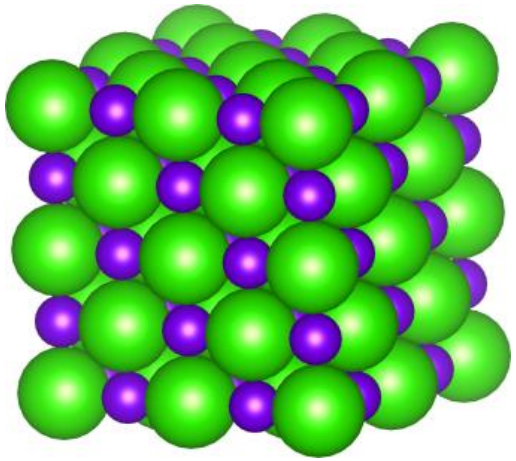
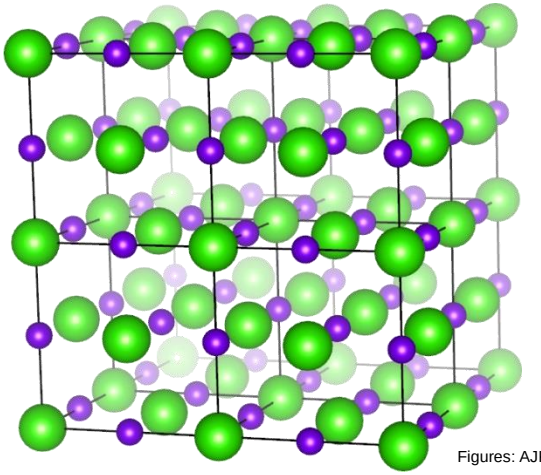
Lecture 1:
Structure of crystalline materials

- Basics of crystalline materials
  - Dimensionality of solids
  - Molecular vs. non-molecular solids
- X-ray diffraction
- Unit cell
- Crystal systems
- Symmetry
  - Point group symmetry and translational symmetry
  - Crystal classes
- Lattice
  - Lattice types and Bravais lattices
- Space groups



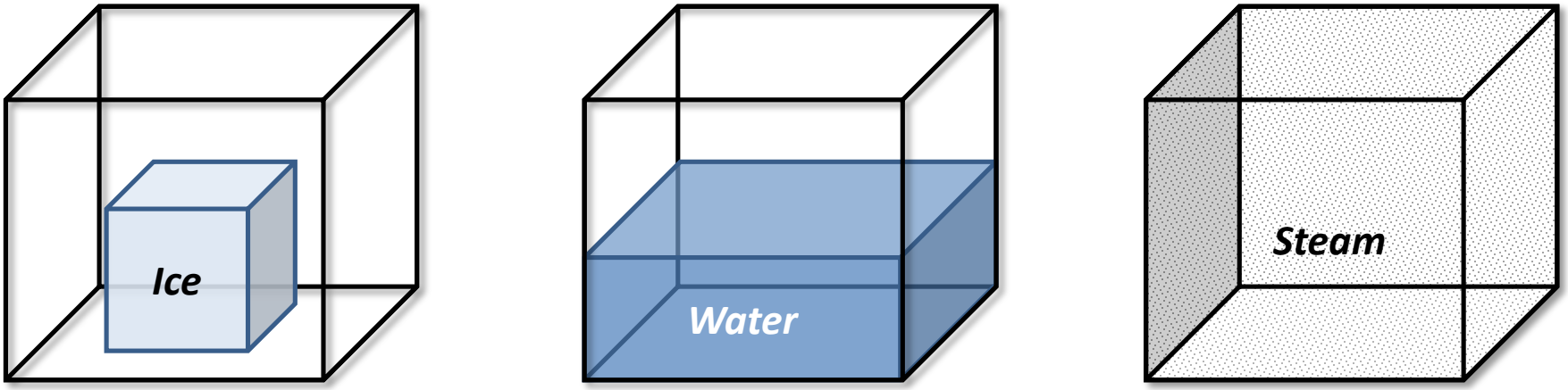


Figures: AJK

Basics of crystalline materials

States of bulk matter

Temperature increases



Figures: AJK

Solid: Adopts and maintains a shape that is independent of the container it occupies.

Liquid: Adopts the shape of the part of the container it occupies and is separated from the unoccupied part of the container by a definite surface.

Gas: immediately fills any container it occupies

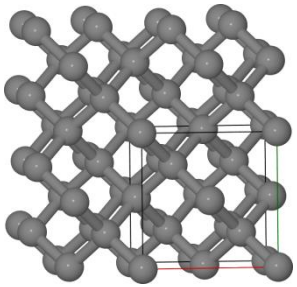
Condensed matter

Fluids (flow in response to forces such as gravity)

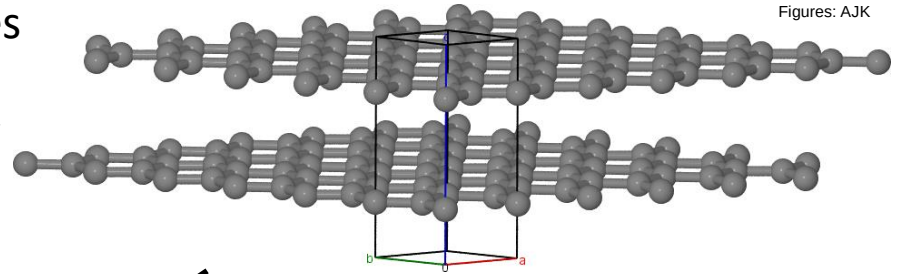
Molecular chemistry

Ref: Atkins' Physical Chemistry, 9th ed. p. 4

Dimensionality of solids



Two 3D allotropes of carbon

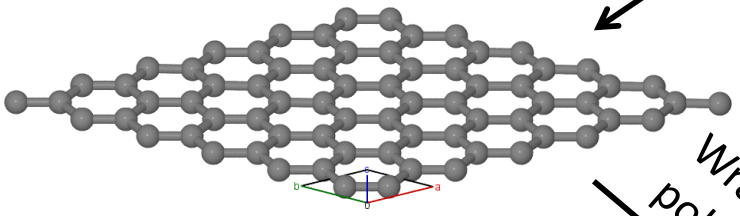


Figures: AJK

Diamond (3D)

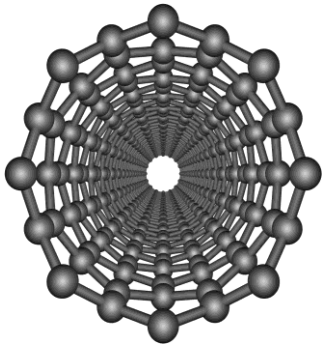
Graphite (3D)

Cut a slab



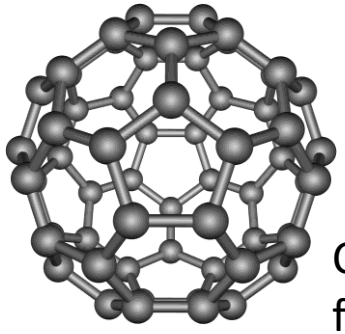
Graphene (2D)

Roll up to a tube



Carbon nanotube (1D)

Wrap up to a polyhedron



Carbon fullerene (0D)

Crystalline materials

- A material is a crystal if it has essentially a ***sharp diffraction pattern*** (IUCr definition)
- The definition includes
  - Periodic crystals
  - Aperiodic crystals
  - Quasicrystals

- ***Periodic*** crystal is a ***regular*** arrangement of atoms in three dimensions. These include
  a) Single crystals
  b) Polycrystals composed of many crystallites

- **Amorphous materials** are non-crystalline and lack long-range order
  - Not discussed on this course

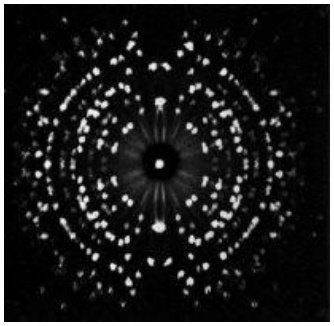


Figure: Susan Lehman / physics.wooster.edu

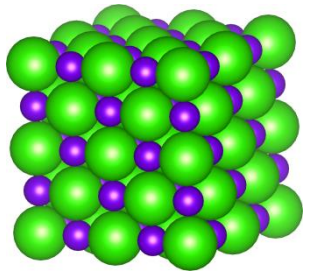
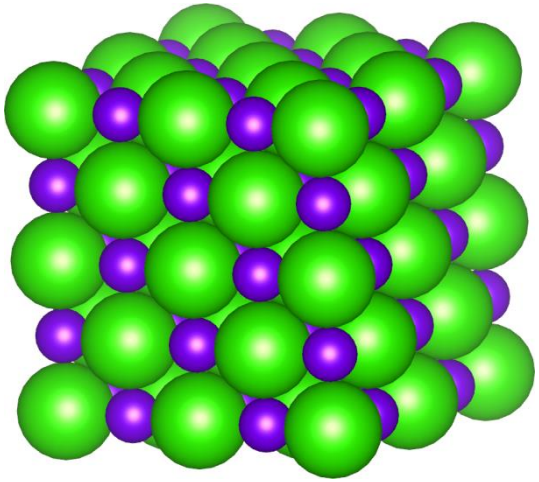


Figure: AJK

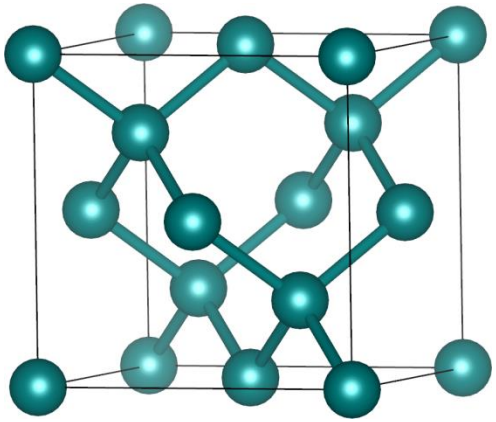
Photo: Virve Karttunen, 2009

Silicon single crystal grown by ***Czochralski process*** (*Deutsches Museum, München*)

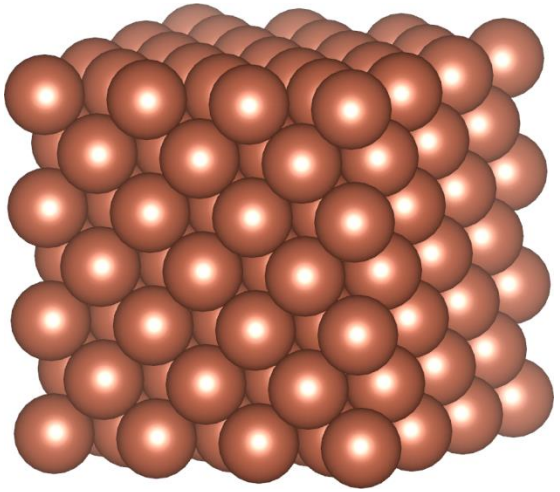
Non-molecular crystalline solids



Ionic bonding
(*e.g.* NaCl)



Covalent bonding
(*e.g.* silicon)



