Chemistry and Physics of Solids – lecture 1

ideal crystal, structure and the lattice, space groups and point groups

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Suggested literature

Richard J.D. Tilley: Understanding Solids, Willey 2013

C. Giacovazzo: Fundamentals of crystallography, Oxford Science Publications 1992

J. I. Gersten: Physics and chemistry of materials, Willey 2001

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Lecture content

- Space lattice
- Crystal systems
- Bravais lattices
- Point groups
- Space groups
- Symmetry operations, matrix based definition
- Equivalent positions

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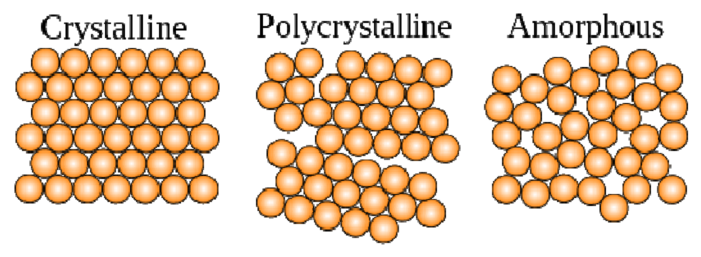
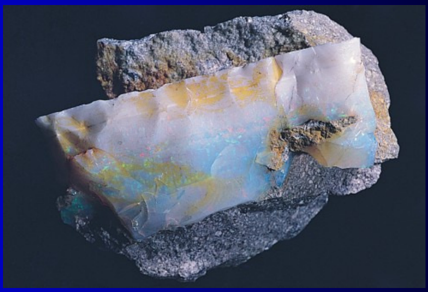
The state of solid state

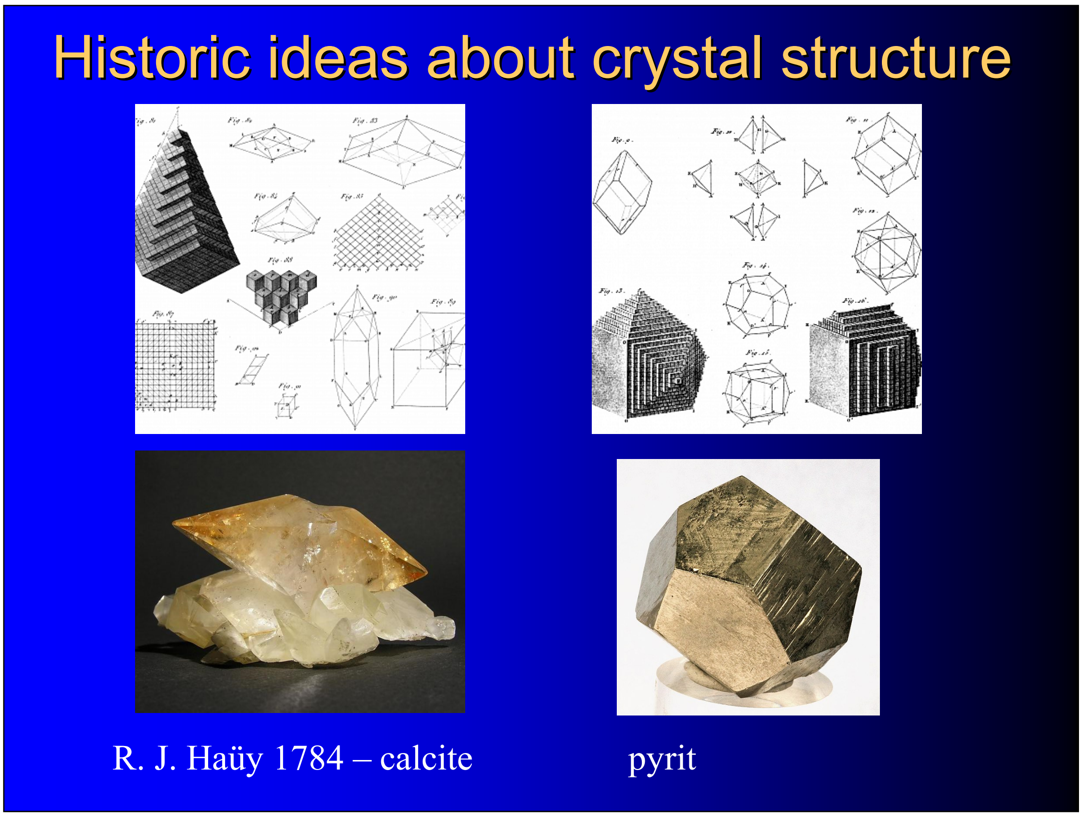


SiO$_2$ in crystal form – quarz



SiO$_2$ in amorphous form – opal

The solid state can exist in several forms , crystalline, polycrystal amorphous. Crystalline form is periodically ordered on long range. Semi crystalline or polycrystalline is ordered only on small range and the amorphous phases are not periodically ordered at all. The substance with the same composition can exist in both crystal and amorphous form. An example is quartz – crystal form of SiO$_2$ and opal, amorphous form of SiO$_2$.



Historic ideas about crystal structure

R. J. Haüy 1784 – calcite

pyrit

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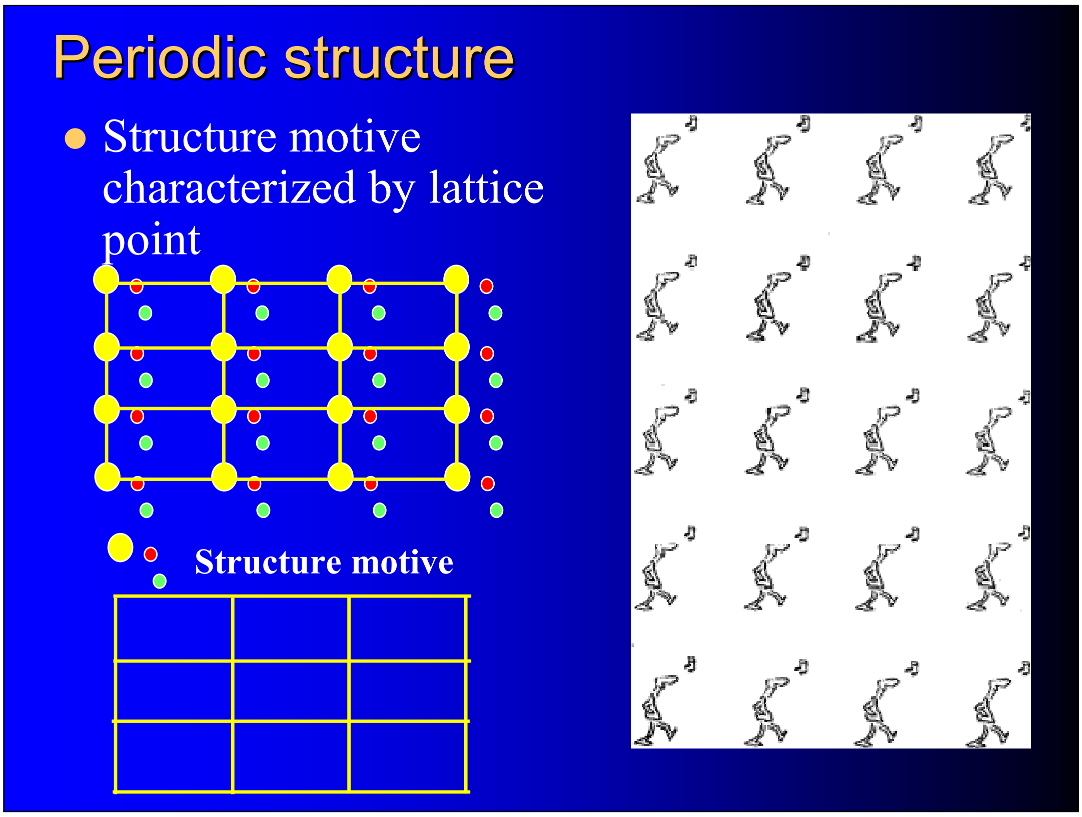
In the past, nothing was known about internal structure of solid p
scientist were fascinated by crystal shapes of minerals. Based on the crystal shapes they had predicted the crystals consist of small elemental bricks witch can build the whole crystal. This prediction based on geometrical analysis was nowadays confirmed to be correct by X-ray structure analysis.



Periodic structure

- Structure motive characterized by lattice point

Structure motive

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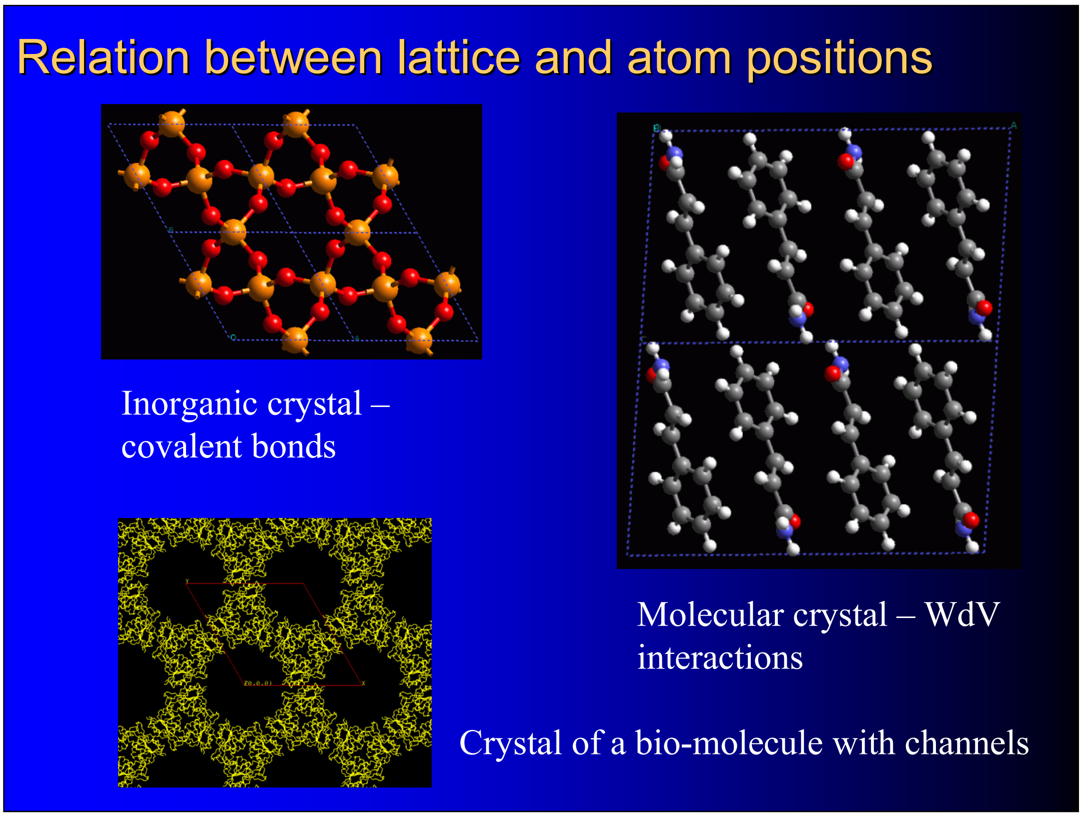
Crystalline solids are based on periodically repenting motive. The typically an atom, a molecule or a cluster of molecules. To simplify the description we characterize the motive position by a point. The points (lattice points) forms a periodic lattice.



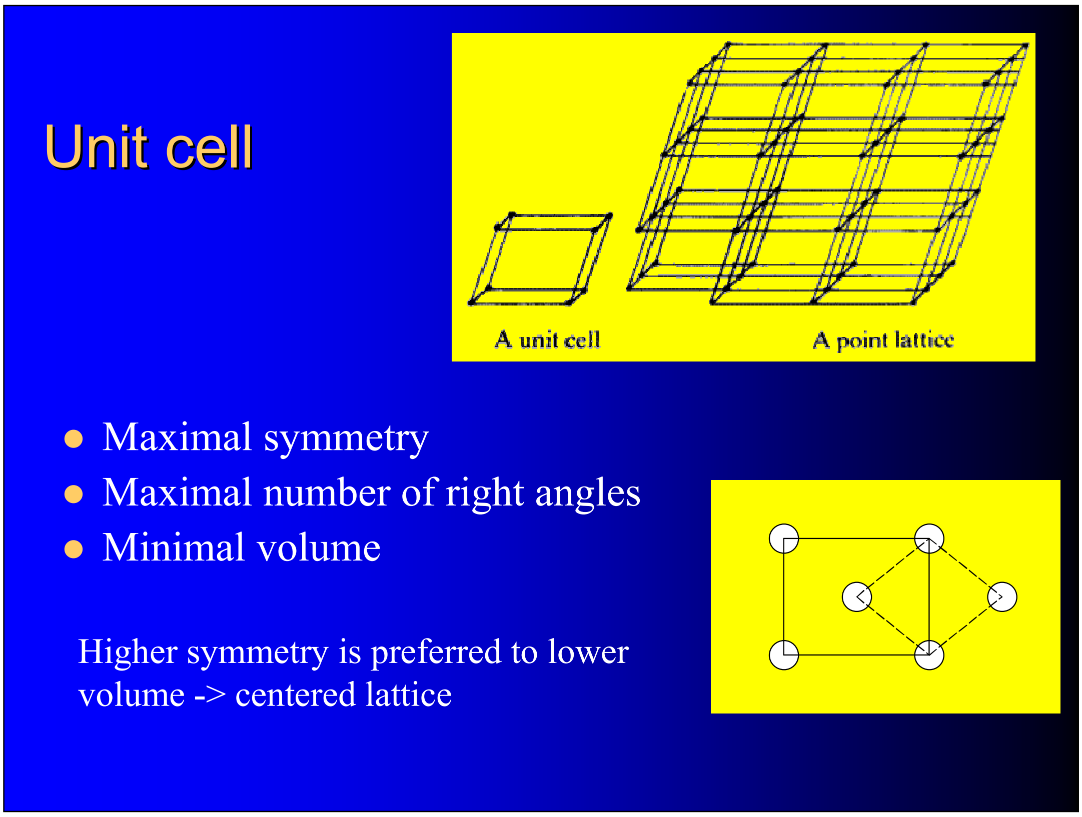
Relation between lattice and atom positions

Inorganic crystal –
covalent bonds

Molecular crystal – WdV
interactions

Crystal of a bio-molecule with channels

For inorganic crystals the motive is typically a group of atoms, bo by covalent, ion or metallic bonds. The typical motive for organic molecules crystal is a single covalent bonded organic molecule, forming so-called molecular crystals. Even big bio molecules can form crystals – such molecules often contain channels full of disordered solvent molecules.



Unit cell

- Maximal symmetry
- Maximal number of right angles
- Minimal volume

Higher symmetry is preferred to lower volume -> centered lattice

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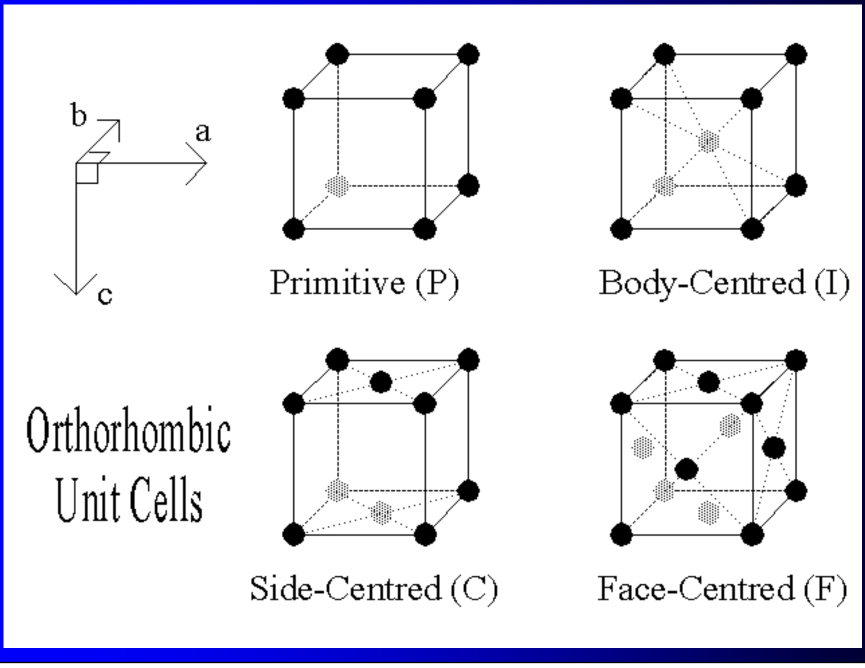
To be able to describe efficiently the periodic structure, we shoul smallest periodic element sufficient for the whole structure generation. This element is called Unit cell. Unit cell should be not only the smallest possible element, but it should reflect the whole symmetry of the structure as well. For this reason we often choose for the structure description a unit with non-minimal volume, the so called centered lattice.

Existing centered lattice – Bravais lattices



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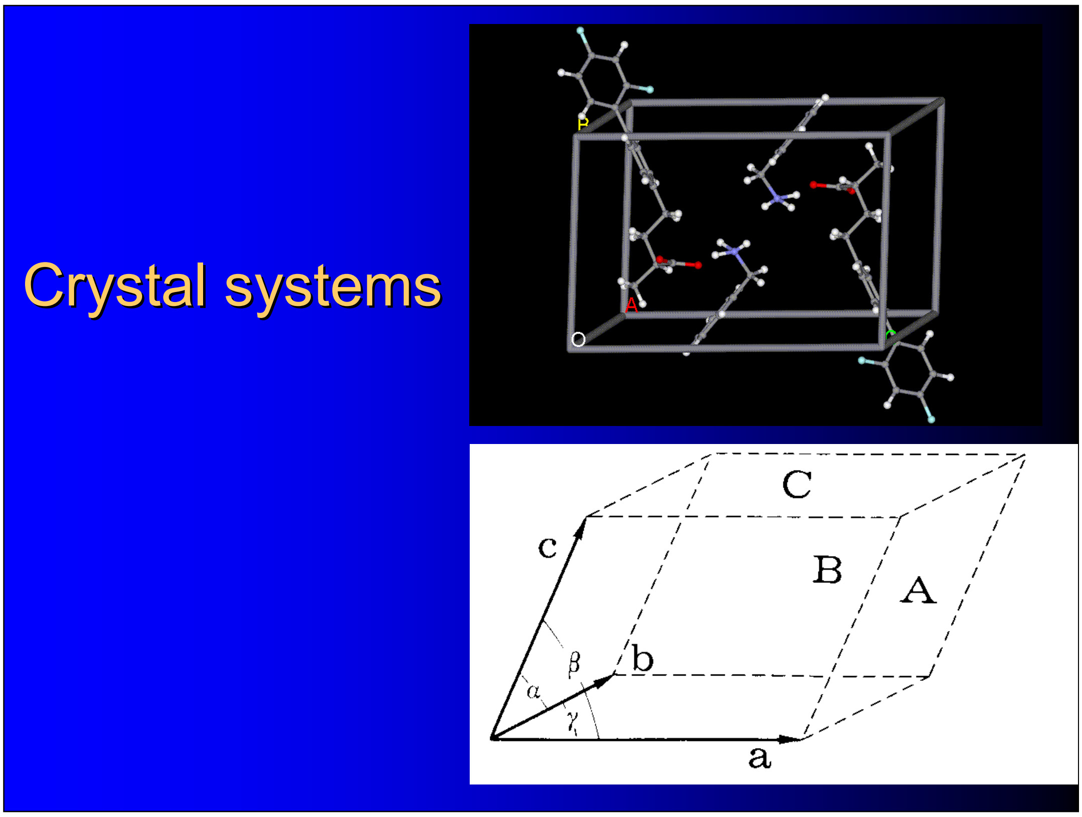
There exist 6 possible centered lattices:

Primitive (P) with one motive in the unit cell.

Side-Centered (A,B,C) with 2 motives in unit cell. For side-centered cell the letters A,B,C are related to the lattice direction in which the cell base is occupied by additional motive.

Body-Centered (I) with 2 motives in unit cell.

Face-Centered (F) with 4 motives in unit cell.



Crystal systems

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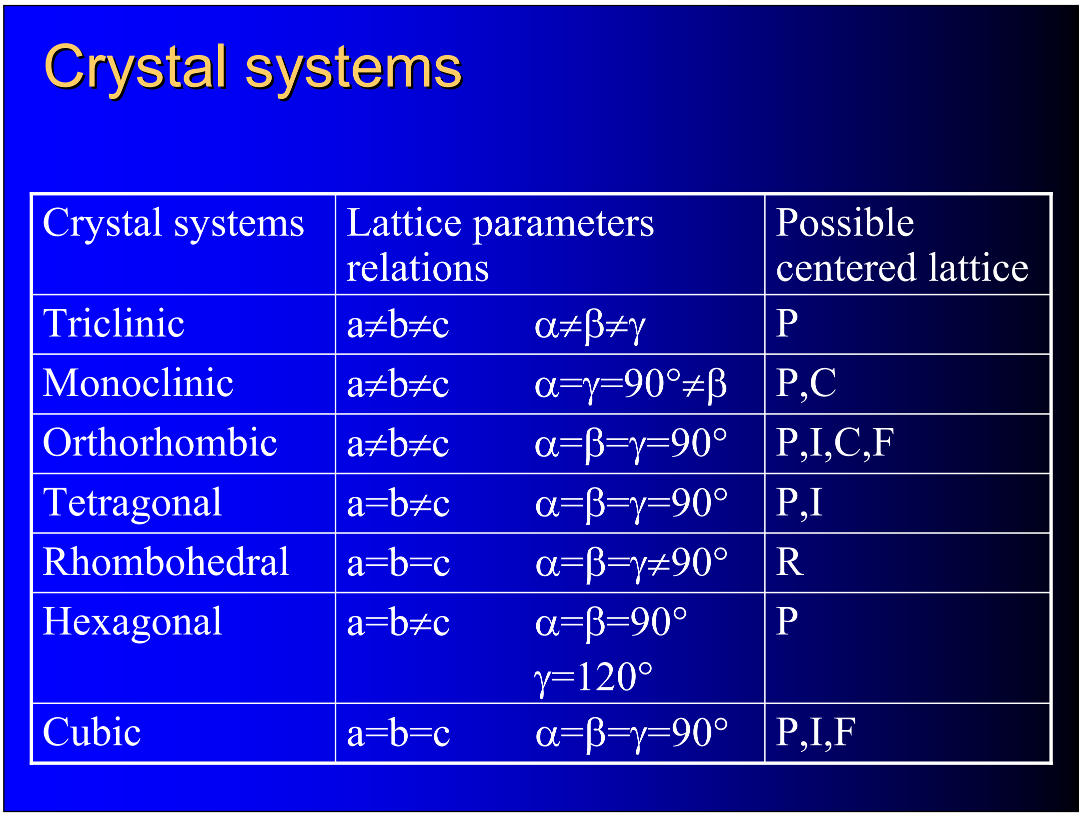
The lattice can be described by 6 lattice parameters:

a, b, c – the lengths' of the lattice edges.

α, β, γ – the angles between b and c, a and c, and a and b vectors respectively.



Crystal systems

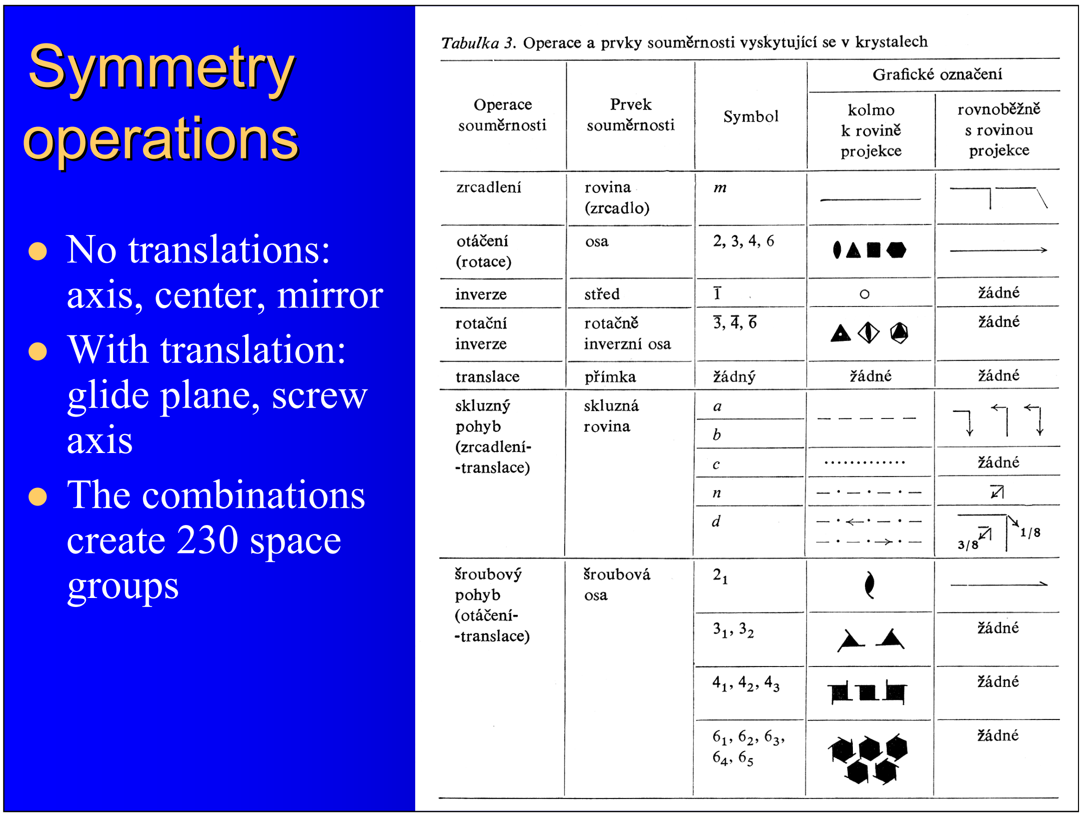
Crystal systems	Lattice parameters relations		Possible centered lattice
Triclinic	a≠b≠c	α≠β≠γ	P
Monoclinic	a≠b≠c	α=γ=90°≠β	P,C
Orthorhombic	a≠b≠c	α=β=γ=90°	P,I,C,F
Tetragonal	a=b≠c	α=β=γ=90°	P,I
Rhombohedral	a=b=c	α=β=γ≠90°	R
Hexagonal	a=b≠c	α=β=90° γ=120°	P
Cubic	a=b=c	α=β=γ=90°	P,I,F

Based on the relation between lattice parameters, we can sort all crystal systems. In each crystal system only selected centered lattice can exist. The reason is some system/centration combination (e.g. F centered monoclinic cell) can be described by smaller unit cell without any symmetry loss. It should be noticed that the rhombohedral structures can be described as hexagonal and the choice of hexagonal/rhombohedral system is partially optional. The table shows the crystal system sorted from the lower symmetry (triclinic) to the highest one (cubic).

Groups of symmetry – another level of structure description

Name	Use	Number
Plane groups	2D crystal description	17
Point groups	External crystal shape description (no translations elements included)	32
Space groups	Internal structure description	230

In addition to the periodic symmetry described by the unit cell, th additional symmetry inside the unit cell. Possible combinations of symmetry are called symmetry groups. In 2D there can exist 17 plane groups able to describe internal symmetry of 2D crystals. The so-called point groups (there may be 32 of them) can describe external symmetry of crystals and symmetry of their physical properties. Point groups do not include translation symmetry operation. Finally, the symmetry of 3D crystals can be described by 230 possible combinations of symmetry operations called space groups.



Symmetry operations

- No translations: axis, center, mirror
- With translation: glide plane, screw axis
- The combinations create 230 space groups

Tabulka 3. Operace a prvky souměrnosti vyskytující se v krystalech

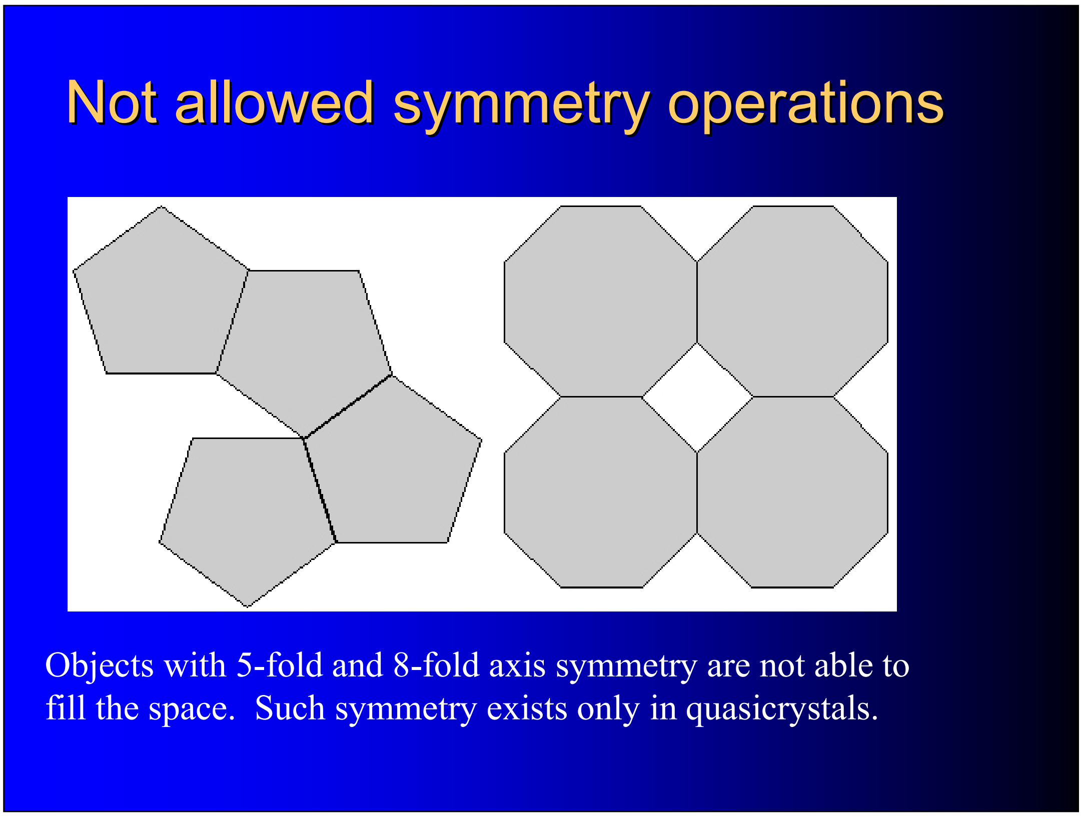
Operace souměrnosti	Prvek souměrnosti	Symbol	Grafické označení: kolmo k rovině projekce	Grafické označení: rovnoběžně s rovinou projekce
zrcadlení	rovina (zrcadlo)	*m*	———	⌐
otáčení (rotace)	osa	2, 3, 4, 6	⬮ ▲ ■ ⬢	⟶
inverze	střed	$\bar{1}$	○	žádné
rotační inverze	rotačně inverzní osa	$\bar{3}, \bar{4}, \bar{6}$		žádné
translace	přímka	žádný	žádné	žádné
skluzný pohyb (zrcadlení--translace)	skluzná rovina	*a*	– – – – –	
		b		
		c	·············	žádné
		n	— · — · — · —	
		d	— · ← · — · — — · — · → · —	3/8 1/8
šroubový pohyb (otáčení--translace)	šroubová osa	2_1		⟶
		3_1, 3_2		žádné
		4_1, 4_2, 4_3		žádné
		6_1, 6_2, 6_3, 6_4, 6_5		žádné

The 230 space groups are created by a combination of symmetry

They can be divided into 2 groups: The one without translation and the one with translation.

No translation is a part of: mirror (m), rotation axis (2,3,4,6), center of symmetry (-1) and axis of inversion (-3,-4,-6).

Translation is a part of: glide plane (a,b,c,n,d) and screw axis (2_1 3_1 3_2 4_1 4_2 4_3 6_1 6_2 6_3 6_4 6_5).



Not allowed symmetry operations

Objects with 5-fold and 8-fold axis symmetry are not able to fill the space. Such symmetry exists only in quasicrystals.

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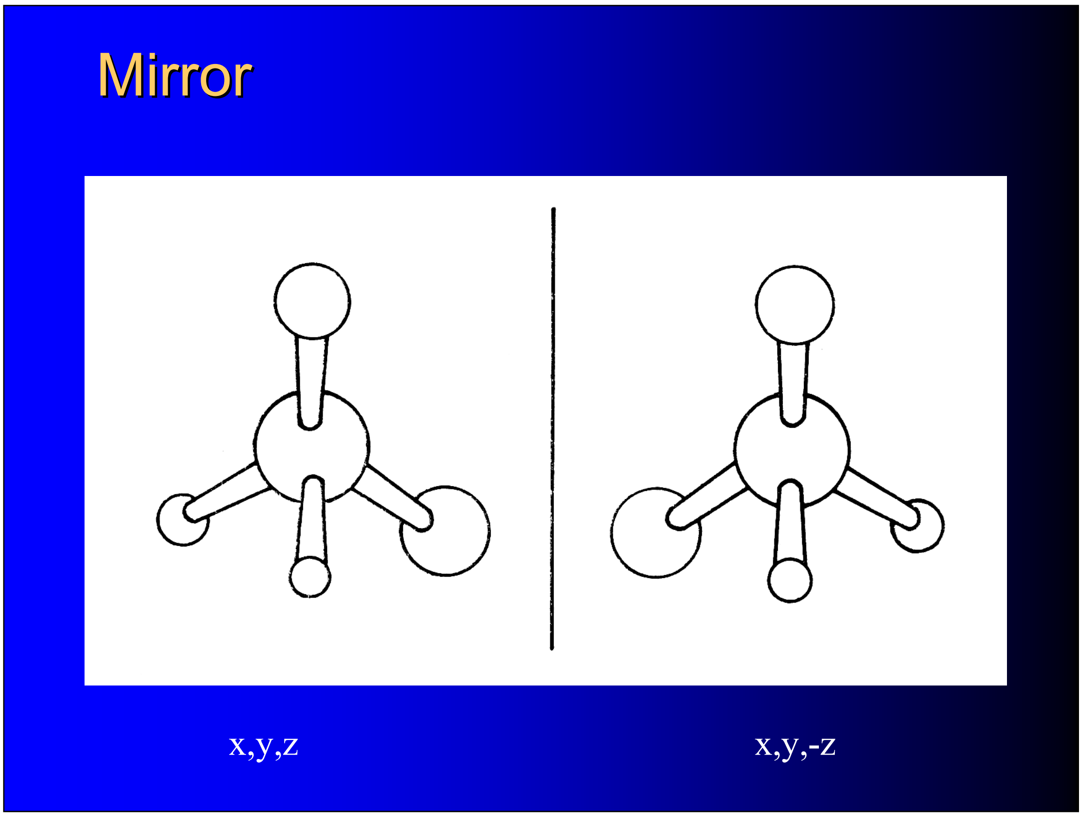
Only the symmetry operation listed on previous slide can describe 3D periodic objects. Symmetry operations like 5 fold axis or 8 fold axis generate shapes that are not able to fill space. Such symmetry operation exists only in special non-standard crystals – quasicrystals.



Mirror

x,y,z

x,y,-z

The mirror operation (m) simply mirrors the motive. It means tha coordinates are converted to x,y,-z for mirror perpendicular to c/z axis. For chiral molecules the mirror reverts chirality.

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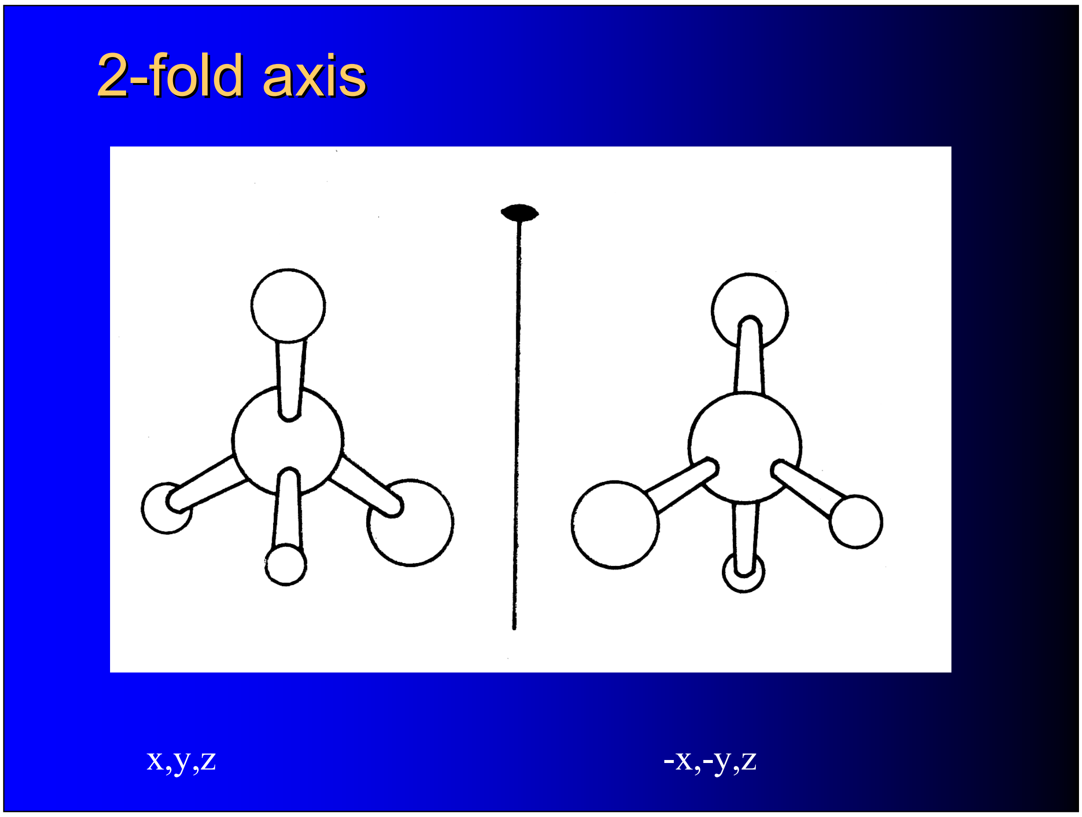
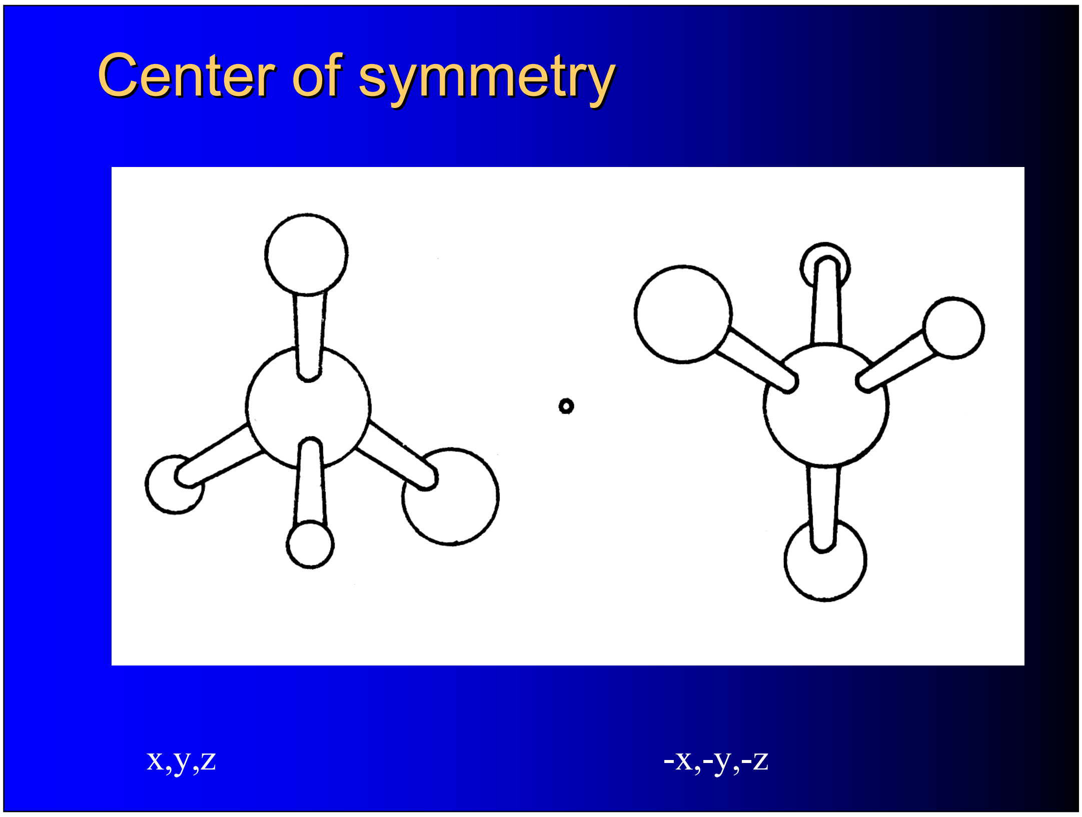


2-fold axis

x,y,z

-x,-y,z

2-fold axis rotates the molecule. From x,y,z coordinates it genera
axis parallel to c/z direction. The chiral centers are not changed.



Center of symmetry

x,y,z

-x,-y,-z

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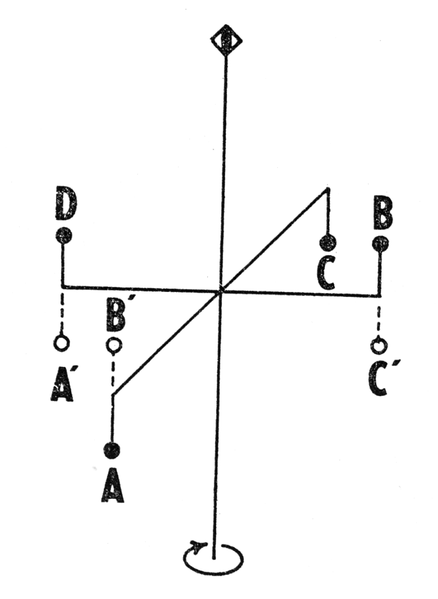
The center of symmetry reverts the molecule. From x,y,z it gener coordinates. It reverts chirality of chiral molecules.

axis of inversion



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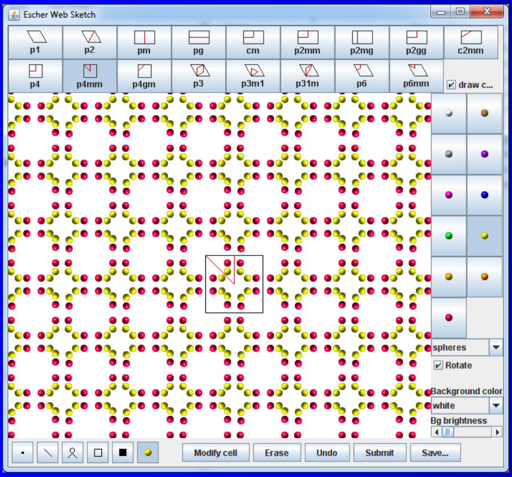
The axis of inversion rotate the motive and then apply a mirror op
Generated positions can be found in the International crystallographic tables (see later).

Plane groups

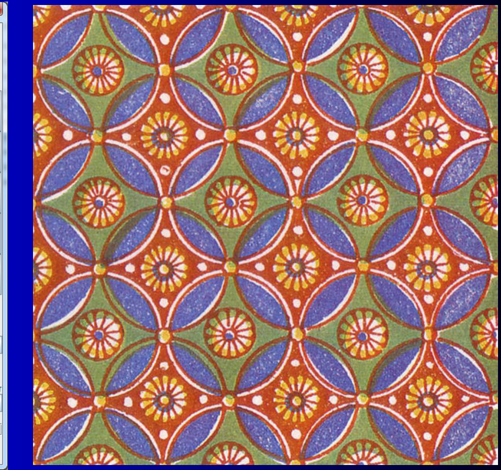


☑ draw c...

spheres

☑ Rotate

Background color
white



The operation symmetry without translation is sufficient to descri

groups. The plane groups can be used for description of 2D crystals or decorative motives printed on textile materials.

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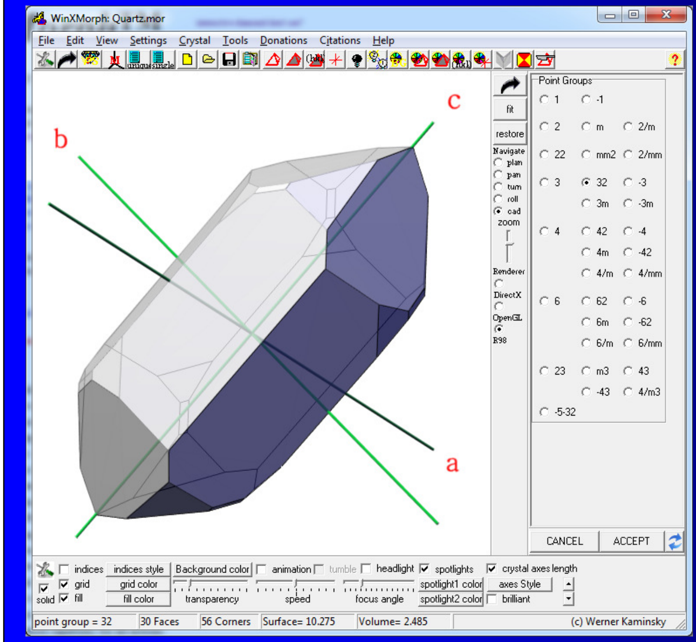
Point groups – quartz



Point Groups: ● 32

point group = 32 | 30 Faces | 56 Corners | Surface= 10.275 | Volume= 2.485 | (c) Werner Kaminsky

Quartz crystal
Point group 32

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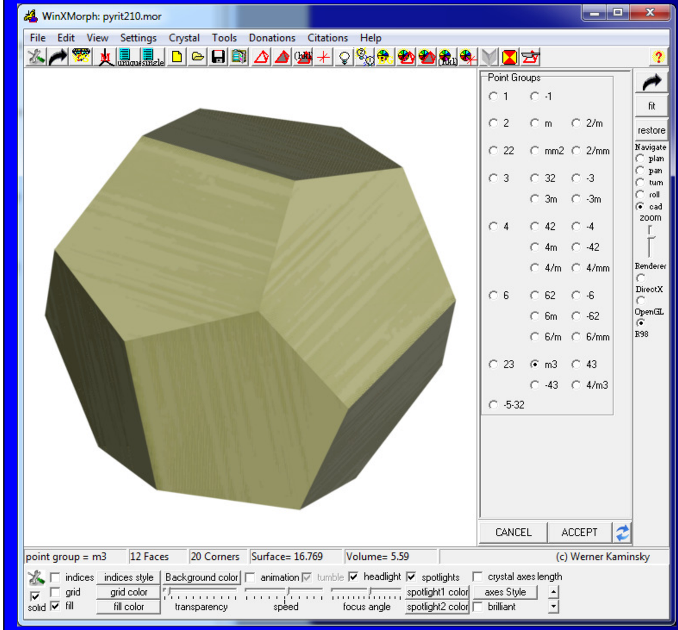
The operation symmetry without translation is sufficient to descri groups. The point groups can describe the shape of crystals and the symmetry of the solid phase physical properties. Such properties are e.g. hardness, color, piezoelectricity etc. … Known space group can help to generate the shape of hypothetical crystals (in this case quartz crystallizing in point group 32).

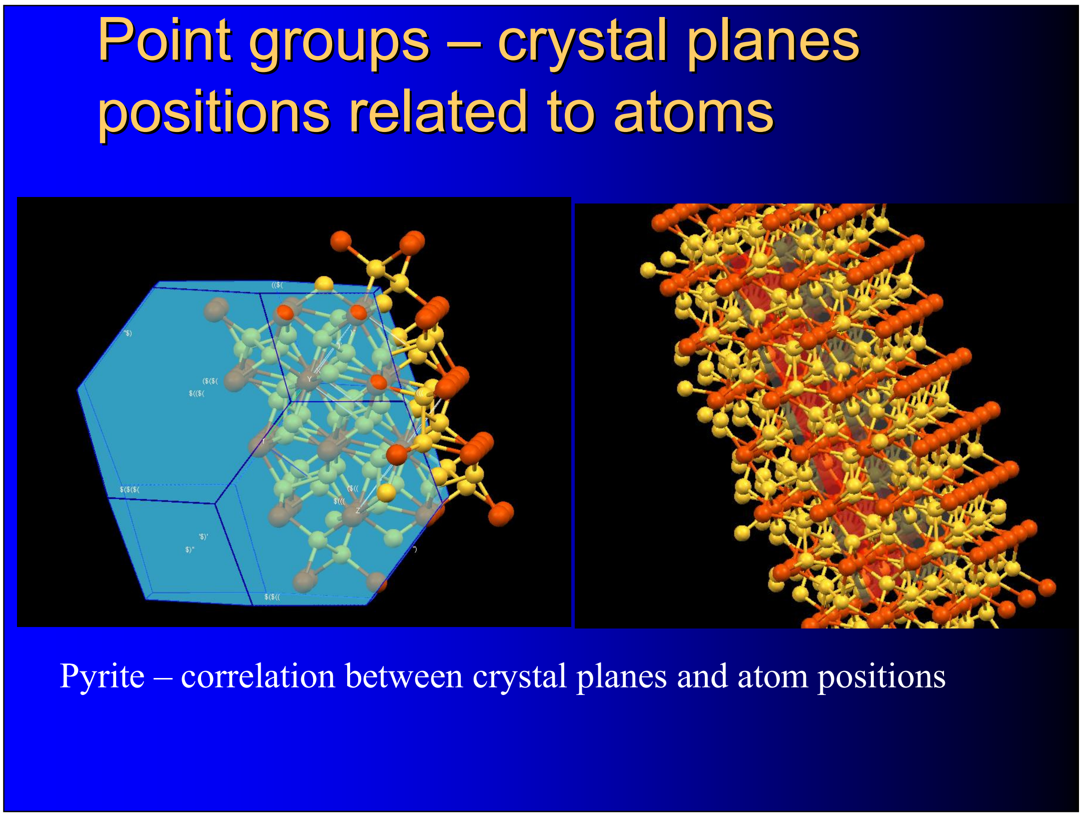
Point groups - pyrite



point group = m3 | 12 Faces | 20 Corners | Surface= 16.769 | Volume= 5.59 | (c) Werner Kaminsky

Pyrite crystal
Point group m3

This slide shows how point group m3 can be used for generating crystal shape of pyrite.



