European Funds
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INSTITUTE OF METALLURGY
AND MATERIALS SCIENCE
POLISH ACADAMY OF SCIENCES

European Union
European Social Fund

Characterization of material structure by the X-ray diffraction III
Fundamentals of crystallography. Part II

Project WND-POWR.03.02.00-00-I043/16

International interdisciplinary PhD Studies in Materials Science with English as the language of instruction

Project co-financed by the European Union within the European Social Funds

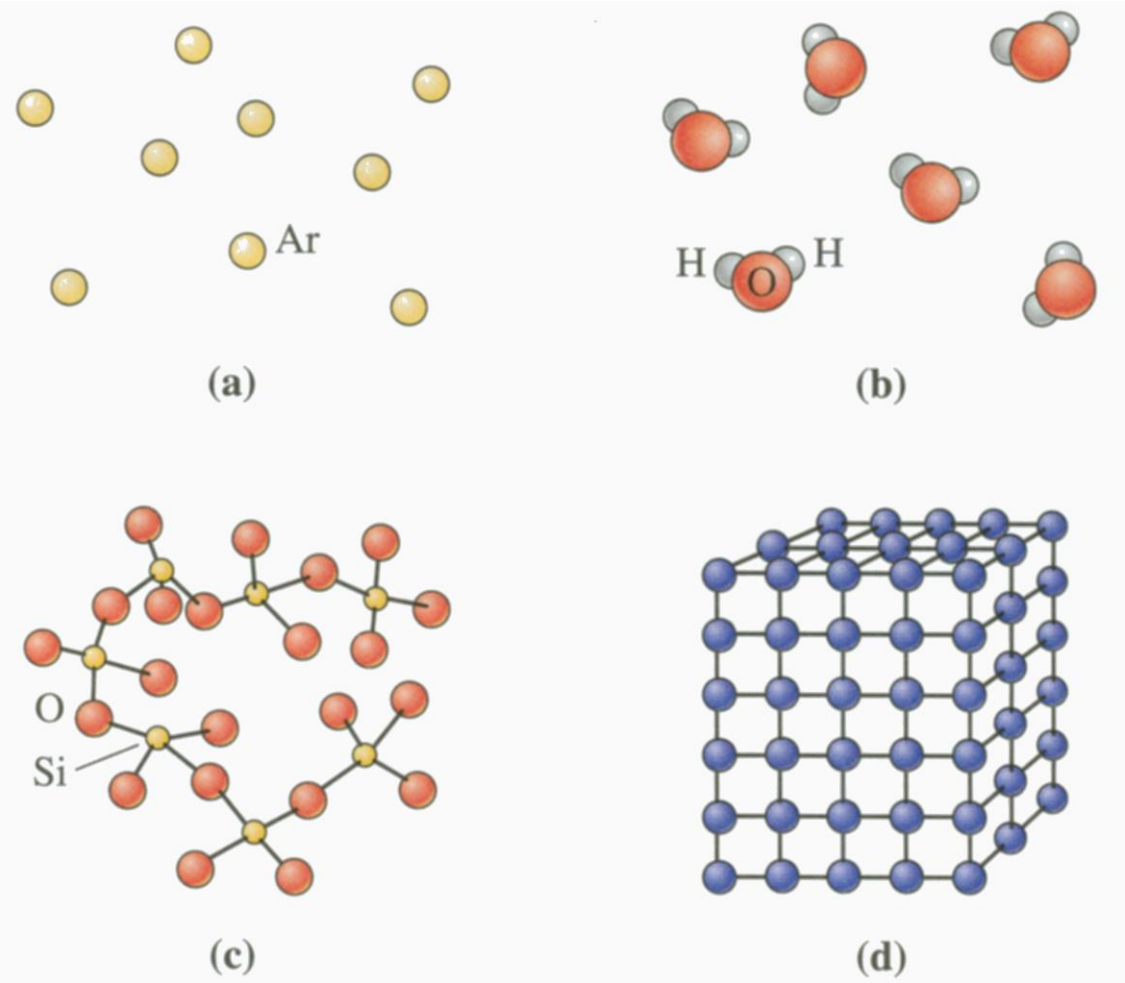
Long-Range and Short-Range Order

Different levels of order in the materials.

(a) Single-atomic gas.

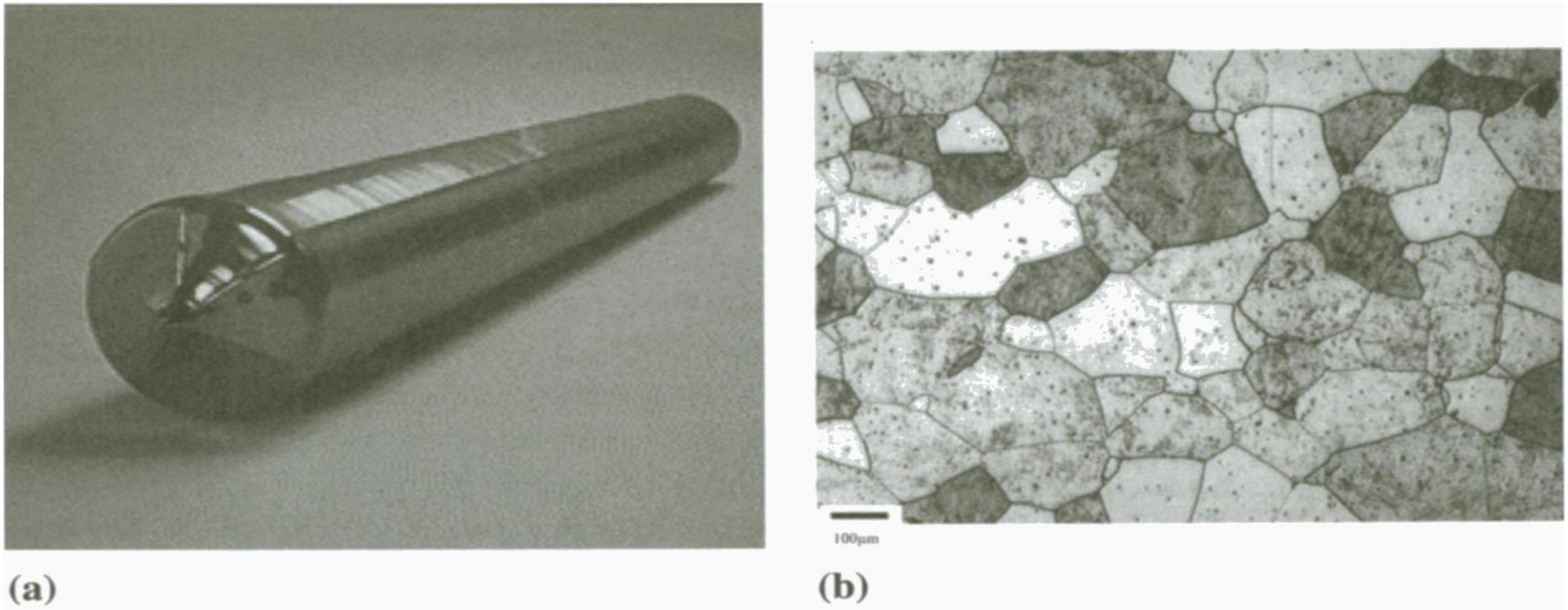
(b and c) Steam and amorphous silicon, short-range ordering.

(d) metals, alloys, many ceramics, long range arrangement of atoms/ions.



Donald R. Askeland, Pradeep P. Phulé „The science and engineering of materials", Thomson 2006.

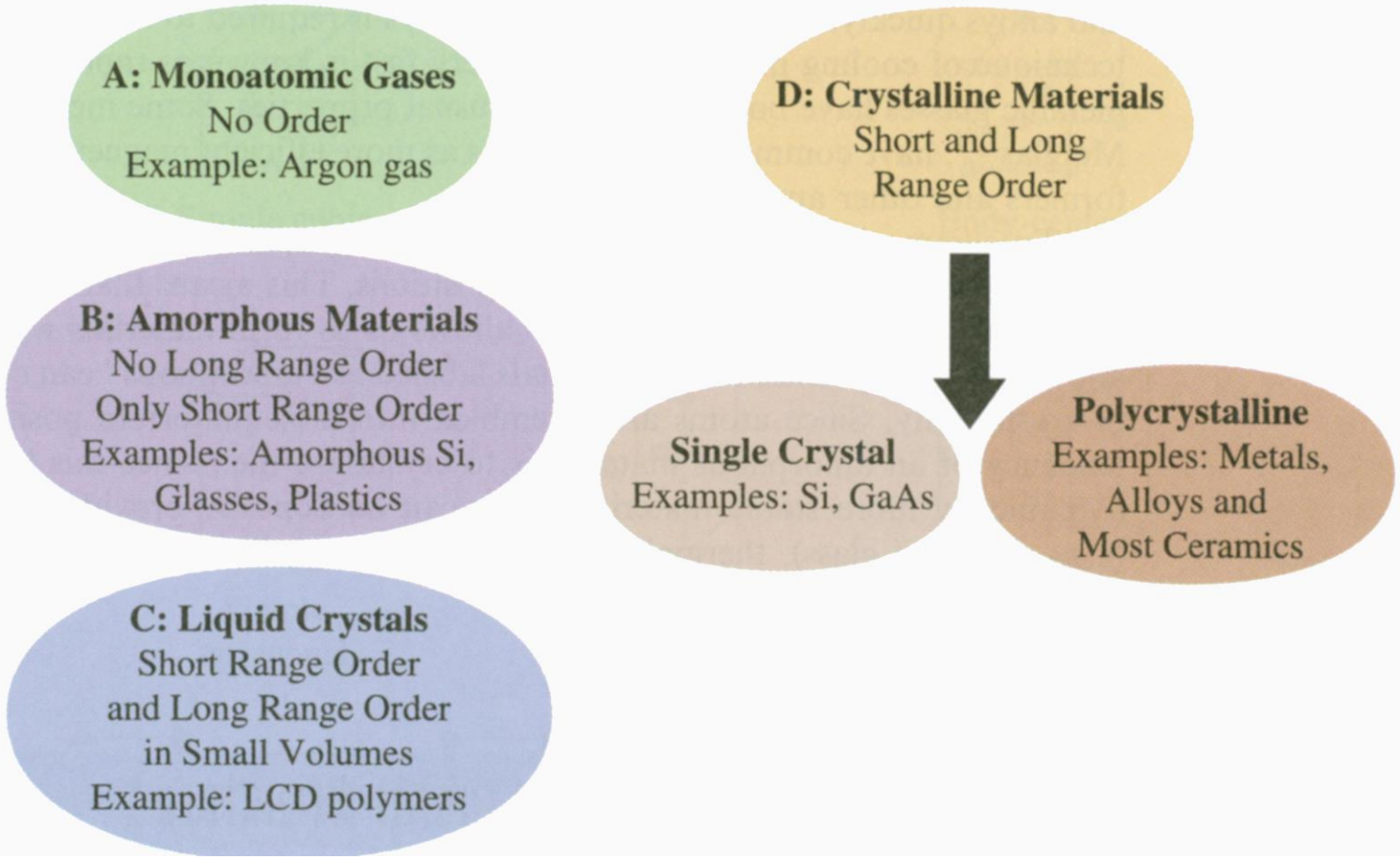
Long-Range and Short-Range Order



(a) Monocrystalline silicon. (b) Microstructure of corrosion-resistant steel.

Donald R. Askeland, Pradeep P. Phulé „The science and engineering of materials”, Thomson 2006.

Classification of materials according to the arrangement of atoms



Donald R. Askeland, Pradeep P. Phulé „The science and engineering of materials", Thomson 2006.

Crystalline body *– condensed matter with 3D ordered structure.*

Properties od crystals (electrical, magnetical, optical and mechanical) are direction dependent (contrary to amorphous bodies).

Single (mono)- or Polycrystals

Single crystals: *mono-phase, non-defected crystalline body, eg.*

- ***sapphire*** *(Al_2O_3 + small amount TiO_2 and Fe_3O_4)*
- ***ruby*** *(Al_2O_3 + small amount Cr_2O_3)*

Polycrystal*: conglomerate of single crystals (micrometer dimension)*

Unit cell

Ideal- and real crystals

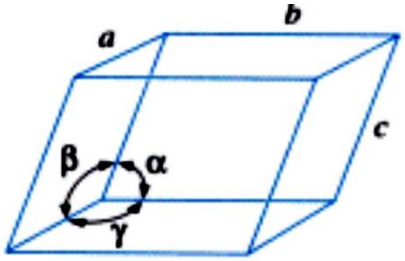
Seven crystallographic systems and fourteen types of lattice

A fundamental feature of the crystalline structure is that the atoms are arranged at intervals of periodic repetition in at least three unequal and non-plane directions.

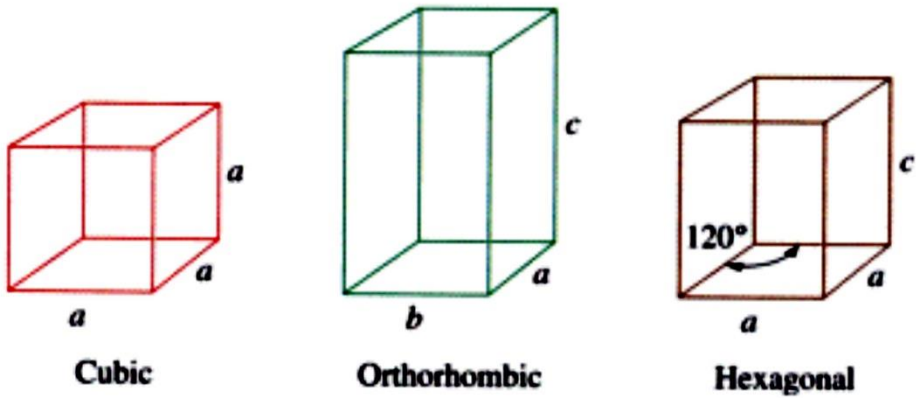
Due to the orderly arrangement of atoms, small groups of atoms form repetitive patterns.

The simplest element, called an unit cell, is usually selected to describe the crystalline structure.

The geometry of the unit cell.



The edge lengths of the unit cell and the values of the angles between the edges are called lattice constants or lattice parameters.



Seven crystallographic systems and fourteen types of lattice

Description of crystalline structures using unit cells → all possible structures have been reduced to seven unit cells differing in shape (seven crystallographic systems). When describing crystalline structures, it is helpful to consider a set of points, lattice nodes, and not atoms forming a crystal. **The characteristic feature of a set of such points is that each point has the same environment.** The lattice created by these points is called a point lattice or Bravais lattice.

There are 14 different point lattices.

Regarding the values of lattice constants of the crystals and symmetry of spatial lattice various ***crystallographic systems*** have been defined. Lattice periods ***a, b, c*** and angles α, β and γ.

