MSE-238
Structure of Materials

Week 2 – crystallography I

Spring 2025

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Overview

- Lattice and motif
- Symmetry (as a first introduction, more next week)
- The hard sphere model: coordination and interstitial sites
- Crystals formed by metals
- Ionic and covalent crystals

- → Hammond Chapter 1

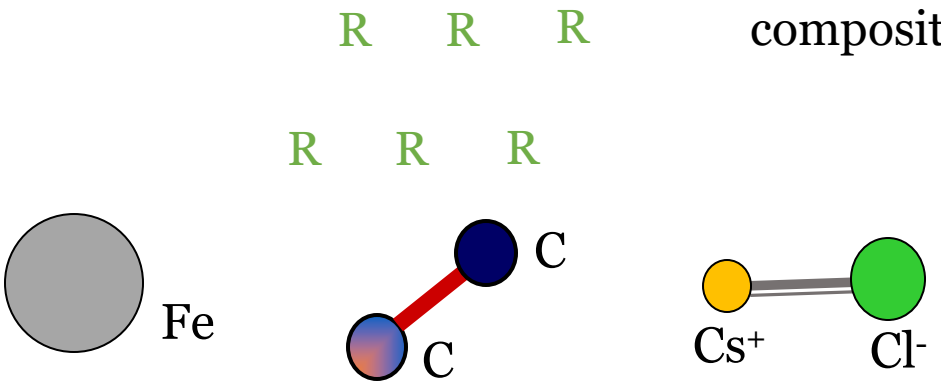
Crystalline material

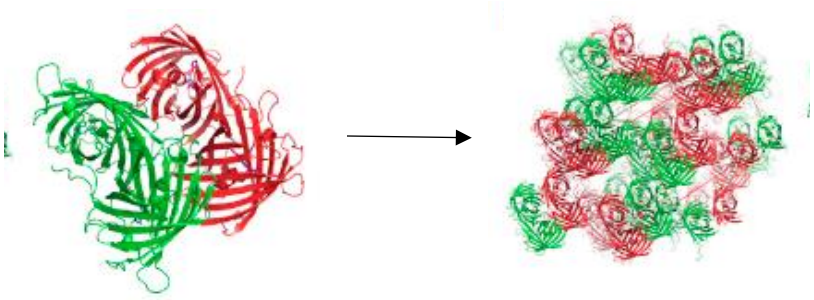
- recap Definition: A **crystalline material** is a material characterized by a **regular arrangement of atoms** or group of atoms over "large" distances, i.e. a crystal displays translational symmetry over a long range.
  In a crystal it is always possible to **identify a group of atoms or molecules** (can be also one atom) that **repeats** itself periodically **on a grid** in space.

Crystal = Motif + Lattice

- in 2D

Motif: repeating "unit of pattern"
here represented by R
atom, group of atoms, molecules → chemical composition





photoactivatable fluorescent protein
h41pkve6 → can be crystalized

Crystalline material

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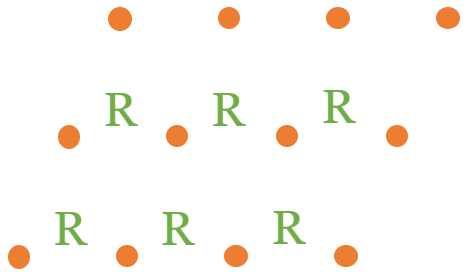

Motif: repeating "unit of pattern"
here represented by R
atom, group of atoms, molecules → chemical composition

Lattice: (imaginary) grid, intersections
→ lattice points
can be placed anywhere, but always in the same position with respect to the motif
in each point of the lattice, the crystal appears identical, **translational symmetry** in between

Crystalline material

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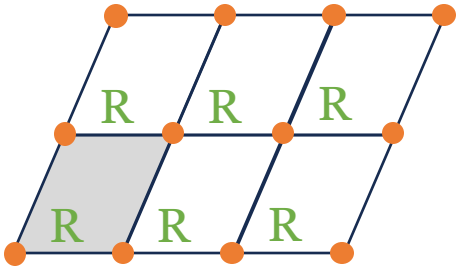
Crystal = Motif + Lattice

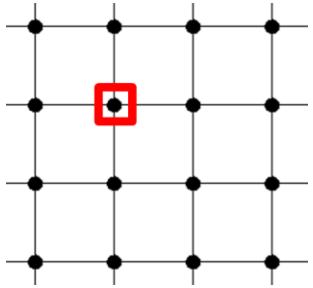
- in 2D



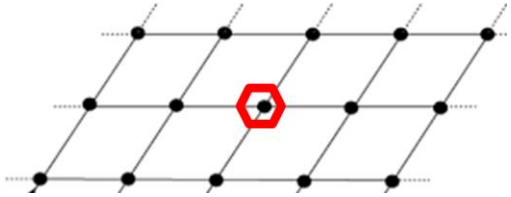
unit cell: arbitrary ways of joining up the lattice points.
primitive unit cell: smallest possible unit, contains one lattice point (here 4 times $1/4^{th}$)
conventional unit cell: larger unit cell, chose to reflect the crystal's symmetry better
contain more than one lattice points
makes visualization and classification of crystal structure easier

Crystal symmetry

- symmetry present in the crystal is determined by
  - how the translation is done

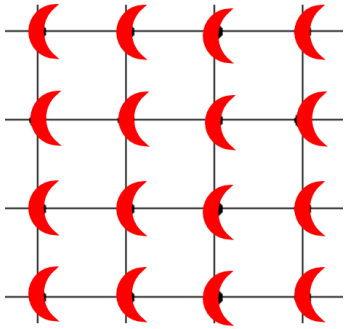


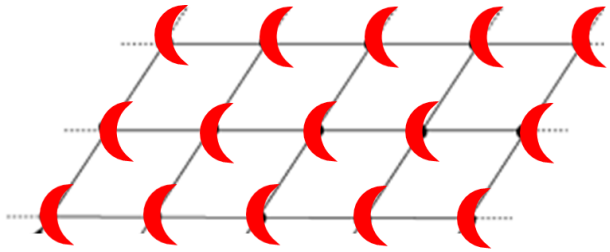
4-fold
rotation axis



6-fold
rotation axis

  - character of the motif

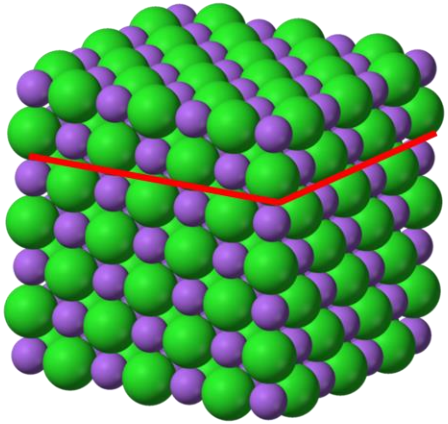




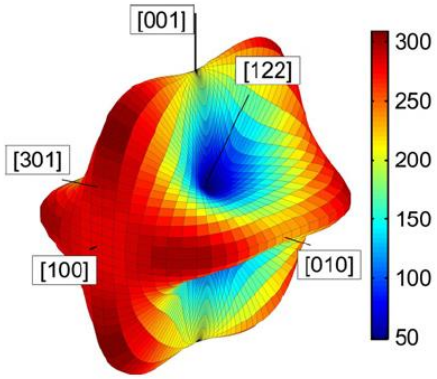
only 1-fold symmetry left!

Crystal symmetry

- Symmetry plays an important role in material science. Most material properties are anisotropic which means that their properties depend upon direction or angular orientation of crystals. Examples are chemical resistance, the ability to get charged when stressed (piezoelectricity) or fracture toughness.



in crystal of NaCl cleavage along planes parallel to cube faces

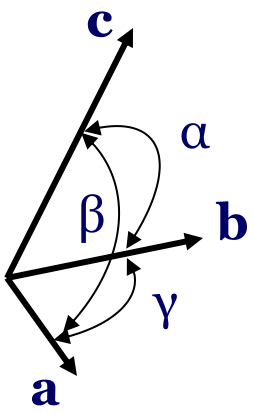


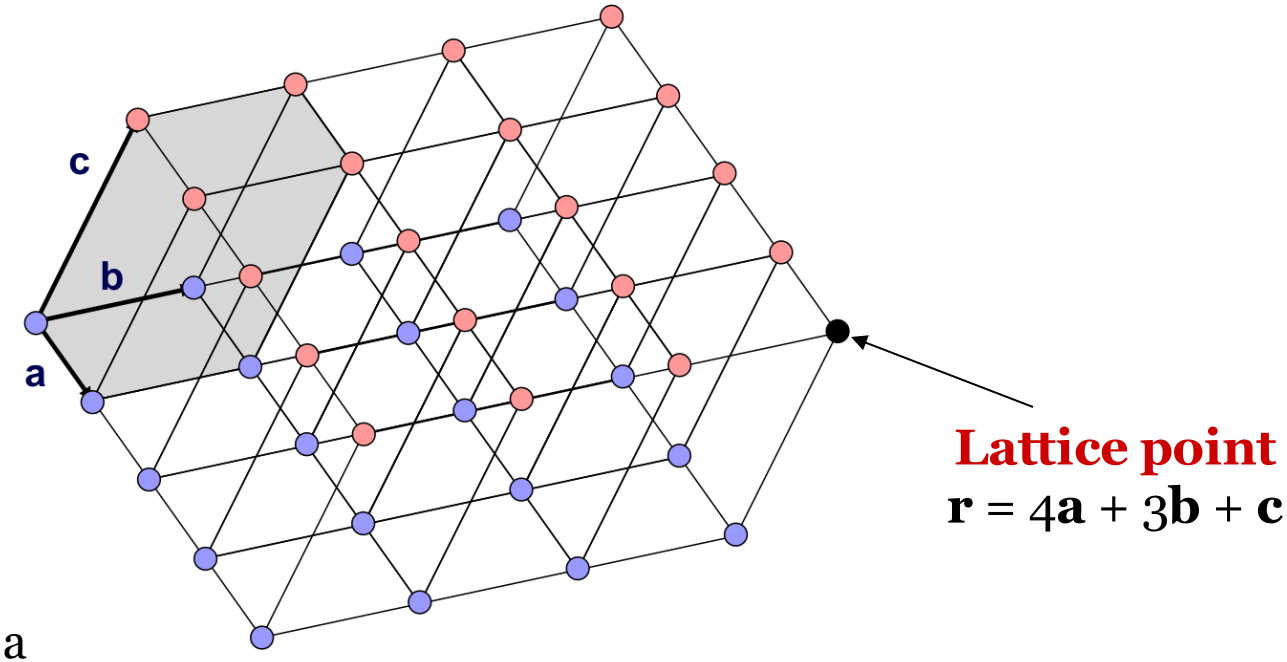
modulus of elasticity for single crystal elastic constant of cementite (Fe^3C)

