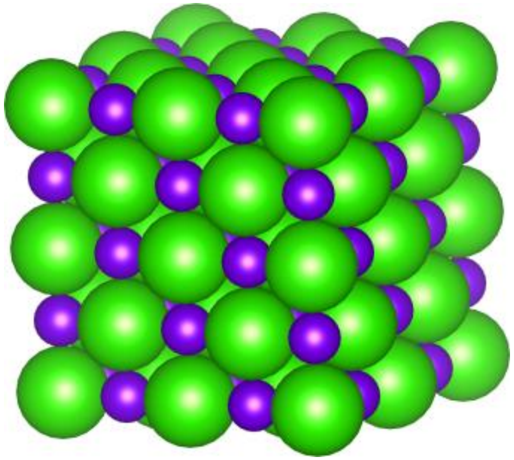
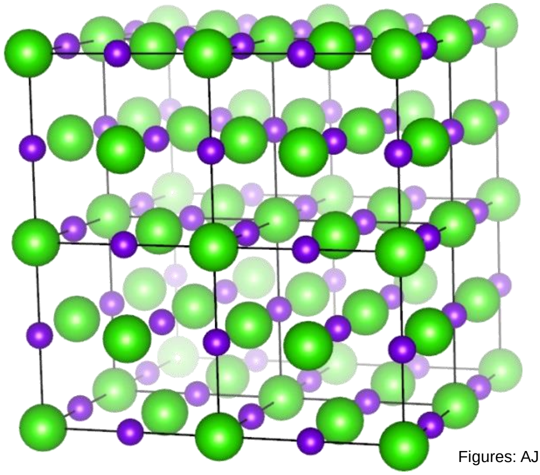
# Lecture 1:
# Structure of crystalline materials

- 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

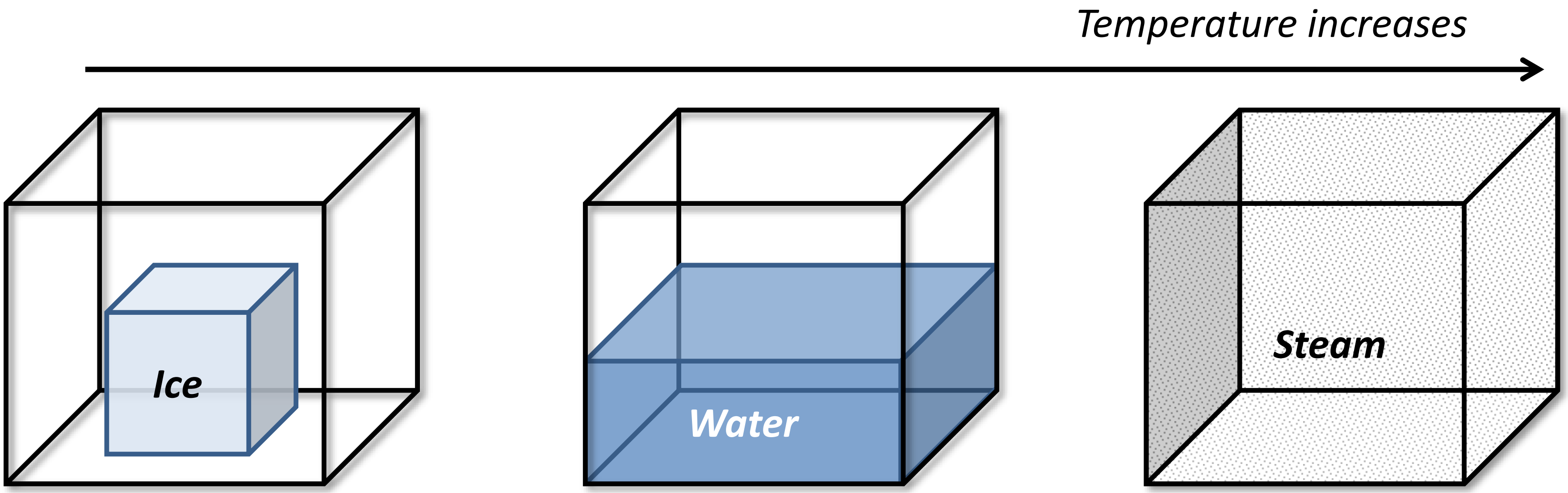




Figures: AJK

# Basics of crystalline materials

# States of bulk matter



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

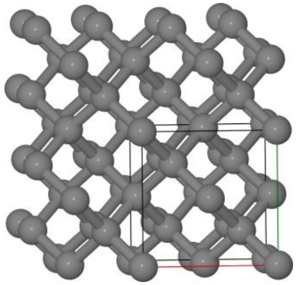
*Condensed matter*

*Fluids (flow in response to forces such as gravity)*

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

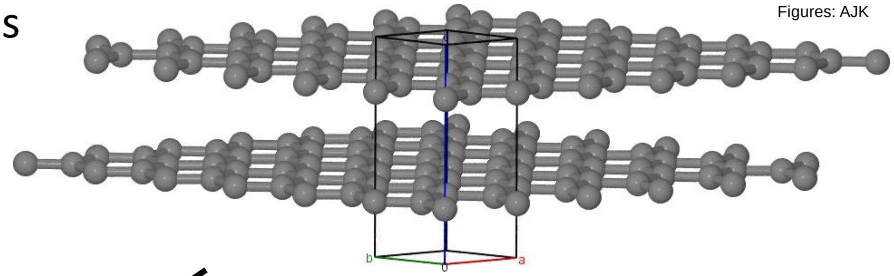
# Dimensionality of solids

Figures: AJK



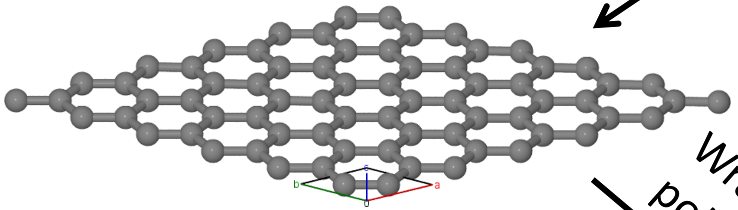
Diamond (3D)

Two 3D allotropes of carbon



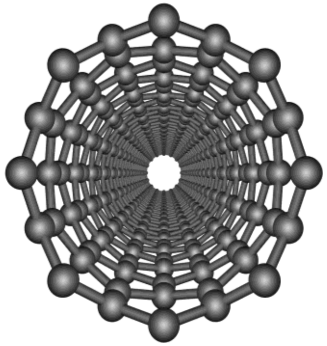
Graphite (3D)

Cut a slab



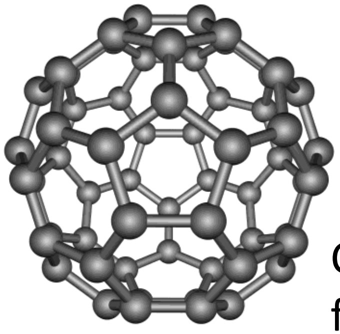
Graphene (2D)

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

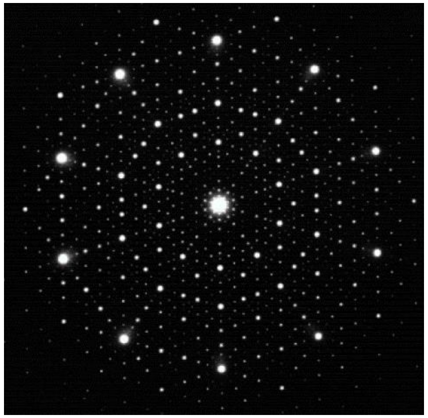
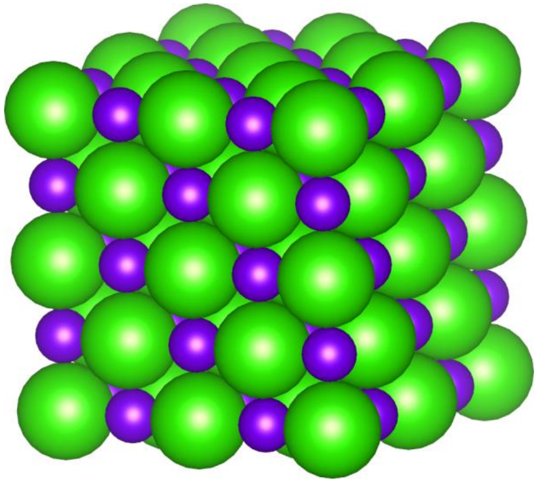


