Welcome to
CHE 384T: Computational Methods in Materials Science

A Brief Introduction to Crystallography

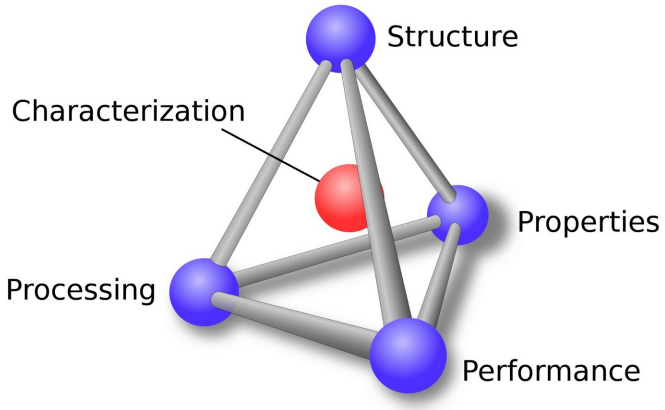
LeSar App. B1-B5

The University of Texas at Austin
McKetta Department
of Chemical Engineering
Cockrell School of Engineering

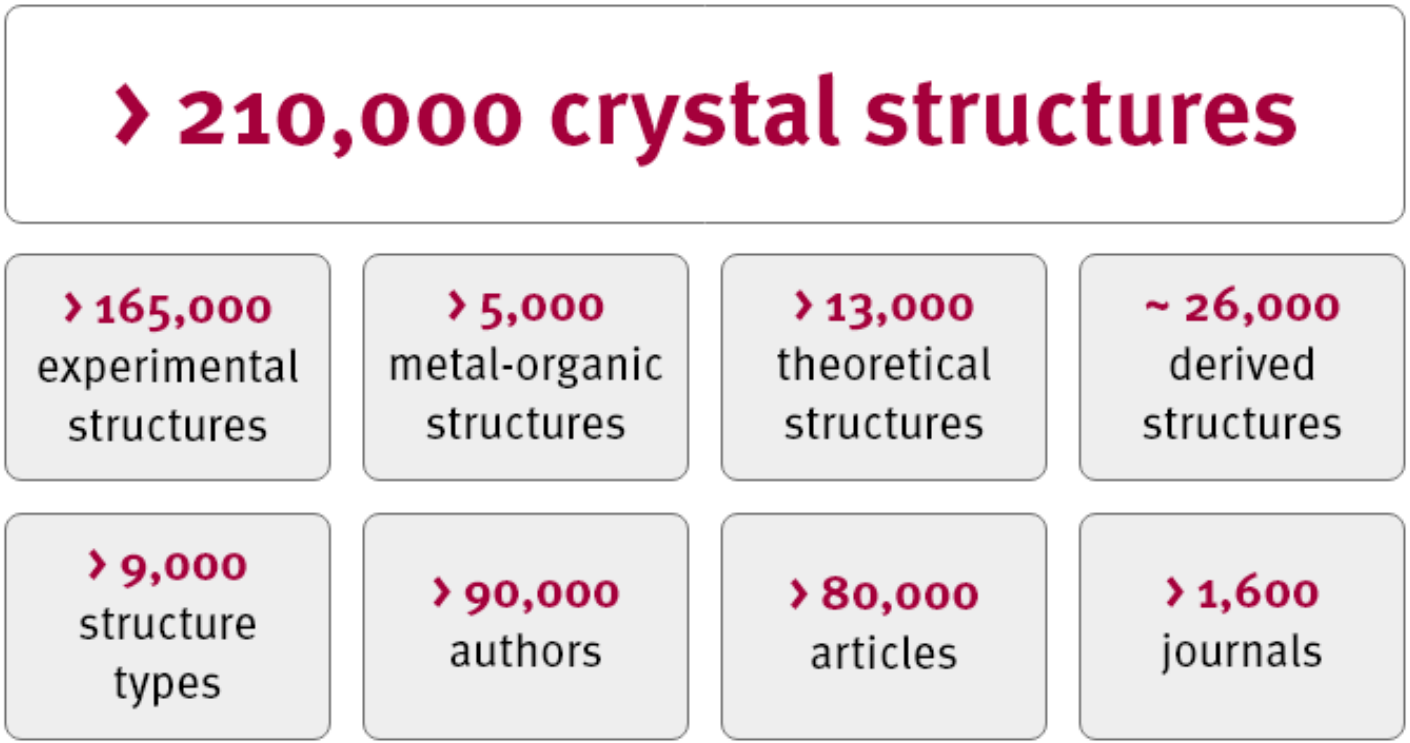
Lecture Outline

Crystal structure
- Unit cell
- Bravais Lattices
- Example Crystal structures from the cubic space group