Weisser et al Acta Materialia 59 (2011) 4448

Crystalline material

- in 3D: Bravais Lattice

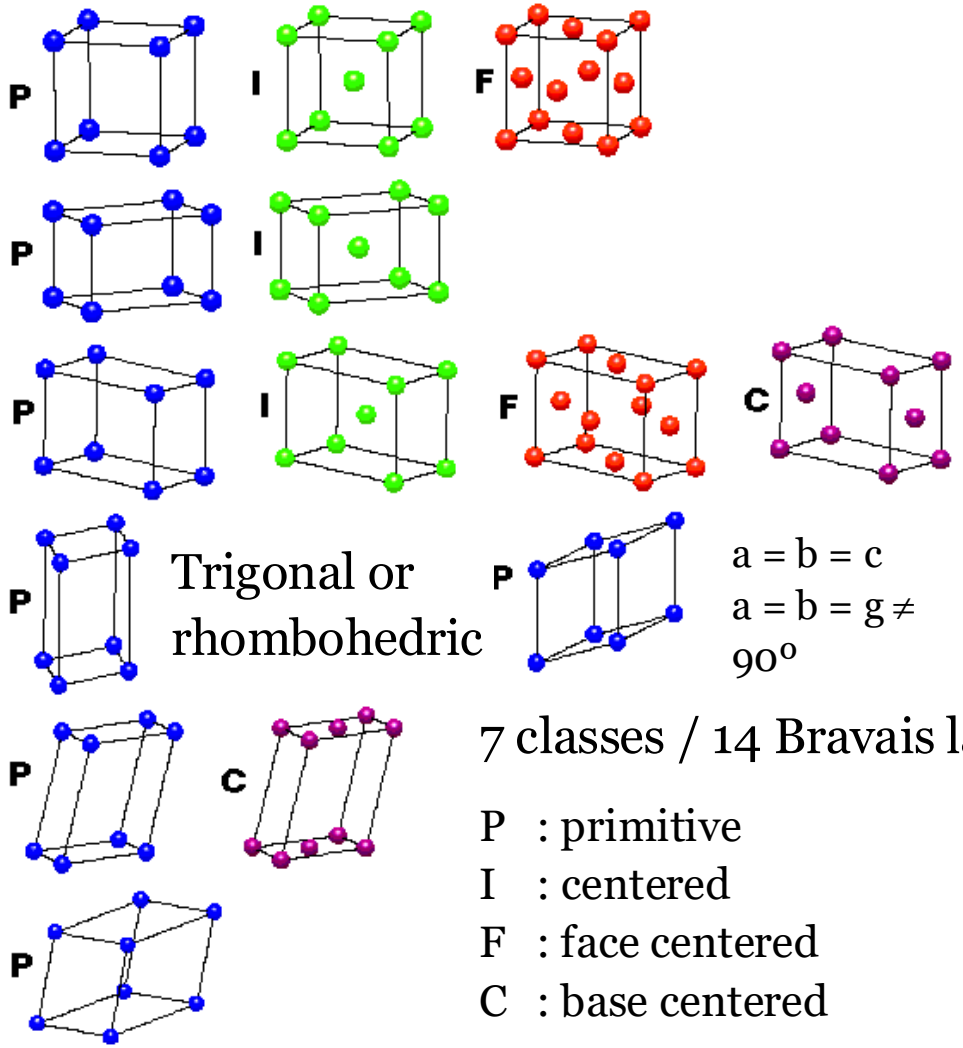




set of 3 vectors
form the basis:
every lattice point is a
linear combination with
relative integers as
coefficients

7 crystal systems – 14 Bravais Lattice

Cubic	a = b = c a = b = g = 90°
Tetragonal	a = b ≠ c a = b = g = 90°
Orthorhombic	a ≠ b ≠ c a = b = g = 90°
Hexagonal	a = b ≠ c a = b = 90°; g = 120°
Monoclinic	a ≠ b ≠ c a = g = 90° ≠ b
Triclinic	a ≠ b ≠ c a ≠ b ≠ g



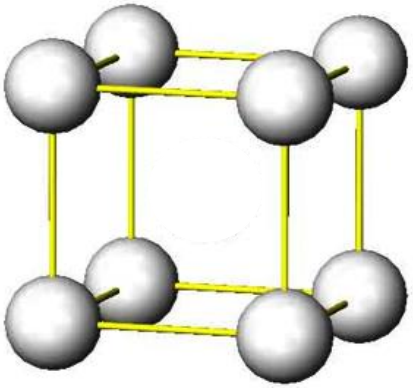
7 classes / 14 Bravais lattice

P : primitive
I : centered
F : face centered
C : base centered

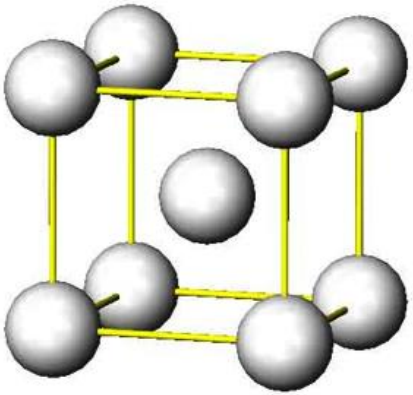
http://www.chem.ox.ac.uk/icl/heyes/structure_of_solids/lecture1/Bravais.gif

The cubic system

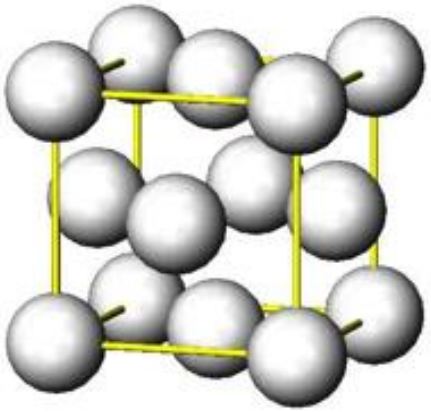
- The cubic system has three Bravais lattices



Primitive Cubic



Body-centered Cubic

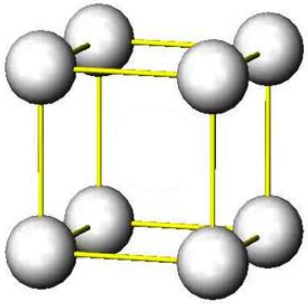


Face-centered Cubic

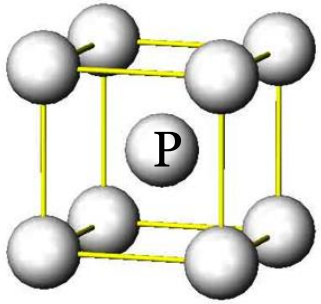
The cubic system: unit cells

primitive unit cell: smallest possible unit, contains one lattice point
conventional unit cell: larger unit cell, chose to reflect the crystal's symmetry better
contain more than one lattice points (and motifs)
makes visualization and classification of crystal structure easier

(**a**,**b**,**c**) is not a basis for BCC, P has the coordinates (1/2, 1/2, 1/2)



Primitive cubic
basis: (**a**,**b**,**c**)

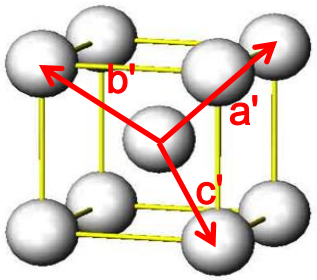


$$\vec{a}' = \frac{1}{2}(-\vec{a} + \vec{b} + \vec{c})$$

$$\vec{b}' = \frac{1}{2}(\vec{a} - \vec{b} + \vec{c})$$

$$\vec{c}' = \frac{1}{2}(\vec{a} + \vec{b} - \vec{c})$$

Body-centered cubic
basis: (**a'**,**b'**,**c'**)



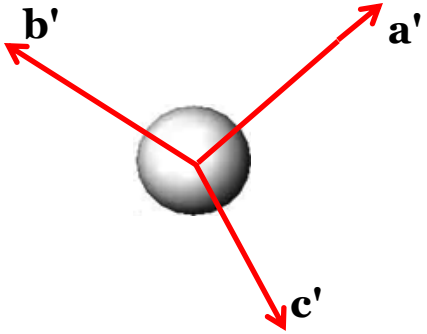
The cubic system: body-centered cubic (bcc)

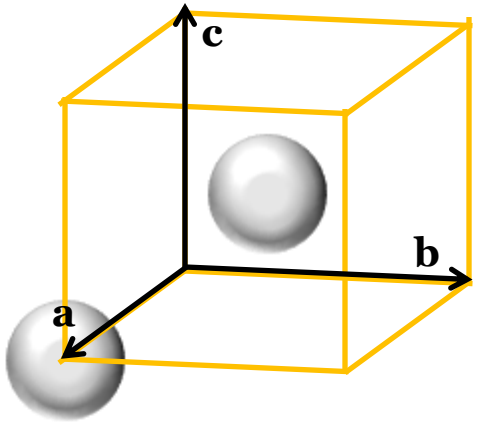
Primitive cell

- Find the motif;
- Translate it along the BCC lattice;

Convetional cell

- Find the motif;
- Place it within the Conventional cell;
- Translate the cell along the orthonormal basis **a**, **b** and **c** of the cubic system;





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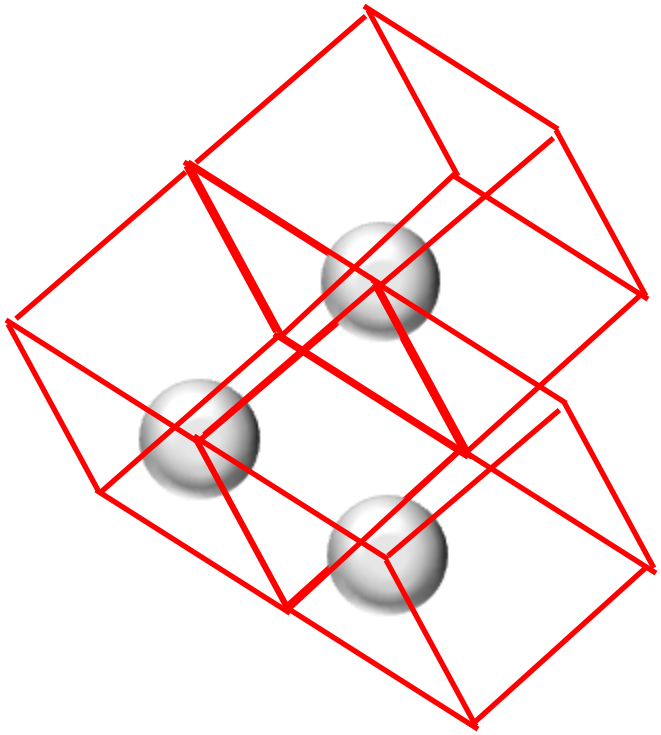