Figure: D. Shechtman/NIST

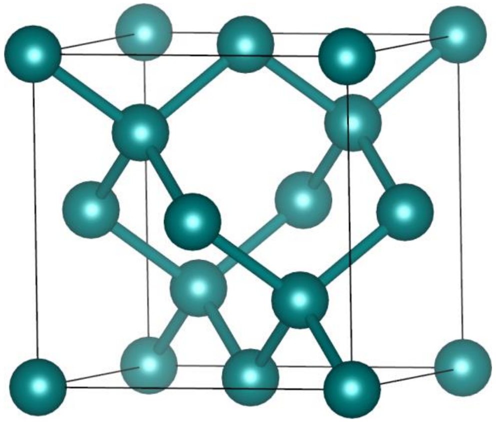
Photo: Virve Karttunen

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

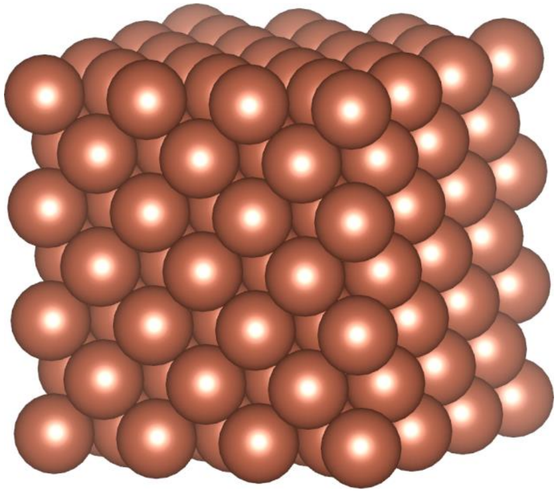
# Non-molecular crystalline solids



***Ionic bonding***
(*e.g.* NaCl)



***Covalent bonding***
(*e.g.* silicon)



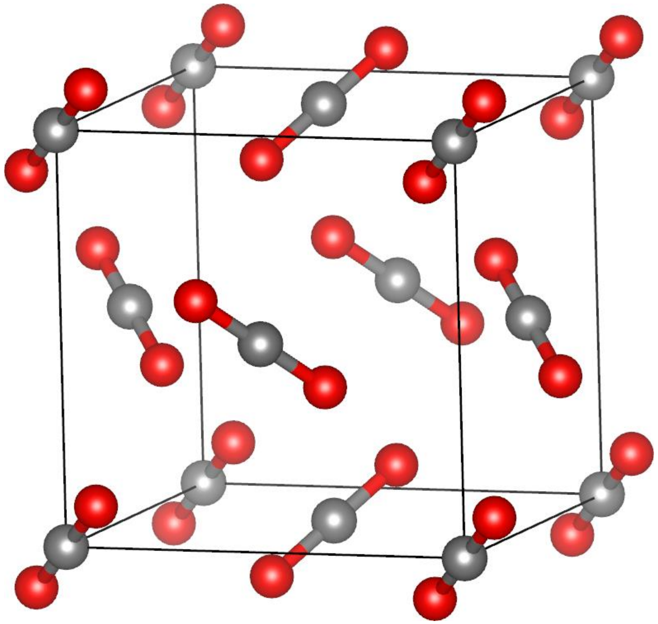
Figures: AJK

***Metallic bonding***
(*e.g.* copper)

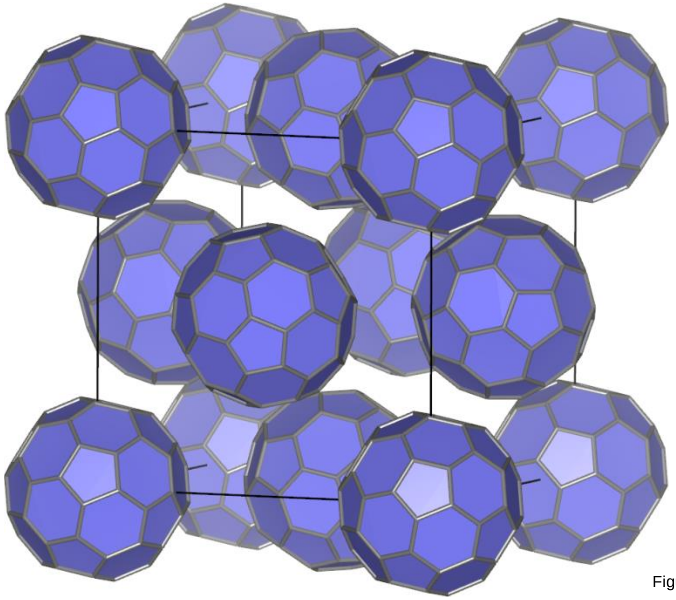
- Coordination polymers such as ***metal-organic frameworks*** show covalent bonding of metal atoms and organic molecules
- Coordination polymers are challenging the traditional classifications of solid state structures (see *e.g.* review of H. Furukawa *et al.*, *Science* **2013**, *341*, 1230444).