Point groups – crystal planes positions related to atoms

Pyrite – correlation between crystal planes and atom positions

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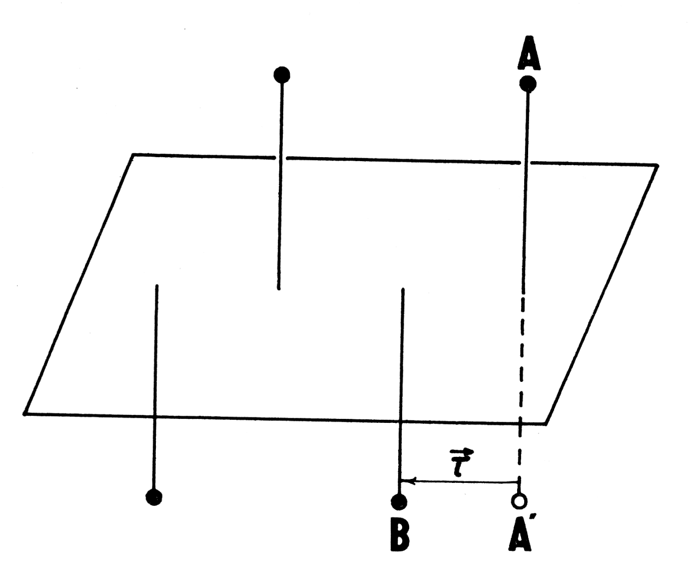
The point group describes the symmetry of atom planes orientatio the crystal planes. They can describe the differences in chemical properties of different planes. A plane with hydrophilic atoms can have e.g. different solubility in water than other one. Software tools like program Mercury can show the atom orientation according to different crystal planes and clarify the effect.

Glide plane



x,y,z

x,1/2+y,-z

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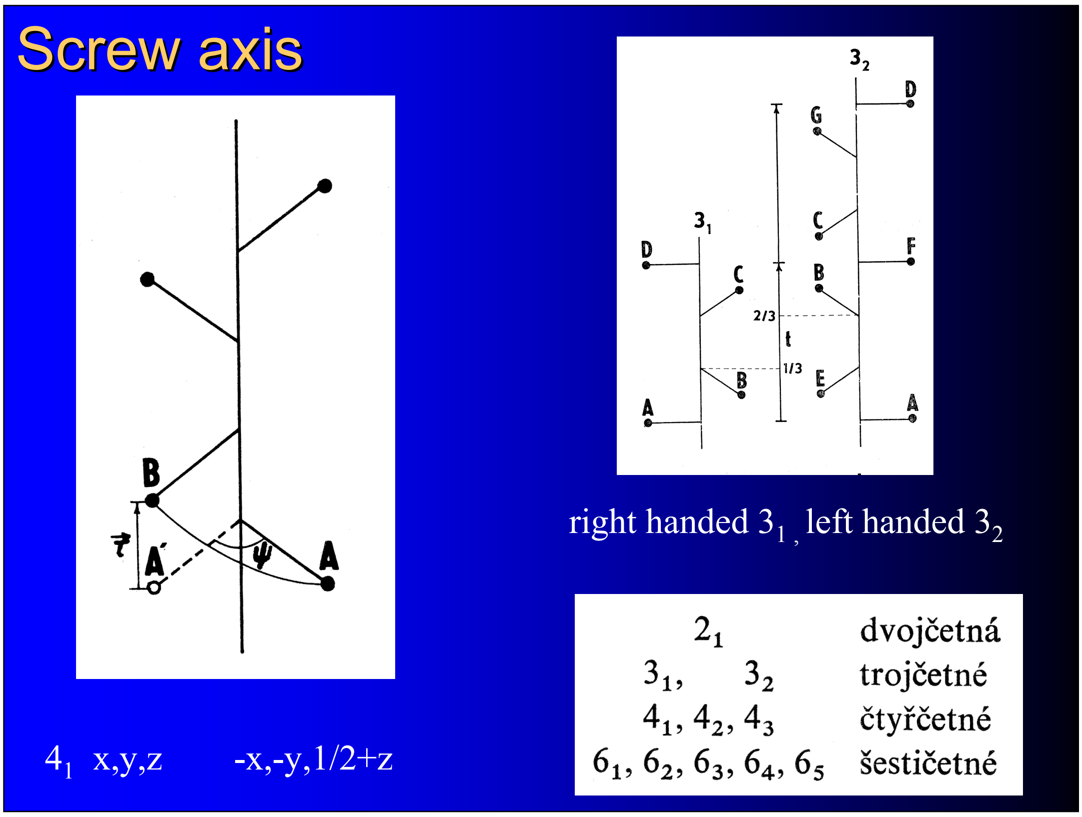
Let us go back to space groups. If we extend the already discussed operation by translation, we can get glide planes. Glide plane (a,b,c,n,d) are a combination of a mirror and a translation in a given direction (e.g. ½ in b axis -> b plane). The b glide plane generates from the motive in x,y,z position a motive in x,1/2+y,-z The operations reverts chirality.



Screw axis

right handed 3_1 , left handed 3_2

2_1	dvojčetná
3_1, 3_2	trojčetné
4_1, 4_2, 4_3	čtyřčetné
6_1, 6_2, 6_3, 6_4, 6_5	šestičetné

4_1 x,y,z -x,-y,1/2+z

The combination of transition and rotation axis results in screw a axis generates from the atom in x,y,z position an atom in –x,1/2+y,-z position (axis in c/y direction). The 3_1 and 3_2 axis differs in the rotation direction. Generally the axis generates something like the stars in old cylindrical towers. Operation does not revert chirality.

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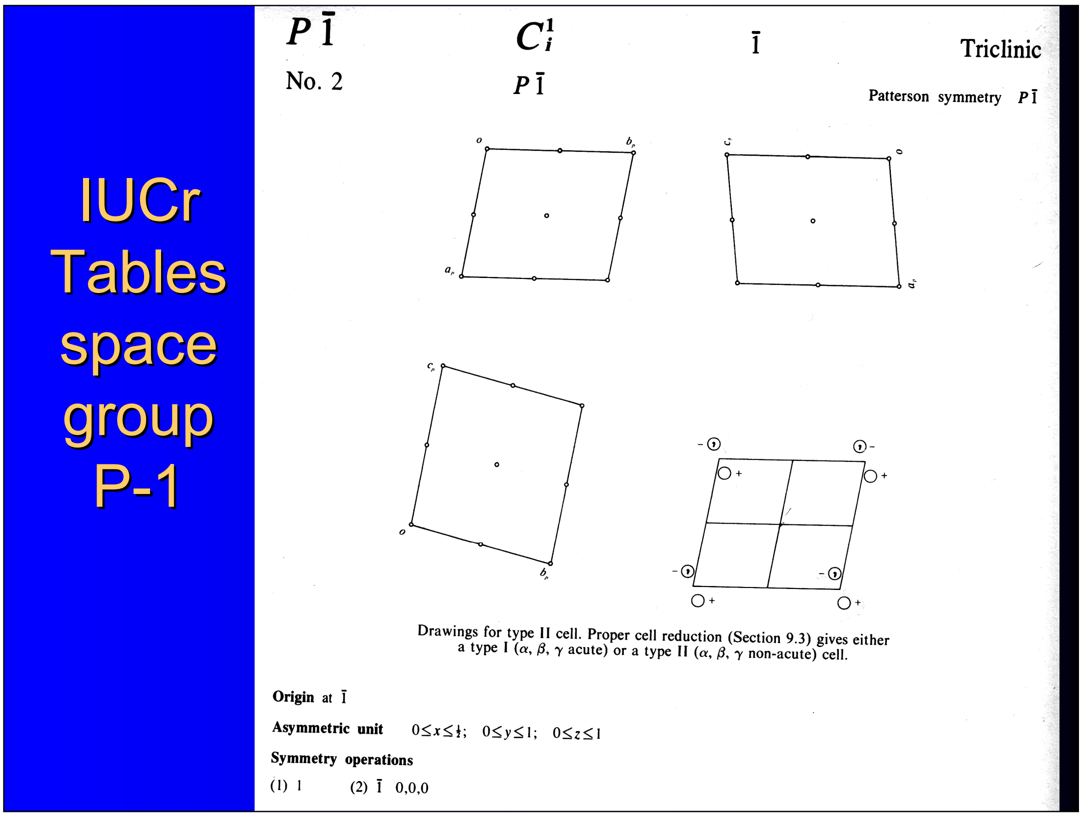

IUCr Tables space group P-1

$P\bar{1}$ C_i^1 $\bar{1}$ Triclinic

No. 2 $P\bar{1}$

Patterson symmetry $P\bar{1}$

Drawings for type II cell. Proper cell reduction (Section 9.3) gives either a type I (α, β, γ acute) or a type II (α, β, γ non-acute) cell.

Origin at $\bar{1}$

Asymmetric unit $0 \le x \le \frac{1}{2}$; $0 \le y \le 1$; $0 \le z \le 1$

Symmetry operations

(1) 1 (2) $\bar{1}$ 0,0,0

For each space group all information can be found in Internationa ray crystallography. For each group you can find there the group symbol (P-1), the corresponding crystallographic system (Triclinic), the group number (2) and location of the symmetry operation in the unit cell. It is clear from the symbol that this is the Bravais lattice (P). The tables should show the position of the motives (x,y,z and –x,-y,-z) for P-1.

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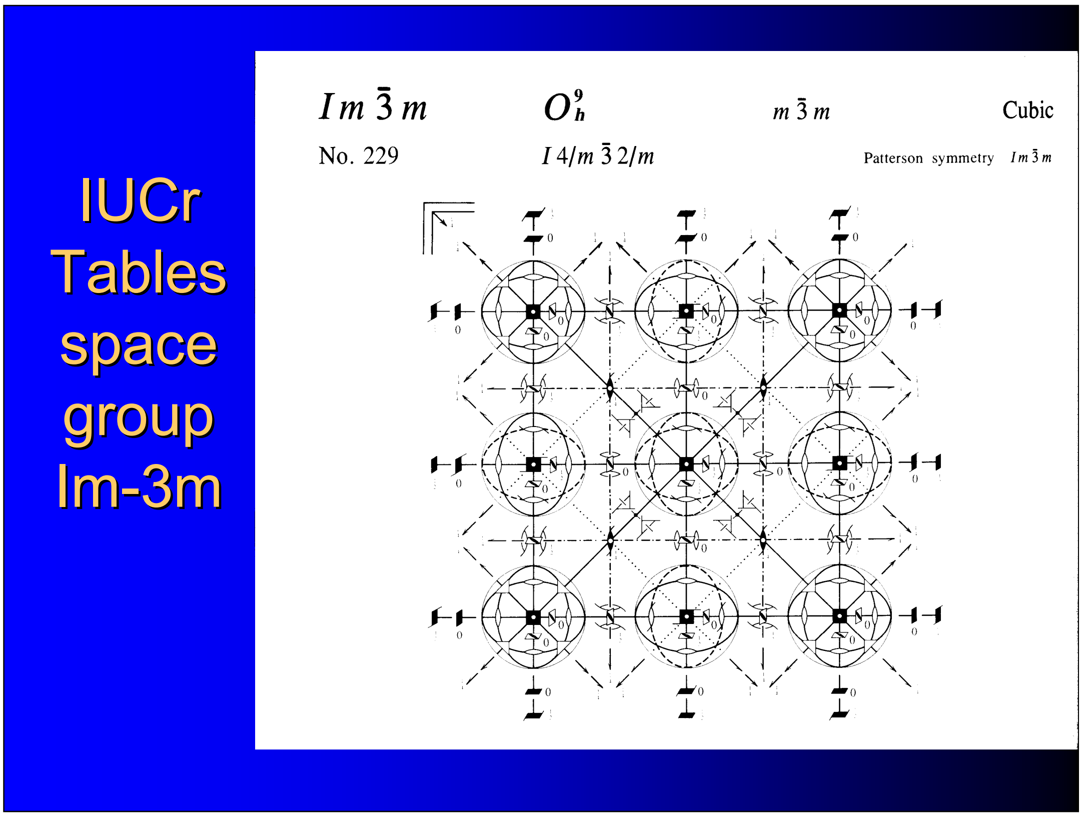

IUCr Tables space group Im-3m

$Im\bar{3}m$ O_h^9 $m\bar{3}m$ Cubic

No. 229 $I\,4/m\,\bar{3}\,2/m$ Patterson symmetry $Im\bar{3}m$

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An example of more complex group with more symmetry elemen number 229, cubic system, symbol I m -3 m. You can see presence of 4-fold. 3-fold and 2 fold axes in both normal and screw forms. Glide planes and mirrors are present as well.

Group Im-3m – 96 positions

96	l	1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $\bar{x},y,\bar{z}$	(4) $x,\bar{y},\bar{z}$
			(5) z,x,y	(6) $z,\bar{x},\bar{y}$	(7) $\bar{z},\bar{x},y$	(8) $\bar{z},x,\bar{y}$
			(9) y,z,x	(10) $\bar{y},z,\bar{x}$	(11) $y,\bar{z},\bar{x}$	(12) $\bar{y},\bar{z},x$
			(13) $y,x,\bar{z}$	(14) $\bar{y},\bar{x},\bar{z}$	(15) $y,\bar{x},z$	(16) $\bar{y},x,z$
			(17) $x,z,\bar{y}$	(18) $\bar{x},z,y$	(19) $\bar{x},\bar{z},\bar{y}$	(20) $x,\bar{z},y$
			(21) $z,y,\bar{x}$	(22) $z,\bar{y},x$	(23) $\bar{z},y,x$	(24) $\bar{z},\bar{y},\bar{x}$
			(25) $\bar{x},\bar{y},\bar{z}$	(26) $x,y,\bar{z}$	(27) $x,\bar{y},z$	(28) $\bar{x},y,z$
			(29) $\bar{z},\bar{x},\bar{y}$	(30) $\bar{z},x,y$	(31) $z,x,\bar{y}$	(32) $z,\bar{x},y$
			(33) $\bar{y},\bar{z},\bar{x}$	(34) $y,\bar{z},x$	(35) $\bar{y},z,x$	(36) $y,z,\bar{x}$
			(37) $\bar{y},\bar{x},z$	(38) y,x,z	(39) $\bar{y},x,\bar{z}$	(40) $y,\bar{x},\bar{z}$
			(41) $\bar{x},\bar{z},y$	(42) $x,\bar{z},\bar{y}$	(43) x,z,y	(44) $\bar{x},z,\bar{y}$
			(45) $\bar{z},\bar{y},x$	(46) $\bar{z},y,\bar{x}$	(47) $z,\bar{y},\bar{x}$	(48) z,y,x

The group I m -3 m generates from one position x,y,z, 96 other p table shows only the 48 one. The rest is generated by the I Bravais lattice from the x+1/2,y+1/2,z+1/2 position.

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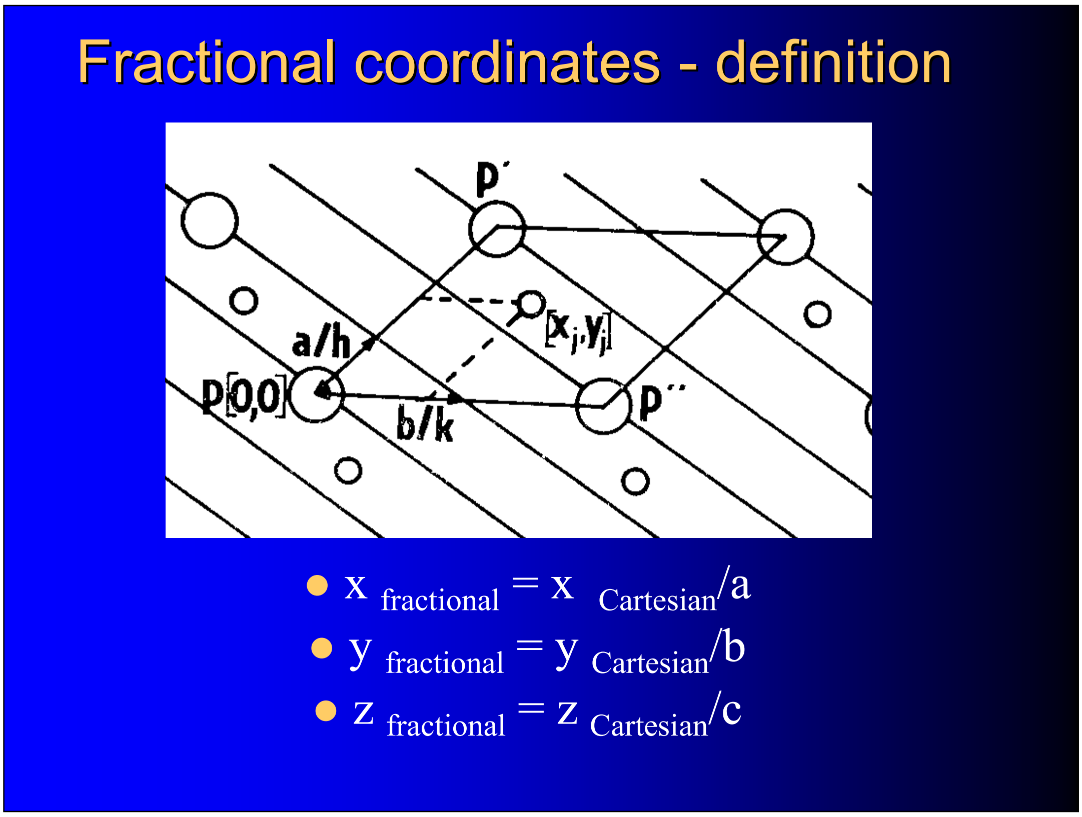

Fractional coordinates - definition

- $x_{\text{fractional}} = x_{\text{Cartesian}}/a$
- $y_{\text{fractional}} = y_{\text{Cartesian}}/b$
- $z_{\text{fractional}} = z_{\text{Cartesian}}/c$

All the equations for symmetry operations from previous slides c for units used in crystallography – the fractional coordinates. Fractional coordinates are used to describe the atom or motive positions.

The definition of the fractional coordinate is the point position in the direction of edge vector divided by the edge length. For orthorhombic and higher symmetry, the Cartesian coordinates can be simply divided by the cell lengths to get fractional coordinates. The result is typically a value in <0,1> interval. All information about solved crystal structures stored in databases is usually stored in the form of fractional coordinates.

Symmetry operation – matrix notation

Rotation part + Translation part. Symmetry operation 2_1

-1	0	0	0
0	-1	0	0
0	0	1	1/2

(1) x,y,z

(2) -x,-y,z+1/2

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For the use with computer programs, it is more efficient to descri operation as matrixes. The positions as listed in International tables can be generated automatically. The matrixes have a rotation part. The input position is multiplied by the rotation part and then the translation part is added. The table and results show the 2_1 operation parallel with c/z axis.

Symmetry operation – matrix notation

N-fold axis

cos(φ)	-sin(φ)	0	0
sin(φ)	cos(φ)	0	0
0	0	1	0

φ=90°, 4- fold axis

0	-1	0	0
1	0	0	0
0	0	1	0

(1) x,y,z (2) –y,x,z

(2) -x,-y,z (4) y,-x,z

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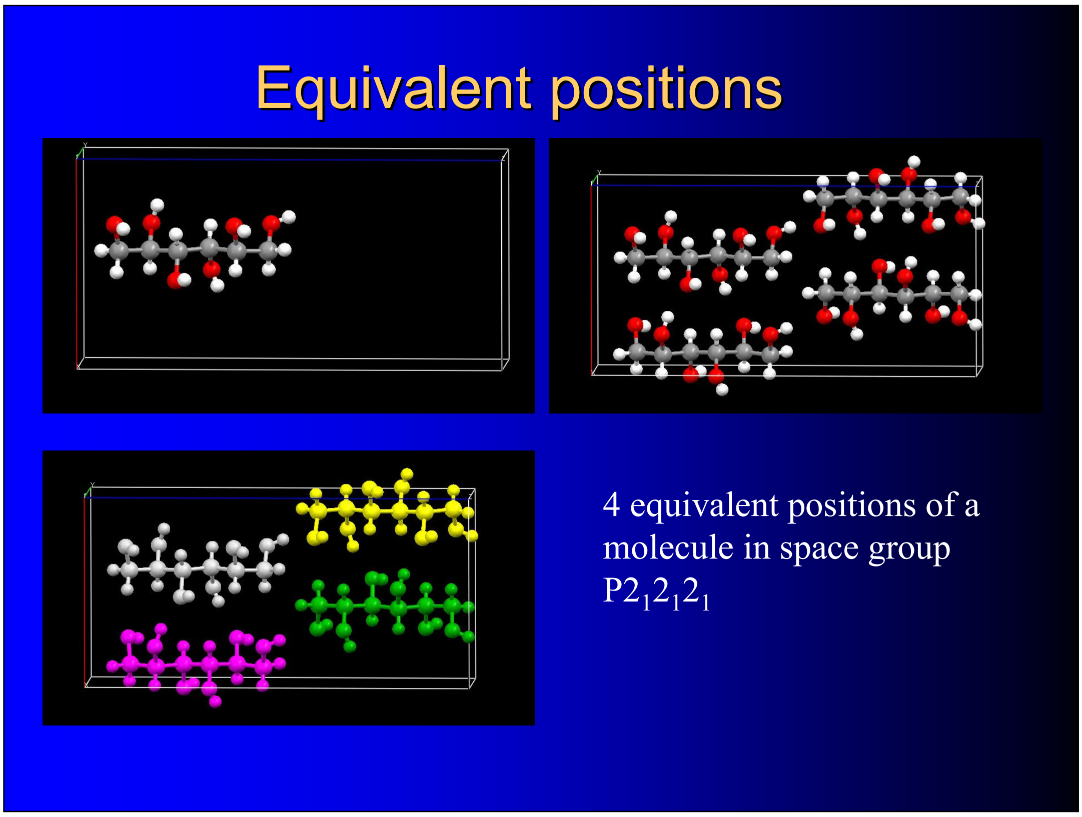
For rotation axis there exists a general matrix formula in which th rotation can be entered to get the result. Formula for 4-fold axis is demonstrated. It should be noted that if you multiply the y,-x,z position by the matrix, you will get x,y,z. 4-fold axes generate only 4 positions.



Equivalent positions

4 equivalent positions of a molecule in space group $P2_12_12_1$

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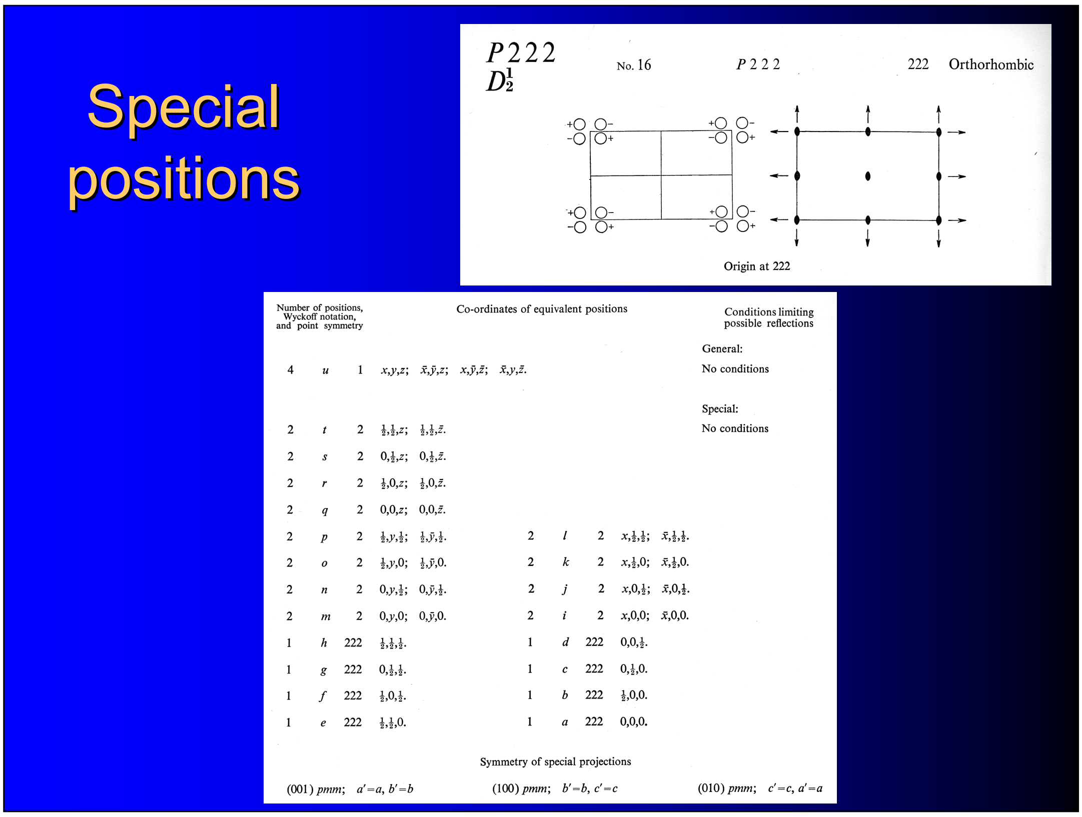
The molecule/motive can be found in the cell in general position symmetry operations generate multiple position where an identical motive is placed. The number of such positions depends on the space group. Such positions are called equivalent position. E.g. space group P 2_1 2_1 2_1 generates 4 equivalent positions.



Special positions

$P222$
D_2^1

No. 16 $P\,2\,2\,2$ 222 Orthorhombic

Origin at 222

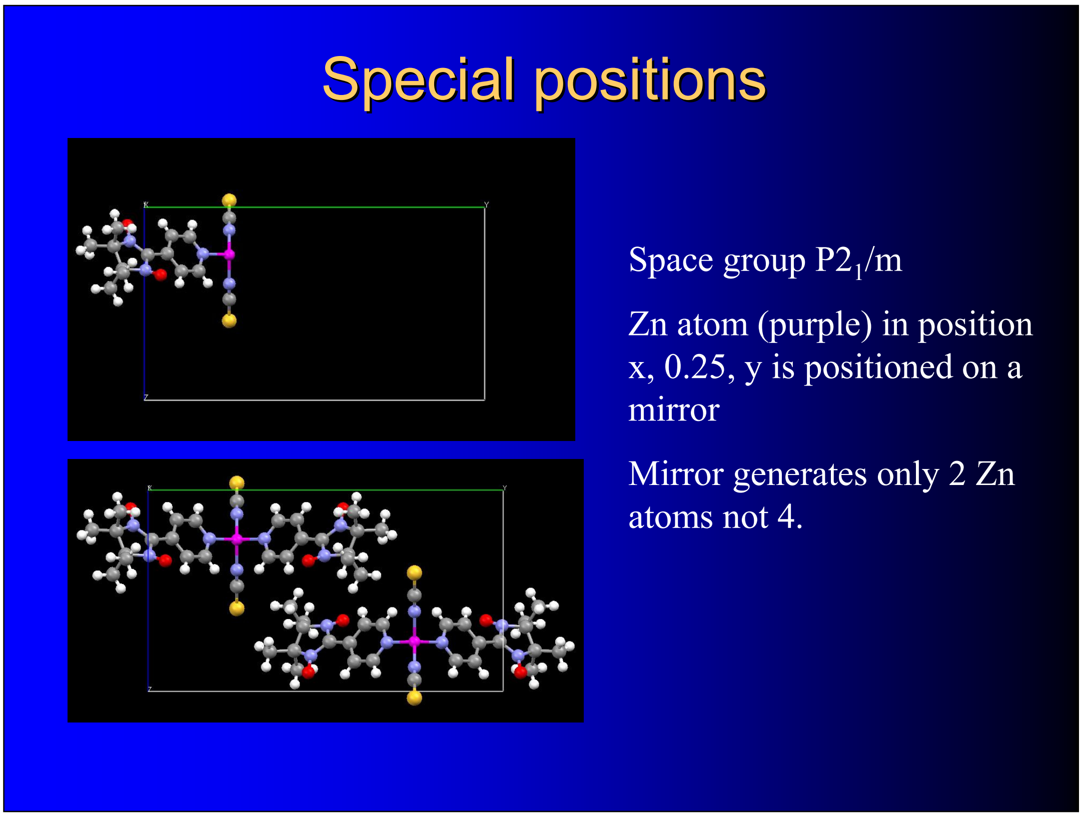
Number of positions, Wyckoff notation, and point symmetry			Co-ordinates of equivalent positions					Conditions limiting possible reflections
								General:
4	*u*	1	$x,y,z;\ \bar{x},\bar{y},z;\ x,\bar{y},\bar{z};\ \bar{x},y,\bar{z}.$					No conditions
								Special:
2	*t*	2	$\frac{1}{2},\frac{1}{2},z;\ \frac{1}{2},\frac{1}{2},\bar{z}.$					No conditions
2	*s*	2	$0,\frac{1}{2},z;\ 0,\frac{1}{2},\bar{z}.$					
2	*r*	2	$\frac{1}{2},0,z;\ \frac{1}{2},0,\bar{z}.$					
2	*q*	2	$0,0,z;\ 0,0,\bar{z}.$					
2	*p*	2	$\frac{1}{2},y,\frac{1}{2};\ \frac{1}{2},\bar{y},\frac{1}{2}.$	2	*l*	2	$x,\frac{1}{2},\frac{1}{2};\ \bar{x},\frac{1}{2},\frac{1}{2}.$	
2	*o*	2	$\frac{1}{2},y,0;\ \frac{1}{2},\bar{y},0.$	2	*k*	2	$x,\frac{1}{2},0;\ \bar{x},\frac{1}{2},0.$	
2	*n*	2	$0,y,\frac{1}{2};\ 0,\bar{y},\frac{1}{2}.$	2	*j*	2	$x,0,\frac{1}{2};\ \bar{x},0,\frac{1}{2}.$	
2	*m*	2	$0,y,0;\ 0,\bar{y},0.$	2	*i*	2	$x,0,0;\ \bar{x},0,0.$	
1	*h*	222	$\frac{1}{2},\frac{1}{2},\frac{1}{2}.$	1	*d*	222	$0,0,\frac{1}{2}.$	
1	*g*	222	$0,\frac{1}{2},\frac{1}{2}.$	1	*c*	222	$0,\frac{1}{2},0.$	
1	*f*	222	$\frac{1}{2},0,\frac{1}{2}.$	1	*b*	222	$\frac{1}{2},0,0.$	
1	*e*	222	$\frac{1}{2},\frac{1}{2},0.$	1	*a*	222	$0,0,0.$	

Symmetry of special projections

(001) *pmm*; $a'=a,\ b'=b$ (100) *pmm*; $b'=b,\ c'=c$ (010) *pmm*; $c'=c,\ a'=a$

BY SA

The individual atom can be placed in the unit cell in the same pos symmetry elements. When an atom is placed e.g. on 2 fold axis, it does not generate a second atom. Instead only 1 atom at this position exists. Such positions of atoms are listed in the International tables. They are called special positions. In space group P 2 2 2 the atom can be placed in general position (4 atoms), on 1x 2-fold axis (2 atoms) or on 2x 2-fold axis (only 1 atom is generated).



Special positions

Space group $P2_1/m$

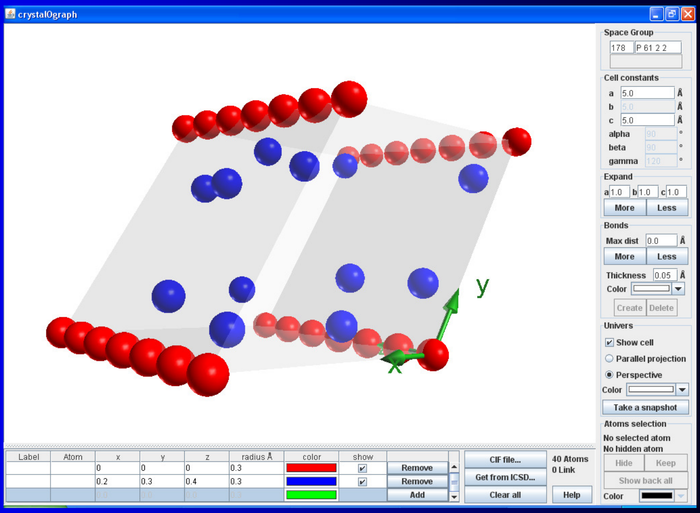
Zn atom (purple) in position x, 0.25, y is positioned on a mirror

Mirror generates only 2 Zn atoms not 4.

CC BY SA

This slide shows a real molecule placed partially in special positi
are in general position => the space group generates 4 of them. The Zn atom is placed on a mirror => only 2 Zn atoms are generated inside the unit cell.

Software used for teaching



Space Group: 178 P 61 2 2

Cell constants
a 5.0 Å
b 5.0 Å
c 5.0 Å
alpha 90 °
beta 90 °
gamma 120 °

Expand: a 1.0 b 1.0 c 1.0

Bonds
Max dist 0.0 Å
Thickness 0.05 Å

Univers
☑ Show cell
○ Parallel projection
● Perspective

Atoms selection
No selected atom
No hidden atom

Label	Atom	x	y	z	radius Å	color	show
		0	0	0	0.3	🟥	☑
		0.2	0.3	0.4	0.3	🟦	☑
		0.0	0.0	0.0	0.3	🟩	

40 Atoms
0 Link

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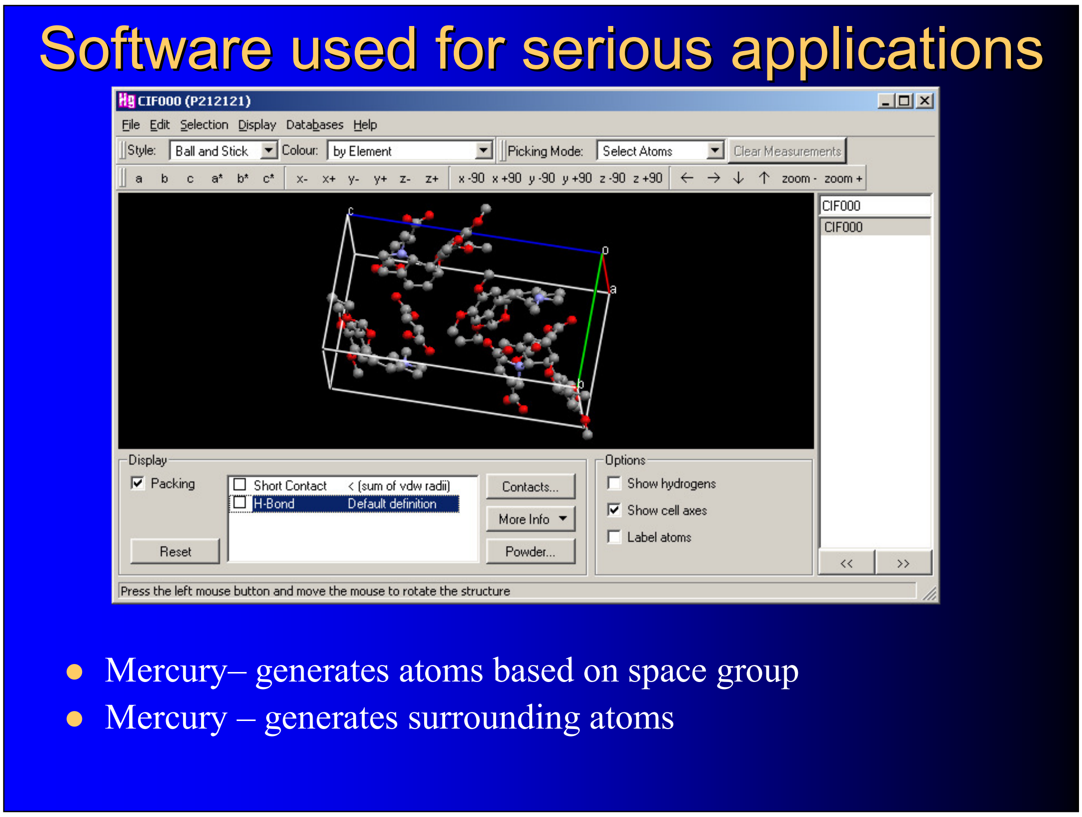
There exist programs for teaching space group and crystallograph
is crystalOgraph (demo will be given during the lecture).



Software used for serious applications

Press the left mouse button and move the mouse to rotate the structure

- Mercury– generates atoms based on space group
- Mercury – generates surrounding atoms

There exist free programs for space group/structure handling. On Mercury – freely available for download from CCDC www: https://www.ccdc.cam.ac.uk/solutions/csd-system/components/mercury/

The code can generate atoms position based on symmetry, measure geometry, visualize crystal cell etc.

It is strongly suggested to download the Mercury software and to try the tutorials.

Chemistry and Physics of Solids– lecture 2

X-ray diffraction, reciprocal lattice

Doc. Michal Hušák dr. Ing.

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Suggested literature

Richard J.D. Tilley: Understanding Solids, Willey 2013

C. Giacovazzo: Fundamentals of crystallography, Oxford Science Publications 1992

J. I. Gersten: Physics and chemistry of materials, Willey 2001

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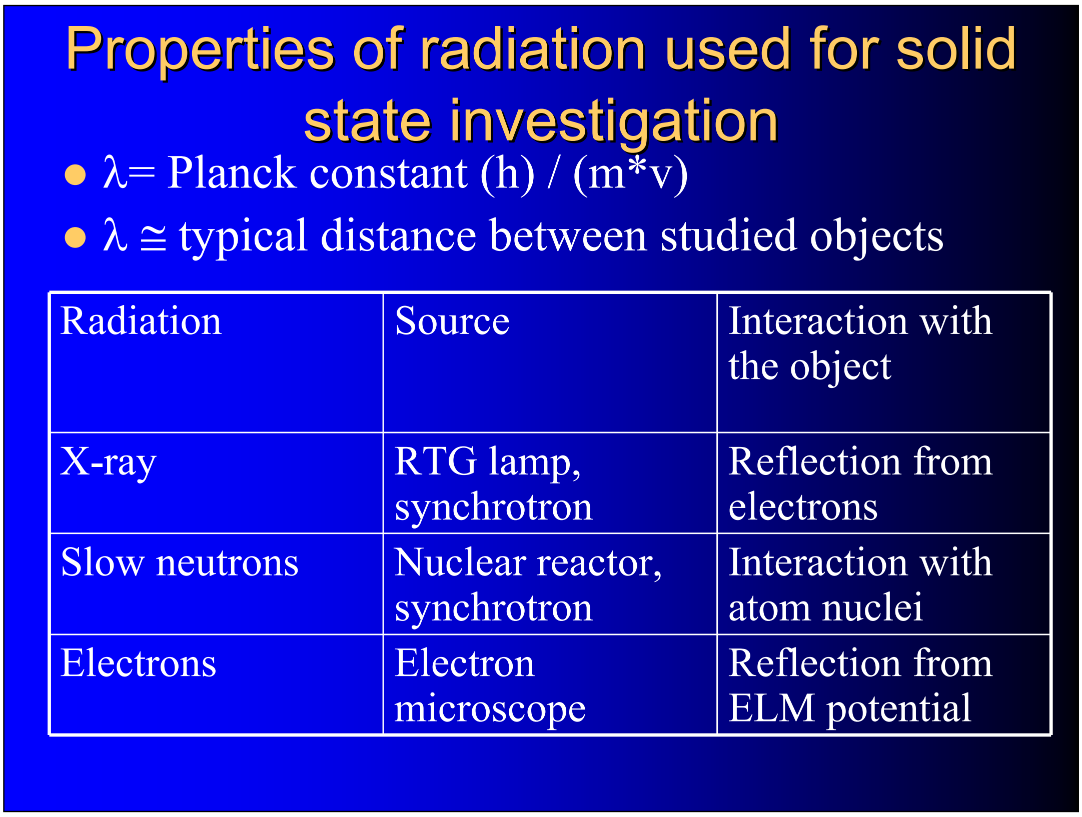
Lecture content

- Interaction of X-ray with solid state
- X-ray diffraction
- Bragg equation
- Planes (hkl)
- Reciprocal space
- Ewald construction
- Diffractometer constructions



Properties of radiation used for solid state investigation

- λ= Planck constant (h) / (m*v)
- $\lambda \cong$ typical distance between studied objects

Radiation	Source	Interaction with the object
X-ray	RTG lamp, synchrotron	Reflection from electrons
Slow neutrons	Nuclear reactor, synchrotron	Interaction with atom nuclei
Electrons	Electron microscope	Reflection from ELM potential

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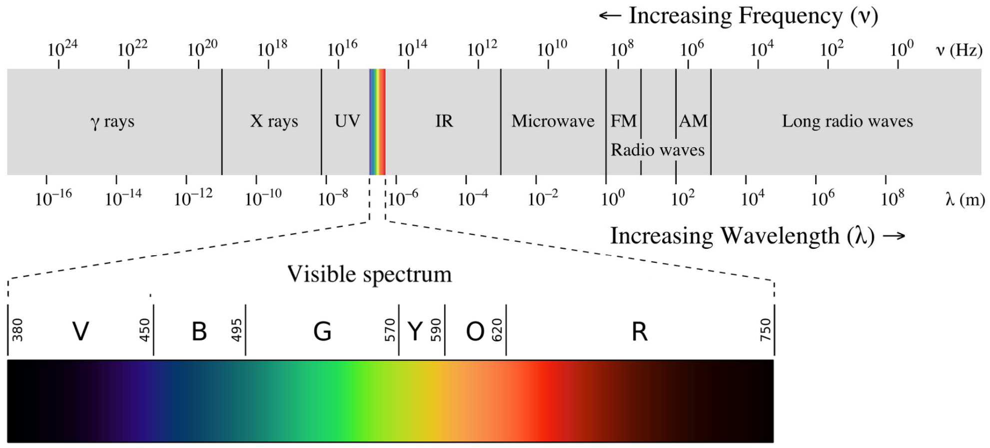
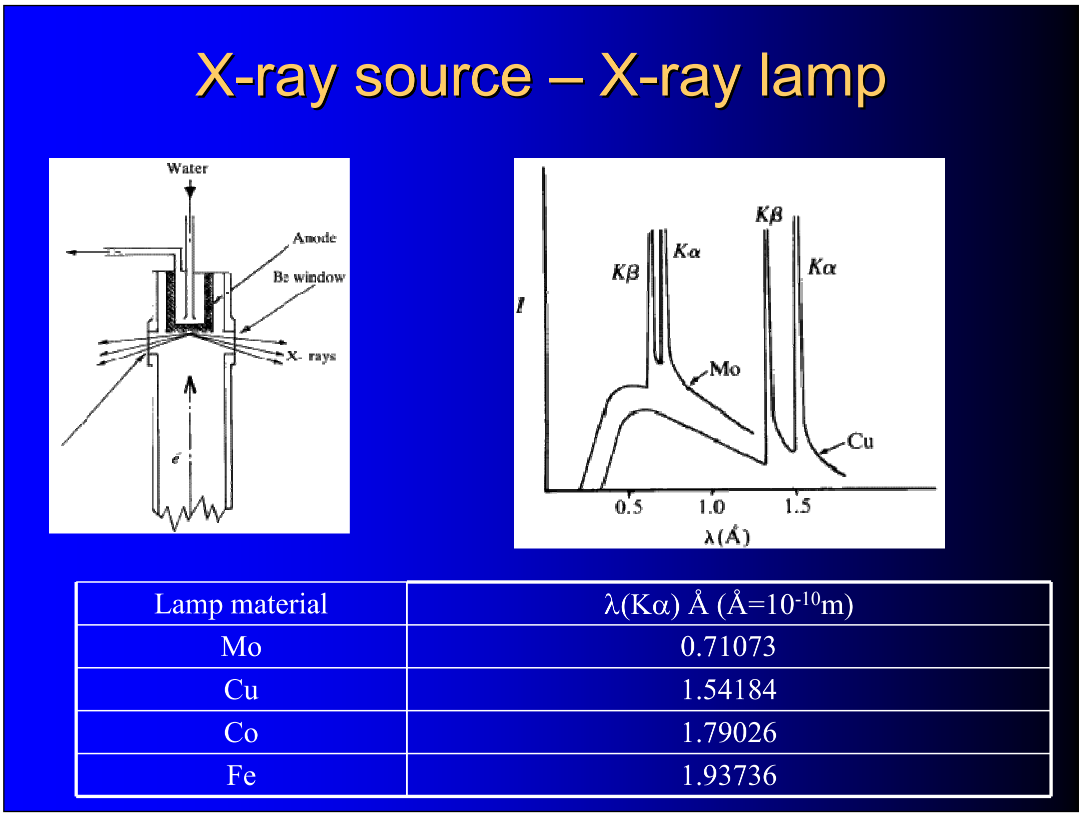
It is impossible to study atomic structure by visible light, e.g. by microscope. The radiation wavelength should be comparable to the studied object size. The typical atom-atom distance is about 10^{-10} m, so we must use a radiation with comparable wavelength. The first choice are photons – X-ray. The wavelength of particles can be adjusted by their velocity – neutrons and electrons can be utilized in this way.

Electromagnetic radiation



The X-ray wavelength is between the UV light and the hard γ rad wavelengths.



X-ray source – X-ray lamp

Lamp material	λ(Kα) Å (Å=10^{-10}m)
Mo	0.71073
Cu	1.54184
Co	1.79026
Fe	1.93736

The typical source of X-ray is an X-ray lamp. The electrons are a voltage difference between cathode and anode. The proper choice of anode material can give monochromatic radiation. Unwanted wavelengths can be eliminated by filters. The typical materials of the X-ray lamp anode are Mo, Cu, Ag, Co, Fe.

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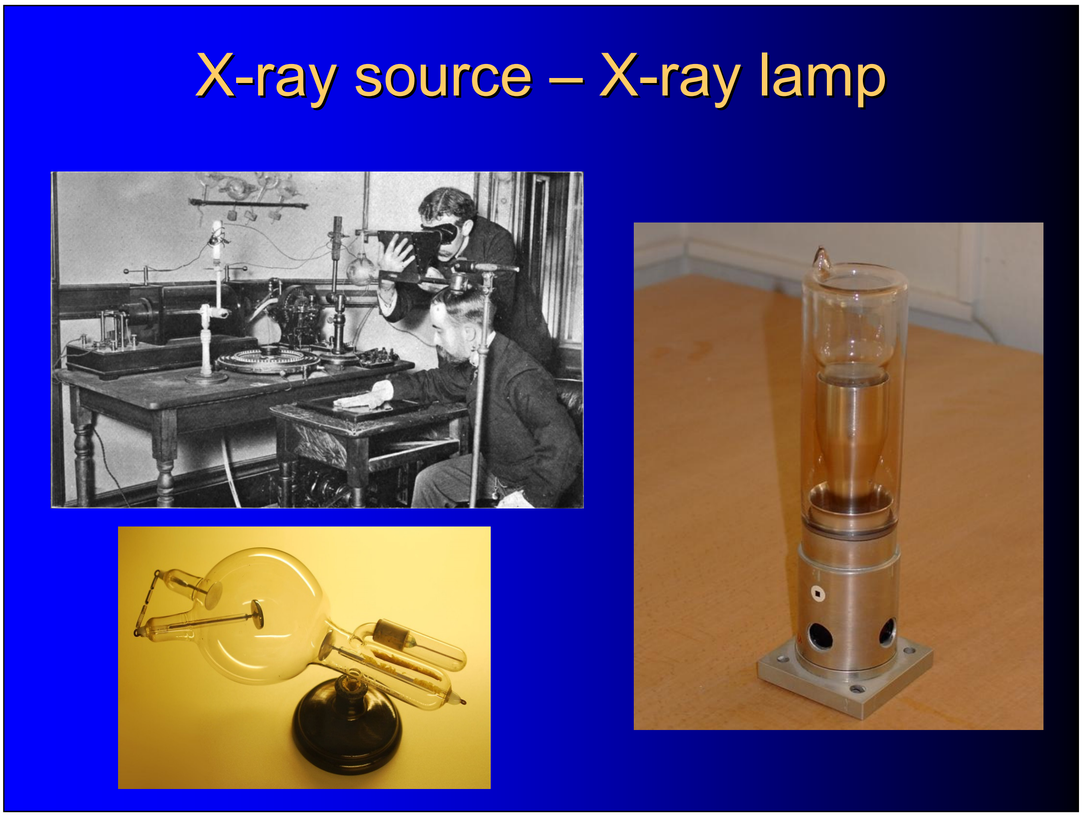
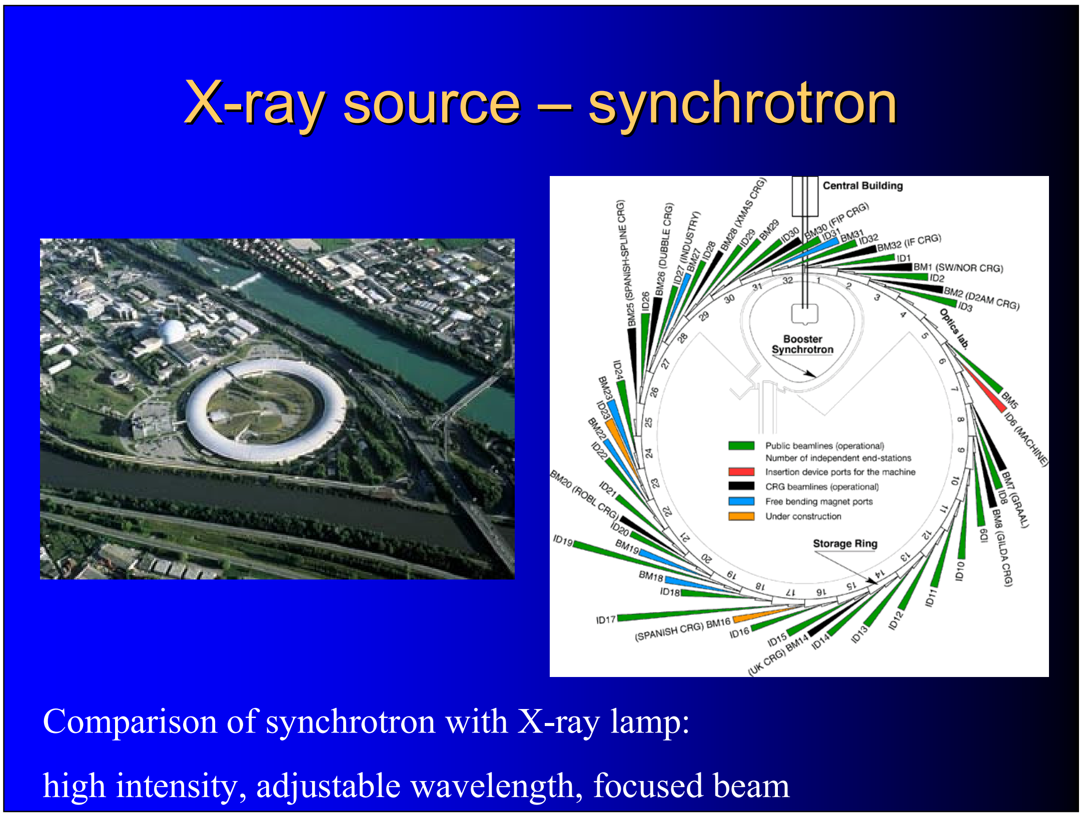


X-ray source – X-ray lamp

BY SA

The left part of the image shows historical models of X-ray lamp construction used in nowadays diffractometers is on the right.