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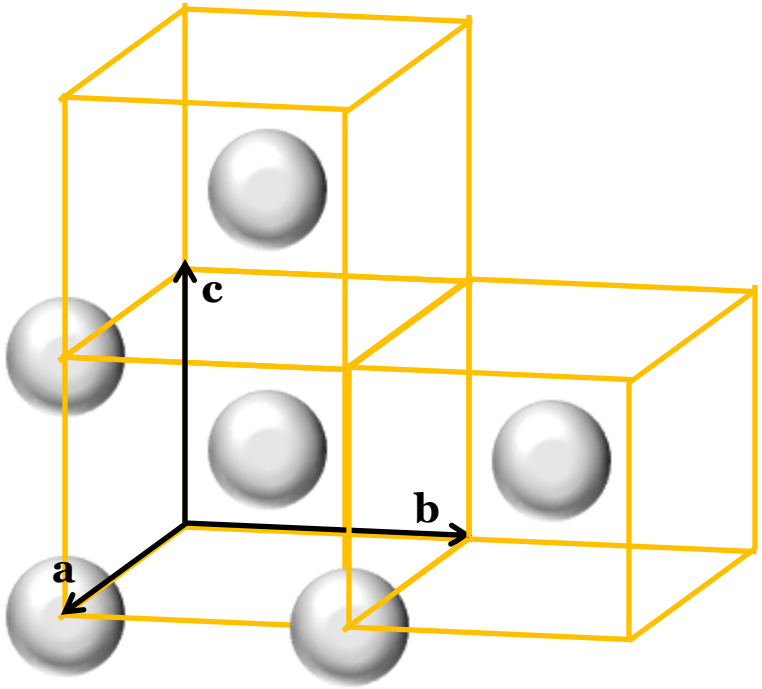

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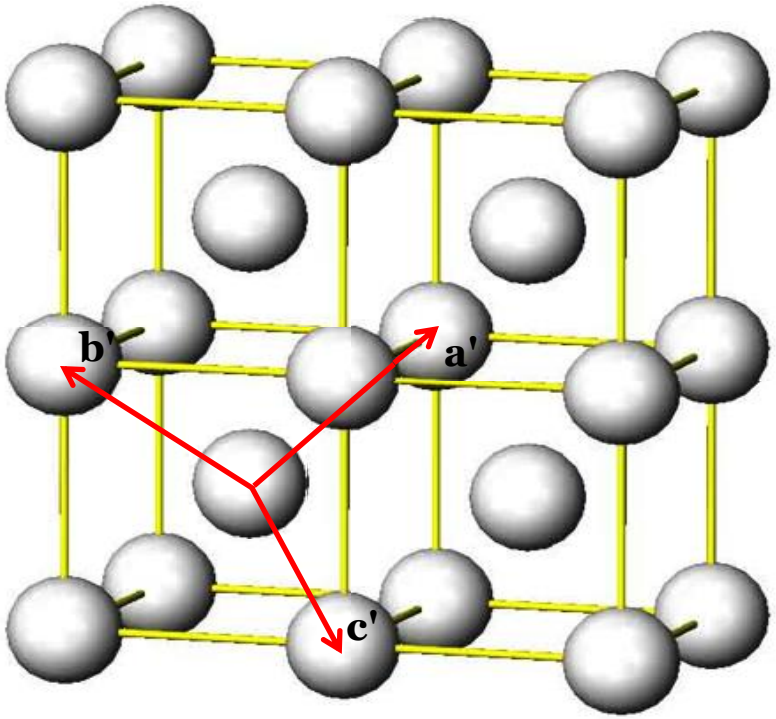

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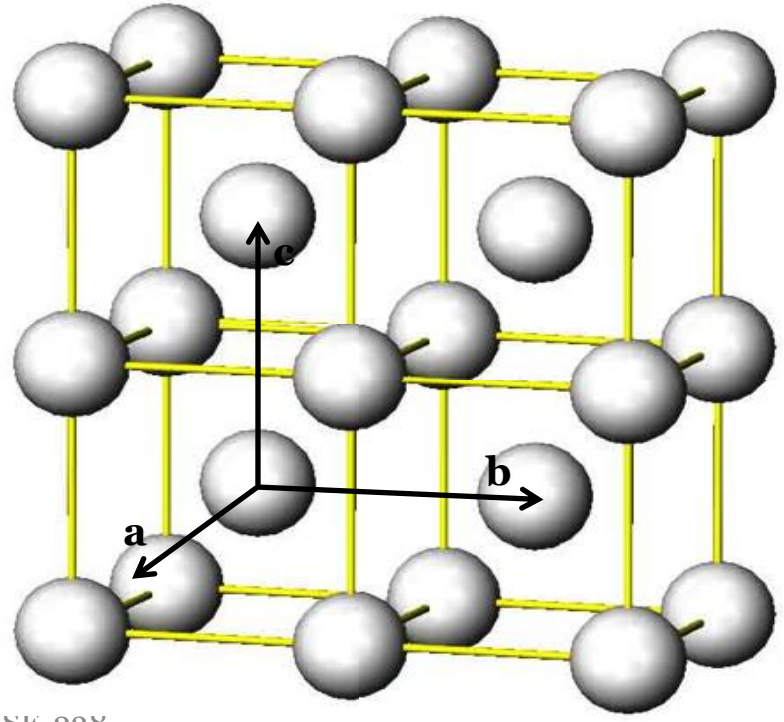
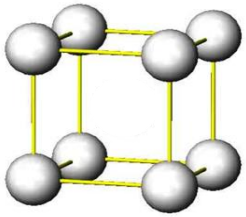
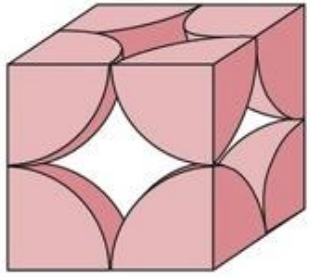


Number of motifs per unit cell

Primitive cubic:

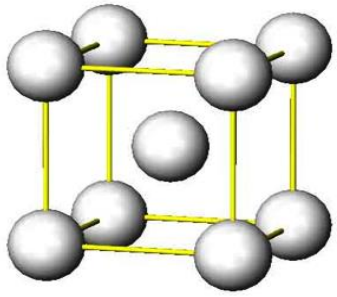
- Motifs at the corners of the cube count for 1/8
- The primitive cell has as expected 1 motif.





Body-centered conventional cell:

- Motifs at the corners of the cube count for 1/8
- The motif inside the cell count for 1.
- Hence the BCC conventional unit cell has 2 motifs.

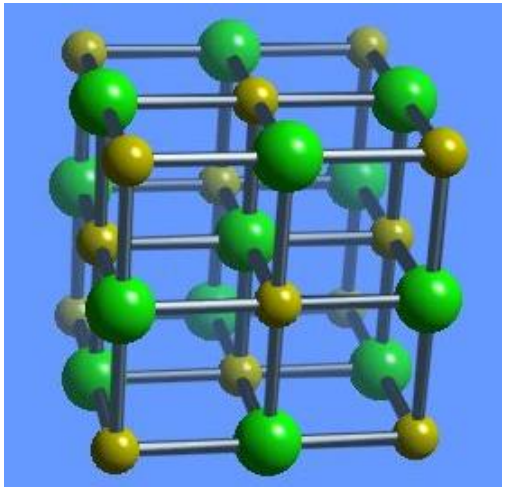


The cubic system

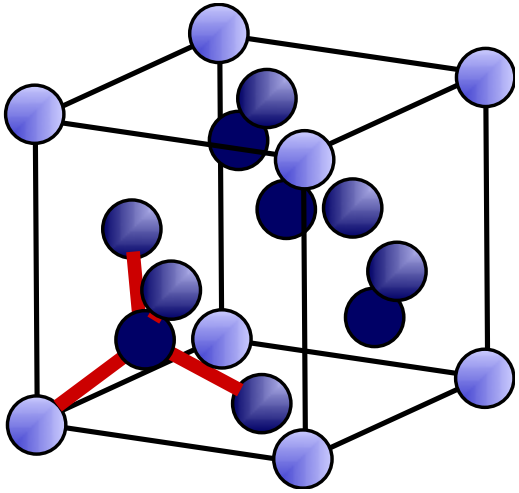
Examples:

Lattice:

Aluminium



NaCl



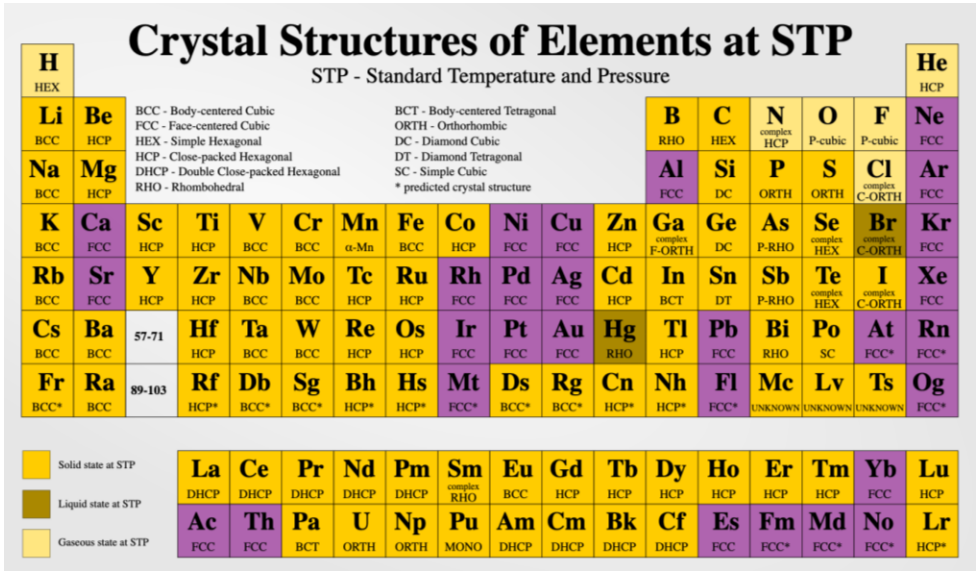
Diamond

Motifs:

