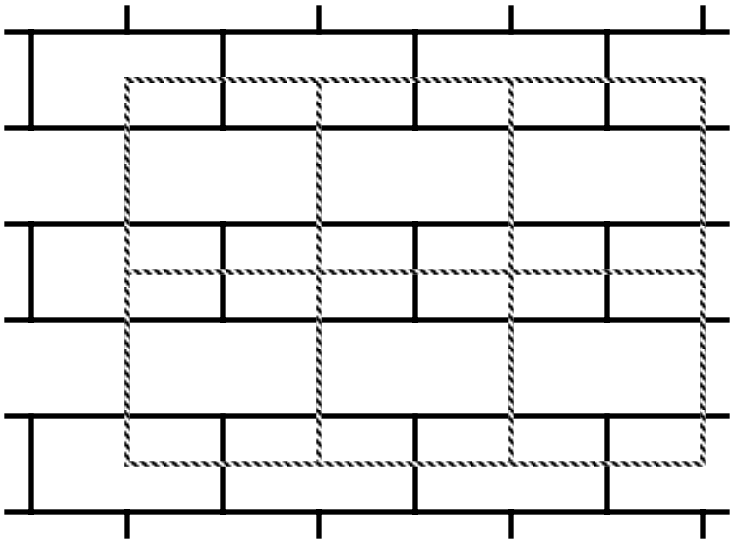
A: Assume a monatomic solid, 10 g/cm^3, 60 g/mol:

$$\frac{6.0\times10^{23}\ \frac{\text{atoms}}{\text{mol}}\ \times 10\ \frac{\text{g}}{\text{cm}^3}\ \times\ 10^{-12}\ \text{cm}^3}{60\ \frac{\text{g}}{\text{mol}}}$$

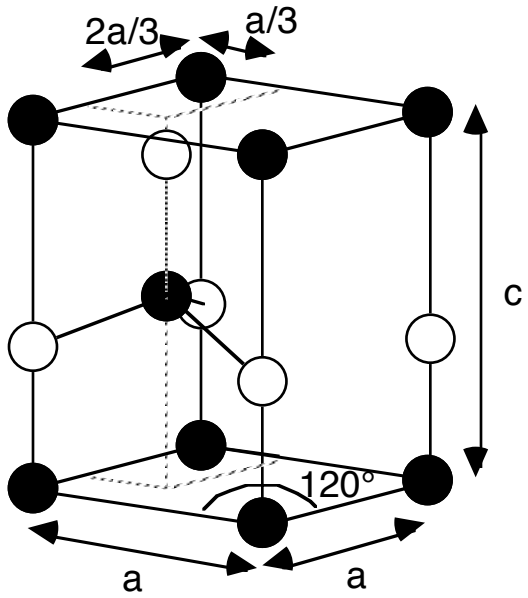
$= 10^{11}$ (*i.e.*, 100 billion) atoms!

LATTICES and CRYSTAL STRUCTURES

- ***Lattice*** (below left)***:***
  - A regular, periodic configuration of points — the ***lattice points*** — in space
  - A ***mathematical construct*** that describes the symmetry of spatially periodic arrangements
  - ***Translation vectors*** between nearest-neighbor lattice points describe the periodicity of the lattice
  - The translation vectors define the lattice's ***unit cell***
  - Lattices can describe the symmetry of …
    - floor tiling • brickwork • wallpaper
    - fabrics • ***crystal structures***
- ***Crystal structure*** (below right)***:***
  - An arrangement of ***atoms*** in space, whose symmetry can be described by a lattice



A cinder-block wall (solid lines) with superimposed 2D lattice (dashed lines)