Brief on Crystallographic notation

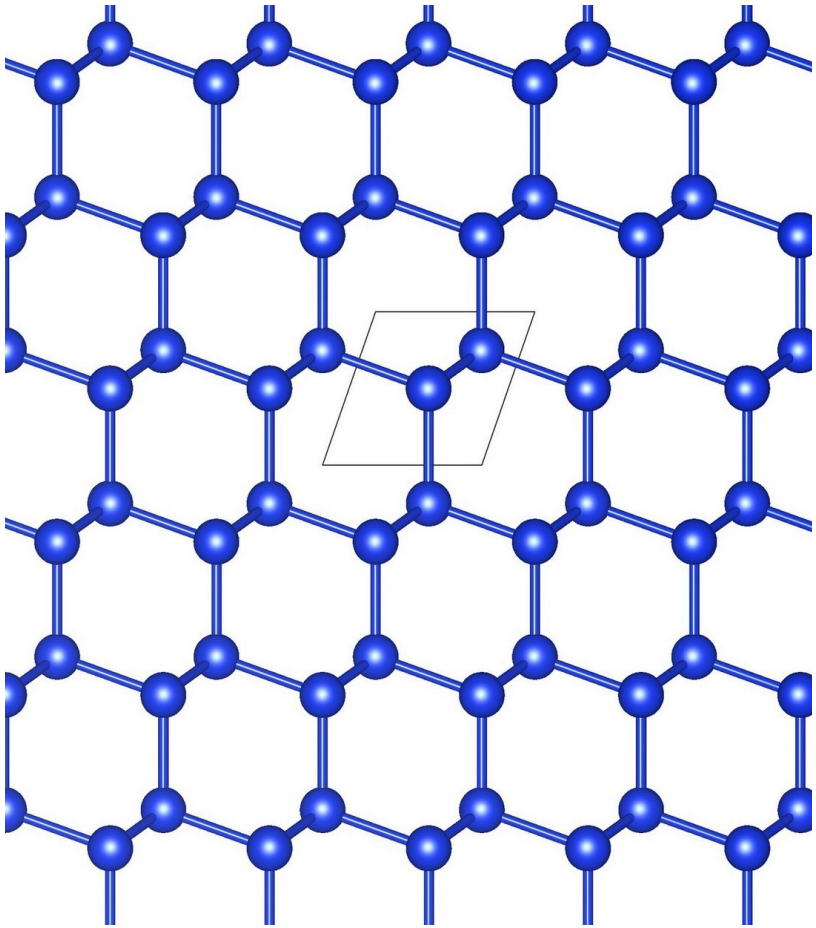


There are a lot of crystal structures out there



ICSD database

Crystals are described by periodicity of the unit cell



Crystal Structure = Basis + Lattice

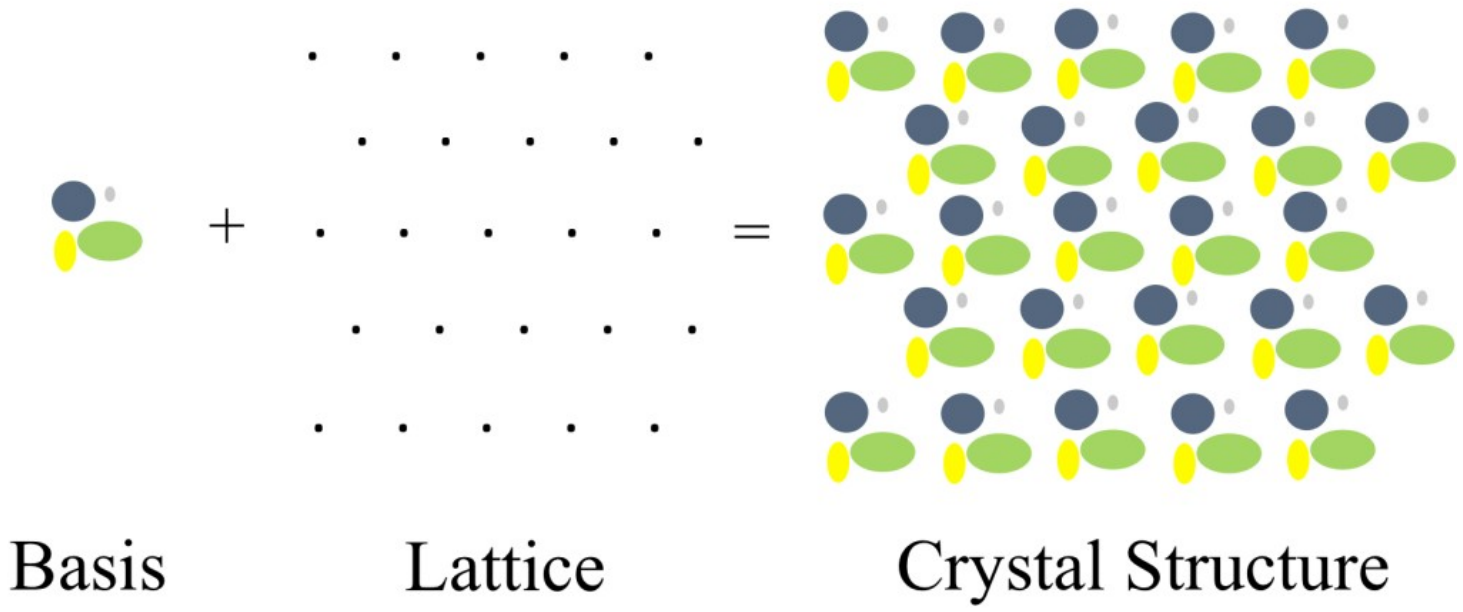
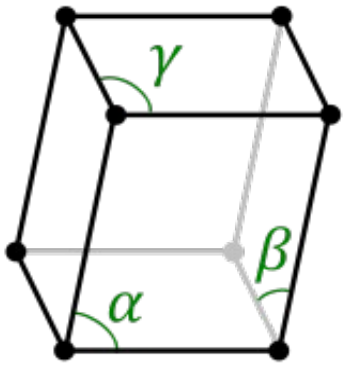


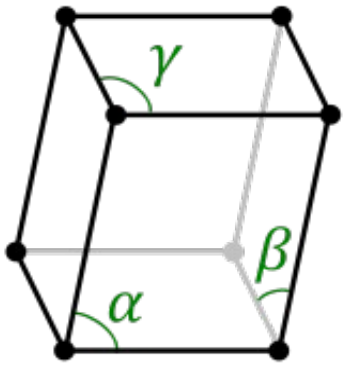
Image from link

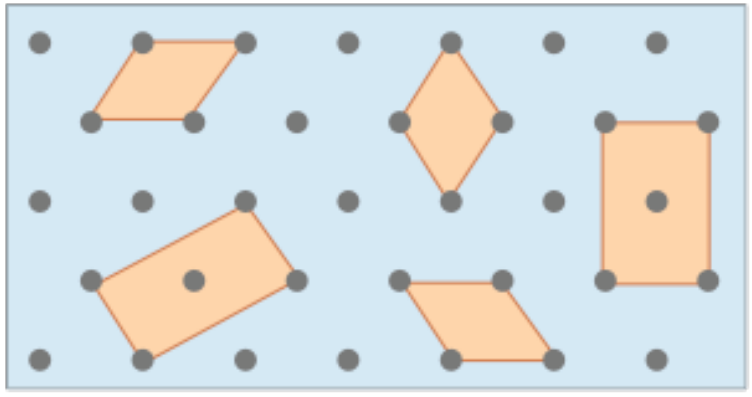
The Unit Cell

$\alpha, \beta, \gamma \neq 90°$



The Unit Cell



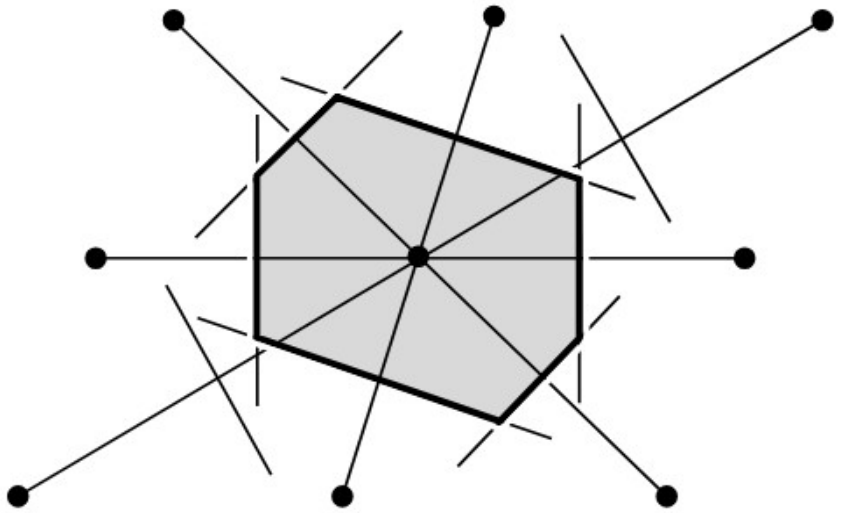


Primitive Unit Cell

Conventional Unit Cell

The Unit Cell

Figure 4 A primitive cell may also be chosen following this procedure: (1) draw lines to connect a given lattice point to all nearby lattice points; (2) at the midpoint and normal to these lines, draw new lines or planes. The smallest volume enclosed in this way is the Wigner-Seitz primitive cell. All space may be filled by these cells, just as by the cells of Fig. 3.