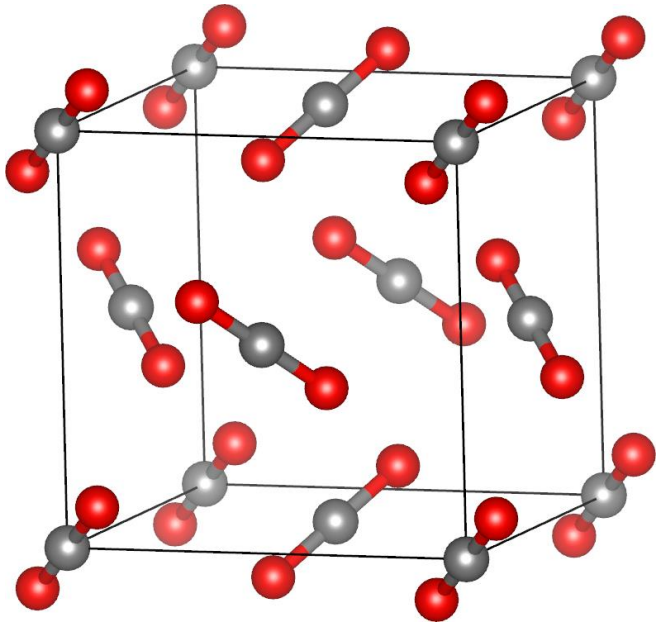
Figures: AJK

Metallic bonding
(*e.g.* copper)

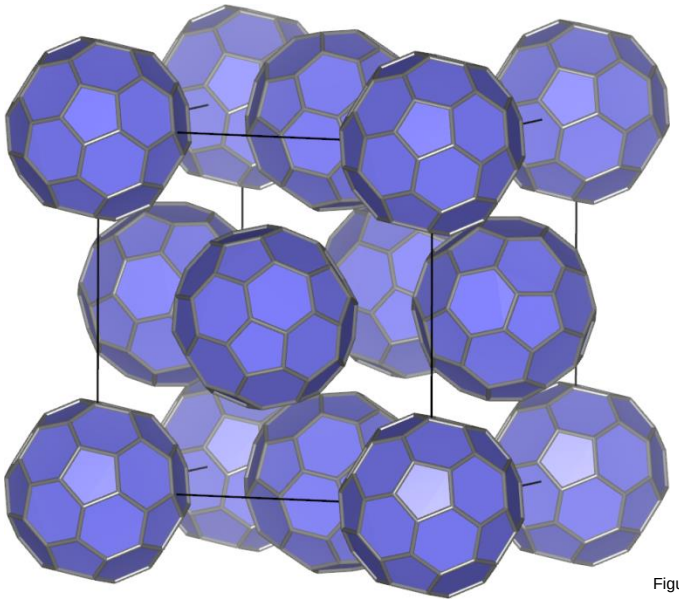
- Coordination polymers such as ***metal-organic frameworks*** show covalent bonding of metal atoms and organic molecules
- They are challenging the traditional classifications of solid state structures (see *e.g.* review of H. Furukawa *et al.*, *Science* **2013**, *341*, 1230444).

Molecular crystalline solids

- Composed of molecules that are held together by (weak) van der Waals forces
- Discussed only little here, but can be interesting for intercalation chemistry
- Much more relevant for small-molecule chemistry
- ***Crystal engineering*** using *e.g.* ***hydrogen*** and ***halogen*** bonding is making the boundary between molecular and non-molecular solids less clear!



Solid CO_2 (space group *Pa*-3, #205)
Acta Cryst. B **1980**, *36*, 2750.

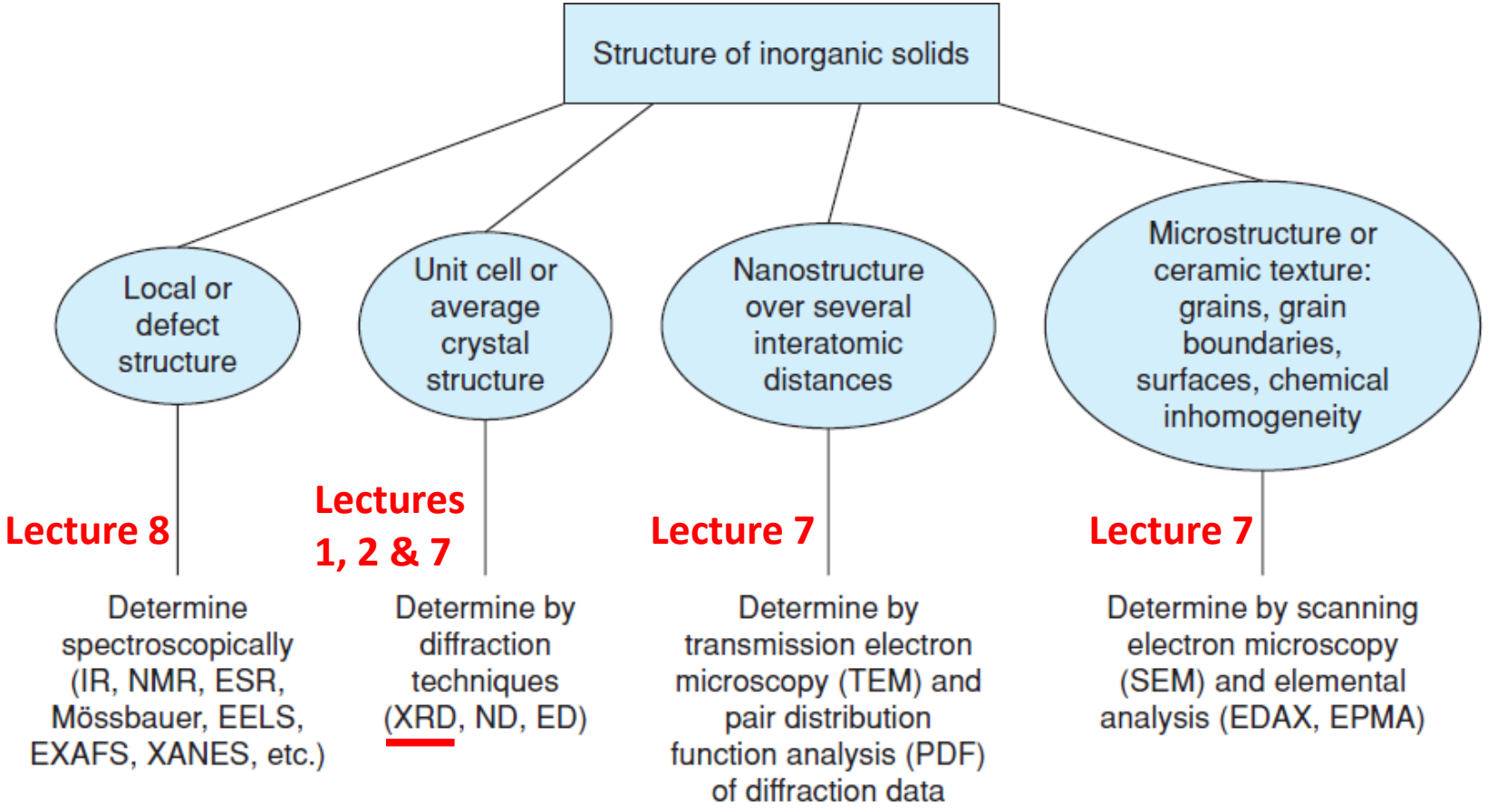


Figures: AJK

Solid C_{60} (space group *Pa*-3, #205)
Nature **1991**, *353*, 147.

Structure determination of crystalline materials

Structure determination



Ref: West p. 230

X-ray diffraction (1)

- X-rays are electromagnetic radiation of wavelength ~1 Å (10^{-10} m)
  - Matches the scale of atomic-level structure!

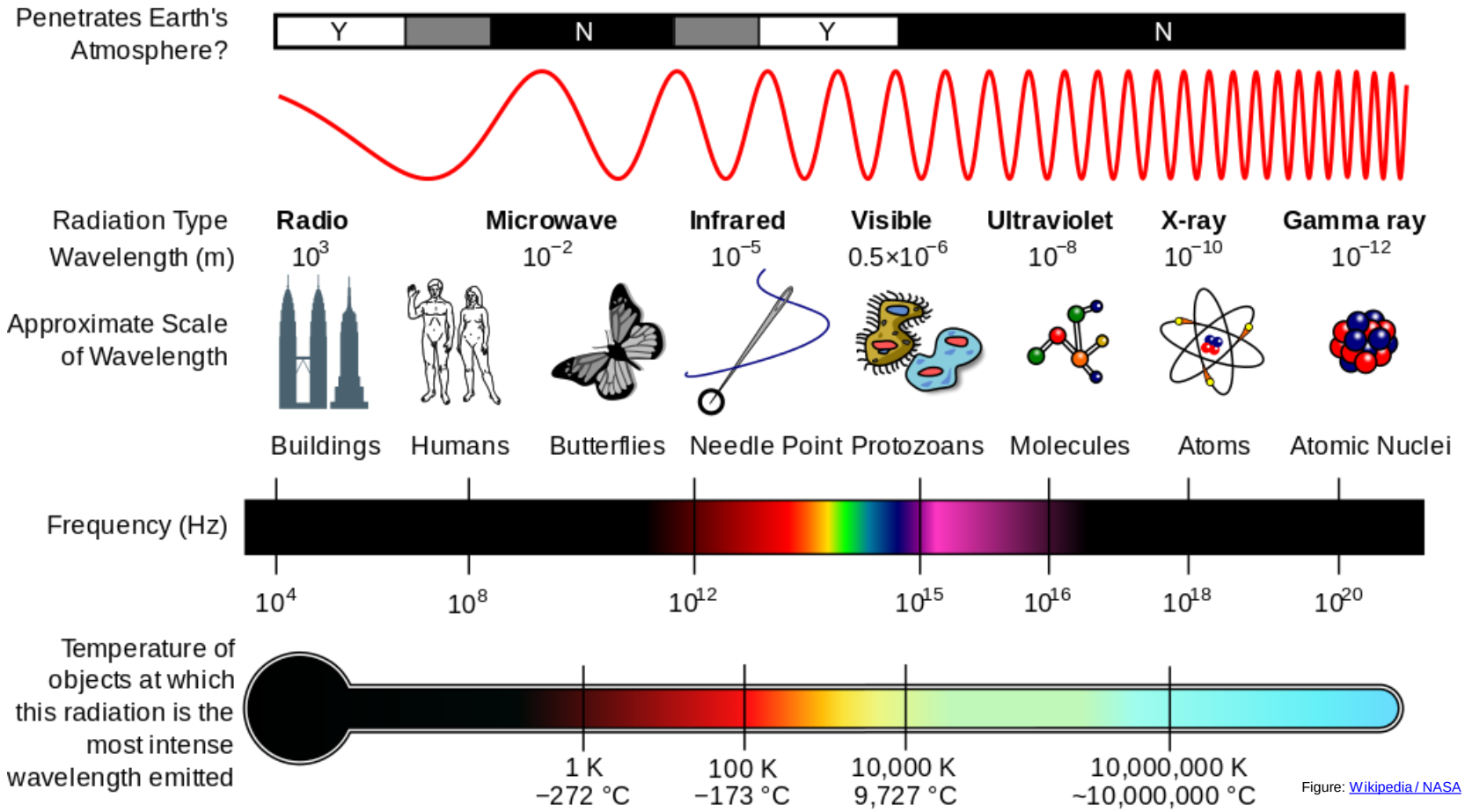


Figure: Wikipedia / NASA

X-ray diffraction (2)