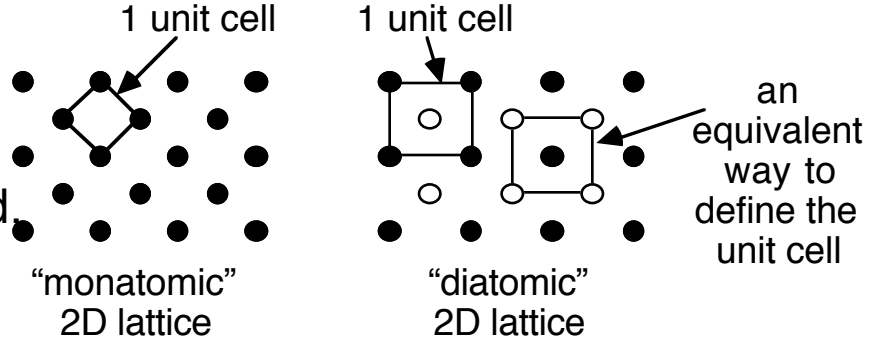
wurtzite structure

UNIT CELL of a lattice

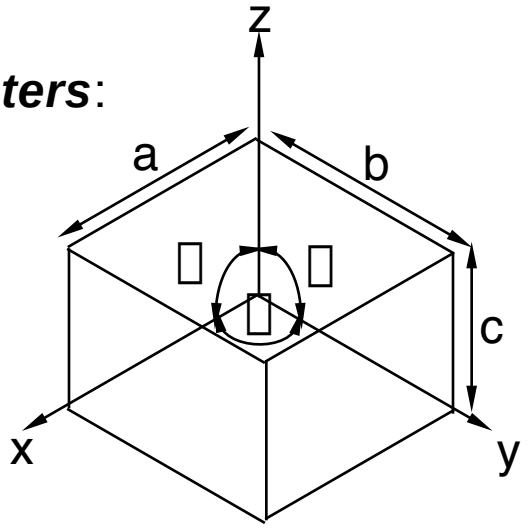
- Polyhedron bounded by the three ***translation vectors*** that describe the periodicity of the lattice

- Smallest grouping of lattice points which describes the…
  - Structure
  - Symmetry

  …of the entire solid.



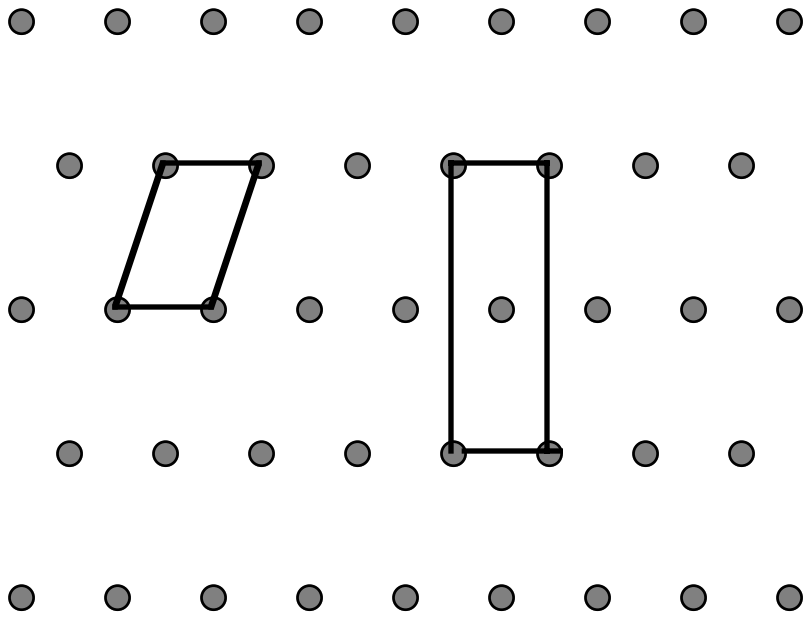
- Described by ***lattice parameters***:
  - Cell dimensions *a, b, c* (lengths of cell edges)
  - Angles α, β, γ between cell edges



PRIMITIVE vs. NON-PRIMITIVE UNIT CELLS

- Primitive unit cell: one (net) lattice point per cell
- Non-primitive unit cells: additional lattice points per cell, within a given crystal class

2-D example:*

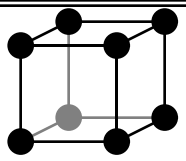
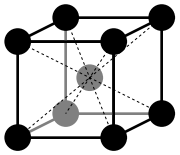
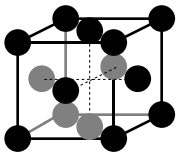
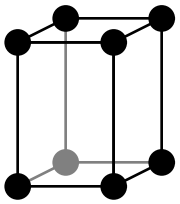
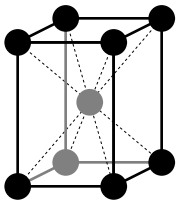
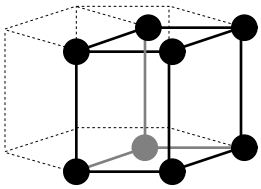
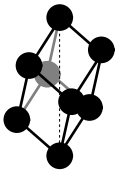