An elementary cell which translation along X, Y, Z reconstruct whole spatial lattice can be distinguished in each of the crystallographic system.

Cells: *primitive* **P**, *centered:* **C** (on basal planes), **F** (face-centered), **I** (spatial-centered)
Each of the ***6(7)*** crystallographic system, dependig on its symmetry, have a strictly defined number of the elementary cells. As it was prooved, there are ***14*** various cells – ***Bravais cells.***

Crystallographic system: **REGULAR** $a_0 = b_0 = c_0$ $\alpha = \beta = \gamma = 90°$

Bravais cells: **P** (primitive), **I** (body centered), **F** (face centered) *fcc*, A1)

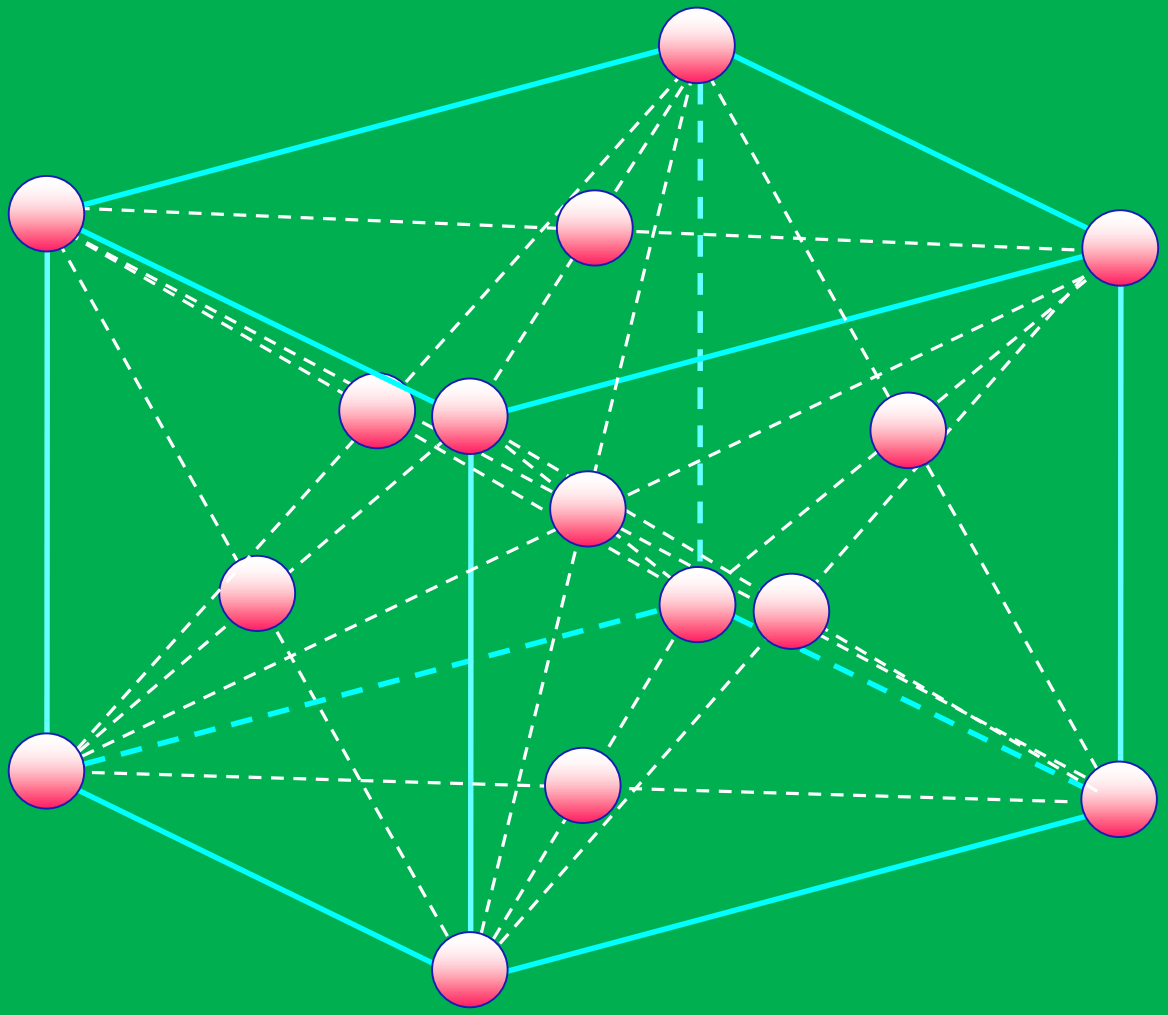


Table 19. PERIODIC TABLE OF THE FACE CENTERED CUBIC ELEMENTS

1 IA	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18 VIIA
	IIA											IIIA	IVA	VA	VIA	VIIA	
		IIIB	IVB	VB	VIB	VIIB	-----	VIII	-----	IB	IIB						10 Ne
												13 Al	14 Si				18 Ar
	20 Ca								28 Ni	29 Cu			32 Ge				36 Kr
	38 Sr							45 Rh	46 Pd	47 Ag							54 Xe
								77 Ir	78 Pt	79 Au			82 Pb				86 Rn

57 La															
89 Ac															

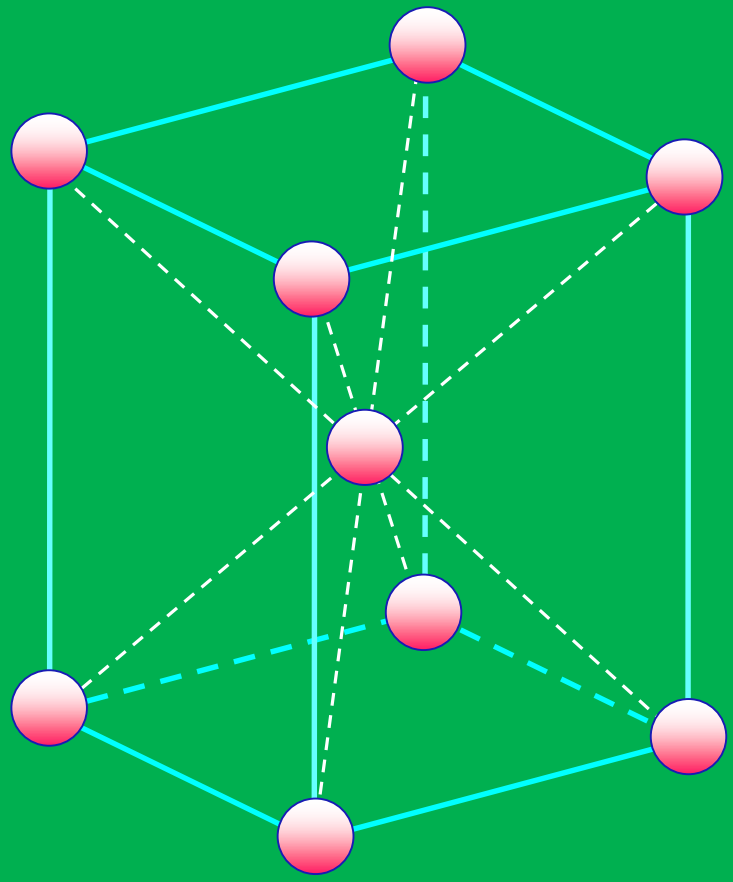
Table 18. PERIODIC TABLE OF THE BODY CENTERED CUBIC ELEMENTS

1 IA	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18 VIIA
	IIA											IIIA	IVA	VA	VIA	VIIA	
3 Li																	
11 Na		IIIB	IVB	VB	VIB	VIIB	-----	VIII	-----	IB	IIB						
19 K				23 V	24 Cr	25 Mn	26 Fe										
37 Rb				41 Nb	42 Mo												
55 Cs	56 Ba			73 Ta	74 W												
87 Fr	88 Ra																

						63 Eu									

Crystallographic system: **TETRAGONAL** $a_0 = b_0 \neq c_0$ $\alpha = \beta = \gamma = 90°$

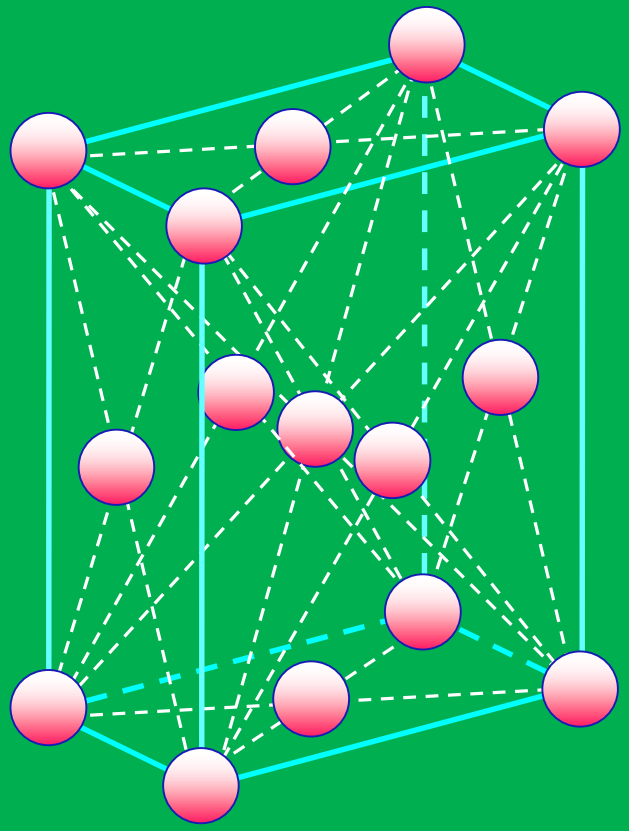
Bravais cells: **P** (primitive) **I** (body centered)



Tetragonal: eg. corundum, *quartz, turmalinum, α-Fe_martensite*

Crystallographic system: **RHOMBOHEDRAL** $a_0 \neq b_0 \neq c_0$ $\alpha = \beta = \gamma = 90°$

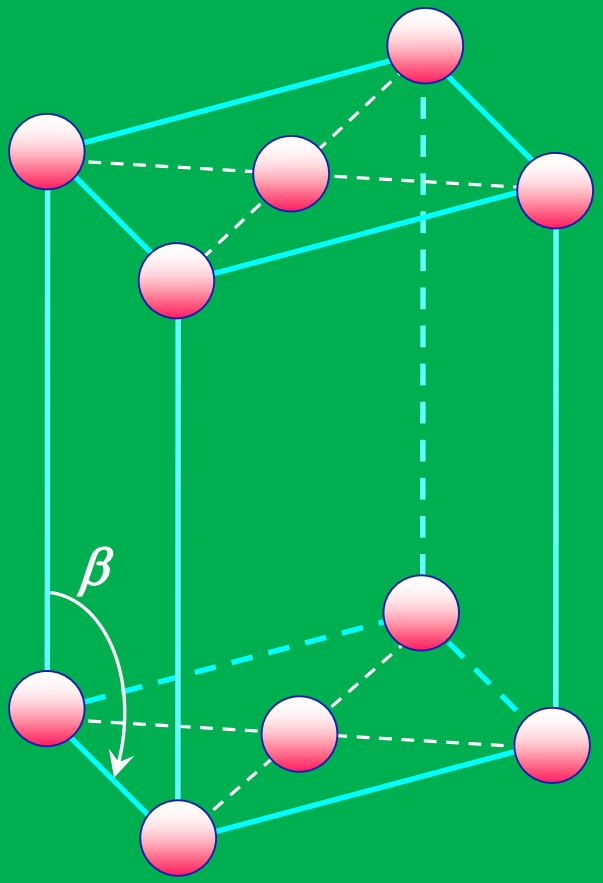
Bravais cells: **P** (primitive) **I** (body-centered) **C** (basal-planes-centered) **F** (face-centered)



Rhombohedral: eg. *topaz, aragonite (variant of $CaCO_3$, eg. Conus Marmoreus)*

Crystallographic system: **MONOCLINIC** $a_0 \neq b_0 \neq c_0$ $\alpha = \gamma = 90°$, $\beta \neq 90°$

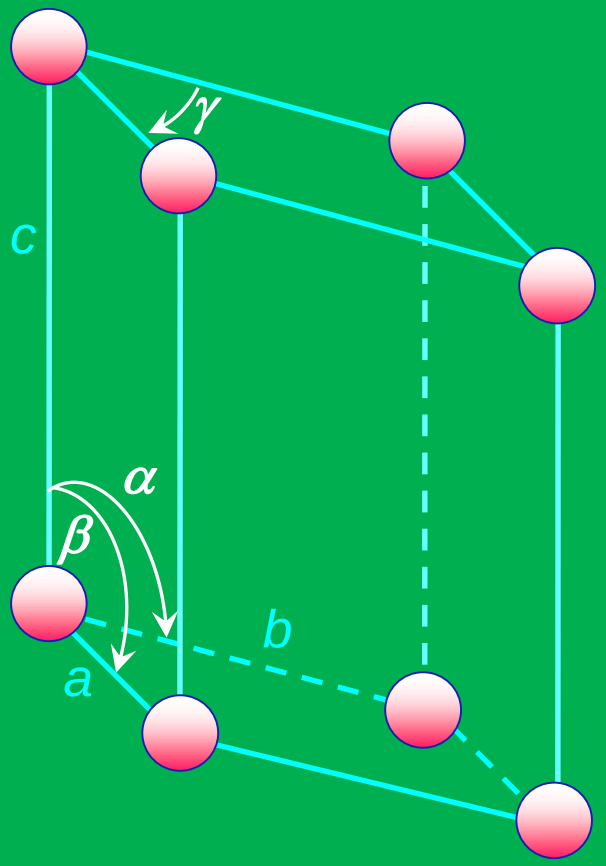
Bravais cells: **P** (primitive) **C** (basal-planes centered)



Monoclinic: eg. *cellulose (crystalline part), jade (nefryt)*

Crystallographic system: **TRICLINIC** $a_0 \neq b_0 \neq c_0$ $\alpha \neq \beta \neq \gamma \neq 90°$

Bravais cells: **P** (primitive)



Triclinic: eg. t*urquoises (turkus), amazonite*

Crystallographic system: **HEXAGONAL** $a_0 = b_0 \neq c_0$ $\alpha = \beta = 90°$, $\gamma = 120°$

Bravais cells: **P** (primitive)

hcp (hexagonal close packed)

$c_0 / a_0 = 1.633$

Ti ($c_0 / a_0 = 1.588$)

Mg ($c_0 / a_0 = 1.624$)

Co ($c_0 / a_0 = 1.623$)

Zn ($c_0 / a_0 = 1.856$)

Cd ($c_0 / a_0 = 1.886$)