- X-rays are produced when high-energy charged particles, *e.g.* electrons accelerated through a voltage of 30 000 V, collide with matter
- For X-ray diffraction experiments, we use *monochromatic* X-rays

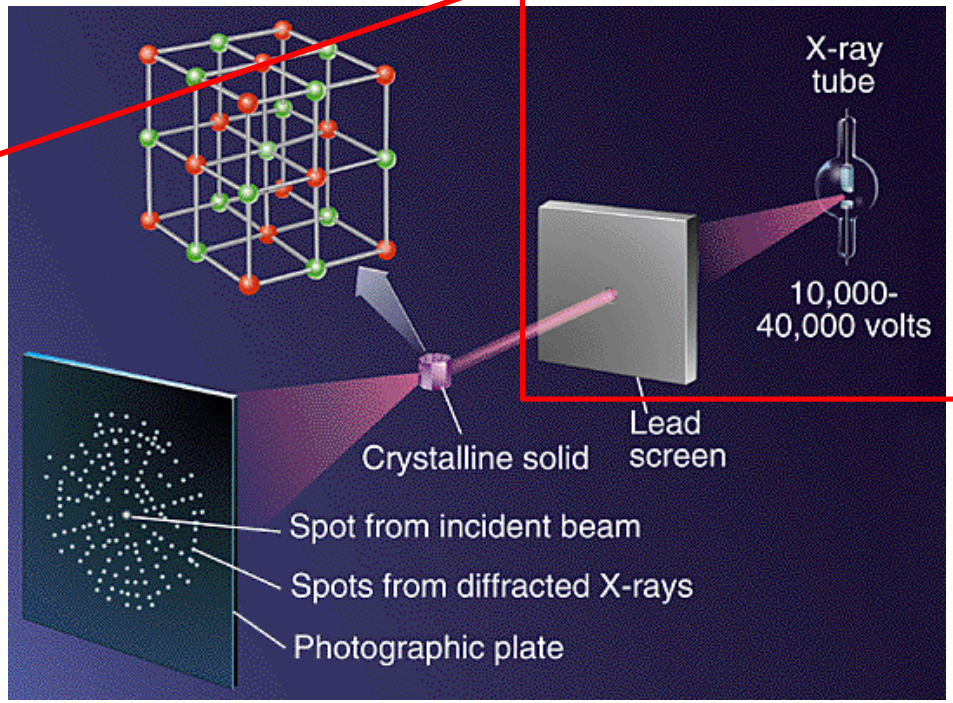


Figure: http://www.scienceiscool.org/solids/intro.html (dead link)

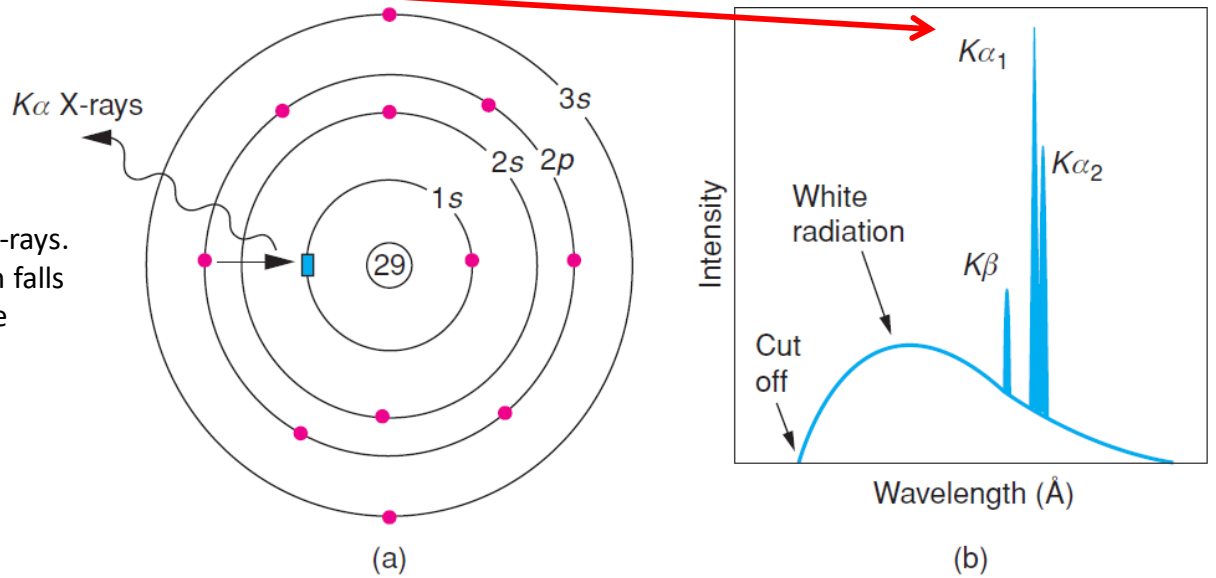


Figure 5.3. (a) Generation of Cu Kα X-rays. A 1s electron is ionised, a 2p electron falls into the empty 1s level (blue) and the excess energy is released as X-rays.

(b) X-ray emission spectrum of Cu

Ref: West p. 233

Bragg's law

- Consider crystals as built up from planes acting as semi-transparent mirrors
- ***Bragg's law***: $2d \sin\theta = n\lambda$, where n = positive integer and λ = wavelength
- When **BL** satisfied, the reflected beams are in-phase and ***interfere constructively***, giving rise to a ***diffraction pattern***, that can be used to solve the crystal structure
- For some simple crystal structures, the planes also correspond to layers of atoms, but this is not generally the case (they are a concept, not physical reality)!

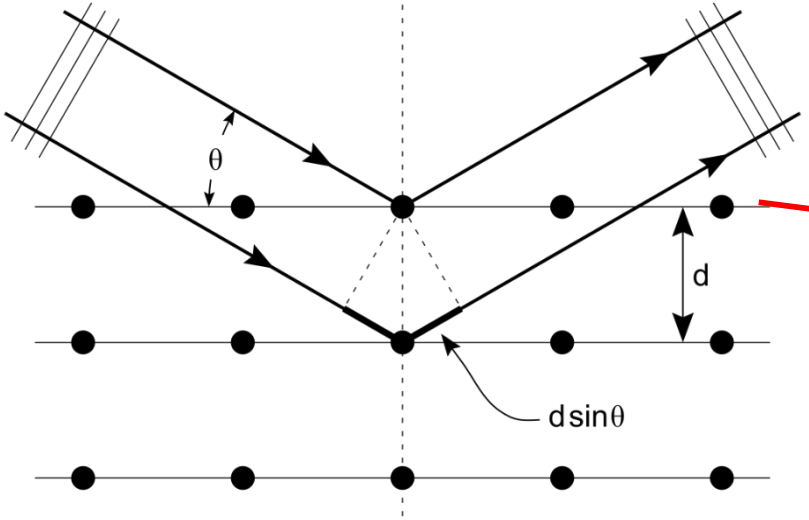


Figure: Wikipedia

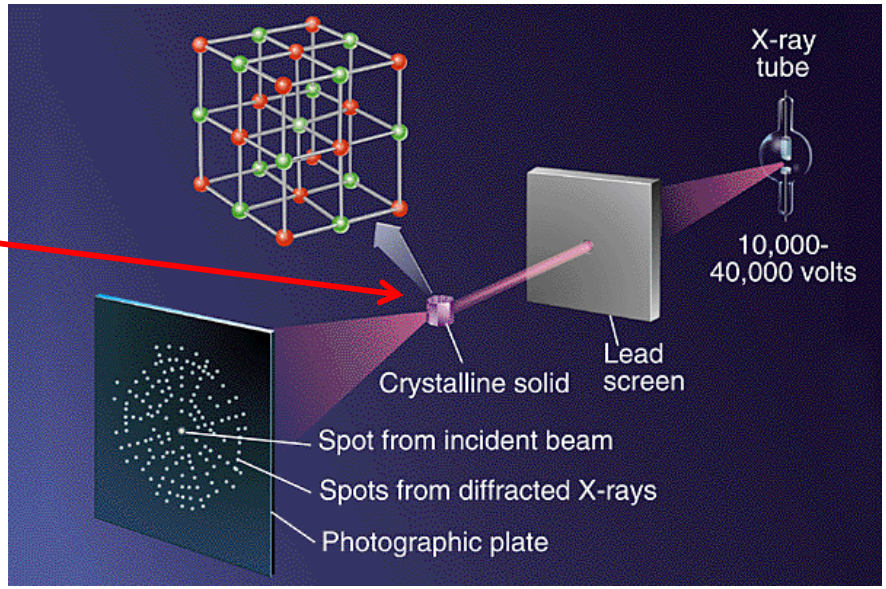
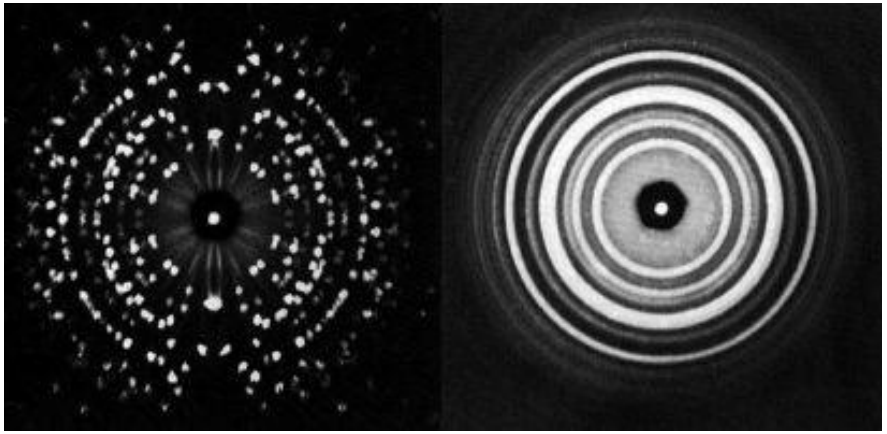


Figure: http://www.scienceiscool.org/solids/intro.html (dead link)

Single crystal vs. powder X-ray

- X-ray diffraction pattern of aluminum single crystal (left) and aluminum powder (right)
- Polycrystalline powder sample has random orientation of crystallites
- 1D summation of 3D diffraction process!
- The crystal structure might be deduced from a powder pattern with ***Rietveld*** refinement (typically requires a good model structure)
- X-ray diffraction powder pattern of crystalline (top) and amorphous (bottom) material