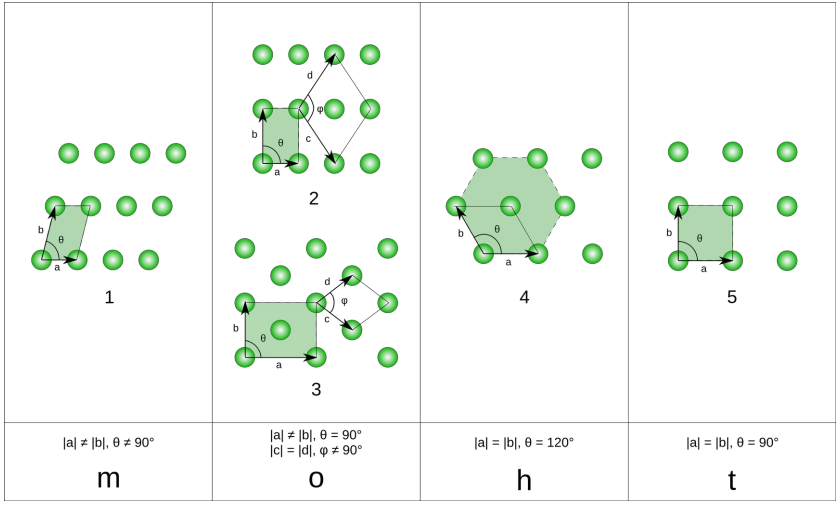
Physics: “Wigner-Seitz cell”

Image from Kittel, Solid-state Physics

Bravais Lattice (in 3D)

Bravais lattice cells	Axes and interaxial angles	Examples
Cubic P, Cubic I, Cubic F	Three axes at right angles; all equal: $a = b = c$; $\alpha = \beta = \gamma = 90°$	Copper (Cu), silver (Ag), sodium chloride (NaCl)
Tetragonal P, Tetragonal I	Three axes at right angles; two equal: $a = b \neq c$; $\alpha = \beta = \gamma = 90°$	White tin (Sn), rutile (TiO_2), β-spodumene ($LiAlSi_2O_6$)
P, C, I, F — Orthorhombic	Three axes at right angles; all unequal: $a \neq b \neq c$; $\alpha = \beta = \gamma = 90°$	Gallium (Ga), perovskite ($CaTiO_3$)
Monoclinic P, Monoclinic C	Three axes, one pair not at right angles, of any lengths: $a \neq b \neq c$; $\alpha = \gamma = 90° \neq \beta$	Gypsum ($CaSO_4 \cdot 2H_2O$)
Triclinic P	Three axes not at right angles, of any lengths: $a \neq b \neq c$; $\alpha \neq \beta \neq \gamma \neq 90°$	Potassium chromate (K_2CrO_7)
Trigonal R (rhombohedral)	Rhombohedral: three axes equally inclined, not at right angles; all equal: $a = b = c$; $\alpha = \beta = \gamma \neq 90°$	Calcite ($CaCO_3$), arsenic (As), bismuth (Bi)
Trigonal and hexagonal C (or P)	Hexagonal: three equal axes coplanar at 120°, fourth axis at right angles to these: $a_1 = a_2 = a_3 \neq c$; $\alpha = \beta = 90°$, $\gamma = 120°$	Zinc (Zn), cadmium (Cd), quartz (SiO_2) [P]

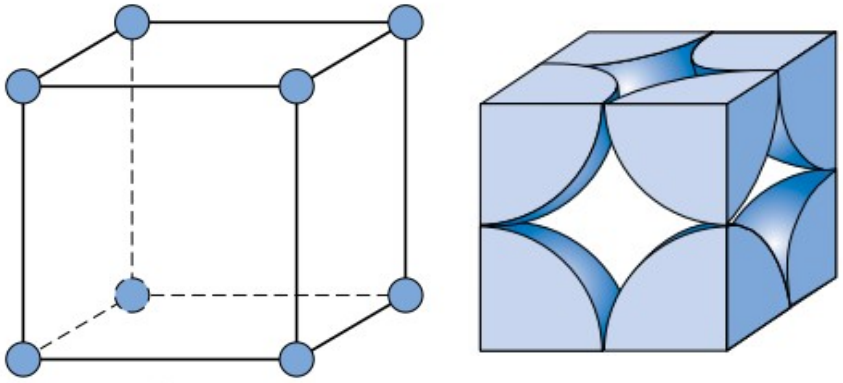
Bravais Lattice (in 2D)



These assume single-atom basis

Cubic crystal structures (monoatomic)

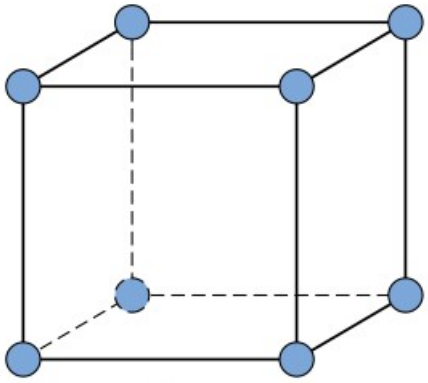
Simple Cubic



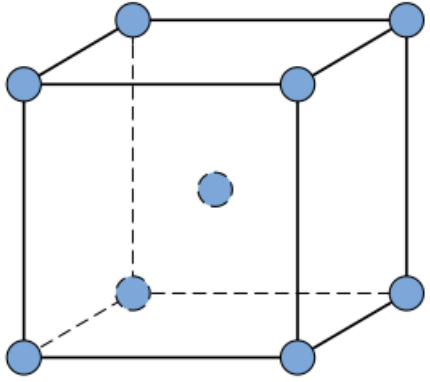
Fractional coordinates

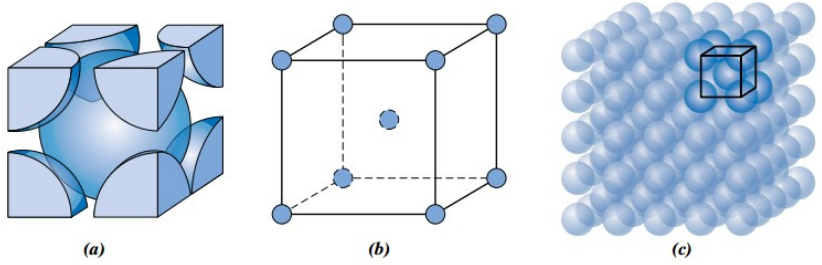
Cubic crystal structures (monoatomic)

Simple Cubic



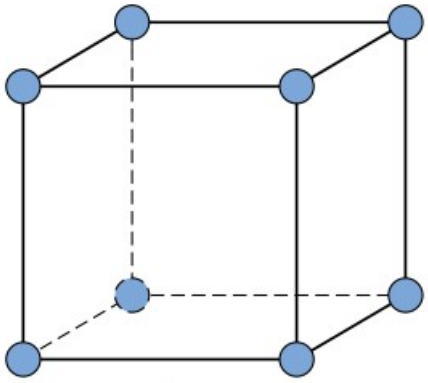
Body-Centered Cubic



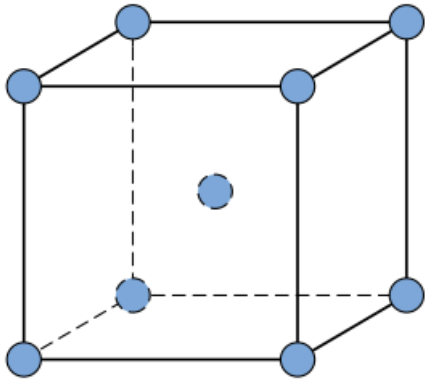


Cubic crystal structures (monoatomic)