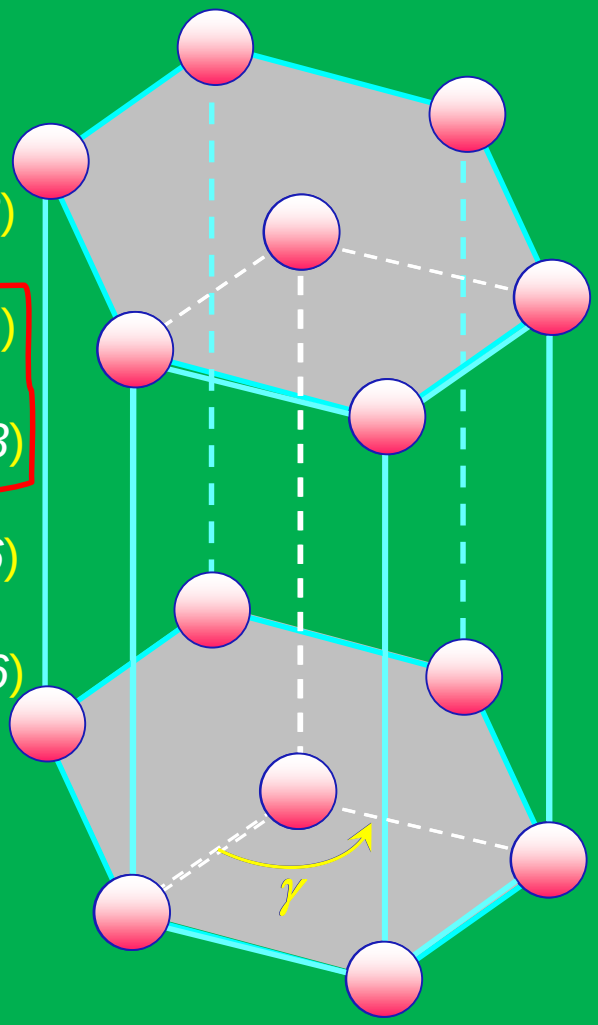


Table 21. PERIODIC TABLE OF THE HEXAGONAL ELEMENTS

1 IA	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18 VIIA
	IIA											IIIA	IVA	VA	VIA	VIIA	
		IIIB	IVB	VB	VIB	VIIB	-----	VIII	-----	IB	IIB		6 C				
															34 Se		
															52 Te		

57 La		59 Pr	60 Nd	61 Pm											
						95 Am	96 Cm	97 Bk							

Table 20. PERIODIC TABLE OF THE HEXAGONAL CLOSE PACKED ELEMENTS

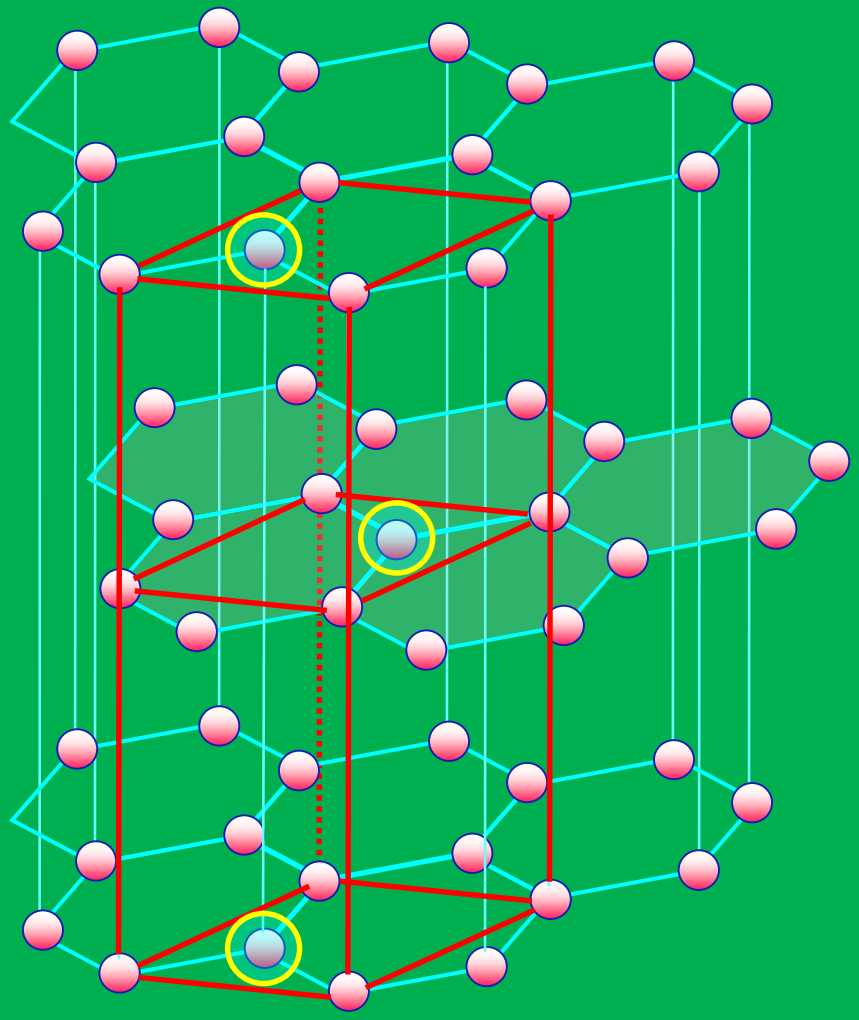
1 IA	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18 VIIA
	IIA											IIIA	IVA	VA	VIA	VIIA	
	4 Be																
	12 Mg	IIIB	IVB	VB	VIB	VIIB	-----	VIII	-----	IB	IIB						
			22 Ti					27 Co			30 Zn						
		39 Y	40 Zr			43 Tc	44 Ru				48 Cd						
			72 Hf			75 Re	76 Os					81 Tl					

								64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm		71 Lu		

Crystallographic system: **HEXAGONAL**

A9 (graphite type structure)

typical layered structure



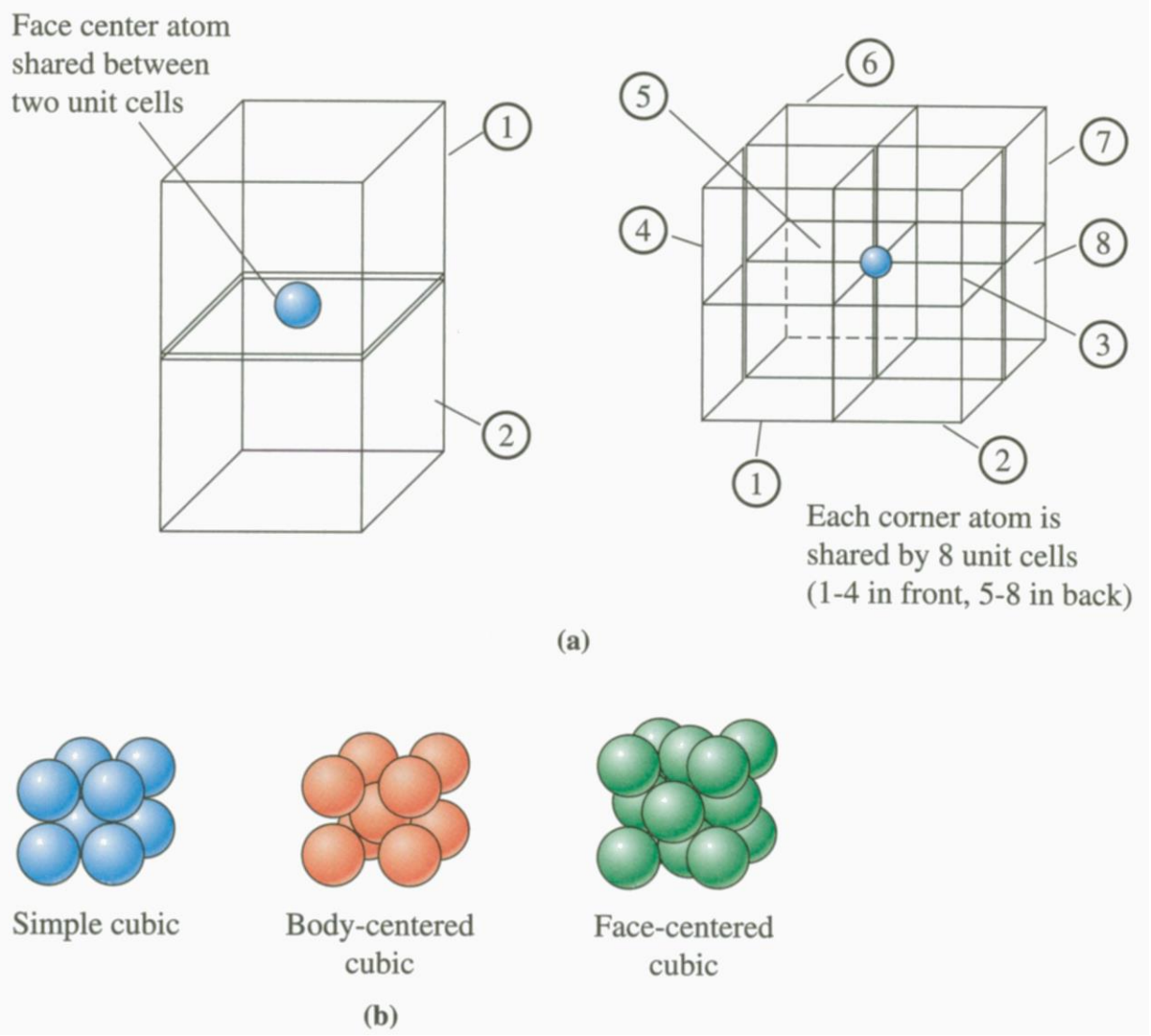
$c_0 / a_0 = 2.76$

Allotropic variety of carbon:

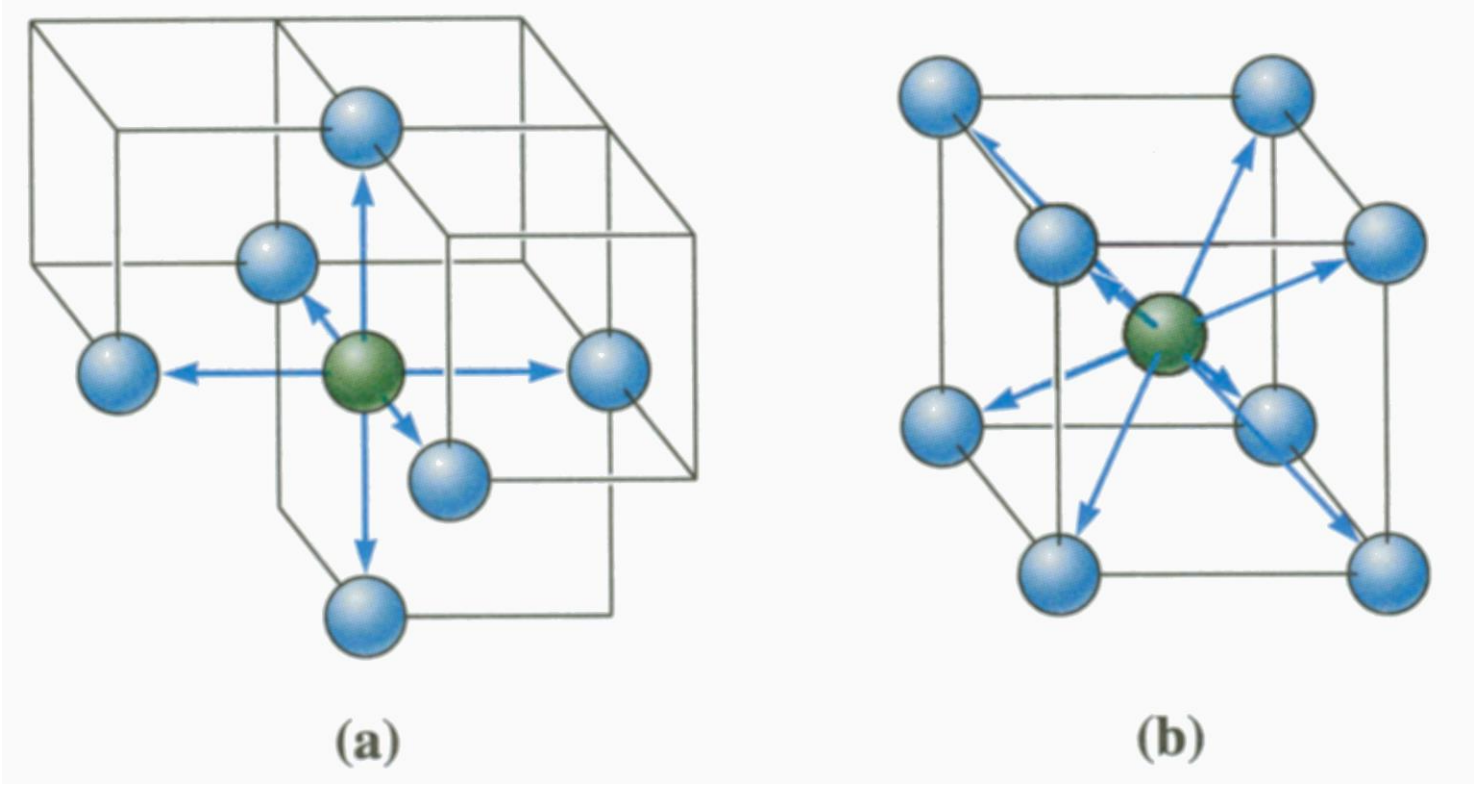
- **Diament** (regular + hexagonal)
- **Graphite** β (rhombohedric ≡ hexagonal)
- **Fulerens** C_{60} (since 1985r)
- **Graphene** (since 2010r)

Graphite-type structures – strong anizotropy of properties: cleavage (łupliwość), thermal expansion, electric conductivity

Atoms in walls and corners of the unit cell.