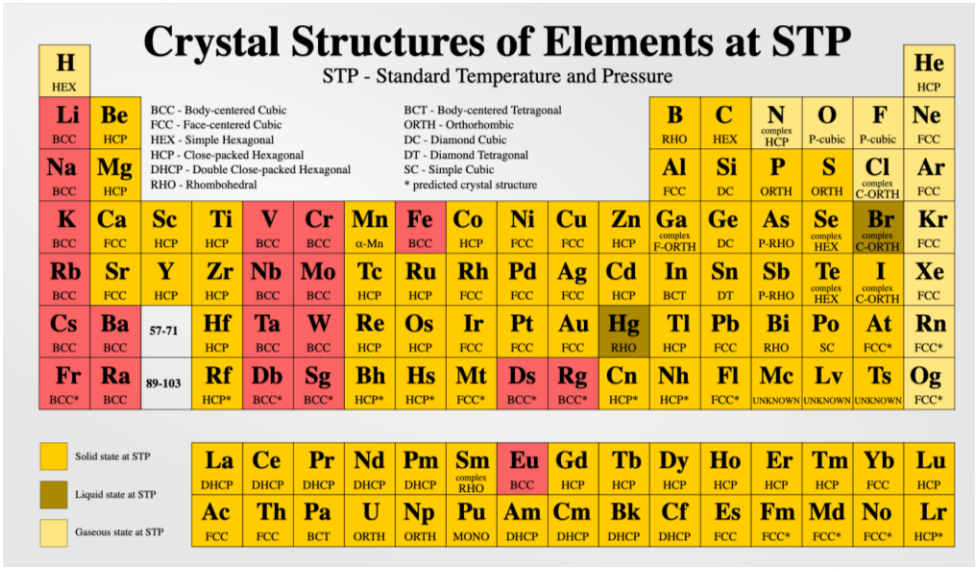
FCC and BCC

- very common crystal structure, for example for single element crystals
- a lot of metals crystalize in fcc or bcc

fcc



bcc



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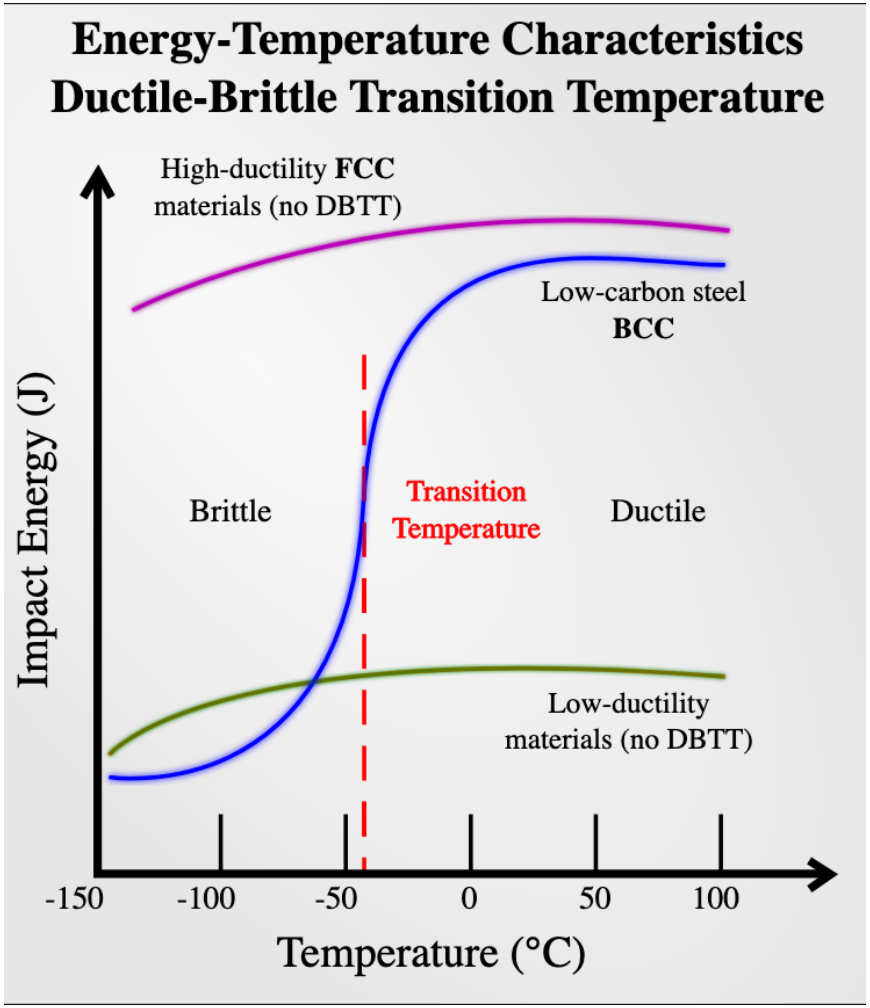
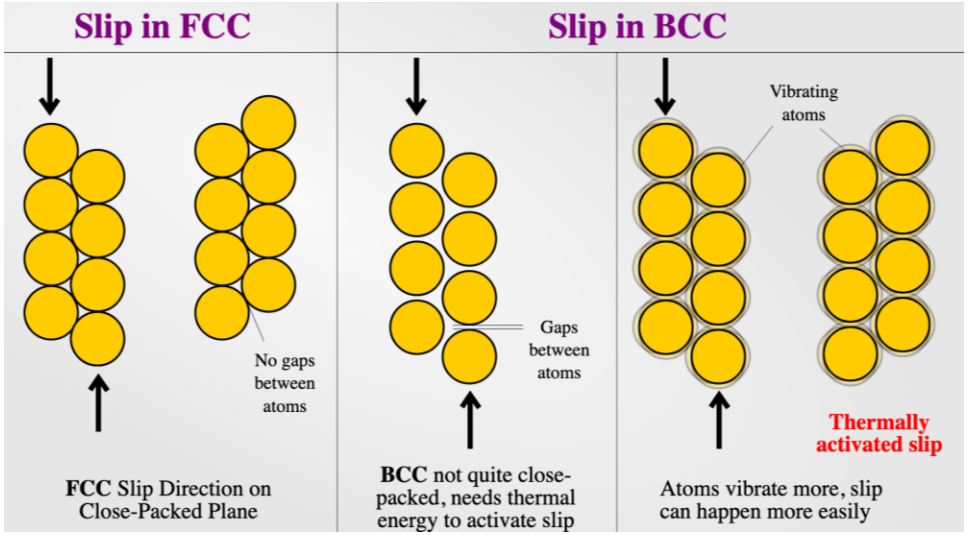
Structure → Property!



FCC metals tend to be more ductile than BCC metals because of their different slip system

BCC metals have a ductile-to-brittle transition



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Packing density

- Represent motif as rigid spheres (hard sphere model) to give insight about the atomic arrangement and resulting properties
  - Packing factor/packing fraction $p = \frac{N_{atoms\ per\ unit\ cell} \times V_{atoms}}{V_{unit\ cell}}$

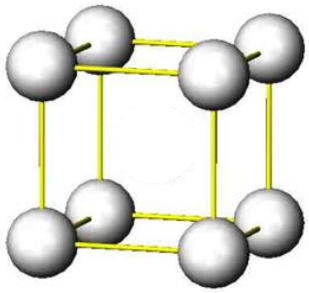
    also called compacity c

  - Density: $\rho = \frac{N_{atoms\ per\ unit\ cell} \times m_{atoms}}{V_{unit\ cell}}$

Packing density

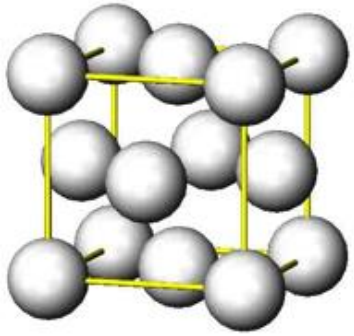
- Represent motif as rigid spheres (hard sphere model) to give insight about the atomic arrangement and resulting properties
  - Packing fraction/packing factor/compacity (last week)