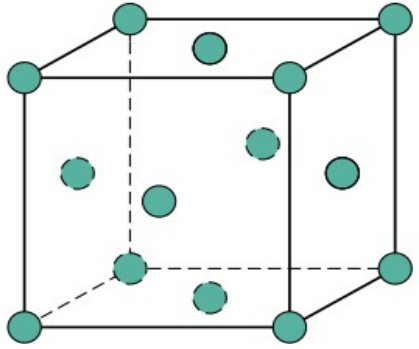
Simple Cubic

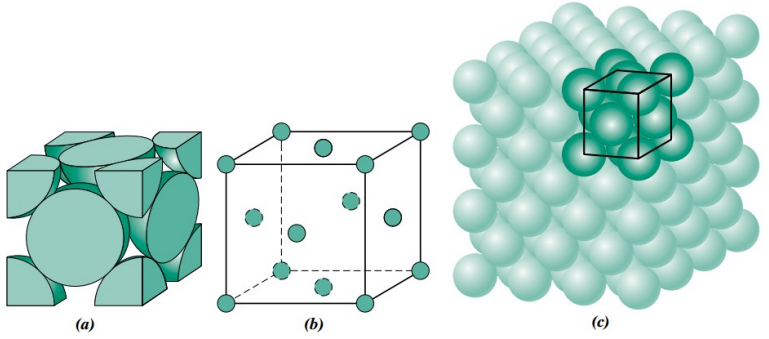


Body-Centered Cubic

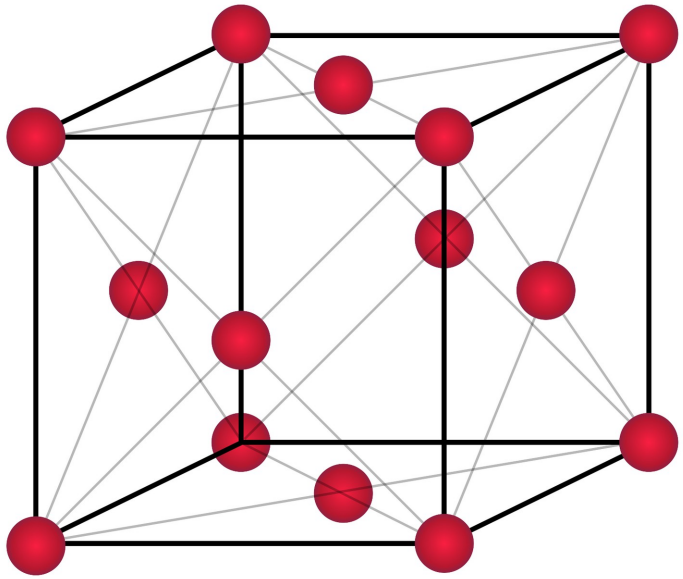


Face-Centered Cubic

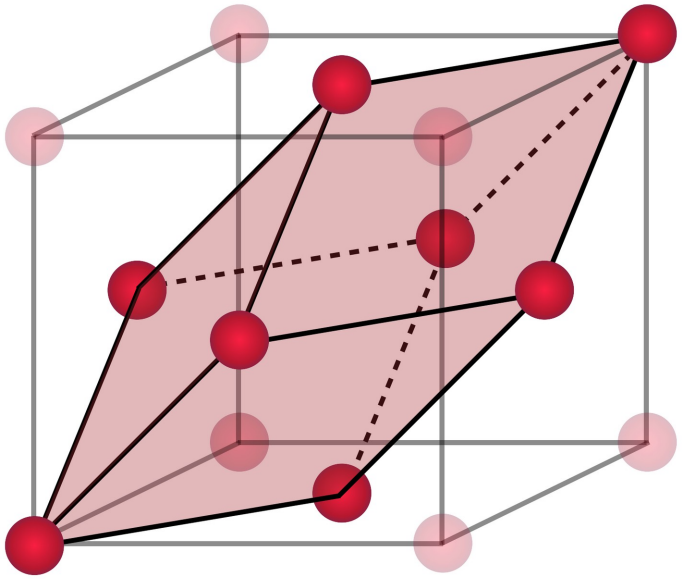




Cubic crystal structures (monoatomic)



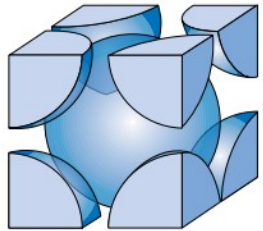
(a) conventional unit cell



(b) primitive unit cell

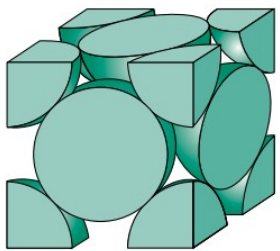
How many (whole) atoms per unit cell?

Body-Centered Cubic



(a)

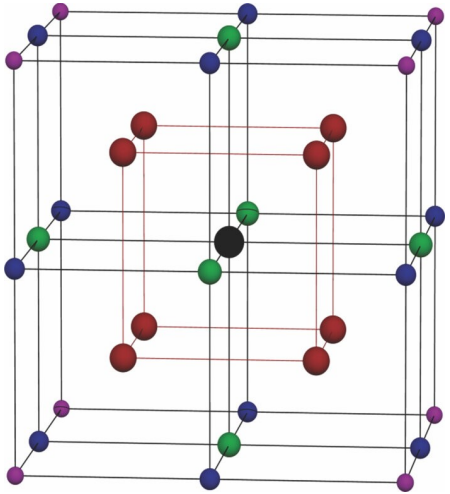
Face-Centered Cubic



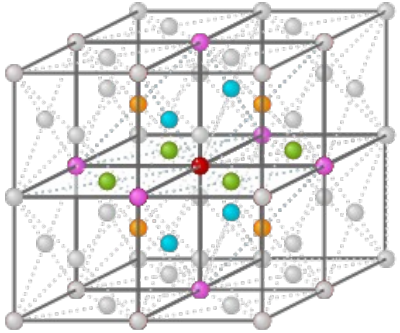
(a)

How many nearest neighbors?

Body-Centered Cubic



Face-Centered Cubic



How many nearest neighbors?

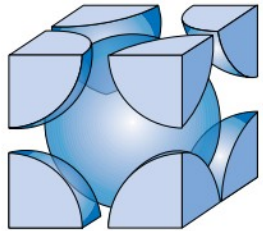
Table 2 Characteristics of cubic lattices[a]

	Simple	Body-centered	Face-centered
Volume, conventional cell	a^3	a^3	a^3
Lattice points per cell	1	2	4
Volume, primitive cell	a^3	$\frac{1}{2}a^3$	$\frac{1}{4}a^3$
Lattice points per unit volume	$1/a^3$	$2/a^3$	$4/a^3$
Number of nearest neighbors	6	8	12
Nearest-neighbor distance	a	$3^{1/2}\,a/2 = 0.866a$	$a/2^{1/2} = 0.707a$
Number of second neighbors	12	6	6
Second neighbor distance	$2^{1/2}a$	a	a
Packing fraction[a]	$\frac{1}{6}\pi$ $=0.524$	$\frac{1}{8}\pi\sqrt{3}$ $=0.680$	$\frac{1}{6}\pi\sqrt{2}$ $=0.740$

Kittel, Solid-state Physics

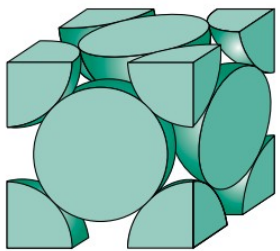
Fractional v cartesian coordinates

Body-Centered Cubic



(a)

Face-Centered Cubic



(a)

What are the fractional coordinates of the basis set atoms of diamond?