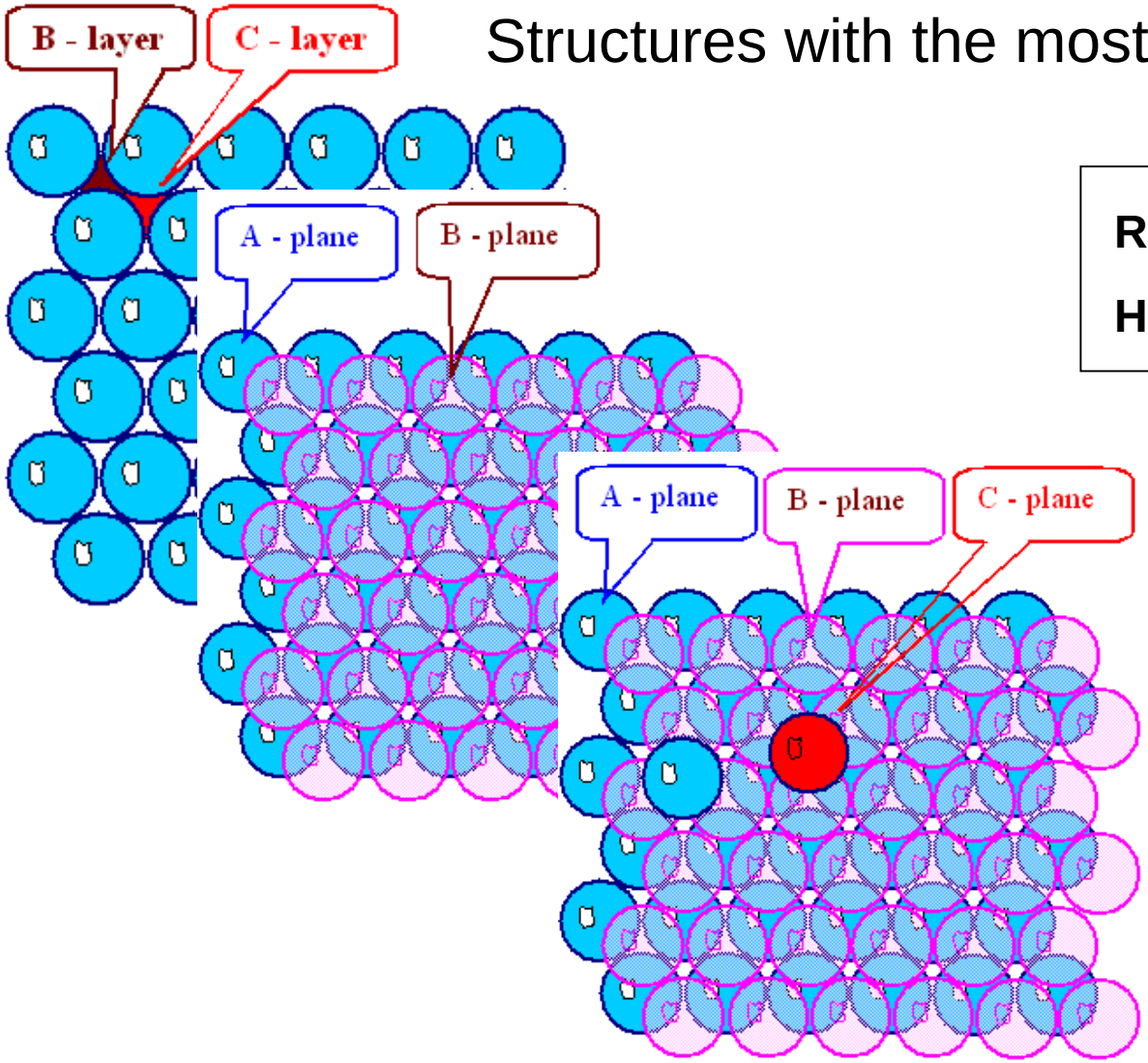


Coordination number



Coordination number → number of nearest neighbours of the atom or ion in the crystalline structure.

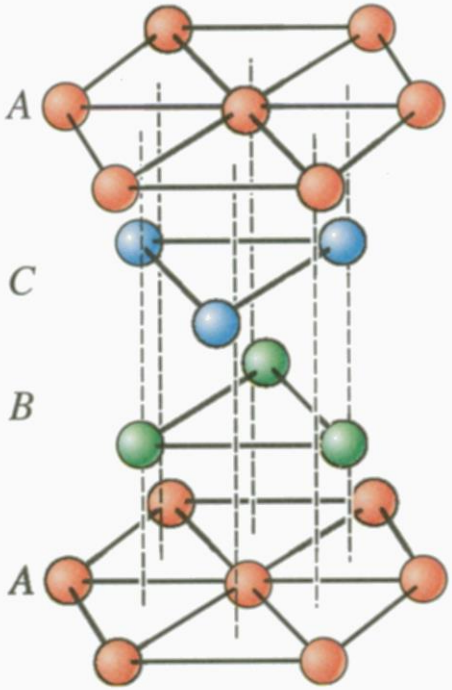
Structures with the most dense packing of atoms

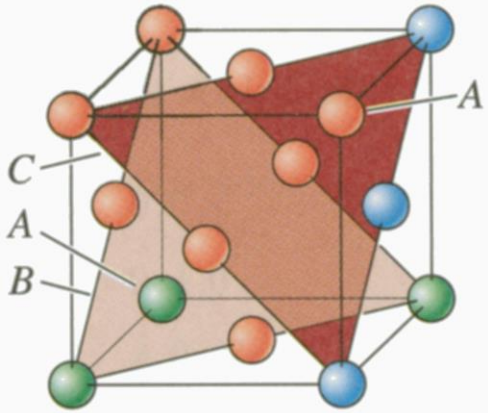


RSC (*fcc*): **ABCABCABCA...**

HZ (*hcp*): **ABABAB...**

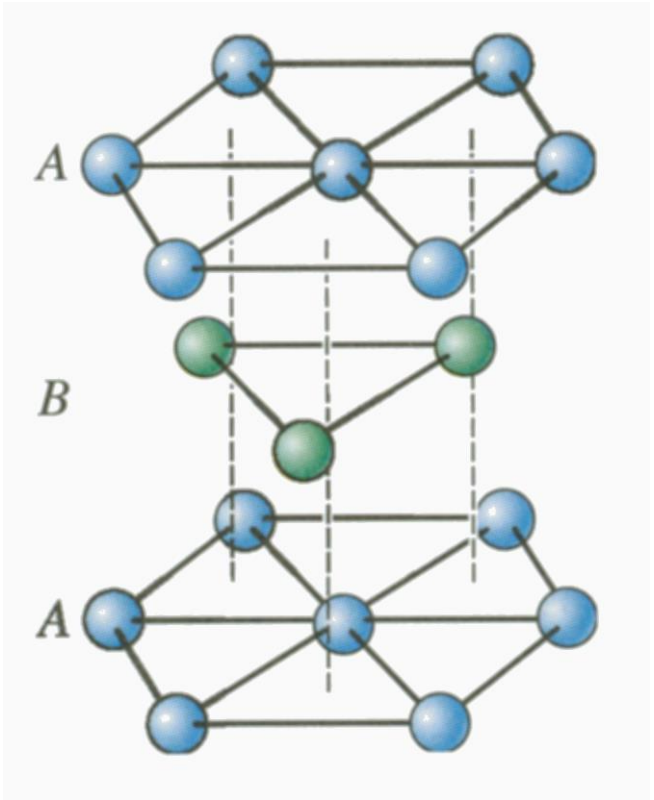
Structures with the most dense packing of atoms





Alignment of the ABCABC in the plane (111) of the FCC lattice.

Alignment of the ABAB in the plane (0001) of the HCP lattice.

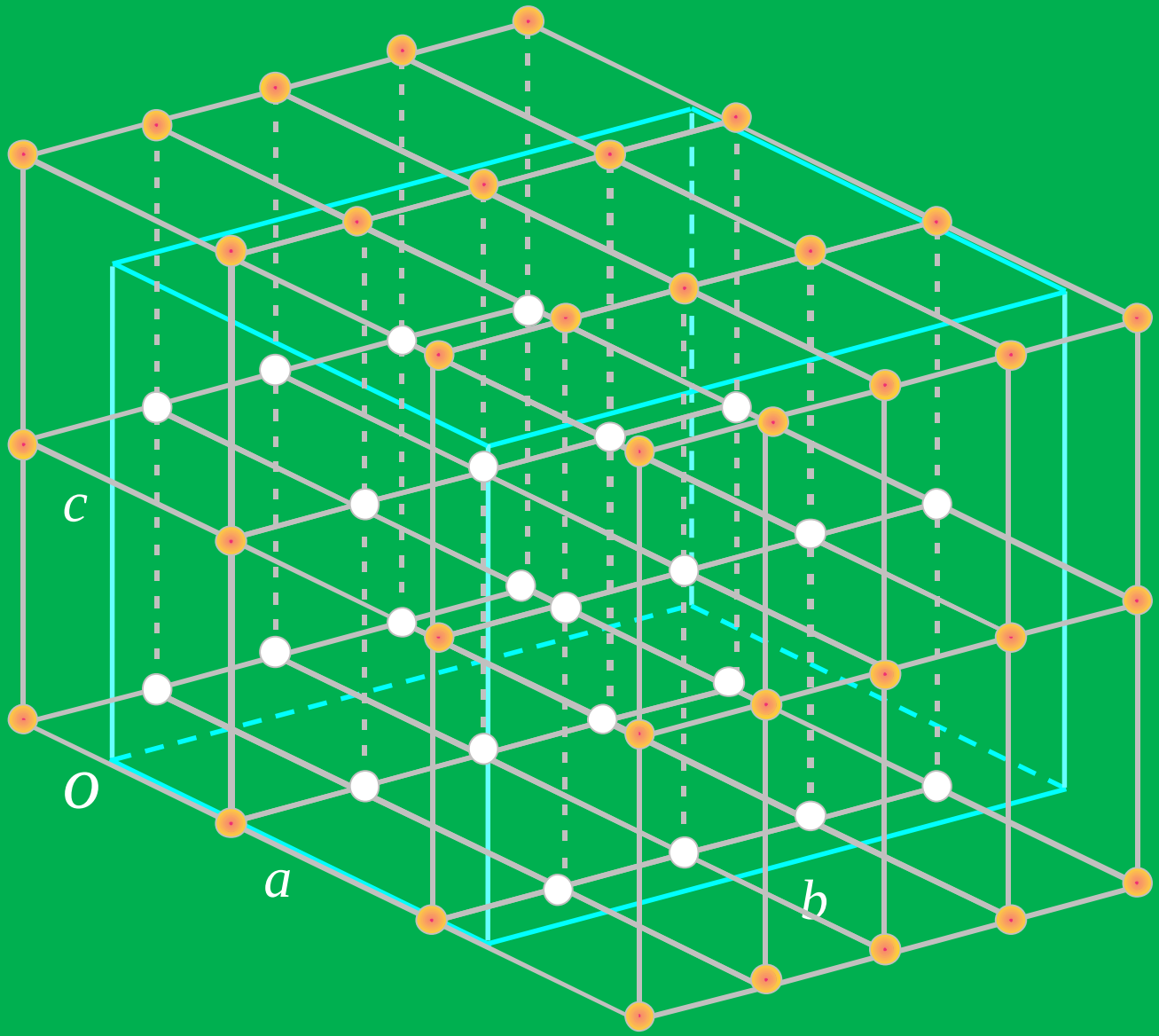


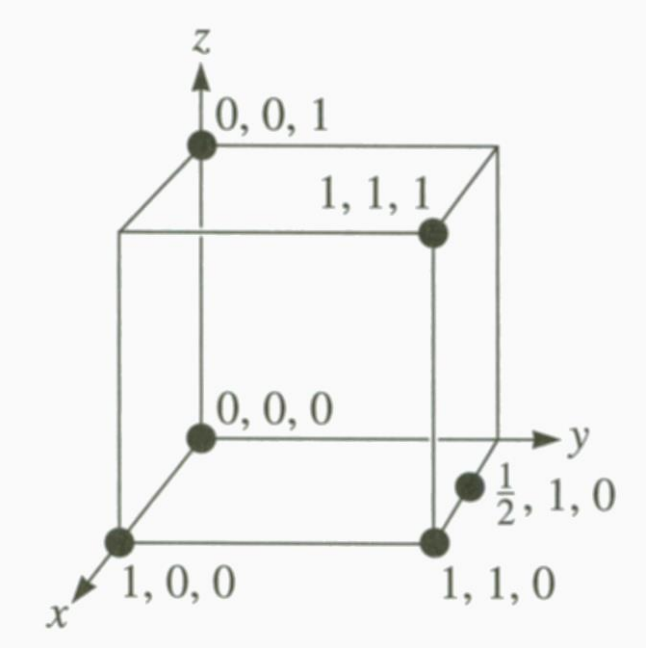
Characteristics of certain crystalline structures

TABLE 3-2 *Crystal structure characteristics of some metals*

Structure	a_0 versus r	Atoms per Cell	Coordination Number	Packing Factor	Examples
Simple cubic (SC)	$a_0 = 2r$	1	6	0.52	Polonium (Po), α-Mn
Body-centered cubic (BCC)	$a_0 = 4r/\sqrt{3}$	2	8	0.68	Fe, Ti, W, Mo, Nb, Ta, K, Na, V, Zr, Cr
Face-centered cubic (FCC)	$a_0 = 4r/\sqrt{2}$	4	12	0.74	Fe, Cu, Au, Pt, Ag, Pb, Ni
Hexagonal close-packed (HCP)	$a_0 = 2r$ $c_0 \approx 1.633a_0$	2	12	0.74	Ti, Mg, Zn, Be, Co, Zr, Cd

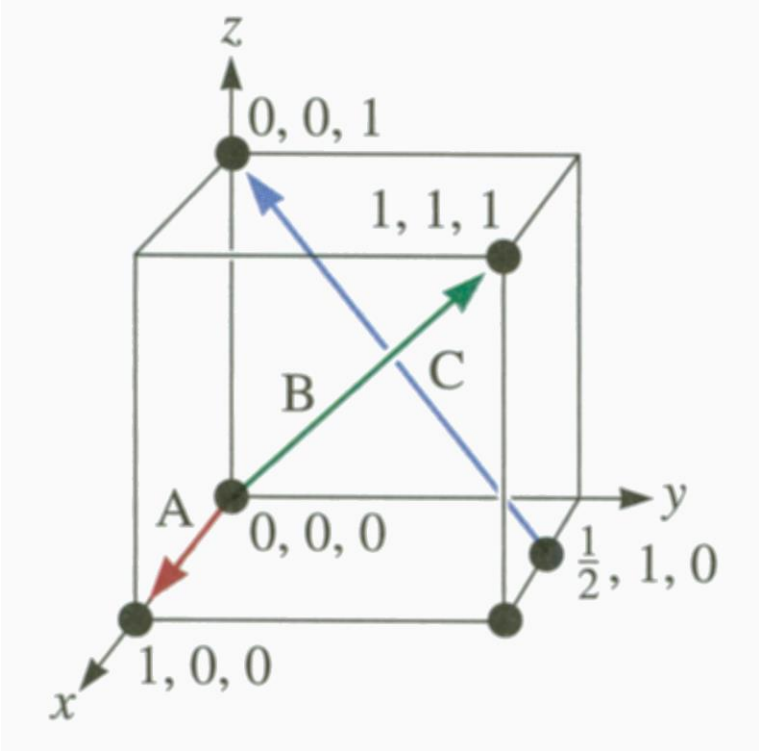
Indexing the crystallographic planes and directions





Coordinates of selected points in the unit cell (positions in units of edge length of the unit cell → unit vectors along the x, y and z axes).

