Crystallography - Structure of metals

Which orders are established?

41680 Introduction to advanced materials

κρυσταλλος	ice
κρυος	icy, frozen

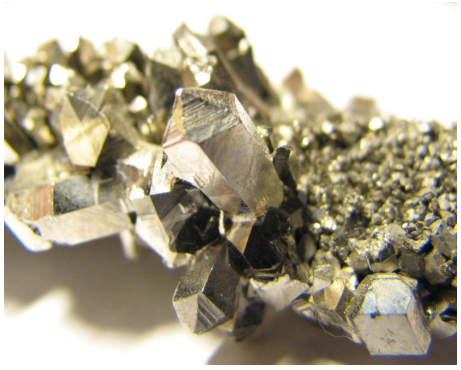
Is

$CuSO_4$

NaCl

DTU Construct
Department of Civil and Mechanical Engineering

Metal crystals

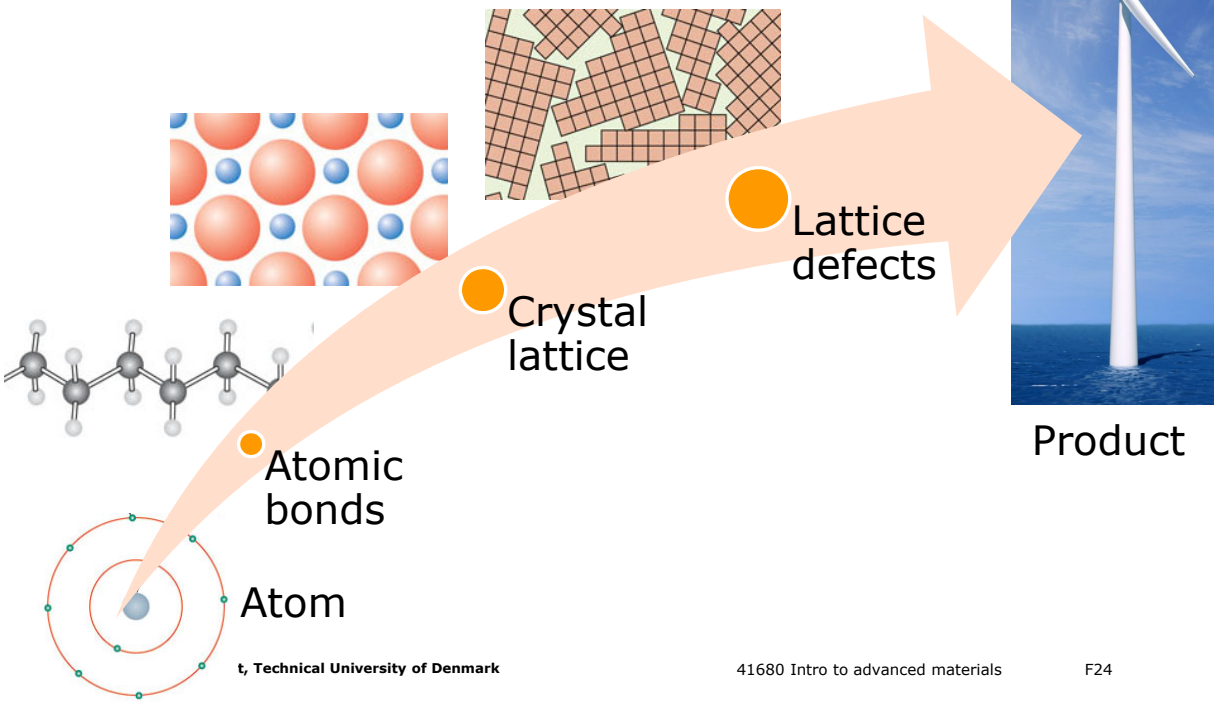


Nb

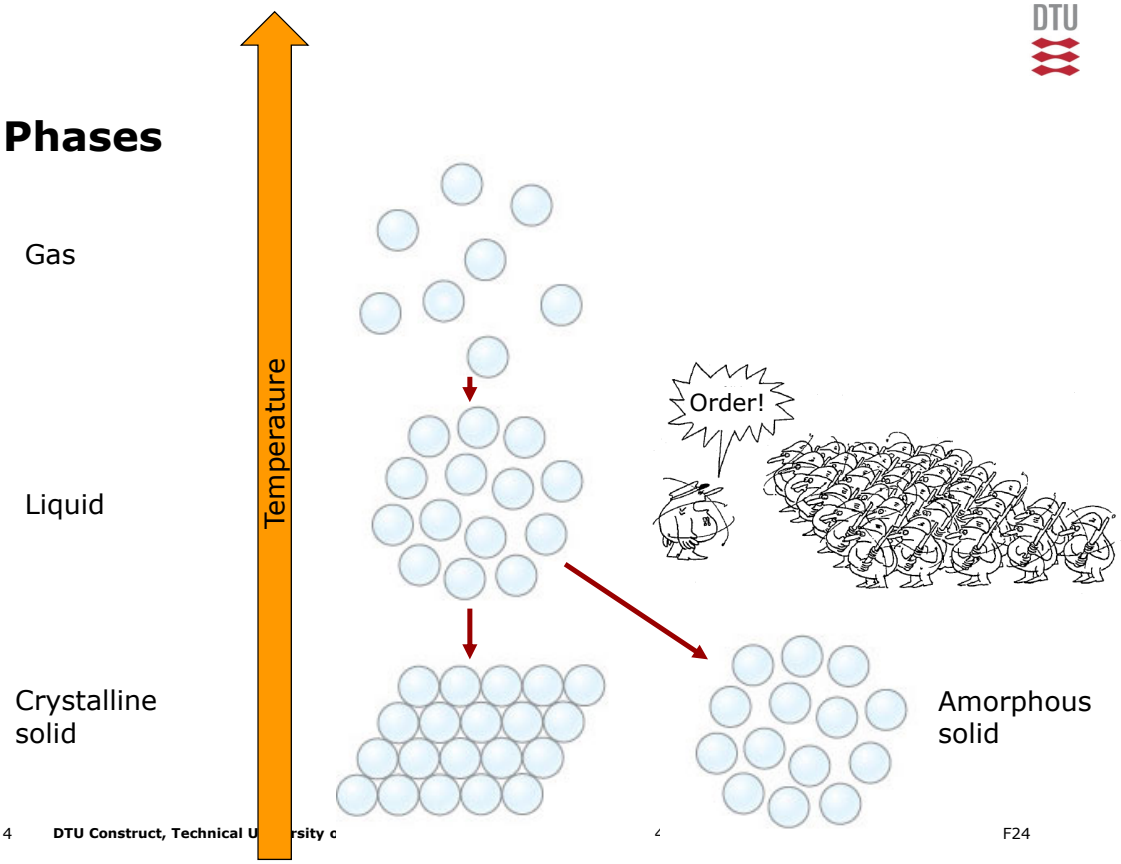
Bi

Pd

Advanced materials
Atoms - Microstructure - Properties

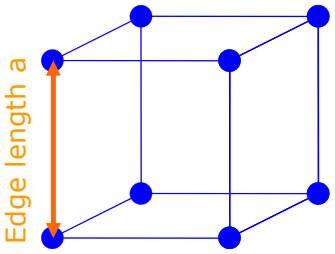


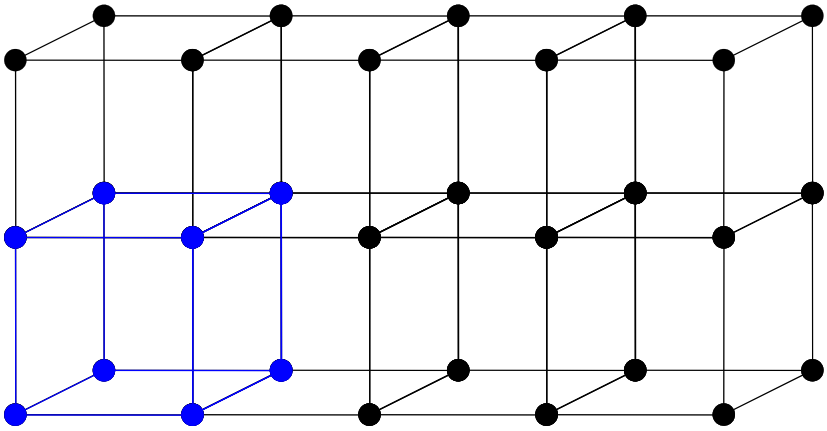
Phases



Crystal structure

- Periodic arrangement of many atoms in 3D
- Regular order on short **and** long ranges
- **Crystalline lattice (many unit cells)**

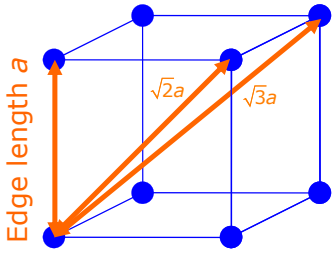


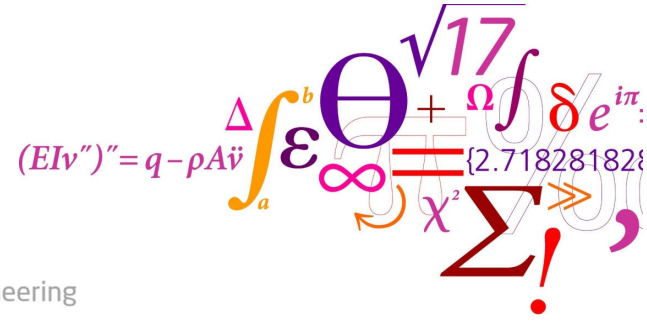


Building block: Unit cell

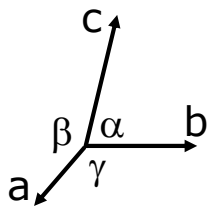
Lattice constant or *lattice parameter*: Edge length of unit cell

Crystalline lattices



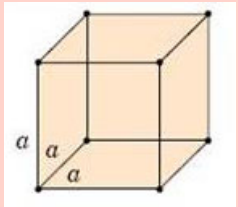
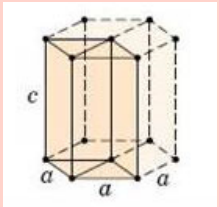
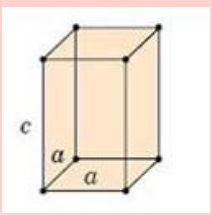
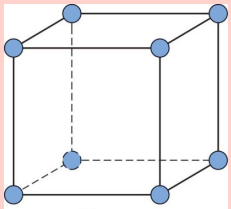