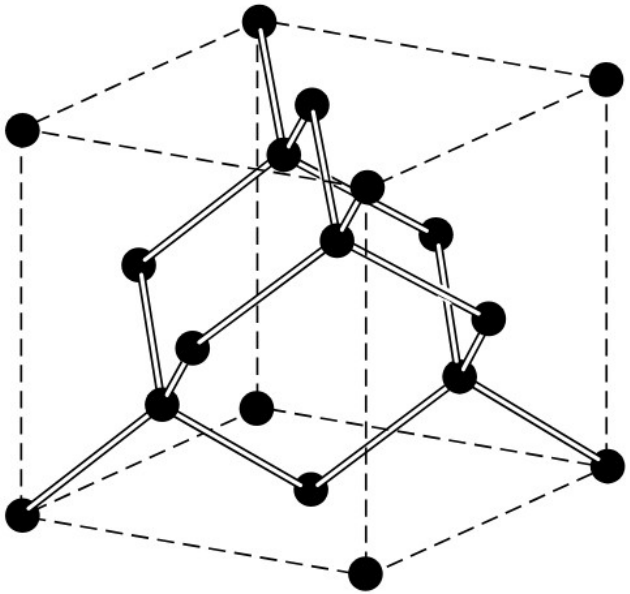
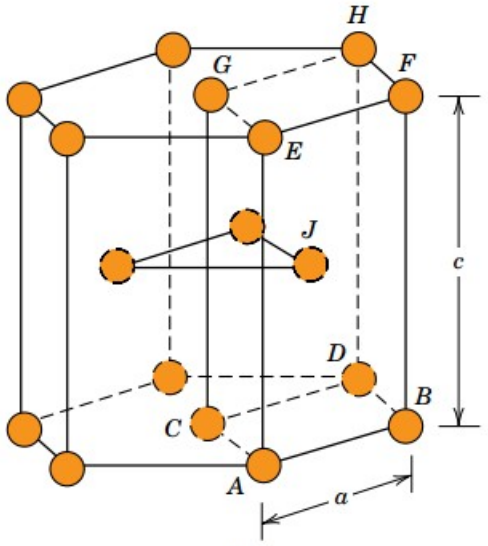
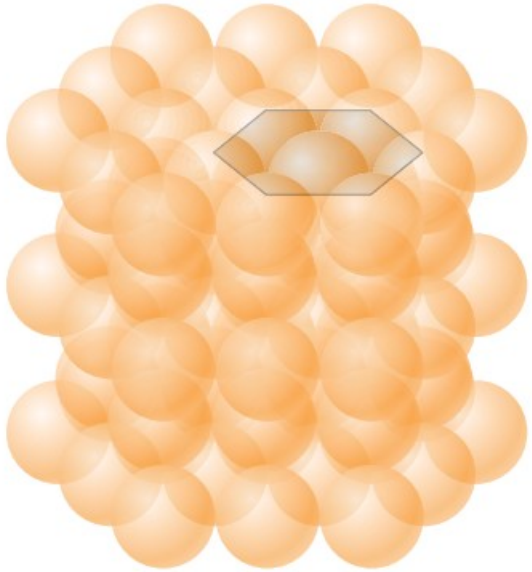


Figure 23 Crystal structure of diamond, showing the tetrahedral bond arrangement.

Hexagonal closed-packed (HCP)

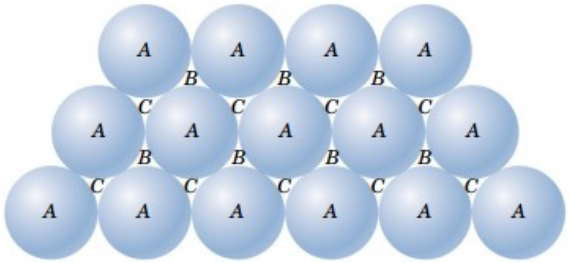


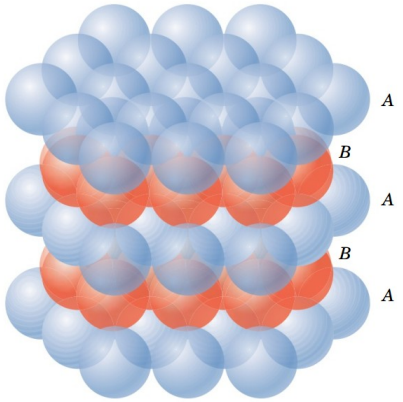
(a)



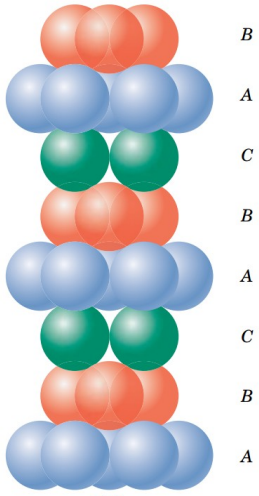
(b)

Relation between HCP & FCC

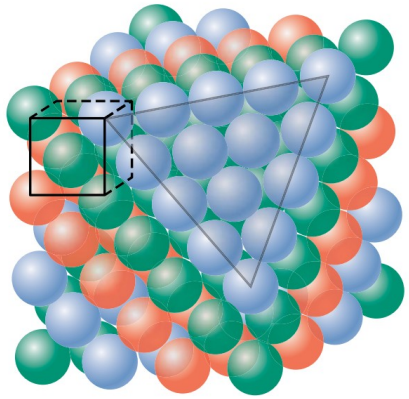




HCP



(a)

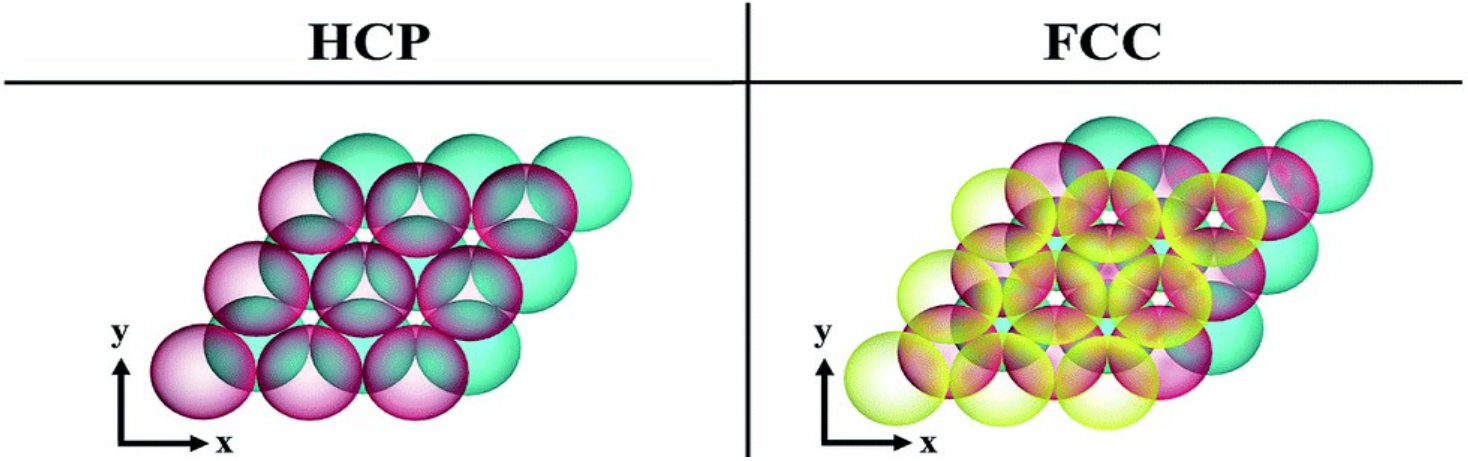


(b)