Lattice directions → coordinates of a point at a straight line parallel to the selected direction and passing through the origin of the coordinate system (e.g. [111]).



Miller indicies – notation of the planes and directions defined in crystallographic lattice based on the unit cell.

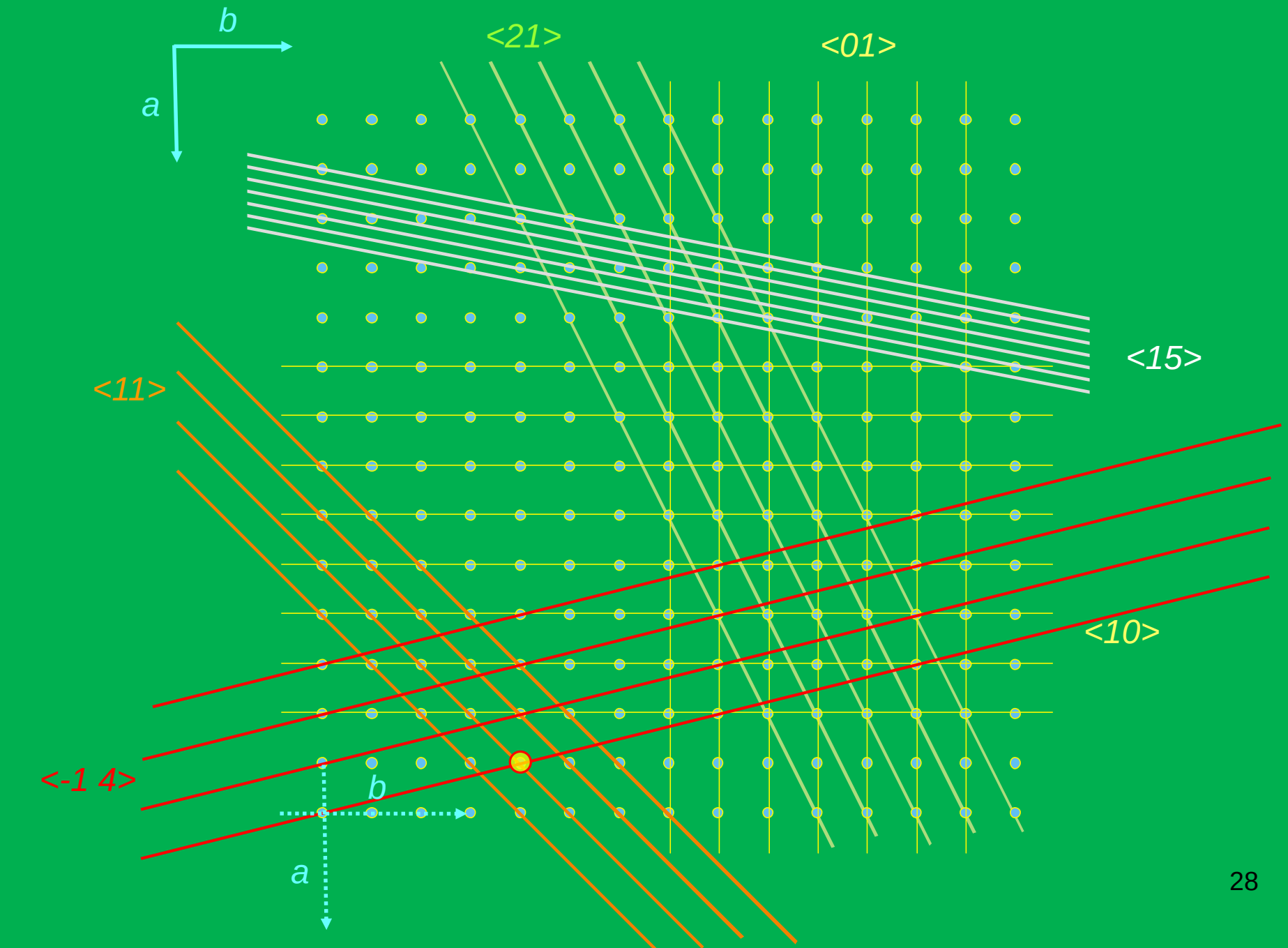
Crystallographic **direction** – fractions of the basal vectors of the lattice cell [uvw], where u, v and w are integers. The family of directions crystallographically equivalent <uvw>.

Crystallographic direction families

TABLE 3-3 Directions of the form ⟨110⟩ in cubic systems

$$\langle 110 \rangle = \begin{Bmatrix} [110] & [\bar{1}\bar{1}0] \\ [101] & [\bar{1}0\bar{1}] \\ [011] & [0\bar{1}\bar{1}] \\ [1\bar{1}0] & [\bar{1}10] \\ [10\bar{1}] & [\bar{1}01] \\ [01\bar{1}] & [0\bar{1}1] \end{Bmatrix}$$

Crystallographic directions in 2-D orthogonal lattice

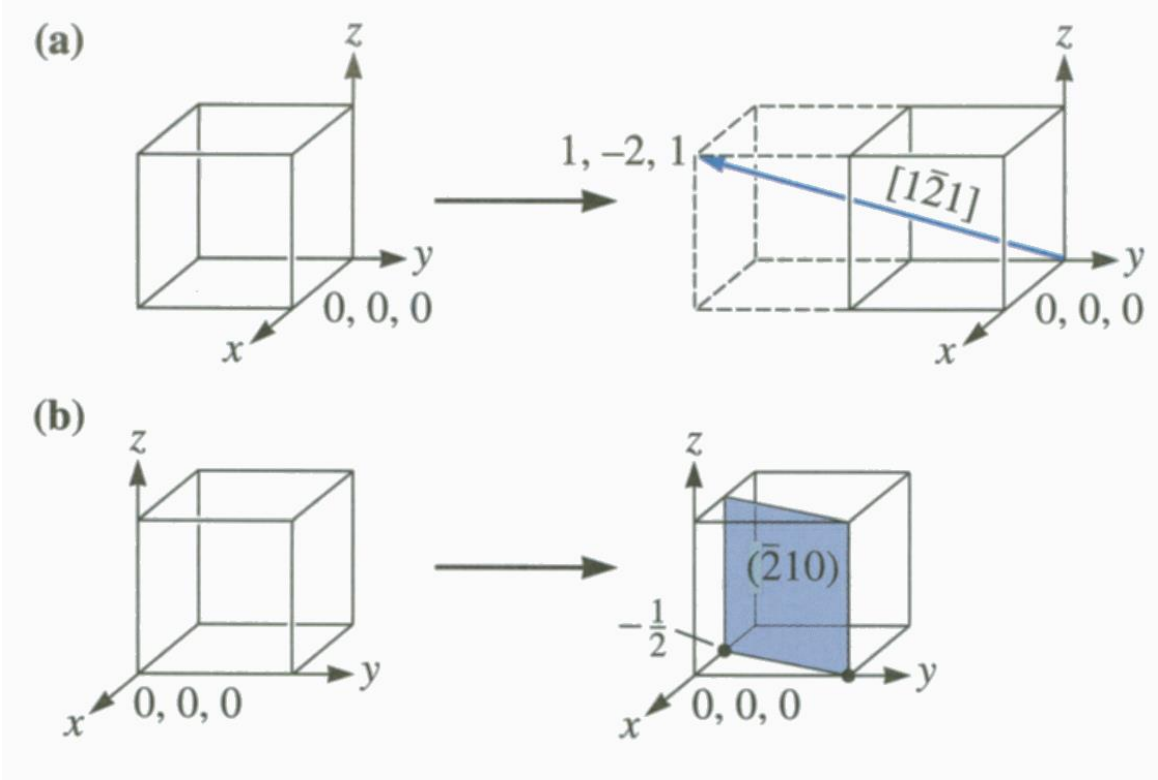


Miller indicies for **lattice planes** are expressed in form (hkl), where h, k, l are complete numbers indicate to how many parts of the basal periods a, b, c are divided by the plane.

(na ile części dana płaszczyzna (najbliższa początku układu) dzieli podstawowe periody na osiach układu współrzędnych).

Family of crystallographically equivalent planes: {hkl}.

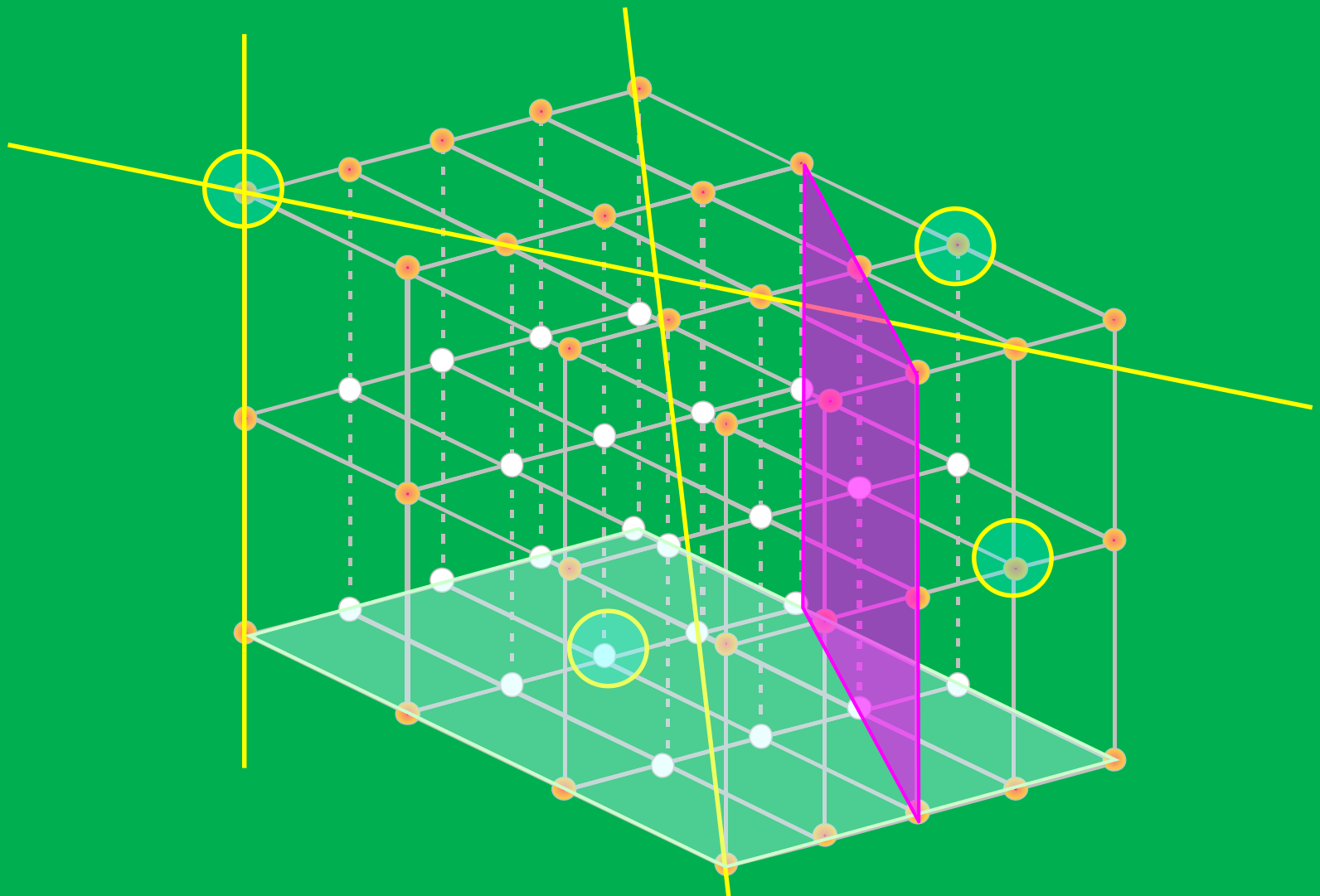
Lattice planes (Miller indices)



To determine the plane indices:

- Determine the length of the segments cut off on the axes of the coordinate system by the plane under consideration,
- State the inverse of these distances,
- Reduce the result to the smallest integers.

Spatial lattice *– infinit conglomeration of ideal elementary cells*
Lattice nods *– points of intersection of edges of the elementary lattice.*
Lattice lines *– lines indicated by selected lattice nodes.*
Lattice planes *– planes indicated by the selected lattice nodes.*
Crystal structure *– way of distribution of atoms (ions, particles) in elementary cell.*



Miller-Bravais Indicies

In 3-digit Miller's notation (planes and directions) for *hexagonal system* the crystallographicaly equivalent planes have various indicies. The inconvenience is not exists in 4-digit Miller-Bravais notation.