X-ray source – synchrotron

Comparison of synchrotron with X-ray lamp:

high intensity, adjustable wavelength, focused beam

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The structure analysis of small crystals or big biological molecule intensity and adjustable wavelength of the radiation. Such source is synchrotron. The electrons circulate in a long evacuated tube. They are accelerated and directed by magnetic fields. The additional energy they get is tangentially emitted. The intensity is several orders of magnitude higher than from X-ray lamp. The photography shows European Synchrotron Radiation Facility (ESRF) in Grenoble, France.

Interaction of a crystal with radiation

- Absorption

$I=I_0*e^{-\mu x}$ Lamber-Beer rule

μ - absorption coefficient , x- length of the ray path

- Fluorescence

$\lambda_{prim}<\lambda_{fluro}$ $E_{prim}>E_{fluor}$

Utilized by X-ray fluorescence analysis (elemental quantitative analytic method)

- Diffraction

λ = constant, vibrating electrons re-emit radiation

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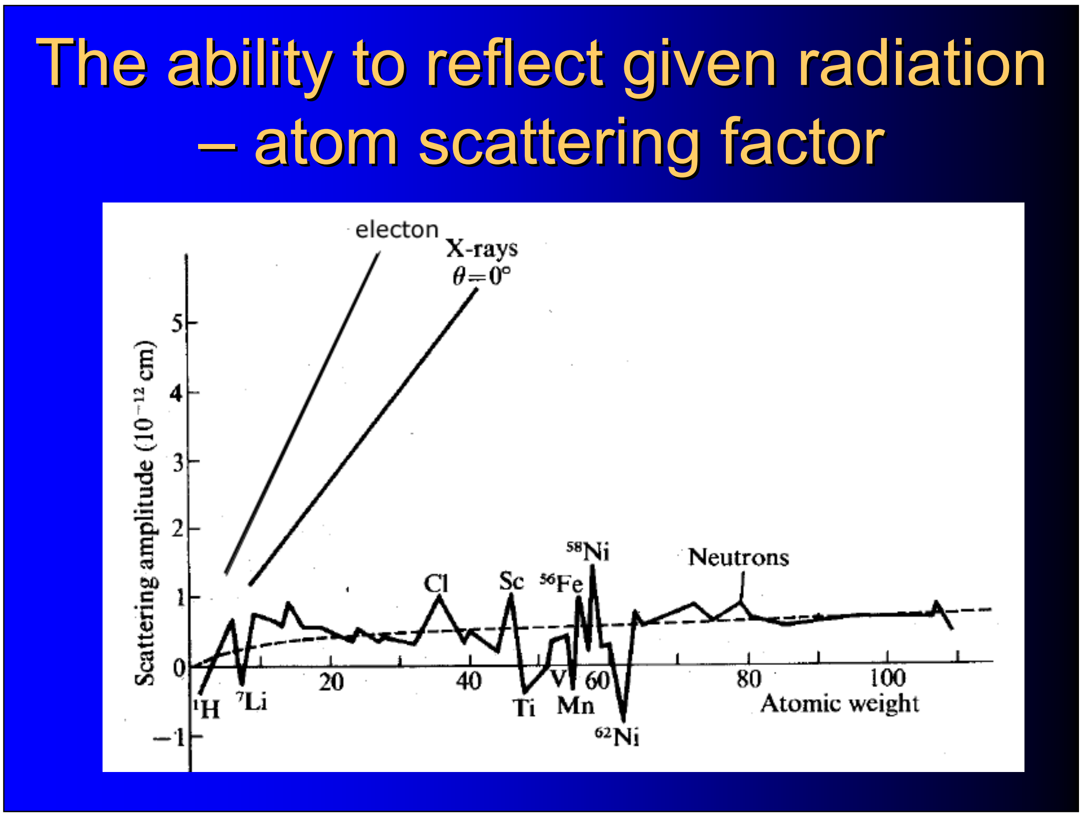
The radiation can interact with the material in 3 different ways. A simply absorbed – this process can be described by Lamber-Beer rule. The second possibility is fluorescence. The material emits a different wavelength (longer λ) than the λ of the incoming light. For the study of crystals, diffraction is the most important feature. The λ does not change and the photons are re-emitted by vibrating electrons.



The ability to reflect given radiation – atom scattering factor

Different atoms differ in the ability to re-emit X-rays. The ability scattering factor. The photons are scattered by electrons, therefore the atom scattering factor depends linearly on the number of elements electrons (and the position in the periodic table). The best scatters are heavy atoms like U, Pb, the worse one is H.

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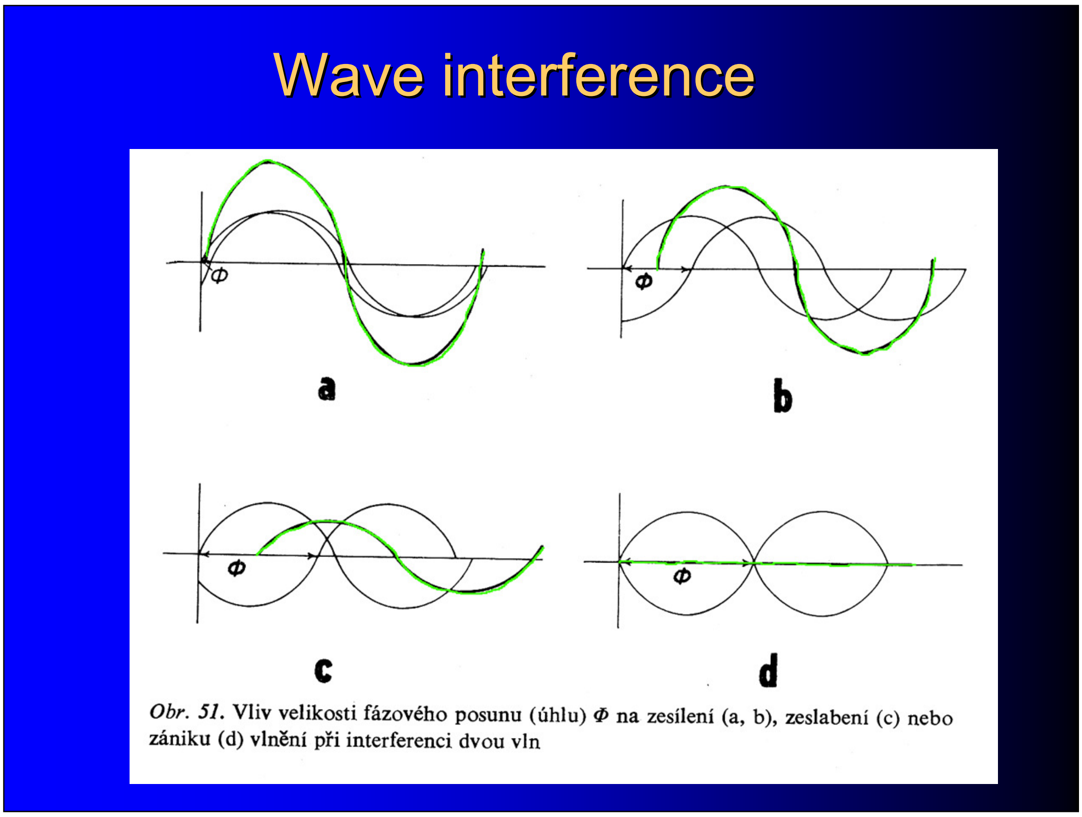
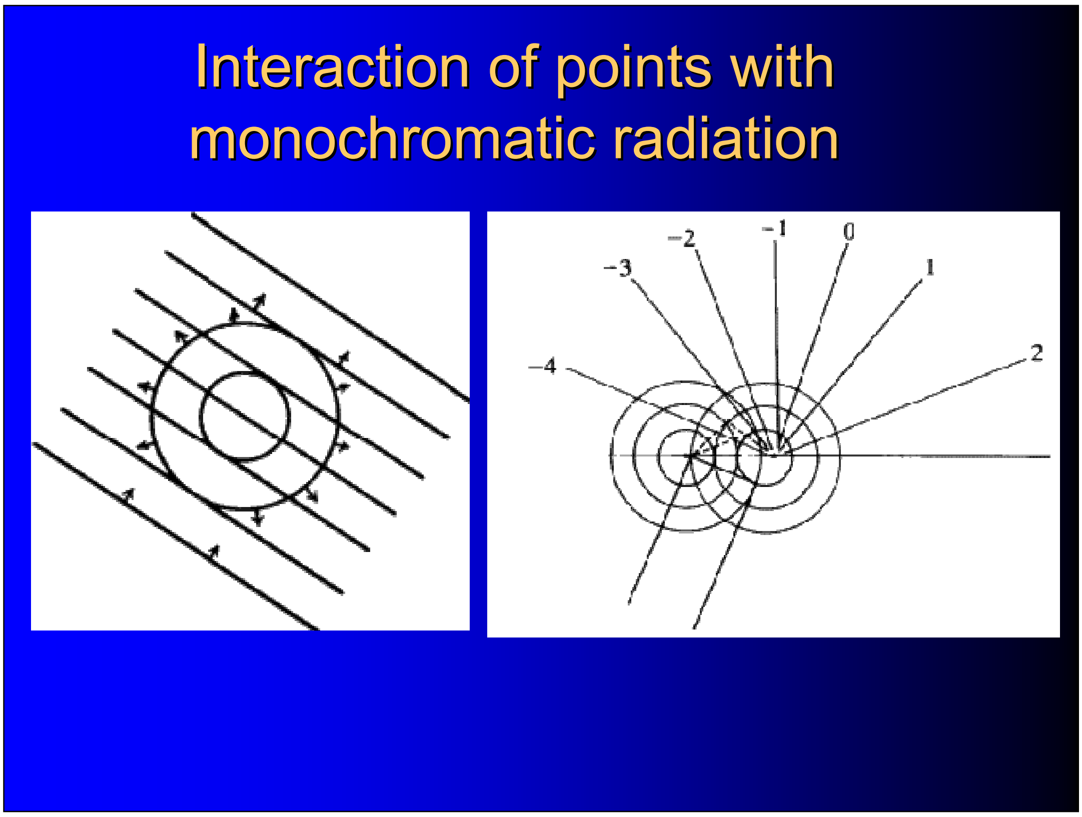


Wave interference

Obr. 51. Vliv velikosti fázového posunu (úhlu) Φ na zesílení (a, b), zeslabení (c) nebo zániku (d) vlnění při interferenci dvou vln

Waves with identical wavelength can interfere together in differe their phase shift. The intensity can be amplified (a), partially amplified of partially reduced (b,c). Phase shift of 1/2 wavelength (1π) can result in waves intensity reduction to 0.



Interaction of points with monochromatic radiation

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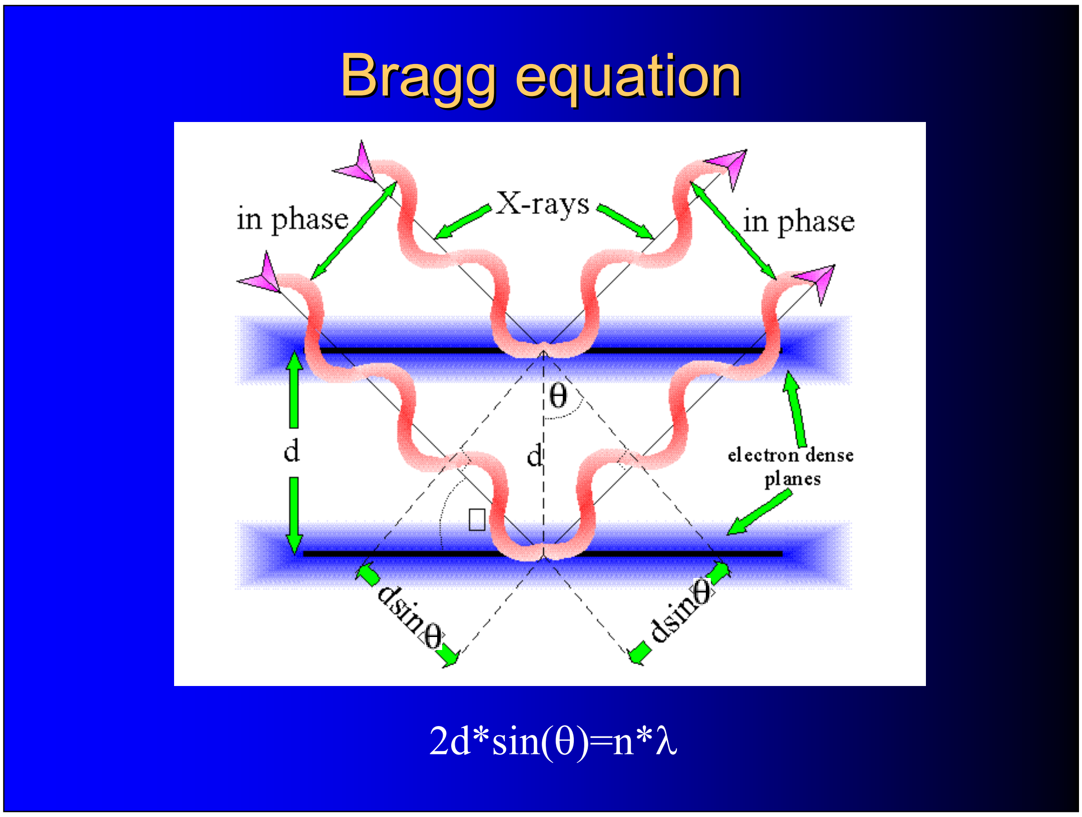
There exists only certain direction is space in which the waves m
phase. The atoms generate wave-like circles. The waves meet in phase only in certain direction.

Water waves interference - analogy

A real life analogy can be several ducks sitting periodically on a p waves generated by several ducks interfere in phase, a tsunami can be theoretically generated. Unfortunately, the two in this photo cannot make the job.

BY SA



Bragg equation

$$2d*\sin(\theta)=n*\lambda$$

The direction of the waves satisfying the “to be in phase” conditi derived from the Bragg equation. The 2 waves must differ in $n*\lambda$ ($n*2\pi$) to be in phase. This is the $d*\sin(\theta)$+ $d*\sin(\theta)$+ distance from the image. If we have 2 planes in distance *d* filled by lattice points the angle of X-ray diffraction can be calculated from the right-angel triangles in the image and the sine function.

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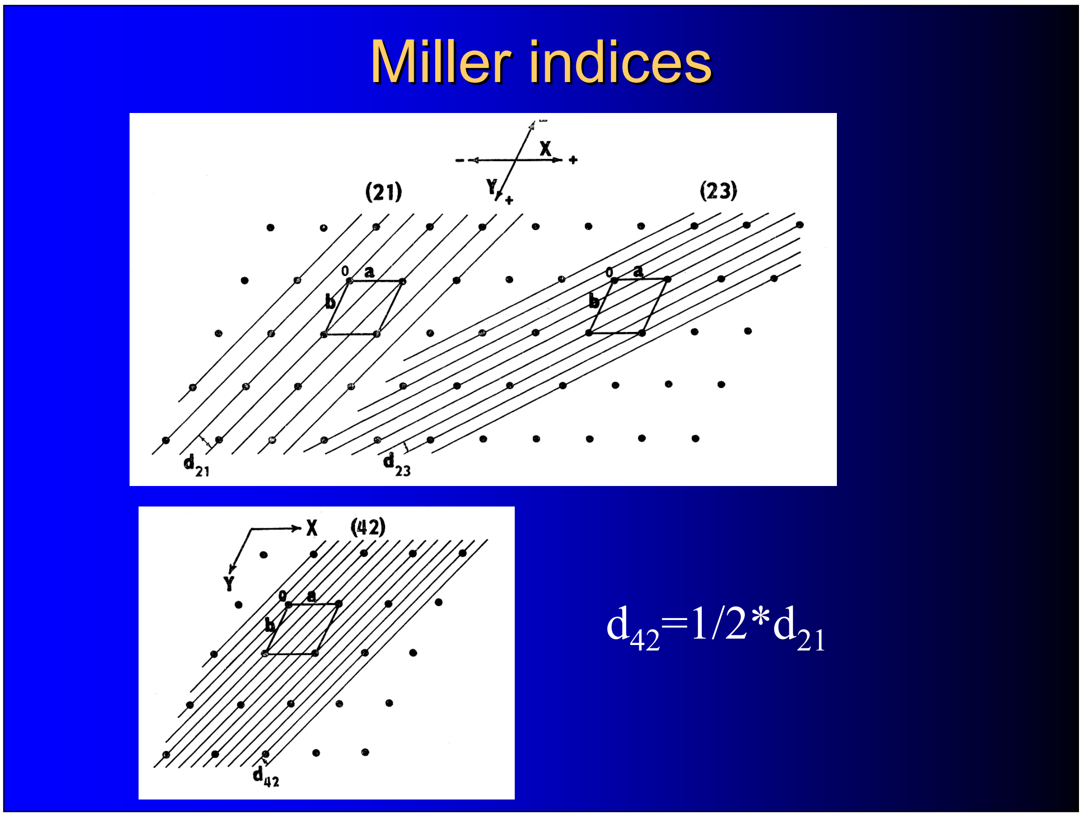

Miller indices

$d_{42}=1/2*d_{21}$

There exist infinite number of planes going through all lattice poi to speak about planes filled by lattice points, we must have a terminology to identify such a plane. Each plane is identified by 3 Miller indices – (h,k,l). The value of the Miller indices is a reciprocal to the distance in with intersect the plane on the unit cell axes. Planes witch intersect the axes in infinity (parallel to the axes) have Miller indices 0 (1/∞). Not to be forced to use the n in Bragg equation we use in calculations planes parallel to existing one (e.g. (4,2,0) parallel to (2,1,0)).

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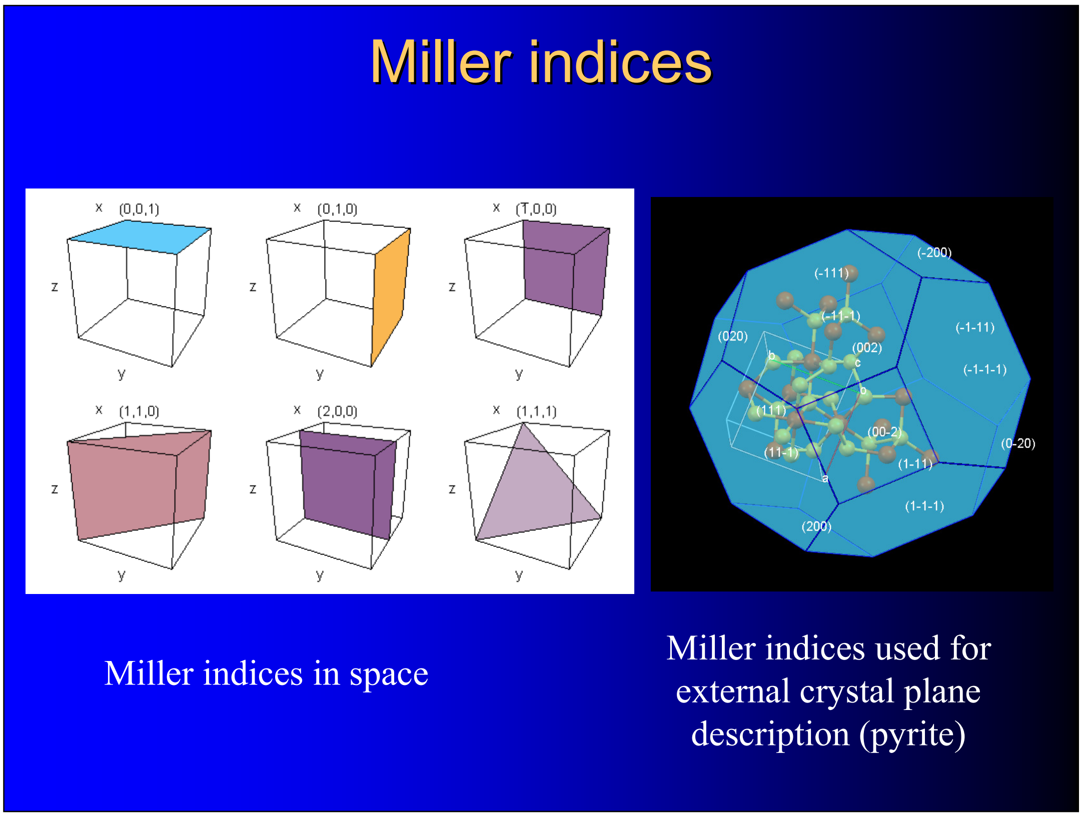


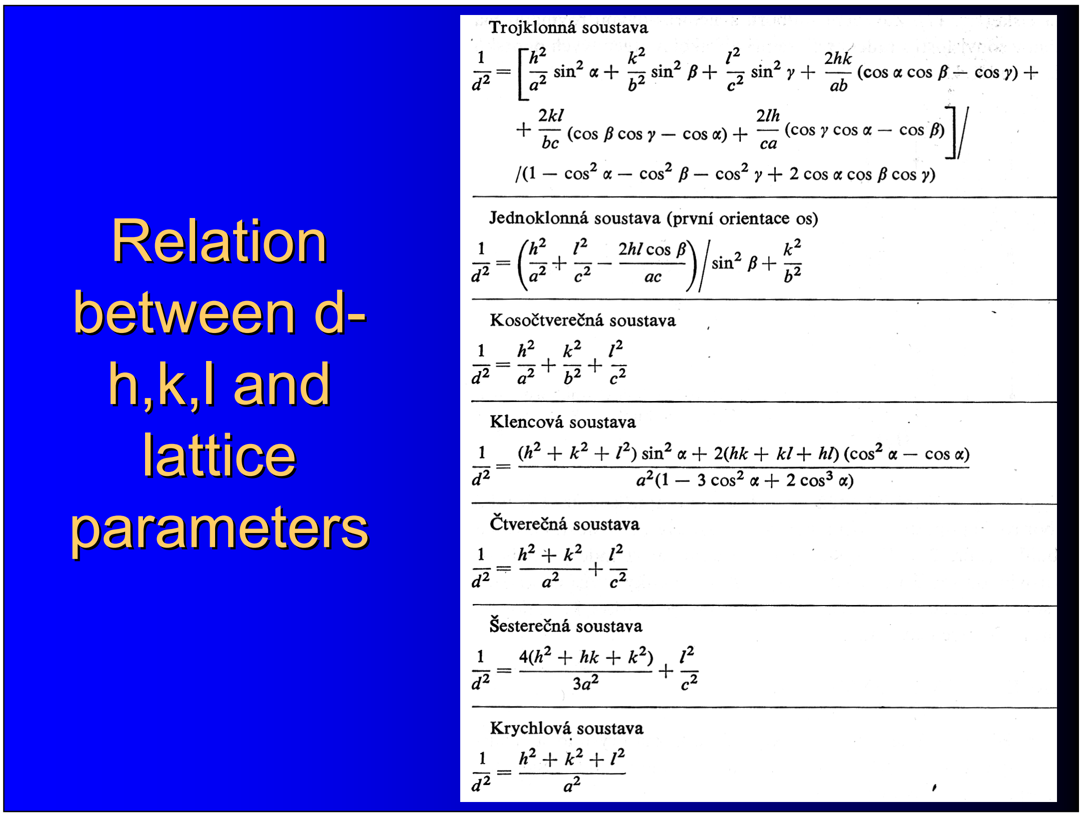
Miller indices

Miller indices in space

Miller indices used for external crystal plane description (pyrite)

BY SA

The image on the left shows different planes going through the ur (2,0,0) plane does not go through any lattice points, but it is parallel with (1,0,0) and satisfies the diffraction condition in Bragg equation for n=2. Another use for Miller indices is the description of crystal planes on macroscopic crystals. Each crystal plane on a crystal is perpendicular to a layer of lattice points inside the crystal and can be assigned by corresponding Miller indices.



Relation between d-h,k,l and lattice parameters

Trojklonná soustava

$$\frac{1}{d^2} = \left[\frac{h^2}{a^2}\sin^2\alpha + \frac{k^2}{b^2}\sin^2\beta + \frac{l^2}{c^2}\sin^2\gamma + \frac{2hk}{ab}(\cos\alpha\cos\beta - \cos\gamma) + \right.$$

$$\left. + \frac{2kl}{bc}(\cos\beta\cos\gamma - \cos\alpha) + \frac{2lh}{ca}(\cos\gamma\cos\alpha - \cos\beta)\right] \Big/$$

$$/(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)$$

Jednoklonná soustava (první orientace os)

$$\frac{1}{d^2} = \left(\frac{h^2}{a^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right) \Big/ \sin^2\beta + \frac{k^2}{b^2}$$

Kosočtverečná soustava

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Klencová soustava

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + kl + hl)(\cos^2\alpha - \cos\alpha)}{a^2(1 - 3\cos^2\alpha + 2\cos^3\alpha)}$$

Čtverečná soustava

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

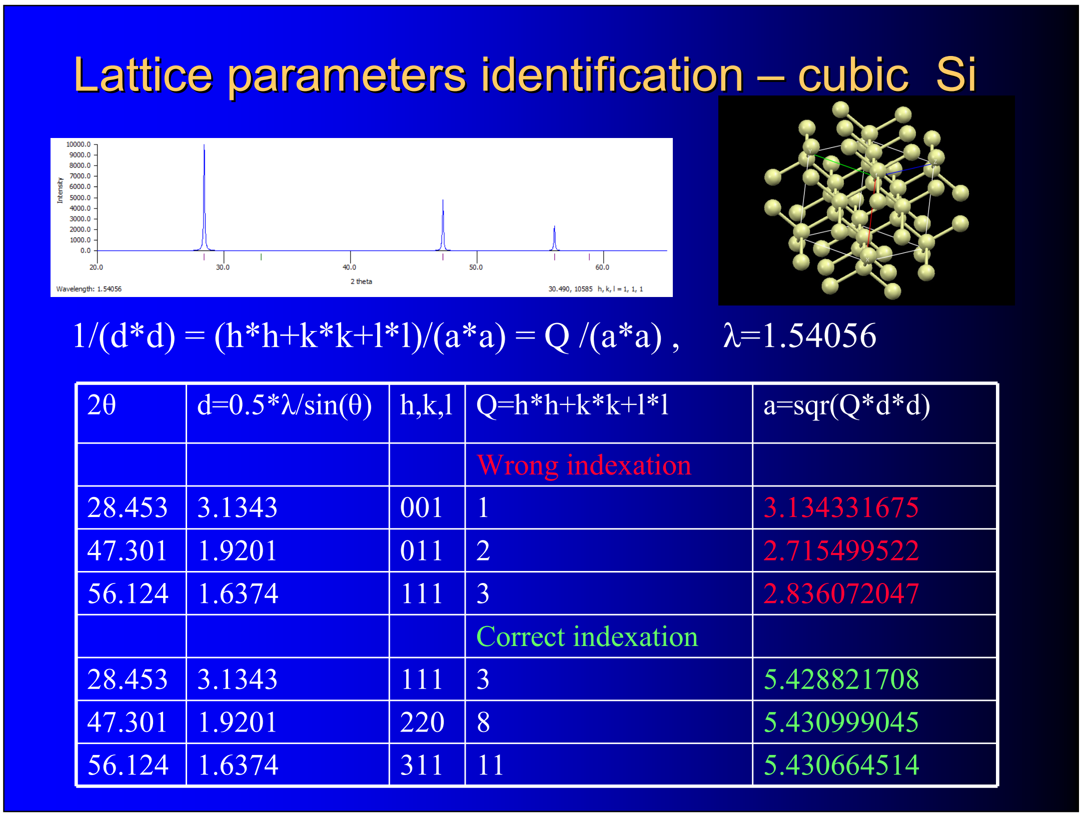
Šesterečná soustava

$$\frac{1}{d^2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2}$$

Krychlová soustava

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

For each crystal system there exists a relation between inter-plana Muller indices and lattice parameters. We can calculate the d value from the Bragg equation. If we have enough d values and corresponding Miller indices (h,k,l) we can solve the equations and calculate lattice parameters.



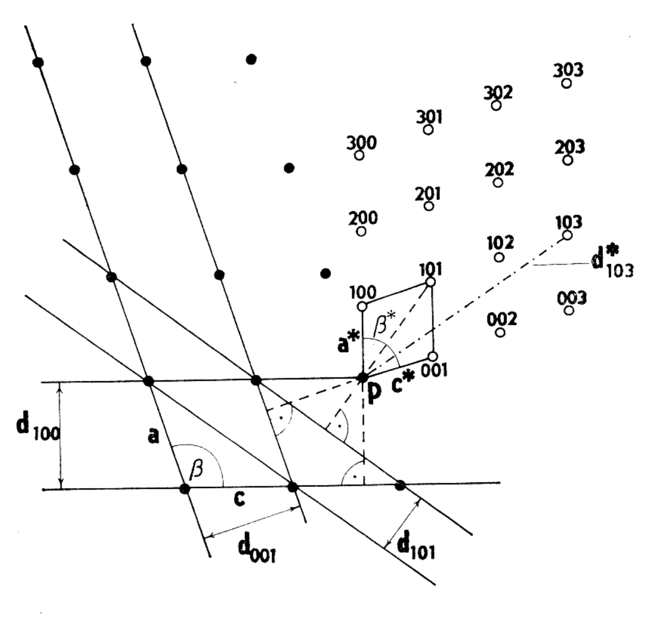
Lattice parameters identification – cubic Si

1/(d*d) = (h*h+k*k+l*l)/(a*a) = Q /(a*a) , λ=1.54056

2θ	d=0.5*λ/sin(θ)	h,k,l	Q=h*h+k*k+l*l	a=sqr(Q*d*d)
			Wrong indexation	
28.453	3.1343	001	1	3.134331675
47.301	1.9201	011	2	2.715499522
56.124	1.6374	111	3	2.836072047
			Correct indexation	
28.453	3.1343	111	3	5.428821708
47.301	1.9201	220	8	5.430999045
56.124	1.6374	311	11	5.430664514

The question is how to get the correct Muller indices (h,k,l). h,k,l whole number (integer). We can try to solve the lattice equation for different integers. When we get in all cases the same lattice parameters, the problem is solved. The slide shows lattice parameters determination for cubic crystalline silicon.

Reciprocal lattice



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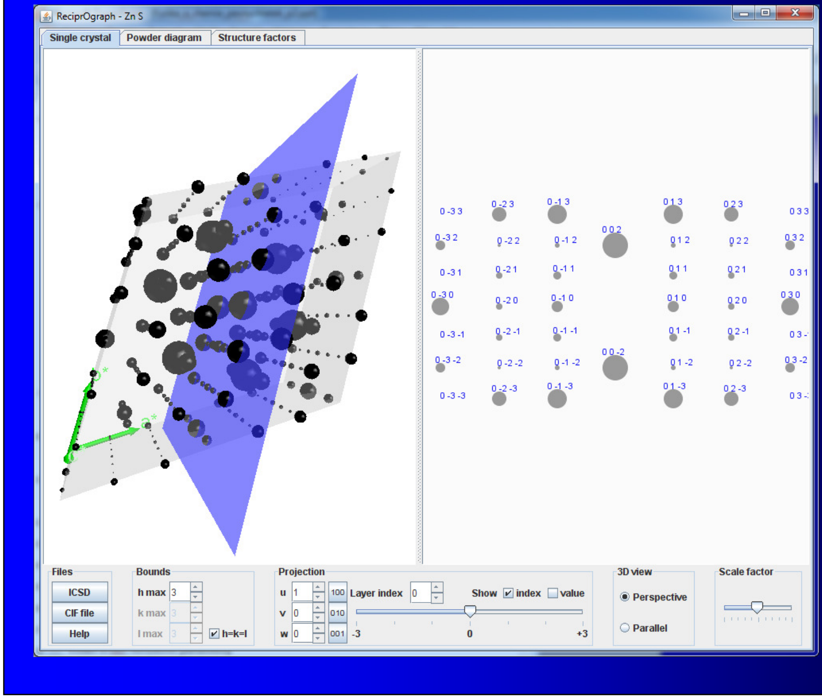
To be able to geometrically predict the diffraction direction a tran
the Real lattice was developed = the Reciprocal lattice. The Reciprocal lattice is constructed in the following way: We choose a real lattice point (P). We make a line perpendicular to the selected plane. On this line we find a point in 1/d distance from the previously selected lattice point (P). The reciprocal lattice is created by points which can be assigned by Miller indices – each point characterizes a set of plane from the crystal. See that e.g. (2,0,0) point is further from origin than (1,0,0) due to the 1/d construction.

Reciprocal lattice

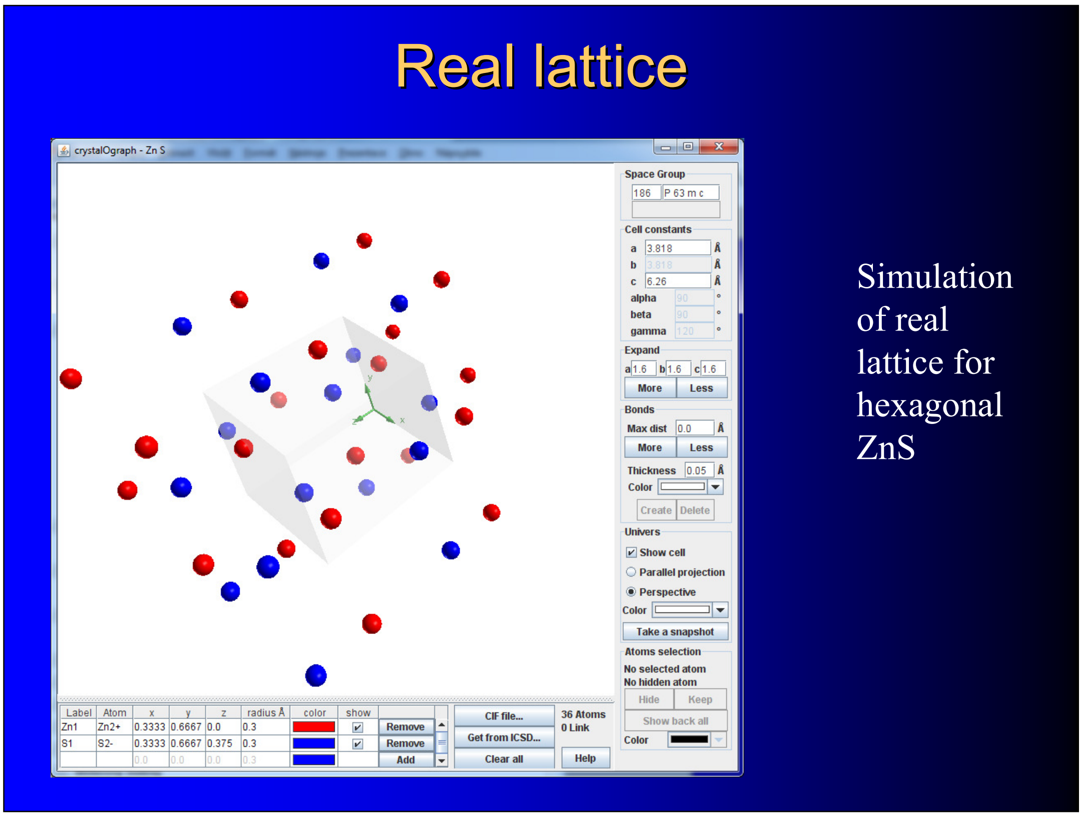


h max 3
k max 3
l max 3
☑ h=k=l
u 1 100
v 0 010
w 0 001
Layer index 0
Show ☑ index ☐ value
● Perspective
○ Parallel

Simulation of weighted reciprocal lattice for hexagonal ZnS

This simulation code shows the Reciprocal lattice in the space. T characterize a group of planes instead of positions of motives created by atoms. The lattice is infinite … The size of the points (weighting) is related to Structure factor which will be described later.

Real lattice


crystalOgraph - Zn S

Space Group: 186 P 63 m c

Cell constants
a 3.818 Å
b 3.818 Å
c 6.26 Å
alpha 90 °
beta 90 °
gamma 120 °

Expand: a 1.6 b 1.6 c 1.6

Bonds
Max dist 0.0 Å
Thickness 0.05 Å

Univers
☑ Show cell
○ Parallel projection
● Perspective

Atoms selection
No selected atom
No hidden atom

Label	Atom	x	y	z	radius Å	color	show
Zn1	Zn2+	0.3333	0.6667	0.0	0.3	🟥	☑
S1	S2-	0.3333	0.6667	0.375	0.3	🟦	☑
		0.0	0.0	0.0	0.3	🟦	

36 Atoms
0 Link

Simulation of real lattice for hexagonal ZnS

On the other hand the Real space lattice is formed by lattice point
motives/atoms location.

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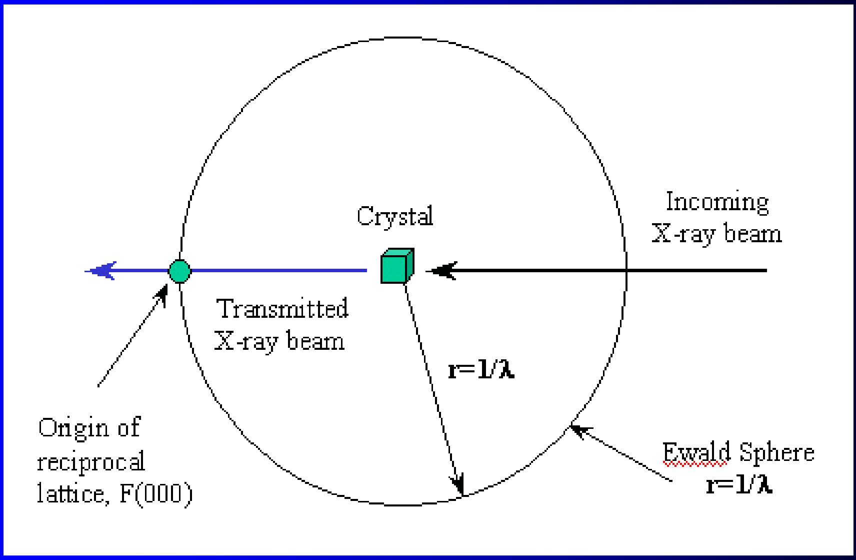
Ewald construction – Ewald sphere



Crystal

Incoming
X-ray beam

Transmitted
X-ray beam

r=1/λ

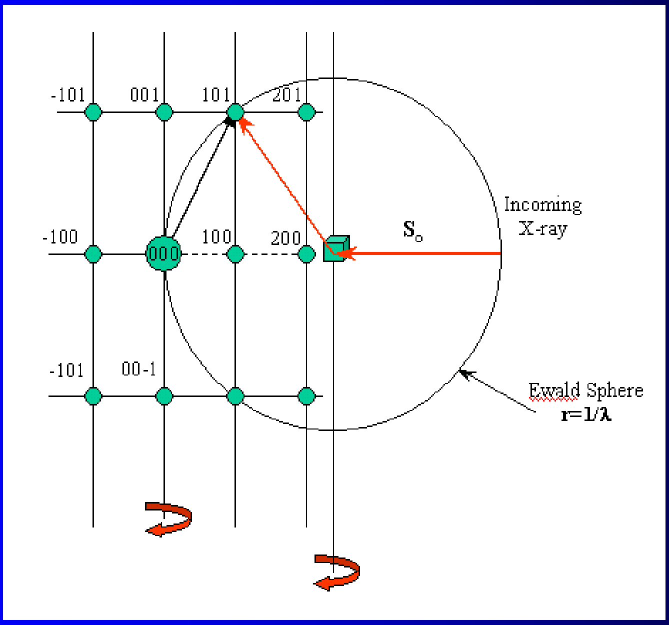
Origin of
reciprocal
lattice, F(000)

Ewald Sphere
r=1/λ

cc BY SA

The Reciprocal lattice can be utilized for diffraction direction pre combination with Ewald sphere geometrical construction. The Ewald sphere has a 1/λ radius. We place I crystal in the center of the sphere and the (0,0,0) point of Reciprocal lattice on the sphere (in opposite direction than the incoming X-ray).

Ewald construction – reciprocal lattice



The rotation of the crystal according to X-ray direction is identica
the reciprocal lattice along the (0,0,0) point.

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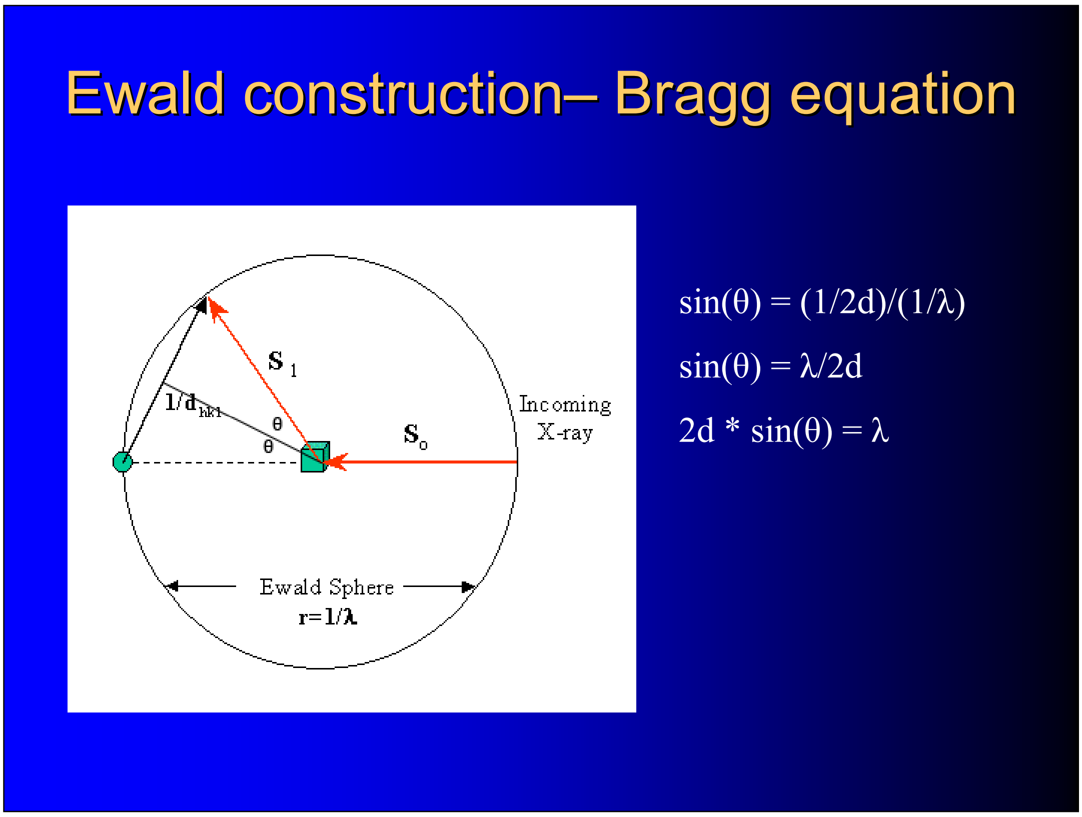


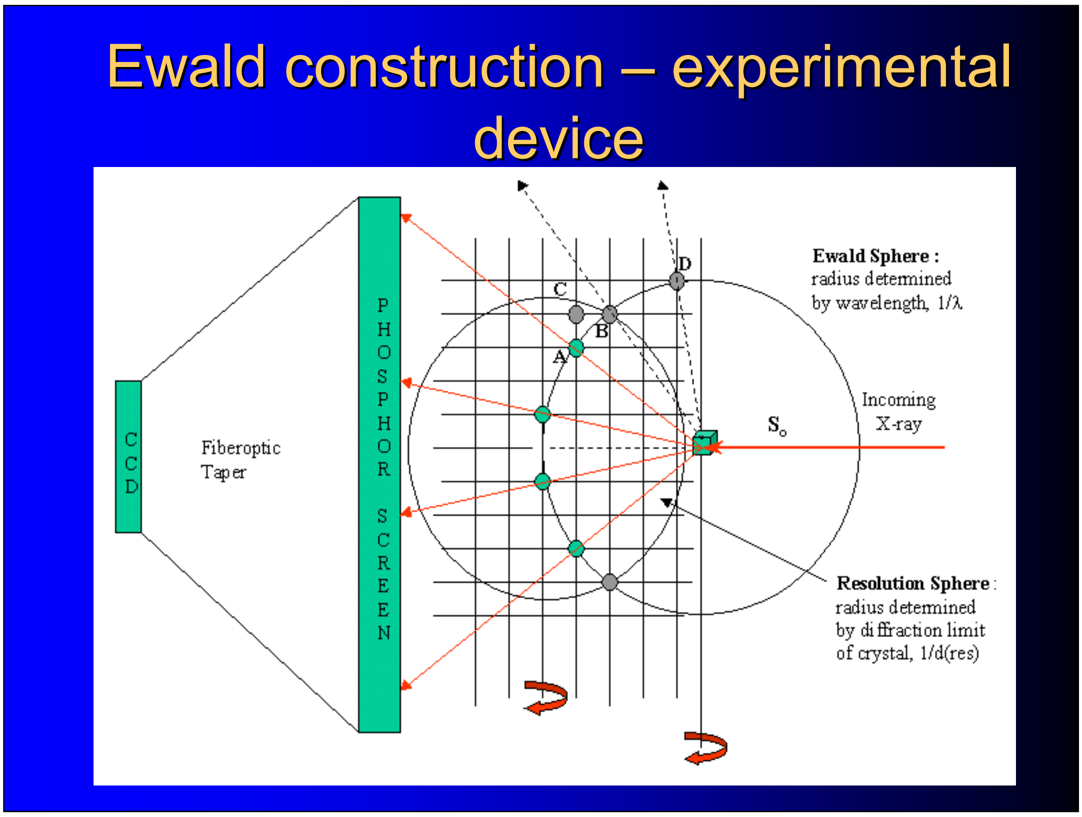
Ewald construction– Bragg equation

$\sin(\theta) = (1/2d)/(1/\lambda)$

$\sin(\theta) = \lambda/2d$

$2d * \sin(\theta) = \lambda$

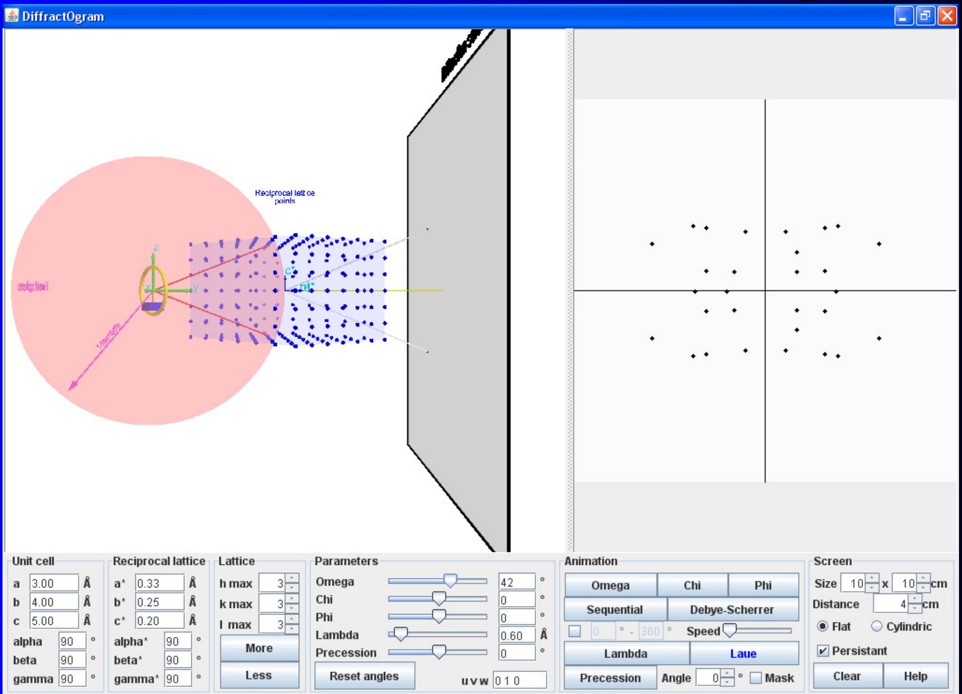
Let us inspect the situation when a reciprocal lattice point crosses sphere. The distance of such point from (0,0,0) is $1/d_{hkl}$. In the image we can see 2 x right triangles. The hypotenuse length is 1/λ. Based on the sine function definition we can derive the dependence between d and θ angle. It is identical to Bragg equation. We can geometrically determine the 2θ angle fulfilling the diffraction condition in this way.



Ewald construction – experimental device

The Ewald construction can be utilized for modelling the key X-r instrument – single crystal diffractometer with area detector. The phosphor screen detects X-ray diffractions in the red lines direction.

Software simulation diffractOgram



Unit cell
a 3.00 Å
b 4.00 Å
c 5.00 Å
alpha 90 °
beta 90 °
gamma 90 °

Reciprocal lattice
a* 0.33 Å
b* 0.25 Å
c* 0.20 Å
alpha* 90 °
beta* 90 °
gamma* 90 °

Lattice
h max 3
k max 3
l max 3

Parameters
Omega 42 °
Chi 0 °
Phi 0 °
Lambda 0.60 Å
Precession 0 °
u v w 0 1 0

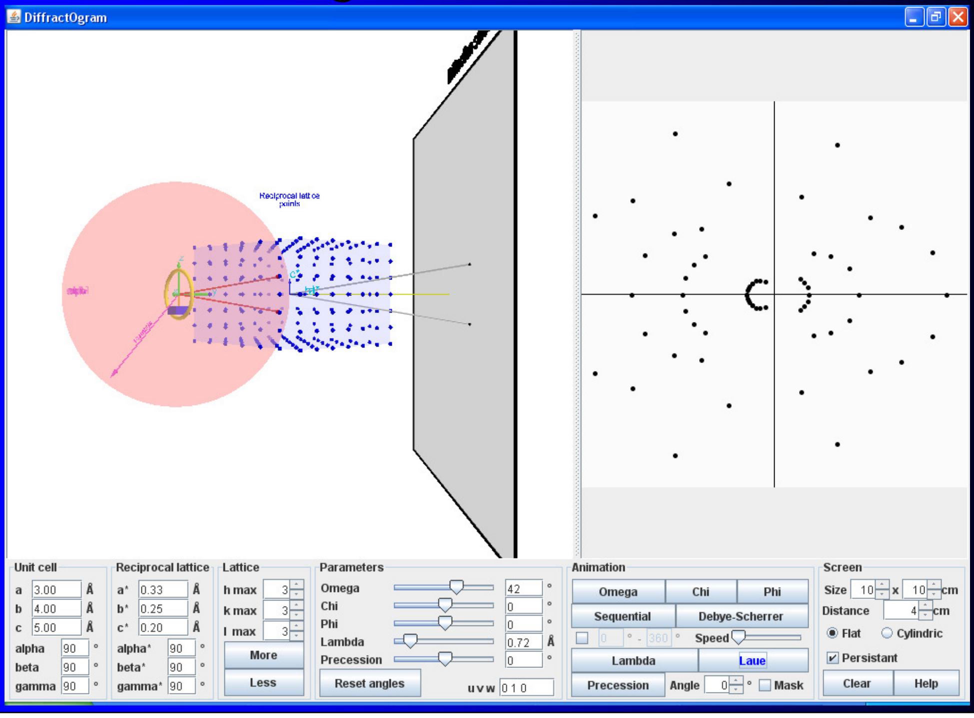
Animation
☐ 0 ° - 360 °
Angle 0 ° ☐ Mask

Screen
Size 10 x 10 cm
Distance 4 cm
● Flat ○ Cylindric
☑ Persistant

The reciprocal lattice can be used inside a graphical software sim diffraction experiments. The software makes it possible to rotate the crystal and change the wavelength. The most common experiments work with fixed wavelength and moving crystal.