- Every lattice point lies at the intersection of a vertical mirror line and a horizontal mirror line
- The primitive cell (left) can replicate the lattice, …
- … but the ***non-primitive cell*** (right), though larger***, is preferred*** because it possesses the full horizontal and vertical mirror symmetry of the lattice
- Similar logic extends to 3-D lattices — the ***Bravais lattices***

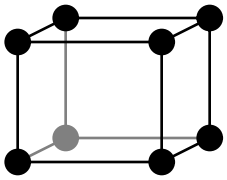
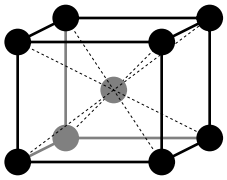
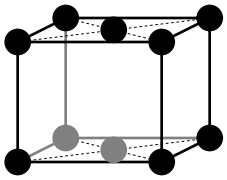
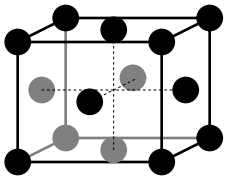
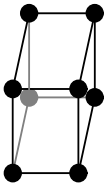
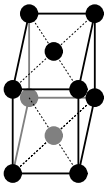
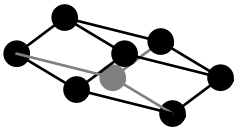
*) After D. W. Oxtoby, H. P. Gillis, and N, H. Nachtrieb, *Principles of Modern Chemistry,* 5th ed., p. 752. Thomson Learning, 2002.

THE BRAVAIS LATTICES (start)

Only unit cells with certain geometries will continuously fill three-dimensional space — the *Bravais lattices*

Class (a.k.a. System)	Type	Minimum lattice points occupied	Unit cell
Cubic $a = b = c$ $\alpha = \beta = \gamma = 90°$	Simple (a.k.a. "primitive")	0 0 0	
	Body-centered	0 0 0 $\frac{1}{2}\frac{1}{2}\frac{1}{2}$	
	Face-centered	0 0 0 $\frac{1}{2}\frac{1}{2}0$ $\frac{1}{2}0\frac{1}{2}$ $0\frac{1}{2}\frac{1}{2}$	
Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = 90°$ (*four*-fold symmetry)	Simple	0 0 0	
	Body-centered	0 0 0 $\frac{1}{2}\frac{1}{2}\frac{1}{2}$	
Hexagonal $a = b \neq c$ $\alpha = \beta = 90°$ $\gamma = 120°$ (*six*-fold symmetry)	Simple	0 0 0	
Rhombohedral $a = b = c$ $\alpha = \beta = \gamma \neq 90°$ (each face is a *rhomb*us)	Simple	0 0 0	

THE BRAVAIS LATTICES (end)

Class (a.k.a. System)	Type	Minimum lattice points occupied	Unit cell
Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$ (*ortho*gonal axes)	Simple	0 0 0	
	Body-centered	0 0 0 $\frac{1}{2}\frac{1}{2}\frac{1}{2}$	
	Base-centered	0 0 0 $\frac{1}{2}\frac{1}{2}0$	
	Face-centered	0 0 0 $\frac{1}{2}\frac{1}{2}0$ $\frac{1}{2}0\frac{1}{2}$ $0\frac{1}{2}\frac{1}{2}$	
Monoclinic $a \neq b \neq c$ $\alpha = \gamma = 90° \neq \beta$ (*one* inc*lin*ed axis)	Simple	0 0 0	
	Base-centered	0 0 0 $\frac{1}{2}\frac{1}{2}0$	
Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$ (*three* inc*lin*ed axes)	Simple	0 0 0	
Total: ***7 crystal systems***		Total: ***14 Bravais lattices***	