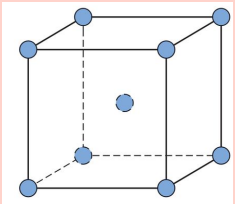
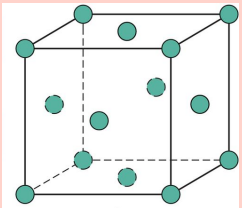


Crystal structures
7 crystal systems

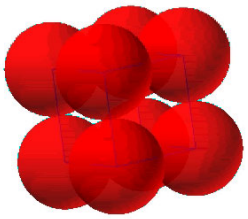


Crystal System	Axial Relationships	Interaxial Angles	Unit Cell Geometry
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	
Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	

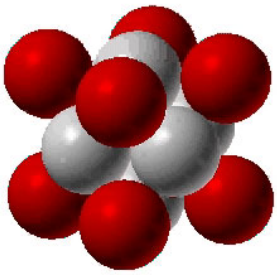
Crystal structures
Relevant Bravais lattices

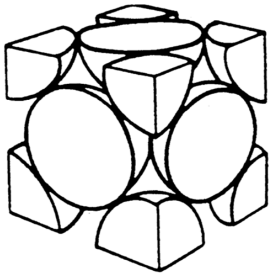
Cubic system	Hexagonal system	Tetragonal system
		
Simple cubic (sc)	**Body-centered cubic (bcc)**	**Face-centered cubic (fcc)**
		

Cubic lattices – primitive and non-primitive unit cells

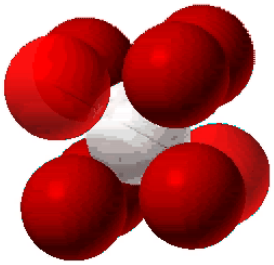


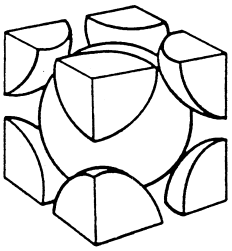
simple cubic (sc)





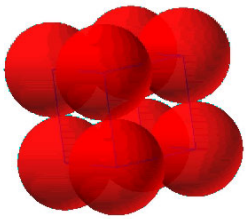
face-centered cubic (fcc)



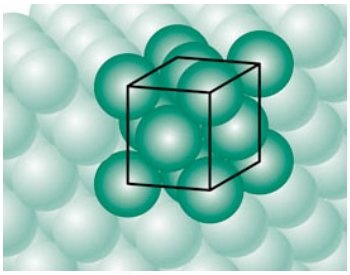


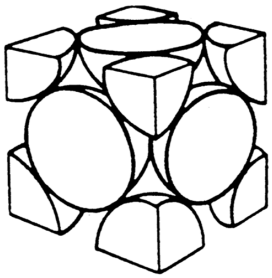
body-centered cubic (bcc)

Cubic lattices – primitive and non-primitive unit cells

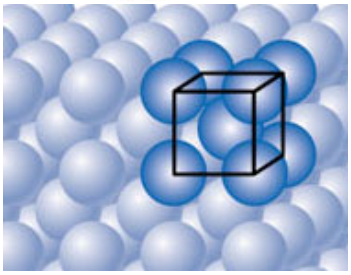


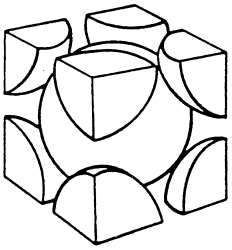
simple cubic (sc)