# 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)
*Acta Cryst. B* **1980**, *36*, 2750.

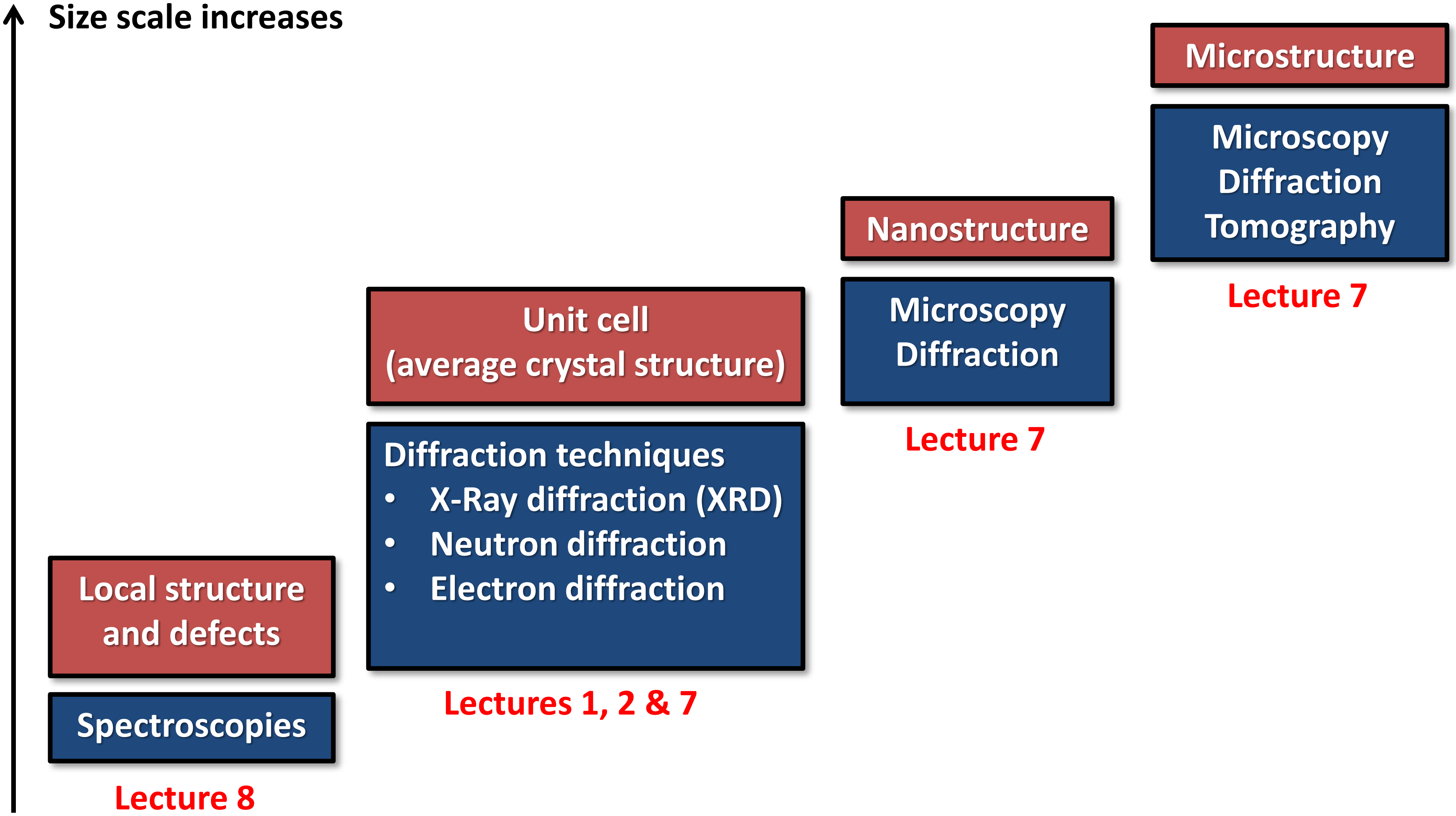


Figures: AJK

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

# Structure determination of crystalline materials

# Structure determination



**Size scale increases**

**Local structure and defects**

**Spectroscopies**

**Lecture 8**

**Unit cell (average crystal structure)**

**Diffraction techniques**
- **X-Ray diffraction (XRD)**
- **Neutron diffraction**
- **Electron diffraction**

**Lectures 1, 2 & 7**

**Nanostructure**

**Microscopy**
**Diffraction**

**Lecture 7**

**Microstructure**

**Microscopy**
**Diffraction**
**Tomography**

**Lecture 7**

Ref: West p. 230

# X-ray diffraction

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

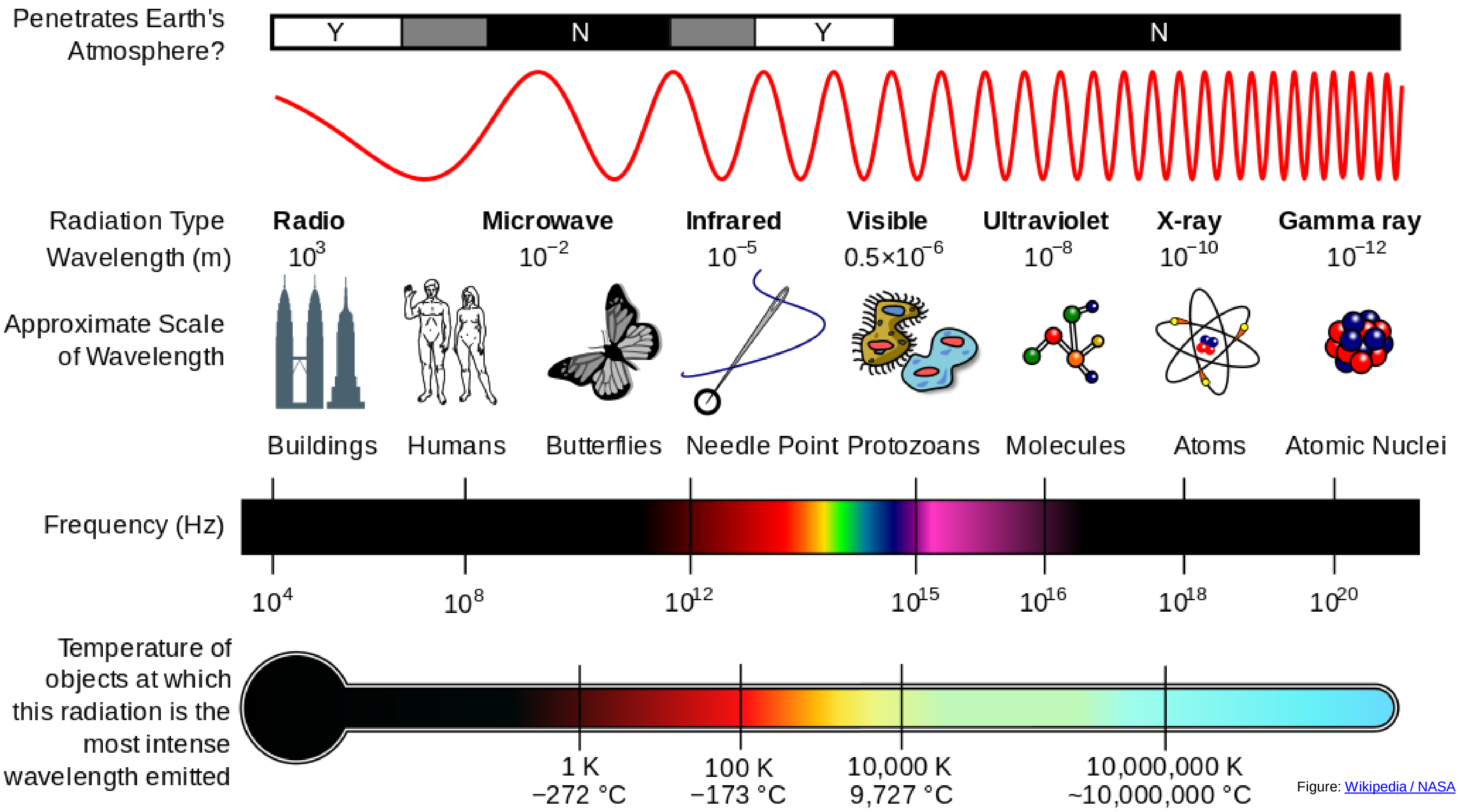
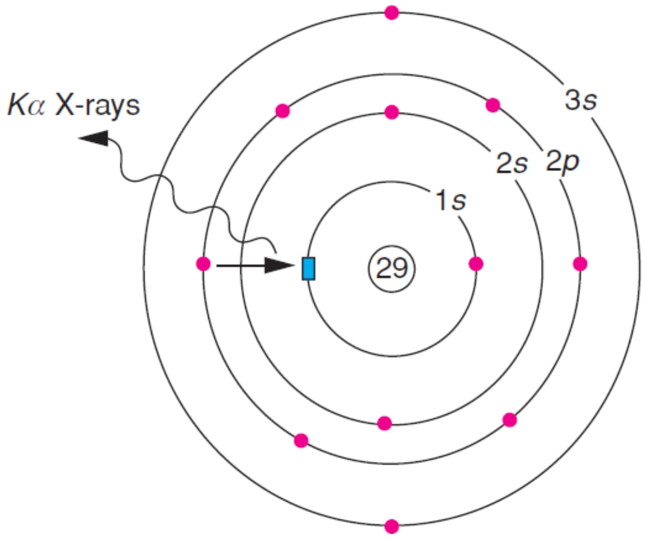


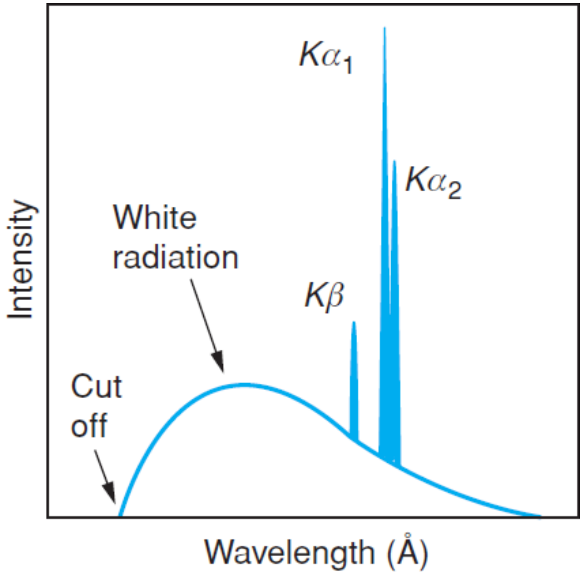
Figure: Wikipedia / NASA

# Generation of X-rays

- X-rays are produced with X-ray tubes (vacuum tubes converting electricity into X-rays).
- In an X-ray tube, high-energy charged particles, such as electrons accelerated through a voltages of 60 keV, collide with matter.
- For X-ray diffraction experiments monochromatic X-rays are used.



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.



Full X-ray emission spectrum of Cu. Particular wavelength, for example **Cu Kα** can be isolated with a monochromator and then used for X-ray diffraction.

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 $\lambda$ = 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)!

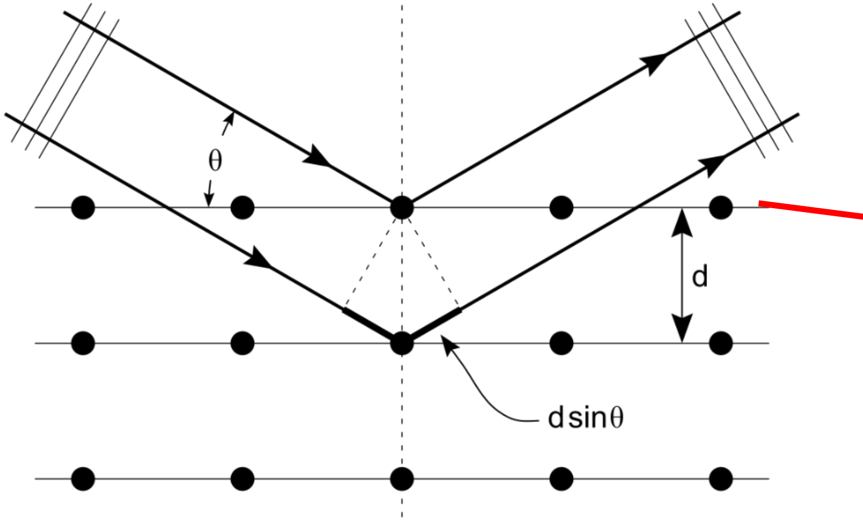


Figure: Wikipedia

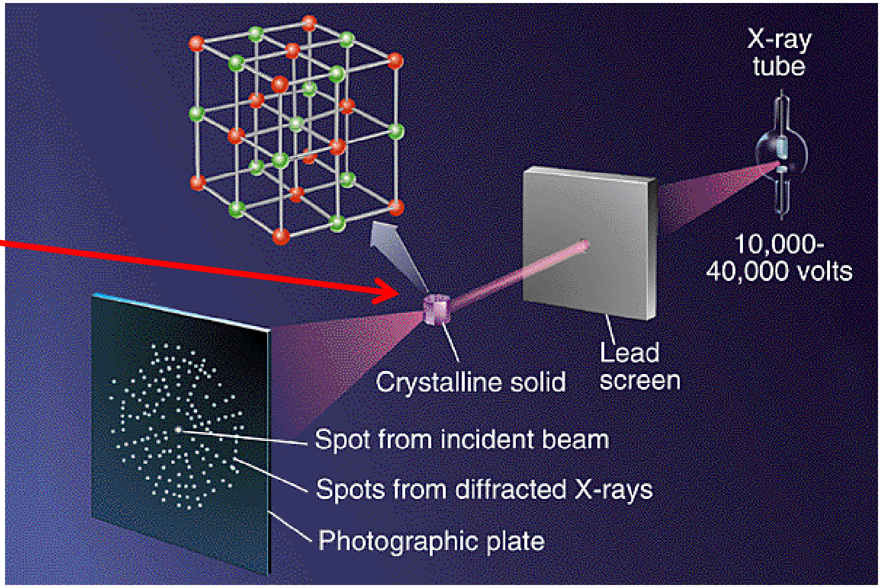
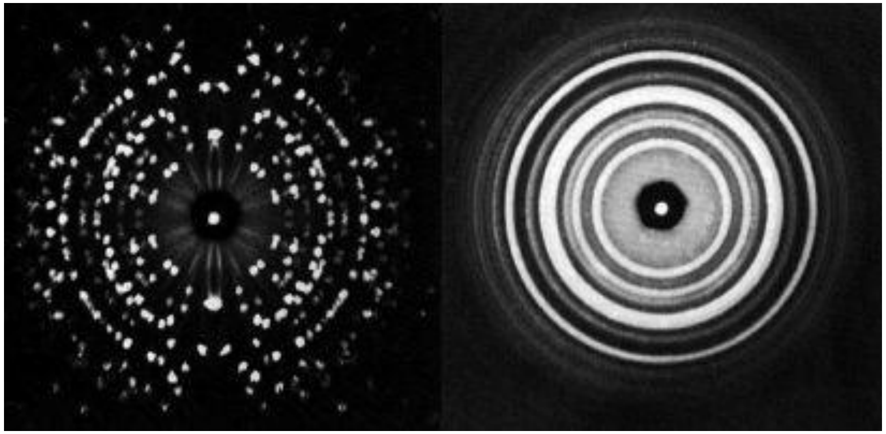