From a LATTICE to a CRYSTAL STRUCTURE

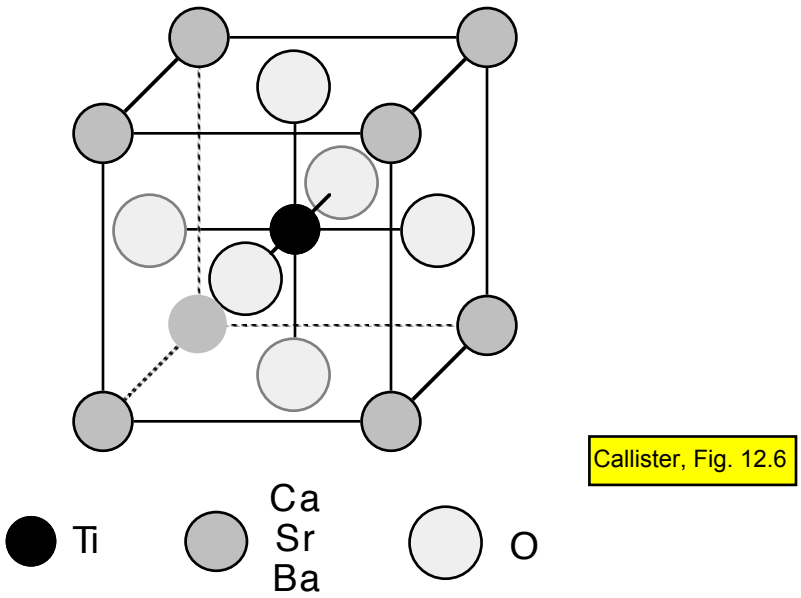
Given the lattice that corresponds to a particular crystal, describing the crystal structure involves listing the ***locations of atoms*** in the unit cell, which may be at:

- ***vertices*** (corners)
- ***edges***
- ***faces***
- ***interior*** positions

- There may be >1 atom per lattice point:

  Example: ***perovskite*** ($CaTiO_3$) is …

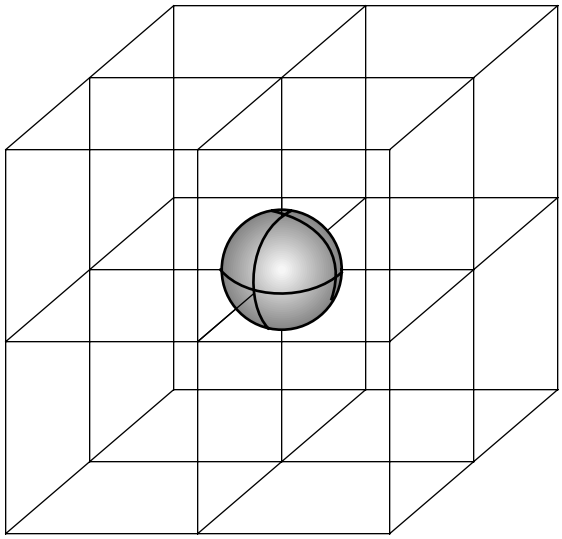
  - … ***primitive cubic***
    - Not body-centered, because the atom at the corners differs from that at the body center
    - Not face-centered, for similar reasoning
  - … with ***five atoms per lattice point*** (one Ca, one Ti, and three O)



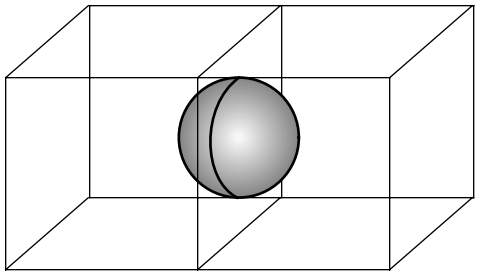
Callister, Fig. 12.6

COUNTING ATOMS in a UNIT CELL

- Atoms on ***corners*** are shared by ***eight*** unit cells



- Atoms on ***faces*** are shared by ***two*** unit cells



[After C. E. Mortimer, *Chemistry — A Conceptual Approach*, 3rd Ed., p. 213. D. Van Nostrand, New York, 1975.

(Also: ***edge*** atoms are shared by ***four*** unit cells)

Q.: How many lattice points (atoms) does a single face-centered cubic cell contain?

A.: $8 \frac{\text{corners occupied}}{\text{cell}} \times \frac{1}{8} \frac{\text{atom}}{\text{corner}} = \mathbf{1}$

$6 \frac{\text{faces occupied}}{\text{cell}} \times \frac{1}{2} \frac{\text{atom}}{\text{face}} = \mathbf{3}$

total of $\mathbf{4} \frac{\mathbf{atoms}}{\mathbf{cell}}$

How to specify DIRECTIONS in a lattice:

1) Draw a vector, through the origin, that is parallel to the direction of interest.