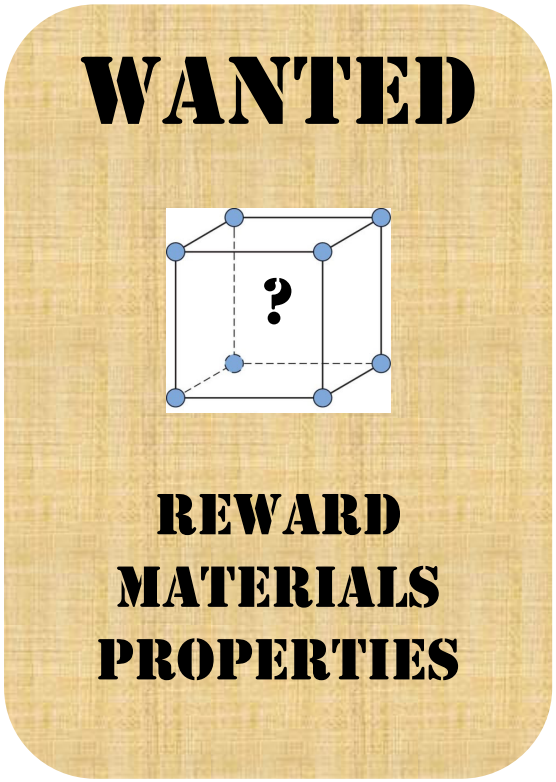


face-centered cubic (fcc)

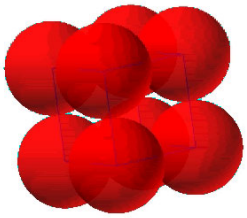




body-centered cubic (bcc)

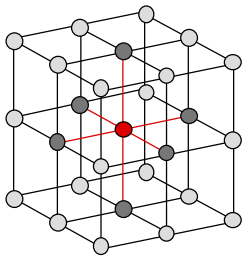


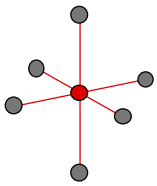
Simple cubic lattice (primitive cubic lattice)



- Hard sphere model
- Close-packed direction <100>
- Atomic packing factor

$$APF = \frac{\text{Volume of atoms}}{\text{Volume unit cell}} = \frac{N_{at}\left[\frac{4\pi}{3}R_{at}^3\right]}{a^3} = \frac{8\frac{1}{8}\left[\frac{4\pi}{3}\left(\frac{a}{2}\right)^3\right]}{a^3} = \frac{\pi}{6} \approx 0.52$$





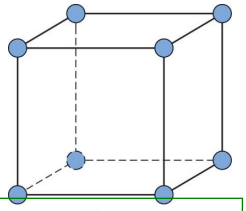
- Number of atoms in unit cell

$$N_{at} = 8\frac{1}{8} = 1$$

- Number of nearest neighbors (Coordination number)

6

Wanted
Simple cubic lattice



I
- Atoms in unit cell
- Coordination number (# nearest neighbors)

III
- Ratio between edge length and atomic radius

  $a/R =$
- Atomic packing factor

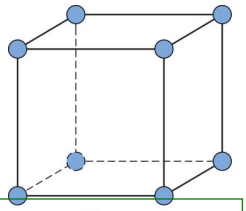
  $APF =$
- Closest packed direction

  < >
- Closest packed planes

  { }
  - ○ Close-packed
  - ○ Not close-packed

II
- Along edges
  - ○ Atoms touch each other
  - ○ Atoms do not touch each other
    - – Distance between centers
    - – Distance between neighbors
- Along face diagonals
  - ○ Atoms touch each other
  - ○ Atoms do not touch each other
    - – Distance between centers
    - – Distance between neighbors
- Along volume diagonals
  - ○ Atoms touch each other
  - ○ Atoms do not touch each other
    - – Distance between centers
    - – Distance between neighbors

Wanted
Simple cubic lattice



I
- Atoms in unit cell: 1
- Coordination number (# nearest neighbors): 6

III
- Ratio between edge length and atomic radius

  $a/R = 2$
- Atomic packing factor

  $APF = \pi/6 \approx 0.52$
- Closest packed direction

  <100>
- Closest packed planes

  {100}
  - ○ Close-packed
  - ☒ Not close-packed

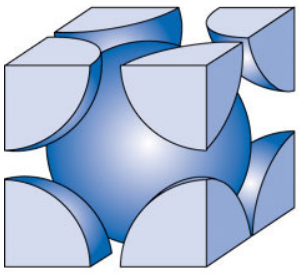
II
- Along edges
  - ☒ Atoms touch each other
  - ○ Atoms do not touch each other
    - – Distance between centers: a
    - – Distance between neighbors: 0
- Along face diagonals
  - ○ Atoms touch each other
  - ☒ Atoms do not touch each other
    - – Distance between centers: $\sqrt{2}a$
    - – Distance between neighbors: $\sqrt{2}a - 2R$
- Along volume diagonals
  - ○ Atoms touch each other
  - ☒ Atoms do not touch each other
    - – Distance between centers: $\sqrt{3}a$
    - – Distance between neighbors: $\sqrt{3}a - 2R$

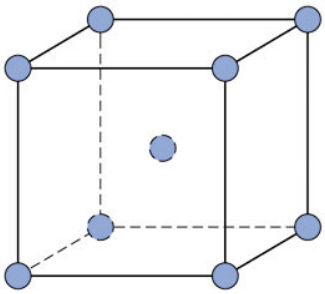
Cubic lattices - comparison

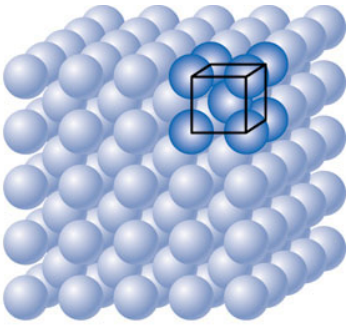
	*	Close-packed direction	Neighbor closest to origin	Atomic dia-meter 2*R*	Atomic packing factor	Coordi-nation number	Examples
sc	1	<100>	[100]*a*	*a*	0.52	6	only α-Po
bcc							
fcc							

* Number of atoms in unit cell Lattice parameter *a*

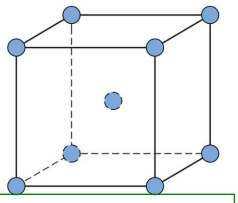
Body-centered cubic lattice







Wanted
Body-centered cubic lattice



I
- Atoms in unit cell
- Coordination number (# nearest neighbors)

III
- Ratio between edge length and atomic radius

  $a/R =$
- Atomic packing factor

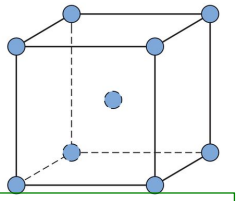
  $APF =$
- Closest packed direction

  < >
- Closest packed planes

  { }
  - ○ Close-packed
  - ○ Not close-packed

II
- Along edges
  - ○ Atoms touch each other
  - ○ Atoms do not touch each other
    - – Distance between centers
    - – Distance between neighbors
- Along face diagonals
  - ○ Atoms touch each other
  - ○ Atoms do not touch each other
    - – Distance between centers
    - – Distance between neighbors
- Along volume diagonals
  - ○ Atoms touch each other
  - ○ Atoms do not touch each other
    - – Distance between centers
    - – Distance between neighbors