Figure: Susan Lehman / physics.wooster.edu



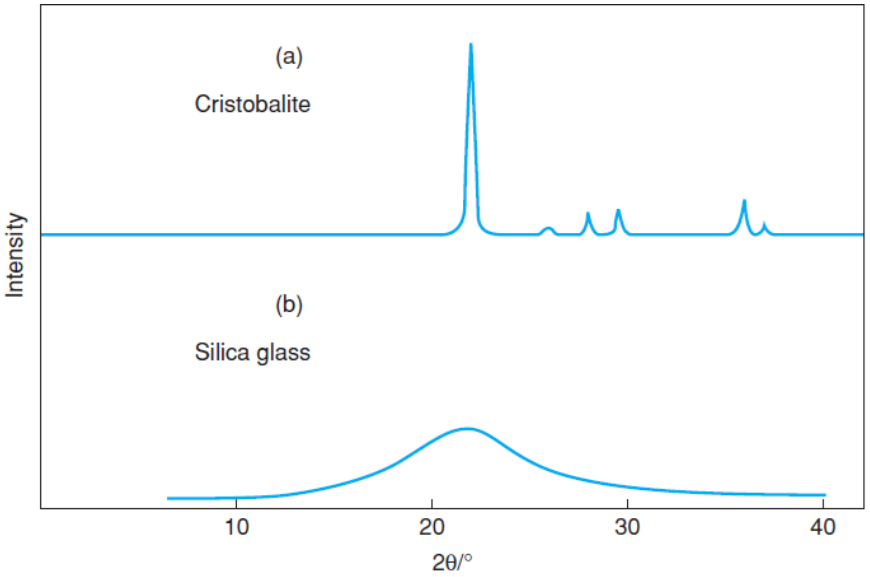


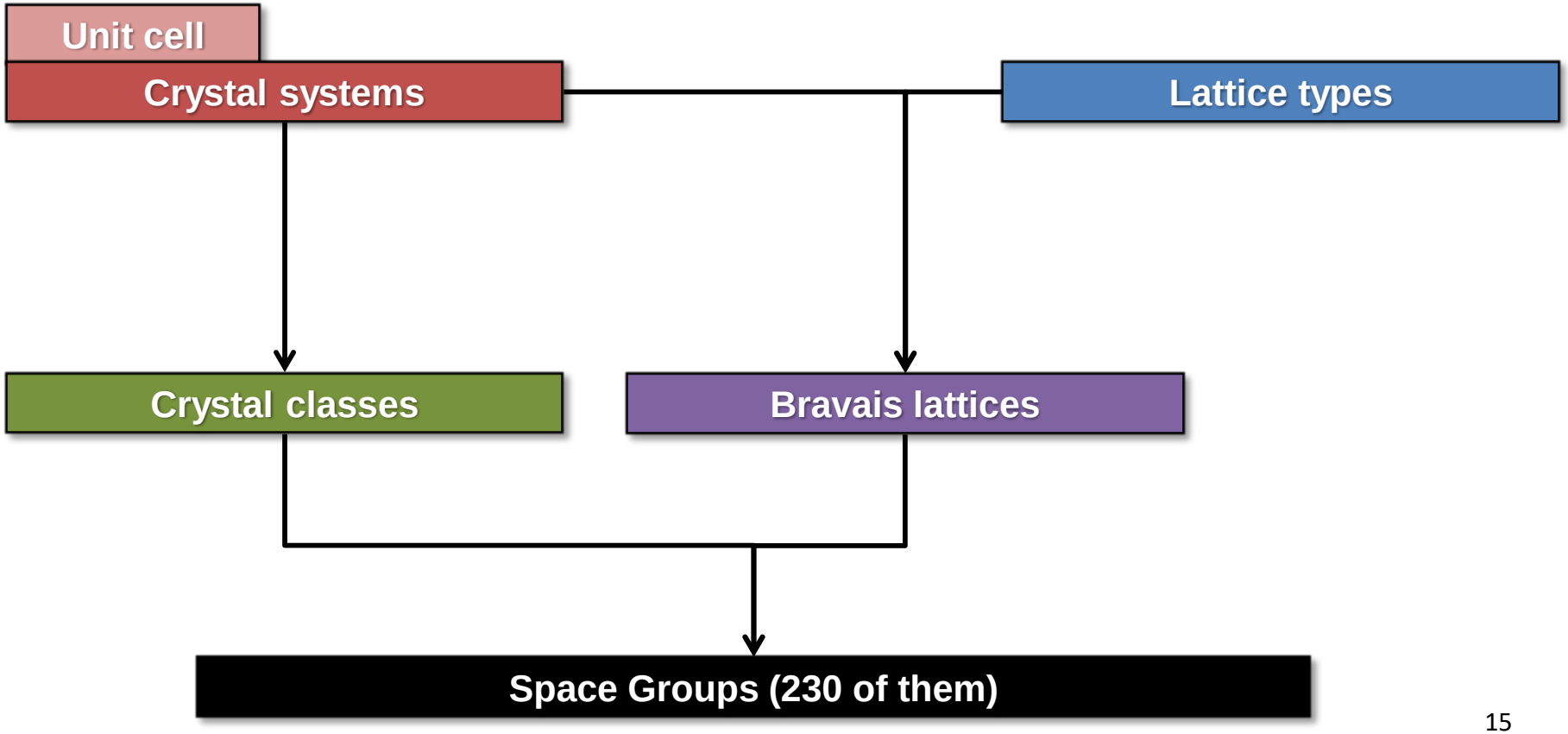
Figure 5.15 *X-ray powder diffraction patterns of (a) cristobalite and (b) glassy SiO_2; Cu Kα radiation.*

Ref: West p. 245

Key concepts for crystal structures

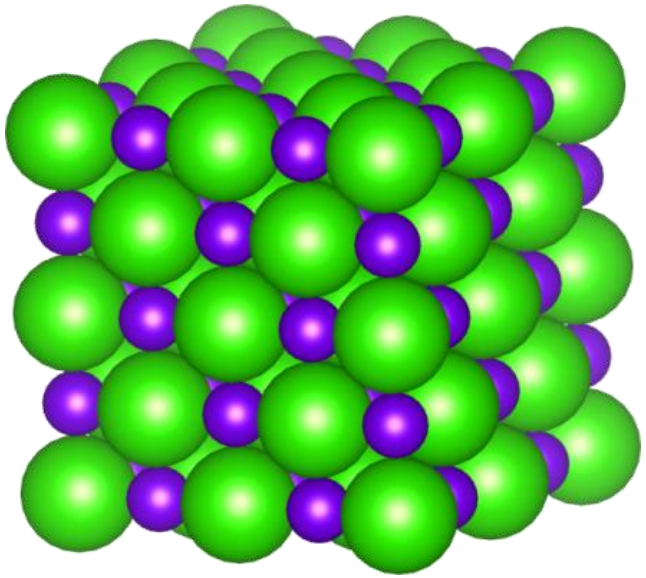
Key concepts for crystal structures

- To describe crystal structures, we will need the key concepts outlined below
- The following slides will introduce the concepts one by one, culminating in the concept of a **space group**

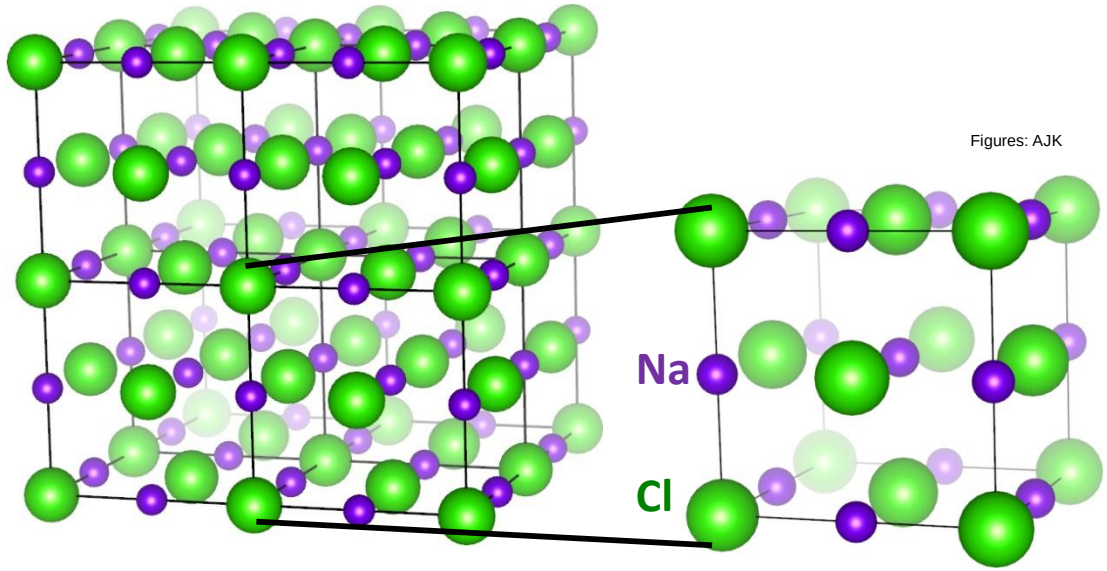


Unit cell

- ***Crystal***: Regular arrangement of atoms in three dimensions
- The regular arrangement can be represented by a repeat unit called the ***unit cell***
- ***Unit cell***: The smallest repeating unit which shows the ***full symmetry*** of the crystal



NaCl crystal: Regular arrangement of Na and Cl (space-filling representation)



NaCl crystal (non-space-filling representation

NaCl unit cell

Crystal systems

Figure 1.3 *(a) The seven crystal systems and their unit cell shapes;* **a, b, c, α, β, γ = Lattice parameters**

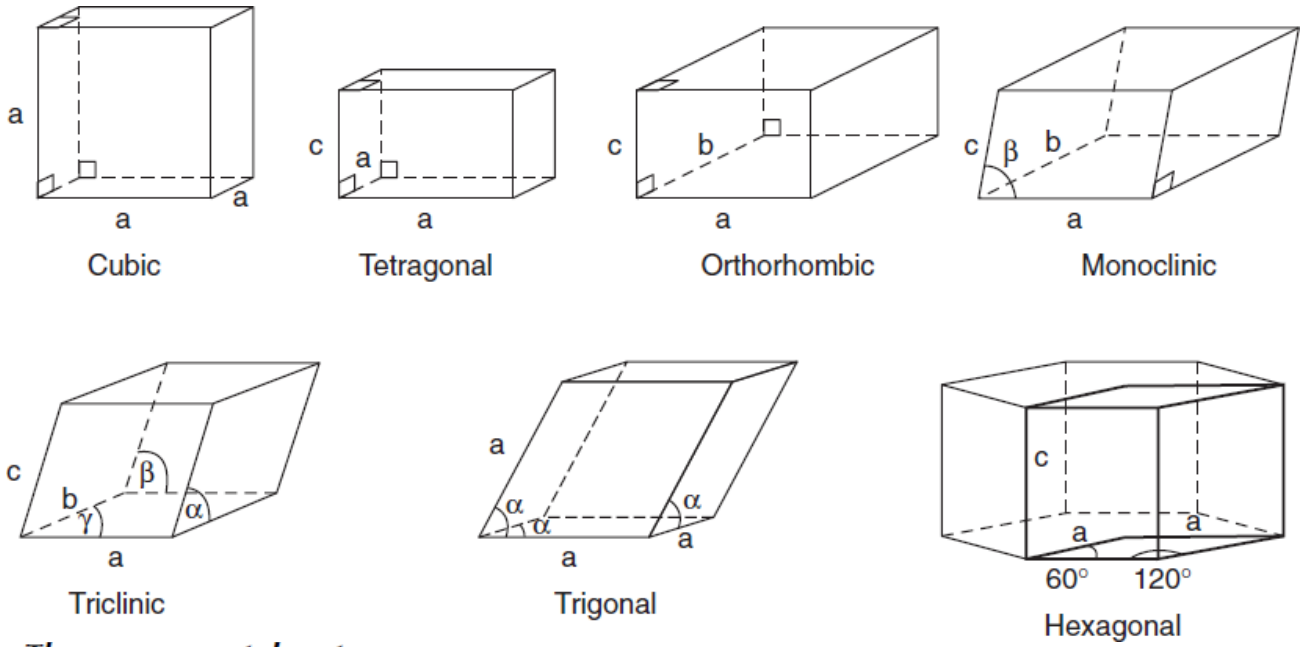


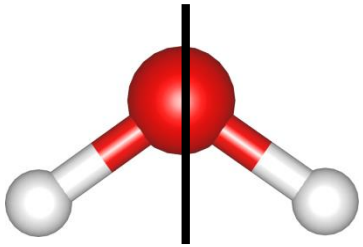
Table 1.1 ***The seven crystal systems***