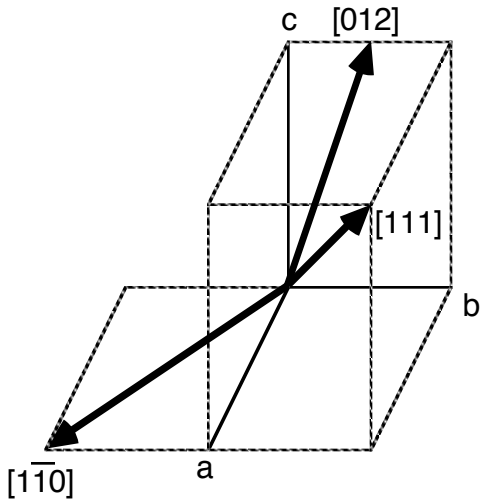
2) Determine the *projections* (components) of the vector along the three axes.

OR

Determine the *coordinates* of any point on the vector.

3) Multiply the resulting three numbers by a *common factor* to convert them to the smallest possible integers.

4) Enclose the resulting three integers in *square brackets*: [ ].



How to specify PLANES in a lattice:

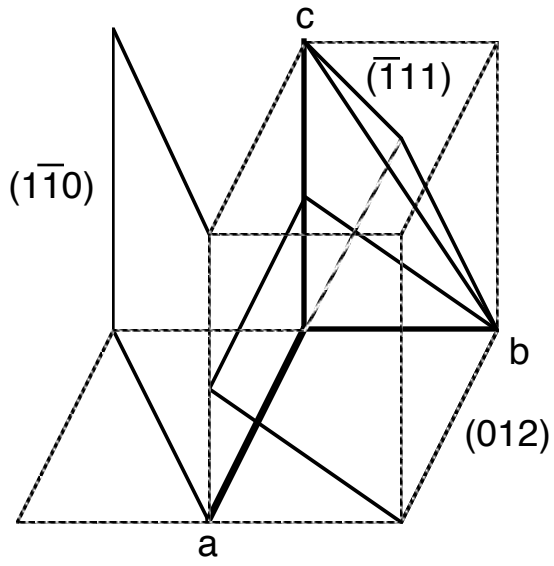
1) Choose a plane that does not contain the origin.

2) Determine the *intercepts* of the plane on the three axes.

3) Take the *reciprocals* of the intercepts.

4) Multiply the reciprocals by the smallest common factor that will clear all fractions.

5) Enclose the resulting integers — the *Miller indices* — in parentheses: $(h\,k\,\ell)$.



POINTS ON PLANES

Stated w/o proof: A point with coordinates x,y,z is on a plane with Miller indices $(h\,k\,\ell)$ if and only if

$$hx + ky + \ell z = 1$$

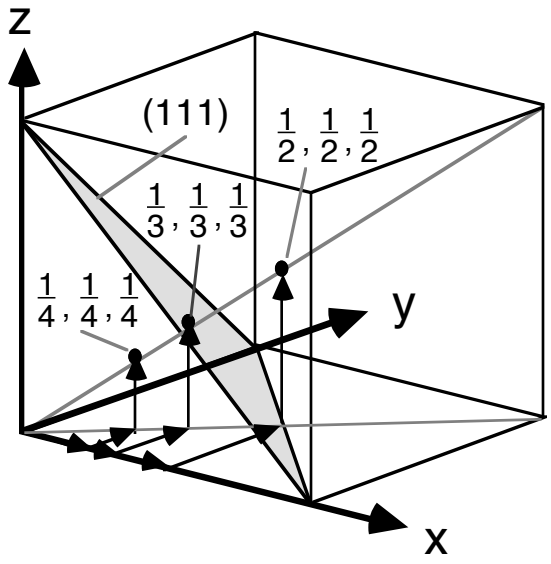
(true for all crystal systems).