Wanted
Body-centered cubic lattice



I
- Atoms in unit cell: 2
- Coordination number (# nearest neighbors): 8

III
- Ratio between edge length and atomic radius

  $a/R = 4/\sqrt{3}$
- Atomic packing factor

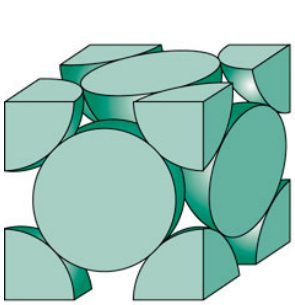
  $APF = 2\frac{4\pi}{3}\left(\frac{\sqrt{3}}{4}\right)^3 = \frac{\pi\sqrt{3}}{8} \approx 0.68$
- Closest packed direction

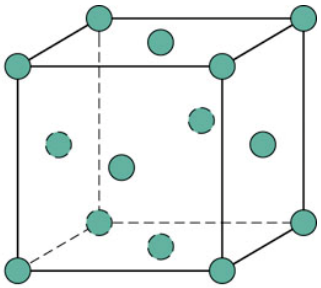
  <111>
- Closest packed planes

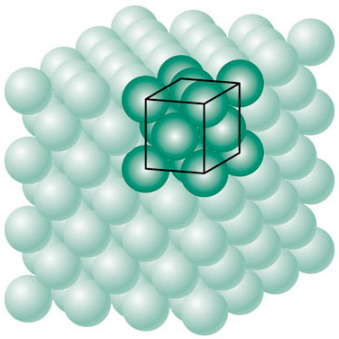
  {110}
  - ○ Close-packed
  - ☒ Not close-packed

II
- Along edges
  - ○ Atoms touch each other
  - ☒ Atoms do not touch each other
    - – Distance between centers: a
    - – Distance between neighbors: $a - 2R$
- Along face diagonals
  - ○ Atoms touch each other
  - ☒ Atoms do not touch each other
    - – Distance between centers: $\sqrt{2}a$
    - – Distance between neighbors: $\sqrt{2}a - 2R$
- Along volume diagonals
  - ☒ Atoms touch each other
  - ○ Atoms do not touch each other
    - – Distance between centers: $\sqrt{3}a/2$
    - – Distance between neighbors: 0

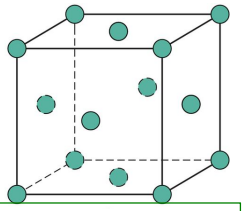
Face-centered cubic lattice







Wanted
Face-centered cubic lattice



I
- Atoms in unit cell
- Coordination number (# nearest neighbors)

III
- Ratio between edge length and atomic radius

  $a/R =$

- Atomic packing factor

  $APF =$

- Closest packed direction

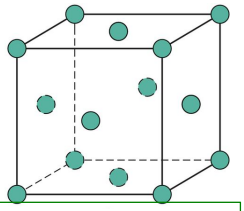
  < >

- Closest packed planes

  { }
  - Close-packed
  - Not close-packed

II
- Along edges
  - Atoms touch each other
  - Atoms do not touch each other
    - Distance between centers
    - Distance between neighbors
- Along face diagonals
  - Atoms touch each other
  - Atoms do not touch each other
    - Distance between centers
    - Distance between neighbors
- Along volume diagonals
  - Atoms touch each other
  - Atoms do not touch each other
    - Distance between centers
    - Distance between neighbors

Wanted
Face-centered cubic lattice



I

- Atoms in unit cell: 4
- Coordination number (# nearest neighbors): 12

III

- Ratio between edge length and atomic radius

$$a/R = 4/\sqrt{2}$$

- Atomic packing factor

$$APF = 4\frac{4\pi}{3}\left(\frac{\sqrt{2}}{4}\right)^3 = \frac{\pi\sqrt{2}}{6} \approx 0.74$$

- Closest packed direction: <110>
- Closest packed planes: {111}
  - [x] Close-packed
  - [ ] Not close-packed

II

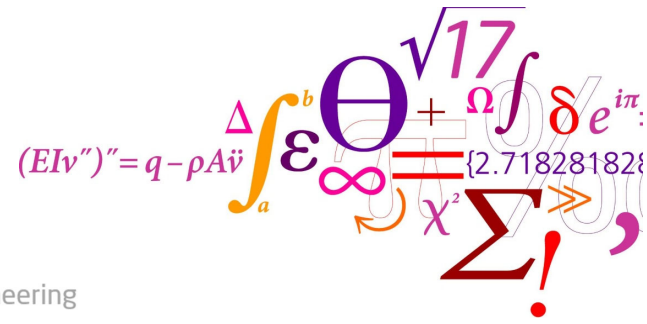
- Along edges
  - [ ] Atoms touch each other
  - [x] Atoms do not touch each other
    - Distance between centers: a
    - Distance between neighbors: $a - 2R$
- Along face diagonals
  - [x] Atoms touch each other
  - [ ] Atoms do not touch each other
    - Distance between centers: $\sqrt{2}a/2$
    - Distance between neighbors: 0
- Along volume diagonals
  - [ ] Atoms touch each other
  - [x] Atoms do not touch each other
    - Distance between centers: $\sqrt{3}a$
    - Distance between neighbors: $\sqrt{3}a - 2R$

DTU

Atomic packing and density

Can the mass density of a material be obtained by dividing the atomic mass be the atomic volume?

$$\rho_{theo} = \frac{m_{at}}{V_{at}}$$



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Masse density

1. Naïve idea

$$\rho_{theo} = \frac{m_{at}}{V_{at}} = \frac{m_{at}}{\frac{4\pi}{3} R_{at}^3} \text{ ???}$$

2. Crystalline lattice

$$\rho = \frac{N_{at} m_{at}}{V_{unitcell}} = \frac{N_{at} m_{at}}{a^3}$$

3. Atomic packing factor

$$APF = \rho / \rho_{theo}$$

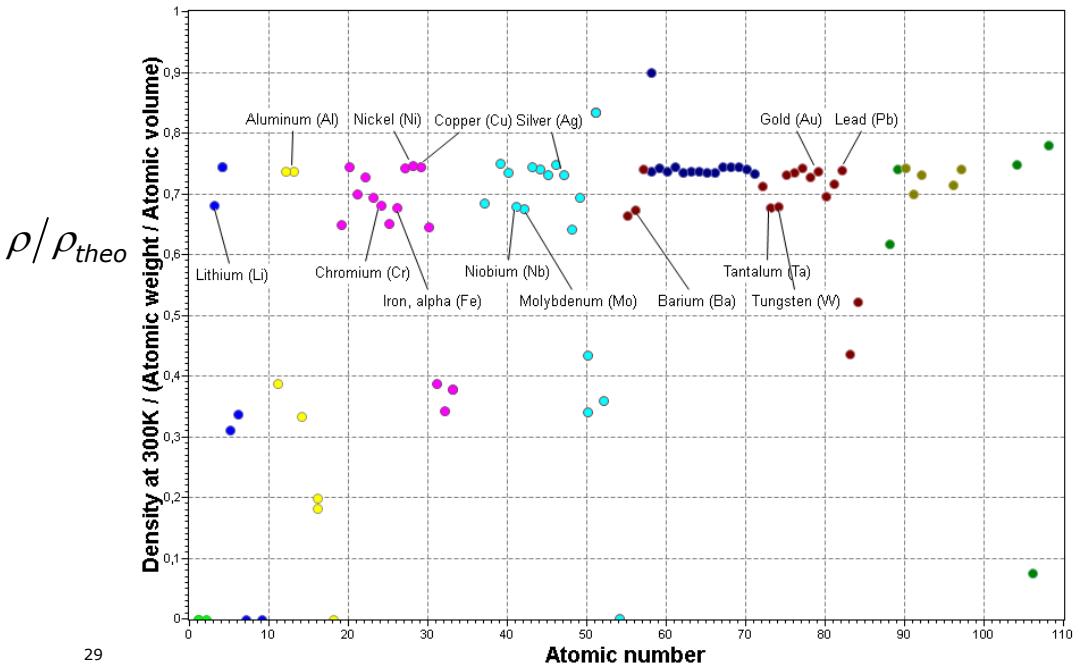
m_{at} atomic mass
V_{at} atomic volume
R_{at} atomic radius
N_{at} number of atoms in cell
a edge length of unit cell
ρ_{theo} theoretical density
ρ mass density in lattice