BY SA

diffractOgram – Laue method



Unit cell
a 3.00 Å
b 4.00 Å
c 5.00 Å
alpha 90 °
beta 90 °
gamma 90 °

Reciprocal lattice
a* 0.33 Å
b* 0.25 Å
c* 0.20 Å
alpha* 90 °
beta* 90 °
gamma* 90 °

Lattice
h max 3
k max 3
l max 3

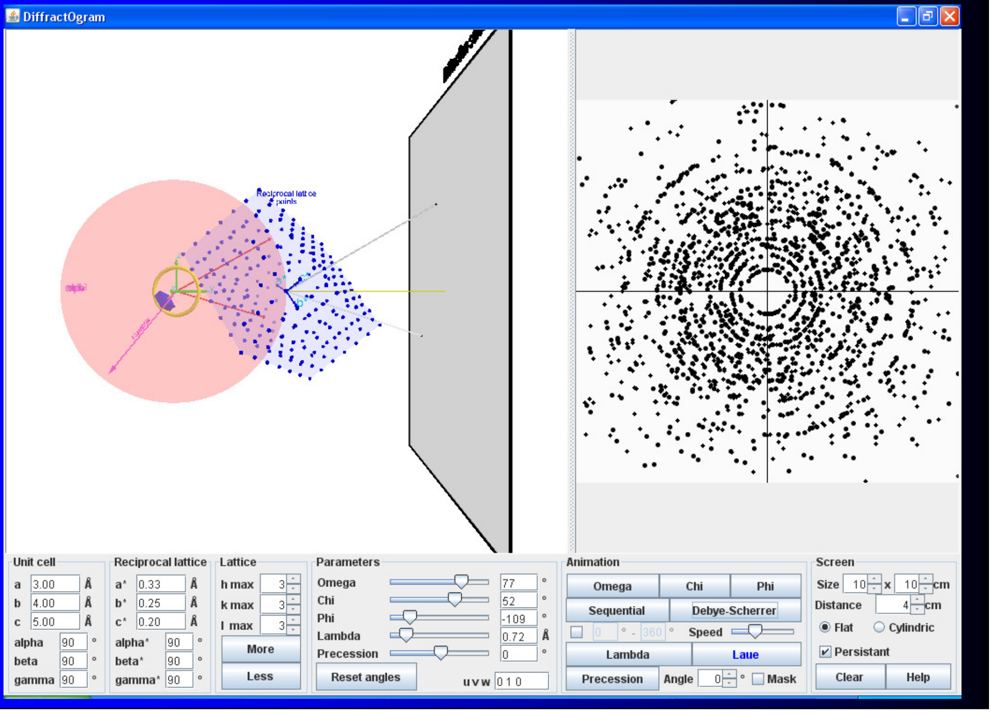
Parameters
Omega 42 °
Chi 0 °
Phi 0 °
Lambda 0.72 Å
Precession 0 °
u v w 0 1 0

Animation
☐ 0 ° - 360 ° Speed
Angle 0 ° ☐ Mask

Screen
Size 10 x 10 cm
Distance 4 cm
● Flat ○ Cylindric
☑ Persistant

We can optionally fix crystal and work with non-monochromatic Such method is called Laue experiment. The results are hard to interpret because we do not know what wavelength we can put in the Bragg equation. For experiments based on Laue diffraction we must know the lattice parameters in advance to be able to calculate the wavelength. The advantage of Laue method is fast measurement of multiple reflection intensity (e.g. for monitoring phase transformations).

diffractOgram - powder



a 3.00 Å
b 4.00 Å
c 5.00 Å
alpha 90 °
beta 90 °
gamma 90 °

a* 0.33 Å
b* 0.25 Å
c* 0.20 Å
alpha* 90 °
beta* 90 °
gamma* 90 °

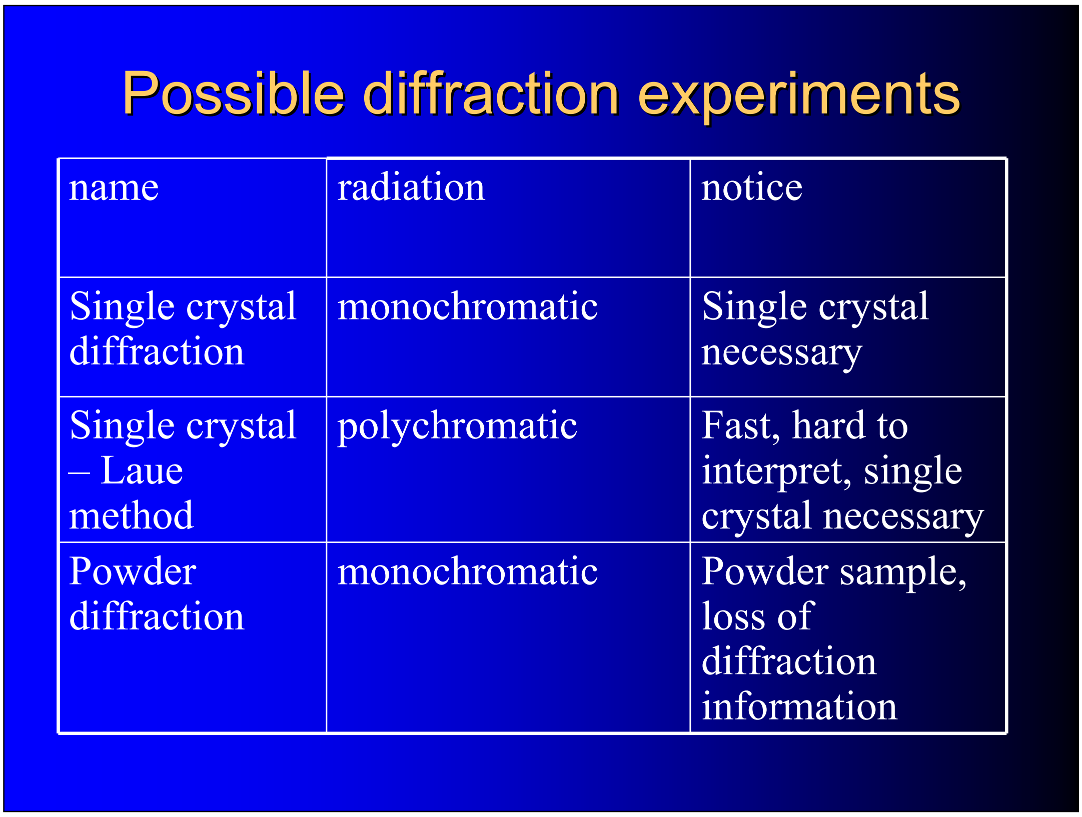
h max 3
k max 3
l max 3

Omega 77 °
Chi 52 °
Phi -109 °
Lambda 0.72 Å
Precession 0 °
u v w 0 1 0

☐ 0 ° - 360 °
Angle 0 °

Size 10 x 10 cm
Distance 4 cm
● Flat ○ Cylindric
☑ Persistant

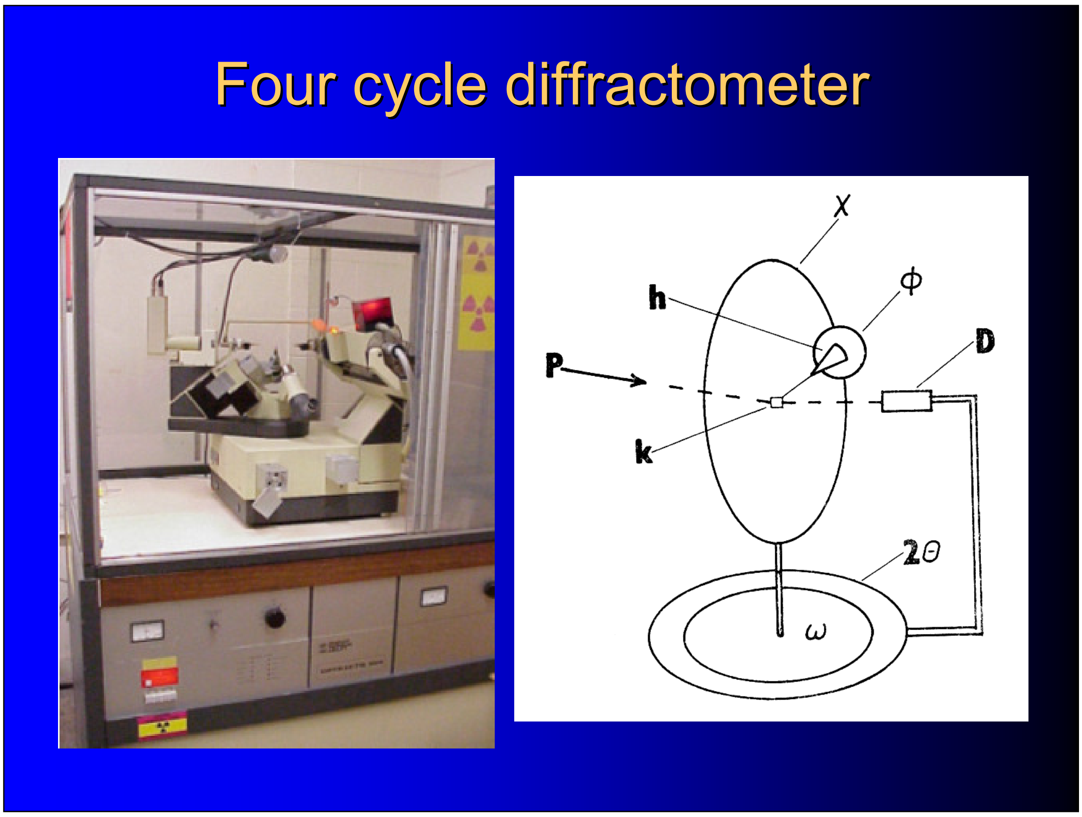
We can put in the position of a single crystal a powder sample. Tl identical to random rotation of a single crystal. The detector will show circles, not discrete points. The result is the so called powder diffractogram.



Possible diffraction experiments

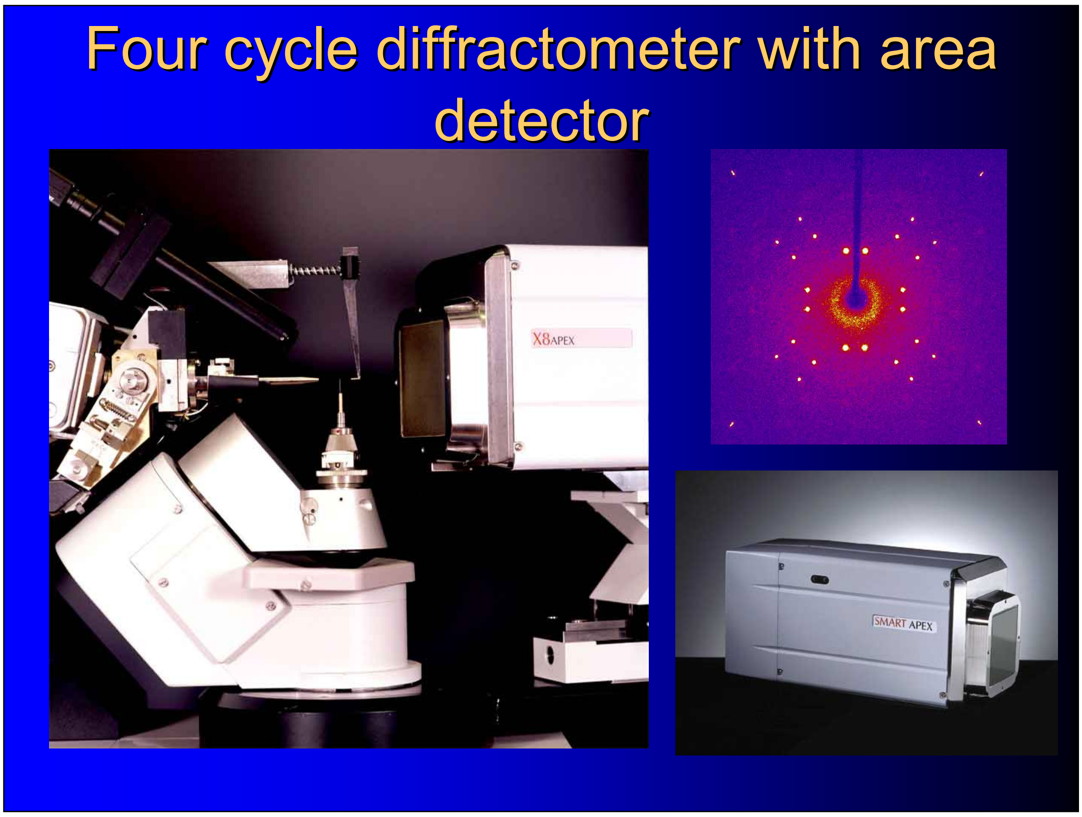
name	radiation	notice
Single crystal diffraction	monochromatic	Single crystal necessary
Single crystal – Laue method	polychromatic	Fast, hard to interpret, single crystal necessary
Powder diffraction	monochromatic	Powder sample, loss of diffraction information

This table summarizes the possible diffraction experiments and th
advantages/disadvantages.



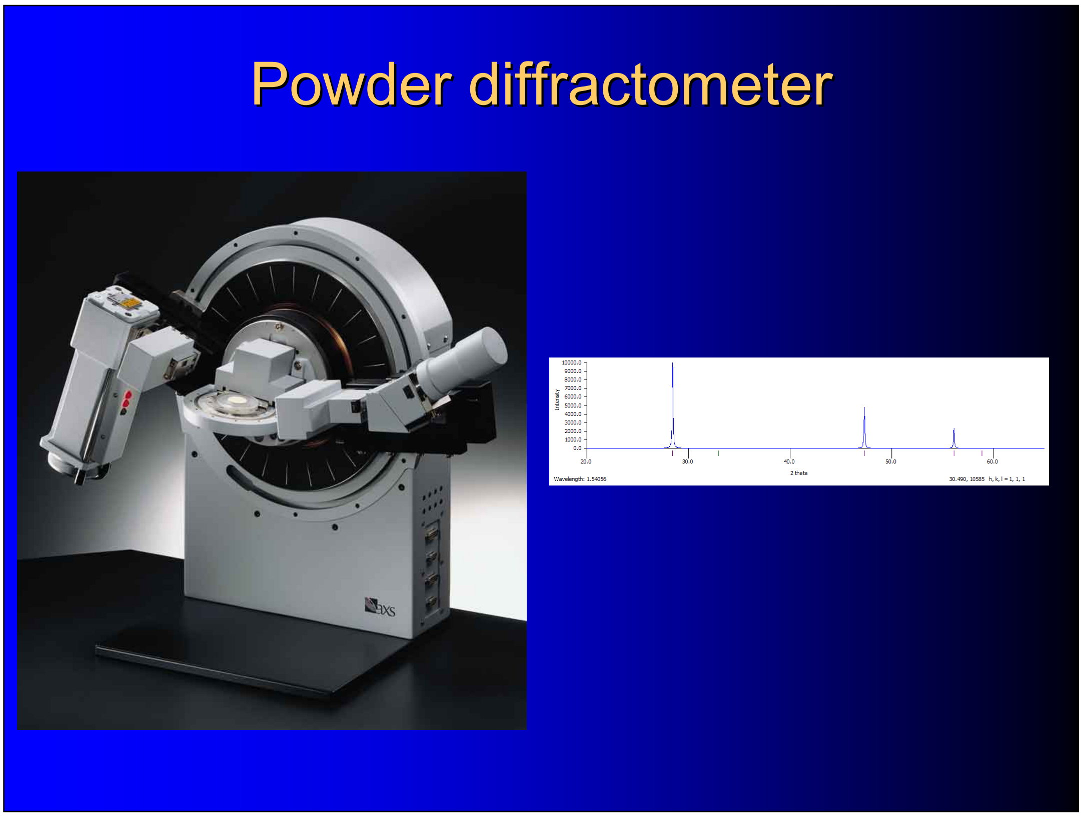
Four cycle diffractometer

Single crystals can be measured by monochromatic radiation on a diffractometer with point detector. The disadvantage of this system is speed – diffraction intensity is measured only in one point.



Four cycle diffractometer with area detector

The construction of four circle diffractometer can be improved by area detector. Such detector measures X-ray intensity in multiple points and speeds up the measurement.



Powder diffractometer

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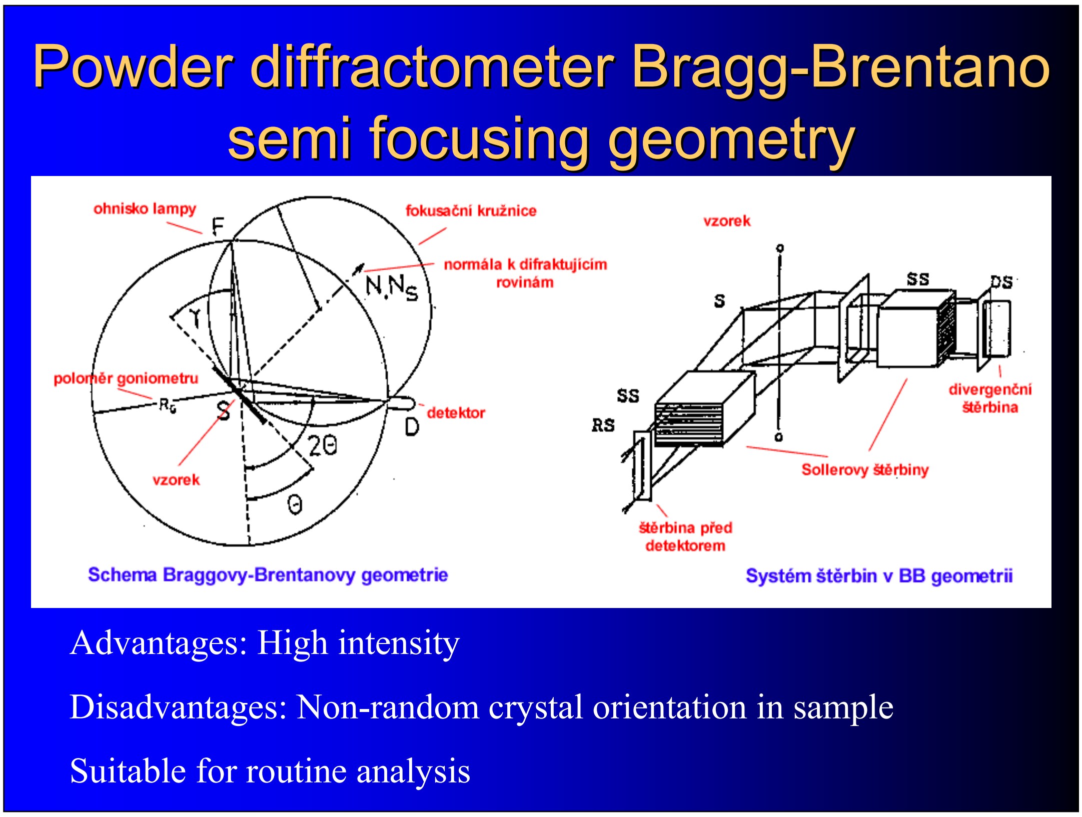
The construction of diffractometer targeted to measure powder sa more simple than four circle diffractometer – only tow circles are used. The result is intensity dependence on the 2θ angle – powder diffractogram.



Powder diffractometer Bragg-Brentano semi focusing geometry

Schema Braggovy-Brentanovy geometrie

Systém štěrbin v BB geometrii

Advantages: High intensity

Disadvantages: Non-random crystal orientation in sample

Suitable for routine analysis

For fast measurement of powder samples an intensity enhancing t developed – Bragg-Brentano geometry. This geometry re-focuses diffracted X-rays from a flat sample to speed up the measurement. It is used mainly for routine fast phase analysis.

Powder diffractometer with area detector

The speed of powder diffractometer can be enhanced by the use o

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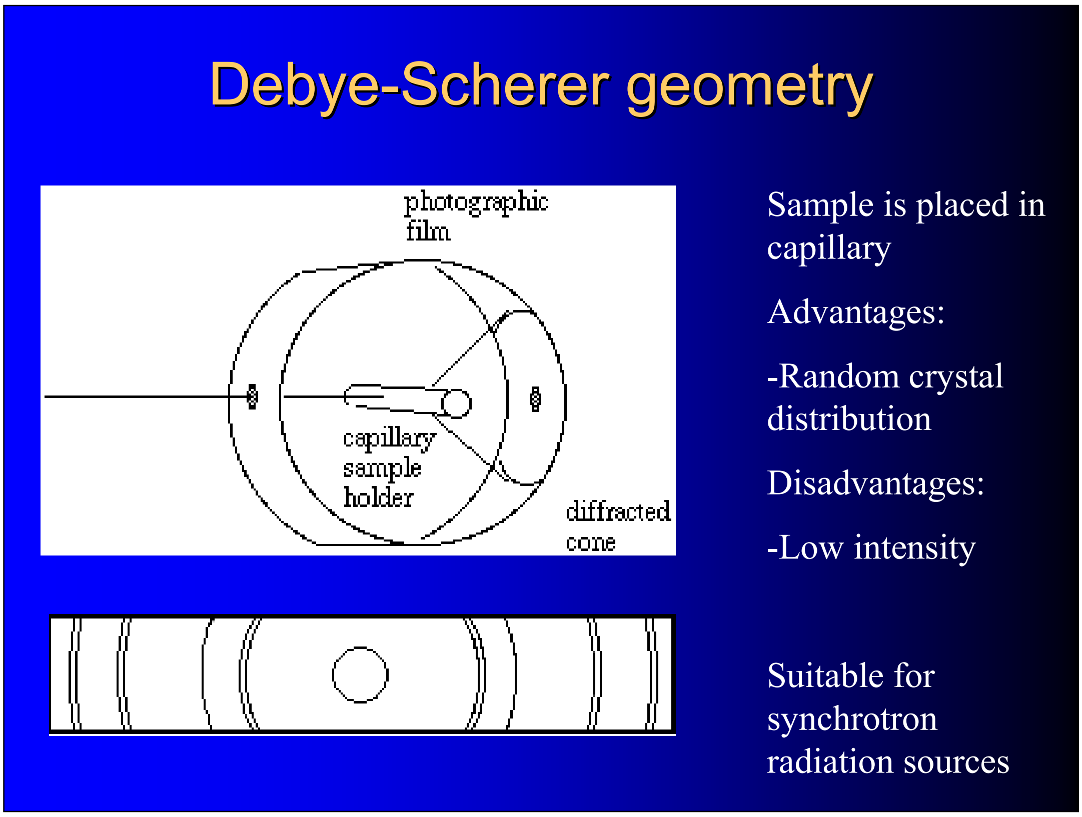


Debye-Scherer geometry

Sample is placed in capillary

Advantages:

-Random crystal distribution

Disadvantages:

-Low intensity

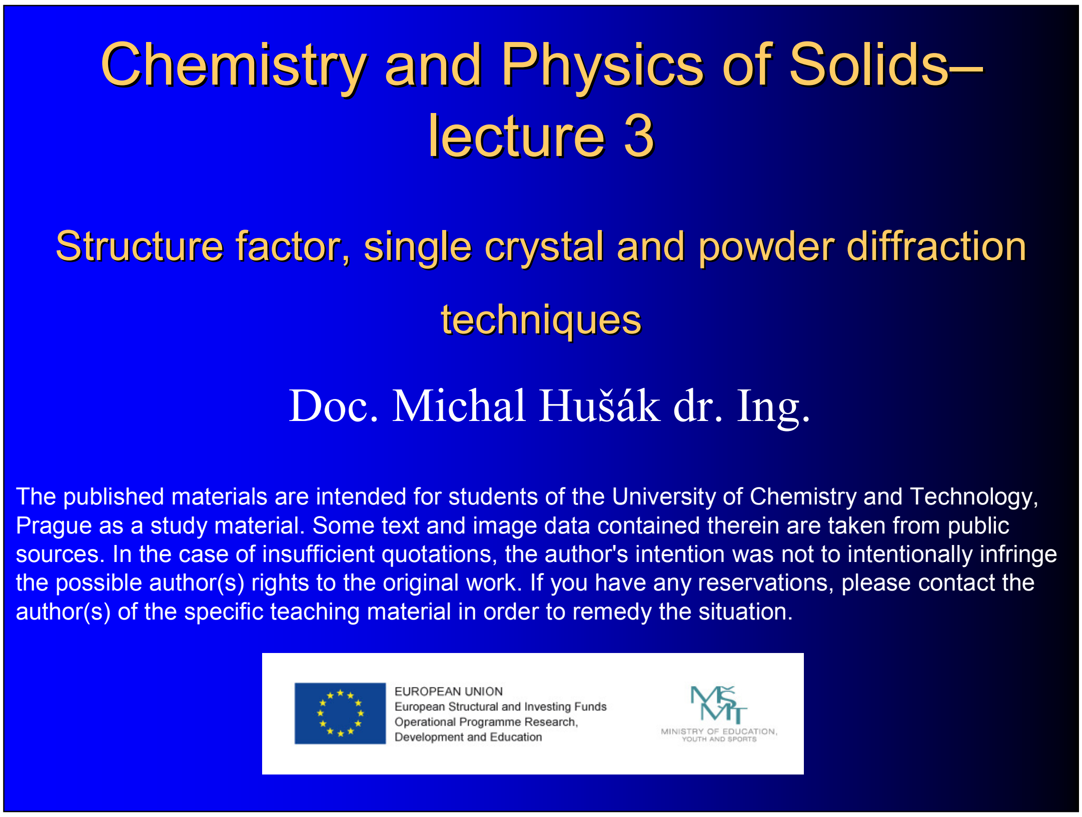
Suitable for synchrotron radiation sources

Another geometry for powder experiments is Debye-Scherer. The
placed in a non diffracting capillary.

Debye-Scherer diffractometer

Debye-Scherer diffractometer at ESRF Grenoble synchrotron facility

Debye-Scherer geometry is typically used in combination with sy ray source. Such measurements are typically targeted on structure solution from powder data.



Chemistry and Physics of Solids– lecture 3

Structure factor, single crystal and powder diffraction techniques

Doc. Michal Hušák dr. Ing.

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Suggested literature

Richard J.D. Tilley: Understanding Solids, Willey 2013

C. Giacovazzo: Fundamentals of crystallography, Oxford Science Publications 1992

J. I. Gersten: Physics and chemistry of materials, Willey 2001

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Lecture content

- Structure factor
- X-ray structure analysis
- Qualitative and quantitative X-ray phase analysis

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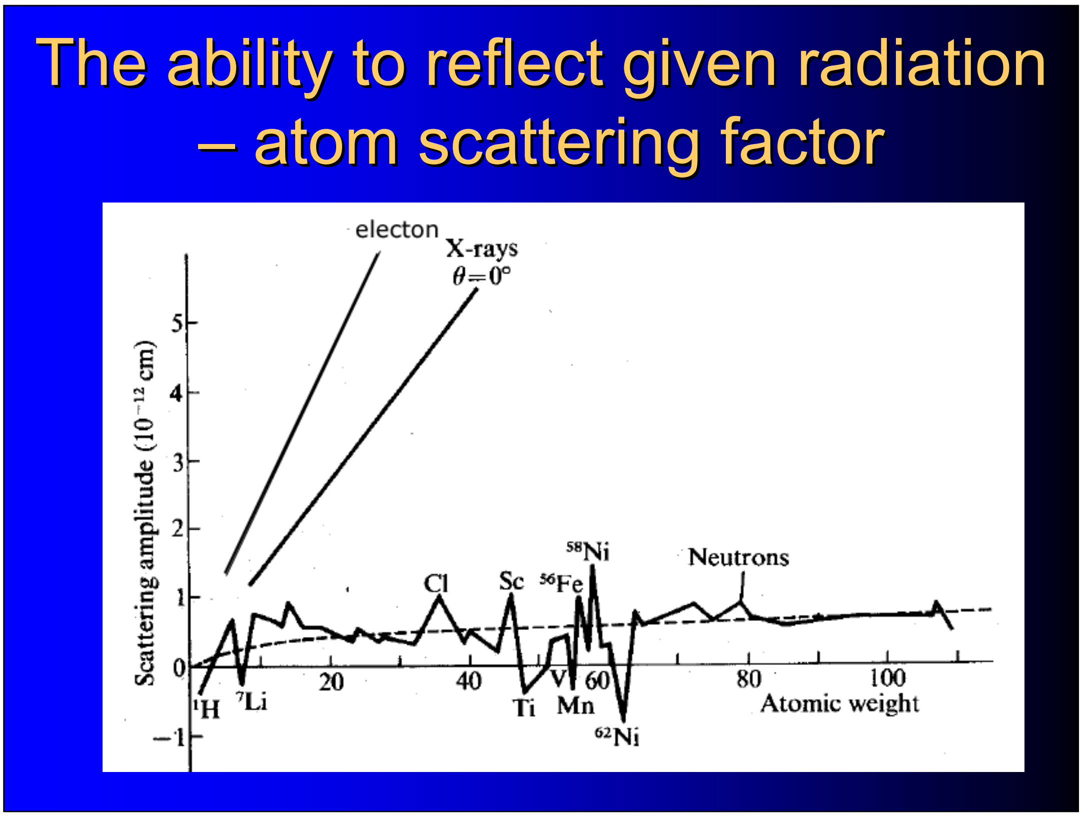
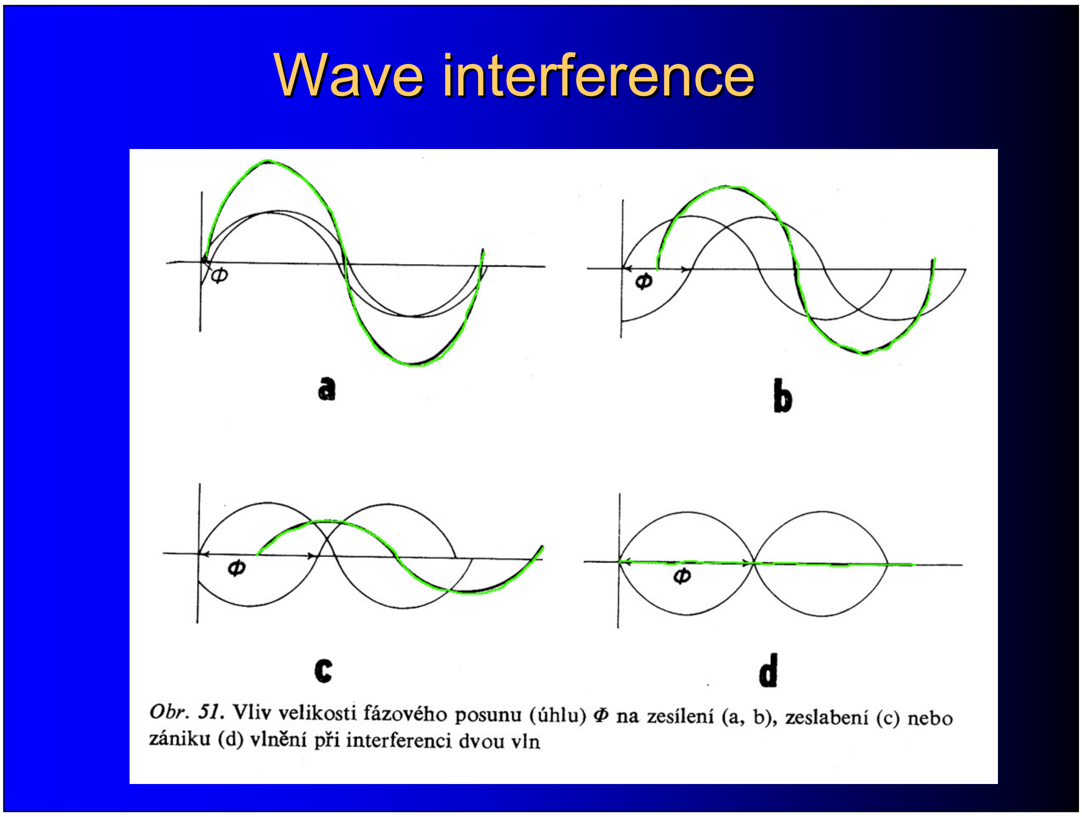


The ability to reflect given radiation – atom scattering factor

BY SA

As already mentioned in the previous lecture, the ability to reflect radiation depends on the reflecting atom type. The X-rays are reflected by electrons. The ability to reflect X-rays depends linearly on atomic number. The property is called atomic scattering factor.



Wave interference

Obr. 51. Vliv velikosti fázového posunu (úhlu) Φ na zesílení (a, b), zeslabení (c) nebo zániku (d) vlnění při interferenci dvou vln

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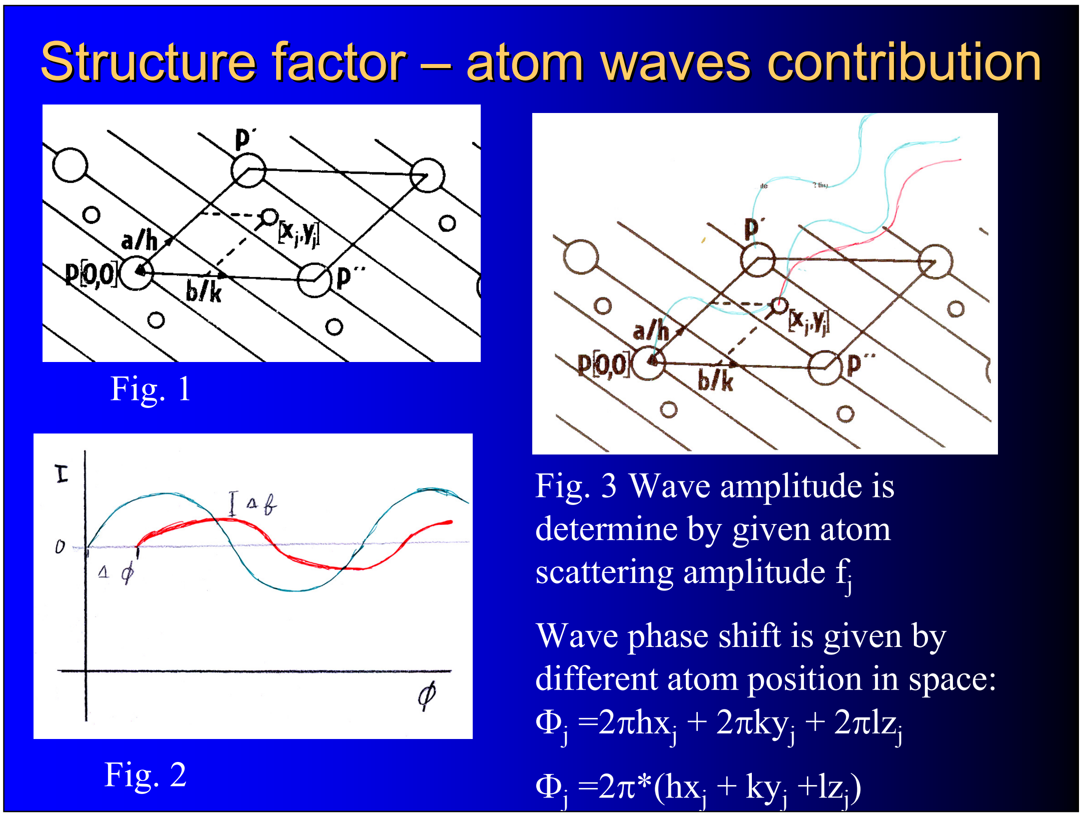
Waves with identical wavelength can interfere together in differe their phase shift. The intensity can be amplified (a), partially amplified of partially reduced (b,c). Phase shift of 1/2 wavelength (1π) can result in waves intensity reduction to 0.



Structure factor – atom waves contribution

Fig. 1

Fig. 2

Fig. 3 Wave amplitude is determine by given atom scattering amplitude f_j

Wave phase shift is given by different atom position in space:

$\Phi_j = 2\pi hx_j + 2\pi ky_j + 2\pi lz_j$

$\Phi_j = 2\pi*(hx_j + ky_j + lz_j)$

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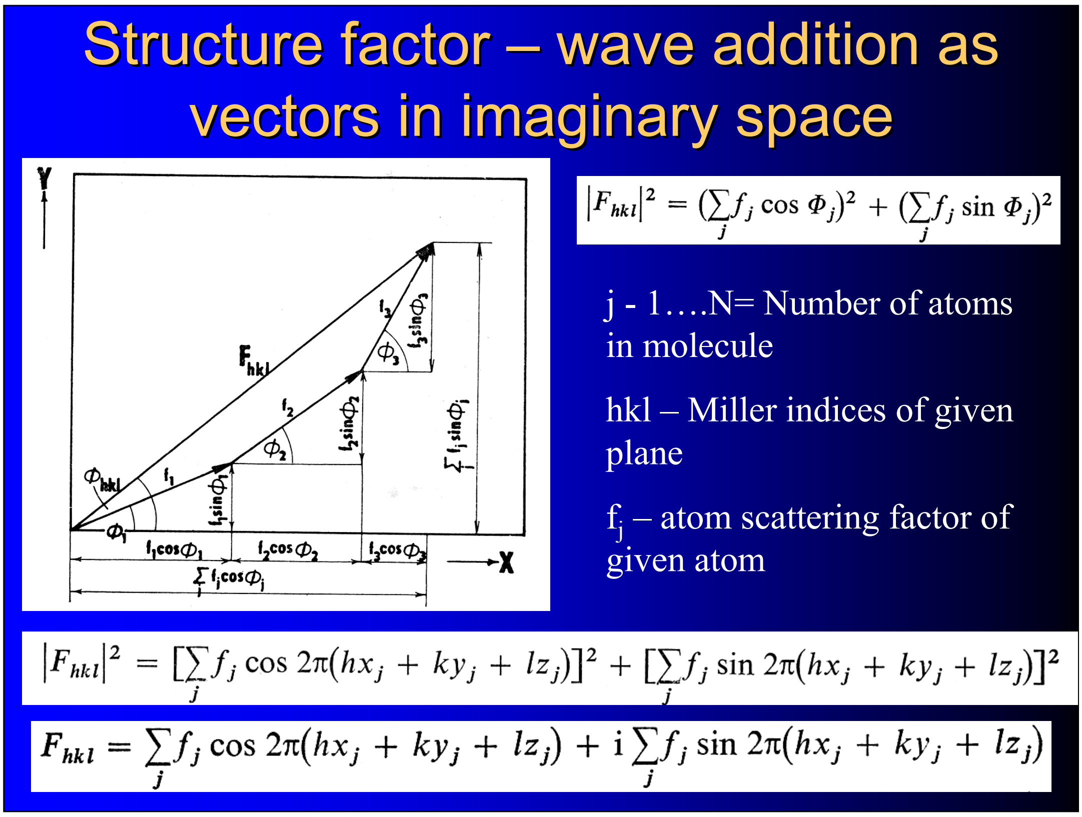
To get the amplitude of a final wave, we must combine waves ge atoms in the structure. The waves will differ in amplitude and in phase shift. The amplitude will be determined by the atom specific atomic scattering factor. Fig 1 shows a theoretical structure formed by 2 atoms : a heavy one in position 0,0,0 and a light one in position x,y,z (fractional coordinates). The light atom wave (red) will have lower amplitude and phase shift according to the heavy atom wave (blue) Fig 2. The waves of heavy atoms will have a phase shift equivalent to 2π to satisfy Bragg equations. The light atom is not in 0,0,0 position, so its phase shift will be determined by its fractional coordinates 2πx , 2πy , 2πz. To be able to work with any planes the final equation for phase shift is 2π(hx+ky+lz).



Structure factor – wave addition as vectors in imaginary space

$$|F_{hkl}|^2 = \left(\sum_j f_j \cos \Phi_j\right)^2 + \left(\sum_j f_j \sin \Phi_j\right)^2$$

j - 1….N= Number of atoms in molecule

hkl – Miller indices of given plane

f_j – atom scattering factor of given atom

$$|F_{hkl}|^2 = \left[\sum_j f_j \cos 2\pi(hx_j + ky_j + lz_j)\right]^2 + \left[\sum_j f_j \sin 2\pi(hx_j + ky_j + lz_j)\right]^2$$

$$F_{hkl} = \sum_j f_j \cos 2\pi(hx_j + ky_j + lz_j) + \mathrm{i} \sum_j f_j \sin 2\pi(hx_j + ky_j + lz_j)$$

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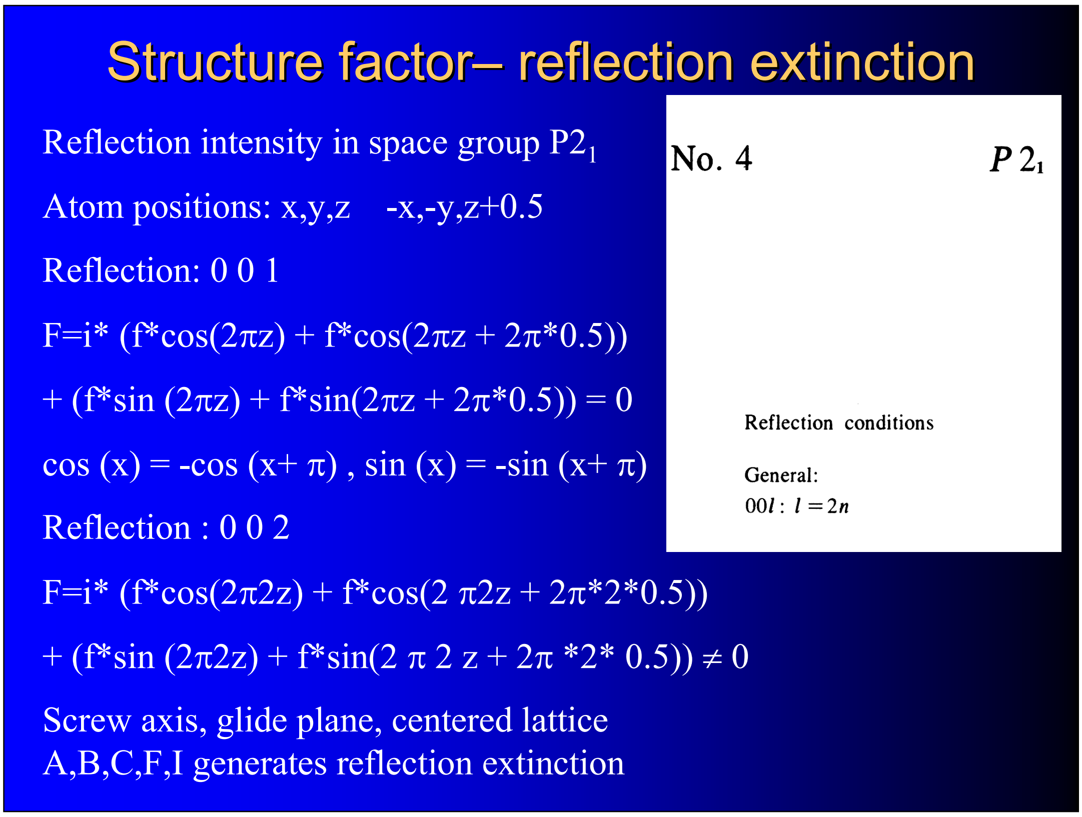
The wave combination can be visualized in imaginary space. Eac as a vector with 2 properties: amplitude (length f) and phase angle Φ. To get final wave (F) properties we must combine together waves from all atoms (j –index). The length of F can be clouted by Pythagorean theorem $F^2=A^2+B^2$. A = sum of cos phase shift multiplied by atomic scattering factors. B = sum of sin phase shift multiplied by atomic scattering factors. The F^2 corresponds to the intensity measured by the diffractometer detector. The structure factor equation gives us the key relation between measured intensity , atom positions (x,y,z) and type (f).



Structure factor– reflection extinction

Reflection intensity in space group $P2_1$

Atom positions: x,y,z   -x,-y,z+0.5

Reflection: 0 0 1

$F = i^* (f^*\cos(2\pi z) + f^*\cos(2\pi z + 2\pi^*0.5))$

$+ (f^*\sin(2\pi z) + f^*\sin(2\pi z + 2\pi^*0.5)) = 0$

$\cos(x) = -\cos(x+\pi)$, $\sin(x) = -\sin(x+\pi)$

Reflection : 0 0 2

$F = i^* (f^*\cos(2\pi 2z) + f^*\cos(2\pi 2z + 2\pi^*2^*0.5))$

$+ (f^*\sin(2\pi 2z) + f^*\sin(2\pi 2z + 2\pi^*2^*0.5)) \neq 0$

Screw axis, glide plane, centered lattice
A,B,C,F,I generates reflection extinction

No. 4 $P2_1$

Reflection conditions

General:
$00l$: $l = 2n$

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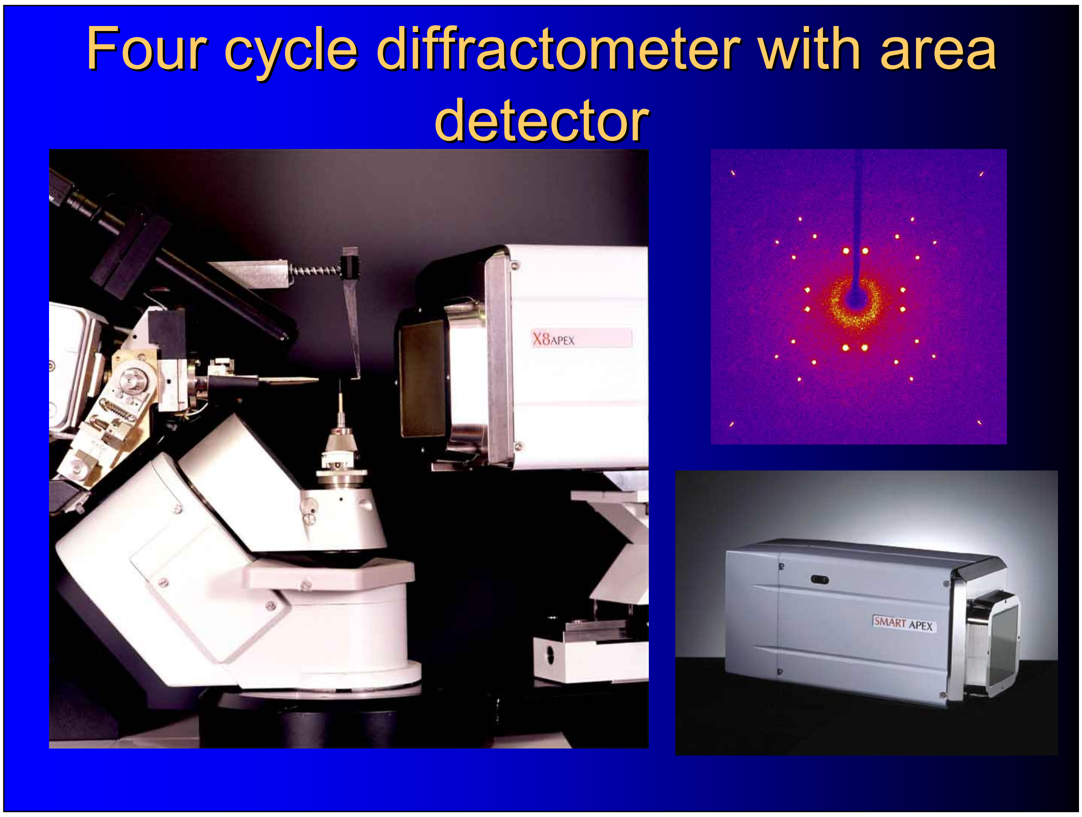
The first useful thing for which we can use structure factor is spac determination. Let us imaging a structure in space group $P2_1$. Such a structure must for each atom in x,y,z, position have another one in –x,-y,z+0.5 (screw axis in z direction). We can calculate the structure factor for (0,0,1) reflection and (0,0,2) reflection. The result is the intensity from (0,0,1), (0,0,3) … will be always 0. This effect can be utilized for space group determination.



Four cycle diffractometer with area detector

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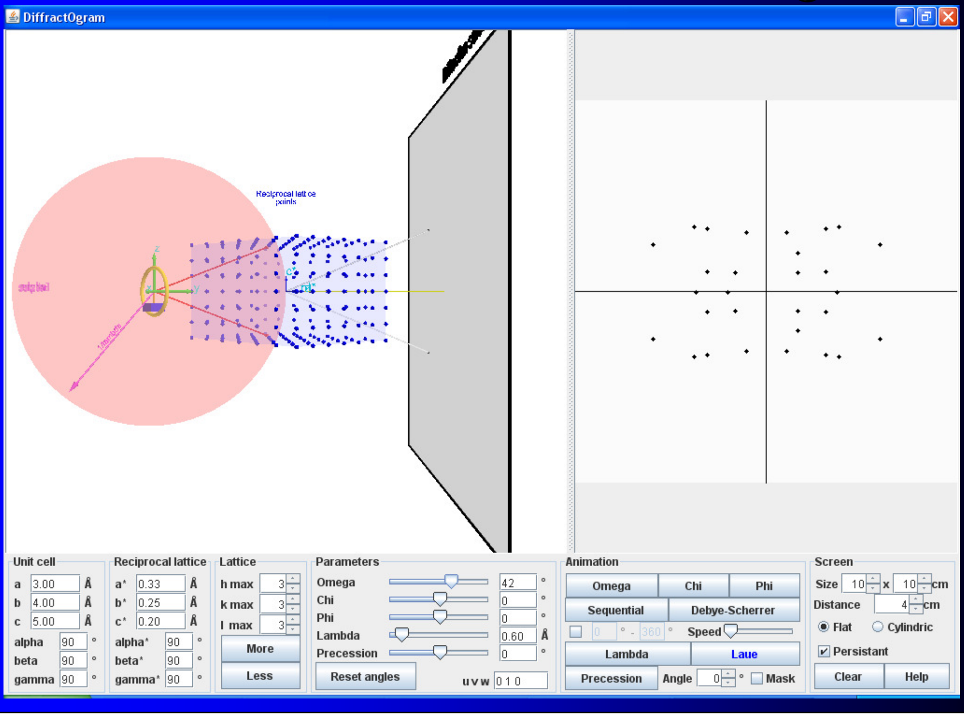
The intensity of diffracted X-rays can be measured on four cycle A small crystal (typically a 0.3 mm size) can be rotated along 4 axes in any direction. The diffracted light is measured by area detector. The principle of area detector is to convert X-rays to visible light and than measure its intensity by CCD sensors.