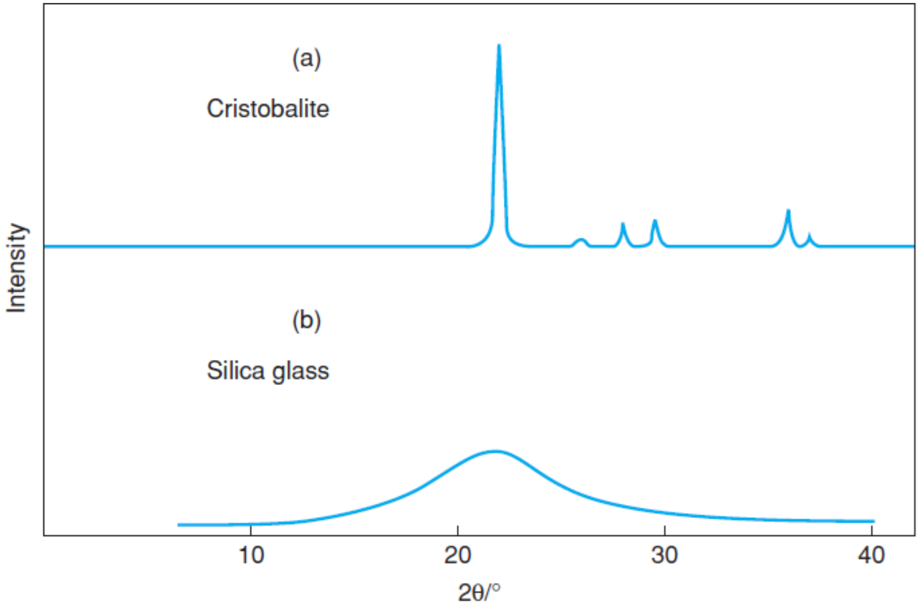
Figure: http://www.scienceiscool.org/solids/intro.html (dead link)

# Single crystal vs. powder X-ray

- The figure shows 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)
- The figure shows Powder X-ray diffraction pattern of crystalline (top) and amorphous (bottom) $SiO_2$

Figure: Susan Lehman / physics.wooster.edu



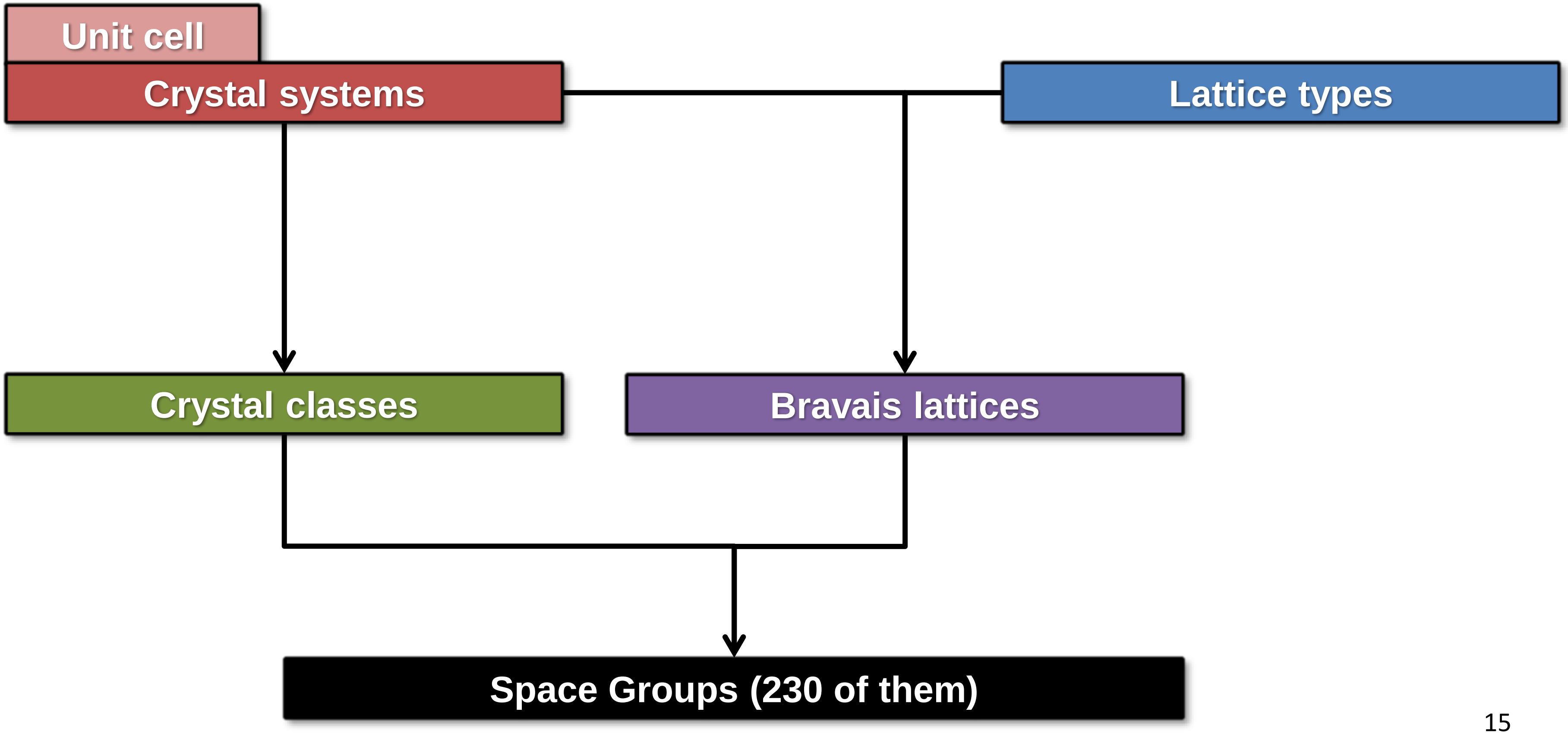


Ref: West p. 245

# 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 systems

Lattice types

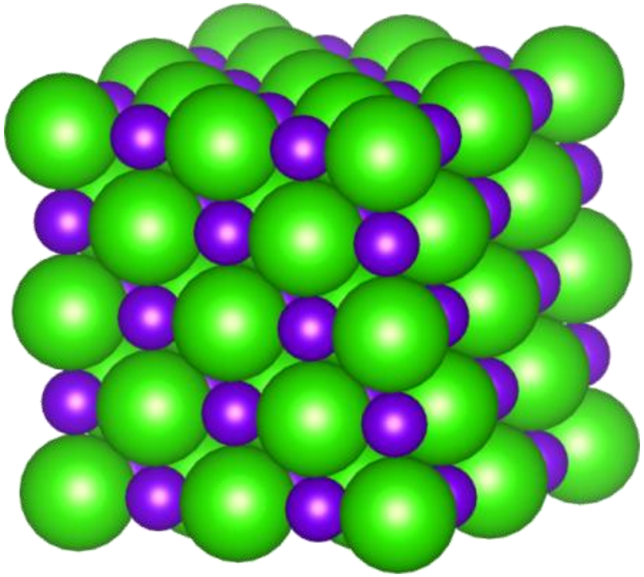
Crystal classes

Bravais lattices

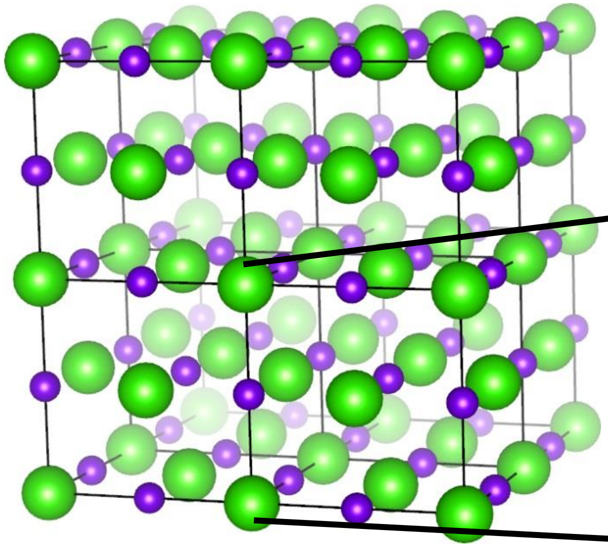
Space Groups (230 of them)

# 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

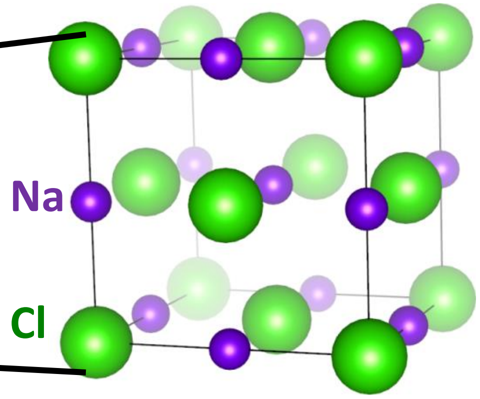


NaCl crystal: Regular arrangement of Na and Cl (space-filling representation)