$$m_{at} = \mu / N_A$$

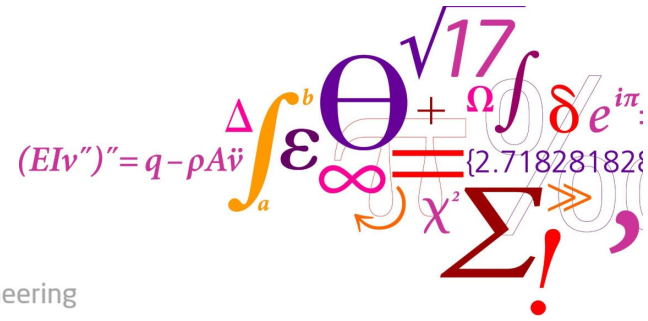
μ molar mass
N_A Avogadro constant

$$\rho = \rho_{theo} = \frac{m_{at}}{V_{at}} = \frac{m_{at}}{\frac{4\pi}{3} R_{at}^3} \text{ ???}$$

Mass density = atomic mass / at. volume ???



Crystallographic notation



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Crystallographic points – notation $n_1n_2n_3$

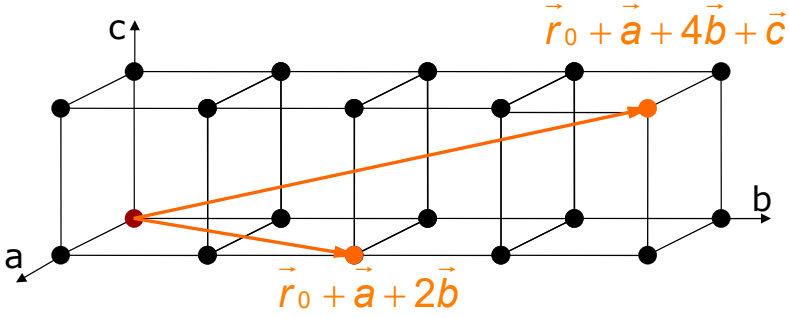
- Point coordinates of atoms (or unit cells)

Atom at origo

$\vec{r}_0 = 0\vec{a} + 0\vec{b} + 0\vec{c}$

All other atoms in crystal lattice

$\vec{r}_n = n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$

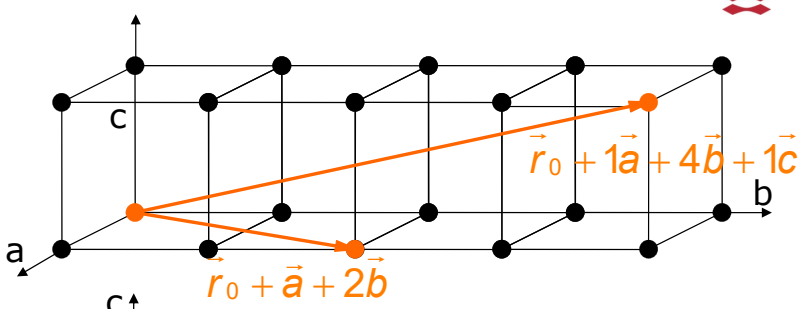


- Translation symmetry
- Unit cell
- n_1, n_2, n_3 integer numbers

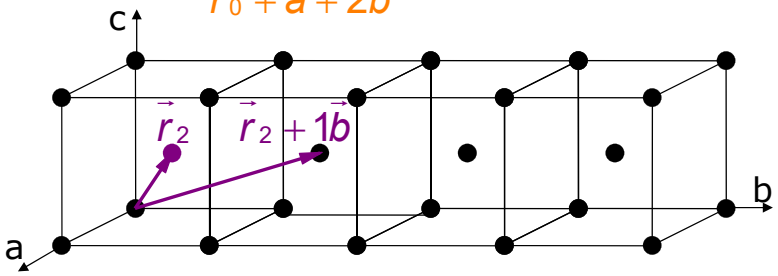
Simple (primitive) unit cell:
Only one atom in unit cell

Crystal structure

$\vec{r}_0 = 0\vec{a} + 0\vec{b} + 0\vec{c}$



$\vec{r}_2 = \frac{1}{2}\vec{a} + \frac{1}{2}\vec{b} + \frac{1}{2}\vec{c}$



crystal: $\vec{r}_n = n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$

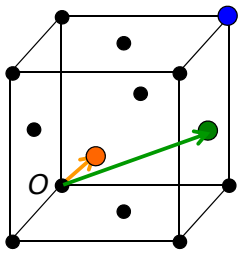
- Translation symmetry
- Unit cell
- n Integer

basis: $\vec{r}_j = x_j\vec{a} + y_j\vec{b} + z_j\vec{c}$

- basis of unit cells
- x,y,z ϵ [0,1] (fractions)

Crystallographic points - exercise

- Find coordinates of the colored points in a face-centered cubic lattice

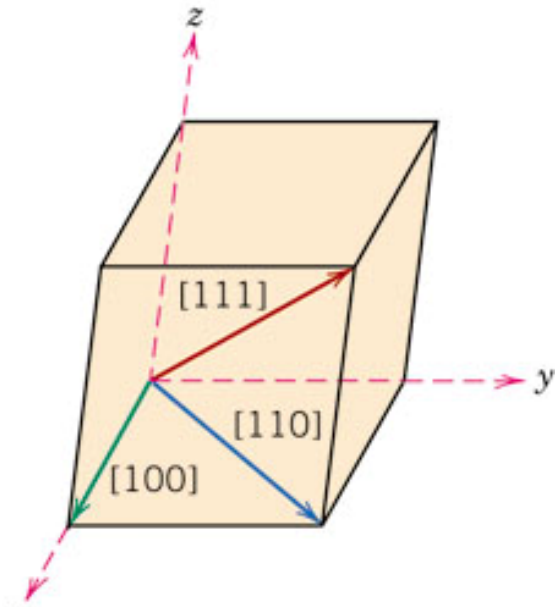


- Find length of the vectors

$$\vec{r} = xa\vec{e}_1 + ya\vec{e}_2 + za\vec{e}_3$$

$$|\vec{r}| = \sqrt{x^2 + y^2 + z^2}\,a$$

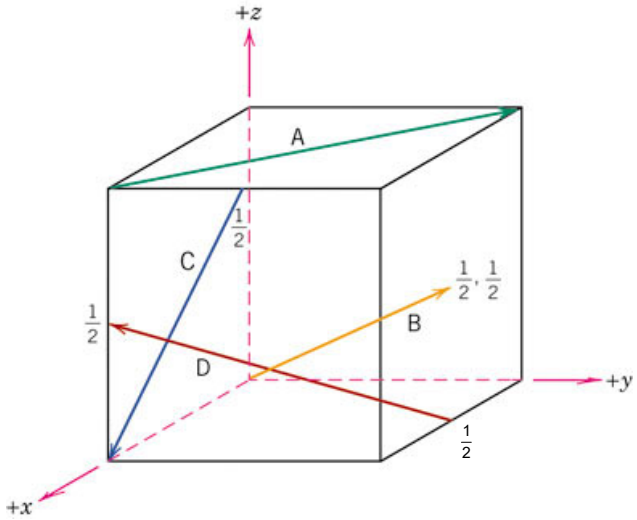
Crystallographic directions – notation [uvw]