Software simulation diffractOgram



Unit cell
a 3.00 Å
b 4.00 Å
c 5.00 Å
alpha 90 °
beta 90 °
gamma 90 °

Reciprocal lattice
a* 0.33 Å
b* 0.25 Å
c* 0.20 Å
alpha* 90 °
beta* 90 °
gamma* 90 °

Lattice
h max 3
k max 3
l max 3

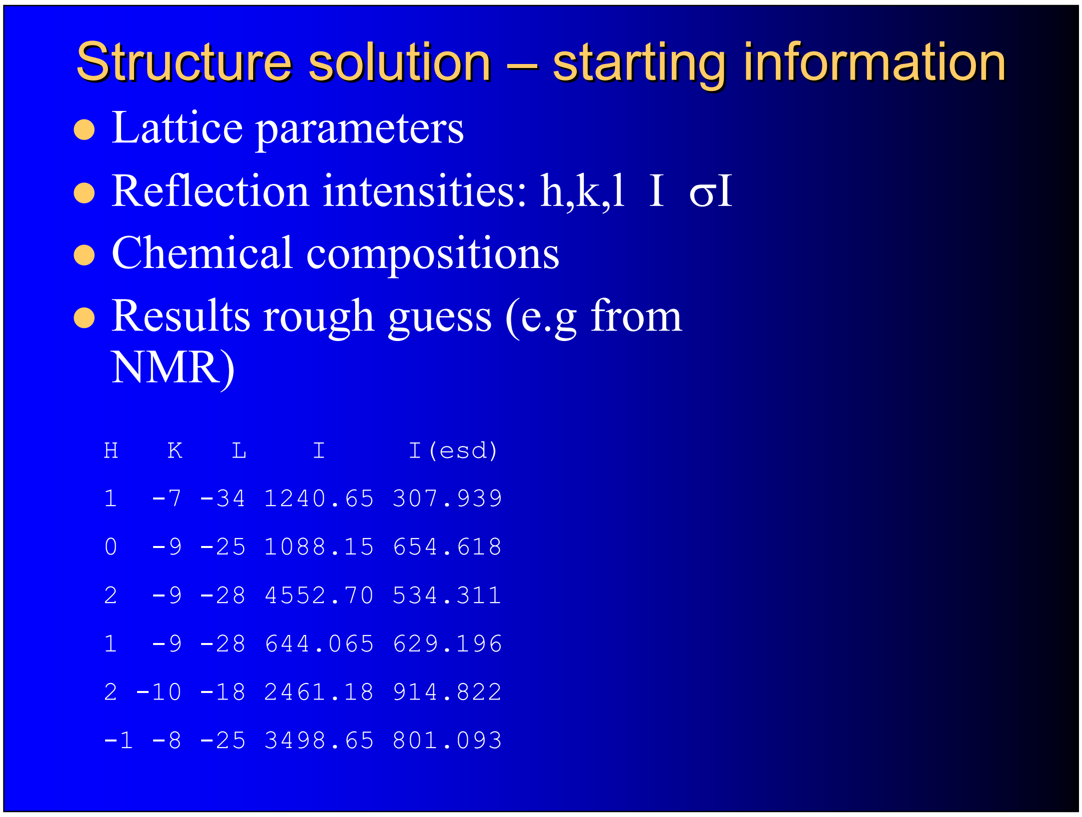
Parameters
Omega 42 °
Chi 0 °
Phi 0 °
Lambda 0.60 Å
Precession 0 °
u v w 0 1 0

Animation
☐ 0 ° - 360 ° Speed
Angle 0 ° ☐ Mask

Screen
Size 10 x 10 cm
Distance 4 cm
● Flat ○ Cylindric
☑ Persistant

The functionality of 4 cycle diffractometer can be simulated by a diffractOgram (see lecture 2).

BY SA

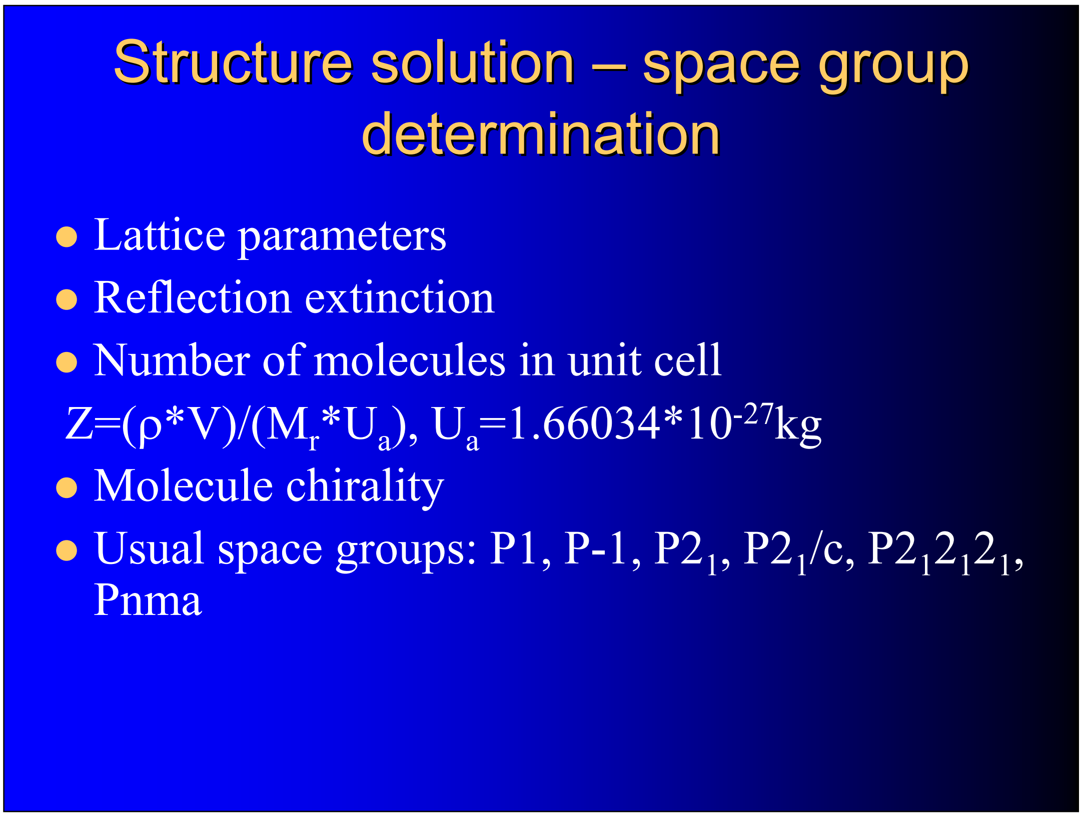


Structure solution – starting information

- Lattice parameters
- Reflection intensities: h,k,l I σI
- Chemical compositions
- Results rough guess (e.g from NMR)

H	K	L	I	I(esd)
1	-7	-34	1240.65	307.939
0	-9	-25	1088.15	654.618
2	-9	-28	4552.70	534.311
1	-9	-28	644.065	629.196
2	-10	-18	2461.18	914.822
-1	-8	-25	3498.65	801.093

At the beginning of crystal structure solution, we have access typ following information: lattice parameters, intensity of several reflections as measured by single crystal diffractometer, elementary analysis and at least some guess about the molecule shape.



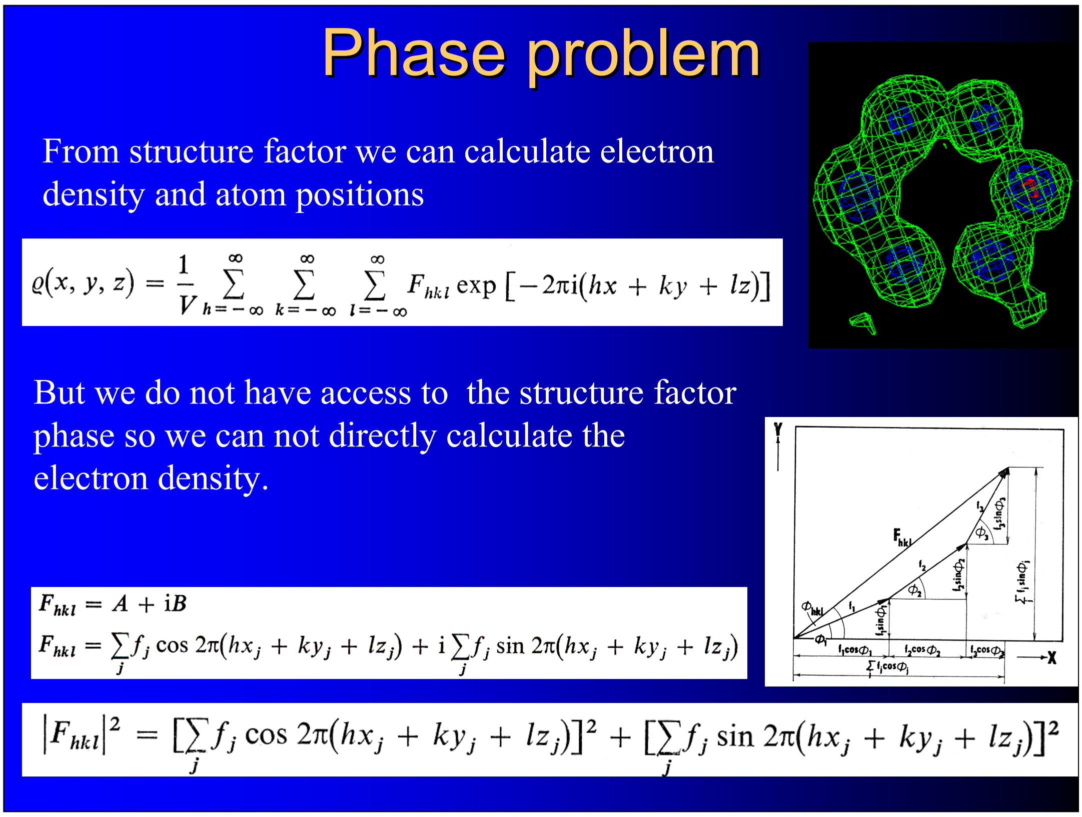
Structure solution – space group determination

- Lattice parameters
- Reflection extinction
- Number of molecules in unit cell

$Z=(\rho*V)/(M_r*U_a)$, $U_a=1.66034*10^{-27}$kg

- Molecule chirality
- Usual space groups: P1, P-1, $P2_1$, $P2_1/c$, $P2_12_12_1$, Pnma

Before we go on with structure solution, we must identify the spa lattice parameters we can identify the crystal system. In given crystal systems only selected space groups occur. From missing (extinct) reflection we can identify symmetry elements with translation (see Structure factor). From the molecule formula and density we can calculate the number of molecule sin the unit cell. Only 2 molecules in unit cell e,g, avoids 4-fold axis presence. A presence of chiral center avoid presence of symmetry elements avoiding chirality. In addition organic s prefer to occur only in some selected space groups (inorganic one crystals in any one).



Phase problem

From structure factor we can calculate electron density and atom positions

$$\varrho(x, y, z) = \frac{1}{V}\sum_{h=-\infty}^{\infty}\sum_{k=-\infty}^{\infty}\sum_{l=-\infty}^{\infty} F_{hkl}\exp\left[-2\pi i(hx + ky + lz)\right]$$

But we do not have access to the structure factor phase so we can not directly calculate the electron density.

$$F_{hkl} = A + iB$$

$$F_{hkl} = \sum_j f_j \cos 2\pi(hx_j + ky_j + lz_j) + i\sum_j f_j \sin 2\pi(hx_j + ky_j + lz_j)$$

$$|F_{hkl}|^2 = \left[\sum_j f_j \cos 2\pi(hx_j + ky_j + lz_j)\right]^2 + \left[\sum_j f_j \sin 2\pi(hx_j + ky_j + lz_j)\right]^2$$

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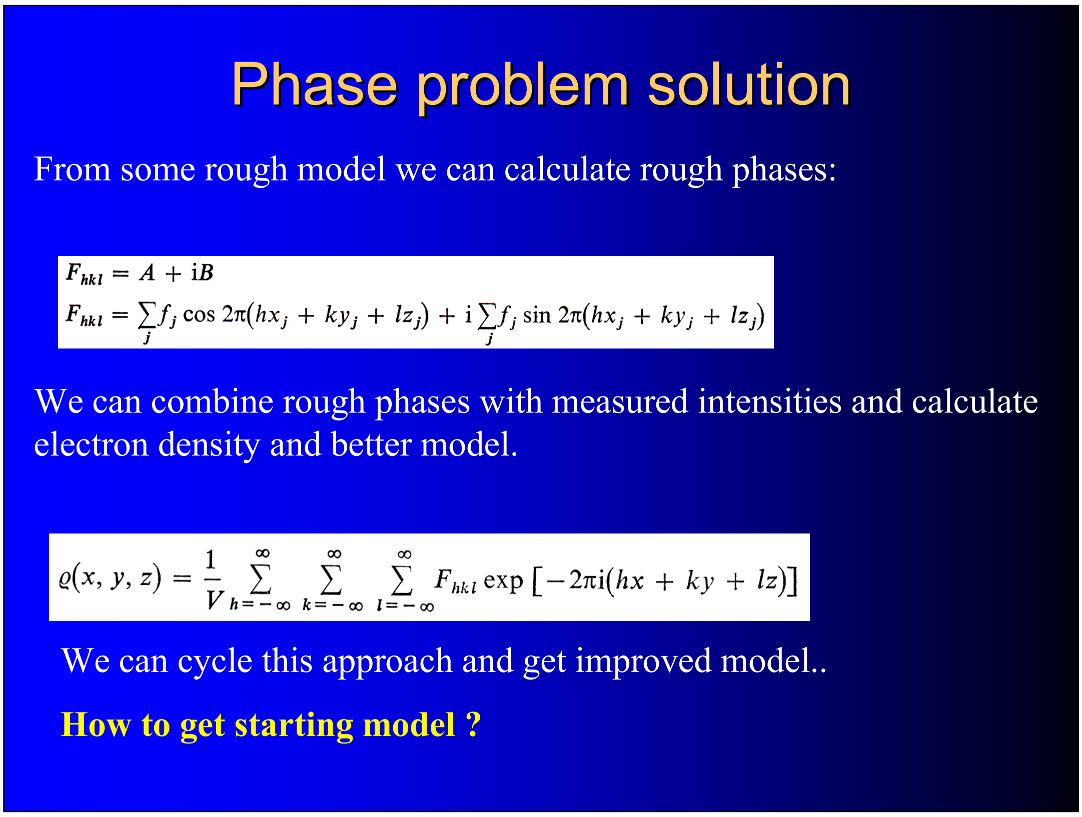
It is possible to calculate from the structure factor an electron den Electron density can be directly interpreted as atom positions. Unfortunately, to be able to make this calculation we need to know both intensity and the phase shift of the F (final wave). The phase shift cannot be experimentally measured. We can measure only the final wave intensity. This issue is called Phase problem.



Phase problem solution

From some rough model we can calculate rough phases:

$$F_{hkl} = A + \mathrm{i}B$$

$$F_{hkl} = \sum_j f_j \cos 2\pi(hx_j + ky_j + lz_j) + \mathrm{i}\sum_j f_j \sin 2\pi(hx_j + ky_j + lz_j)$$

We can combine rough phases with measured intensities and calculate electron density and better model.

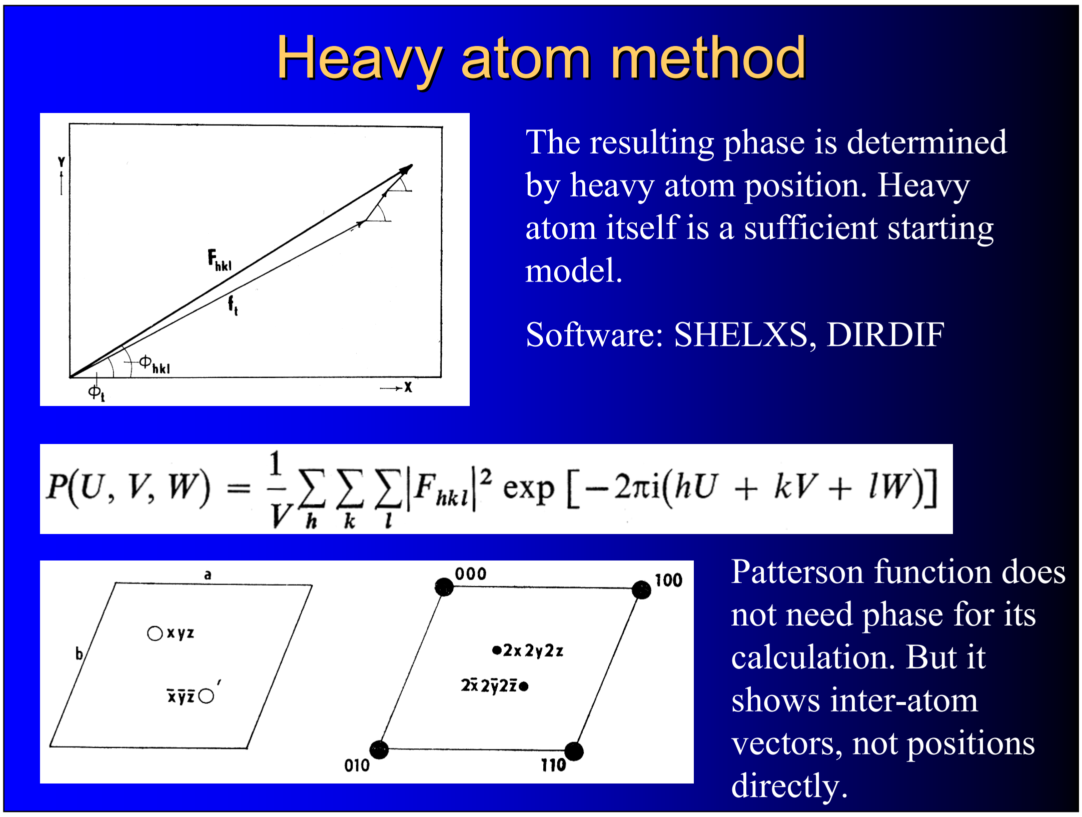
$$\varrho(x, y, z) = \frac{1}{V}\sum_{h=-\infty}^{\infty}\sum_{k=-\infty}^{\infty}\sum_{l=-\infty}^{\infty} F_{hkl}\exp\left[-2\pi\mathrm{i}(hx + ky + lz)\right]$$

We can cycle this approach and get improved model..

How to get starting model ?

BY SA

When we know the atom position, we can calculate the unknown combine such potentially unknown phases with experimental intensities. The result can be used to calculate electron density map and to improve the model. Such a cycling can help to finalize the model. The key question is how to get any starting model at all ?



Heavy atom method

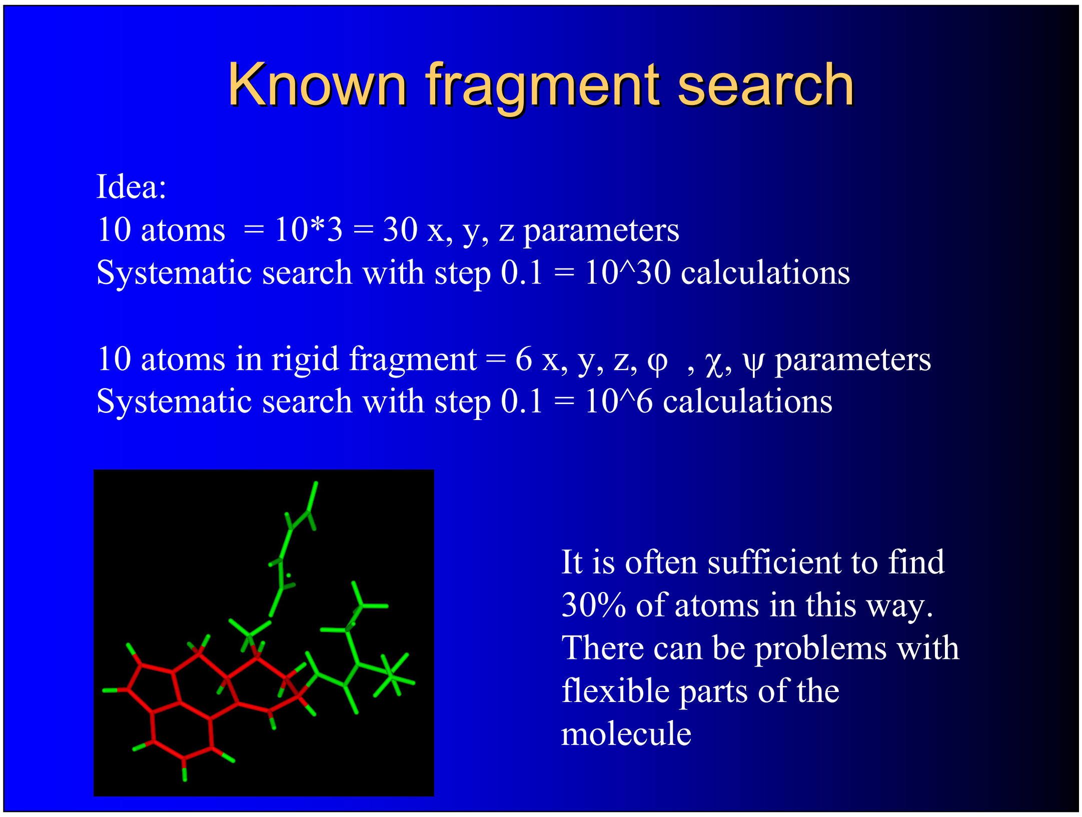
The resulting phase is determined by heavy atom position. Heavy atom itself is a sufficient starting model.

Software: SHELXS, DIRDIF

$$P(U, V, W) = \frac{1}{V}\sum_h \sum_k \sum_l |F_{hkl}|^2 \exp\left[-2\pi i(hU + kV + lW)\right]$$

Patterson function does not need phase for its calculation. But it shows inter-atom vectors, not positions directly.

The phase of the final structure factor is primarily determined by the most heavy atoms (with high atomic scattering factor). The position of heavy atoms itself can be a good enough starting model. Without knowledge of phases we can calculate the so called Patterson function from the data intensities only. The maxima on Patterson functions show no atom positions but inter-atom vector distances. There exist software and methods how to derive the positions of heavy atoms from the maximum peaks on Patterson map.



Known fragment search

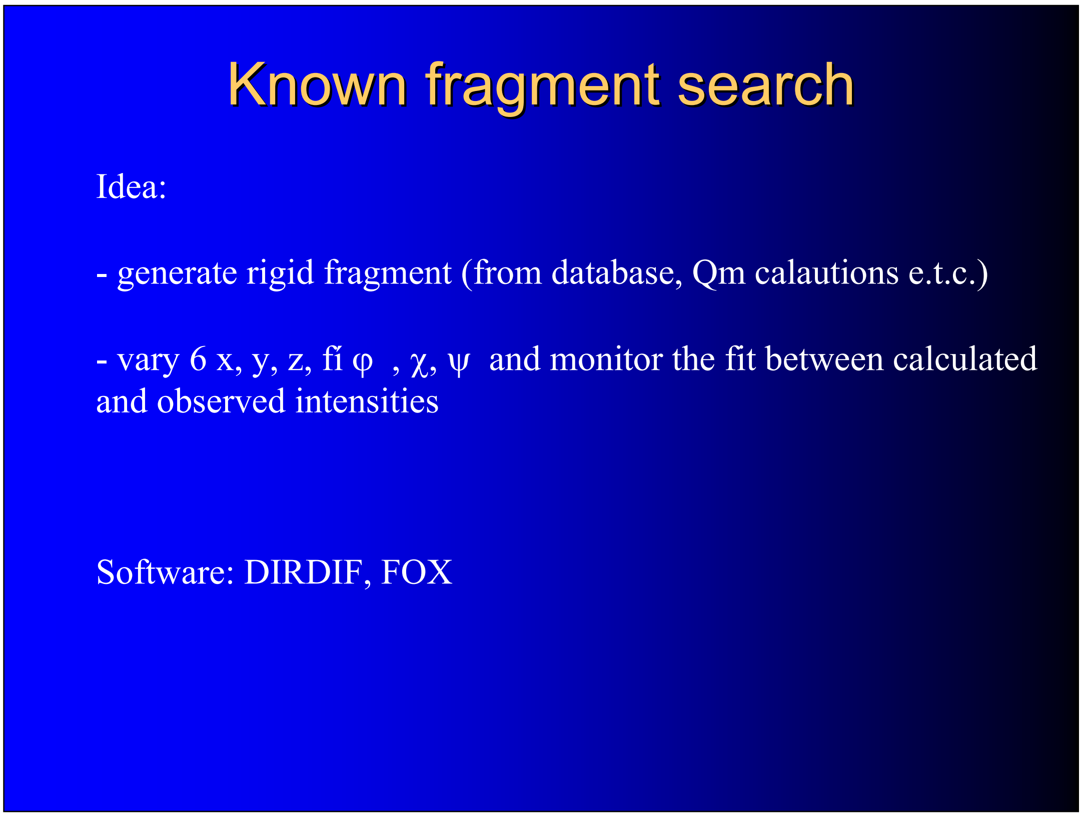
Idea:
10 atoms = 10*3 = 30 x, y, z parameters
Systematic search with step 0.1 = 10^30 calculations

10 atoms in rigid fragment = 6 x, y, z, φ , χ, ψ parameters
Systematic search with step 0.1 = 10^6 calculations

It is often sufficient to find 30% of atoms in this way. There can be problems with flexible parts of the molecule

BY SA

Another method how to get a starting model is fragment search. V atoms positions randomly and check whether the model is correct (by comparison of calculated and observed structure factors intensities). Even for 10 atoms such calculation is too computationally expensive to give results within reasonable time. When we place one atom somewhere in space the next atom cannot be anywhere – the structure has a restricted geometry given by typical inter-atomic distances, angles and torsion angles. The position of a rigid fragment from any number of atoms can be described by only 6 parameters. Random search through 6 parameter is an easy task …



Known fragment search

Idea:

- generate rigid fragment (from database, Qm calautions e.t.c.)

- vary 6 x, y, z, fi φ , χ, ψ and monitor the fit between calculated and observed intensities

Software: DIRDIF, FOX

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The structure solution based on fragment search is simple – gener a starting fragment (from similar structure, from molecular modelling) and than find its position in unit cell. The rest of the structure (non-rigid parts) can be found later from electron density map.

Direct (statistic) methods

Electron density properties:
- it is never less than 0
- it is localized in points/speheres

It is possible to determine equations between phases of intensive reflections

Sayre formula:

$$s(F_{h'k'l'}) \approx s(F_{hkl})\, s(F_{h'-h,k'-k,l'-l})$$

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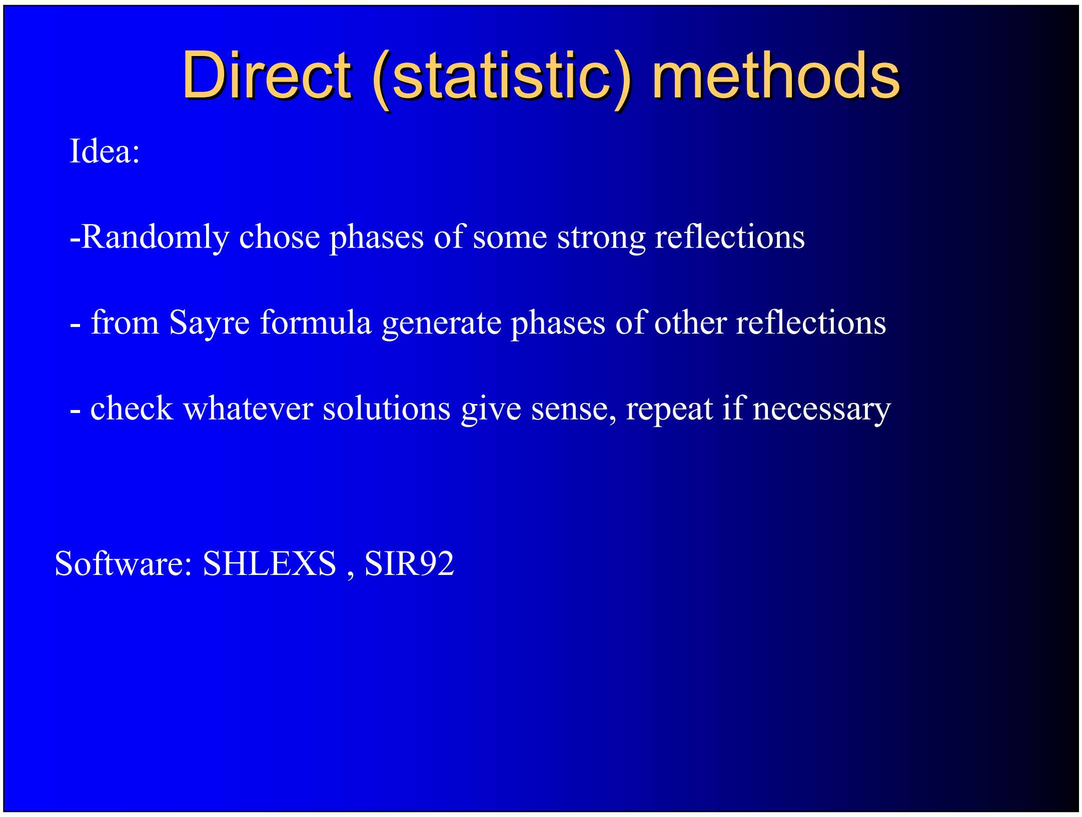
Another method for solving phase problem are direct methods. T based on the electron density property – it can never be less than zero. In addition electrons are usually localized in spheres surround atoms. Based on this assumption several formulas giving relations between phases of different structure factors can be derived.



Direct (statistic) methods

Idea:

-Randomly chose phases of some strong reflections

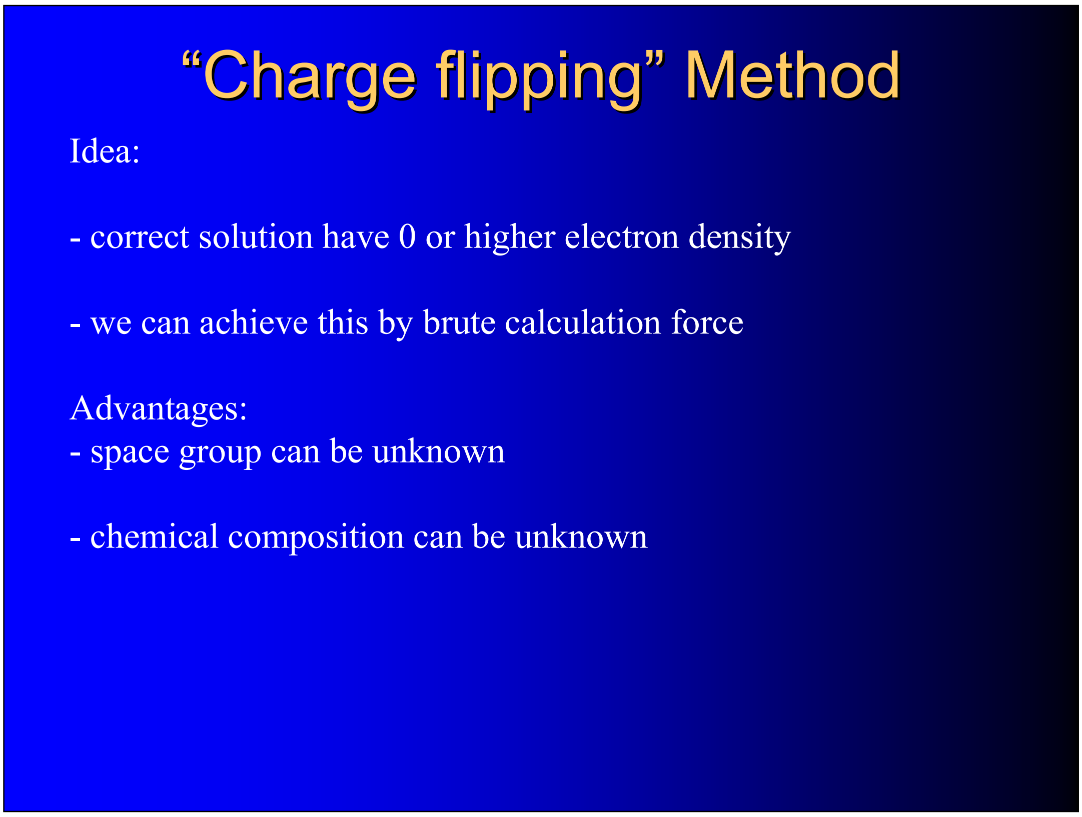
- from Sayre formula generate phases of other reflections

- check whatever solutions give sense, repeat if necessary

Software: SHLEXS , SIR92

BY SA

The derived formulas are used in following way: We chose rando
few (typical 3 – triplet) structure factors. Based on this phases we derive phases of other structure factors. When we get electrons density map giving sense we are done, elsewhere we must chose another set of random phases for a test.



“Charge flipping” Method

Idea:

- correct solution have 0 or higher electron density

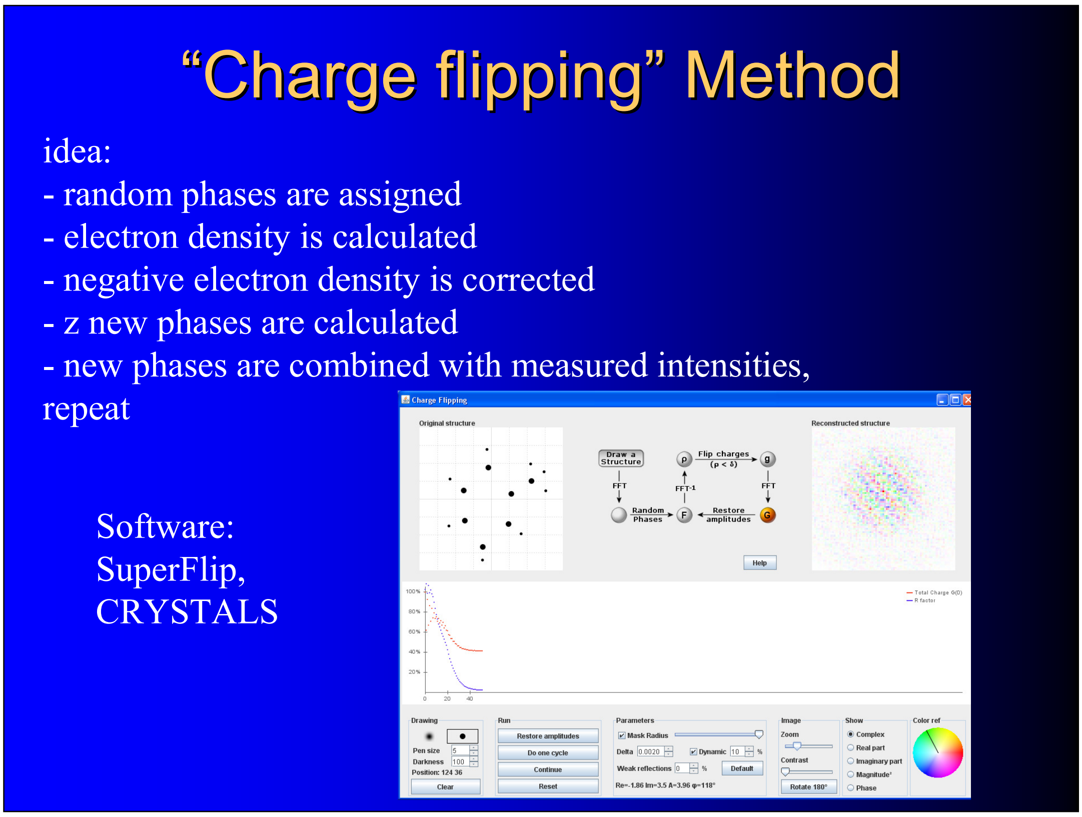
- we can achieve this by brute calculation force

Advantages:

- space group can be unknown

- chemical composition can be unknown

A modern variant of the direct method is the so-called “Charge fl
based only on the assumption that the electron density cannot be less than 0.



“Charge flipping” Method

idea:

- random phases are assigned
- electron density is calculated
- negative electron density is corrected
- z new phases are calculated
- new phases are combined with measured intensities, repeat

Software:
SuperFlip,
CRYSTALS

Pen size 5
Darkness 100
Position: 124 36

☑ Mask Radius
Delta 0.0020
☑ Dynamic 10 %
Weak reflections 0 %
Re=-1.86 Im=3.5 A=3.96 φ=118°

● Complex
○ Real part
○ Imaginary part
○ Magnitude²
○ Phase

The slide shows how the “Charge flipping” method works. A free
charge_flip.jar exists for graphical demonstration.

BY SA

Structure refinement

$$|F_c| = |F_c(p_1 \dots p_n)|$$

Calculated structure factor depends on model parameters

We want to minimize square of calculated and observed intensities.

$$\sum_{hkl} w_{hkl}\left[|F_0| - |F_c(p_1 \dots p_n)|\right]^2 = \min$$

Taylor expansion and conversion to system of linear equation is used (numeric math methods).

$$\sum_{hkl} 2w_{hkl}\left[|F_0| - |F_c(p_1^0 \dots p_n^0)| - \frac{\partial|F_c|}{\partial p_1}\Delta p_1 - \dots - \frac{\partial|F_c|}{\partial p_n}\Delta p_n\right]\frac{\partial|F_c|}{\partial p_j} = 0$$

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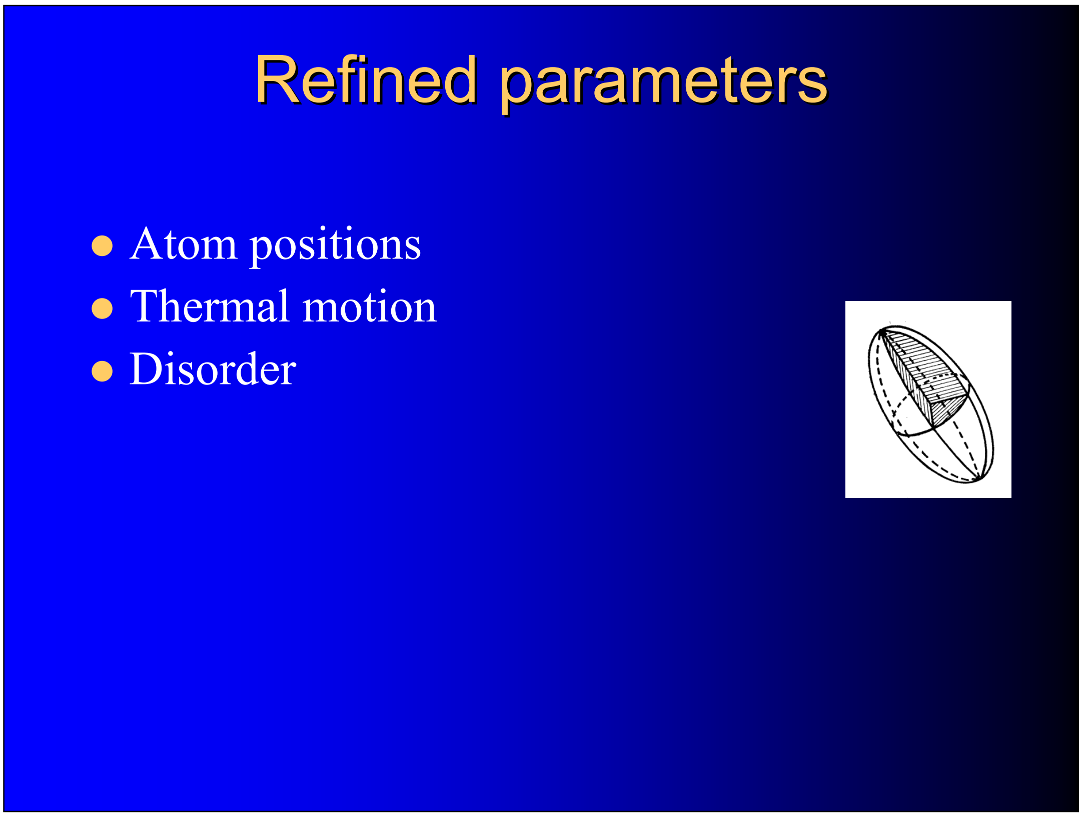
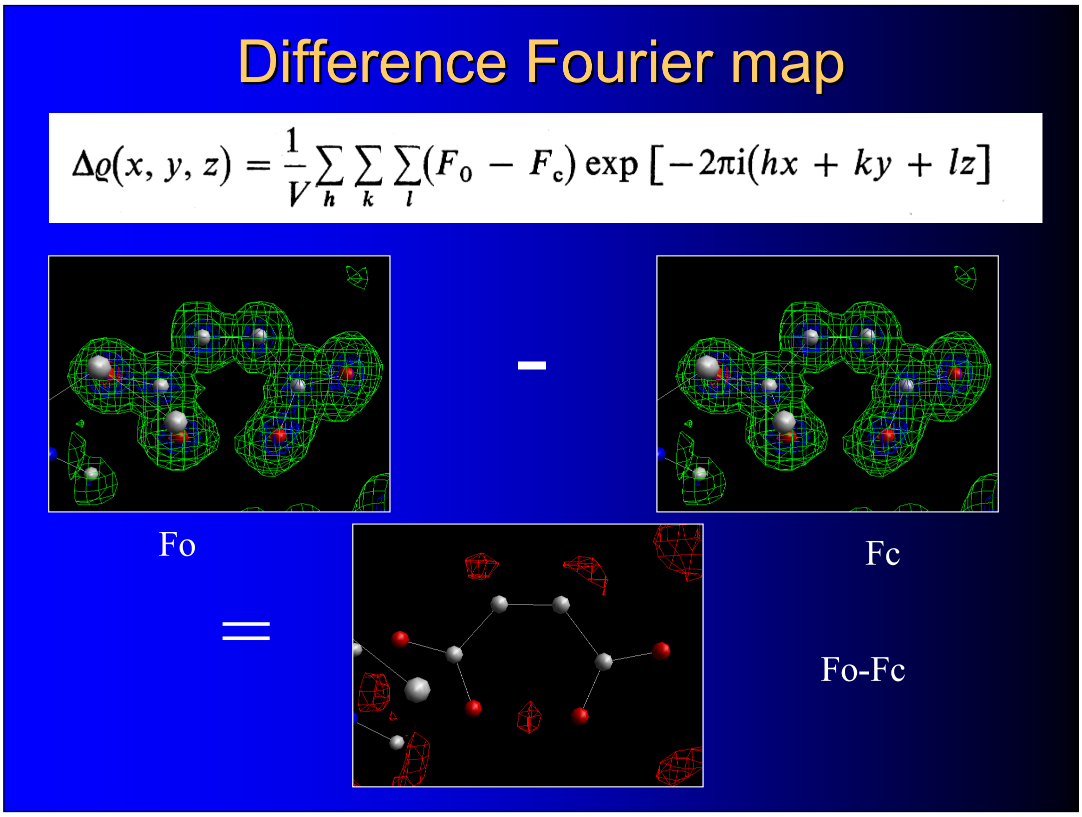
The last step of structure determination is Structure refinement. W optimize the structure model to find an agreement between calculated and measured structure factors intensities. The equations are non-linear so the solution is based on Taylor expansion and repeated solution of linear equations.



Refined parameters

- Atom positions
- Thermal motion
- Disorder

During the refinement we can modify the following parameters o atom positions, description of their thermal motion, disorder (multiple possible locations of one atom)



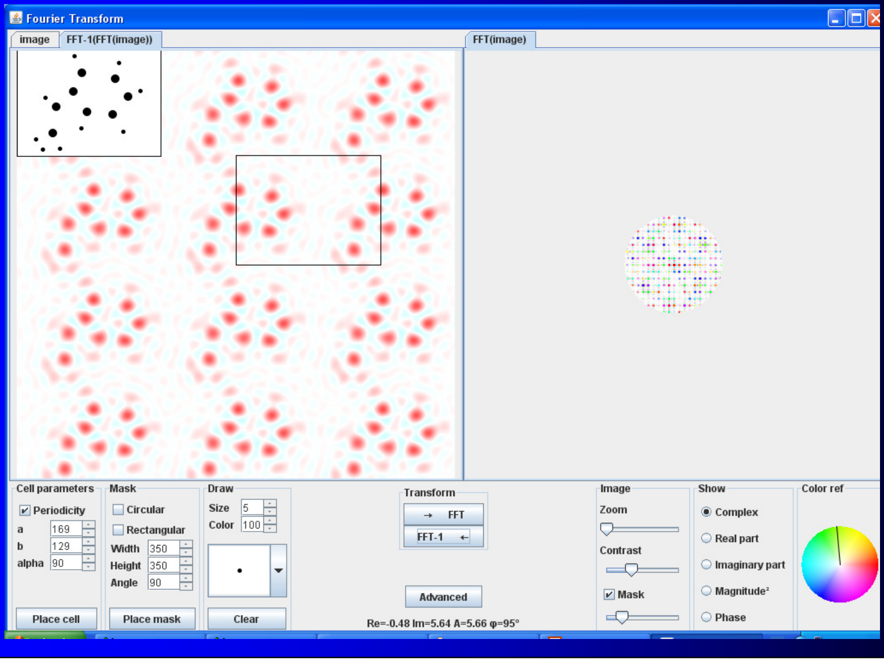
Difference Fourier map

$$\Delta\varrho(x, y, z) = \frac{1}{V}\sum_{h}\sum_{k}\sum_{l}(F_0 - F_c)\exp\left[-2\pi i(hx + ky + lz)\right]$$

cc BY SA

At the and of the structure solution a check for possible missing a performed. Electron density calculated from our model will be subtracted from electron density calculated from experimental data. The difference (difference Fourier map) shows often missing atoms – typically hydrogen.

Results quality limits – finite number of reflections



☑ Periodicity
a 169
b 129
alpha 90

☐ Circular
☐ Rectangular
Width 350
Height 350
Angle 90

Size 5
Color 100

Re=-0.48 Im=5.64 A=5.66 φ=95°

☑ Mask

● Complex
○ Real part
○ Imaginary part
○ Magnitude²
○ Phase

The quality of the result is limited by the number of measured int perfect electron density map can be calculated only from infinite number of measured diffraction intensities. With the help of forward and reverse Fourier calculations, the influence of the intensities number on the map quality can be visualized.

BY SA

Model quality evaluation

- R a Rw factors
- Residual electron density
- Errors of parameters (e.s.d.)
- Chemical sense of the result

$$R = \frac{\sum_{hkl} \left| |F_0| - |F_c| \right|}{\sum_{hkl} |F_0|}$$

$$wR = \sqrt{\left(\frac{\sum_{hkl} w_{hkl} (|F_0| - |F_c|)^2}{\sum_{hkl} w_{hkl} |F_0|^2} \right)}$$

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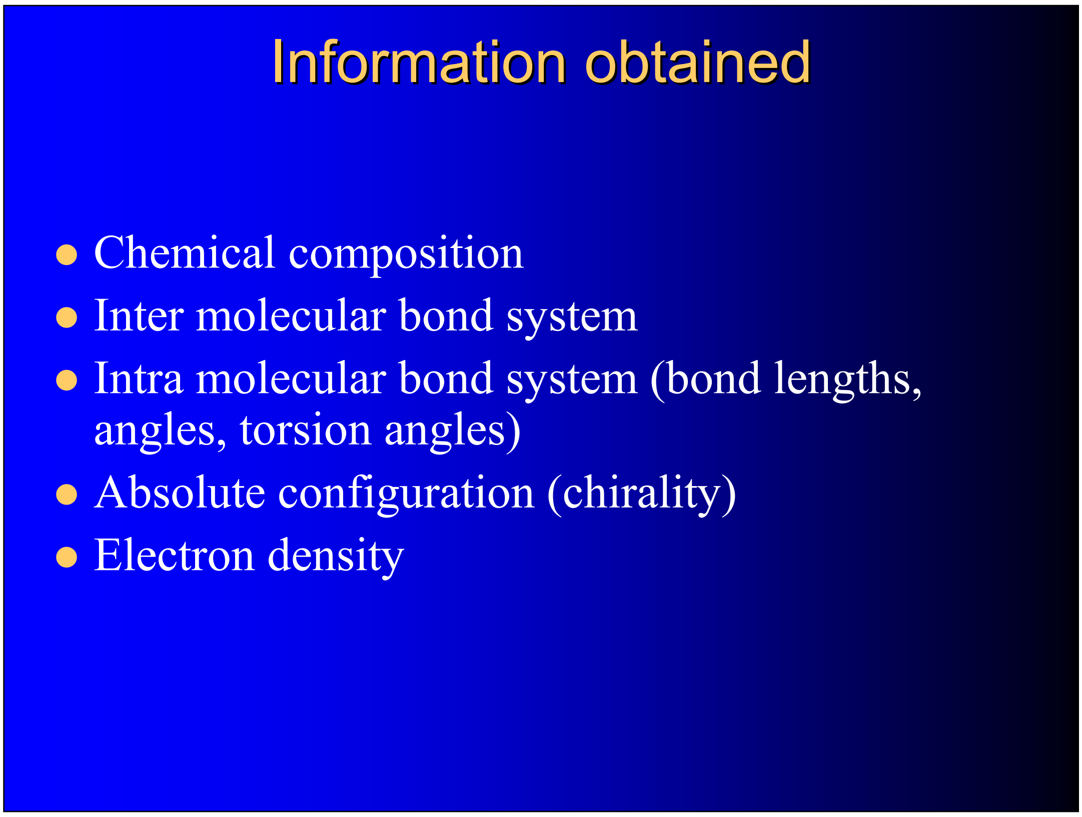
The quality of the structure model can be determined by comparis diffraction intensities calculated form the model and measured intensities. Quantitative measure as so-called R factors. Other quality indicators: residual electron density, errors of geometry parameters, general molecular geometry sense.