NaCl crystal (non-space-filling representation

Figures: AJK



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**

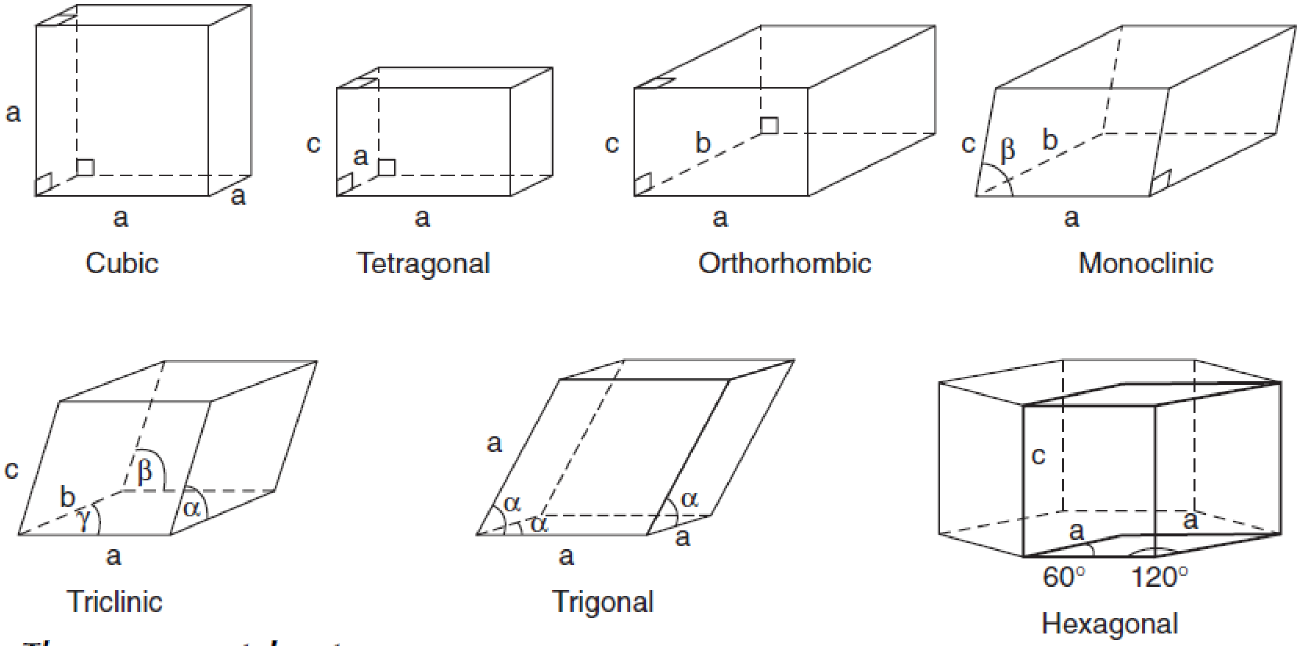


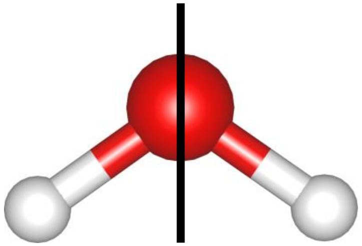
*Table 1.1* *The seven crystal systems*

| 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



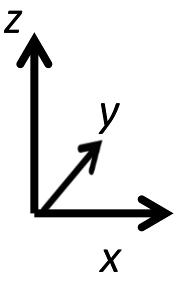
Mirror plane in a water molecule

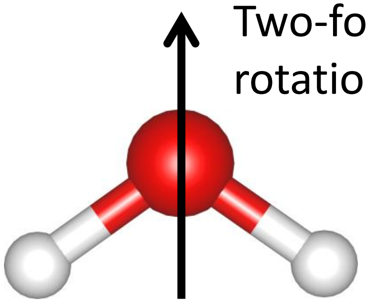
Figure: AJK

# 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 symmetry elements that are present

| Symmetry element | Symmetry operation | Schönflies symbol |
|---|---|---|
| Symmetry plane (mirror plane) | Reflection through plane | $\sigma$ |
| 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 | $S_n$ |

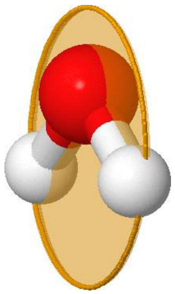




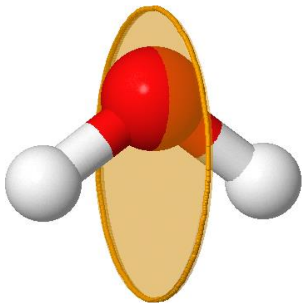
Two-fold proper rotation axis $C_2$

$H_2O$ (point group $C_{2v}$)

Mirror plane $\sigma_{yz}$



Mirror plane $\sigma_{xz}$



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) | $m$ | $\sigma$ |
| Inversion | $\bar{1}$ | $i$ |
| Proper axis (rotation) | $n$ = 2, 3, 4, 6 | $C_n$ |
| Improper axis (improper rotation) | – | $S_n$ |
| | | |
| **Elements only in crystals** | | |
| Inversion axis (point symmetry) | $\bar{n} = \bar{3}, \bar{4}, \bar{6}$ | – |
| Glide plane (includes translation) | *a, b, c, d, n* | – |
| Screw axis (includes translation) | $2_1$, $3_1$, etc. | – |

*(Inversion axis, glide plane, and screw axis explained in more detail in extra slides)*

# 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 | $1, \bar{1}$ | $C_1, C_i$ |
| Monoclinic | $2, m, 2/m$ | $C_2, C_s, C_{2h}$ |
| Orthorhombic | $222, mm2, mmm$ | $D_2, C_{2v}, D_{2h}$ |
| Tetragonal | $4, \bar{4}, 4/m, 422, 4mm, \bar{4}2m, 4/mmm$ | $C_4, S_4, C_{4h}, D_4, C_{4v}, D_{2d}, D_{4h}$ |
| Trigonal | $3, \bar{3}, 32, 3m, \bar{3}m$ | $C_3, S_6\ (C_{3i}), D_3, C_{3v}, D_{3d}$ |
| Hexagonal | $6, \bar{6}, 6/m, 622, 6mm, \bar{6}m2, 6/mmm$ | $C_6, C_{3h}, C_{6h}, D_6, C_{6v}, D_{3h}, D_{6h}$ |
| Cubic | $23, \bar{4}3m, m\bar{3}, 432, m\bar{3}m$ | $T, T_d, T_h, O, O_h$ |

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

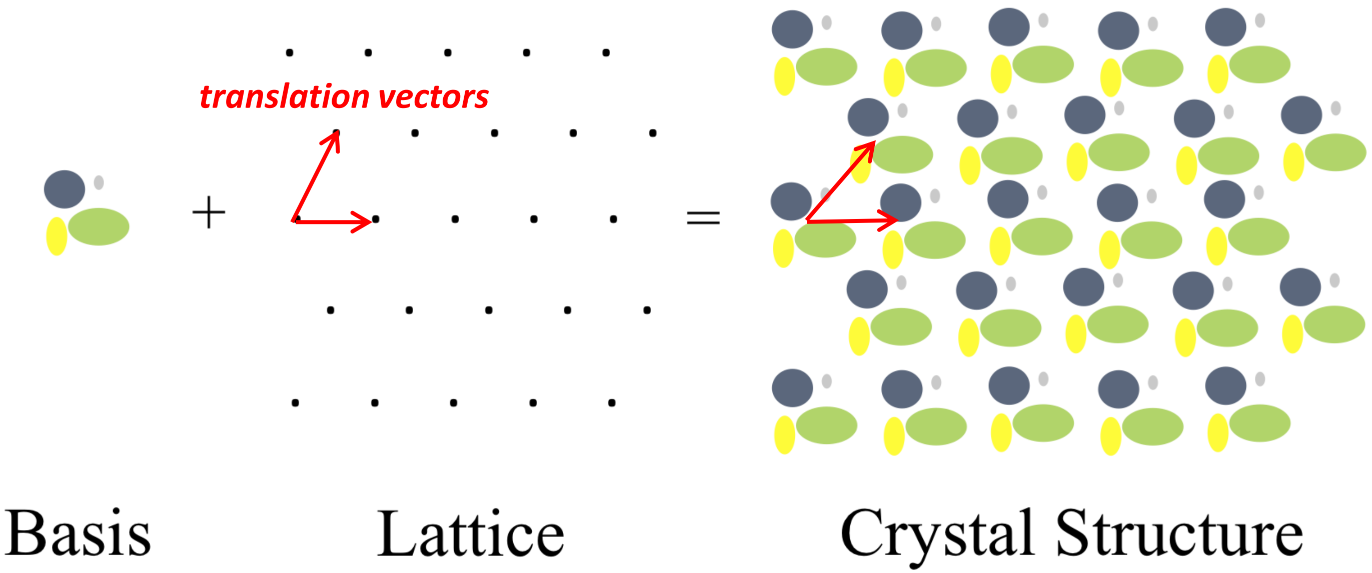
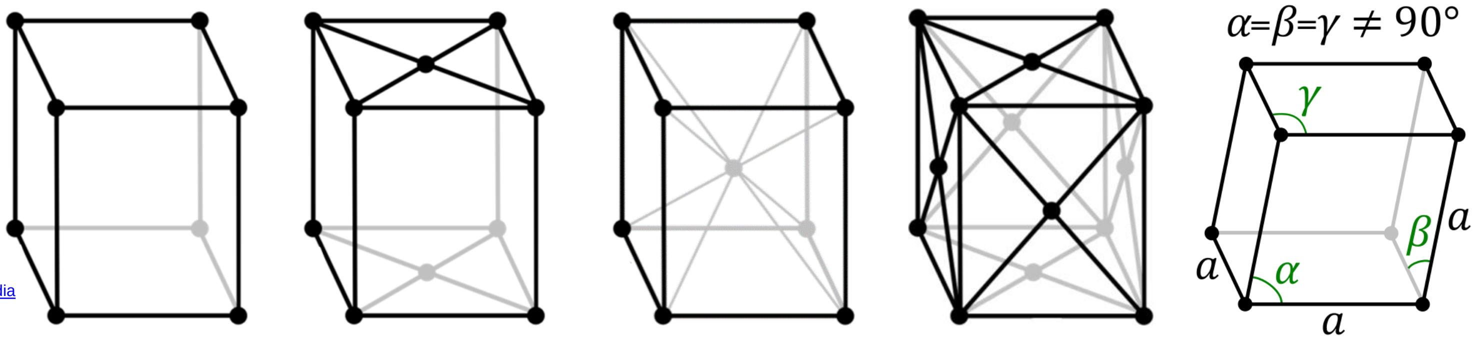