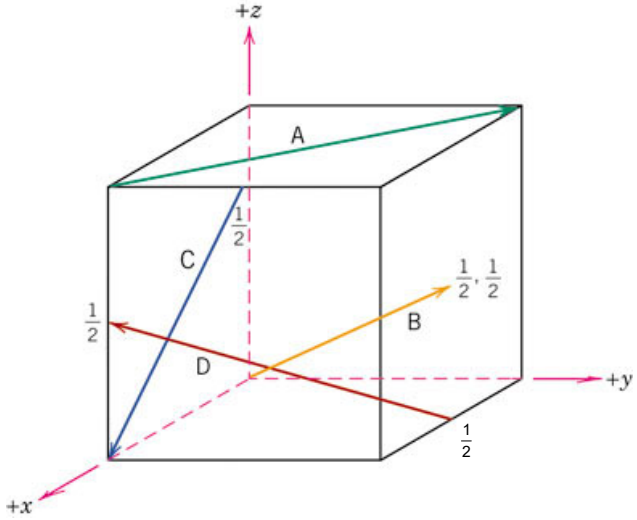
Recipe for crystallographic direction [uvw]

1. Choose origin, typically lower left corner in the back of unit cell. This becomes 000.
2. Draw vector from origin to lattice point as end point in the desired direction.
3. Find the three components of the vector along the three axes of the unit cell (length determined as multiples or fractions of the lattice constants).
4. Re-calculate the resulting components to obtain integers (by multiplication with appropriate numbers).
5. The three integers (indices uvw) are written without separation within square brackets [uvw].

Exercise



Exercise

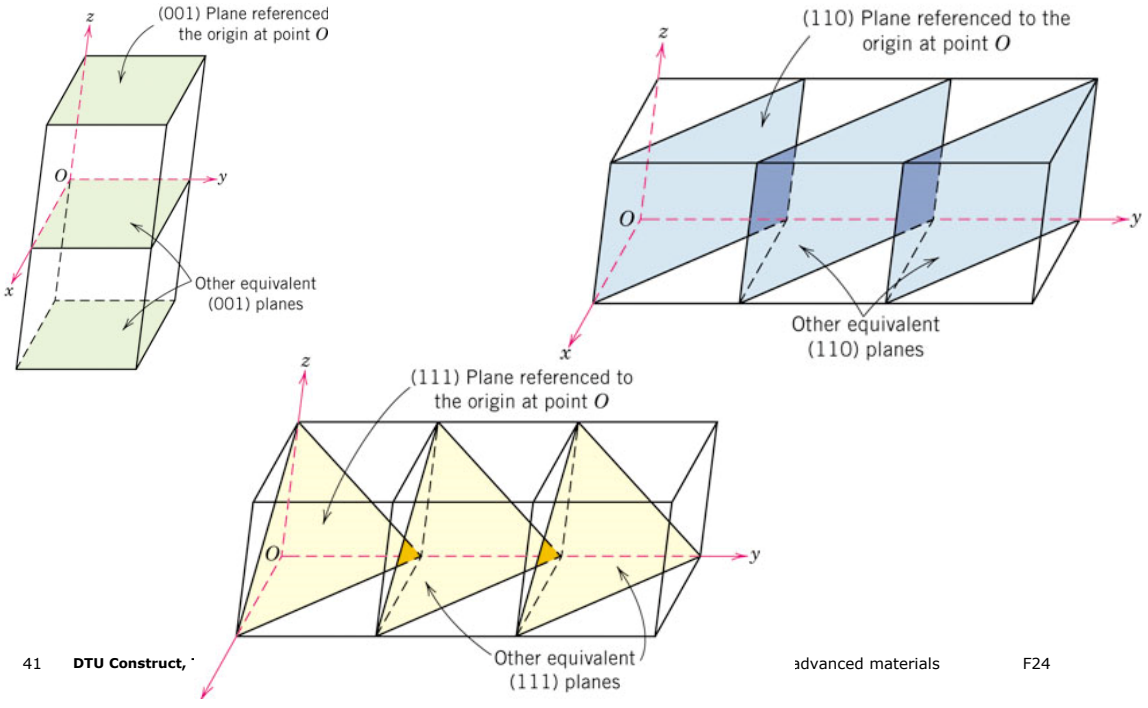


	x	y	z	
A	-1	1	0	$[\bar{1}\,10]$
B integers	½ 1	1 2	½ 1	$[121]$
C integers	0 0	-½ -1	-1 -2	$[0\,\bar{1}\,\bar{2}]$
D integers	½ 1	-1 -2	½ 1	$[1\bar{2}1]$

Recipe for crystallographic direction [uvw]

1. Choose origin, typically lower left corner in the back of unit cell. This becomes 000.
2. Draw vector from origin to lattice point as end point in the desired direction.
3. Find the three components of the vector along the three axes of the unit cell (length determined as multiples or fractions of the lattice constants).
4. Re-calculate the resulting components to obtain integers (by multiplication with appropriate numbers).
5. The three integers (indices uvw) are written without separation within square brackets [uvw].
6. If one of the indices becomes negative, it is indicated by a bar on top of it, e.g. [u$\bar{v}$w].
7. If one of the indices is 10 or above, it is separated by a dot from the next [10.12].
8. If not the specific direction, but all crystallographic equivalents are meant, angle brackets are used ⟨uvw⟩.

Crystallographic planes Miller indices (hkl)



Recipe for crystallographic plane (hkl)

1. Origo must not be on plane - may require to move origo.
2. Find intersections of plane with axis of unit cell.
3. If plane does not intersect an axis (because both are parallel), this is accounted as infinity (∞).
4. Determine intersection as fractions or multiples of the lattice constants taking into account the sign (+ or −)

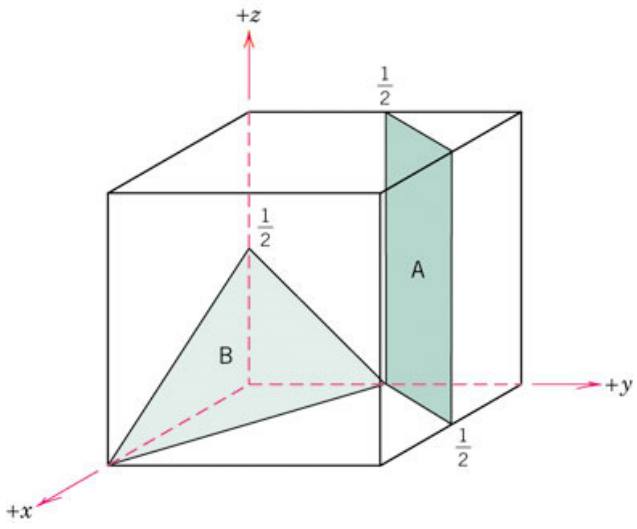
	h	**k**	**l**
Intersection	x-axis 1/2	y-axis -1	z-axis infinity