primitive cubic



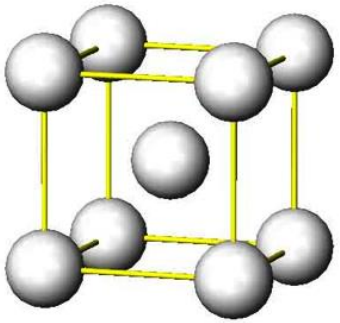
52%

face centered cubic



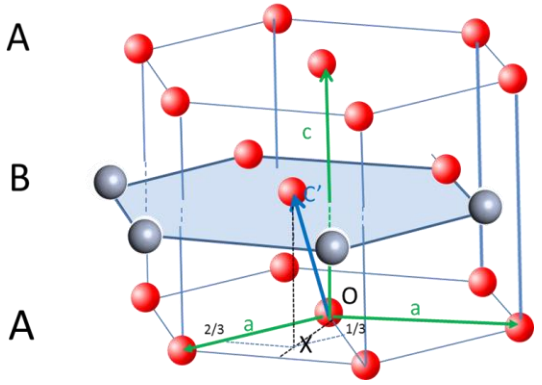
74%

body centered cubic



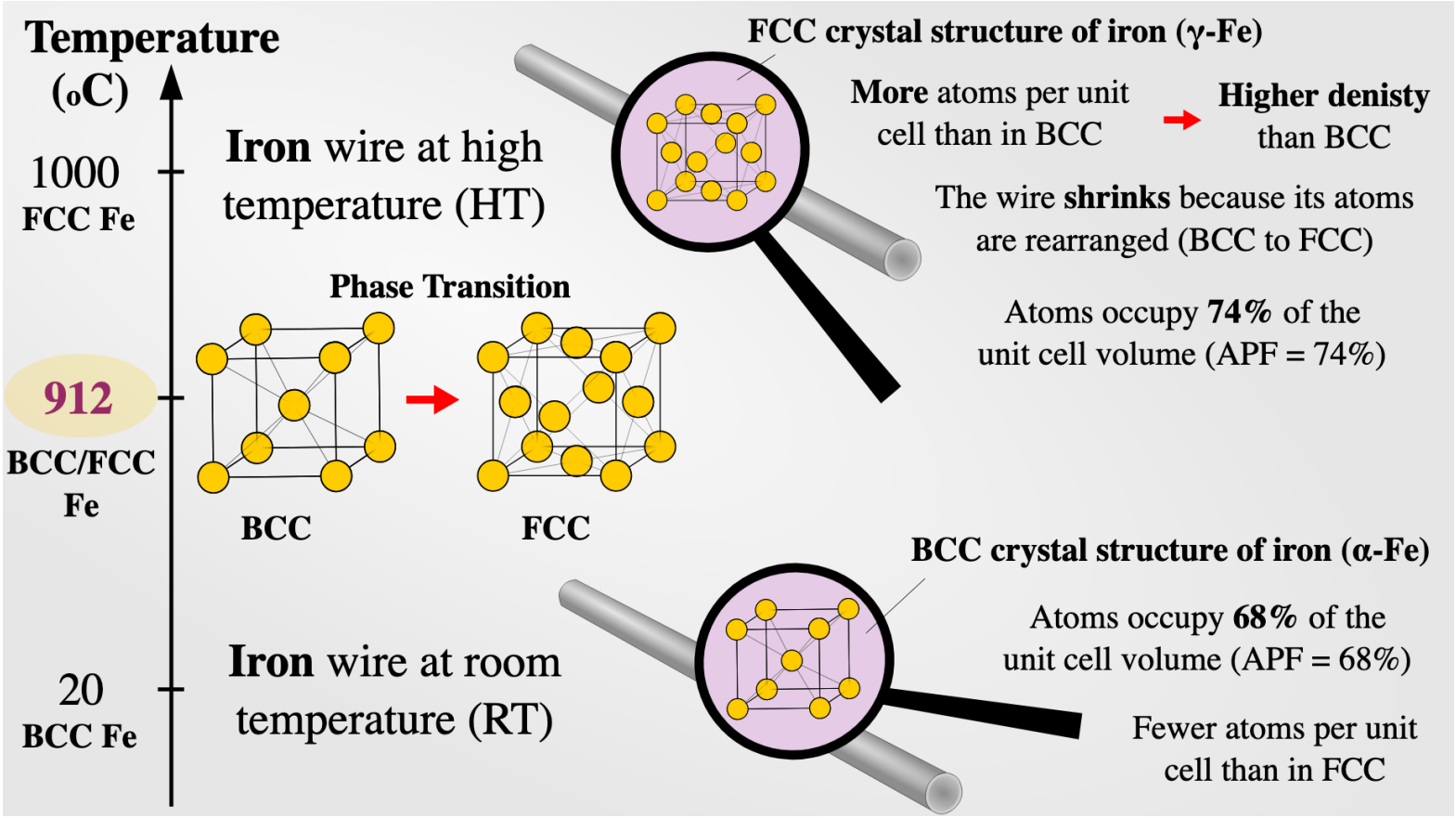
68%

hexagonal closed packed



74%

Polymorphism of Iron



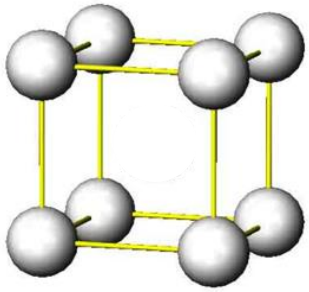
austenite

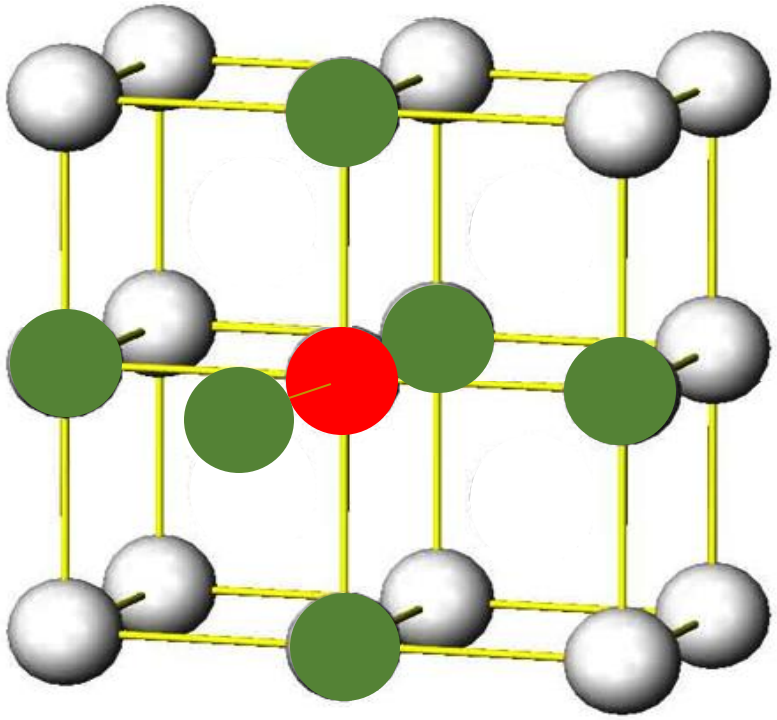
ferrite

Coordination number

- Represent motif as rigid spheres (hard sphere model) to give insight about the atomic arrangement and resulting properties
  - Packing fraction/packing factor/compacity (last week)
  - Density
  - coordination number: number of closest neighbors

for primitive cubic

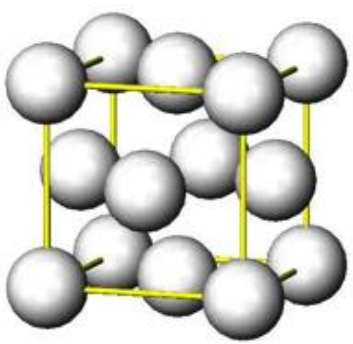


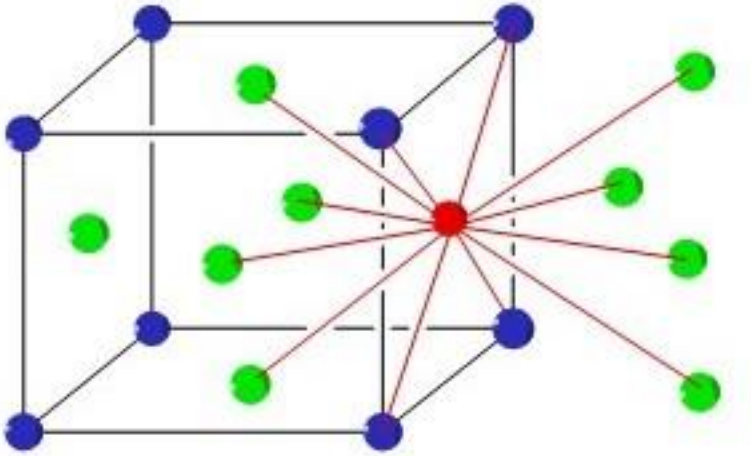


Coordination: 6

Coordination

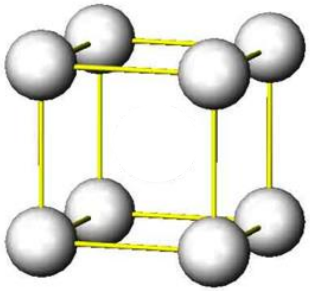
- Face-centered Cubic: Coordination: 12



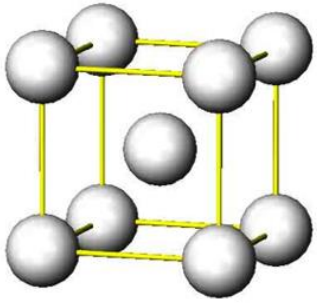


Coordination

- Coordination number:



6



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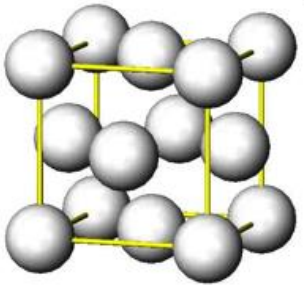
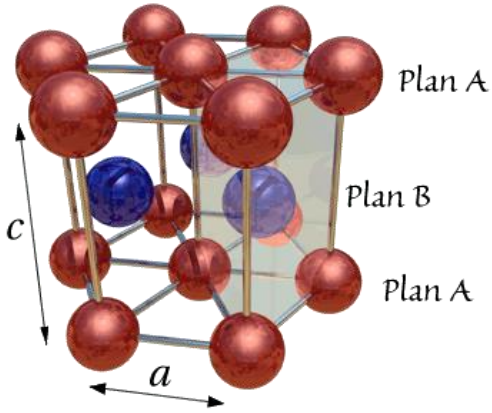


12



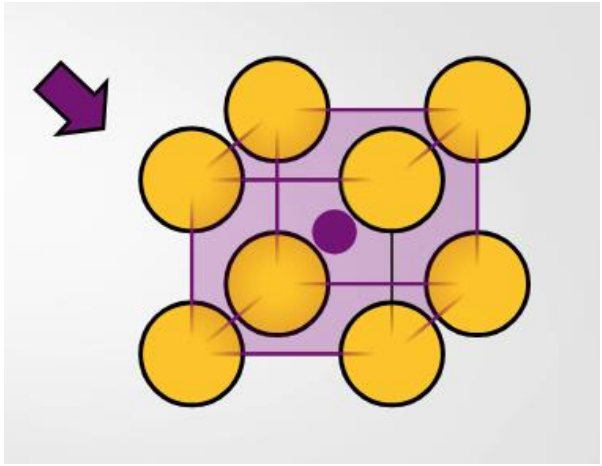
Hexagonal close-packed :

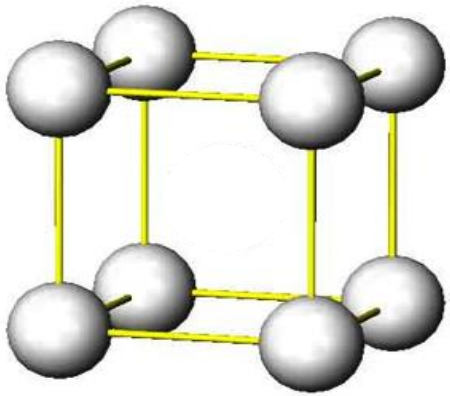
-Coordination: 12

Interstitial Sites

- Crystal structures have a certain packing density, and hence also a free volume where voids exist called interstitial sites.
- Interstitial sites play a very important role in atomic diffusion, as a material can host another smaller atom as is the case in steel (Fe+C).