Figure: Andreas Mulyo

# Lattice types

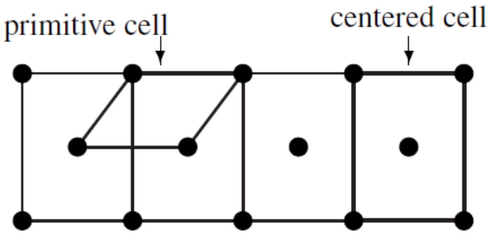
- Every crystal structure belongs to one of five ***lattice types***:
  - The balls are lattice points, ***not*** atoms!



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)*)



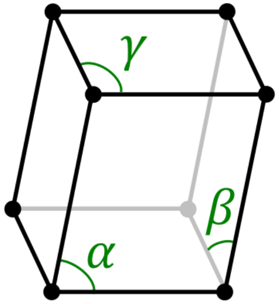
Ref: Müller p. 8

# Bravais lattices (1)

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

***Triclinic***

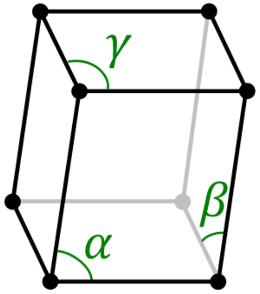
$\alpha, \beta, \gamma \neq 90°$



**P**

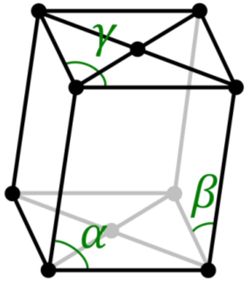
***Monoclinic***

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



**P**

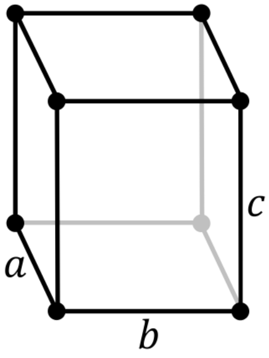
$\beta \neq 90°$
$\alpha, \gamma = 90°$



**C**

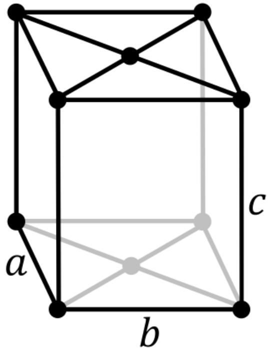
***Orthorhombic***

$a \neq b \neq c$



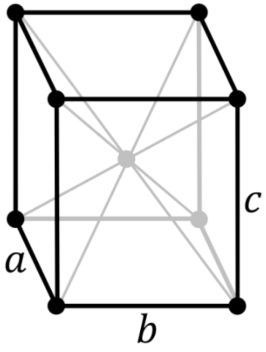
**P**

$a \neq b \neq c$



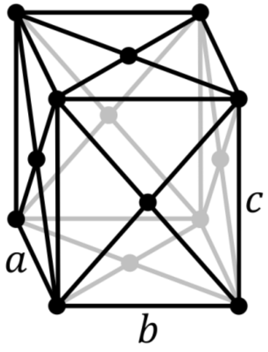
**C**

$a \neq b \neq c$



**I**

$a \neq b \neq c$

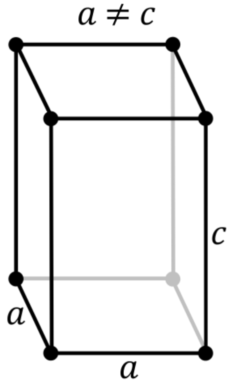


**F**

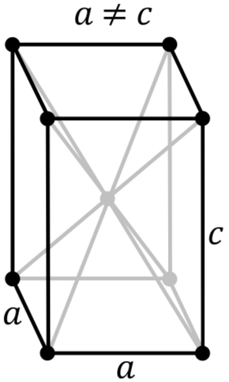
Figures: Wikipedia

# Bravais lattices (2)

### *Tetragonal*

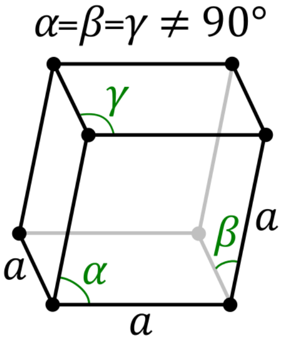


***P***



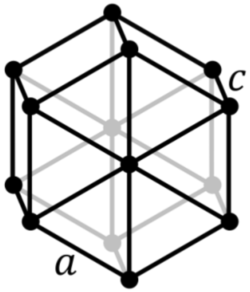
***I***

### *Rhombohedral*



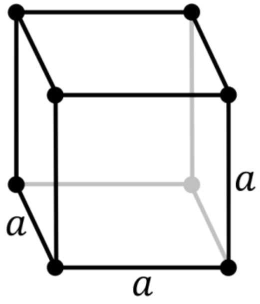
***R***

### *Hexagonal*

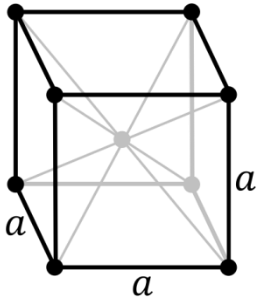


***P***

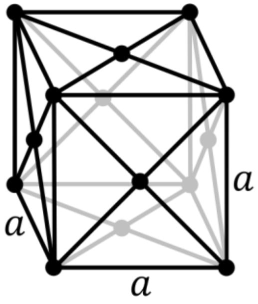
### *Cubic*



***P***



***I (bcc)***



***F (fcc)***

Figures: [Wikipedia]

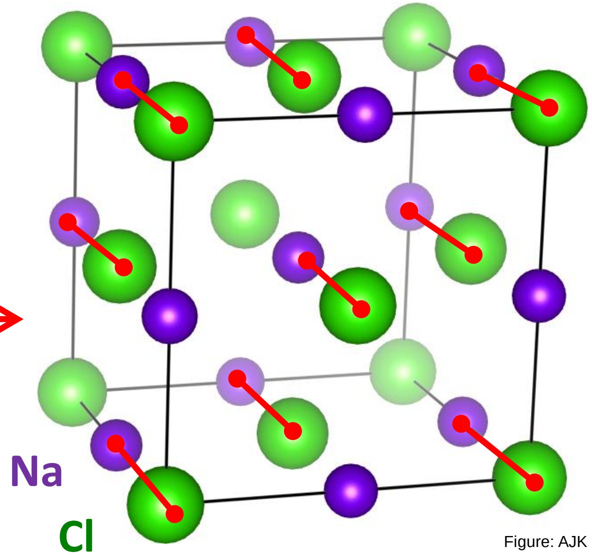
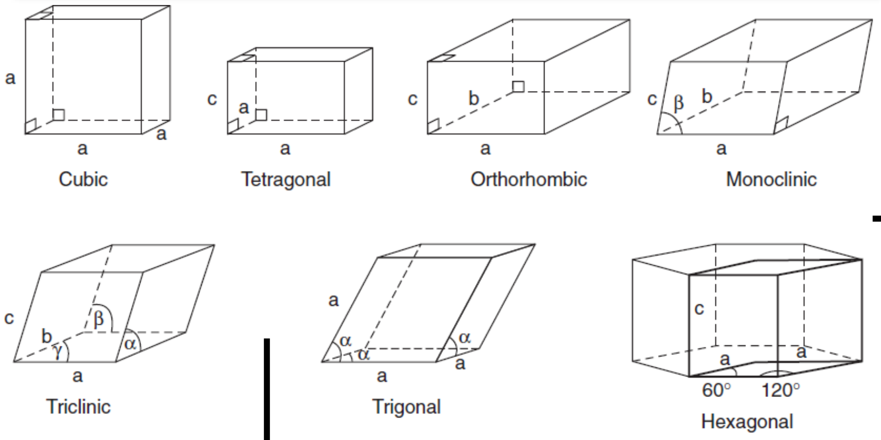