So, for example, of the following points,

$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ is NOT on (111) $\left(\Leftarrow hx + ky + \ell z = \frac{3}{4}\right)$

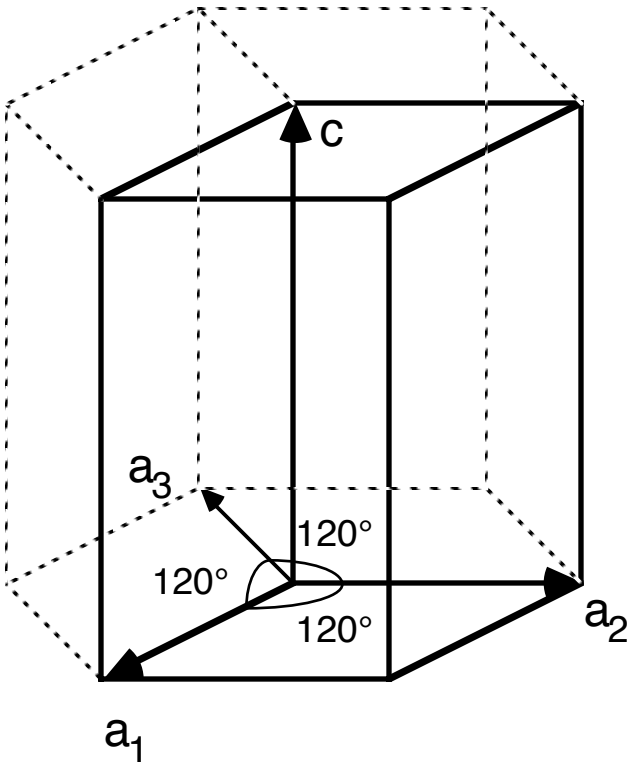
$\frac{1}{3}, \frac{1}{3}, \frac{1}{3}$ IS on (111) $\left(\Leftarrow hx + ky + \ell z = 1\right)$

$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ is NOT on (111) $\left(\Leftarrow hx + ky + \ell z = \frac{3}{2}\right)$

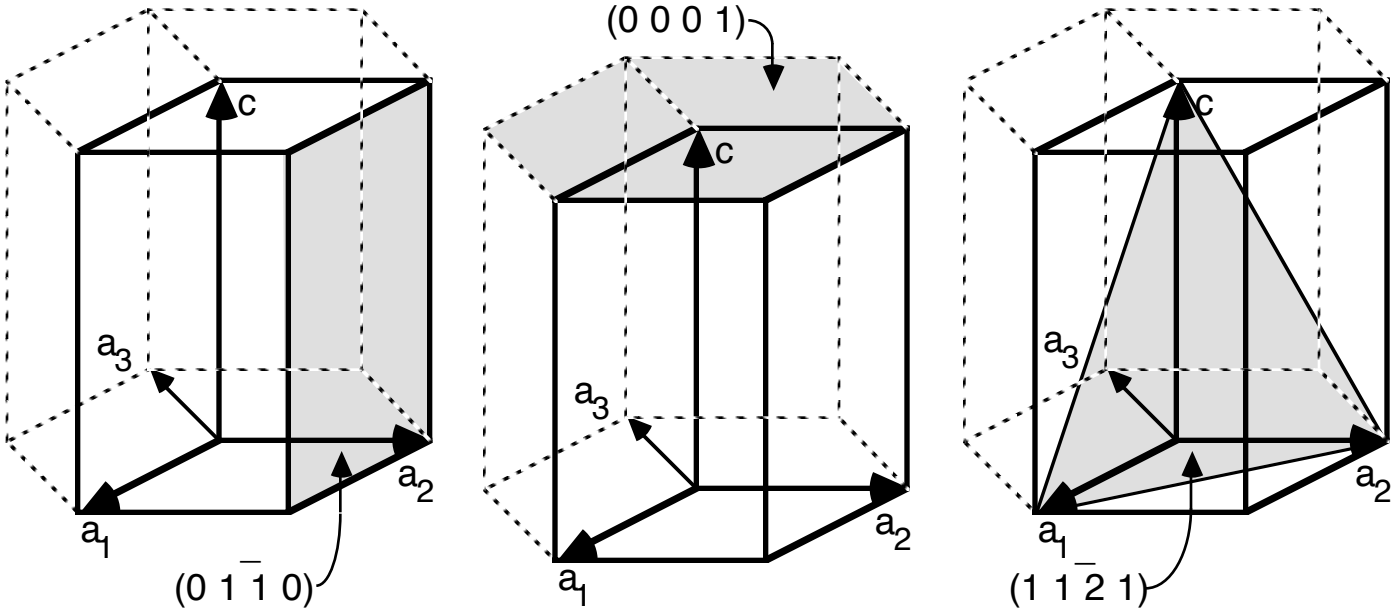


MILLER-BRAVAIS INDICES for planes in hexagonal lattices (start)