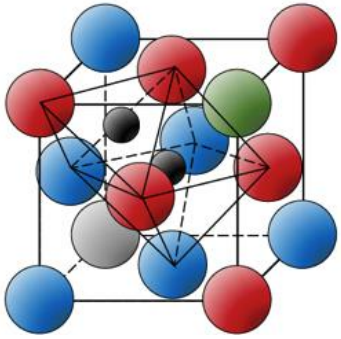
- Primitive cubic:
  - cubic interstitial site in between 8 atoms





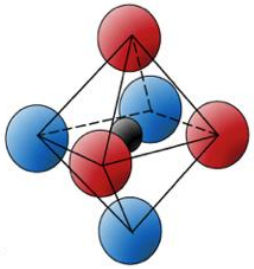
Interstitial Sites

- The FCC structure, has two main interstitial sites:



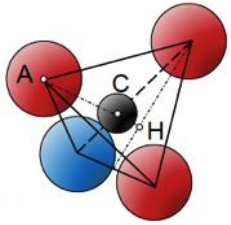
Octahedral: at the center of the conventional cell

Coordination number: 6

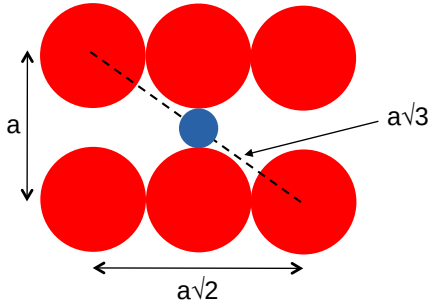


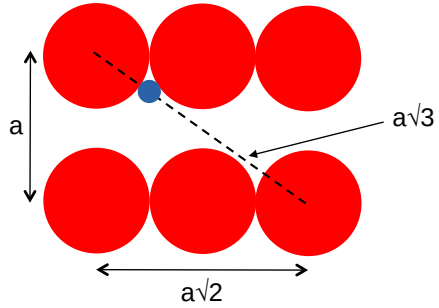
8x Tetrahedral: at 1/4 of the diagonal of the cube

Coordination number: 4



In the planes:





→ Exercise: size comparison of interstital sites in different structures

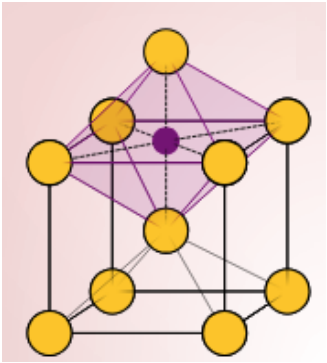
Interstitial Sites

- Interstitial sites in the BCC:

6x Octahedral: centered around each of the six BCC cell faces

e.g. center (1/2,1/2,0)

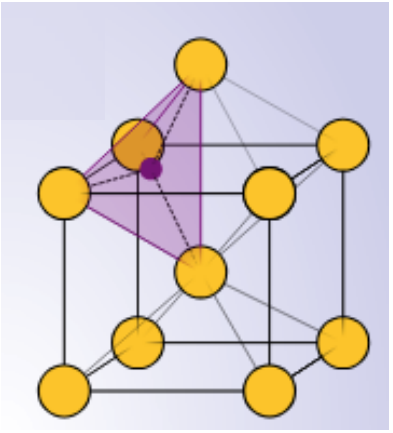
Coordination number: 6



12x Tetrahedral: at midpoint of the edges

e.g. center (1/2,1/4,0)

Coordination number: 4

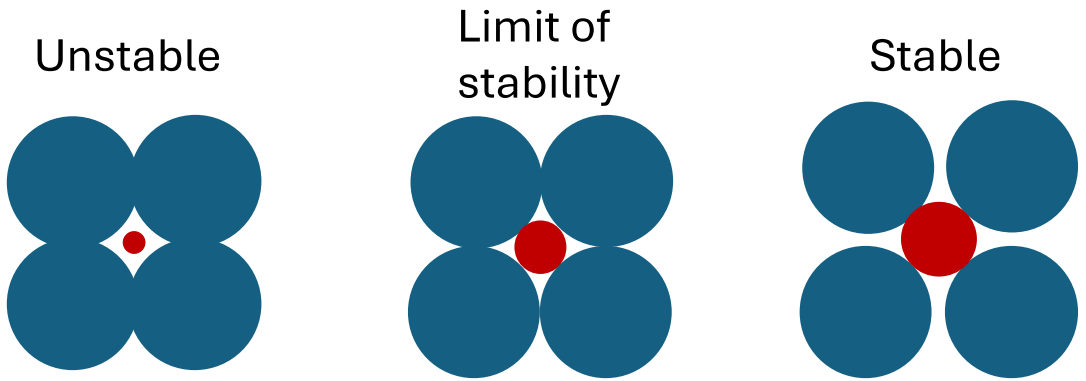


both Octahedral and Tetrahedral sites are irregular!
the coordination atom closer to the interstitial site determine what size can fit

→ Exercise on Iron FCC and BCC

Interstitial Sites: Ionic crystals

- The notion of interstitial sites can also be used to estimate what the crystal structure could be of ionic crystals.
- Different rules exist regarding the relative size of the Anions and the Cations in the molecules and their charges (take valence into account).
- For two atoms (NaCl, ClCs, ZnS etc…), a first rule called the Radius Ratio rule, or first Pauling rule, establishes a formula that defines the coordination number depending on the ratio of the radius of the cation to the one of the anion:
- $\rho = \frac{r_+}{r_-}$
- Based on the hard sphere model, it predicts that if the cation is too small, anions get too close to each other which lead to an unstable structure due to repulsive forces.



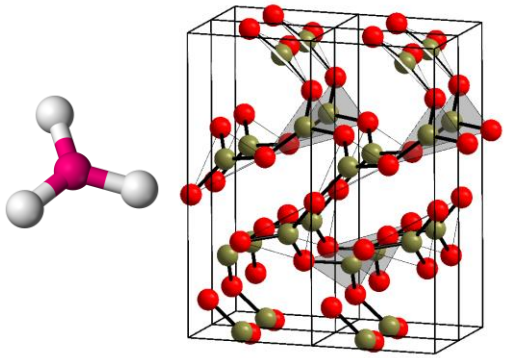
Interstitial Sites: Ionic crystals

At the limit of stability, geometric consideration can give a condition on the ratio to have a certain coordination, in other words a certain number of cations surrounding an anion (and vice versa).

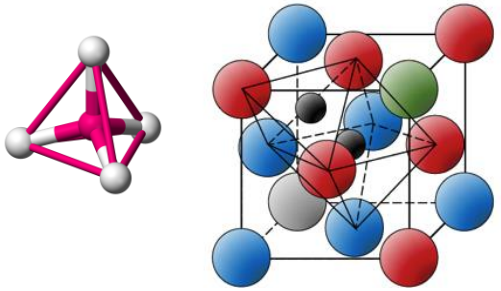
The formula is given by : $\rho = \sqrt{\frac{12}{12-CN}} - 1$, where CN = coordination number

→ Exercise for geometrical consideration

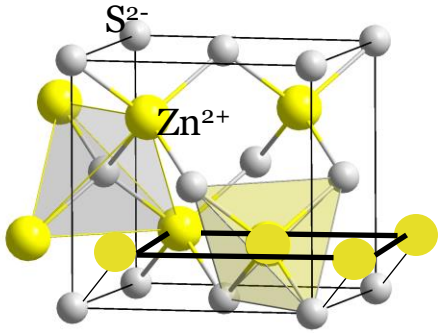
- For $0.1547 < \rho < 0.2247$,
  - $CN = 3$
  - Type of void: triangular planar
  - Example: B_2O_3 (trigonal)



- For $0.2247 < \rho < 0.4142$,
  - $CN = 4$
  - Type of void: Tetrahedral
  - Example: ZnS, CuCl, GaAs



Void in FCC



Zincblende structure

Two interpenetrating FCC structures shifted along ¼ of the diagonal

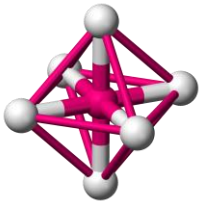
Interstitial Sites: Ionic crystals

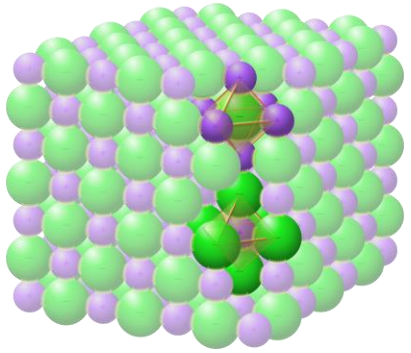
For $0.4142 < \rho < 0.7320$:

$CN = 6$

Type of void: Octahedral

Example: NaCl, MgO



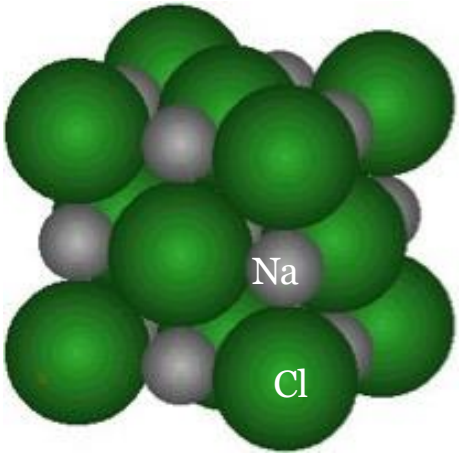


Rock salt structure

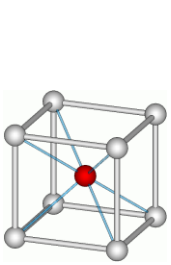
Na Cl

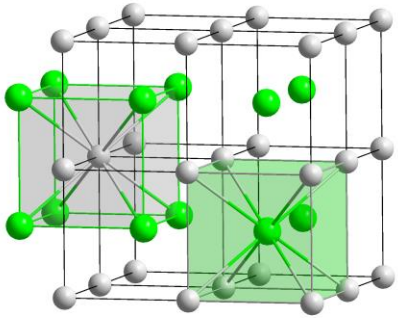
R_{Na+} = 1.02 Å

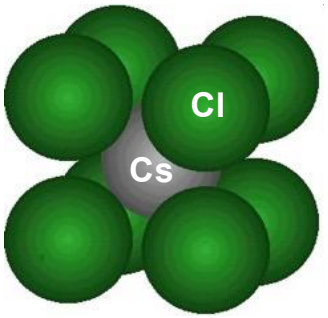
R_{Cl-} = 1.81 Å



- For $0.7320 < \rho < 1$:
  - $CN = 8$
  - Type of void: Cubic
  - Example: CsCl







CsCl structure

Cs Cl

R_{Cs+} = 1.67 Å

R_{Cl-} = 1.81 Å

Ionic crystals

- The ratio rule presented above enables to predict the crystal structure fairly well given its simplicity: in some studies, in a set of over 5000 oxides, 66% of coordination environments agree with Pauling's first rule.
- Many exceptions do exist: Oxides formed with alkali or alkali-earth meta, or cations that contain multiple cation coordination are common deviations from this rule.
- The discrepancy lies also mostly in the polar, and not strictly ionic, nature of bonds inside the crystals.
- There are other rules, such as, for example:
    - The electrostatic valence rule looks at the strength of the electrostatic force as a function of the charge and the coordination number.