Plane (HKiL), where *H*, *K*, *i* and *L* are complete numbers, where i = -(H + K)

$$H = h$$
$$K = k$$
$$i = -(h + k)$$
$$L = l$$

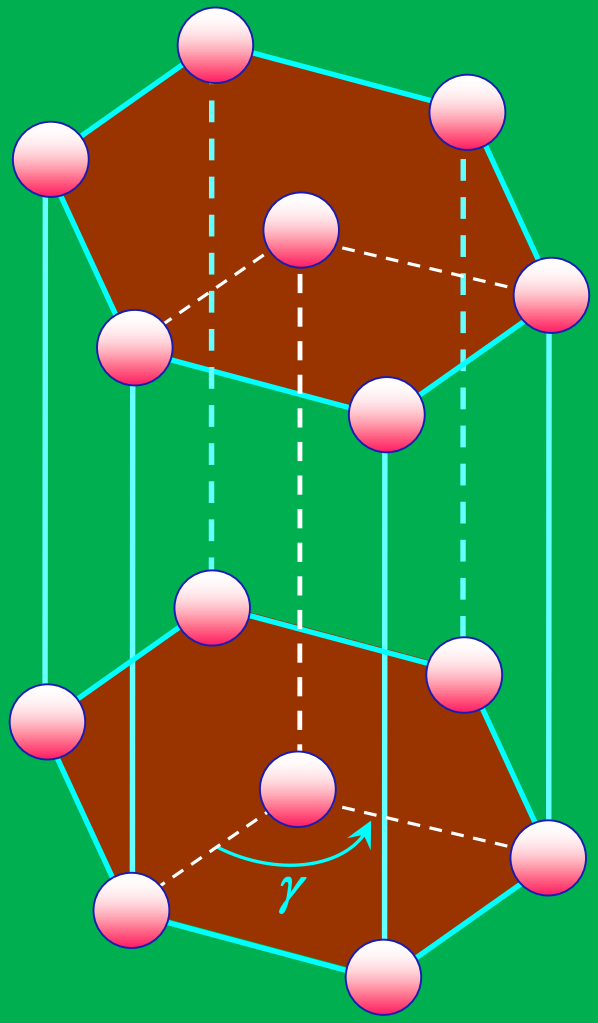
Direction expressed as [UVTW] where *U*, *V*, *T* and *W* are complete numbers, additionally **T** = -(**U** + **V**), ...but indicies of directions *can not be derived directly* from the equivalent Miller indicies

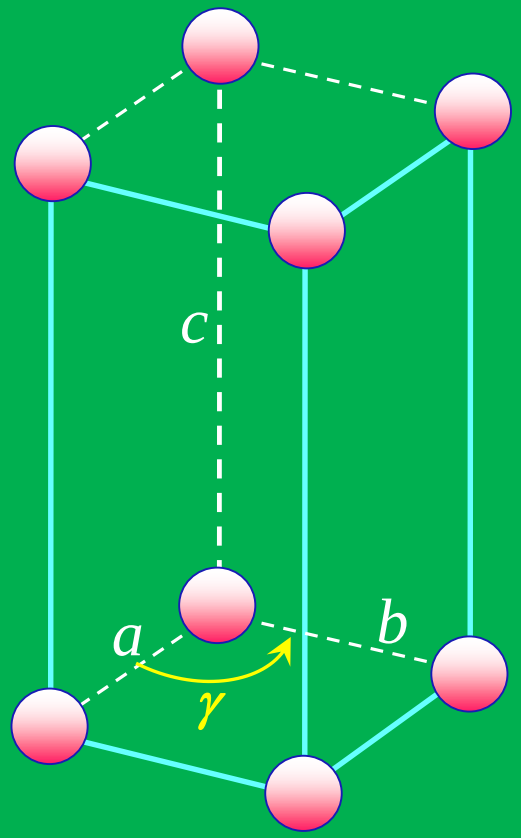
$$\boldsymbol{U} = (2u - v)/3$$
$$\boldsymbol{V} = (2v - u)/3$$
$$\boldsymbol{T} = -(u + v)/3$$
$$\boldsymbol{W} = w$$

Crystallographic system: **HEXAGONAL** $a_0 = b_0 \neq c_0$ $\alpha = \beta = 90°$, $\gamma = 120°$

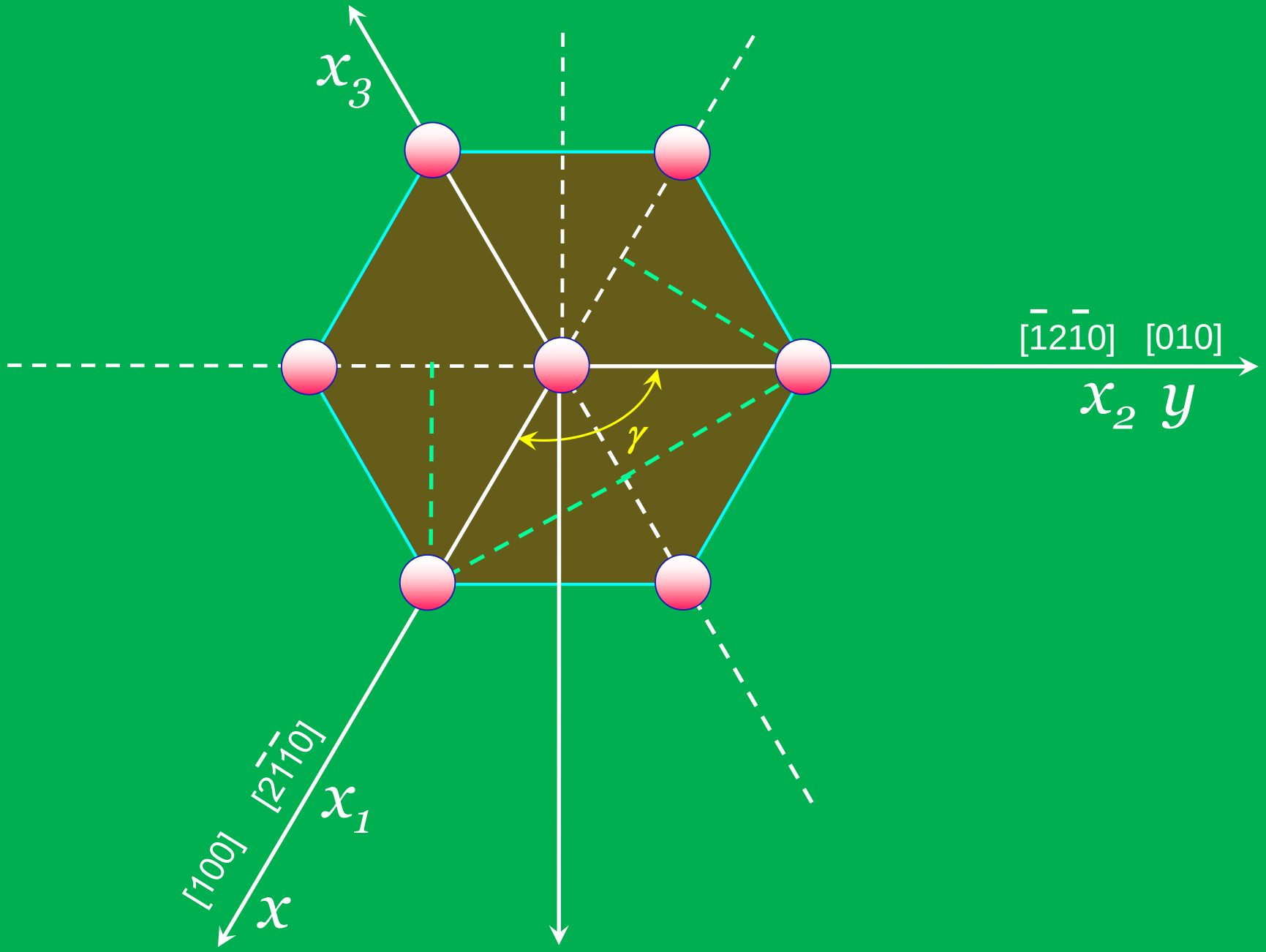
Bravais cells: **P** (primitive)

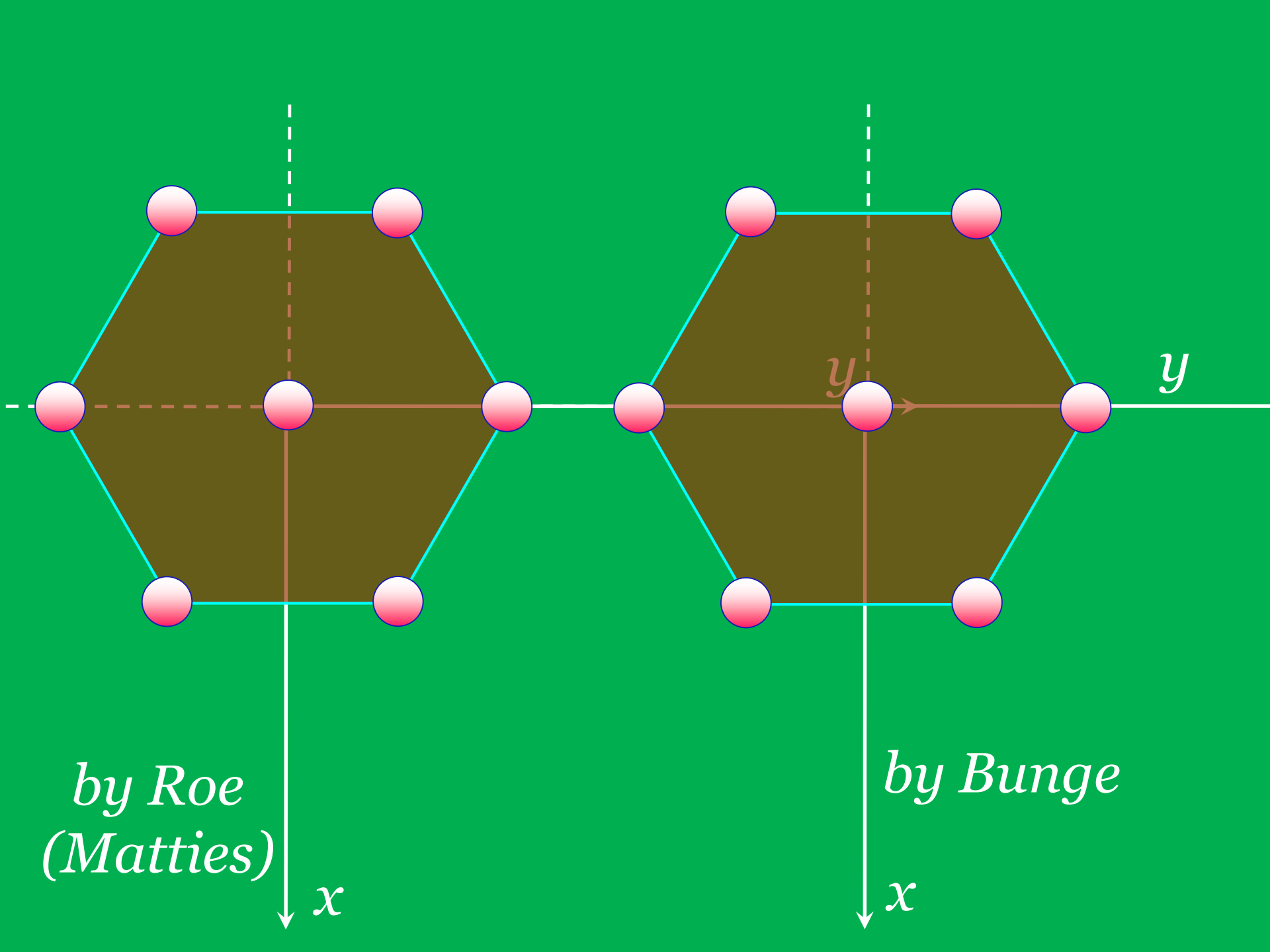
$c_0 / a_0 = 1.633$



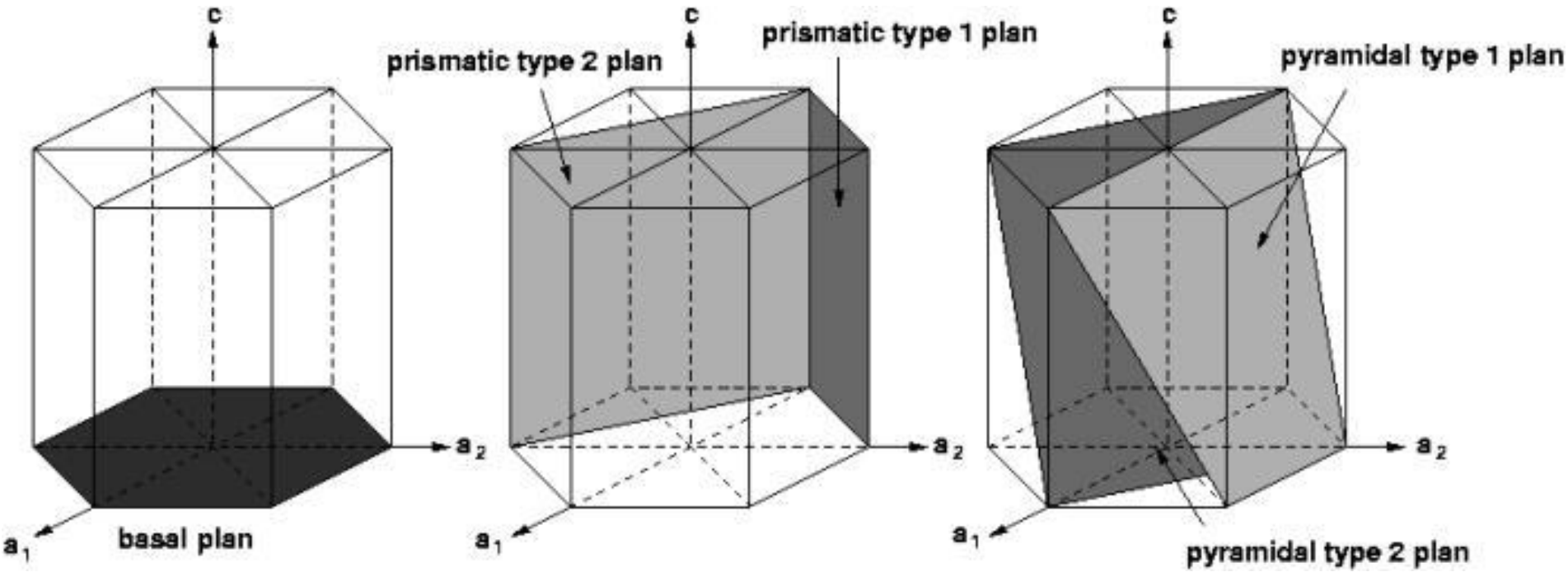


Crystallographic system: **HEXAGONAL** $a_0 = b_0 \neq c_0$ $\alpha = \beta = 90°$, $\gamma = 120°$