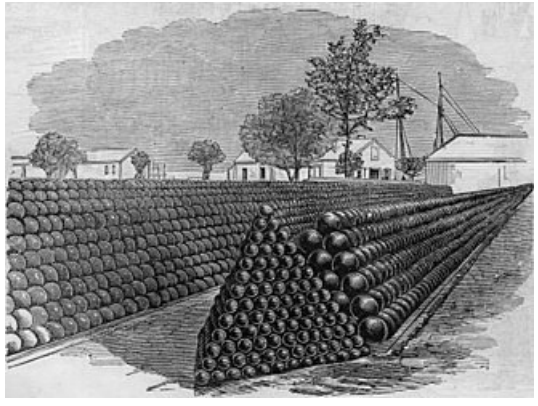
FCC

3D animation #1
3D animation #2

Relation between HCP & FCC



N.A. Mahynski et al. Soft Matter, 2015,11, 280-289 10.1039/C4SM02191F



The Cannonball problem
Youtube video: Hard sphere packing problem

Front HCP, Rear FCC
(Image from Yvette Cendes, CC0)

Non-crystalline systems

Polycrystalline materials

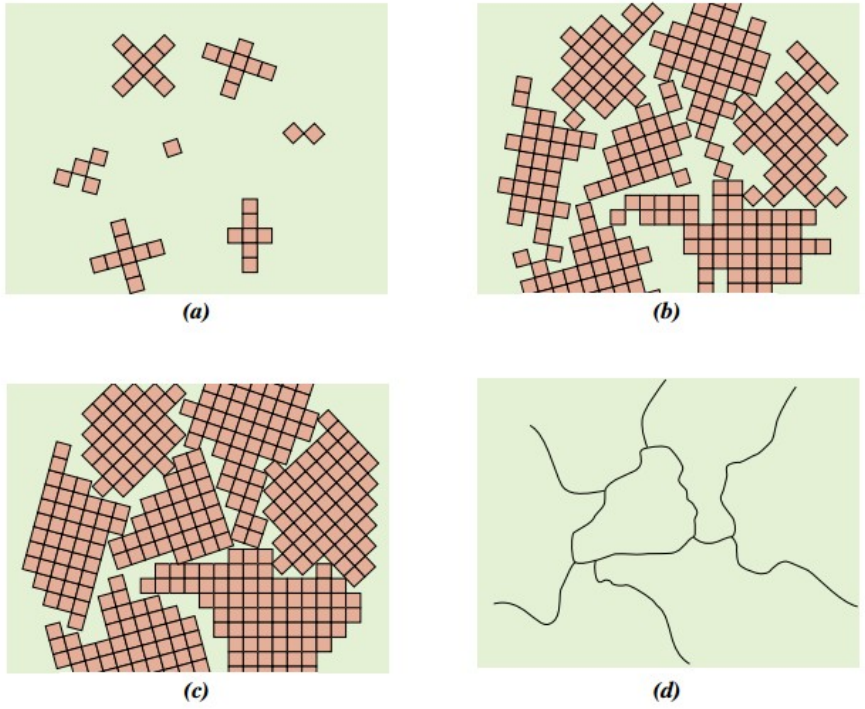


Figure 3.20 Schematic diagrams of the various stages in the solidification of a polycrystalline material; the square grids depict unit cells. (*a*) Small crystallite nuclei. (*b*) Growth of the crystallites; the obstruction of some grains that are adjacent to one another is also shown. (*c*) Upon completion of solidification, grains having irregular shapes have formed. (*d*) The grain structure as it would appear under the microscope; dark lines are the grain boundaries. (Adapted from W. Rosenhain, *An Introduction to the Study of Physical Metallurgy*, 2nd edition, Constable & Company Ltd., London, 1915.)

Non-crystalline systems

Amorphous materials

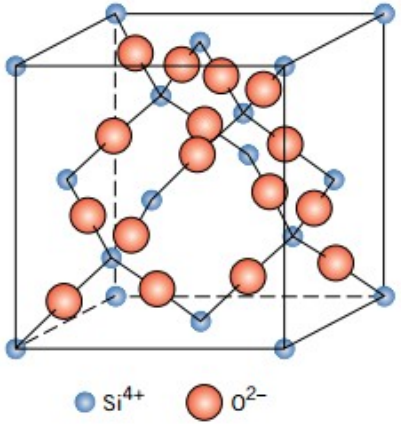


Figure 12.10 The arrangement of silicon and oxygen atoms in a unit cell of cristobalite, a polymorph of SiO_2.

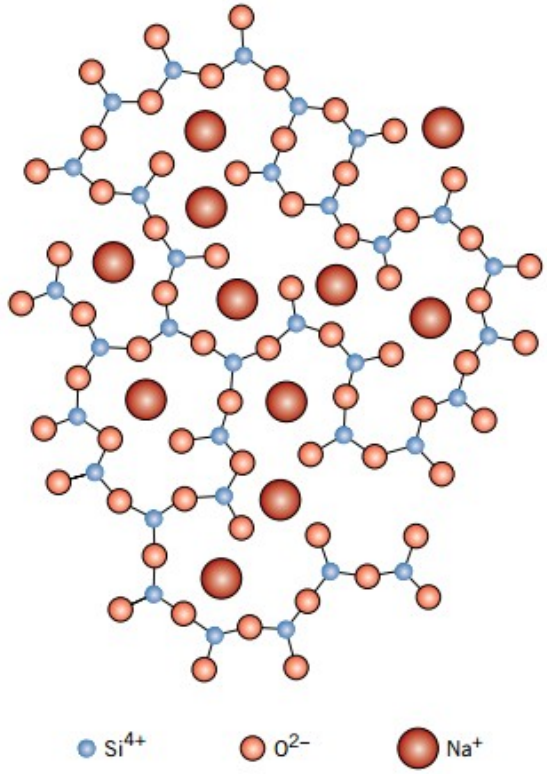


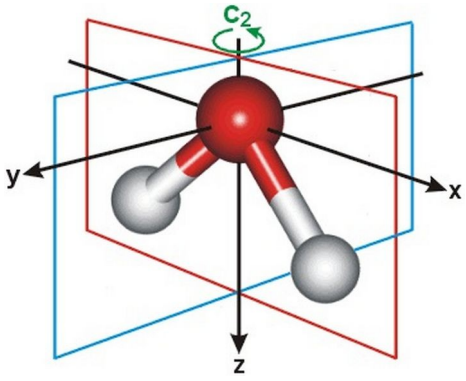
Figure 12.11 Schematic representation of ion positions in a sodium–silicate glass.

A side note on space groups

Neumann's principle:
'the symmetry elements of any physical property of a crystal must include the symmetry elements of the point group of the crystal'.