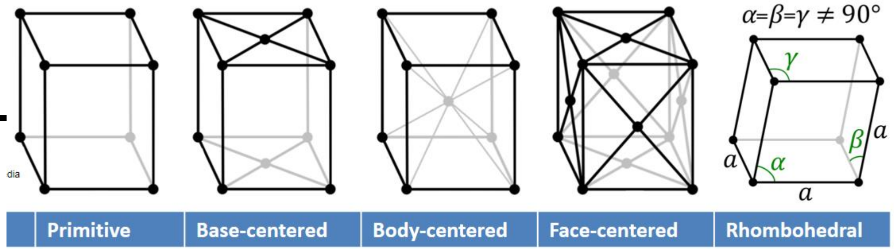
Figure: AJK

fcc, basis: Cl + Na

# Crystal systems (7 of them)



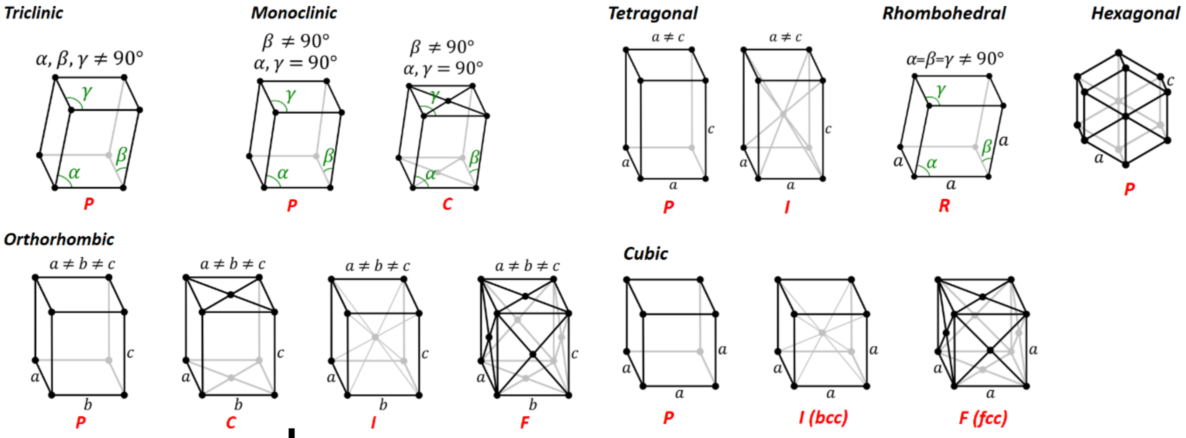
# Lattice types (5 of them)



# 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 | $222, mm2, mmm$ |
| Tetragonal | $4, \bar{4}, 4/m, 422, 4mm, \bar{4}2m, 4/mmm$ |
| Trigonal | $3, \bar{3}, 32, 3m, \bar{3}m$ |
| Hexagonal | $6, \bar{6}, 6/m, 622, 6mm, \bar{6}m2, 6/mmm$ |
| 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

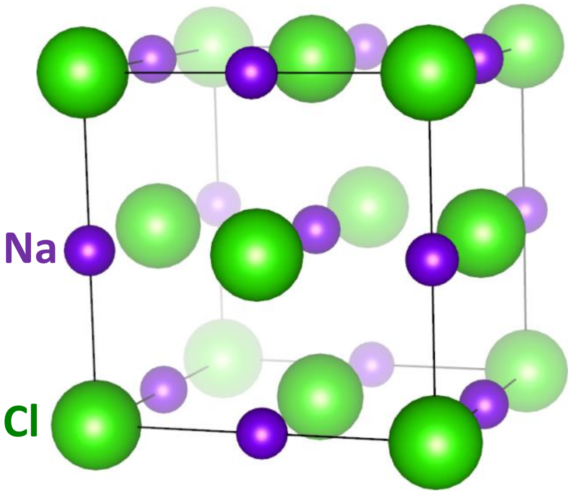
- The **32** crystal classes and **14** Bravais lattices give rise to **230** space groups
- The Hermann-Mauguin symbol for the space group of NaCl: $\boldsymbol{Fm\bar{3}m}$ (or ***Fm*-3*m***)
- The symbol begins with a capital letter *P, A, B, C, F, I,*or *R,* specifying the presence of ***translational 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

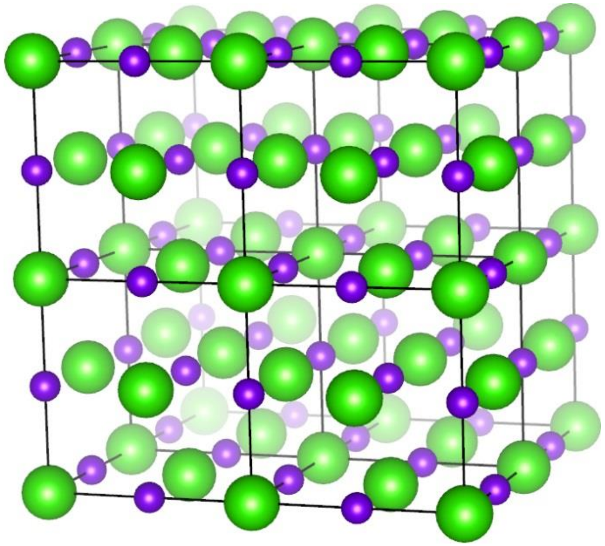
- A crystal structure is defined by
  - Space group
  - Lattice parameters
  - Atomic coordinates (positions) in fractional coordinates ($0.0 \leq x,y,z < 1.0$)
  - Normally only ***symmetry-independent*** atoms in the ***asymmetric unit*** are listed
- For example, NaCl (ICSD code 655785)
  - ***Fm*-3*m***
  - $a = b = c =$ **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 $Z = 4$



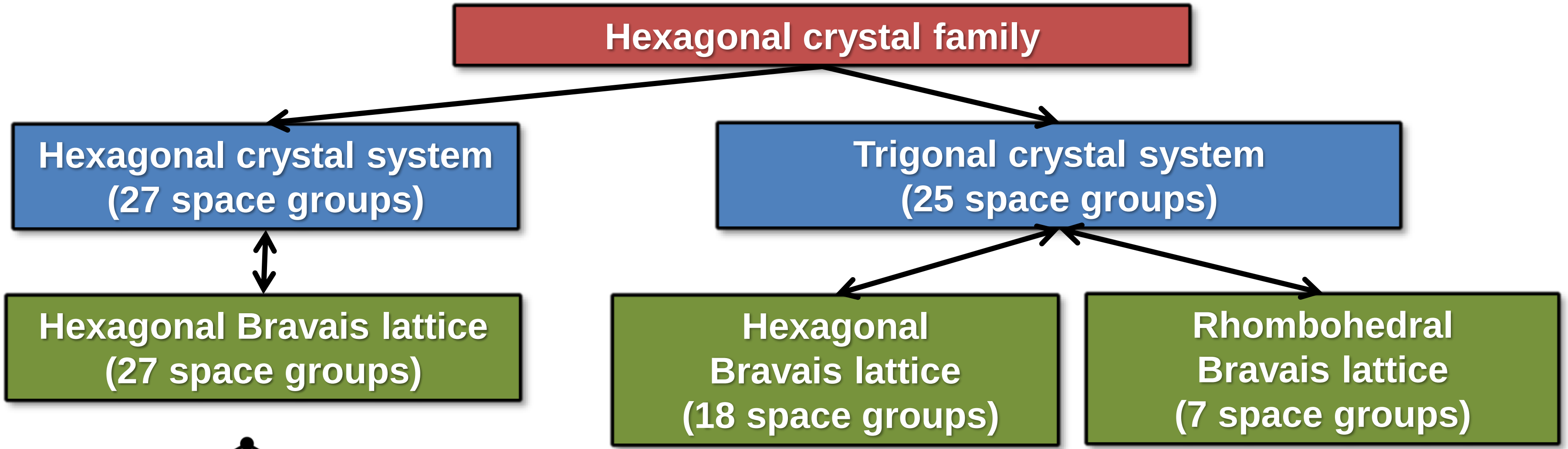
Figures: AJK



# Extra slides

“Nice-to-know”-type material that is not needed for completing the exercises

# More details on trigonal crystal system



**Hexagonal crystal family**

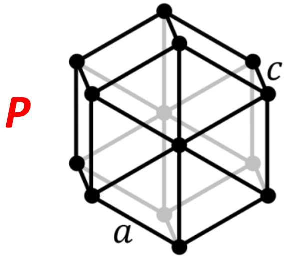
**Hexagonal crystal system**
**(27 space groups)**

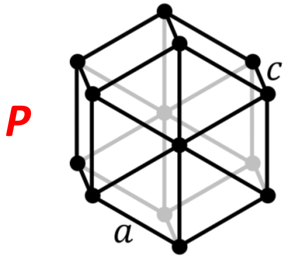
**Trigonal crystal system**
**(25 space groups)**

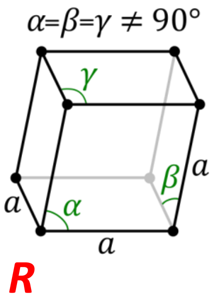
**Hexagonal Bravais lattice**
**(27 space groups)**

**Hexagonal**
**Bravais lattice**
**(18 space groups)**

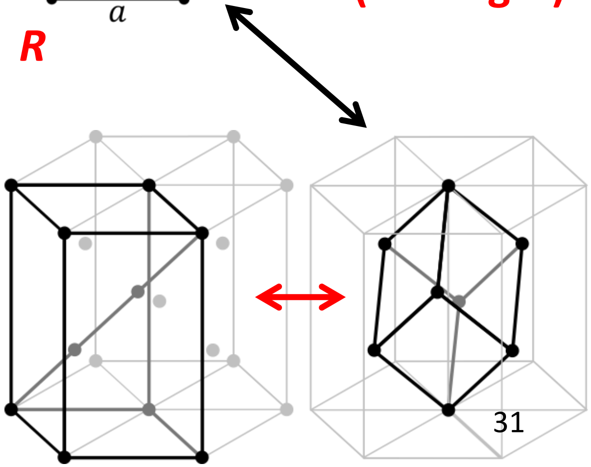
**Rhombohedral**
**Bravais lattice**
**(7 space groups)**