Crystal system	Unit cell shape[b]	Essential symmetry	Allowed lattices
Cubic	$a = b = c, \alpha = \beta = \gamma = 90°$	Four threefold axes	P, F, I
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90°$	One fourfold axis	P, I
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90°$	Three twofold axes or mirror planes	P, F, I, A (B or C)
Hexagonal	$a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$	One sixfold axis	P
Trigonal (a)	$a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$	One threefold axis	P
Trigonal (b)	$a = b = c, \alpha = \beta = \gamma \neq 90°$	One threefold axis	R
Monoclinic[a]	$a \neq b \neq c, \alpha = \gamma = 90°, \beta \neq 90°$	One twofold axis or mirror plane	P, C
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90°$	None	P

Ref: West p. 3-4

Symmetry

- The most characteristic feature of any crystal structure is its ***symmetry***
- The shape of the unit cell is not enough to determine the crystal system. It is the symmetry of the unit cell that really determines the crystal system
  - For example, a ”pseudocubic” crystal structure could have $a = b = c$ and $\alpha = \beta = \gamma = 90°$, but it would not possess the correct cubic symmetry
- In the context of crystals, we will encounter two types of symmetry:
  - **Point group symmetry** (both in crystals and molecules)
  - **Translational symmetry** of the crystal lattice (only in crystals)
- We describe the symmetry properties of crystals and molecules in terms of:
  - **Symmetry elements** (for example, a mirror plane)
  - **Symmetry operations** (the actual process of applying a symmetry element)
- In crystals and molecules, a symmetry operation transfers an atom into a new spatial position that cannot be distinguished from its original position



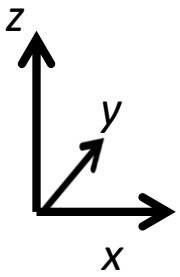
Mirror plane in a water molecule

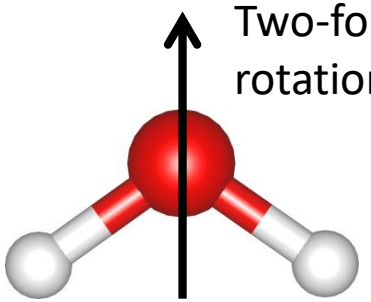
Figure: AJK

Point group symmetry

- In point group symmetry operations, at least one point stays unchanged during the symmetry operation
- For learning point group symmetry, we will utilize the Symmetry@Otterbein website: https://symotter.org/
- The **point group** of a molecule is based on the present symmetry elements

Synmmetry element	Symmetry operation	Schönflies symbol
Symmetry plane (mirror plane)	Reflection through plane	σ
Inversion	Every point *x,y,z* translated to *-x,-y,-z*	*i*
Proper axis (rotation)	Rotation about axis by 360/*n* degrees	C_n
Improper axis (improper rotation)	Rotation by 360/*n* degrees followed by reflection through plane perpendicular to rotation axis	S_n

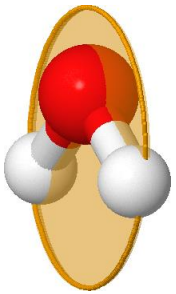




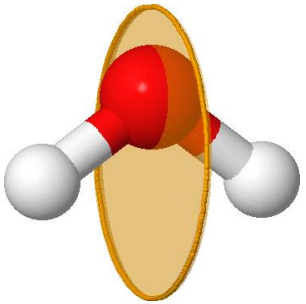
Two-fold proper rotation axis C_2

H_2O (point group C_{2v})

Mirror plane σ_{yz}



Mirror plane σ_{xz}



Figures: AJK

Symmetry elements in crystals

- Crystals may display rotational symmetries 2, 3, 4, and 6, not others
- In crystallography, the symmetries are labeled with ***Hermann–Mauguin*** symbols
- Crystals show several symmetry elements that are not present in molecules

Symmetry element	Hermann-Mauguin symbol (crystals)	Schönflies symbol (molecules)
Symmetry plane (mirror plane)	m	σ
Inversion	$\overline{1}$	i
Proper axis (rotation)	n = 2, 3, 4, 6	C_n
Improper axis (improper rotation)	–	S_n
Elements only in crystals		
Inversion axis (point symmetry)	$\overline{n}$ = $\overline{3}$, $\overline{4}$, $\overline{6}$	–
Glide plane (includes translation)	a, b, c, d, n	–
Screw axis (includes translation)	2_1, 3_1, etc.	–

Crystal symmetry: Inversion axis

- Denoted by $\bar{n}$. Rotation of 360° / *n* followed by inversion.
- $\bar{1}$ = equal to inversion center
- $\bar{2}$ = equal to mirror plane (*m*)
- $\bar{3}$, $\bar{4}$, $\bar{6}$ are actual inversion axes
- For example, $\bar{3}$ inversion axis (equal to S_6 improper rotation):

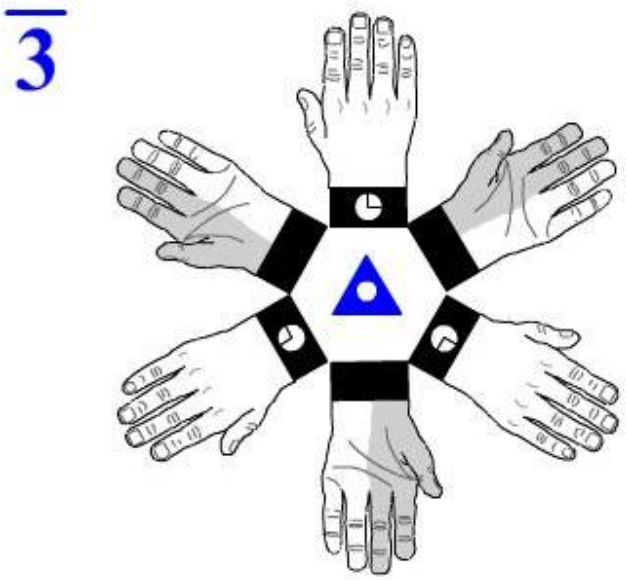


Figure: Margaret E. Kastner,
http://www.crystallographiccourseware.com/

Crystal symmetry: Glide plane

- Reflection followed by a translation
  - Simple glide planes are denoted as *a*, *b*, *c* (axis of the glide)
  - *n* glide: reflection followed by translation of 1/2 along ***two*** cell edges
  - *d* glide (diamond glide): reflection followed by translation of 1/4 along ***two*** cell edges

Glide plane (parallel to *a*, reflection followed by a translation of ½*a*)

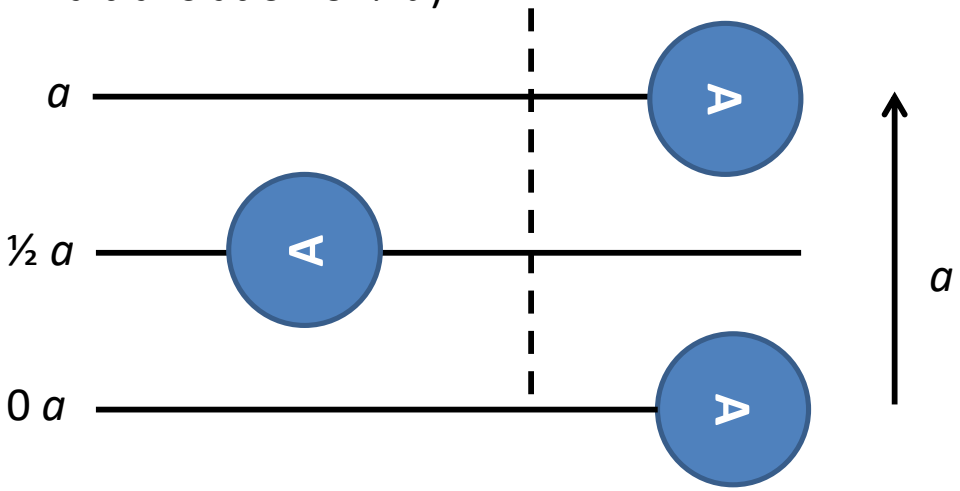
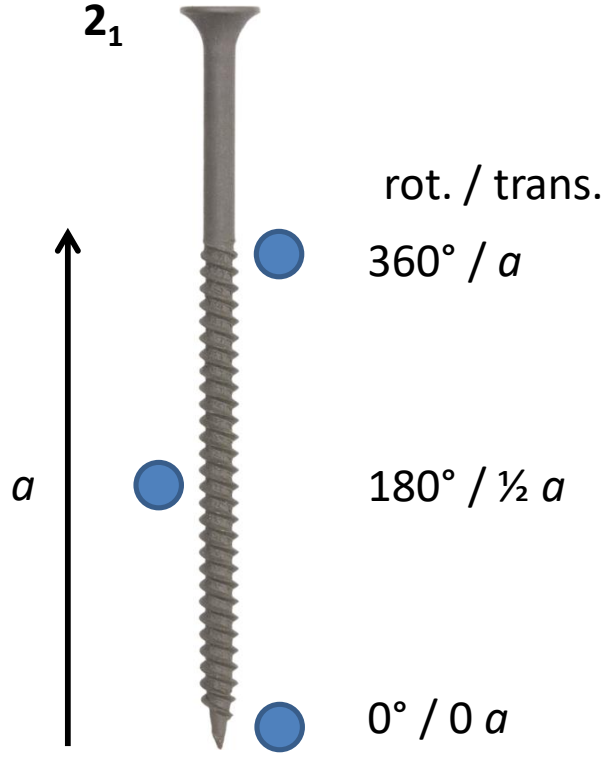


Figure: AJK

Crystal symmetry: Screw axis

- Combination of rotation and translation, denoted as x_y:
  - Rotation of 360° / *x*; translation of *y* / *x* units along the screw axis
  - 2_1 screw axis: rotation of 360° / 2 = 180°; translation of 1/2 units
  - 4_2 screw axis: rotation of 360° / 4 = 90°; translation of 2/4 = 1/2 units



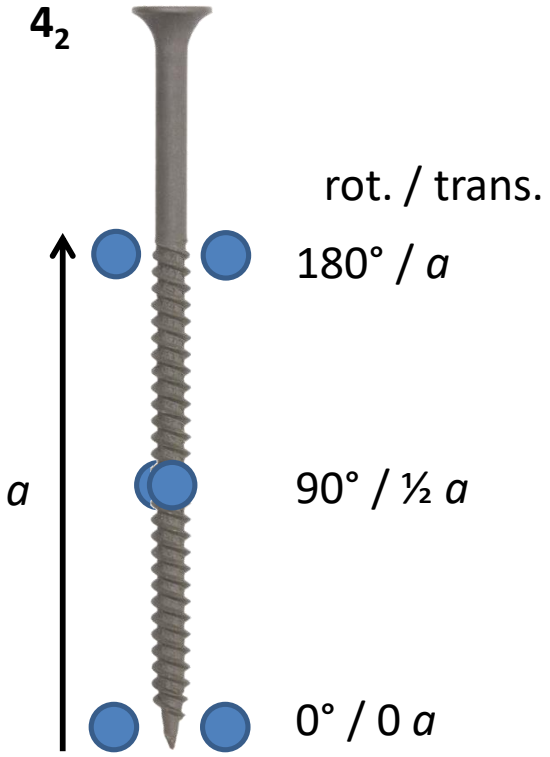


Figure: AJK. Inpisred by: Margaret E. Kastner, http://www.crystallographiccourseware.com/