- Define a set of *four* basis vectors, a_1, a_2, a_3, and c as shown at right:
- Determine the ***intercepts*** of the plane of interest on the four basis vectors
- Take the ***reciprocals*** of the intercepts
- Multiply the reciprocals by the smallest common factor that will ***clear all fractions***
- Enclose in parentheses ***(h k i l)***



Examples:



- Note: the relationship between a_1, a_2, and a_3 is such that

$$-i = h + k$$

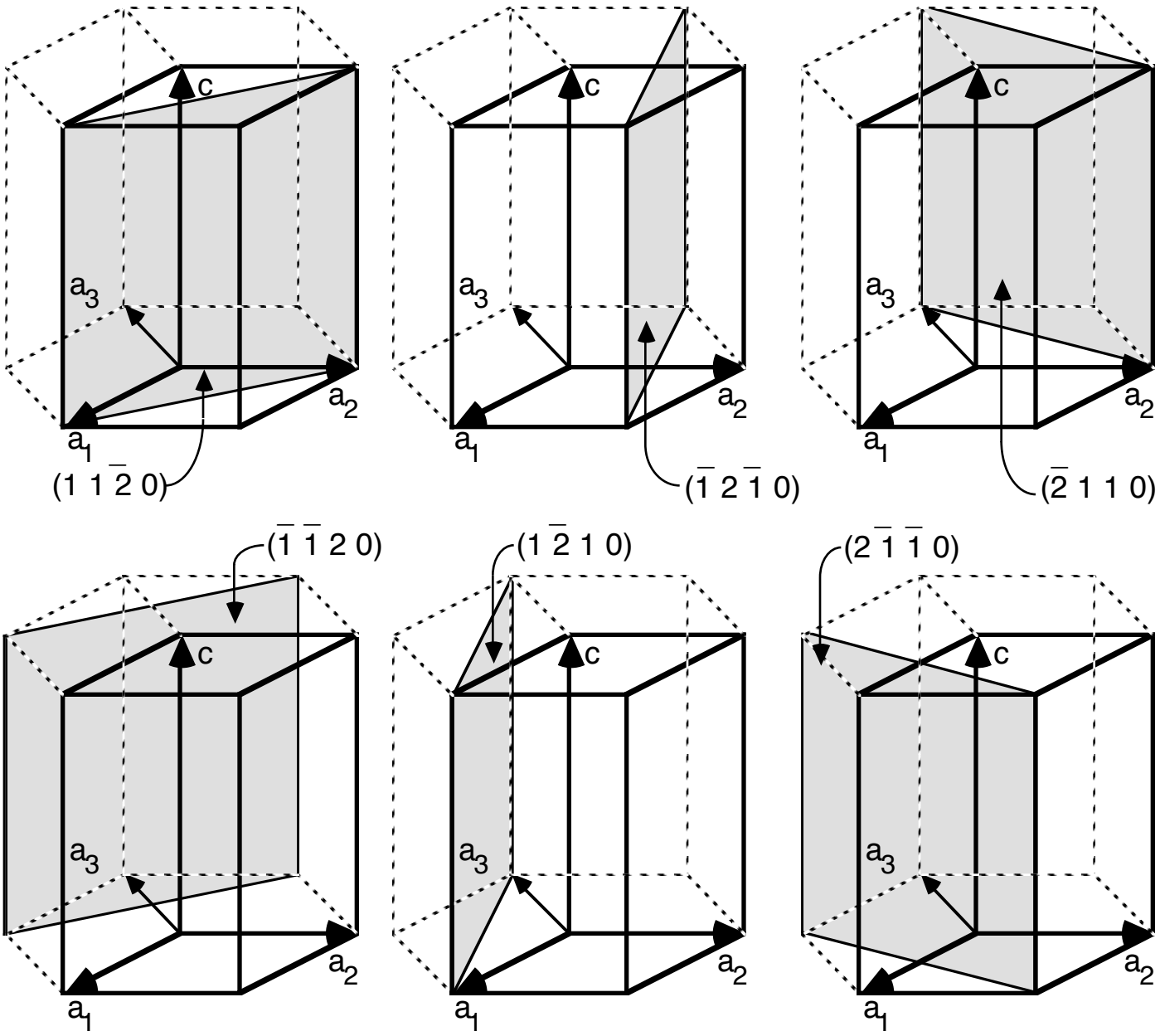
MILLER-BRAVAIS INDICES (end)

Q: Why bother with an extra index?