Space group:
combination of crystallographic point groups + Bravais lattice
(230 combinations in 3D, if count chiral structures distinct)

Example: crystallographic point group of water molecule



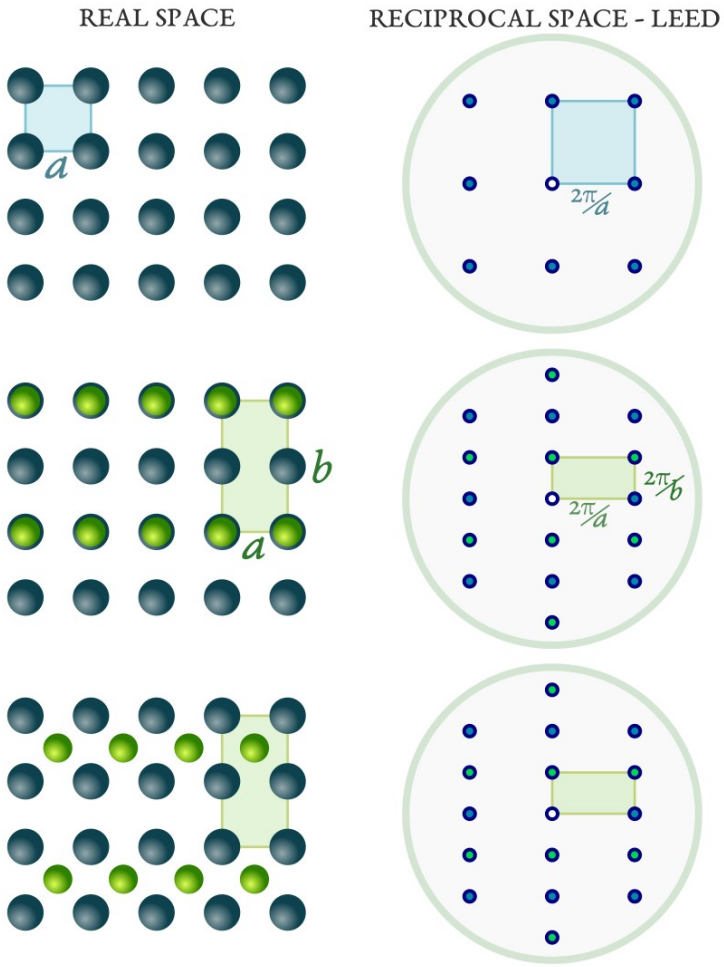
Common notation: Hermann-Mauguin or Schoeflies used

Looking up info on space space groups
e.g., http://img.chem.ucl.ac.uk/sgp/medium/sgp.htm

A side note on Reciprocal Space:

The electron density is a periodic function of the lattice

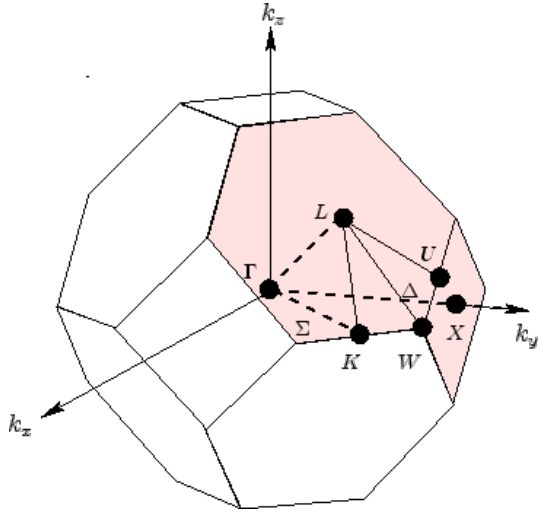
A side note on Reciprocal Space:



$$\mathbf{b}_1 = \frac{2\pi}{V}\,\mathbf{a}_2 \times \mathbf{a}_3$$

$$\mathbf{b}_2 = \frac{2\pi}{V}\,\mathbf{a}_3 \times \mathbf{a}_1$$

$$\mathbf{b}_3 = \frac{2\pi}{V}\,\mathbf{a}_1 \times \mathbf{a}_2$$



Reciprocal cell of FCC lattice, aka first Brillouin Zone

$$\mathbf{G} = v_1\mathbf{b_1} + v_2\mathbf{b_2} + v_3\mathbf{b_3}$$

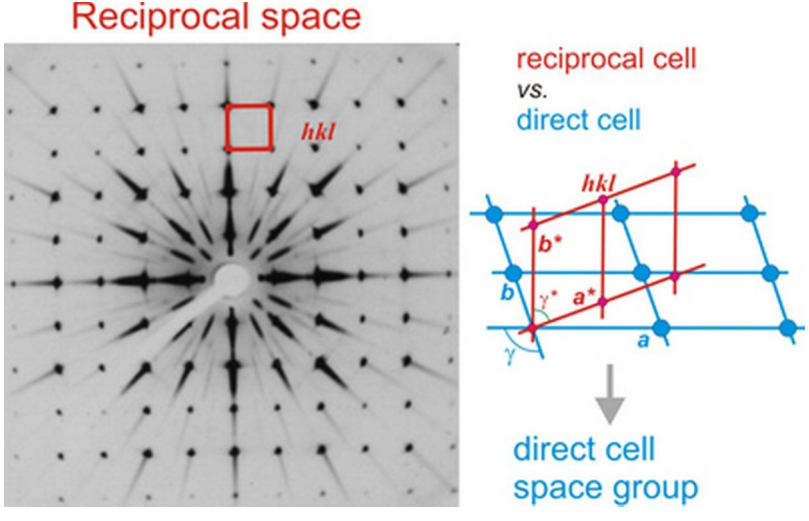
A side note on Reciprocal Space:

Why bother with reciprocal space?

Falls out naturally in the math (complex exponentials)

Corresponds to experimental measurements
(where you probe the sample with light or beam source)