Screw: pngimg.com (CC-BY-NC 4.0)

Crystal classes

- By combining the seven crystal systems and 32 crystallographic point groups, we obtain the following 32 **crystal classes**:

Crystal system	Crystal classes (point groups) in Hermann-Mauguin notation	Crystal classes (point groups) in Schönflies notation
Triclinic	$1, \overline{1}$	C_1, C_i
Monoclinic	$2, m, 2/m$	C_2, C_s, C_{2h}
Orthorhombic	$222, mm2, mmm$	D_2, C_{2v}, D_{2h}
Tetragonal	$4, \overline{4}, 4/m, 422, 4mm, \overline{4}2m, 4/mmm$	$C_4, S_4, C_{4h}, D_4, C_{4v}, D_{2d}, D_{4h}$
Trigonal	$3, \overline{3}, 32, 3m, \overline{3}m$	$C_3, S_6\ (C_{3i}), D_3, C_{3v}, D_{3d}$
Hexagonal	$6, \overline{6}, 6/m, 622, 6mm, \overline{6}m2, 6/mmm$	$C_6, C_{3h}, C_{6h}, D_6, C_{6v}, D_{3h}, D_{6h}$
Cubic	$23, \overline{4}3m, m\overline{3}, 432, m\overline{3}m$	T, T_d, T_h, O, O_h

Ref: Müller p. 24, Wikipedia

Lattice

- The most characteristic feature of any crystal structure is its ***symmetry***
  1. Point group symmetry (discussed above)
  2. ***Translational symmetry*** of the ***crystal lattice***
- Crystal structure = ***basis*** (atoms) + crystal lattice

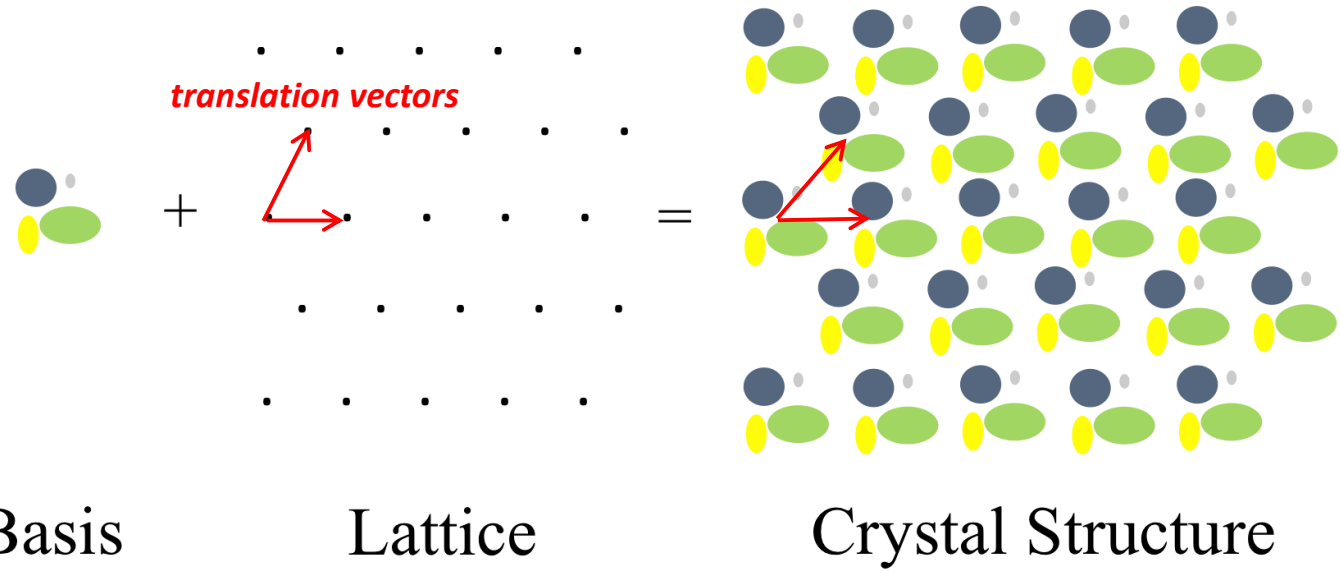
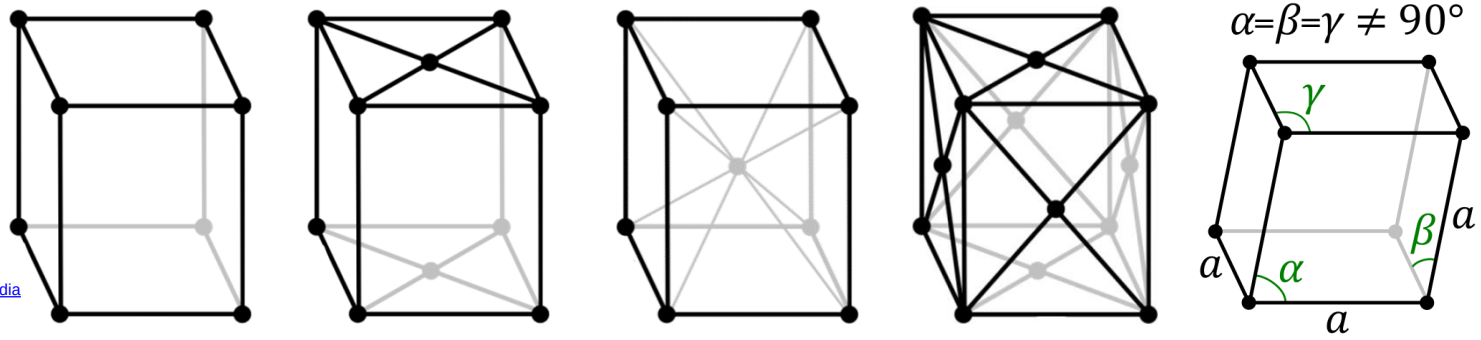


Figure: Andreas Mulyo

Lattice types

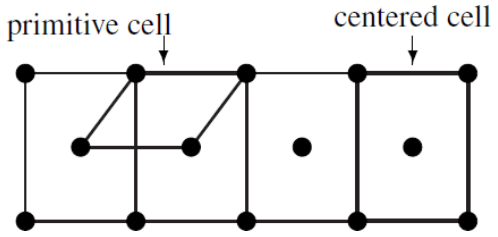
- Every crystal structure belongs to one of five ***lattice types***:
  - The balls are lattice points, ***not*** atoms!



Figures: Wikipedia

Lattice type	Primitive	Base-centered	Body-centered	Face-centered	Rhombohedral
Symbol	*P*	*A* / *B* / *C*	*I*	*F*	*R*
V(C-cell)/*V*(P-cell)	1	2	2	4	3

- ***Primitive unit cell***: unit cell with the smallest possible volume
- ***Centered unit cell***: the smallest repeating unit which shows the full symmetry of the crystal
- The centered unit cell is 2, 3, or 4 times larger than the primitive cell (table: *V(C-cell)/V(P-cell)*)



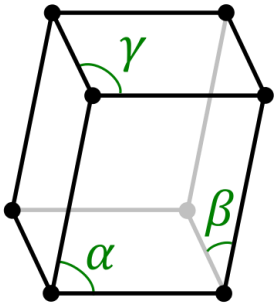
Ref: Müller p. 8

Bravais lattices (1)

- By combining 7 crystal systems and 5 lattice types we obtain 14 ***Bravais lattices***

Triclinic

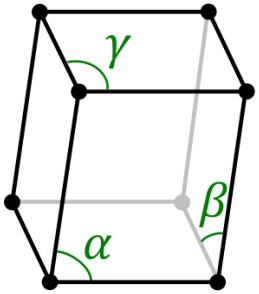
$\alpha, \beta, \gamma \neq 90°$



P

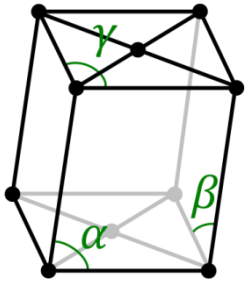
Monoclinic

$\beta \neq 90°$
$\alpha, \gamma = 90°$



P

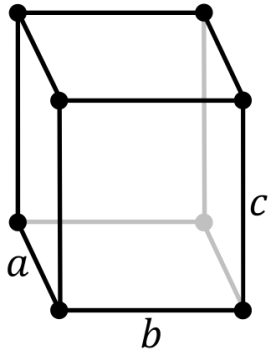
$\beta \neq 90°$
$\alpha, \gamma = 90°$



C

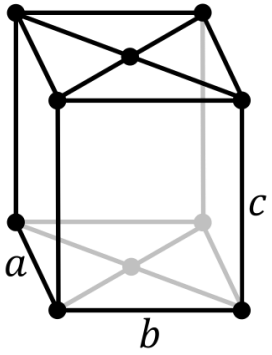
Orthorhombic

$a \neq b \neq c$



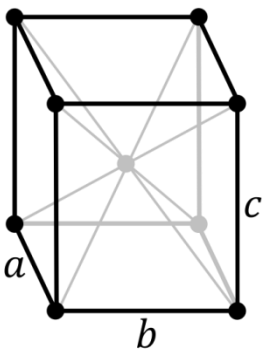
P

$a \neq b \neq c$



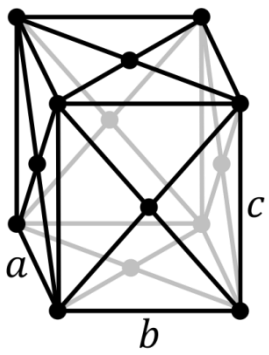
C

$a \neq b \neq c$



I

$a \neq b \neq c$

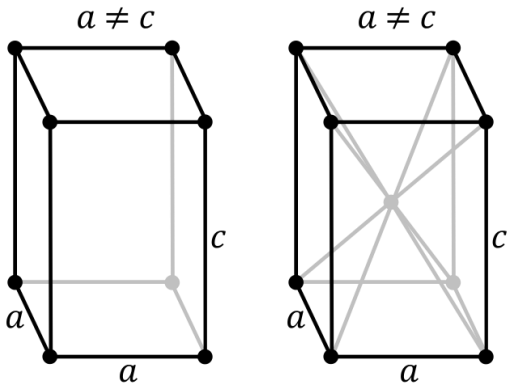


F

Figures: Wikipedia

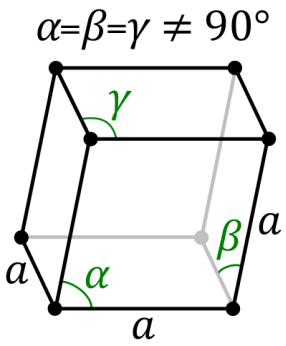
Bravais lattices (2)