A: Now planes in the same ***family*** are identified by ***permutations*** of the (first three) indices, as with Miller indices for the other systems:

e.g. {11$\bar{2}$0} consists of

(1 1 $\bar{2}$ 0) ($\bar{1}$ 2 $\bar{1}$ 0) ($\bar{2}$ 1 1 0) ($\bar{1}$ $\bar{1}$ 2 0) (1 $\bar{2}$ 1 0) (2 $\bar{1}$ $\bar{1}$ 0)

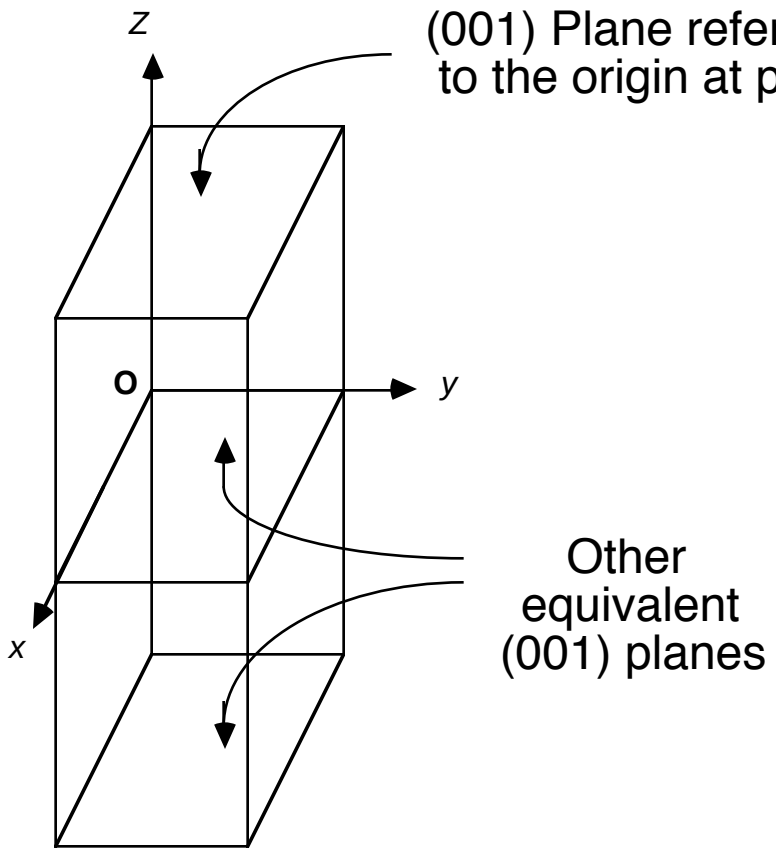


EQUIVALENT PLANES

Callister, Figure 3.9

Equivalent planes: planes that are identical to each other by virtue of the ordinary translational symmetry of the lattice;

i.e., they can be generated by translating the unit cell along its base vectors by integral multiples of the respective lattice parameter



FAMILIES OF PLANES & DIRECTIONS

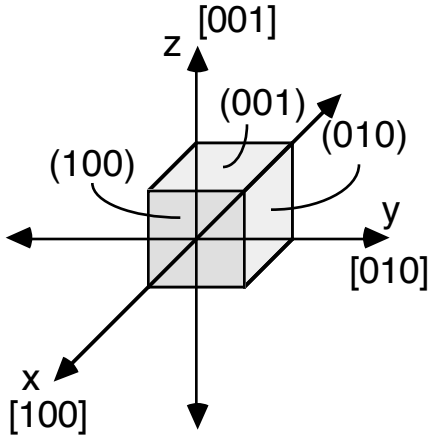
- Also called ***planes of a form*** and ***directions of a form***

- Are identical to each other by the internal symmetry of the cell (vs. equivalent planes, which are related by the translational symmetry of the lattice):

  e.g., in the cubic class,

  the cell ***faces*** lie on planes of a form

  the cell ***edges*** are along directions of a form



Cube faces — (100), (010), (001) — belong to the family of {100} planes

Cube edges — [100], [010], [001] — belong to the family of <100> directions

<u>But note</u>: in the *tetragonal* class,

[100] and [010] belong to the <100> family, but [001] doesn't

(100) and (010) belong to the {100} family, but (001) doesn't