y
y
by Roe
(Matties)
x
by Bunge
x

Typical planes for hexagonal system



Project WND-POWR.03.02.00-00-I043/16

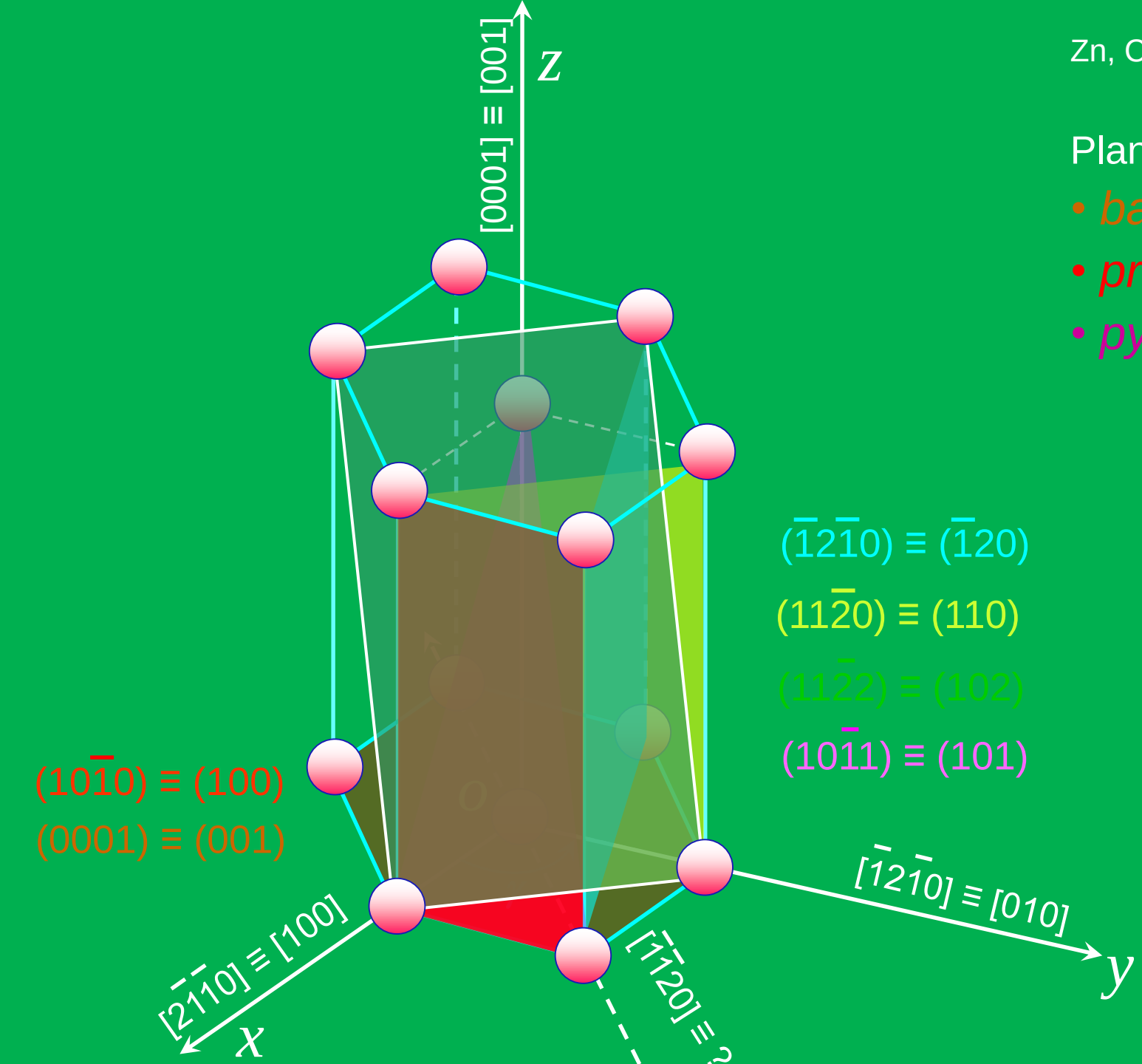
International interdisciplinary PhD Studies in Materials Science with English as the language of instruction

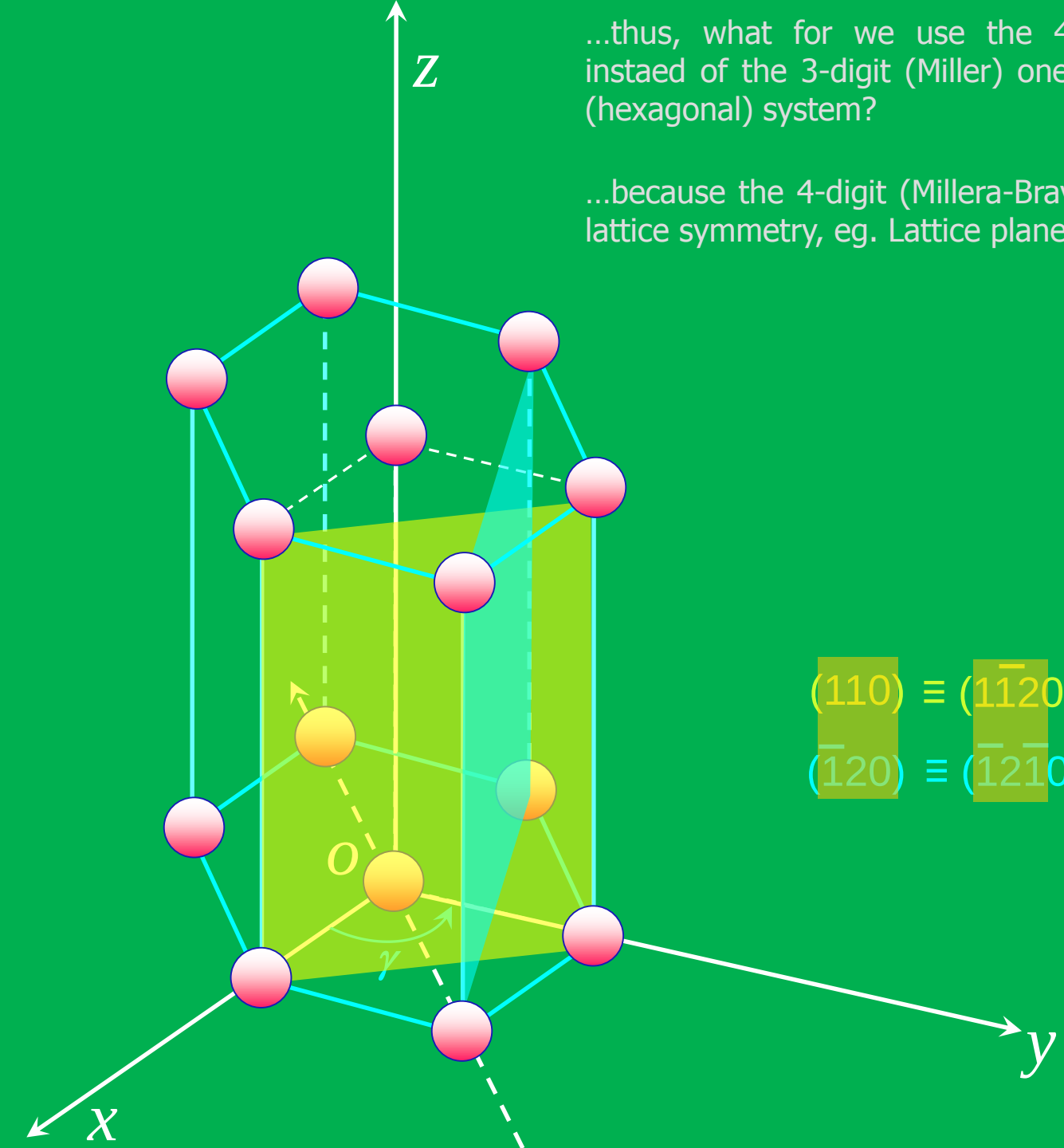
Project co-financed by the European Union within the European Social Funds

Zn, Cd, Mg, Co, Ti, Zr

Planes:

- *basal,*
- *prismatic,*
- *pyramidal*





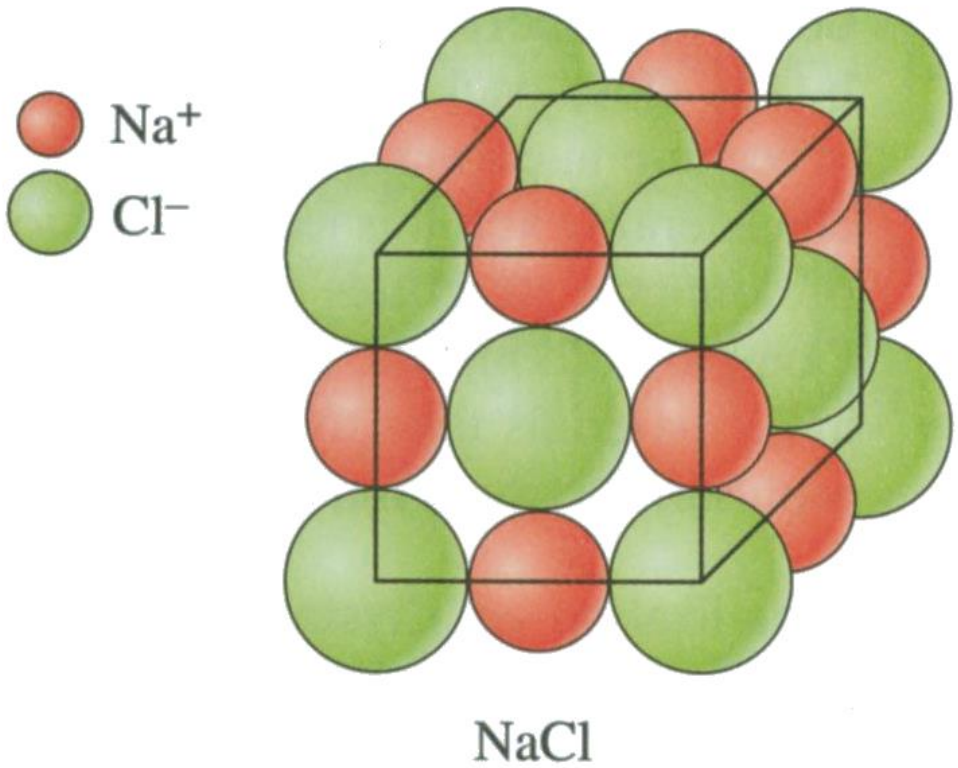
…thus, what for we use the 4-digit (Millera-Bravais) indicies instaed of the 3-digit (Miller) one if the both describe the same (hexagonal) system?

…because the 4-digit (Millera-Bravais) indicies better express the lattice symmetry, eg. Lattice planes (110) and (-1 2 0)

$(110) \equiv (11\bar{2}0)$

$(\bar{1}20) \equiv (\bar{1}2\bar{1}0)$

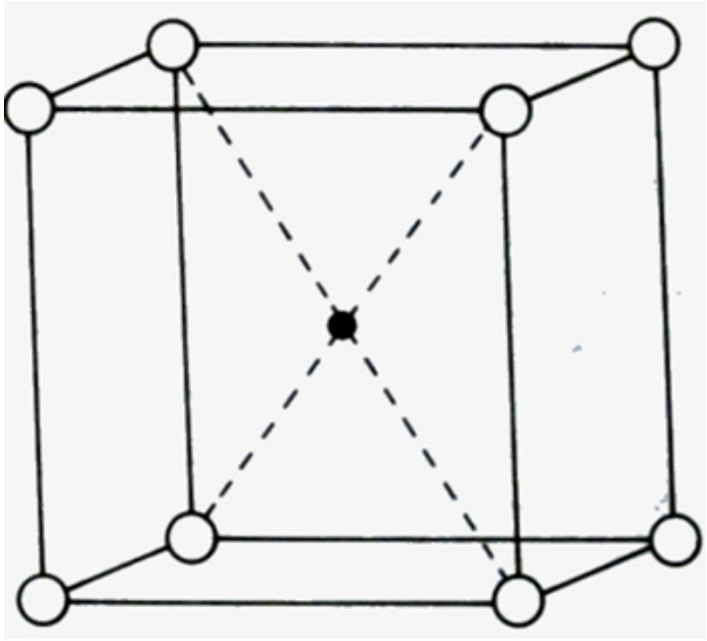
Structure of ceramics



NaCl

Sodium chloride structure, two-ion unit cell (Na+ and Cl-) per lattice point, cubic face-centred.

Interstice voids



Location of interstices in the CP structure:

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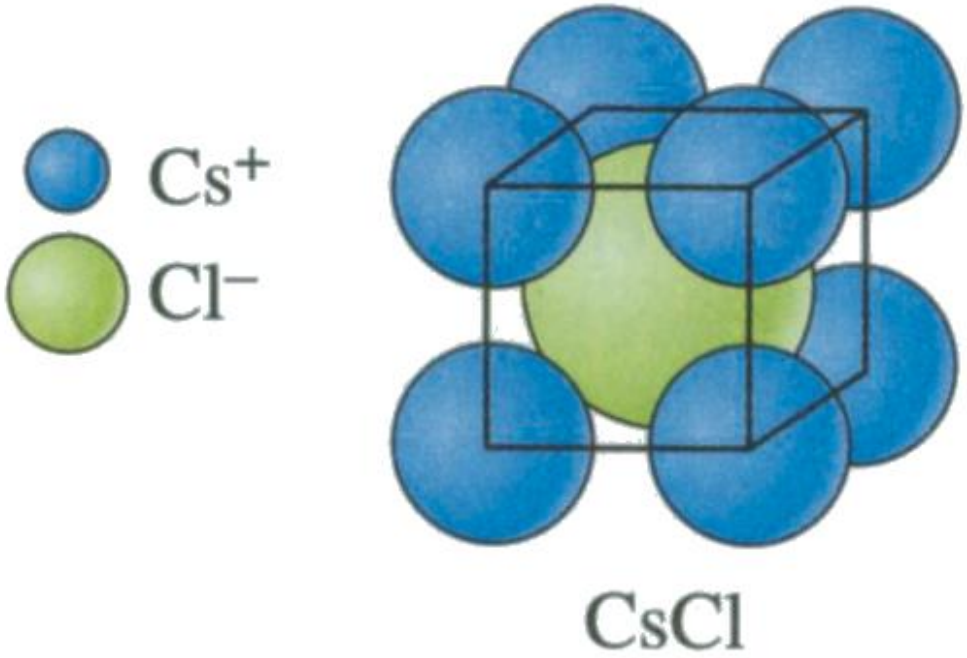
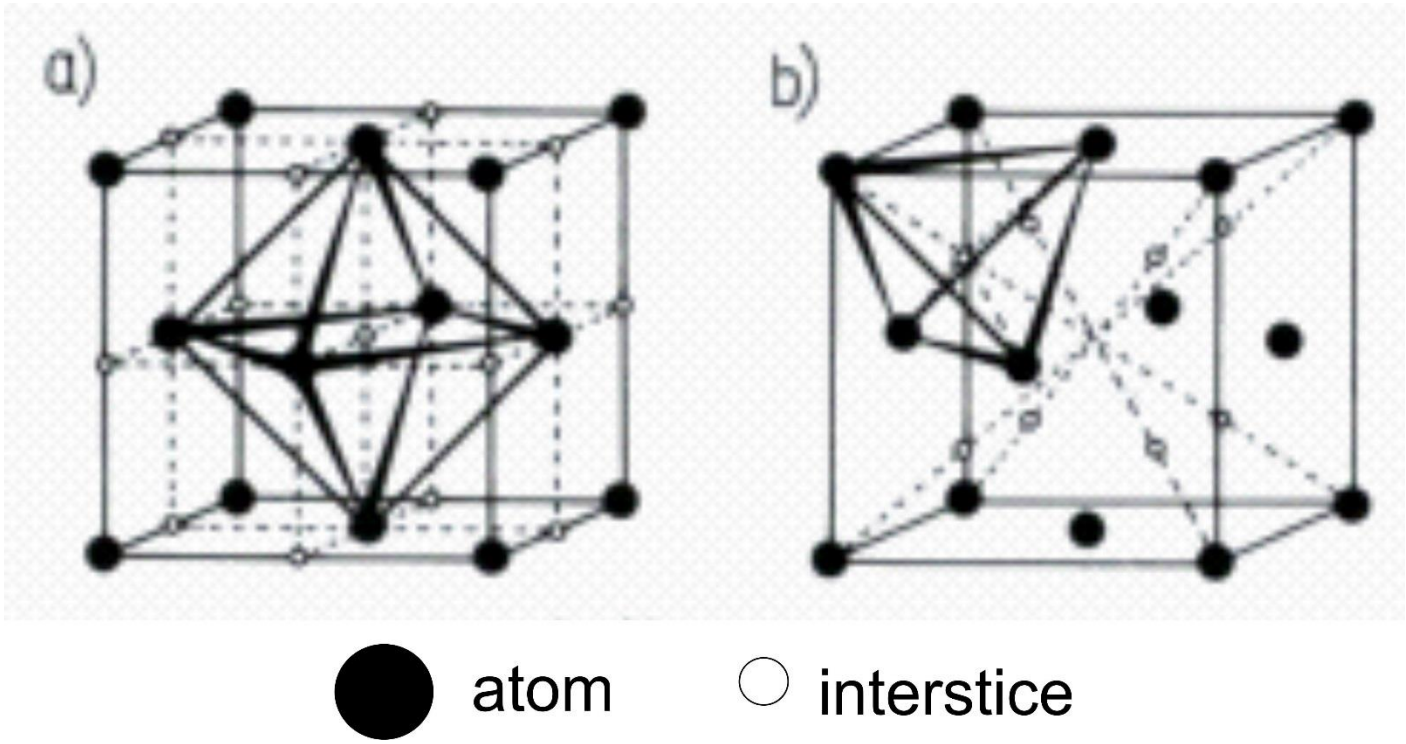
Ionic ceramic materials (ionic crystals)

Typical ionic ceramics are chemical compounds of metals with non-metals.