Cations with oxide O^{2-} ion

Cation	Radius ratio	Cation C.N.	Electrostatic bond strength	Anion C.N.
Li^{+}	0.34	4	0.25	8
Mg^{2+}	0.47	6	0.33	6
Sc^{3+}	0.60	6	0.5	4

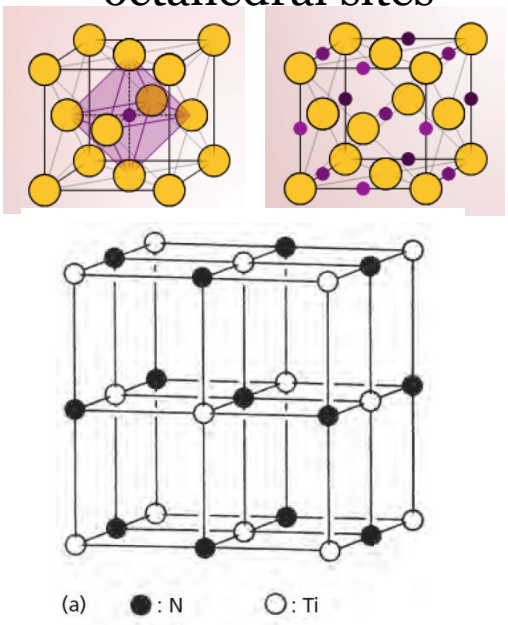
- Other geometric rules exist but they are accurate only in 13% of cases, limiting their use.

Interstitial compounds

- Metal hydrides, nitrides, borides, carbides, etc., in which the radius ratio of the (small) non-metallic atoms to the (large) metal atoms is small, provide good examples of interstitial compounds.
- However usually the interstitial atoms are oversized (in terms of radius ratio) and push apart the structure → not strictly closed packed

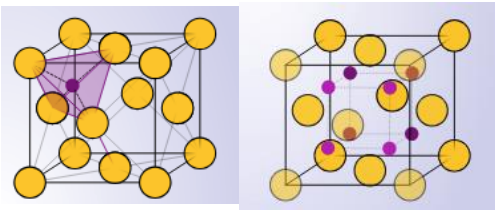
Example: FCC

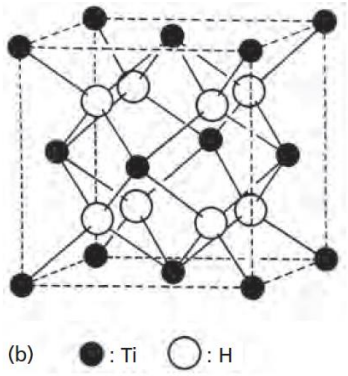
octahedral sites



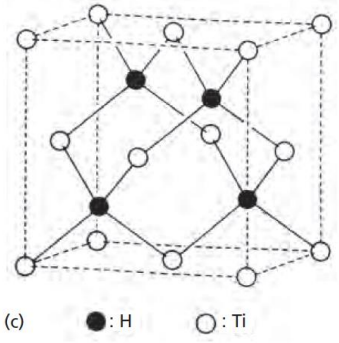
TiN: hard ceramic coating

tetrahedral sites





TiH_2



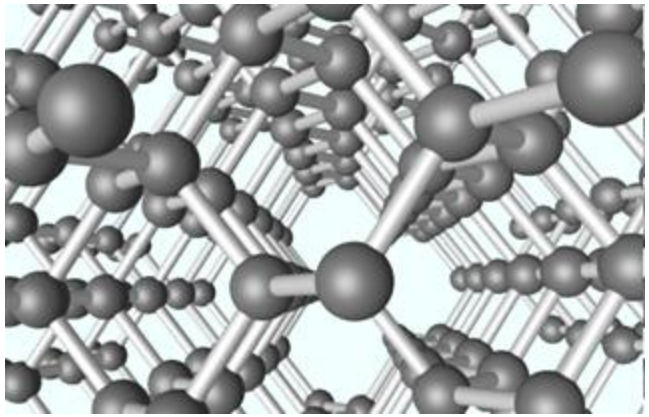
TiH

brittle and hard, powder

Covalent crystals and covalent/ionic crystals

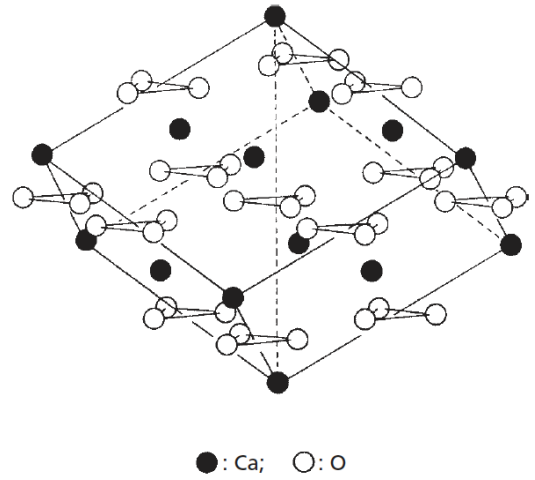
- While ionic crystals and crystals with metallic bonds usually take closed packed forms, the structure of covalent crystals is dictated by the directional covalent bond and the configuration of the atomic orbitals
- high strength of covalent and ionic bonds: high hardness

"pure" covalent crystals:
Diamond, Silicon
sp^3 orbitals → tetrahedrally
coordination number: 4



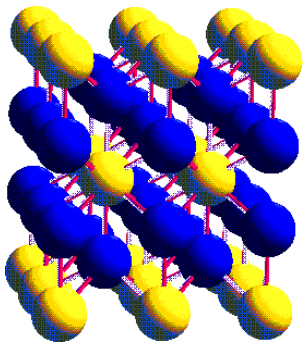
from Exercise week 1:
packing fraction only 34%

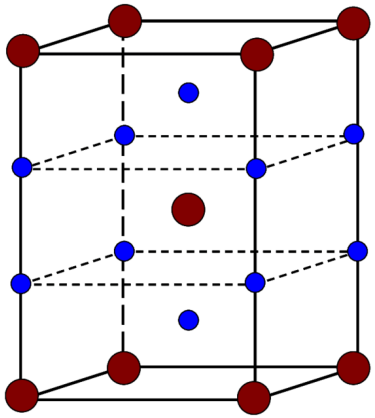
many inorganic crystals
mixture of covalent and ionic bonds
$Ca^+ (CO_3)^-$



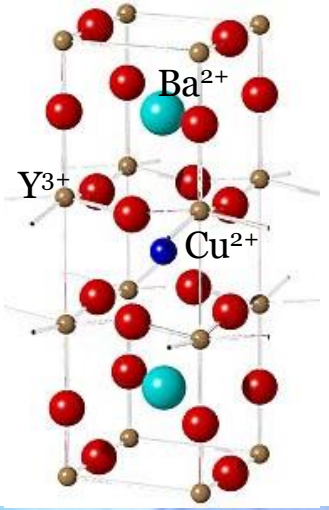
Ceramics

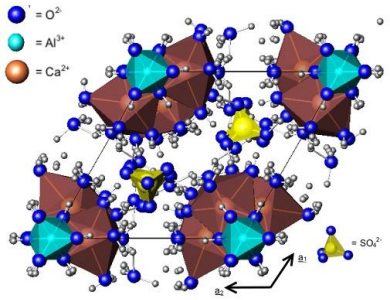
- Ceramics possess ionic or covalent (or polar) bonds that are very strong.
- The structure can be compact like metals but more complex, as it depends on the ionic radius of the different atoms, and their valence.
- As a result, the crystallographic arrangements can be quite complex and they have a **higher ability to be quenched into an amorphous structure.**





$MoSi_2$

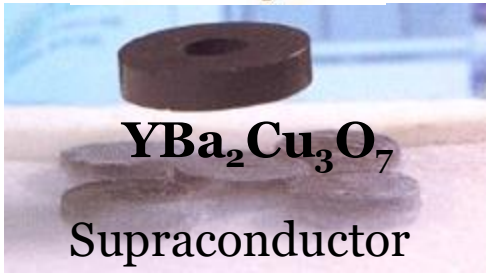




Ettringite structure

structure formed in the early phases of hardening of **cement**

Resistive heating elements



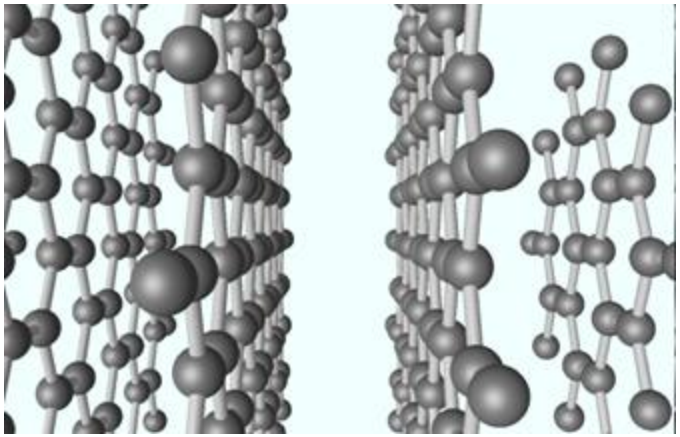
$YBa_2Cu_3O_7$

Supraconductor

Covalent and VDW crystals

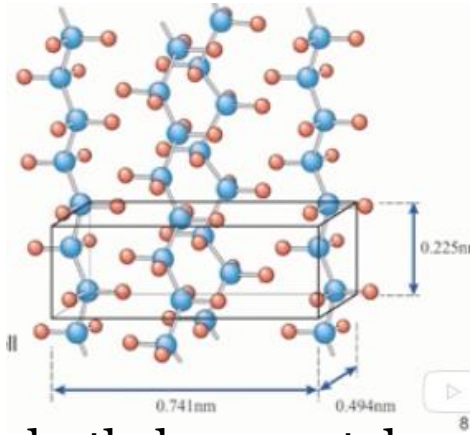
- Layered inorganic structures: covalently bond within a layer, van der Waal bonds between the layers: graphite, talc, mica
- Organic crystal: covalent bonds within molecule, van der Waal (and H-bonds) in between

covalent bond
sp_2 orbital → planar
in between Van der Waal bonds



graphite
→ anisotropic mechanical properties

organic crystals
molecules strongly bond
if they can be arranged regulary form crystal