5. Use the reciprocal value (1/x)

Reciprocal	2	-1	0

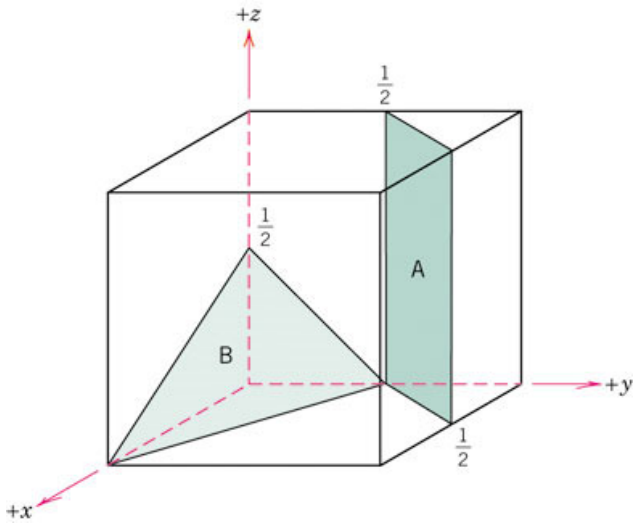
6. Re-calculate the resulting components to obtain integers (by multiplication with appropriate numbers).
7. Denote indices hkl with round brackets (hkl), e.g. $(2\bar{1}0)$
8. If necessary, move origo to avoid too many minuses.
9. If all crystallographic equivalent planes are meant, curly brackets are used {hkl}.

Exercise



Help: http://www.doitpoms.ac.uk/tlplib/miller_indices/index.php

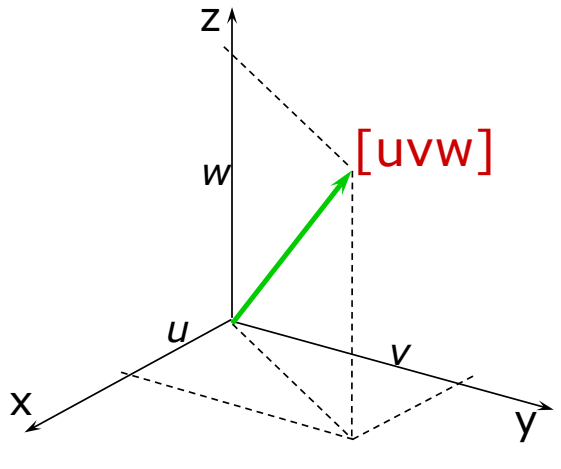
Exercise

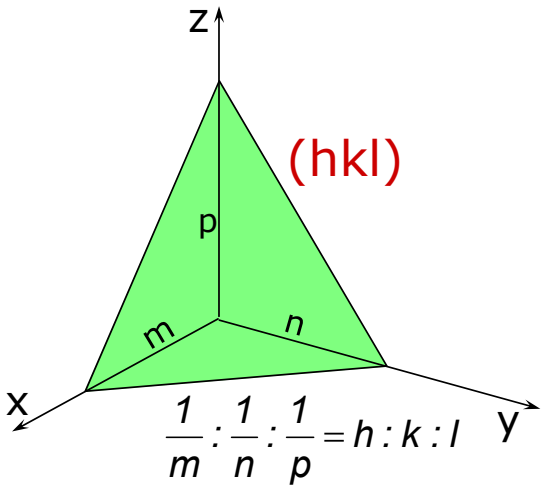


A	x	y	z
Intersection	½	-½	∞
Reciprocal value	2	-2	0
Reduction	1	-1	0
	→	$(1\bar{1}0)$	

B	x	y	z
Intersection	1	½	½
Reciprocal value	1	2	2
Reduction	not required		
	→	(122)	

Crystallographic directions [uvw] og planes (hkl) in a crystal

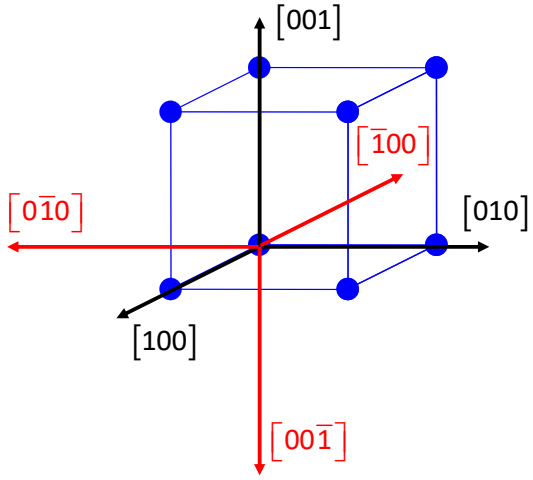




[xyz] ⊥ (xyz) only for cubic lattices

Crystallographically equivalent directions and crystallographically equivalent planes

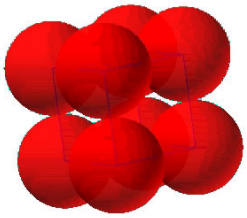
- Simple cubic lattice



- A specific direction [uvw] [square brackets]
- All crystallographically equivalent directions ⟨uvw⟩ ⟨angle brackets⟩

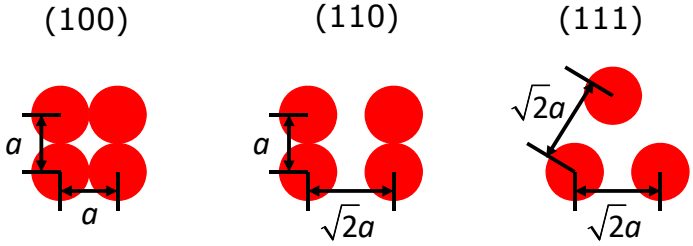
- A specific plane (hkl) (round brackets)
- All crystallographically equivalent planes {hkl} {curly brackets}

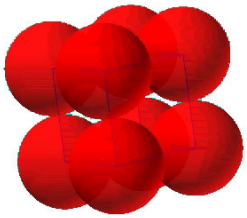
Simple cubic lattice



- Hard sphere model

- Crystallographic planes

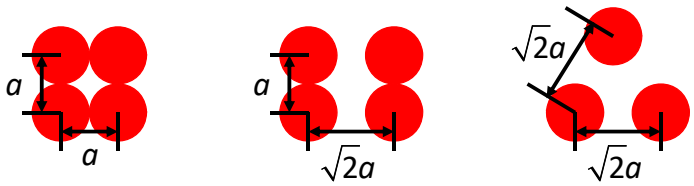




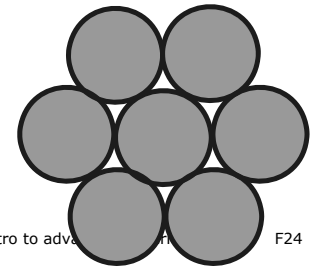
Closest packed planes vs. close-packed planes