Tetragonal



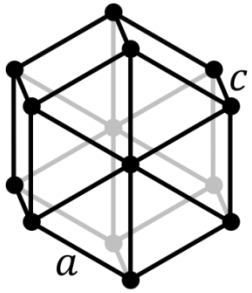
P ***I***

Rhombohedral



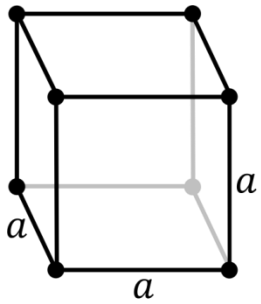
R

Hexagonal

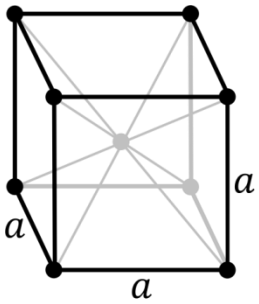


P

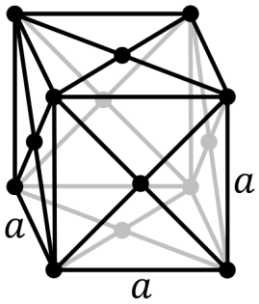
Cubic



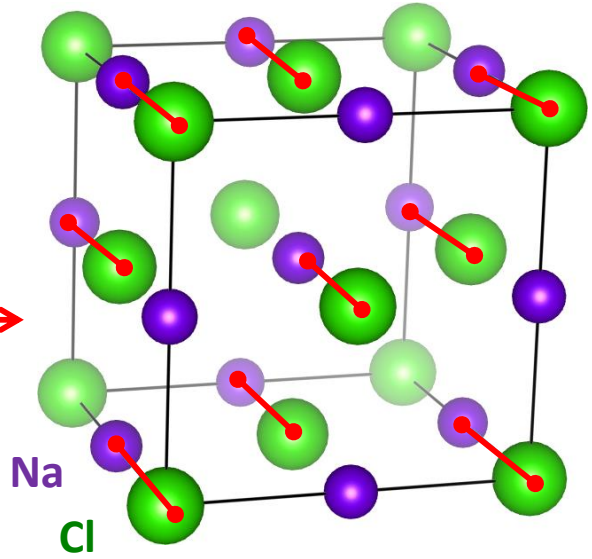
P



I (bcc)



F (fcc)

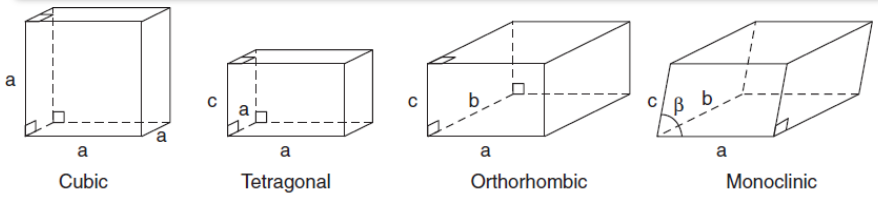


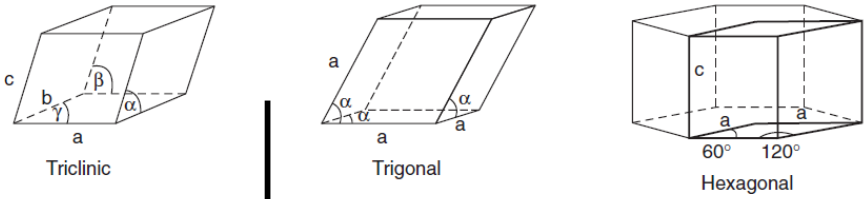
fcc, basis: Cl + Na

Figures: Wikipedia

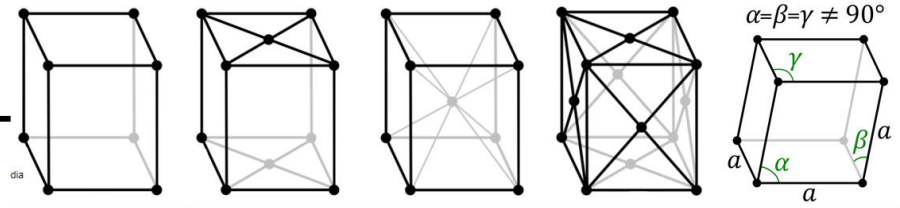
Figure: AJK

Crystal systems (7 of them)





Lattice types (5 of them)

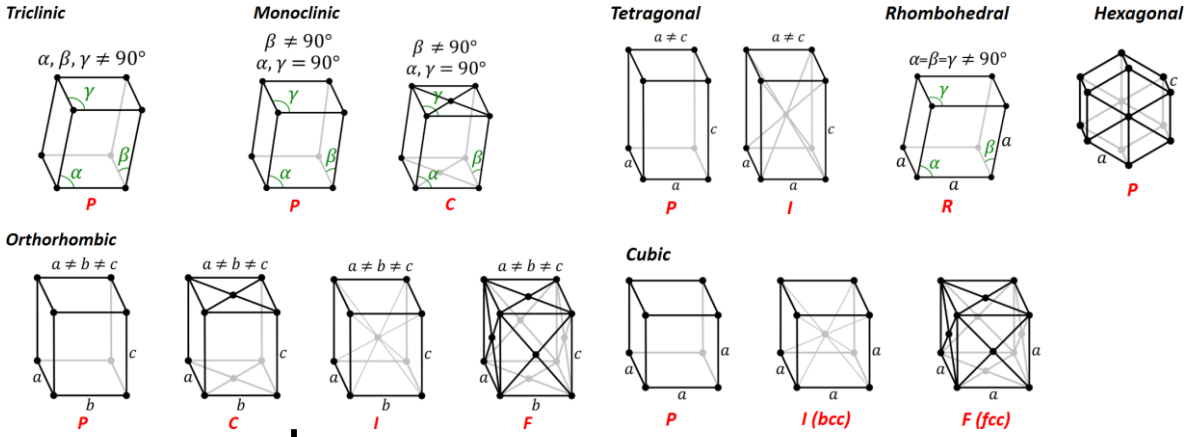


	Primitive	Base-centered	Body-centered	Face-centered	Rhombohedral

Crystal classes (32 of them)

Crystal system	Crystal classes (point groups) in Hermann-Mauguin notation
Triclinic	1, $\bar{1}$
Monoclinic	2, *m*, 2/*m*
Orthorhombic	222, *mm*2, *mmm*
Tetragonal	4, $\bar{4}$, 4/*m*, 422, 4*mm*, $\bar{4}$2*m*, 4/*mmm*
Trigonal	3, $\bar{3}$, 32, 3*m*, $\bar{3}m$
Hexagonal	6, $\bar{6}$, 6/*m*, 622, 6*mm*, $\bar{6}$*m*2, 6/*mmm*
Cubic	23, $\bar{4}3m$, $m\bar{3}$, 432, $m\bar{3}m$

Bravais lattices (14 of them)



Space Groups (230 of them)

Summary: AJK. Individual figures from Wikipedia and West (p 3.)

Space groups

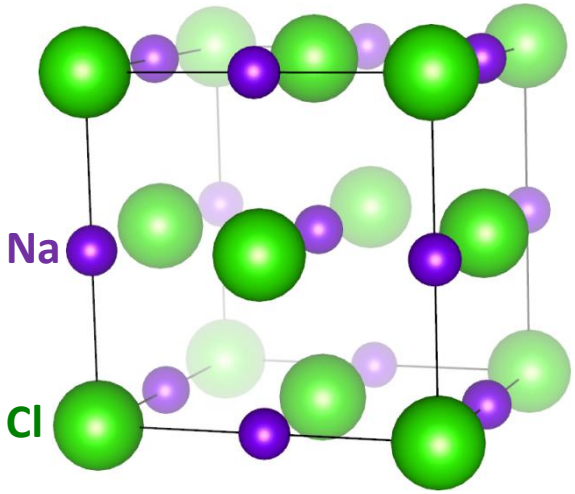
- The **32** crystal classes and **14** Bravais lattices give rise to **230** space groups
- The Hermann-Mauguin symbol for the space group of NaCl: ***Fm$\bar{3}$m*** (or ***Fm-3m***)
- The symbol begins with a capital letter *P, A, B, C, F, I* or *R,* specifying the presence of ***translational symmetry*** in three dimensions and the lattice type (***centering***)
- The letter is followed by a listing of the other symmetry elements
- Some examples:
  - All ***triclinic*** space groups: *P*1 and *P*-1
  - Some ***monoclinic*** space groups: *P*2, *Pm*, *C*2/*c*
  - Some ***hexagonal*** space groups: *P*6, *P*6/*mmm*, *P*6/*mcc*
  - Some ***cubic*** space groups: *Pm*-3*m*, *Im*-3*m*
- Note that some space groups can be defined with ***alternate axes*** and/or ***origin*** (see e.g. orthorhombic SGs in http://img.chem.ucl.ac.uk/sgp/large/ortho.htm)
- Everything about space groups: International Tables of Crystallography
- Good resource: http://img.chem.ucl.ac.uk/sgp/large/sgp.htm
- Wikipedia: https://en.wikipedia.org/wiki/List_of_space_groups

Defining a crystal structure

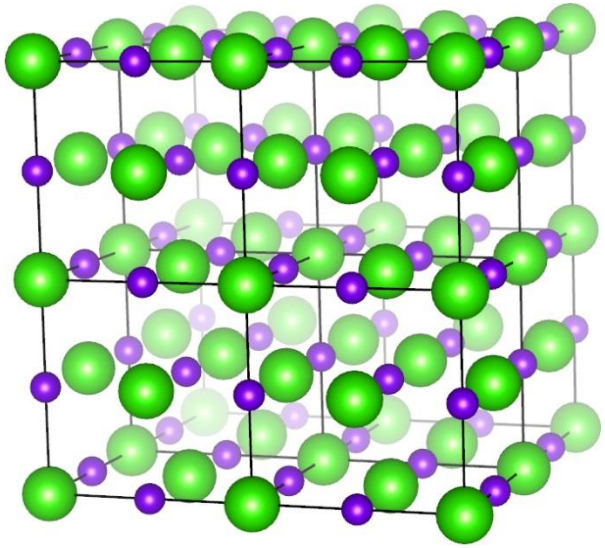
- A crystal structure is defined by
  - Space group
  - Lattice parameters
  - Atomic coordinates (positions) in fractional coordinates ($0.0 \leq x,y,z < 1.0$)
  - Normally only ***symmetry-independent*** atoms in the ***asymmetric unit*** are listed
- For example, NaCl (ICSD code 655785)
  - ***Fm*-3*m***
  - $a = b = c =$ **5.6402** Å ($\alpha = \beta = \gamma =$ **90°** by definition for a cubic space group)
  - Atomic coordinates (x, y, z): **Cl**: 0.0, 0.0, 0.0; **Na**: 0.5, 0.5, 0.5
- Typically, crystal structures are distributed in Crystallographic Information Files (CIF)
- A ***definition*** of a crystal structure is not usually enough to understand the real chemistry. For this, we need a ***description*** of the crystal structure
  - Concepts such as bonding, packing of spheres, coordination, polyhedra, ...