Information obtained

- Chemical composition
- Inter molecular bond system
- Intra molecular bond system (bond lengths, angles, torsion angles)
- Absolute configuration (chirality)
- Electron density

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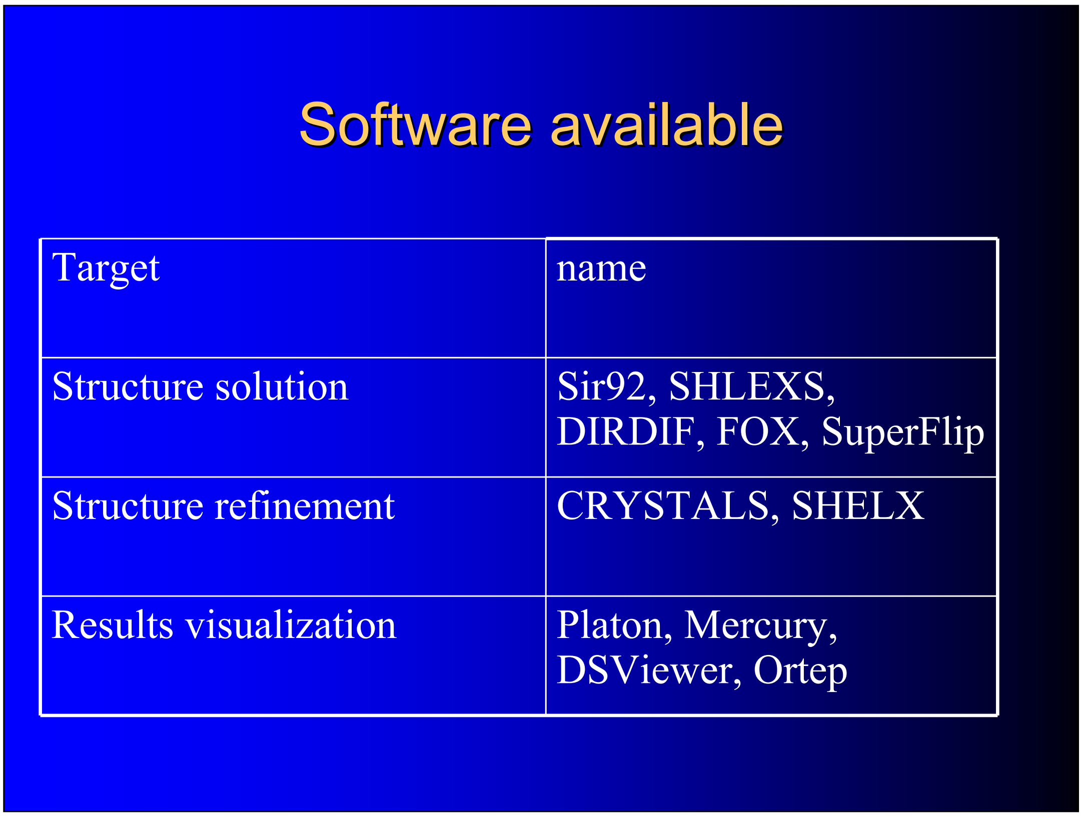
From the structure solution process we can get the following info chemical composition, inter-molecular bond system data, or information about intermolecular geometry, chirality, electron density



Software available

Target	name
Structure solution	Sir92, SHLEXS, DIRDIF, FOX, SuperFlip
Structure refinement	CRYSTALS, SHELX
Results visualization	Platon, Mercury, DSViewer, Ortep

List of existing software for different mentioned tasks.

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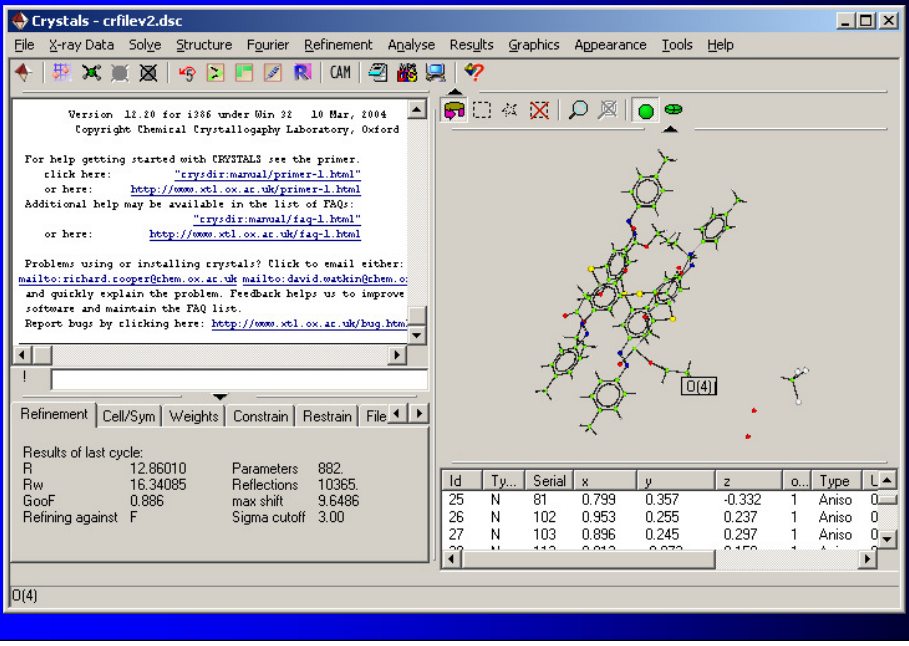
CRYSTALS – software demo



```
        Version  12.20 for i386 under Win 32   10 Mar, 2004
         Copyright Chemical Crystallogaphy Laboratory, Oxford

 For help getting started with CRYSTALS see the primer.
    click here:            "crysdir:manual/primer-1.html"
    or here:        http://www.xtl.ox.ac.uk/primer-1.html
 Additional help may be available in the list of FAQs:
                               "crysdir:manual/faq-1.html"
    or here:           http://www.xtl.ox.ac.uk/faq-1.html

 Problems using or installing crystals? Click to email either:
mailto:richard.cooper@chem.ox.ac.uk mailto:david.watkin@chem.o
 and quickly explain the problem. Feedback helps us to improve
 software and maintain the FAQ list.
 Report bugs by clicking here: http://www.xtl.ox.ac.uk/bug.htm
```

Results of last cycle:

R	12.86010	Parameters	882.
Rw	16.34085	Reflections	10365.
GooF	0.886	max shift	9.6486
Refining against	F	Sigma cutoff	3.00

Id	Ty...	Serial	x	y	z	o...	Type	L
25	N	81	0.799	0.357	-0.332	1	Aniso	0
26	N	102	0.953	0.255	0.237	1	Aniso	0
27	N	103	0.896	0.245	0.297	1	Aniso	0

O(4)

Demo of CRYSTALS software (structure solution, structure refin visualization)

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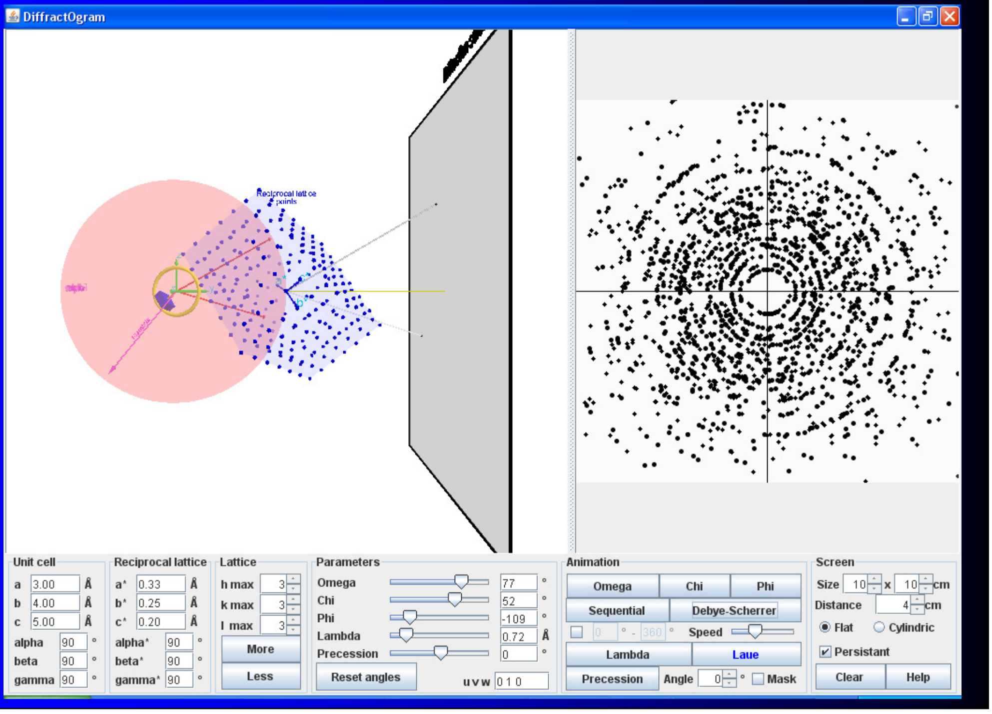
diffractOgram – powder sample



Unit cell: a 3.00 Å, b 4.00 Å, c 5.00 Å, alpha 90 °, beta 90 °, gamma 90 °

Reciprocal lattice: a* 0.33 Å, b* 0.25 Å, c* 0.20 Å, alpha* 90 °, beta* 90 °, gamma* 90 °

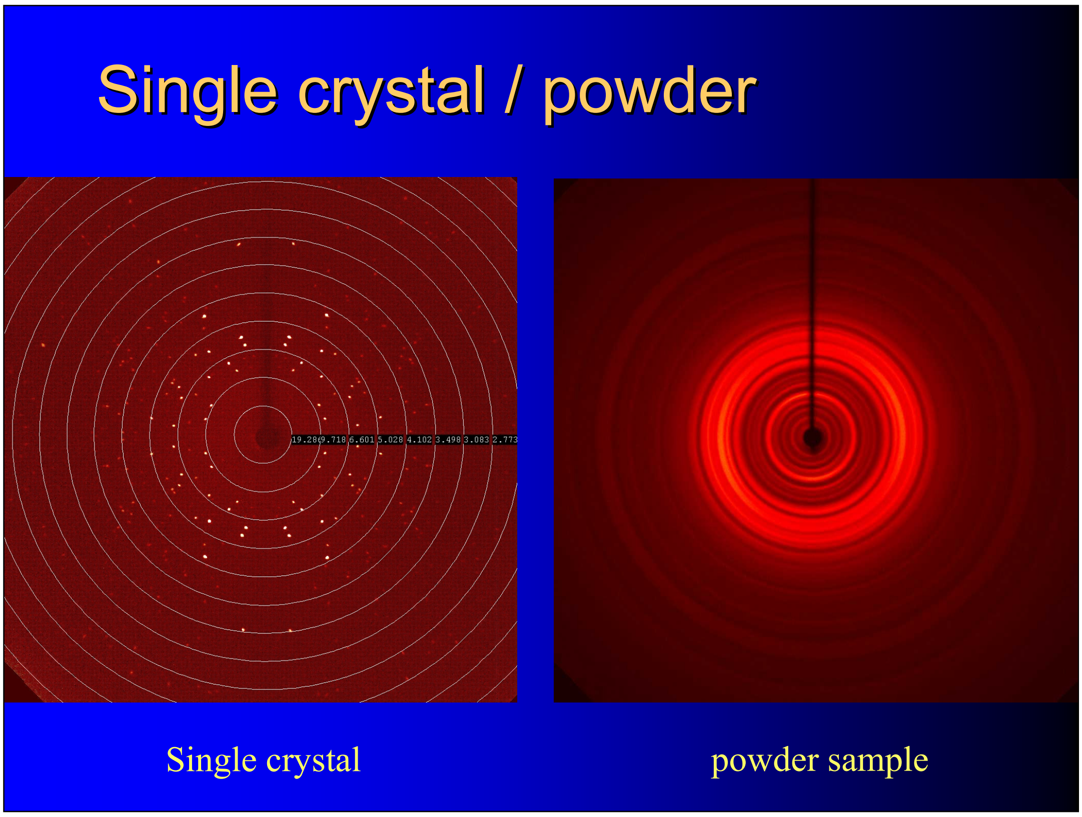
Lattice: h max 3, k max 3, l max 3

Parameters: Omega 77 °, Chi 52 °, Phi -109 °, Lambda 0.72 Å, Precession 0 °, u v w 0 1 0

Animation: ☐ 0 ° - 360 °, Speed, Angle 0 °, ☐ Mask

Screen: Size 10 x 10 cm, Distance 4 cm, ● Flat ○ Cylindric, ☑ Persistant

For random orientation of multiple crystals the 3D diffraction rec
to a 1D powder diffraction record. On 4 circle diffractometer we will see on the detector circles, not separated points.



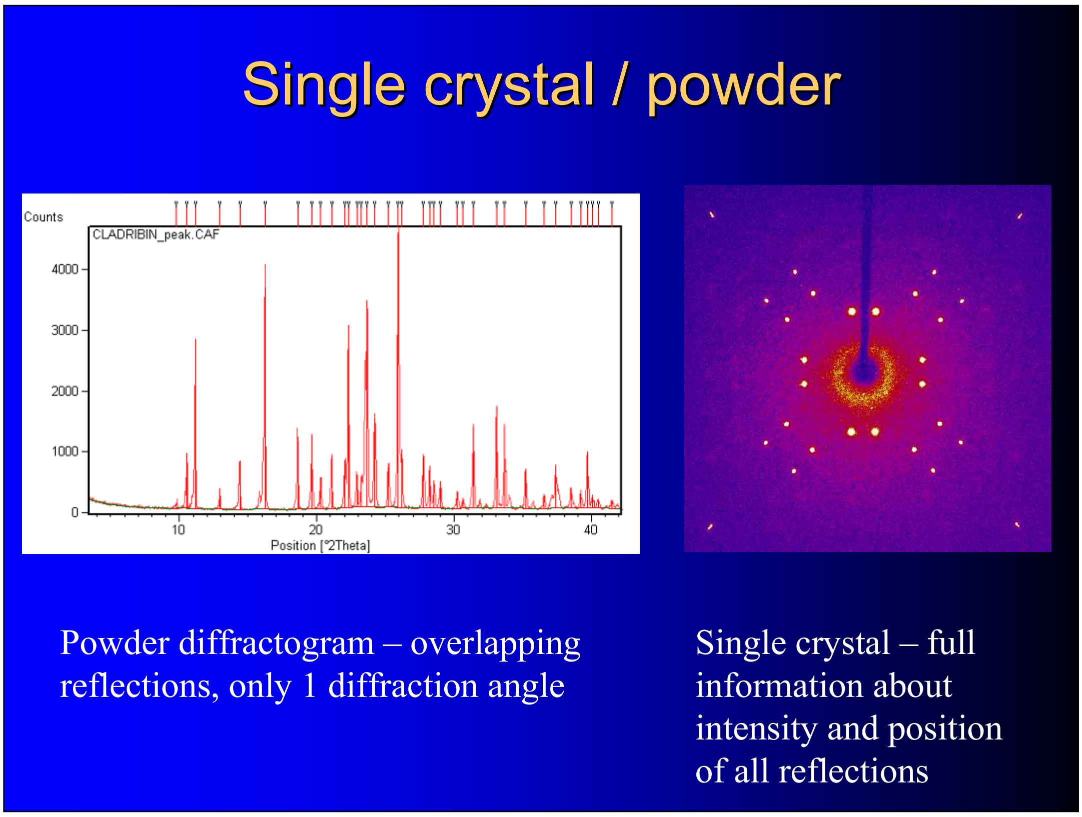
Single crystal / powder

Single crystal

powder sample

The images from area detector illustrate the difference between si
powder sample.

BY SA



Single crystal / powder

Powder diffractogram – overlapping reflections, only 1 diffraction angle

Single crystal – full information about intensity and position of all reflections

The powder data can be described as 1D record – intensity depen

diffraction angle 2θ.

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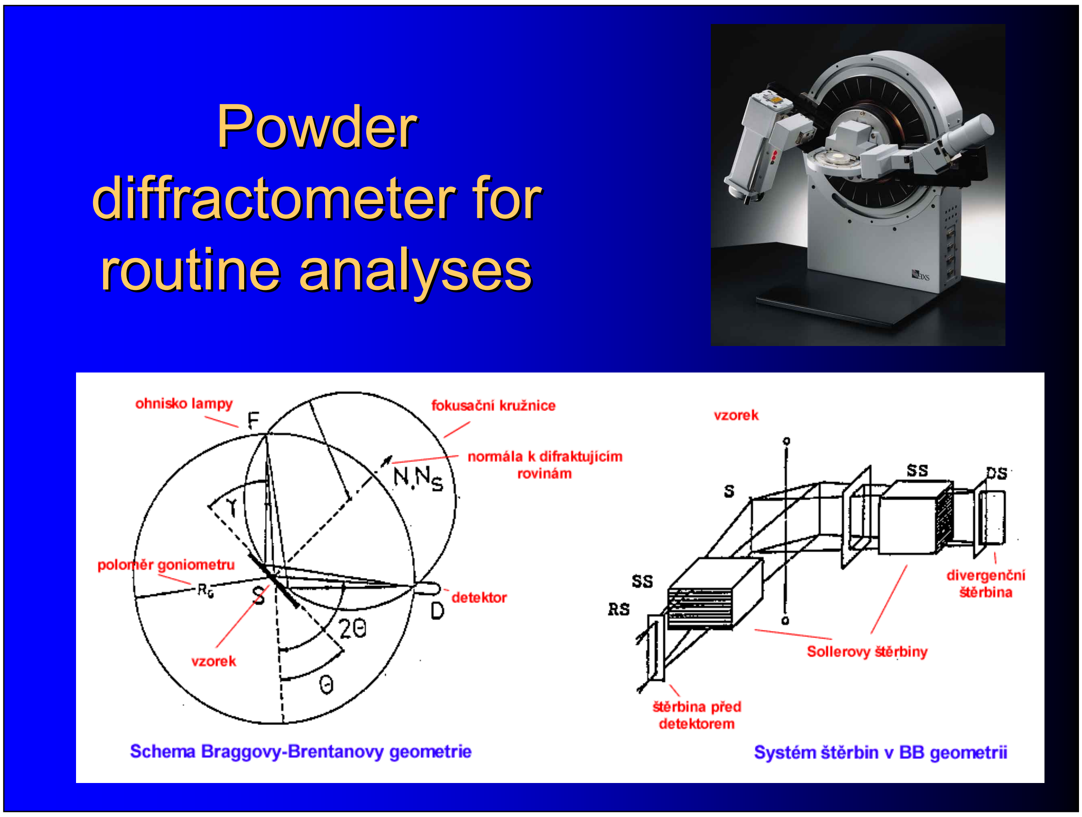

Powder diffractometer for routine analyses

Schema Braggovy-Brentanovy geometrie

Systém štěrbin v BB geometrii

For routine phase analyses we use powder diffractometer with bra semi focusing geometry.

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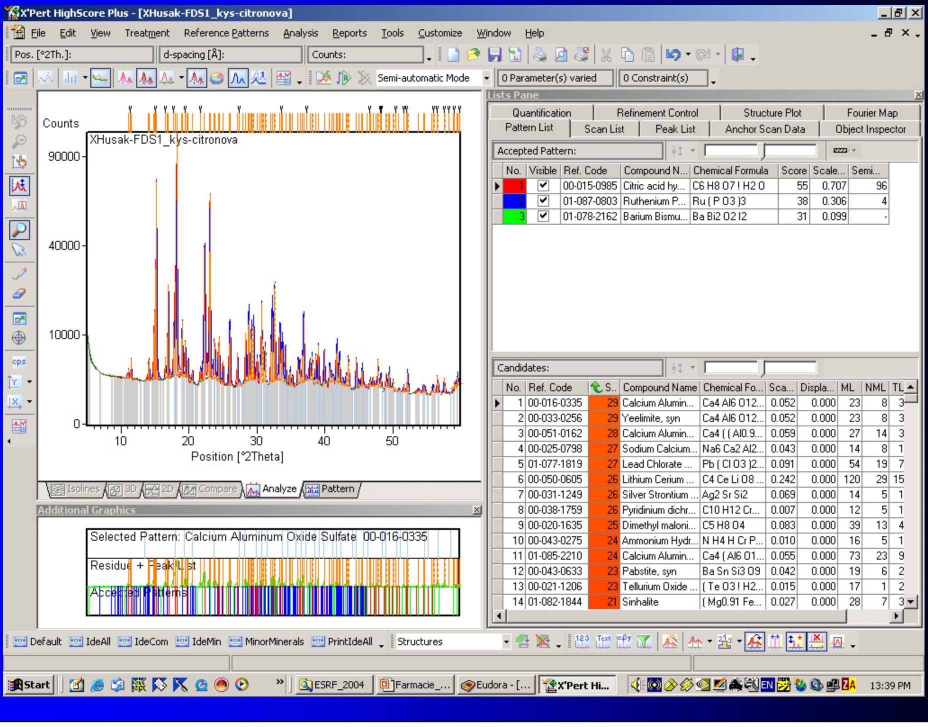
Phase identification



Accepted Pattern:

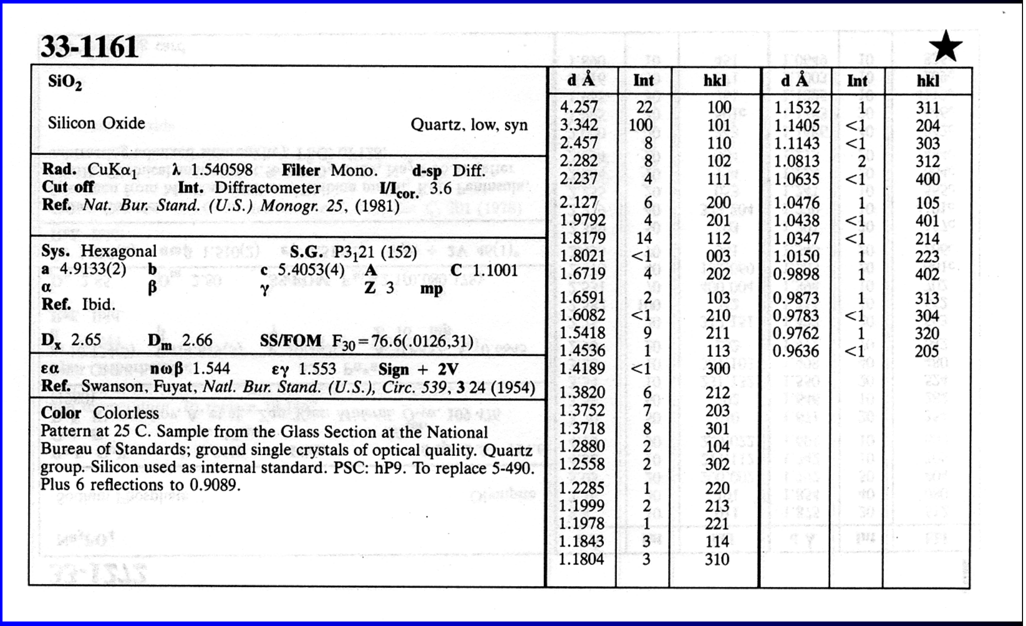
No.	Visible	Ref. Code	Compound N...	Chemical Formula	Score	Scale...	Semi...
1	☑	00-015-0985	Citric acid hy...	C6 H8 O7 ! H2 O	55	0.707	96
2	☑	01-087-0803	Ruthenium P...	Ru (P O3)3	38	0.306	4
3	☑	01-078-2162	Barium Bismu...	Ba Bi2 O2 I2	31	0.099	-

Candidates:

No.	Ref. Code	S..	Compound Name	Chemical Fo...	Sca...	Displa...	ML	NML	TL
1	00-016-0335	29	Calcium Alumin...	Ca4 Al6 O12...	0.052	0.000	23	8	3
2	00-033-0256	29	Yeelimite, syn	Ca4 Al6 O12...	0.052	0.000	23	8	3
3	00-051-0162	28	Calcium Alumin...	Ca4 ((Al0.9...	0.059	0.000	27	14	3
4	00-025-0798	27	Sodium Calcium...	Na6 Ca2 Al2...	0.043	0.000	14	8	1
5	01-077-1819	27	Lead Chlorate ...	Pb (Cl O3)2...	0.091	0.000	54	19	7
6	00-050-0605	26	Lithium Cerium ...	C4 Ce Li O8 ...	0.242	0.000	120	29	15
7	00-031-1249	26	Silver Strontium ...	Ag2 Sr Si2	0.069	0.000	14	5	1
8	00-038-1759	26	Pyridinium dichr...	C10 H12 Cr...	0.007	0.000	12	5	1
9	00-020-1635	25	Dimethyl maloni...	C5 H8 O4	0.083	0.000	39	13	4
10	00-043-0275	24	Ammonium Hydr...	N H4 H Cr P...	0.010	0.000	16	5	1
11	01-085-2210	24	Calcium Alumin...	Ca4 (Al6 O1...	0.055	0.000	73	23	9
12	00-043-0633	23	Pabstite, syn	Ba Sn Si3 O9	0.042	0.000	19	6	2
13	00-021-1206	23	Tellurium Oxide ...	(Te O3 ! H2...	0.015	0.000	17	1	2
14	01-082-1844	21	Sinhalite	(Mg0.91 Fe...	0.027	0.000	28	7	3

The prime use of powder data is phase identification. The positions and intensities of reflections can be automatically compared to a database of diffraction record and present phases can be identified. The image shows a screenshot from commercial High Score Plus software (PanAnalytical) during phase analysis evaluation.

PDF – record



33-1161 ★

SiO_2

Silicon Oxide Quartz, low, syn

Rad. $CuK\alpha_1$ **λ** 1.540598 **Filter** Mono. **d-sp** Diff.
Cut off **Int.** Diffractometer **$I/I_{cor.}$** 3.6
Ref. *Nat. Bur. Stand. (U.S.) Monogr. 25*, (1981)

Sys. Hexagonal **S.G.** $P3_121$ (152)
a 4.9133(2) **b** **c** 5.4053(4) **A** **C** 1.1001
α **β** **γ** **Z** 3 **mp**
Ref. Ibid.

D_x 2.65 **D_m** 2.66 **SS/FOM** $F_{30}=76.6(.0126,31)$

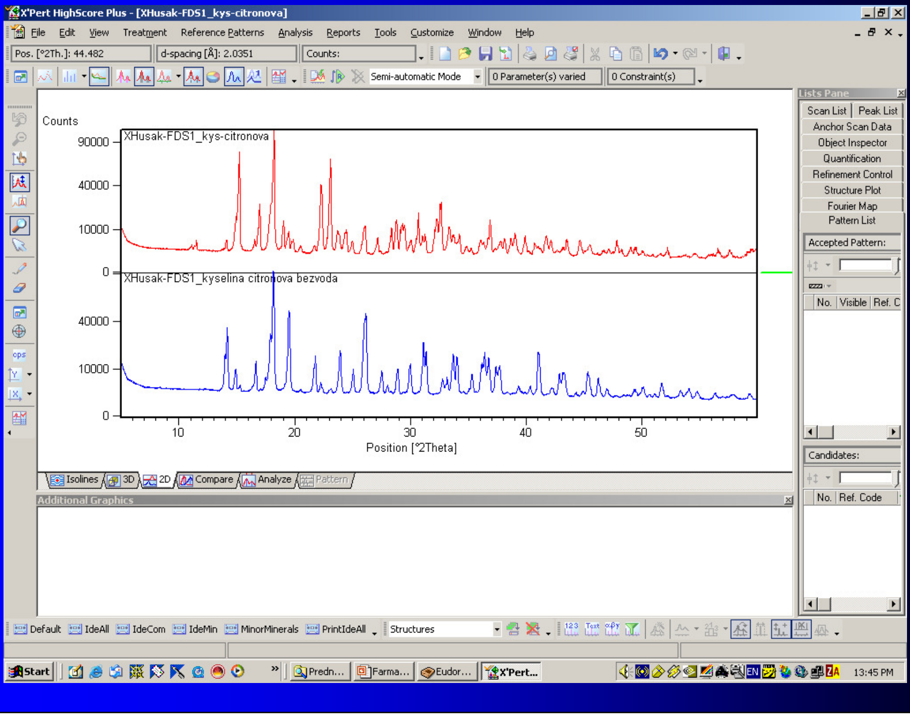
εα **nωβ** 1.544 **εγ** 1.553 **Sign** + **2V**
Ref. Swanson, Fuyat, *Natl. Bur. Stand. (U.S.), Circ. 539*, **3** 24 (1954)

Color Colorless
Pattern at 25 C. Sample from the Glass Section at the National Bureau of Standards; ground single crystals of optical quality. Quartz group. Silicon used as internal standard. PSC: hP9. To replace 5-490. Plus 6 reflections to 0.9089.

d Å	Int	hkl	d Å	Int	hkl
4.257	22	100	1.1532	1	311
3.342	100	101	1.1405	<1	204
2.457	8	110	1.1143	<1	303
2.282	8	102	1.0813	2	312
2.237	4	111	1.0635	<1	400
2.127	6	200	1.0476	1	105
1.9792	4	201	1.0438	<1	401
1.8179	14	112	1.0347	<1	214
1.8021	<1	003	1.0150	1	223
1.6719	4	202	0.9898	1	402
1.6591	2	103	0.9873	1	313
1.6082	<1	210	0.9783	<1	304
1.5418	9	211	0.9762	1	320
1.4536	1	113	0.9636	<1	205
1.4189	<1	300			
1.3820	6	212			
1.3752	7	203			
1.3718	8	301			
1.2880	2	104			
1.2558	2	302			
1.2285	1	220			
1.1999	2	213			
1.1978	1	221			
1.1843	3	114			
1.1804	3	310			

The information about powder diffraction data are stored in PDF (Powder Diffraction Files). The data contains compound identification, reflection position in d-values, relative reflection intensity. Lattice parameters, space group and reference to structure solution are listed if known.

Quantitative phase analysis



Pos. [°2Th.]: 44.482

d-spacing [Å]: 2.0351

Counts:

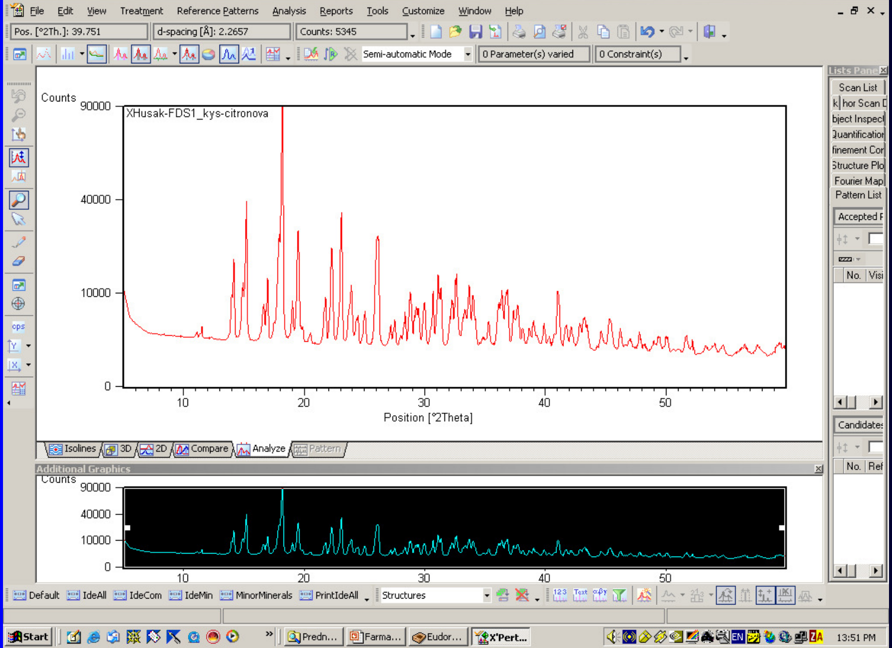
0 Parameter(s) varied

0 Constraint(s)

A mixture of 2 phases gives a record which is a simple summatio
individual records of both phases.

cc BY SA

Quantitative phase analysis



X'Pert HighScore Plus - [XHusak-FDS1_kys-citronova]

Pos. [°2Th.]: 39.751

d-spacing [Å]: 2.2657

Counts: 5345

Semi-automatic Mode

0 Parameter(s) varied

0 Constraint(s)

The image shows a record of 2 different citric acid phases mixed

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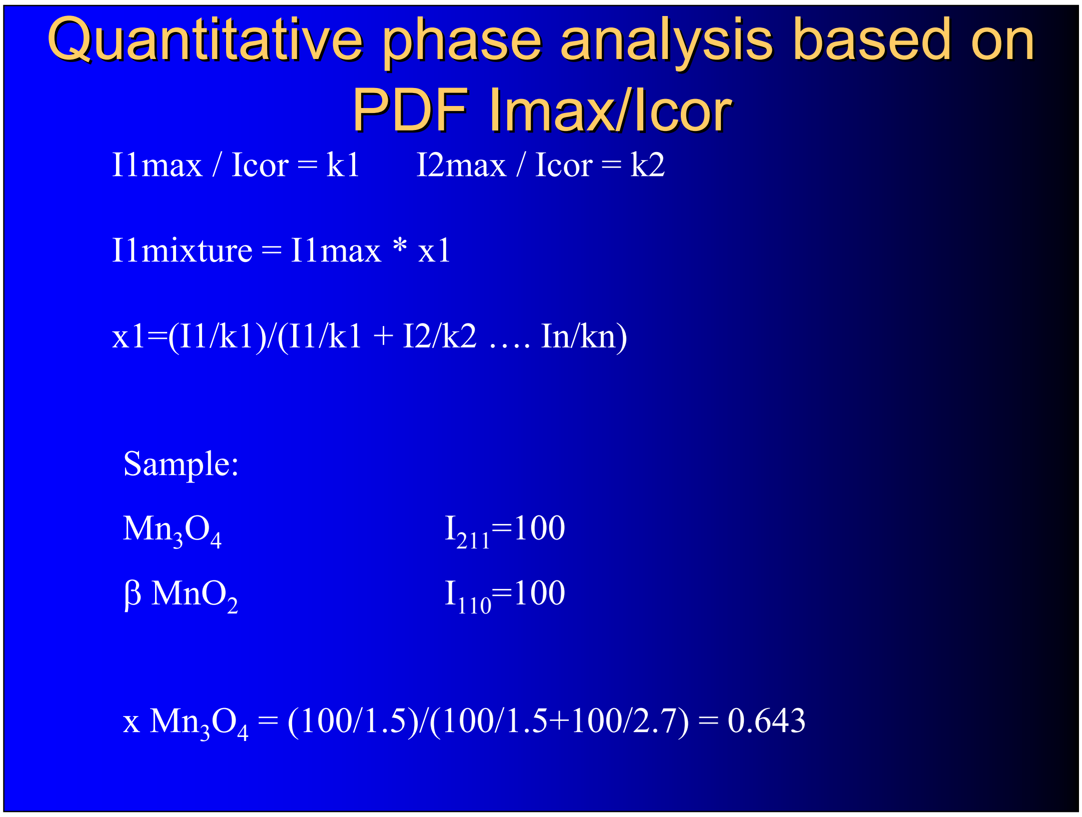

Quantitative phase analysis based on PDF Imax/Icor

I1max / Icor = k1 I2max / Icor = k2

I1mixture = I1max * x1

x1=(I1/k1)/(I1/k1 + I2/k2 …. In/kn)

Sample:

Mn_3O_4	$I_{211}=100$
β MnO_2	$I_{110}=100$

x Mn_3O_4 = (100/1.5)/(100/1.5+100/2.7) = 0.643

For quantitative phase analysis we must at first identify the phase database we can find the so-called corundum number – intensity ratio of maximal intensity line of the phase and corundum intensity in 50:50 mixture. The corundum number can be utilized for quantitative phase analysis – equations on the slide.

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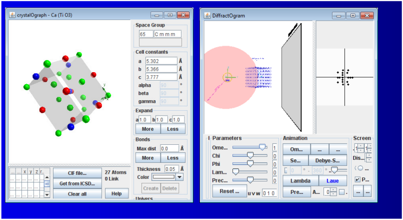
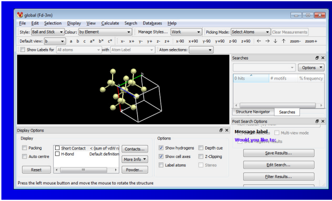
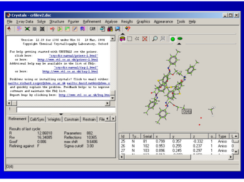
Free software used in the lectures

Name	Screenshot	WWW link
e-Crystallography course (Escher, diffractOgram, crystalOgraph, Charge flipping)		http://escher.epfl.ch/eCrystallography/
CSD Mercury		http://www.ccdc.cam.ac.uk/solutions/csd-system/components/mercury/
CRYSTALS		http://www.xtl.ox.ac.uk/crystals.1.html

List of software used during lectures 1-3 with links to the source.

Chemistry and Physics of Solids – Lecture 4

Introduction to crystal chemistry

The published materials are intended for students of the University of Chemistry and Technology, Prague as a study material. Some text and image data contained therein are taken from public sources. In the case of insufficient quotations, the author's intention was not to intentionally infringe the possible author(s) rights to the original work.

If you have any reservations, please contact the author(s) of the specific teaching material in order to remedy the situation.

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YOUTH AND SPORTS

Crystal chemistry

What does it do?

Lecture 4a

“From all of the physical properties of substances, no one is as constant and remarkable in all respects as the same chemical compounds always accept one and the same geometric form with unusual preci

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Whewell William - History of the inductive sciences, 1869

Crystal chemistry

What does it do?

- Crystal chemistry is essentially inorganic chemistry of crystalline solids. It is the science of crystal structures and their association with the principal of the matter.

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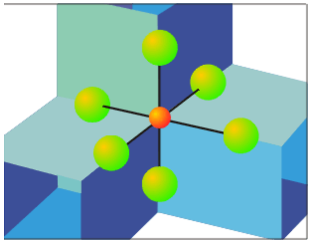
How ???

- It studies structures of crystals - distribution of atoms and their chemical bond in a 3D space.

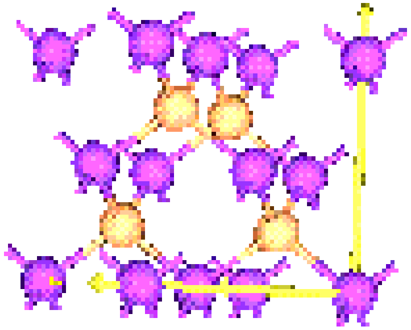
Why ???

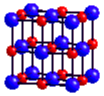
- It tries to influence the dependence of the physical and chemical properties of crystalline substances on their composition.

What to do with that ???



Crystal chemistry





After today's 1st and next 2nd lectures you will know how to:

- Determine the coordinate numbers n-size ratios

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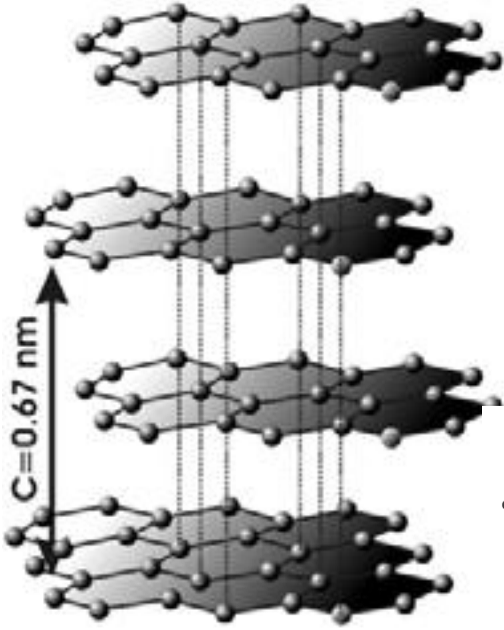
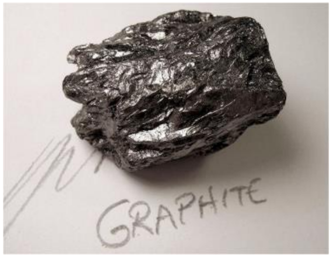
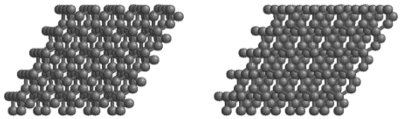
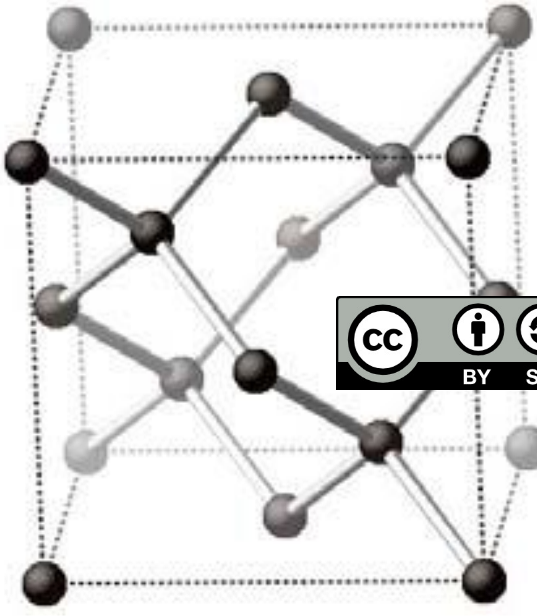
- Derive the structures of ionic, some covalent and most metal compounds from the concept of close packing of atoms or ions
- You will understand the structures of silicates and
- know what solid solutions mean

Crystal chemistry









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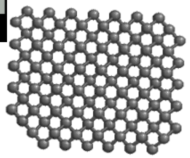
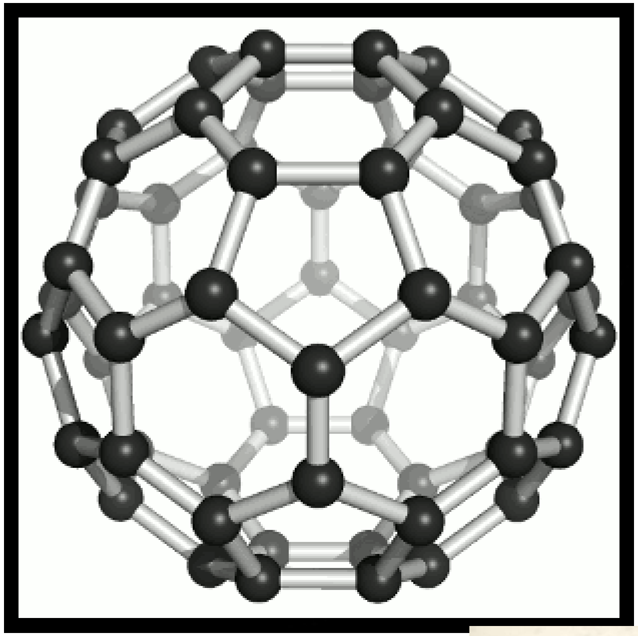
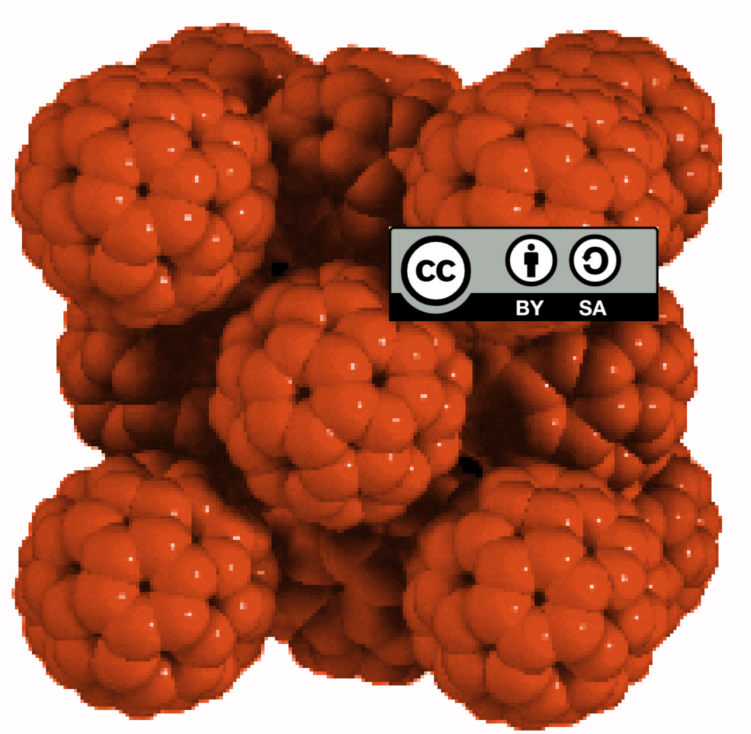


It studies the relationships between the inner structure of the crystals and their physico-chemical properties.
It studies the arrangement of molecules, atoms or ions in crystals and the existing forces between them.

Crystal chemistry



Fullerene



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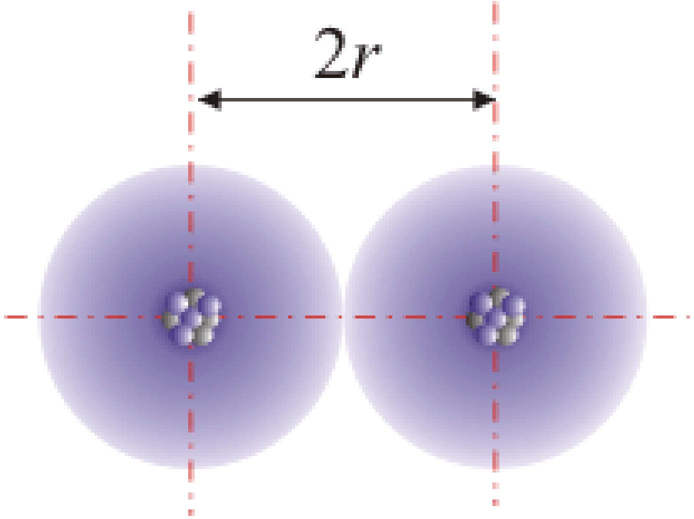
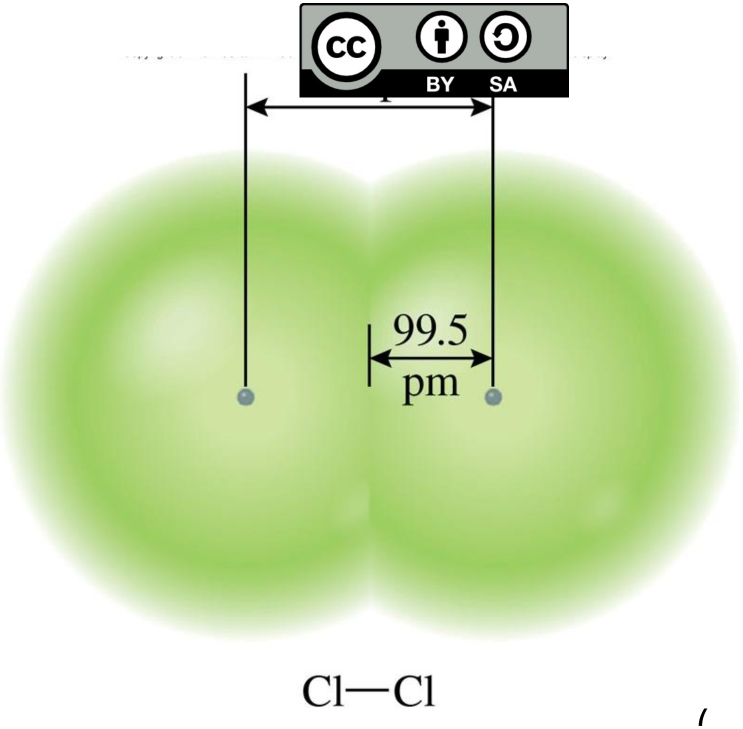
Fullerite

Atomic radius in covalent, metal, ion, and van der Waals bonds

van der Waals radius characterizes the minimum contacts of the atoms, belonging to different molecules. It is counted as half the smallest distance between atoms with van der Waals bond.