- Lattice planes of simple cubic lattice

(100) (110) (111)



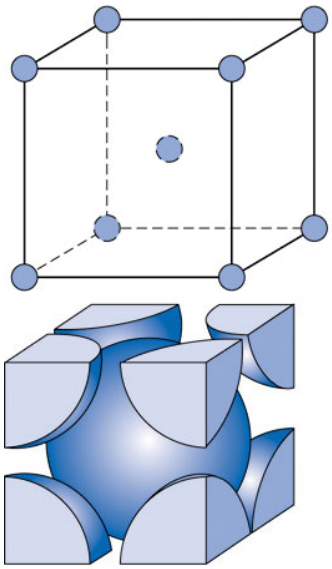
- (100) is the closest packed plane, in other planes the atoms do not touch each other
- But {100} are not close-packed planes, where atoms touch along three directions



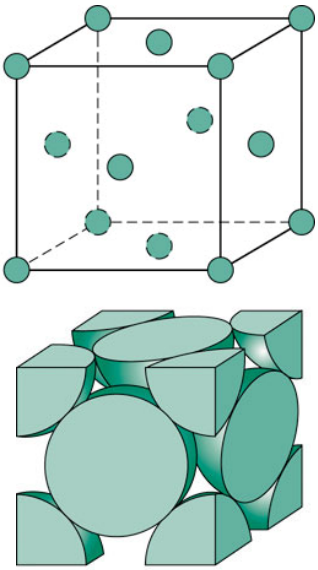
Group exercises

Non-primitive cubic lattices

- Body-centered cubic

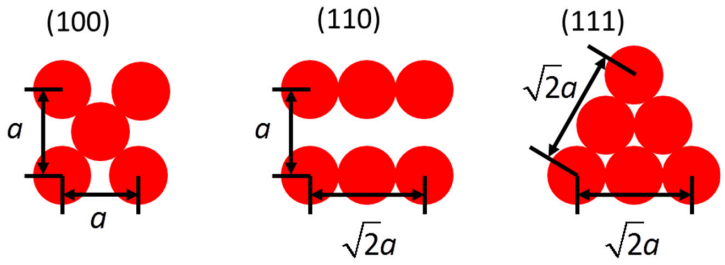


- Face-centered cubic

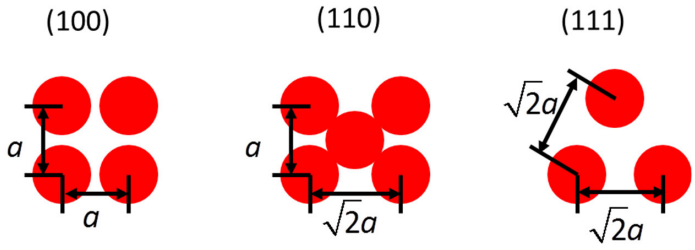


Planes in cubic lattice

- Face centered fcc



- Body centered bcc



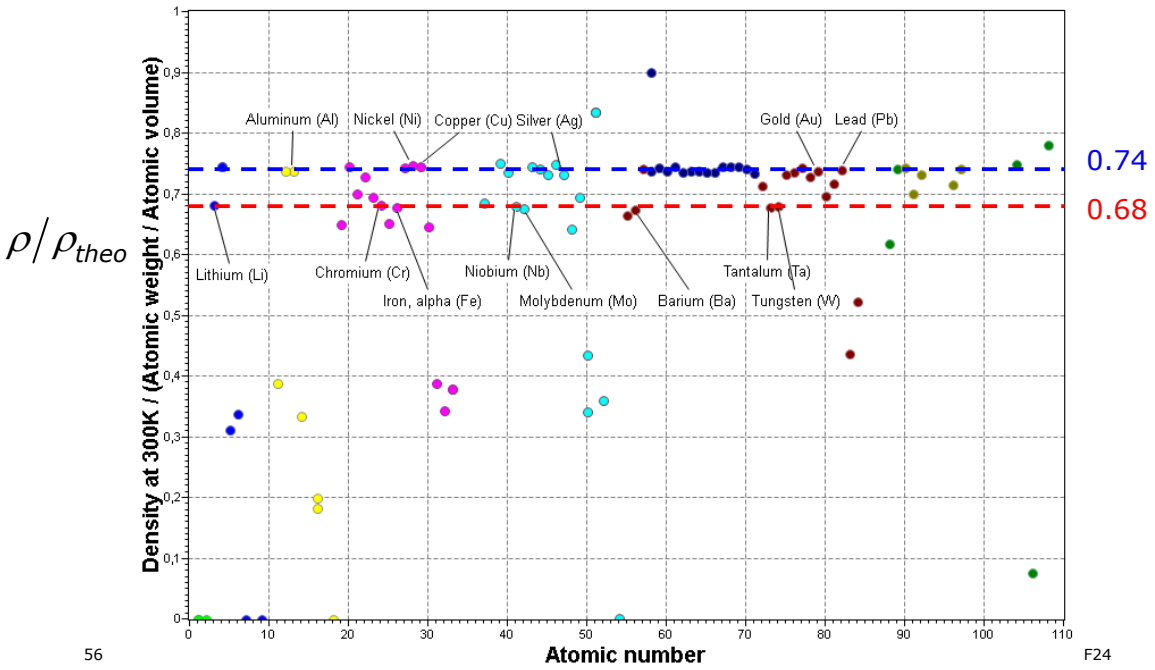
Cubic lattices - comparison

	*	Close-packed direction	Neighbor closest to origin	Atomic dia-meter 2*R*	Atomic packing factor	Coordi-nation number	Examples
sc	1	<100>	[100]*a*	*a*	0.52	6	only α-Po
bcc	2	<111>	[111]*a*/2	$\sqrt{3}a/2$	0.68	8	Cr, W, V, Ta, α-Fe
fcc	4	<110>	[110]*a*/2	$\sqrt{2}a/2$	0.74	12	Al, Cu, Ag, Au, Ni, γ-Fe
	* Number of atoms in unit cell			Lattice parameter *a*			
Random close-packed spheres					0.64		
Ordered close-packed spheres					0.74		

Only fcc is close-packed !

$$\rho \neq \rho_{theo} = \frac{m_{at}}{V_{at}} = \frac{m_{at}}{\frac{4\pi}{3} R_{at}^3} \text{ !!!}$$

Mass density ≠ atomic mass / at. volume !!!



Elements – crystal structures

H																	He
Li hcp	Be											B	C cub	N	O	F	Ne
Na hcp	Mg											Al	Si	P	S	Cl	Ar
K	Ca bcc	Sc fcc	Ti bcc	V	Cr	Mn	Fe fcc	Co fcc	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr bcc	Y bcc	Zr bcc	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn ttg	Sb	Te	I	Xe
Cs	Ba	L	Hf bcc	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl bcc	Pb	Bi	Po	At	Rn
Fr	Ra	A	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

	L	La fcc	Ce fcc	Pr bcc	Nd bcc	Pm bcc	Sm hcp	Eu	Gd bcc	Tb bcc	Dy bcc	Ho	Er	Tm	Yb bcc	Lu
	A	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

	Cubic primitive		Face-centered cubic		Diamond (cubic)
	Body-centered cubic		Hexagonal		Nonmetals