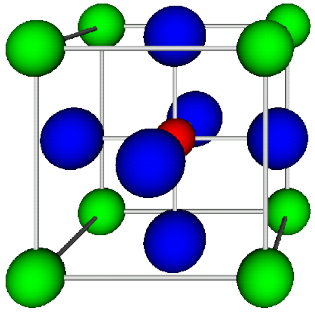


Polyethylene crystal
→ soft materials
→ more in polymer lecture

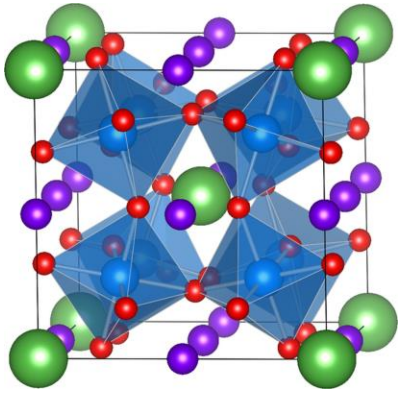
Examples for more complex crystals

Perovskites

ABX3, where:
- **A** is a large cation
- **B** is a smaller metal cation
- **X** is an anion

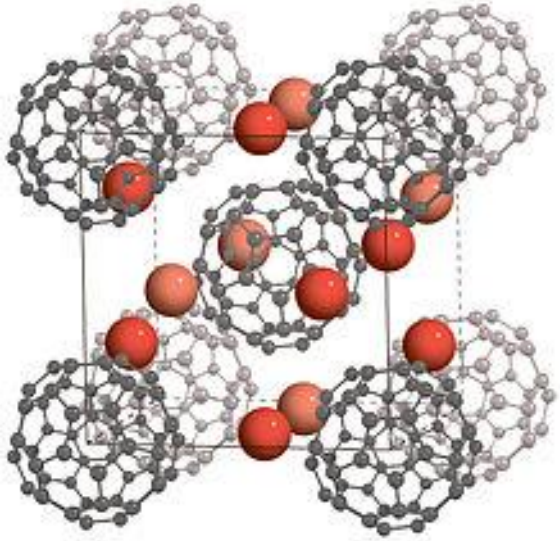


$CaTiO_3$ (Ca=green, O=blue, Ti=red)



Double perovskite structure $AA'_3B_4O_{12}$.

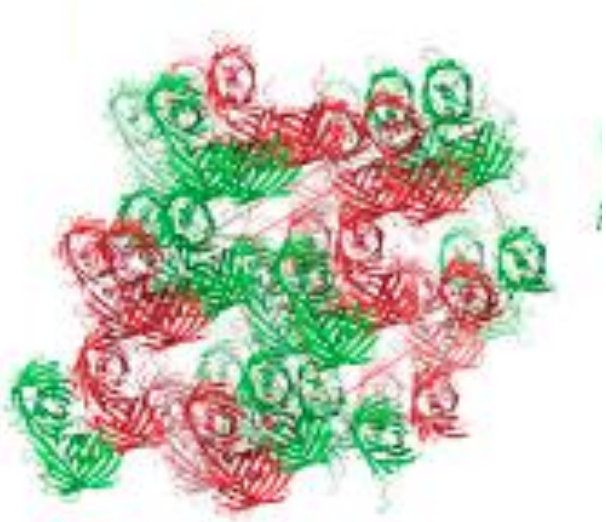
Molecular crystals



alkaline-metal-doped fullerenes such as Cs_3C_{60} crystals superconductive at 33K

http://en.wikipedia.org/wiki/Buckminsterfullerene

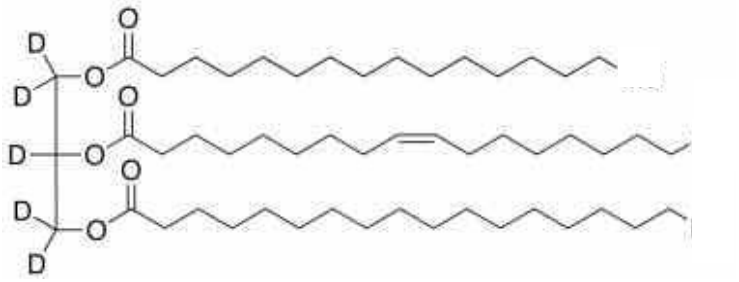
Protein crystal



photoactivatable fluorescent protein h41pkve6

Organic crystal: Chocolate

polymorphism of Triacylglycerol (= cocoa butter)



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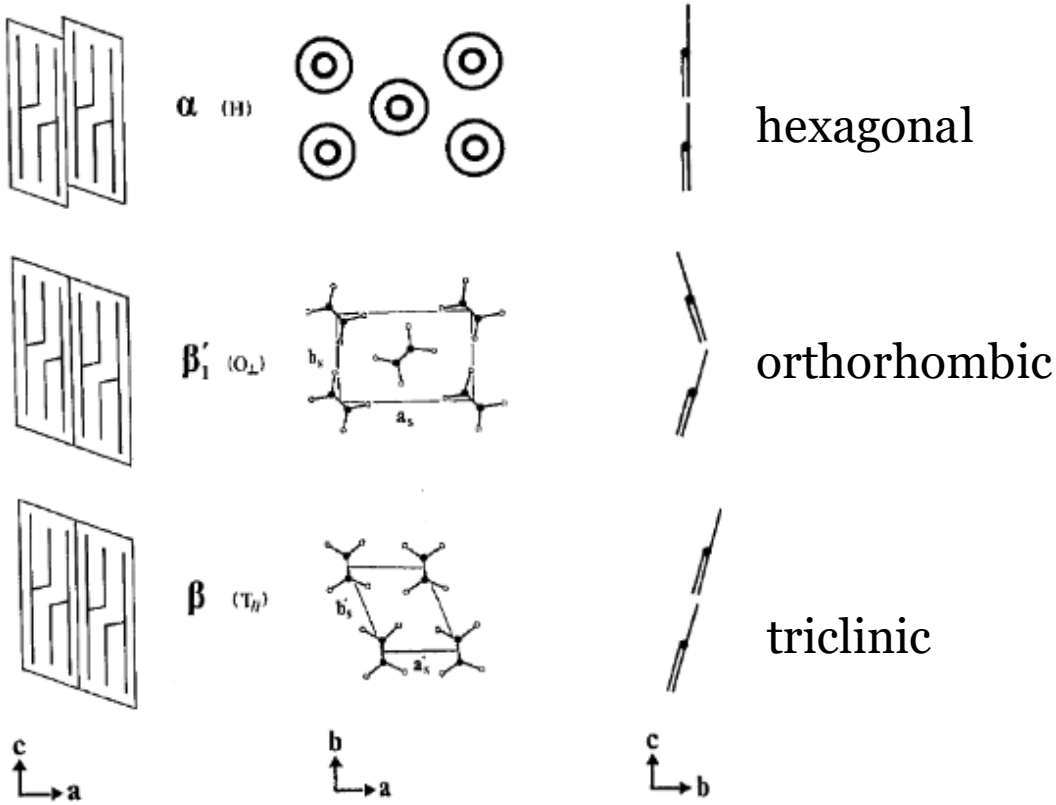
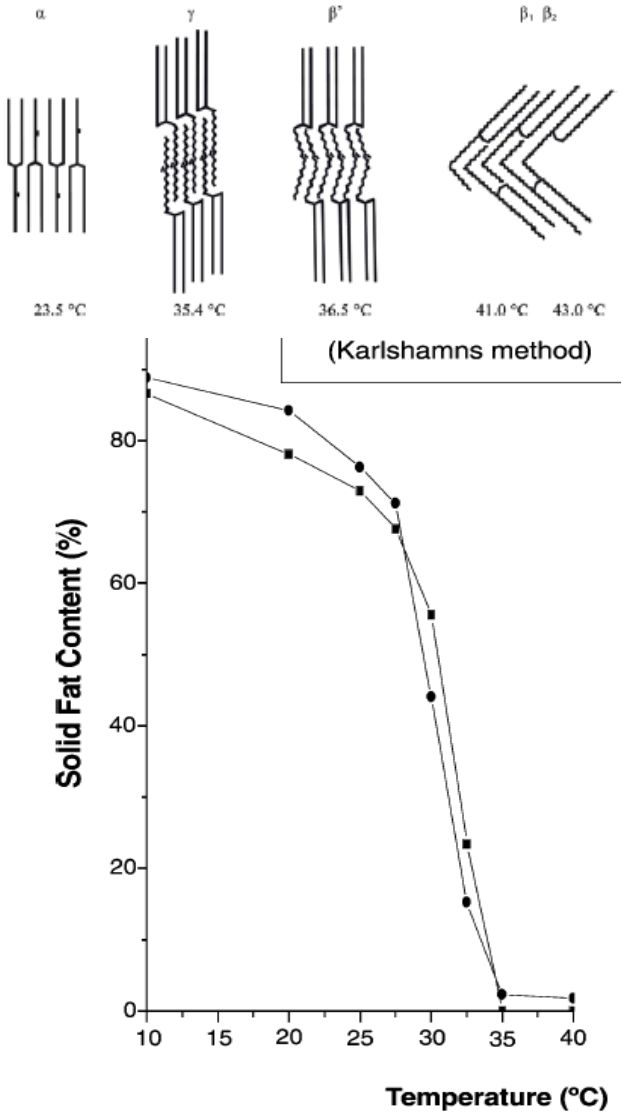


Chocolate

- cacao butter, main component POS and many other triglycerides
- polymorphism: 6 different crystalline forms: γ, α, III, β_{IV}, β_V, β_{VI}
- β_V: desired form due to melting behaviour, gloss, texture and breaking behaviour
  BUT: is not the thermodynamically most stable form
- fat bloom related to recrystallization
  $\beta_V \rightarrow \beta_{VI}$ transition



Summary

- Definition of crystal, lattice and motif
- first introduction to symmetry, crystal systems and Bravais Lattice
  →main topic for next week!
- The cubic system with its three Bravais lattice (primitive cubic, bcc, fcc)
- primitive vs. conventional cells
- Coordination number
- Interstitial Sites
- Ionic crystal and the radius ratio rule
- Covalent crystals