Formula units (Z)

- Counting the contents of a unit cell for NaCl:
- 8 Cl^- ions in the 8 vertices, each belonging to 8 adjacent cells = 8/8 = **1** Cl^- ion in total
- 6 Cl^- ions in the 6 centers of the faces, each belonging to two cells = 6/2 = **3** Cl^- ions
- **1** Na^+ ion in the center of the cell, not shared with other cells
- 12 Na^+ ions in the centers of the 12 edges, each belonging to 4 cells = 12 / 4 = **3** Na^+ ions
- In total **4** Na^+ ions and **4** Cl^- ions
  - NaCl is said to have **4** ”formula units” per unit cell
  - Denoted with $Z = 4$



Figures: AJK

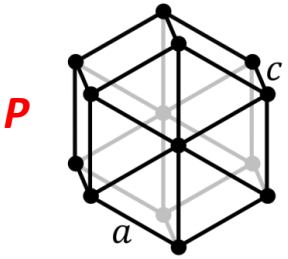


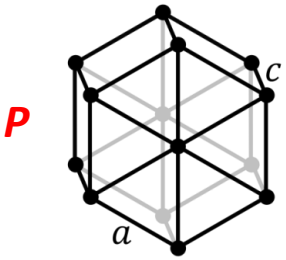
Extra slides

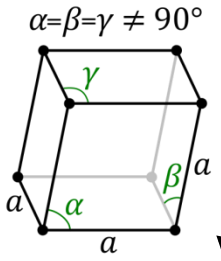
Trigonal crystal system

Hexagonal crystal family

- **Hexagonal crystal system (27 space groups)**
  - **Hexagonal Bravais lattice (27 space groups)**
- **Trigonal crystal system (25 space groups)**
  - **Hexagonal Bravais lattice (18 space groups)**
  - **Rhombohedral Bravais lattice (7 space groups)**





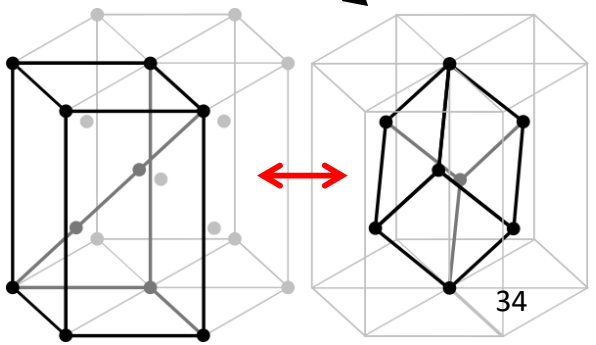


Can also be described with hexagonal unit cell (3 x larger)

Figures: Wikipedia

Table 1.1 ***The seven crystal systems***

Crystal system	Unit cell shape[b]	Essential symmetry	Allowed lattices
Cubic	$a = b = c, \alpha = \beta = \gamma = 90°$	Four threefold axes	P, F, I
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90°$	One fourfold axis	P, I
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90°$	Three twofold axes or mirror planes	P, F, I, A (B or C)
Hexagonal	$a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$	One sixfold axis	P
Trigonal (a)	$a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$	One threefold axis	P
Trigonal (b)	$a = b = c, \alpha = \beta = \gamma \neq 90°$	One threefold axis	R
Monoclinic[a]	$a \neq b \neq c, \alpha = \gamma = 90°, \beta \neq 90°$	One twofold axis or mirror plane	P, C
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90°$	None	P



Quasicrystals (1)

- Quasicrystals exhibit long-range order, but do not have translational periodicity
- Quasicrystals can show ”forbidden” rotational symmetries of 5, 8, 10, 12, etc.
- Discovered by Daniel Schechtman in 1982, Nobel prize 2011 (link)

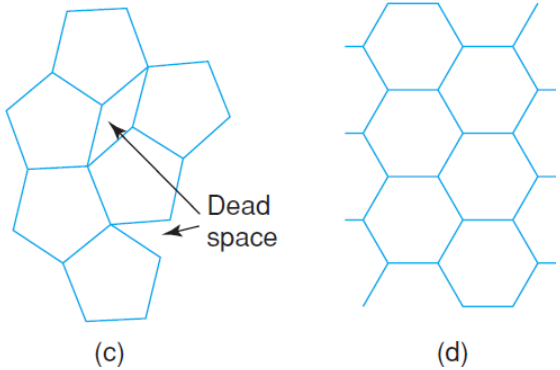


Figure 1.4. (c) the impossibility of forming a complete layer of pentagons; (d) a complete layer of hexagons

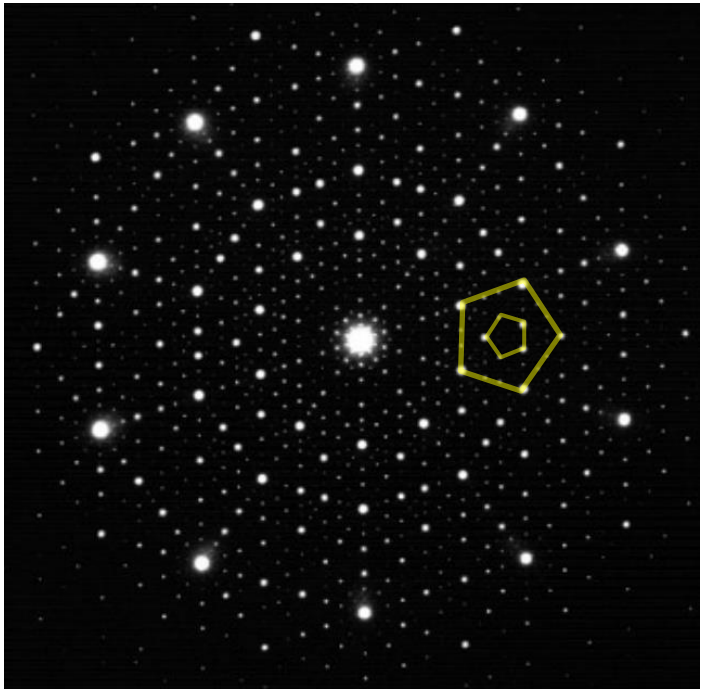


Figure: Nobel committee

Electron diffraction pattern from an icosahedral quasicrystal

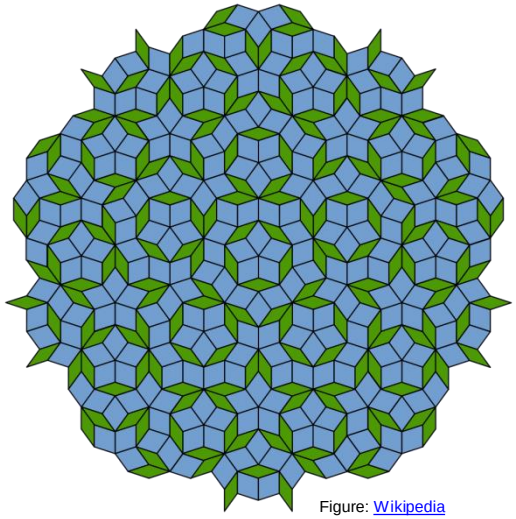


Figure: Wikipedia

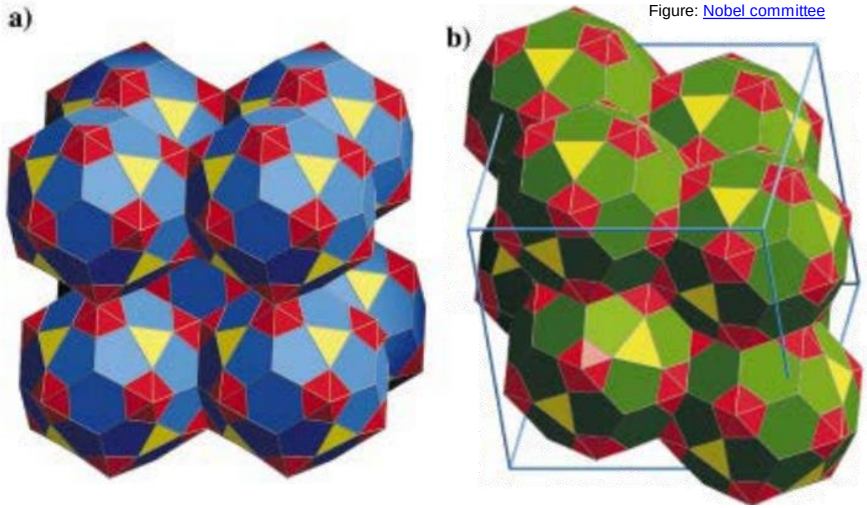
Penrose tiling (no translational periodicity)

Ref: West p. 5-6

Quasicrystals (2)

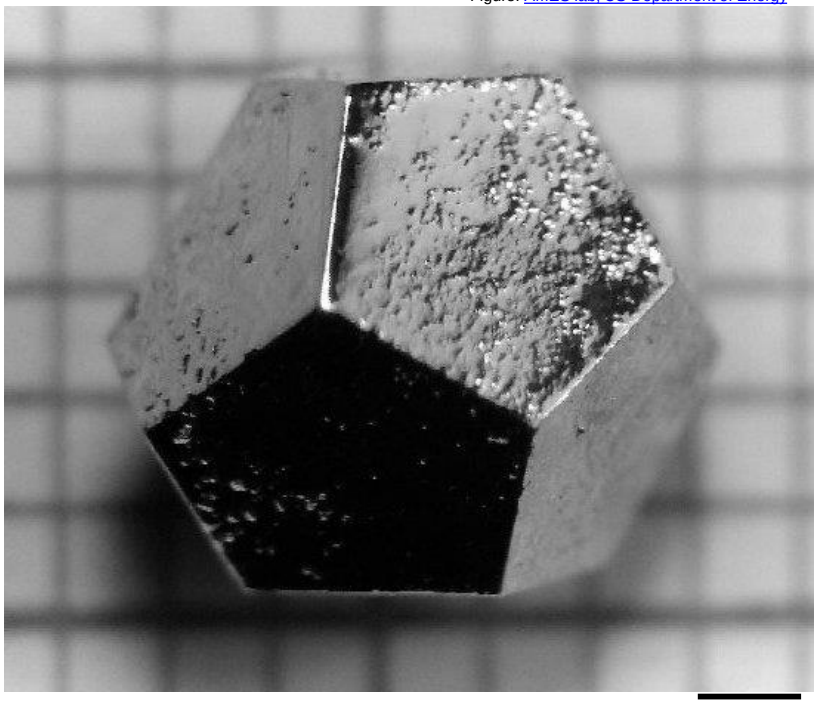
- Icosahedral symmetry is allowed together with translational symmetry in 6-dimensional space
- Refinement of quasicrystal models involves the refinement of the position and shape of the atomic surfaces in 6-dimensional space for icosahedral quasicrystals

Figure: Nobel committee



Polyhedral arrangements in icosahedral quasicrystal ***approximants*** in the system Ca-Cd (*Angew. Chem.* **2001**, *40*, 4037-4039)

Figure: AMES lab, US Department of Energy



Ho-Mg-Zn dodecahedral quasicrystal (*Phys. Rev. B* **1999**, *59*, 308–321)

Perfect crystals do not exist

- Crystal structures from X-ray diffraction are ”average” structures
- Real crystals possess defects (**lecture 13**)
- Point defects, line defects, grain boundaries, stacking faults, bulk defects, etc.
- Some defects can be characterized using techniques other than XRD (**lecture 8**)

Figure 2.2 ***2D representation of a Schottky defect with cation and anion vacancies.***

Ref: West p. 83