**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 |

# Symmetry elements in crystals: 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):

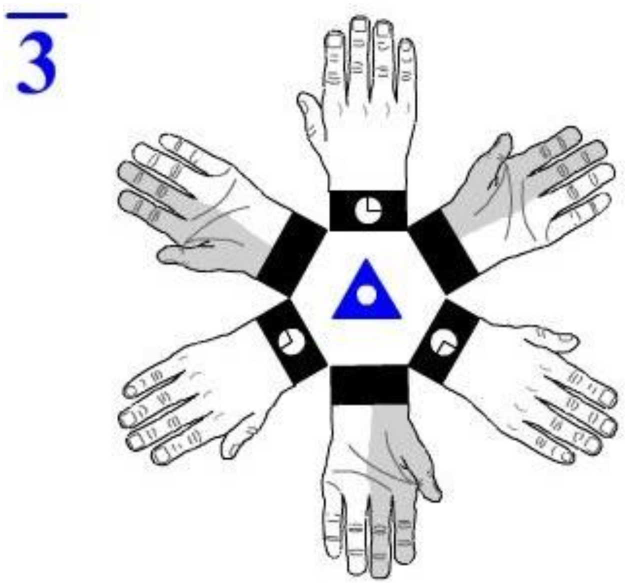


Figure: Margaret E. Kastner,
http://www.crystallographiccourseware.com/

# Symmetry elements in crystals: 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

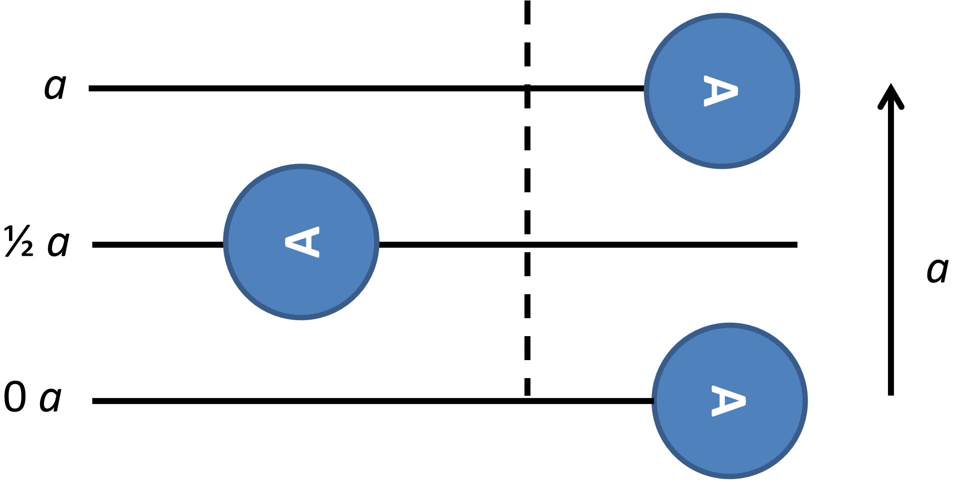
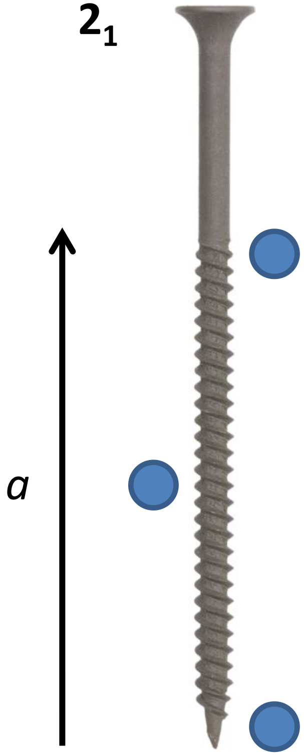


Figure: AJK

# Symmetry elements in crystals: 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

**$2_1$**



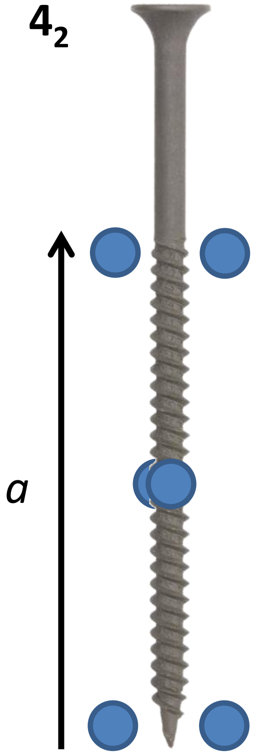
rot. / trans.

360° / *a*

180° / ½ *a*

0° / 0 *a*

**$4_2$**



rot. / trans.

180° / *a*

90° / ½ *a*

0° / 0 *a*

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

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

# 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)

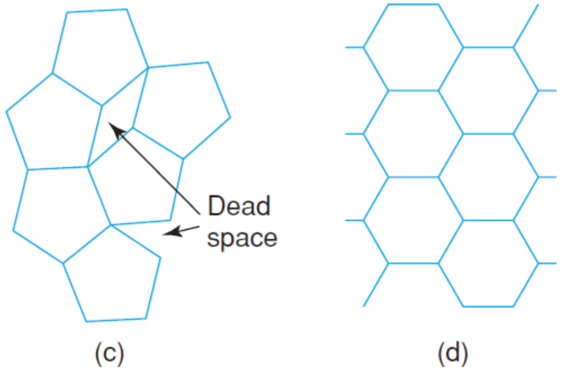


***Figure 1.4.*** (c) the impossibility of forming a complete layer of pentagons; (d) a complete layer of hexagons

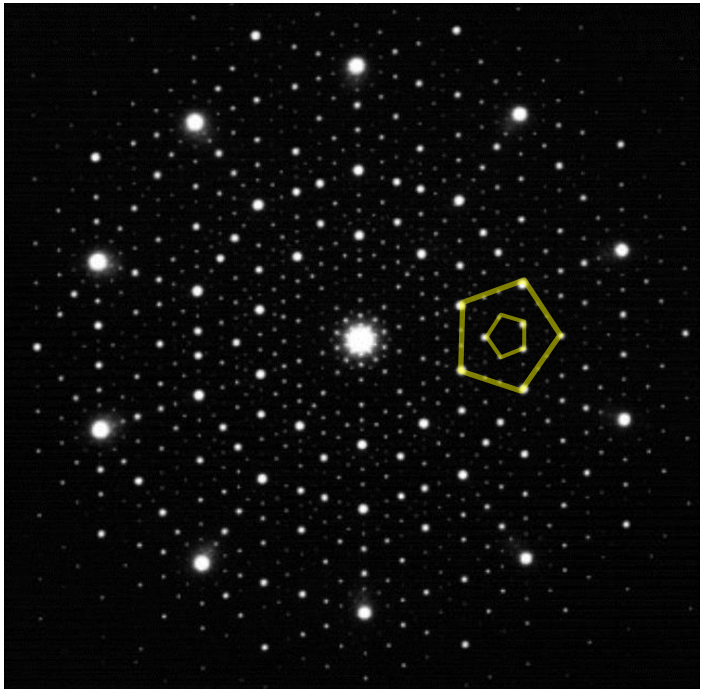


Figure: Nobel committee

Electron diffraction pattern from an icosahedral quasicrystal

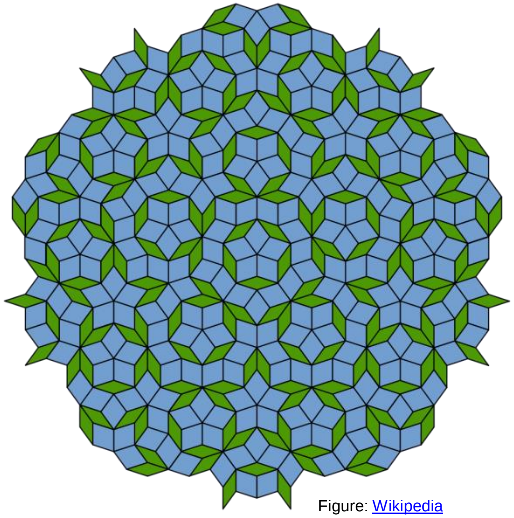


Figure: Wikipedia

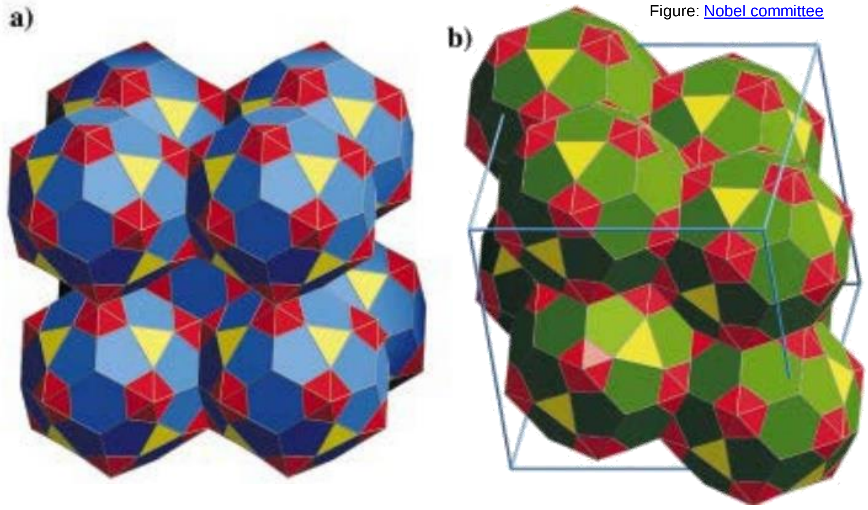
Penrose tiling (no translational periodicity)

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