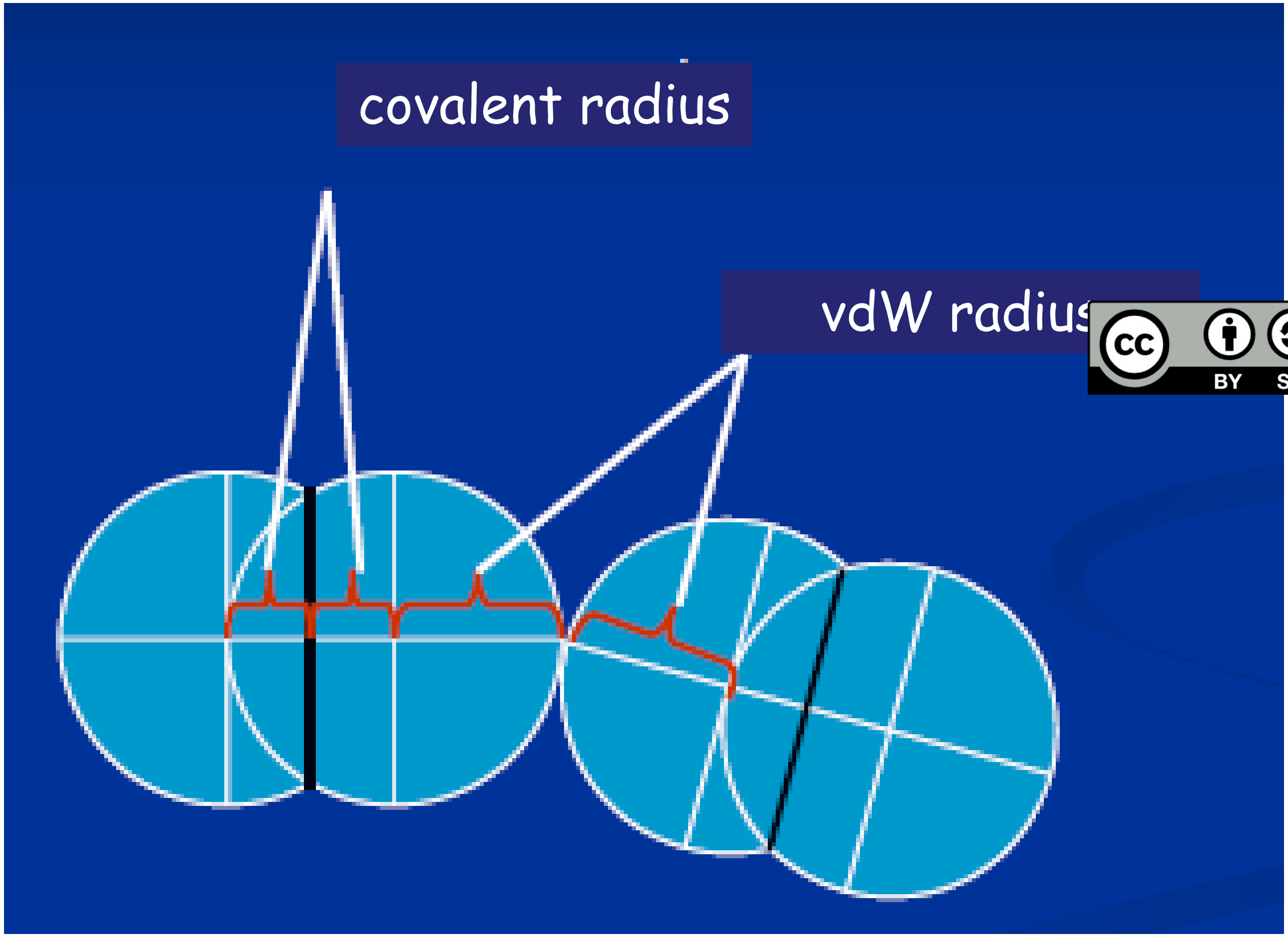


van der Waals radius



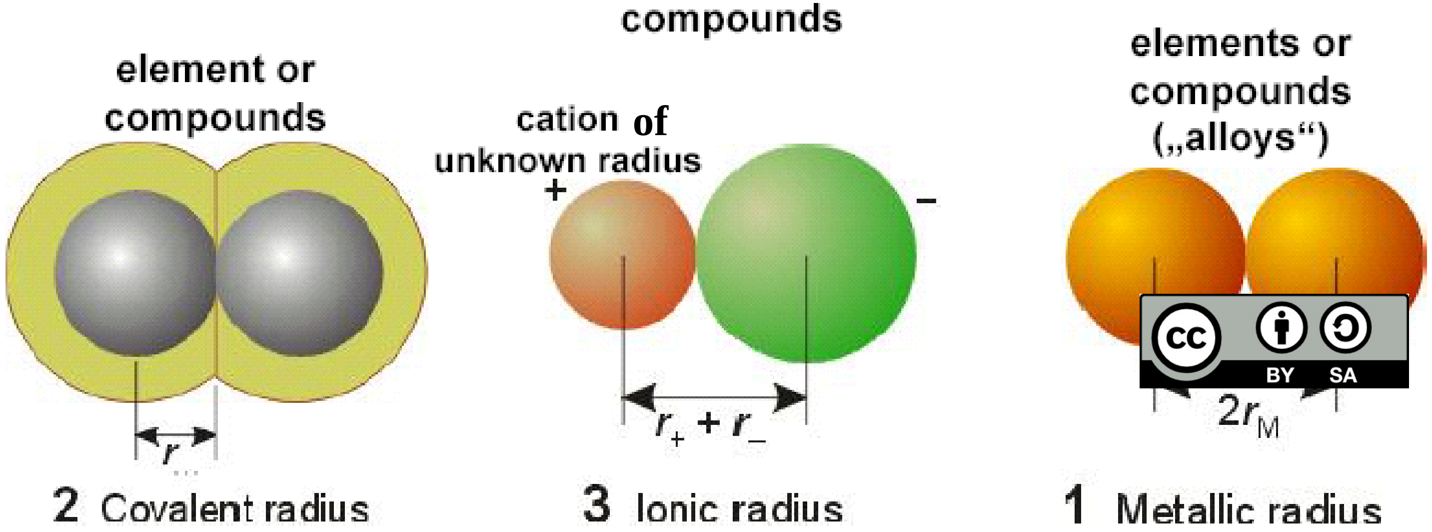
covalent radius

Atomic radius in covalent, metal, ion, and van der Waals bonds



cc BY SA

The type of chemical bond can be derived from the radius



element or compounds

2 Covalent radius

=

d/2 of single bond
in molecule

compounds

cation of unknown radius

3 Ionic radius

=

d – r(F, O…)
problem: reference!

elements or compounds („alloys“)

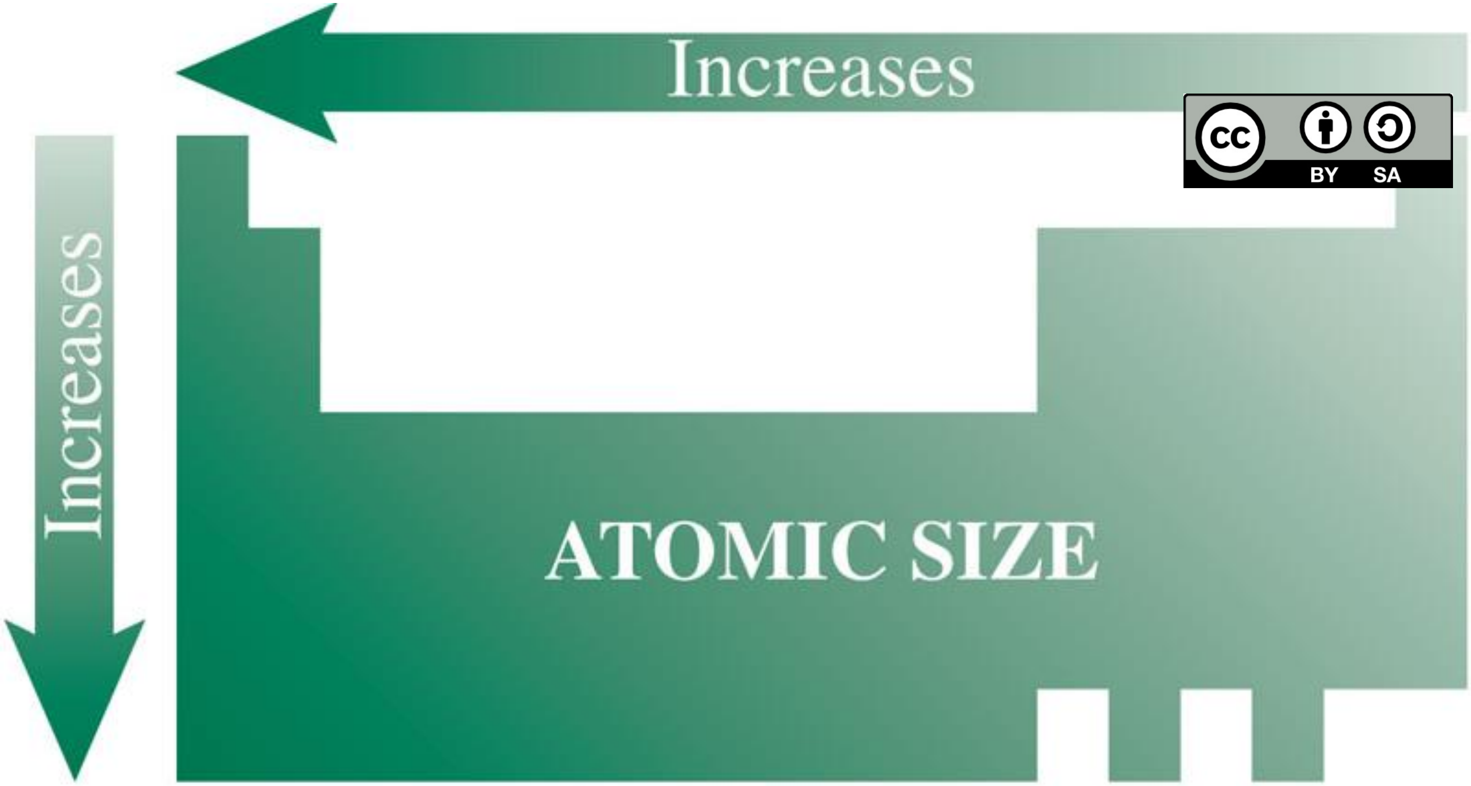
1 Metallic radius

=

d/2 in metal

Trends in atomic sizes

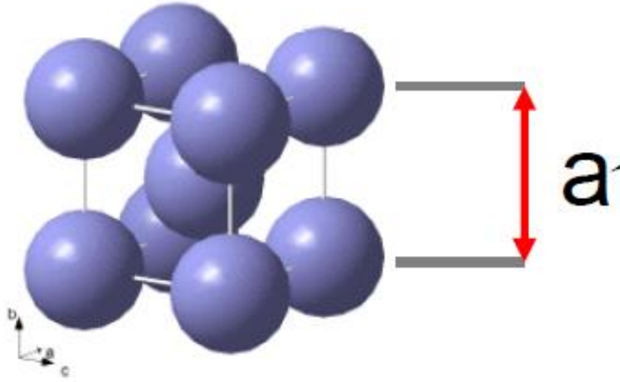
- **The atomic sizes (radius) increase downwards in groups and from right to left in periods.**



CC BY SA

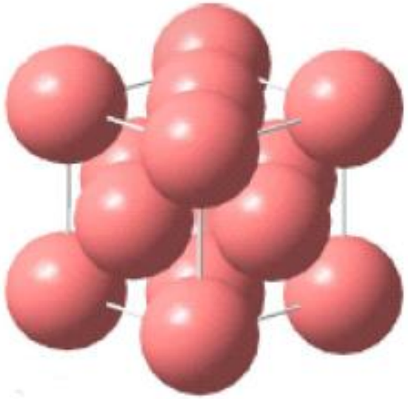
How to determine the radius of an atom in metals?

The edge of the elemental cell is experimentally determined by X-ray diffraction analysis



$$4r = a\sqrt{3}$$

cc BY SA



$$4r = a\sqrt{2}$$

The first estimates of atomic radius were performed by W. Bragg (1920)

Atomic radius derived by crystal chemistry

Although there are different types of chemical bonds and structures, with one type of bond and its order, the dAB distance for a given pair of atoms is maintained at an accuracy of the order of 0.05-0.1 Å. This allows the approximate constant "dimensions" – crystal chemical radii to be assigned to atoms for the given or other type of bond in the first approximation.

BY SA

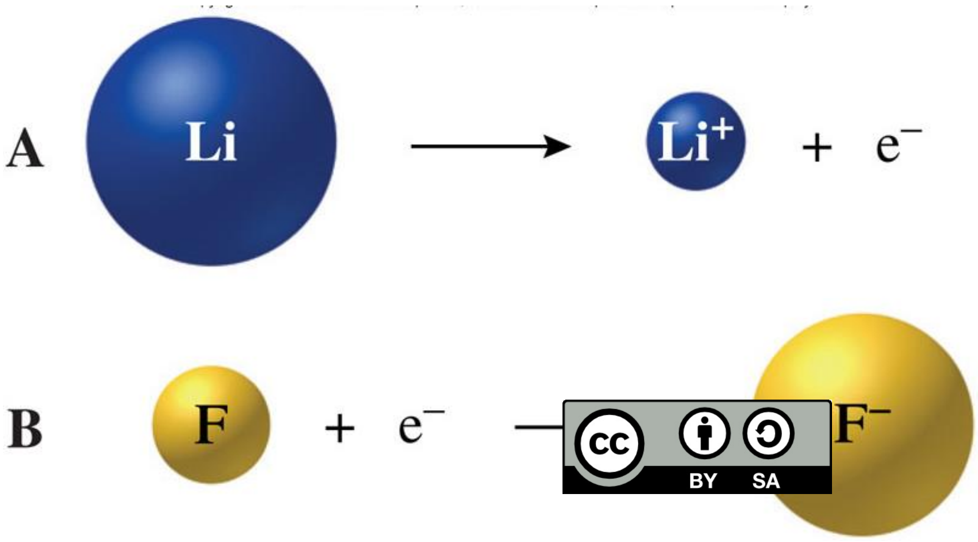
The main characteristic of crystallochemical radii is the reproduction at summation of chemical bond lengths (radius admitivity).

In accordance with the basic types of chemical bonds, four systems differ
crystallochemical radii:
Ionic, covalent, metal and van der Waals

Size of ions

- size of ions

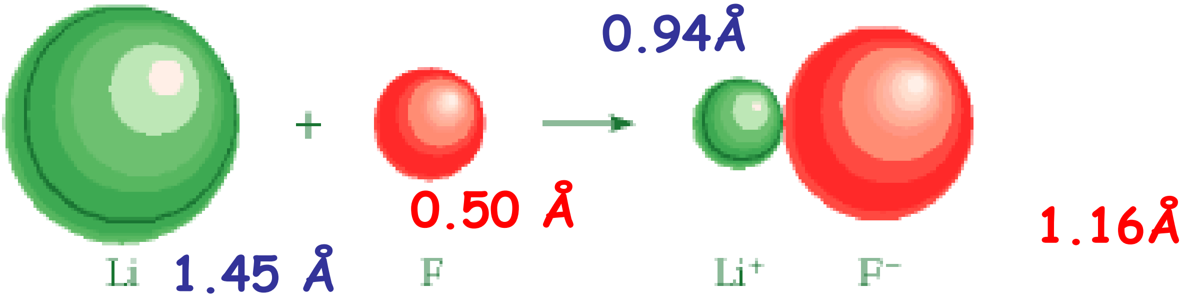
The radius of the atom varies with ion formation



BY SA

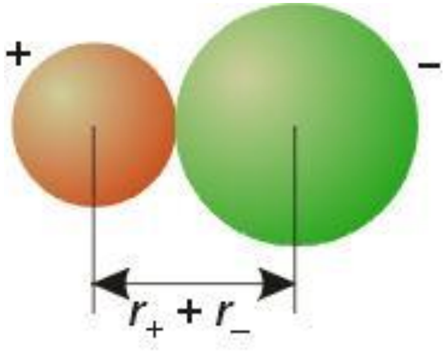
$Li\ (1s^2 2s^1) \rightarrow Li^+\ (1s^2)$

$F\ 1s^2 2s^2 2p^5 \rightarrow F^-\ (1s^2 2s^2 2p^6)$



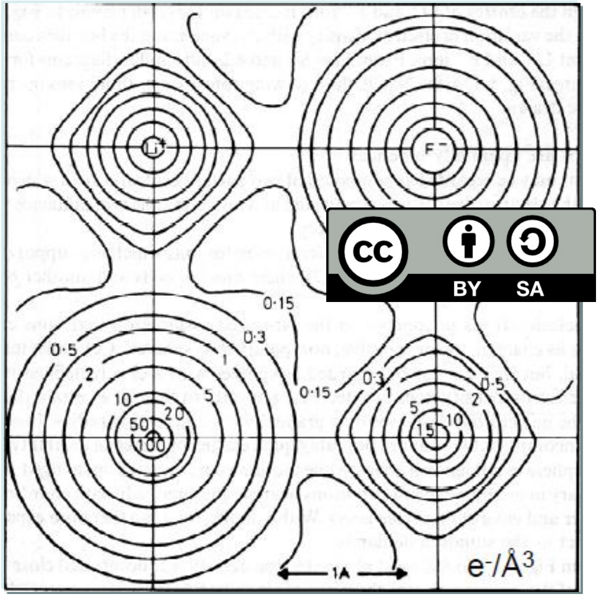
Determination of ionic radii is not clear

ionic radius = d – r(F, O…)



3 Ionic radius

The most important method of the structural analysis: X-ray diffraction



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Electron density along the Li-F axis

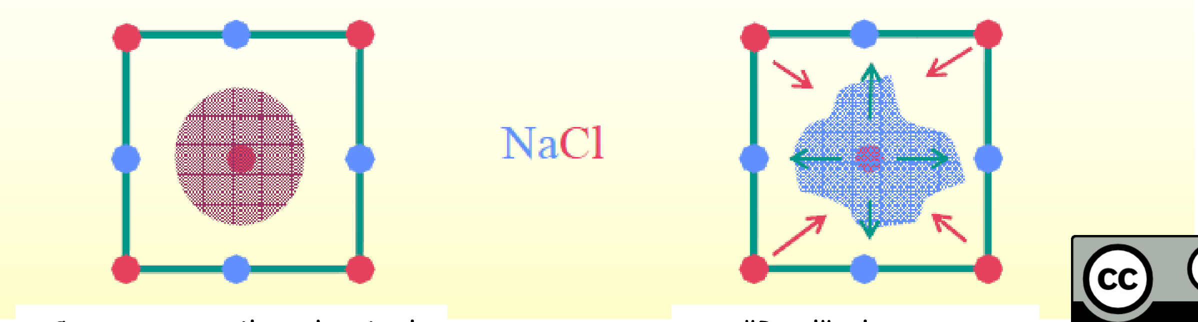
L. Pauling:

- The radius of one ion is fixed - usually an oxygen anion (r (O2-) = 140 pm)
- This value was used to build a consistent value set radii of other ions.

Everything in the world is relative

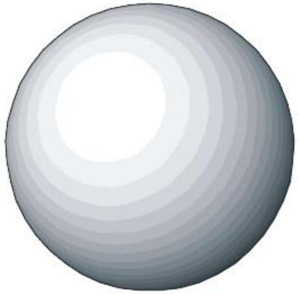
The term radius of atom will be understood as follows:

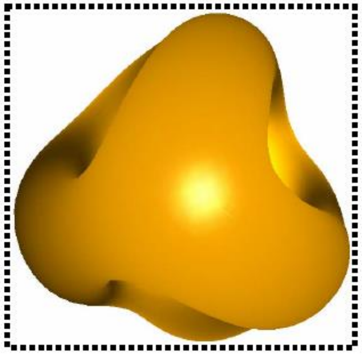
The distribution of electron density is in fact continuous
So what is the "radius"? This is an agreed (conditional) radius



Contemporarily spherical
Electron cloud Cl-

"Real" electron
Cloud Cl-





of electron ion crystals is n covalent or metallic crystals, in particular due to:

1) the presence of a minimum energy density of the electron density along the bond;

2) characteristic shifting of the density of the overlap towards the electronegative atom.

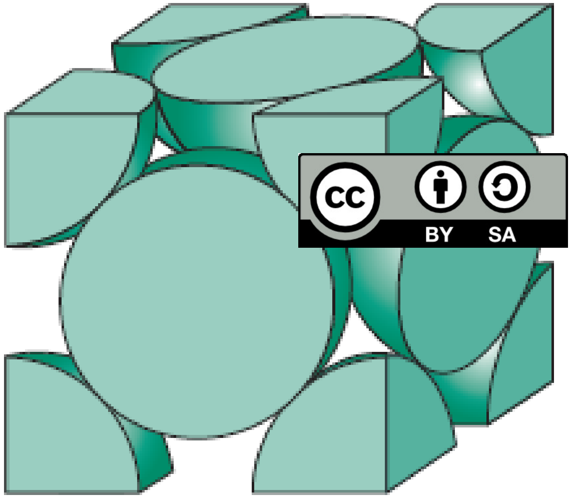
Unfortunately, atoms in the crystal do not look like this...

….. but they look like this

Crystal structure

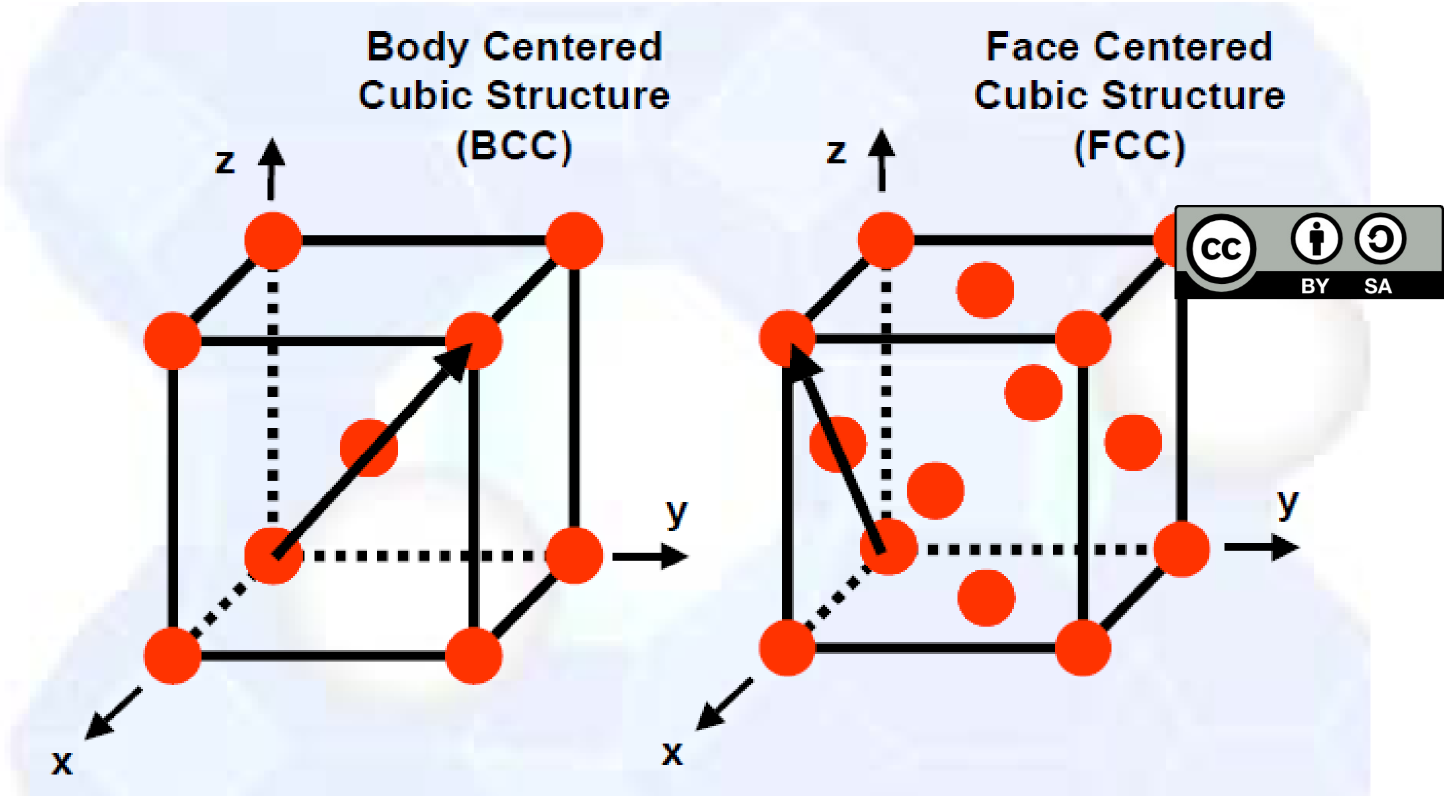
shows how atoms, ions, or molecules are spatially arranged

In describing crystalline structures, we consider atoms as solid (incompressible) spheres having defined diameters; the spheres representing the nearest atoms touch each other



The grid represents a three-dimensional arrangement of points that may not coincide with atomic positions

In which directions of the elemental cells BCC and FCC the atoms touch each other?



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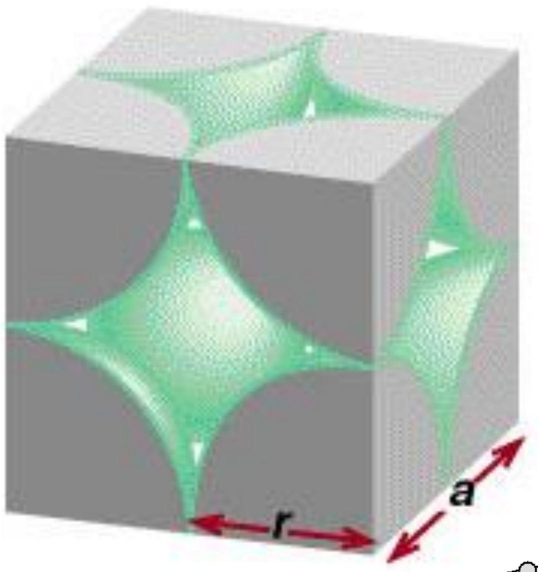
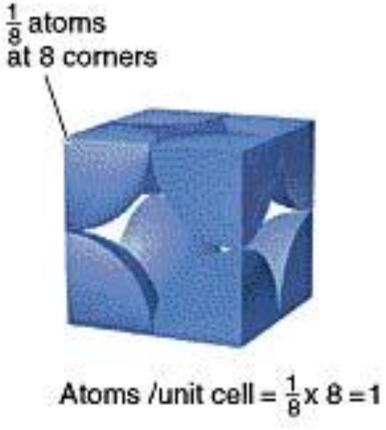
1) Cubic primitive unit cell

8 atoms are at the corners - the atoms touch along the edges, but not along the diagonals. Coordinate number = 6. 4 in the layer, 1 above and 1 under
1 atom / elemental cell (1/8 x 8 atoms)



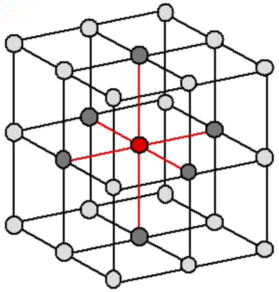
pcc

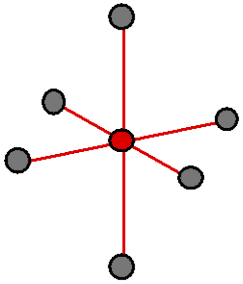
$a = 2r$



- **Rare arrangement due to low packing level. Only Po has this structure**
- **The tou tion of crushing the cube edges**

Coefficient of filling space = 54%





- **Coordinate number = 6 (Number of Nearest Neighbors)**

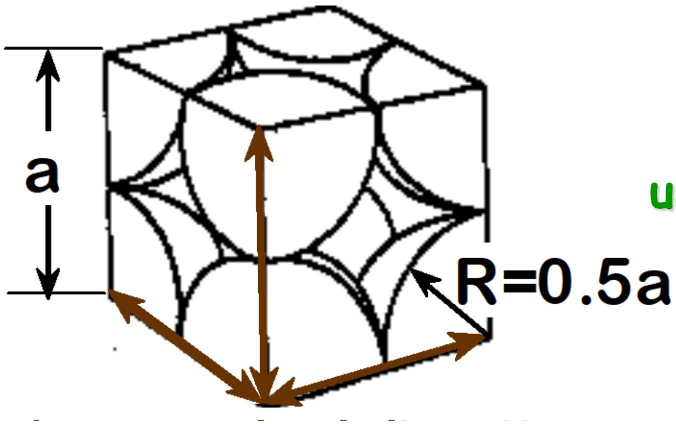
Efficiency of the arrangement

$$EU = \frac{\text{atomic volume in the unit cell*}}{\text{volume of the unit cell}}$$

* suppose rigid spheres

- EU of primitive cubic structure = 0.54

BY SA



Directions closest packing

contains 8 x 1/8 = 1

1 atom/unit cell

atoms

unit cell

Volume

Atom

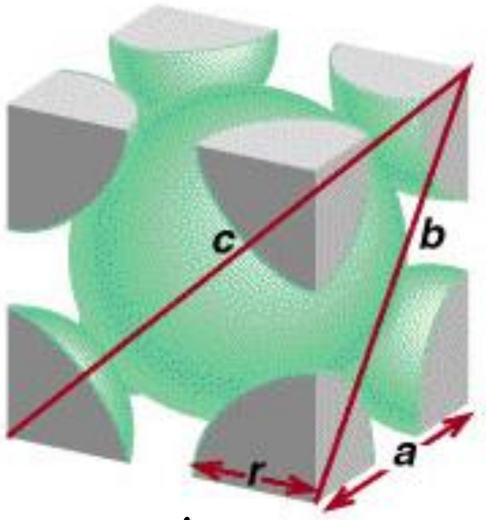
$$EU = \frac{1 \; \frac{4}{3}\pi\,(0.5a)^3}{a^3}$$

volume

unit cell

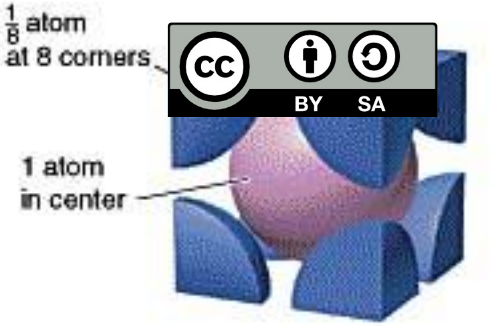
2) Cubic body-centered unit cell

8 atoms located at the corners and 1 atom at the center of the cube - the atoms at the corners touch it. Coordination number = 8 atoms above the center and 4 atoms down. Content: 2 atoms / elemental cell (1/8 x 8 atoms + 1 atom in the center)



bcc

$$
\begin{aligned}
b^2 &= a^2 + a^2 \\
c^2 &= a^2 + b^2 \\
&= 3a^2 \\
c &= \sqrt{3}a = 4r \\
a &= \frac{4r}{\sqrt{3}}
\end{aligned}
$$



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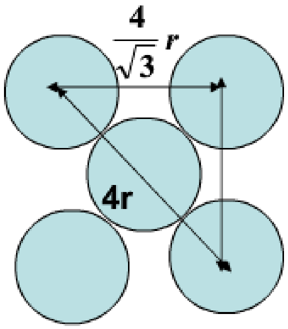
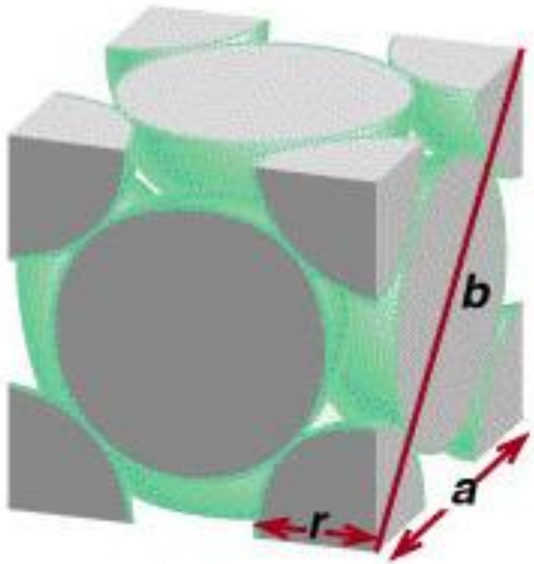
Atoms / unit cell = $(\frac{1}{8} \times 8) + 1 = 2$



Efficiency of the arrangement = 68%

3) Cubic face-centered unit cell

8 atoms are located at the corners of the cube and 6 at the center of each surface - the corner atoms touch the atom in the area not at the edges of each other. Coordination number = 12.4 atoms / elementary cell (1/8 x 8 corner atoms + ½ x 6 atoms in the area).



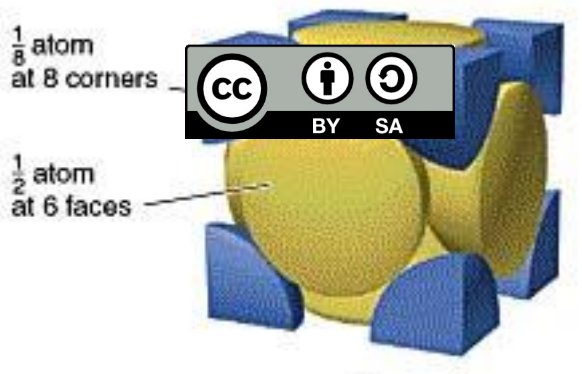
fcc

$$b = 4r$$

$$b^2 = a^2 + a^2$$

$$16r^2 = 2a^2$$

$$a = \sqrt{8}r$$



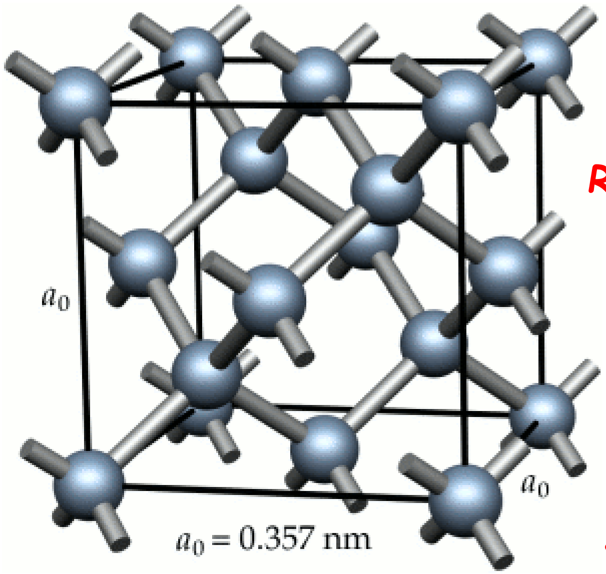
cc BY SA

Atoms / unit cell = $(\frac{1}{8} \times 8) + (\frac{1}{2} \times 6) = 4$

Structure that meets the tightest concept Arrangement with a fill rate of 74%

4) What is the density of packing in the diamond cell

8 atoms are located at the corners of the cube and 6 at the center of each area. 4 atoms are located in ¼ diagonals. Together 8 atoms / elemental cell (1/8 x 8 corner atoms + ½ x 6 atoms in areas + 4 atoms inside).



$$2r = 1/4\, d$$

length of the body diagonal

$$d = \sqrt{a^2 + 2a^2}$$

Radius of the atom in the elementa

cc BY SA

$$r = {}^1\!/_8 \text{ x} \sqrt{3a^2} = \frac{\sqrt{3}}{8}a$$

Density of packing: $\dfrac{8\text{x}\frac{4}{3}\pi r^3}{a^3}$

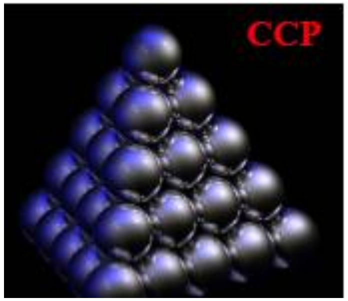
Substitution of r $\dfrac{8\text{x}\frac{4}{3}\pi\left(\frac{a\sqrt{3}}{8}\right)^3}{a^3} = \dfrac{\sqrt{3}\pi}{16}$

The packing density of the diamond structure is 34%

Packing of elements (particles)

Irregular particle shapes can also be struck, but spherical symmetry is much better.

non-periodical packing



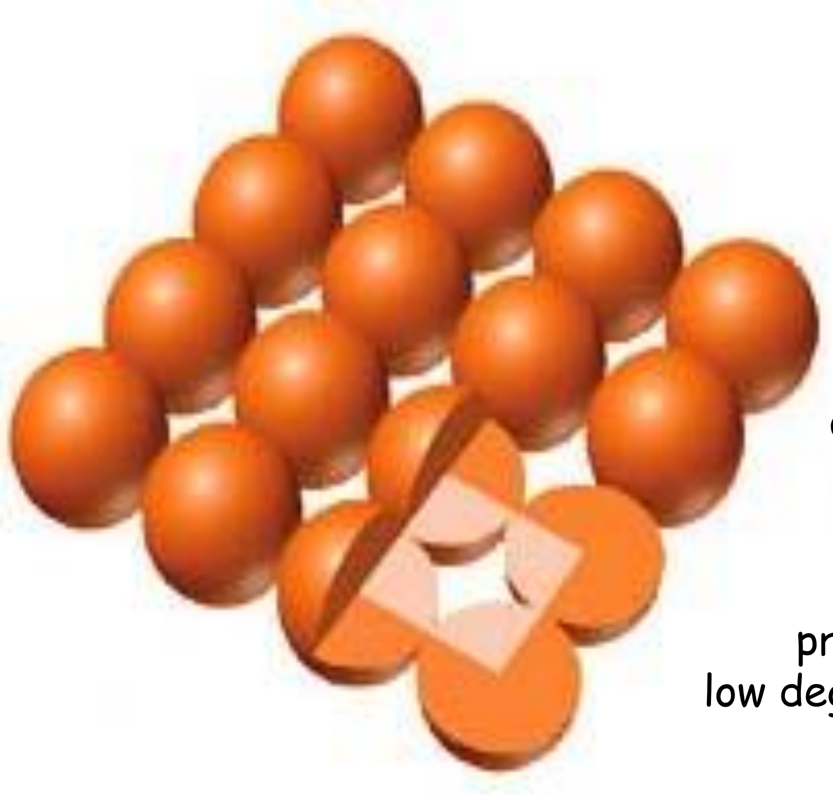
periodical packing

Kepler's presumption

«The crystals are composed of densely arranged spheres »
The assumption is very close to the truth than it would seem.

Crystal systems of close packings

Cubic close packing or cubic face centered - FCC
Prerequisite: atoms - incompressible, hard balls



The square arrangement of solid spheres is not th a close pac

cc BY SA

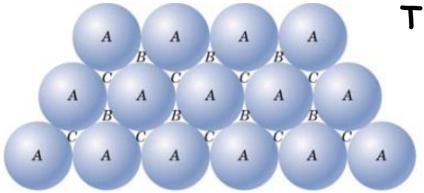
By pushing the atoms into a closer arrangement, triangular gaps occur

primitive packing
low degree of space filling

Square balls arrangement

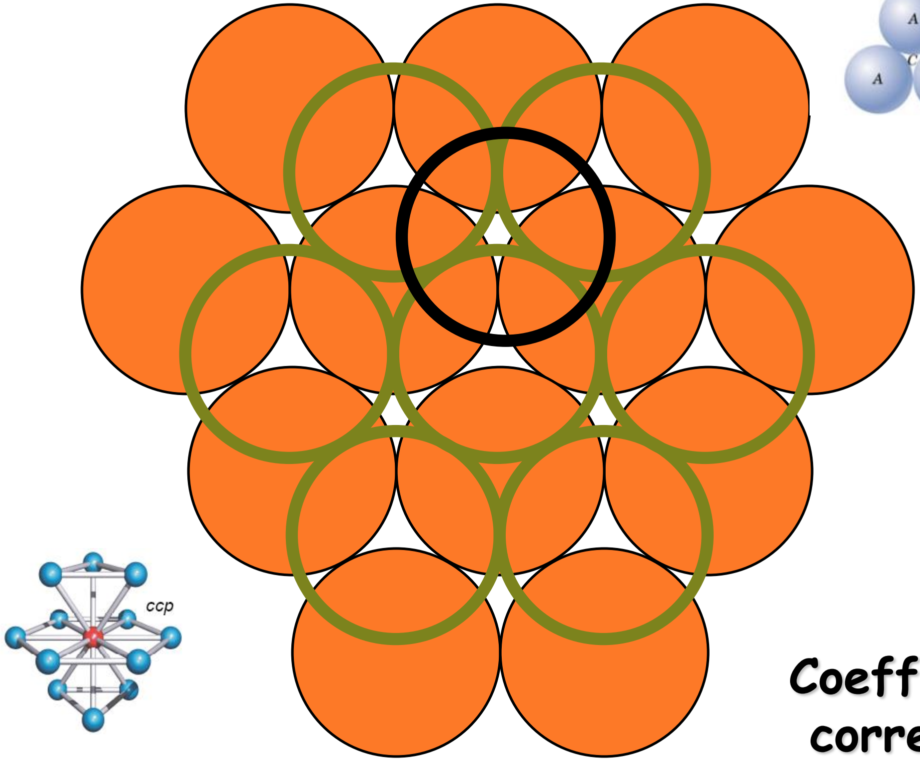
Crystal systems of close packings

Cubic close packing or cubic face centered - FCC
Strukture A1



The most effective method of packing balls of the same size - CCP
- 6 closest neighbors

Coordination number (CN): 6



put the second
triangular space

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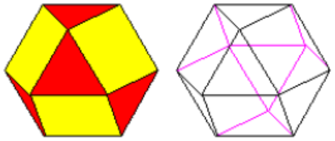
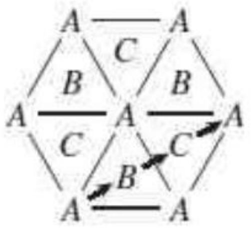
The third layer is over vacant cavities.

Coefficient of filling of the closest packing corresponds to 74%.

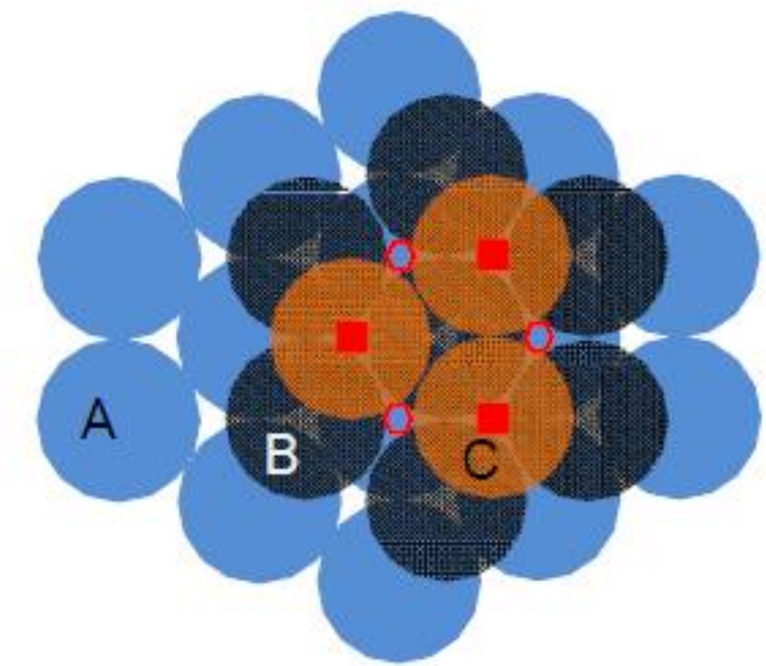


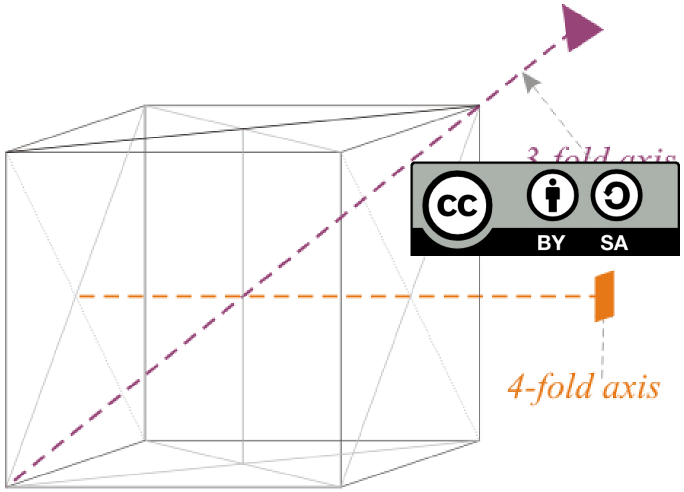
abcabc…



Crystal systems of close packings

Cubic close packing or cubic face centered - FCC
Strukture A1





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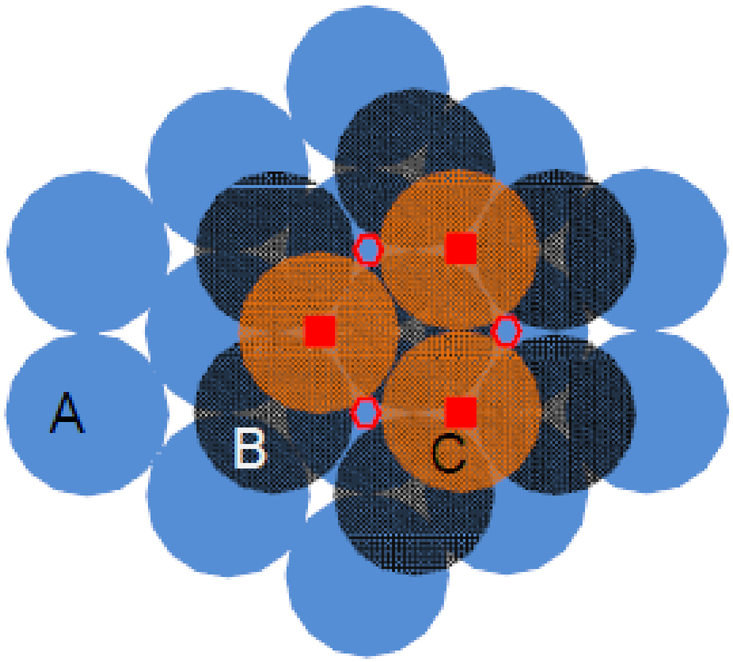
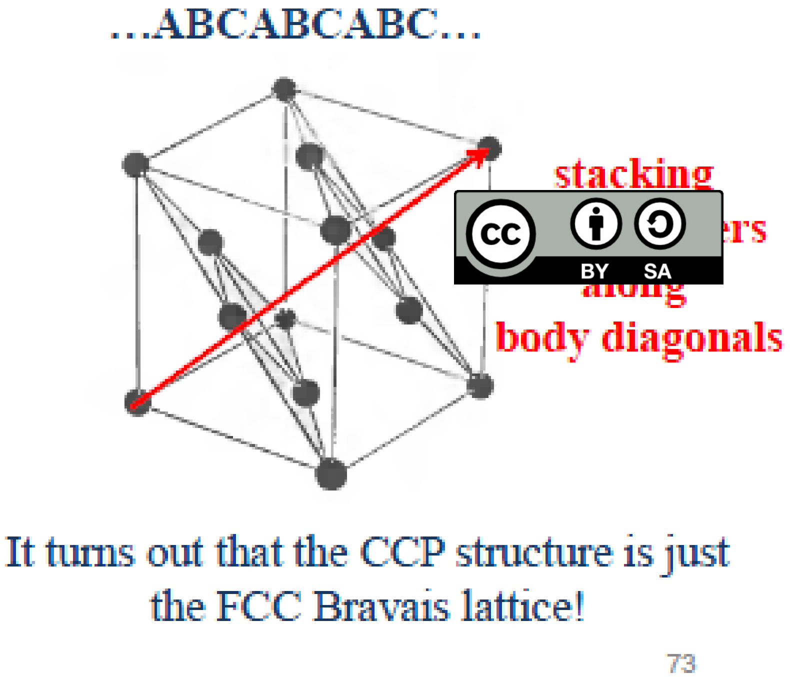
In ABCABC-type packing ... the layers have hexagonal symmetry. Packing leads to the formation of a 3-fold axis with an angle of 54.74 degrees to the original 6-fold axis, and the so-called CCP pattern

(FCC elementary cell)

Crystal systems of close packings

Cubic close packing or cubic face centered - FCC
Strukture A1



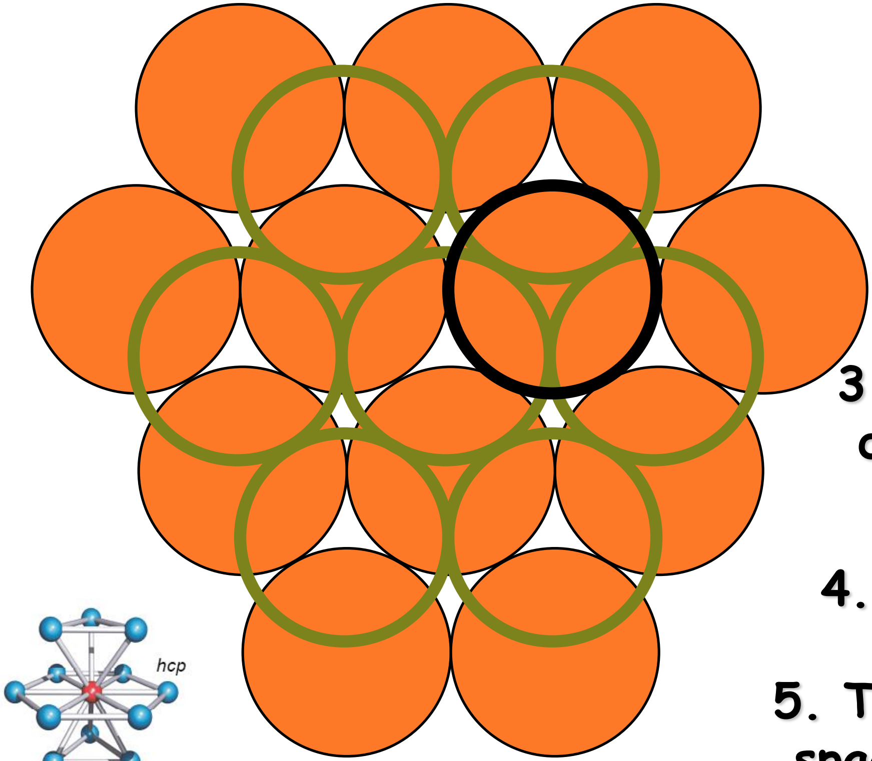


It turns out that the CCP structure is just the FCC Bravais lattice!