Structure of caesium chloride, unit cell with two ions (Cs+ and Cl-) per lattice point, CP structure.

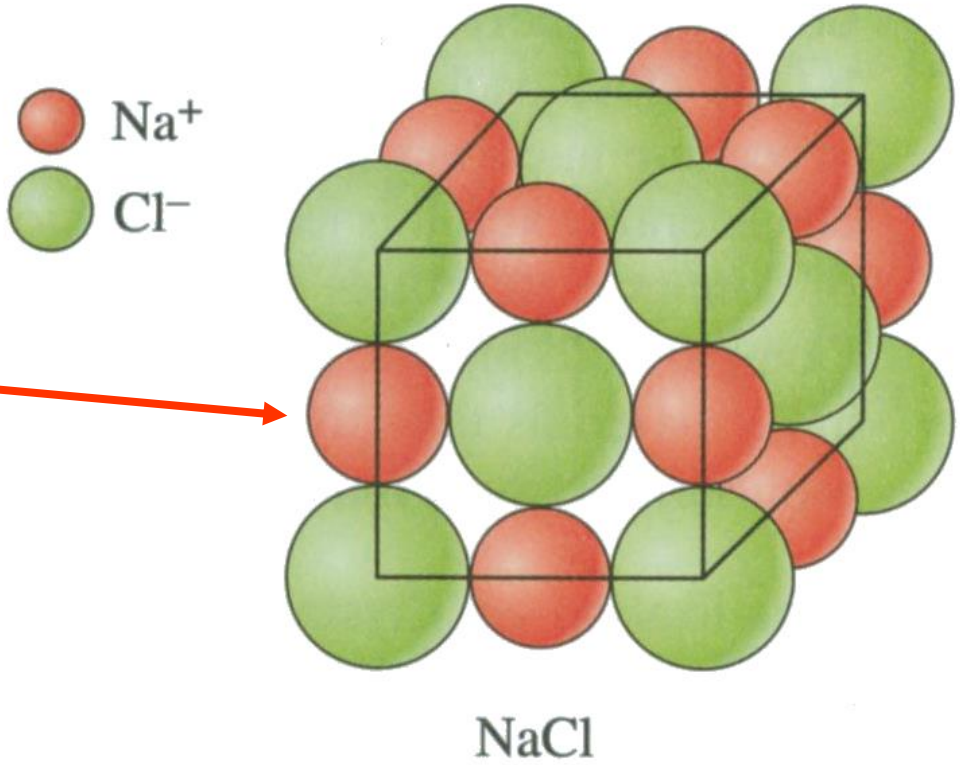
Interstice voids



Location of interstices in the FCC structure:
a) Octaedric interstices, diameter of the gap - 0.414d (d - diameter of the net atom),
b) Tetrahedral interstices, gap diameter 0.225d.

Ionic ceramic materials (ionic crystals)

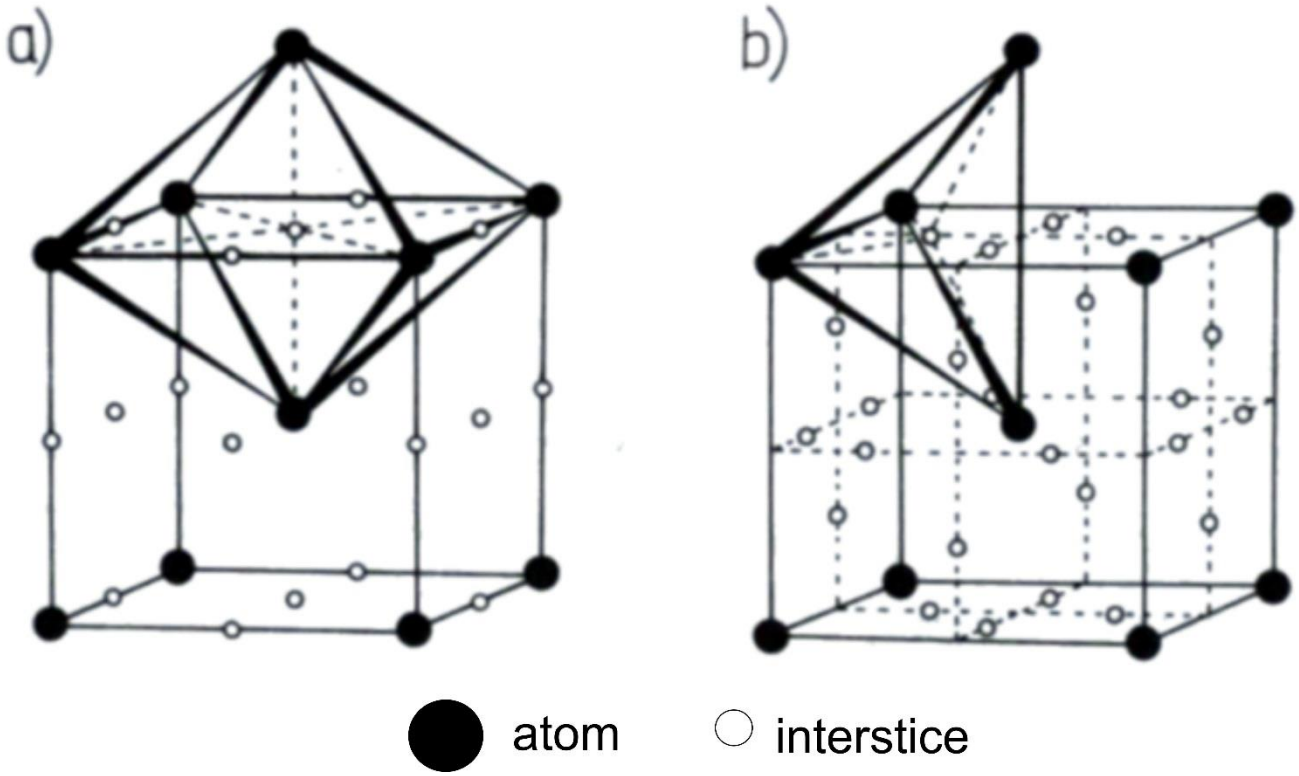
Octaedric interstices



NaCl

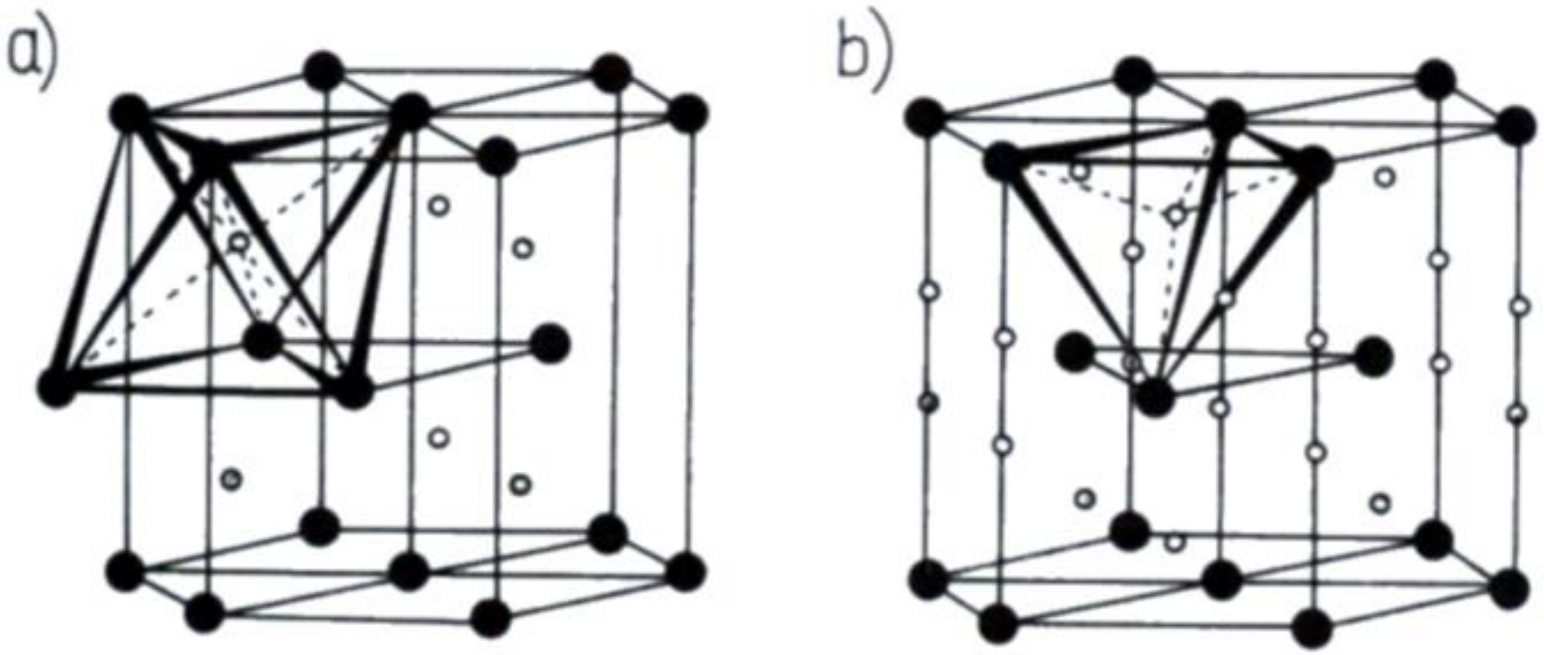
Sodium chloride structure, two-ion unit cell (Na+ and Cl-) per lattice point, FCC structure.

Interstice voids



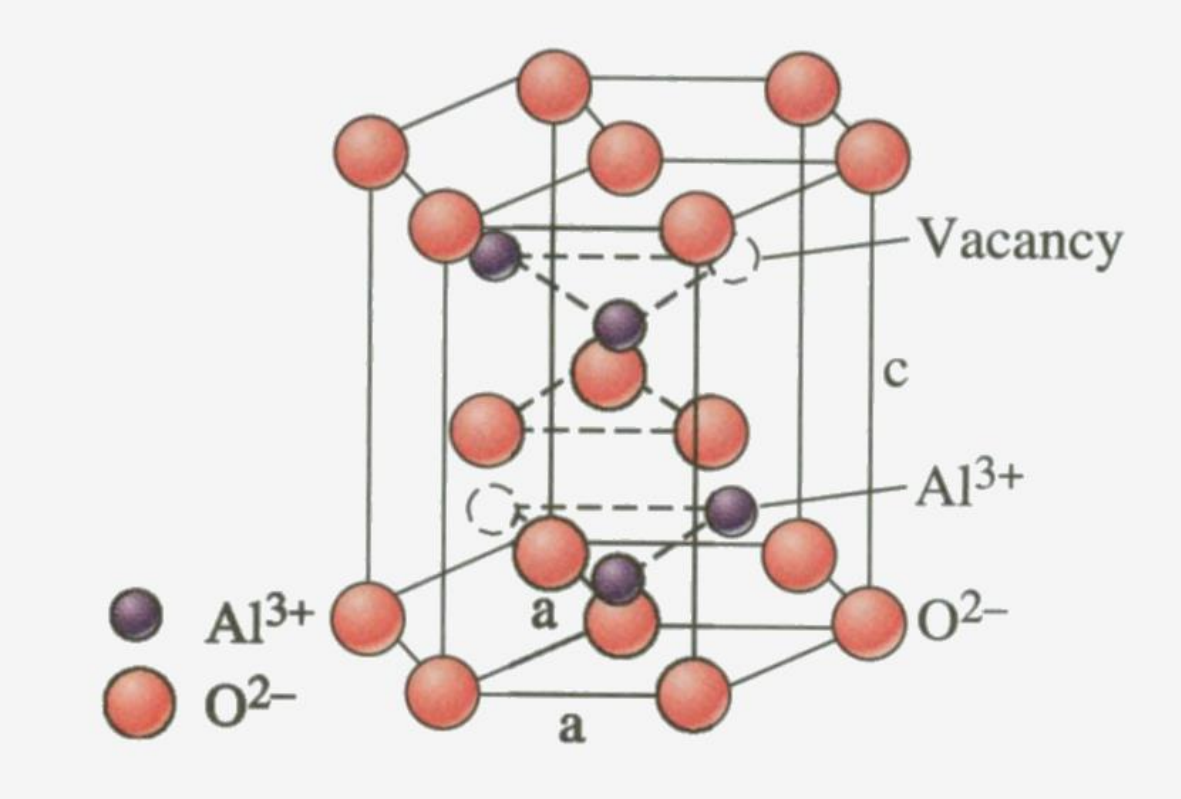
Location of interstices in the BCC structure:
a) Octaedric interstices, diameter of the gap - 0.155d (d - diameter of the lattice atom),
b) Tetrahedral interstices, gap diameter - 0.291d.

Interstice voids



Location of interstices in the HCP structure:
a) Octaedric interstices,
b) Tetrahedral interstices.

Ionic ceramic materials (ionic crystals)



Corundum structure (α-Al2O3), unit cell with oxygen anions in hexagonal positions and Al cations in octaedric interstices.

α-Al2O3 - the most widely (and most frequently) used ceramic material.

European Funds
Knowledge Education Development

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European Social Fund

Thank you

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