X-ray diffraction → Bulk crystal structure



Low-energy electron diffraction (LEED)
→ Surface crystal structure

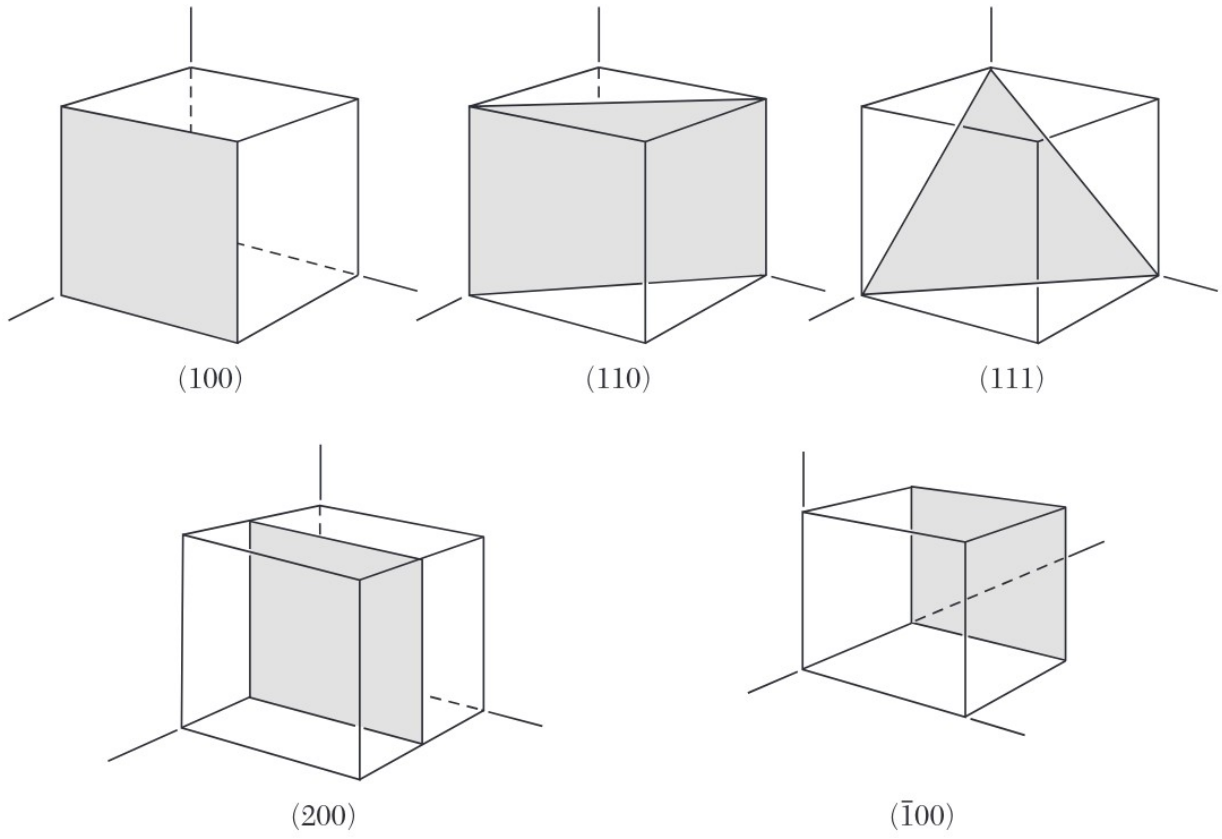


Figure 14 Indices of important planes in a cubic crystal. The plane (200) is parallel to (100) and to (100).

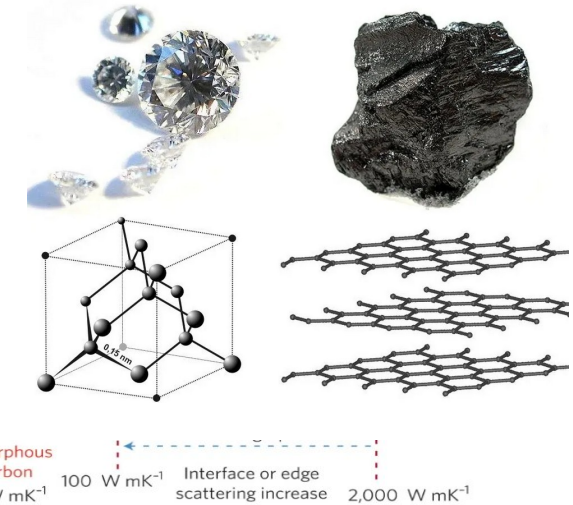
Why is understanding crystallography important?

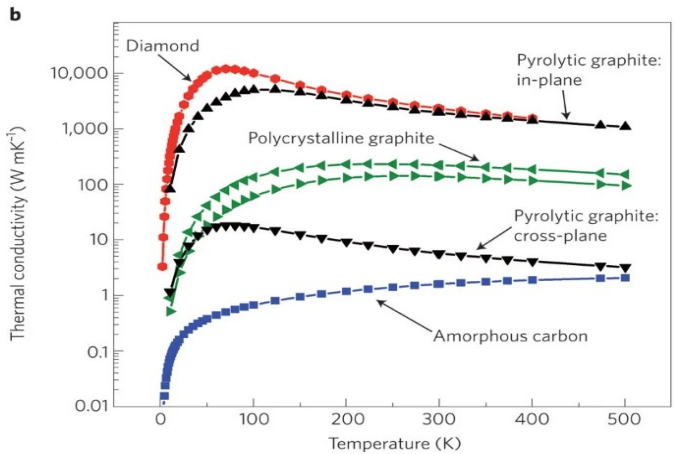
Material anisotropy-
material properties have diretionality

Table 3.4
Modulus of Elasticity Values for Several Metals at Various Crystallographic Orientations

	Modulus of Elasticity (GPa)		
Metal	***[100]***	***[110]***	***[111]***
Aluminum	63.7	72.6	76.1
Copper	66.7	130.3	191.1
Iron	125.0	210.5	272.7
Tungsten	384.6	384.6	384.6

Source: R. W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd edition.

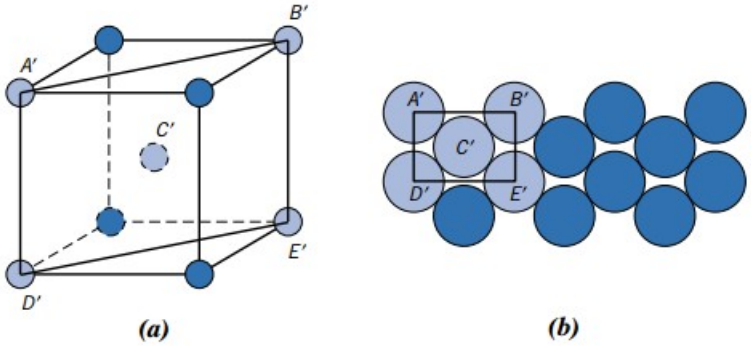


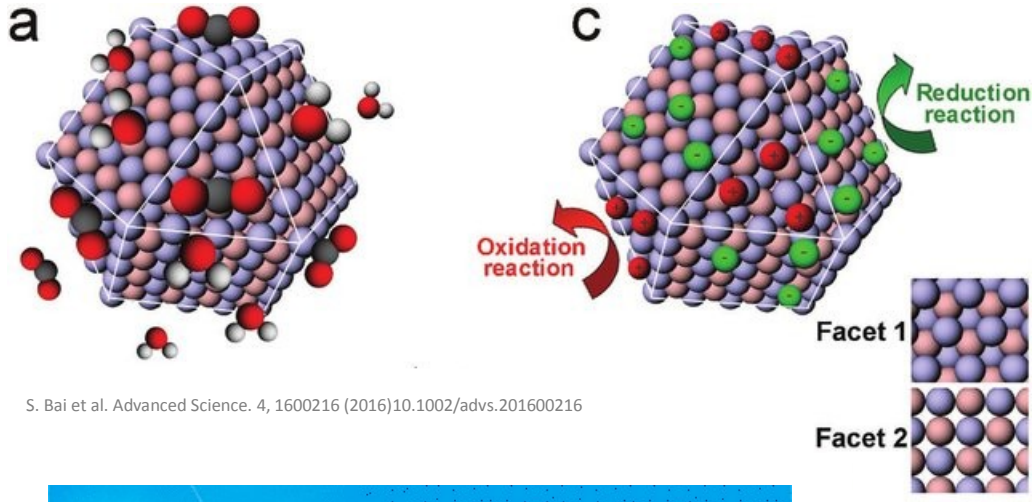


A. Balandin. Nature Mater 10, 569–581 (2011). 10.1038/nmat3064

Crystallographic planes and surface facets

(110) plane for BCC





S. Bai et al. Advanced Science. 4, 1600216 (2016)10.1002/advs.201600216

(110) plane for FCC