In ABCABC-type packing ... the layers have hexagonal symmetry. Packing leads to the formation of a 3-fold axis with an angle of 54.74 degrees to the original 6-fold axis, and the so-called CCP pattern
(FCC elementary cell)

Crystal systems of close packings

Hexagonal close packing HCP layout. Structure A3



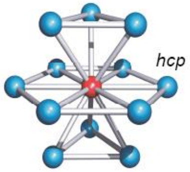
1. Press each row in the first layer in to the closest packing

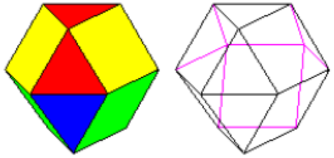
2. Place the second row into triangular spaces

3. The third layer of atoms is located directly above the first layer

4. There is a hexagonal elementary cell

5. The tighter structure has a fill space factor of 74%





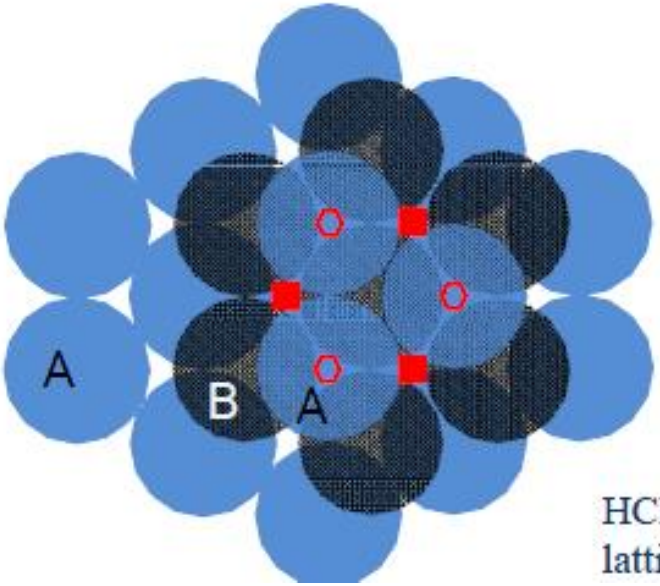
abab…

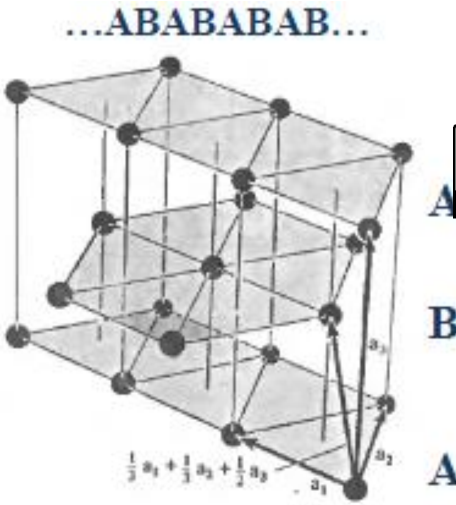
coordination number = 12

(3 above, 6 in row, 3 under)

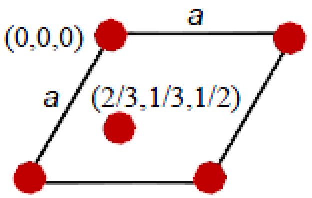
Crystal systems of close packings

Hexagonal close packing HCP layout. Structure A3





HCP is two interpenetrating simple hexagonal lattices displaced by $\mathbf{a}_1/3 + \mathbf{a}_2/3 + \mathbf{a}_3/2$



HCP Strukture in 2D

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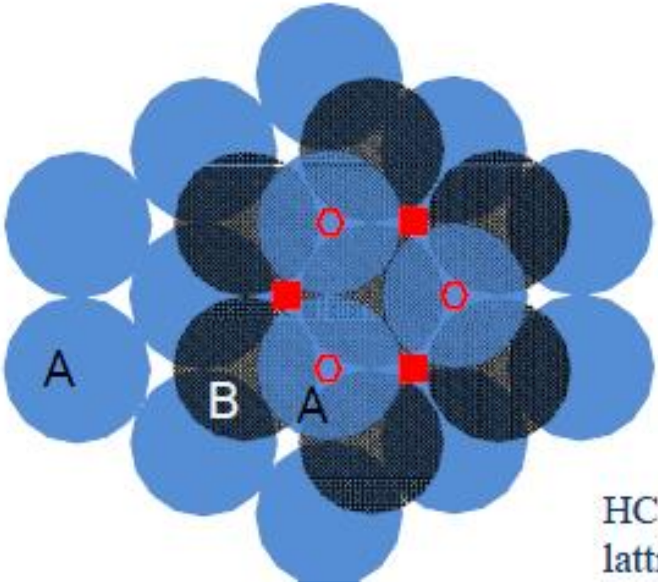
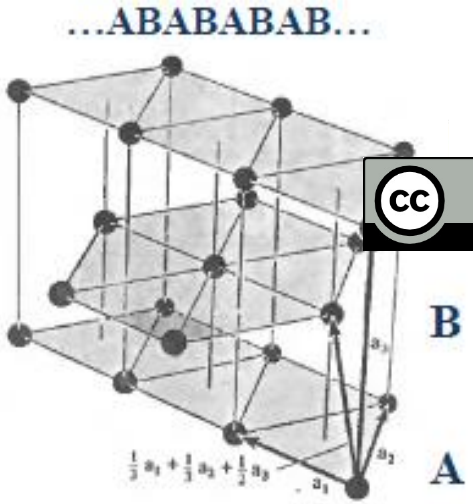
6 atoms in the plane
and 6 atoms off the plane

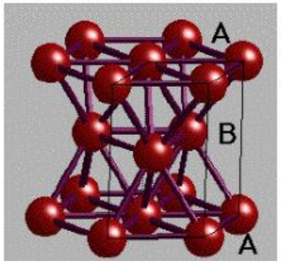
Crystal systems of close packings

Hexagonal close packing HCP layout. Structure A3





HCP is two interpenetrating simple hexagonal lattices displaced by $\mathbf{a}_1/3 + \mathbf{a}_2/3 + \mathbf{a}_3/2$

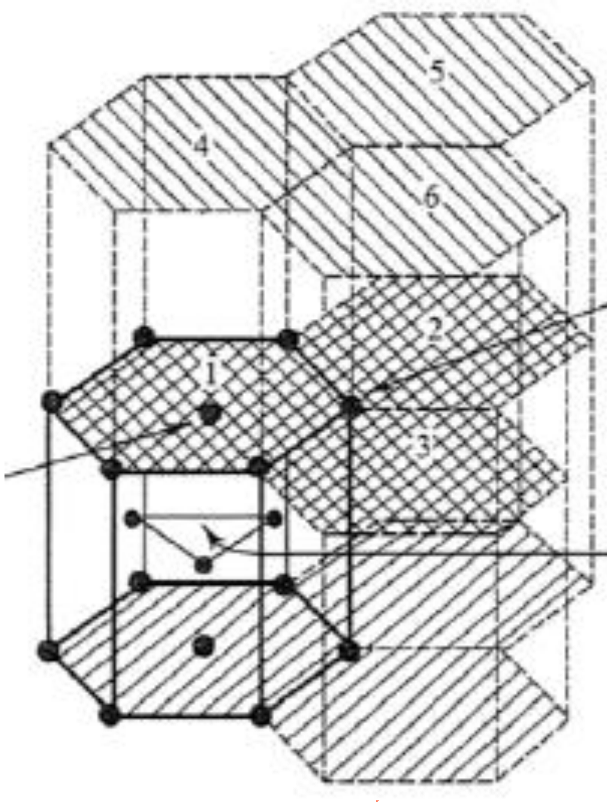


Elementary single hexagonal structure cell with 2 points

cc BY SA

6 atoms in the plane
and 6 atoms off the plane

Structure with Hexagonal Close Packing (HCP) - Unit Cell



is point belong to six unit cells

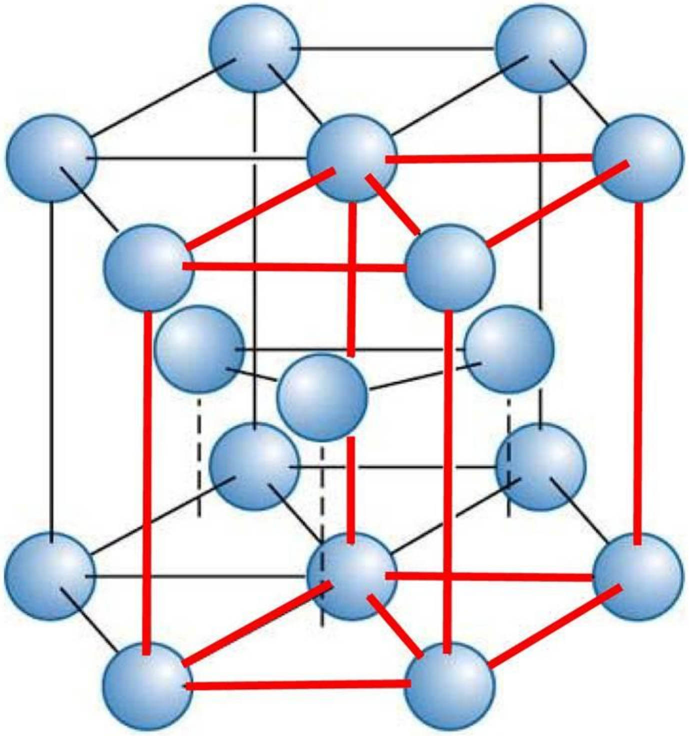
This point belongs to two unit cells

These three poitns belongs to the one unit cell

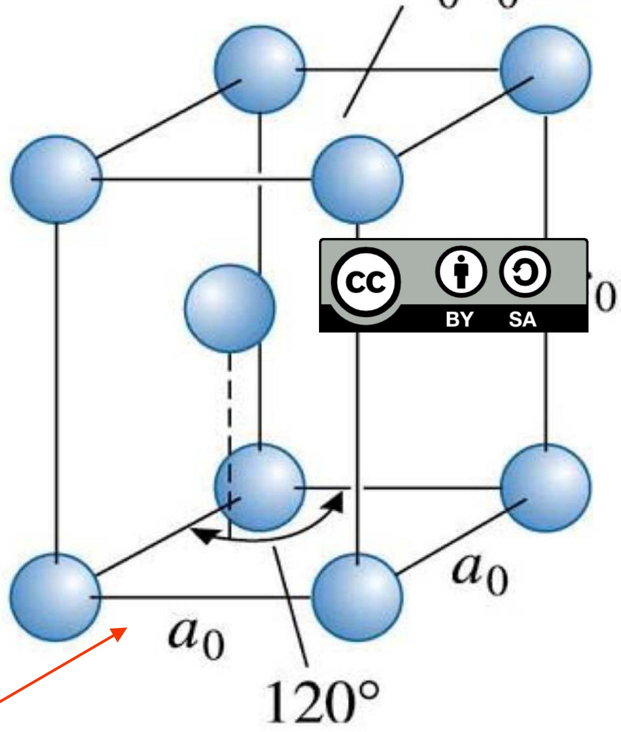
cc BY SA

Examples of elements with HCP structure : α-Ti, Zn, Mg, Be, Co…

Structure with Hexagonal Close Packing (HCP) - Unit Cell



Volume $= a_0^2 c_0 \cos 30°$



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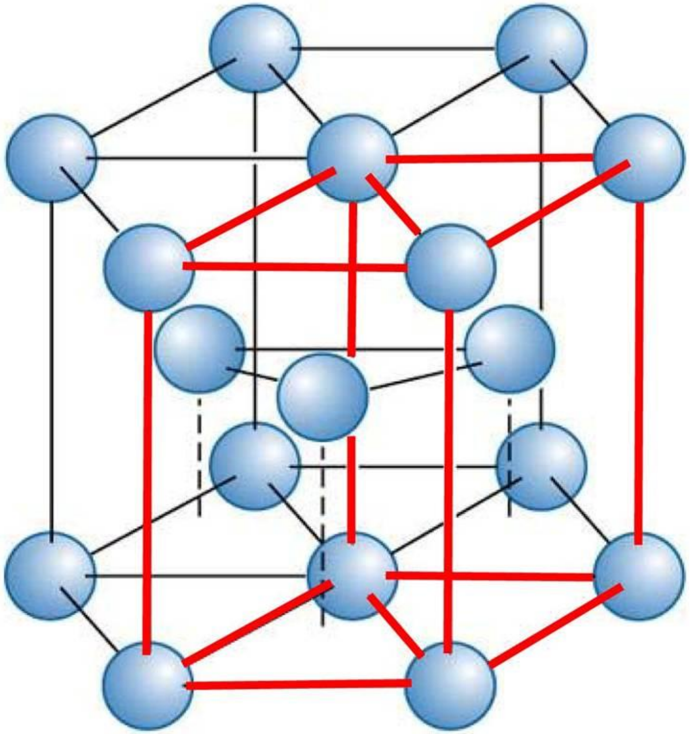
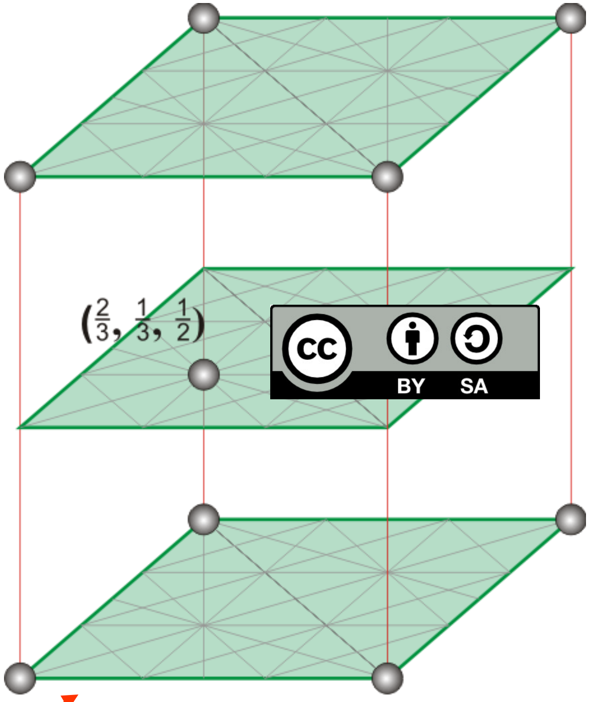
Unit cell of the HCP (rhomboedric)

Examples of elements with HCP structure : α-Ti, Zn, Mg, Be, Co…

Structure with Hexagonal Close Packing (HCP) - Unit Cell





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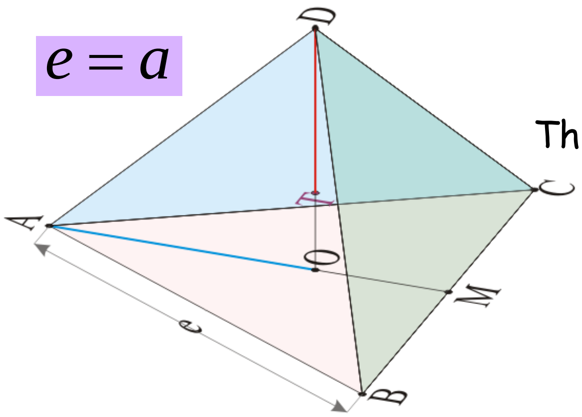
Unit cell of the HCP (*rhomboedric*)

Examples of elements with HCP structure : α-Ti, Zn, Mg, Be, Co…

- The hexagonal lattice contains two atoms or ions (at (0,0,0), (⅔, ⅓, ½)); ...and the HCP structure is created. In this ideal structure, the ratio is c / a ~ 1.632
- Real crystals with HCP often (mostly!) have c/a ratios different from ideal values

Calculation of the ideal c / a ratio

$e = a$



In tetraedra ABCD

$$AD^2 = e^2 = AO^2 + DO^2$$

Almost ideal c/a forMg

Kov	c/a
Cd	1.886
Zn	1.856
Ideal	1.632
Mg	1.624
Co	1.623
[illegible]	1.590
[illegible]	1.588
Be	1.586

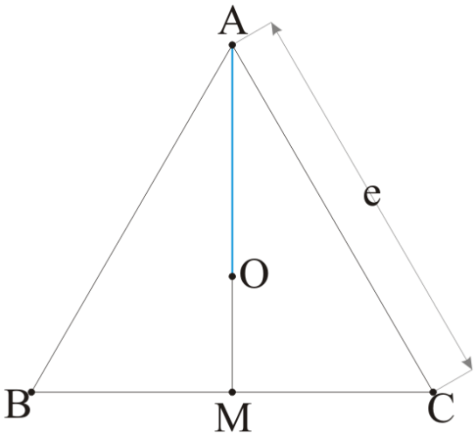
The AO calculation is solved in the triangle below

$c = 2h$

$$e^2 = \frac{e^2}{3} + DO^2 \qquad DO = e\sqrt{\frac{2}{3}} = h$$

ideal c/a

$$\boxed{\frac{c}{a} = \frac{2h}{a} = 2\sqrt{\frac{2}{3}} = 1.632...}$$

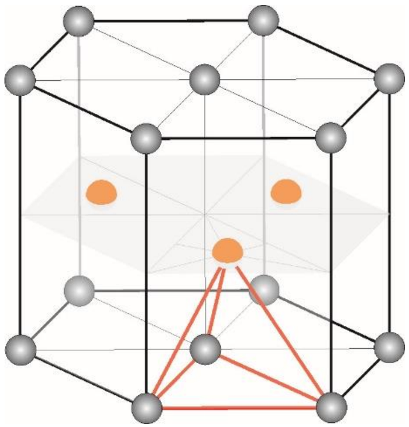


In the triangle ABC

$$e^2 = \frac{e^2}{4} + AM^2$$

$$AM = \frac{\sqrt{3}}{2}e$$

$$AO = \frac{2}{3}AM = \frac{2}{3}\frac{\sqrt{3}}{2}e = \frac{e}{\sqrt{3}}$$



Theoretical density ρ

$$\textbf{density} = \rho = \frac{\text{Mass of Atoms in Unit Cell}}{\text{Total Volume of Unit Cell}}$$

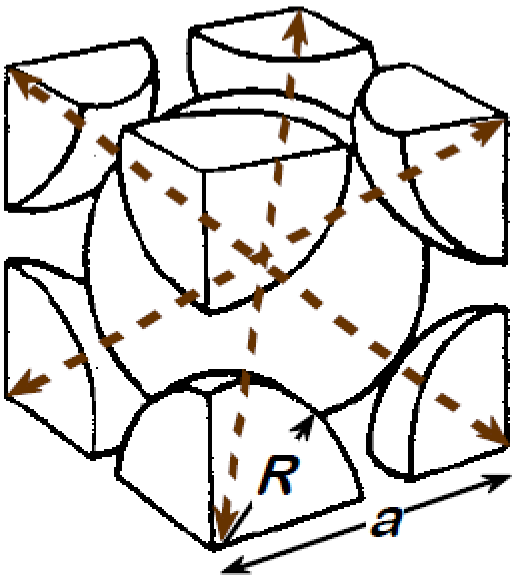
$$\rho = \frac{n\,A}{V_C N_A}$$

BY SA

where

n = number of atoms/unit cell
A = atomic weight
V_C = Volume of unit cell = a^3 for cubic
N_A = Avogadro's number
= 6.023×10^{23} atoms/mol

Theoretical density ρ



- Ex: Cr (BCC)

$A = 52.00$ g/mol

$R = 0.125$ nm

$n = 2$

cc BY SA

$a = 4R/\sqrt{3} = 0.2887$ nm

$$\rho = \frac{\overset{\frac{\text{atoms}}{\text{unit cell}}}{2}\;\overset{\frac{\text{g}}{\text{mol}}}{52.00}}{\underset{\frac{\text{volume}}{\text{unit cell}}}{a^3}\;\underset{\frac{\text{atoms}}{\text{mol}}}{6.023 \times 10^{23}}}$$

$\rho_{\text{theoretical}} = 7.18\ \text{g/cm}^3$

$\rho_{\text{actual}} = 7.19\ \text{g/cm}^3$

Polytypes

The ABCABC ... and ABAB ... sequences are just two of an infinite number of possibilities.
The point is that at each stage of construction there are positions in A, B or C positions
For example:? ABCAB ABCAB ABCAB ...? ABCABCAB ABCABCAB ABCABCAB ...
This is why crystals with larger elemental cells are formed
If the layers are arranged irregularly - then the crystal does not appear

The composition of the substances may move after a certain branch of the diagram and / or may end up after a certain sequence and its repetition results in the formation of a crystal

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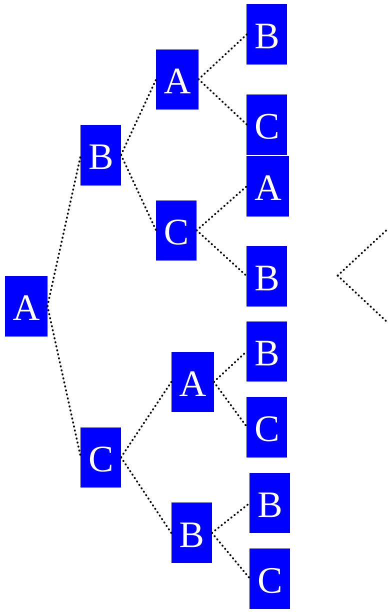
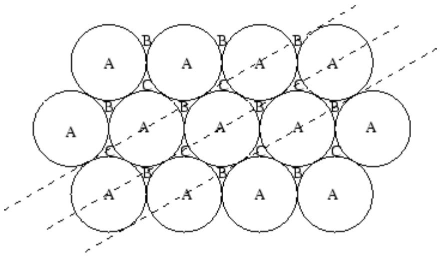


Polytype forms have the same lattice paramete the layer and vary in a perpendicular direction directly proportional to the number of layers in the period.

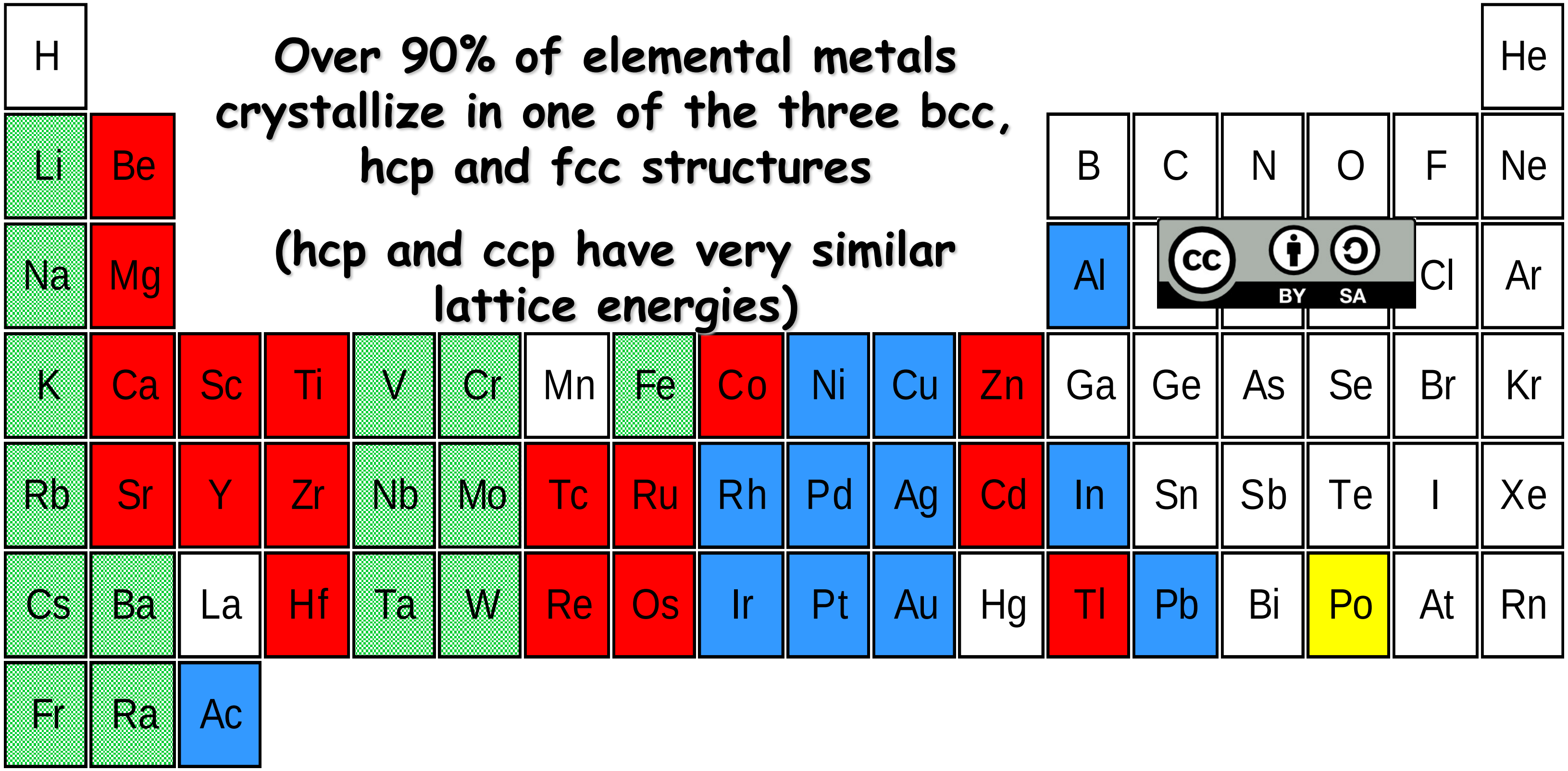
Example: SiC is over 250 polytypes
for example, 6H-SiC, packing sequence: ... ABCACB ...

Some polytypes contain long sequences. For example
174R - 436.7 Å
393R - 989.6 Å



Structure of metals

Some metals are soft and ductile (Au, Ag, Cu, Al etc)? Others are hard (Fe, W, Cr, etc.) Why ????



H																	He
Li 🟩	Be 🟥											B	C	N	O	F	Ne
Na 🟩	Mg 🟥											Al 🟦				Cl	Ar
K 🟩	Ca 🟥	Sc 🟥	Ti 🟥	V 🟩	Cr 🟩	Mn	Fe 🟩	Co 🟥	Ni 🟦	Cu 🟦	Zn 🟥	Ga	Ge	As	Se	Br	Kr
Rb 🟩	Sr 🟥	Y 🟥	Zr 🟥	Nb 🟩	Mo 🟩	Tc 🟥	Ru 🟥	Rh 🟦	Pd 🟦	Ag 🟦	Cd 🟥	In 🟦	Sn	Sb	Te	I	Xe
Cs 🟩	Ba 🟩	La	Hf 🟥	Ta 🟩	W 🟩	Re 🟥	Os 🟥	Ir 🟦	Pt 🟦	Au 🟦	Hg	Tl 🟥	Pb 🟦	Bi	Po 🟨	At	Rn
Fr 🟩	Ra 🟩	Ac 🟦															

Over 90% of elemental metals crystallize in one of the three bcc, hcp and fcc structures

(hcp and ccp have very similar lattice energies)

🟨 Primitive cubic - PS

🟩 BCC

🟦 FCC

🟥 HCP

FCC and HCP metal structures and INM

- Metal structures can be described by the - „closest packing" of atoms in the form of non-pressurized spheres.
- Some INM structures can be derived from binary compounds in which "cavities" in the FCC structure are filled

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Chemistry and Physics of Solids – Lecture 5

Close packing and structure types

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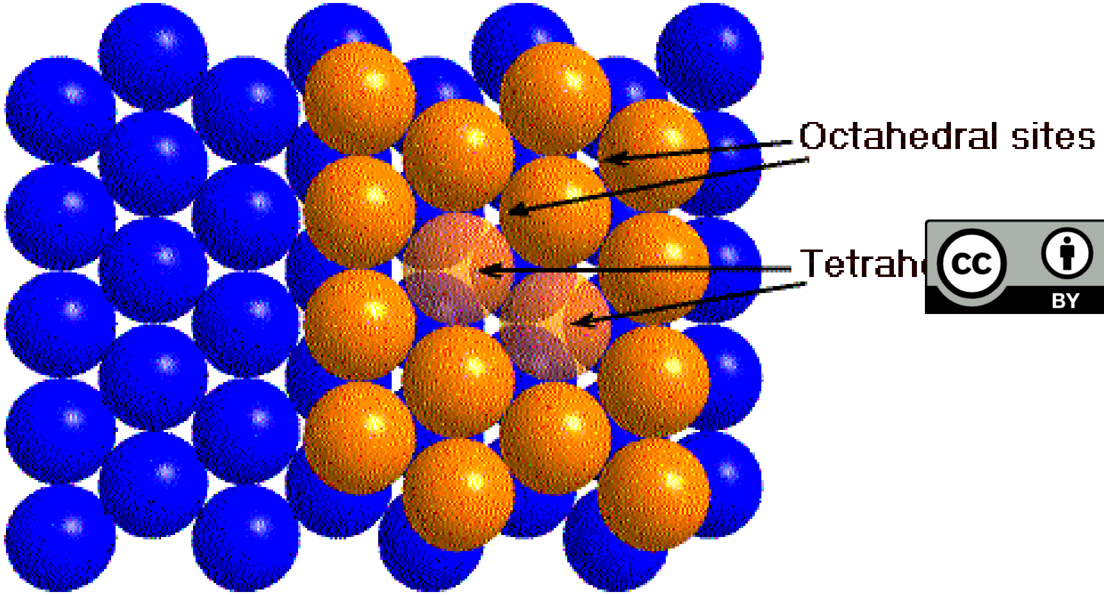
In the closest packings, positions for other atoms appear



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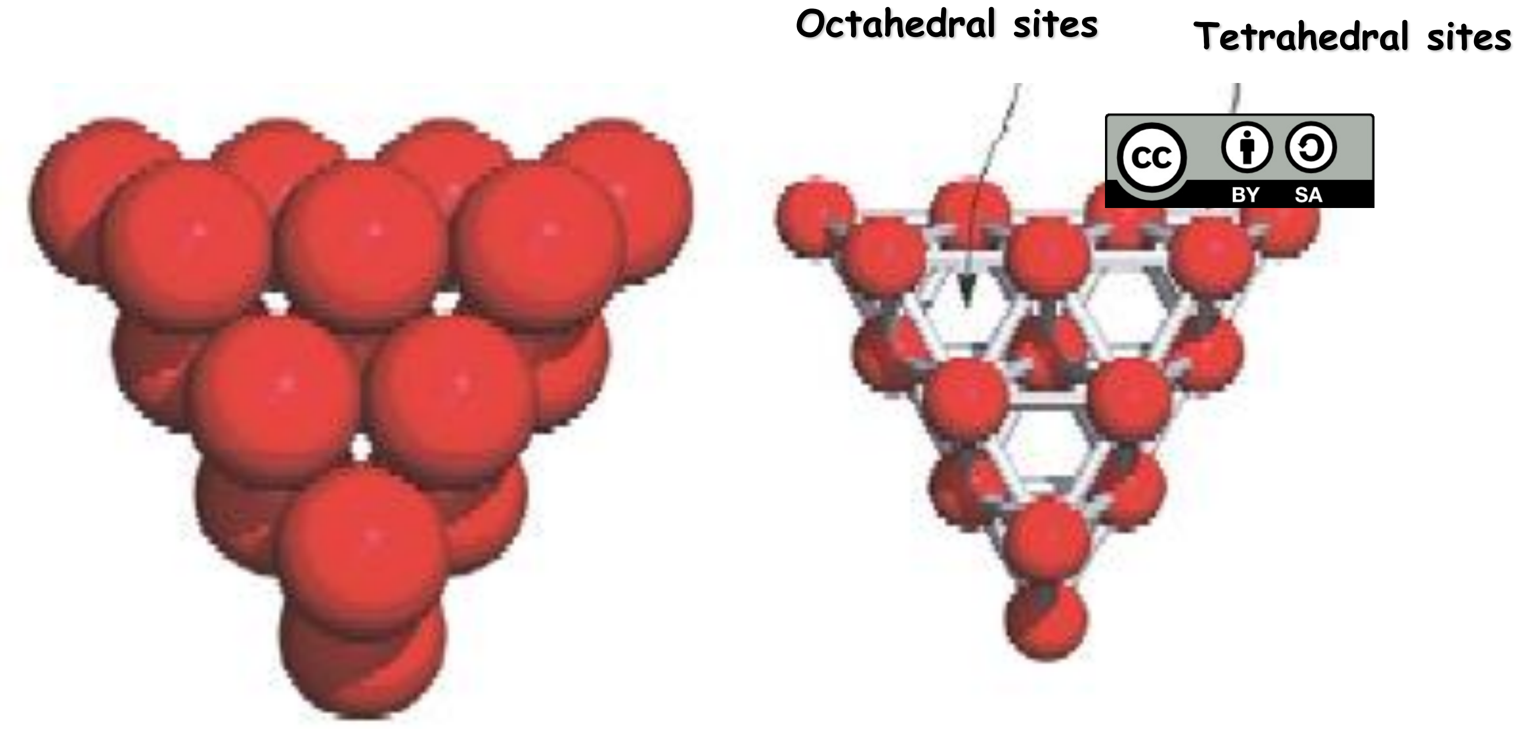
The metal structures correspond to the „closest packing" of the ball symmetry atoms

Many INMs can be derived from binary compounds by filling the "cavities" in the arrangement of atoms or ions.

In the closest packings, positions for other atoms appear



(a) (b)

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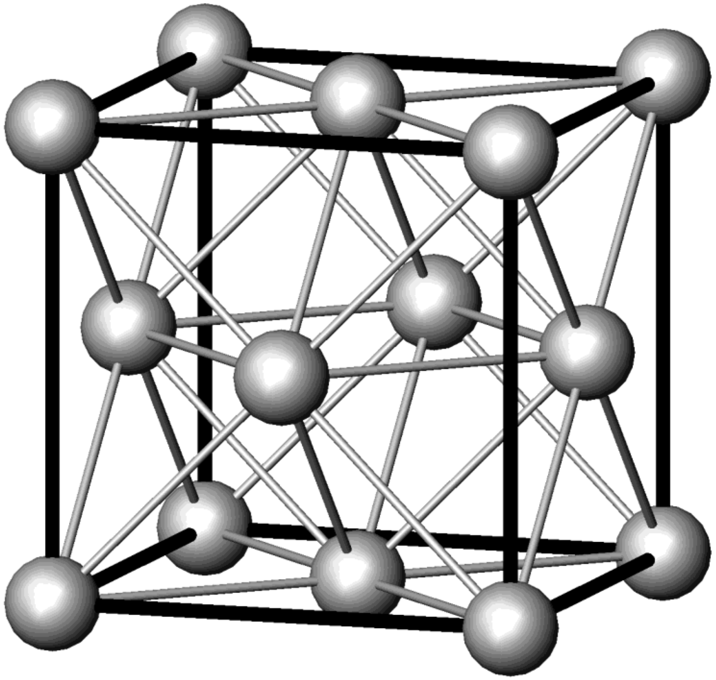
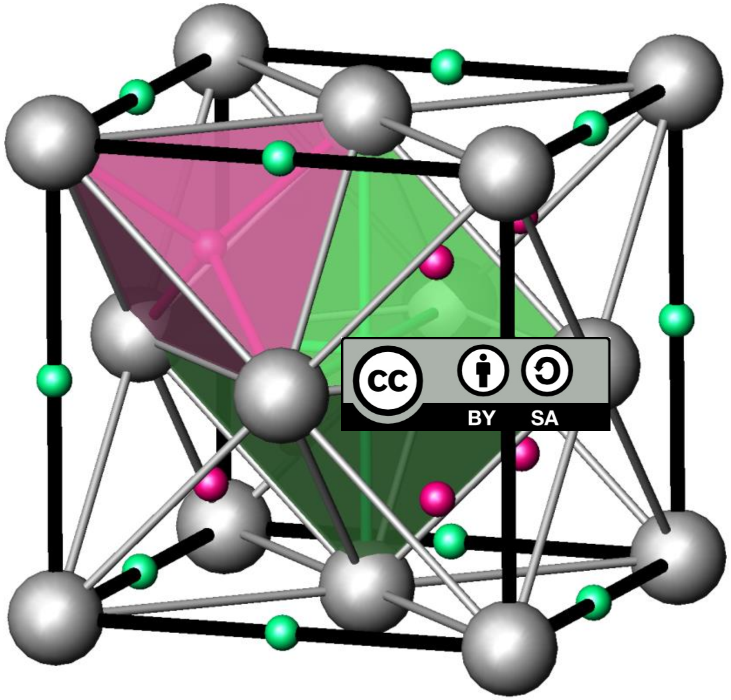
Cubic closest packings



8 tetrahedral positions / unit cell
2 tetrahedral positions / tightly arranged atom



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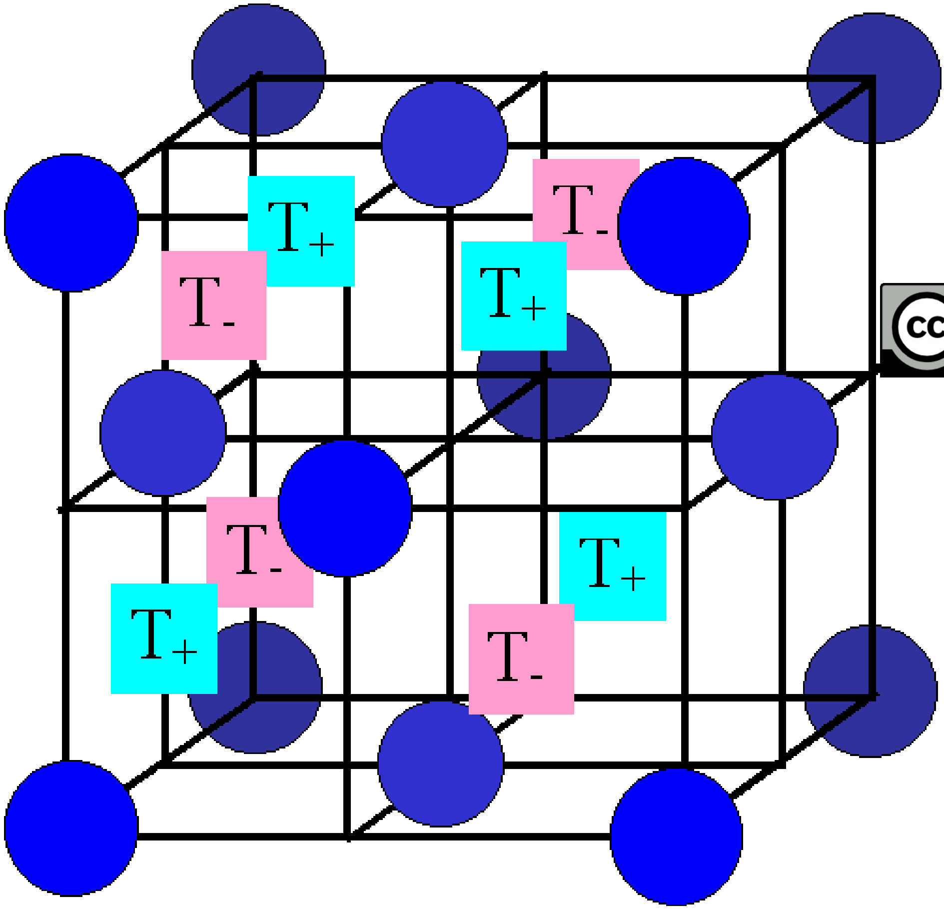
4 octahedral positions / unit cell
1 octahedral position / tightly arranged atom

... 8 tetrahedral positions in the closest cubic packing



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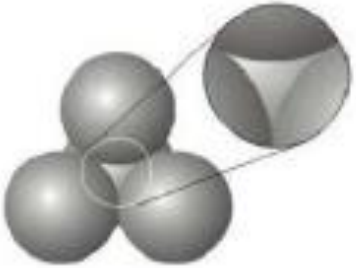
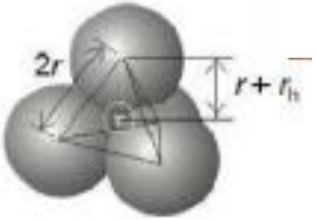
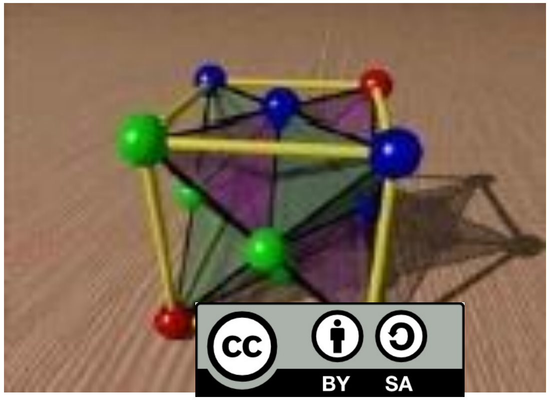
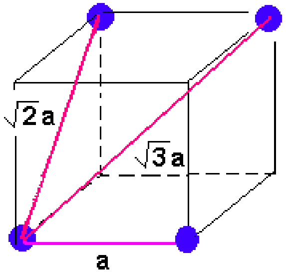
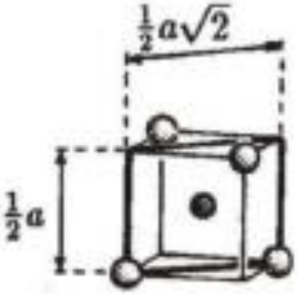
What minimal dimension can the cation have to "fit" into the tetrahedral cavity?

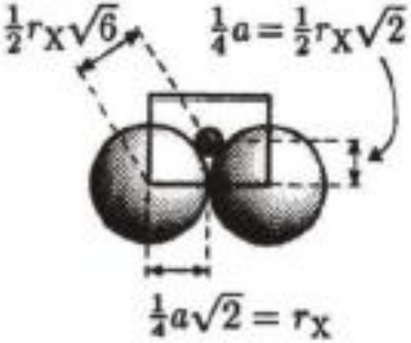








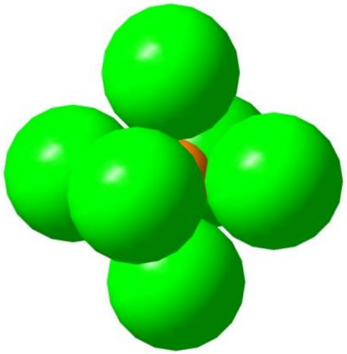


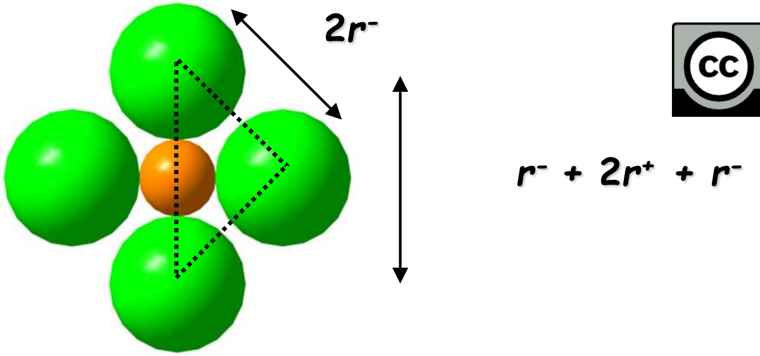


$$
\begin{aligned}
r_M + r_X &= r_X \cdot \tfrac{1}{2}\sqrt{6} \\
r_M/r_X &= \tfrac{1}{2}\sqrt{6} - 1 \\
&= 0,225
\end{aligned}
$$

What is the site of the octahedral cavity?

In the NaCl structure, the Na^+ (r+ = 102 pm) cations occupy the octahedral positions in the cubic Cluster Cl anions (r = 182 µm). Suppose ions are "rigid spheres" with radii r+ and r-. Consider geometry:

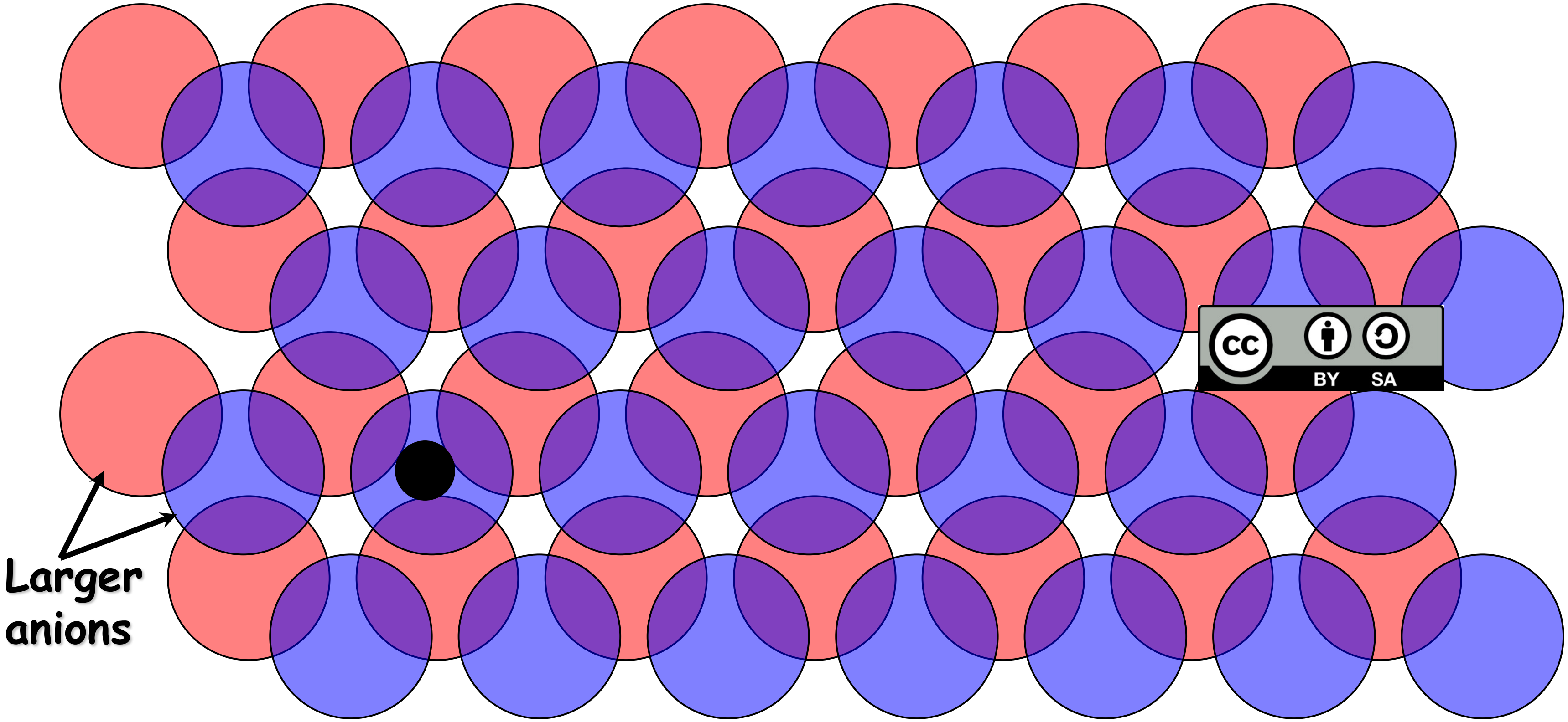




The cation must have contact with the 6 surrounding anions (KC 6), but must also prevent the anions from contacting each other.
Minimum cation radius $(r+)_{min}$:

$$r^- + 2(r^+)_{min} + r^- = \sqrt{2}(2r^-)$$
$$(r^+)_{min} = (\sqrt{2} - 1)\, r^-$$
$$\text{then } (r^+/r^-)_{min} = 0.414$$

Red and blue balls showing the most severe type A and B anions arrangement of layers; where do cations come in?



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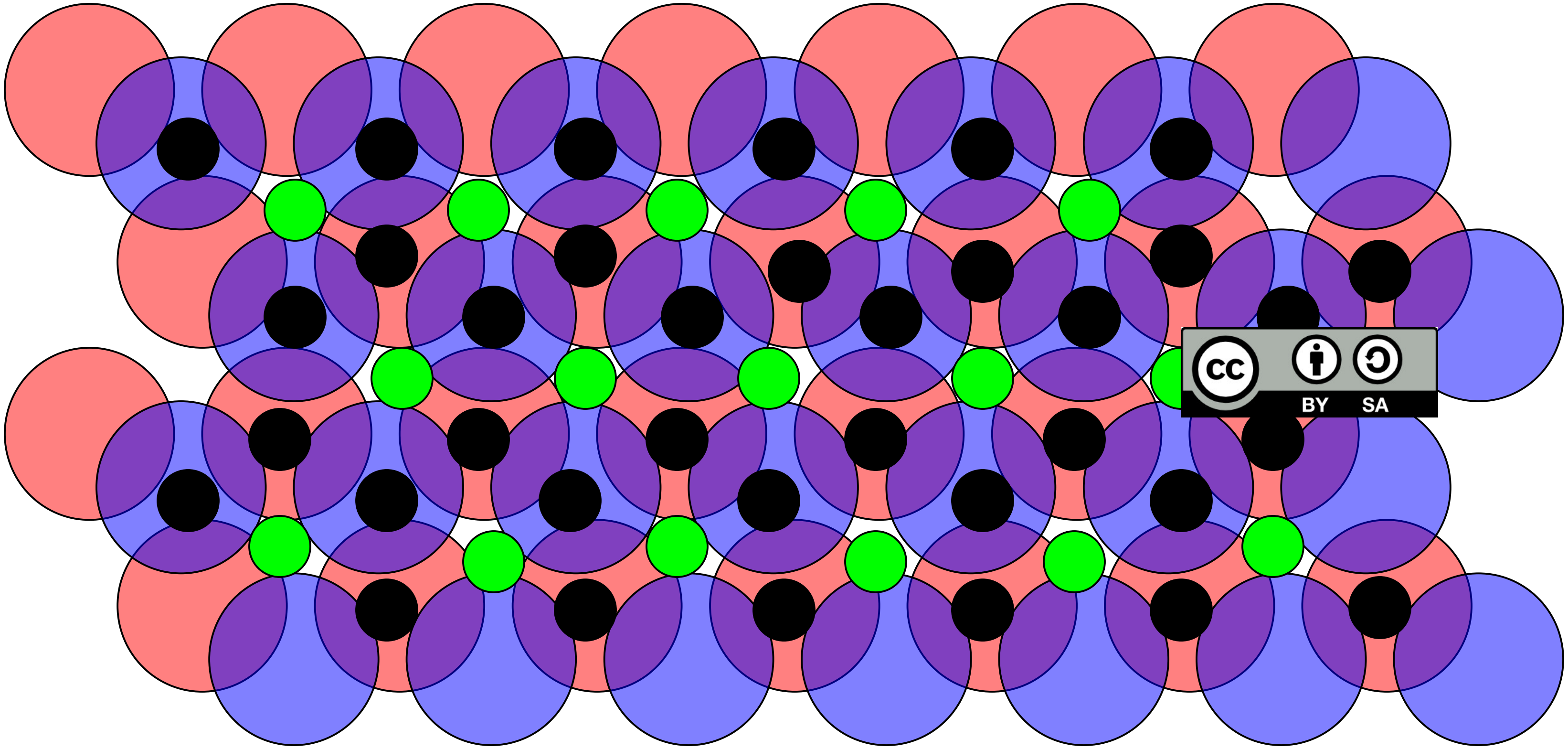
Smaller cations, $r^+/r^- < 0.41$

Larger cations, $r^+/r^- > 0.41$

The cationic cavities Td are smaller than the Oh cavities
Td cavities are 2x more than Oh cavities



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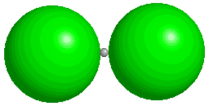
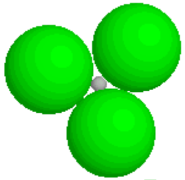
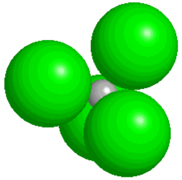
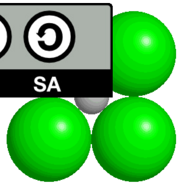
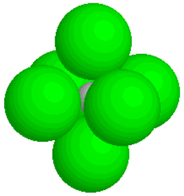
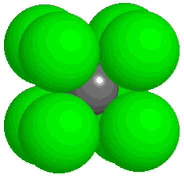
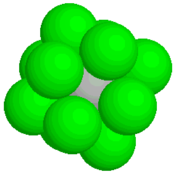
The most common coordinating polyhedra

0.000-0.155	2	Linear	
0.155-0.225	3	Triangle	
0.225-0.414	4	Tetrahedra	
0.414-0.732	4	Square	
0.414-0.732	6	Octahedra	
0.732-1.000	8	Cube	
1.000	12	Closest packing	

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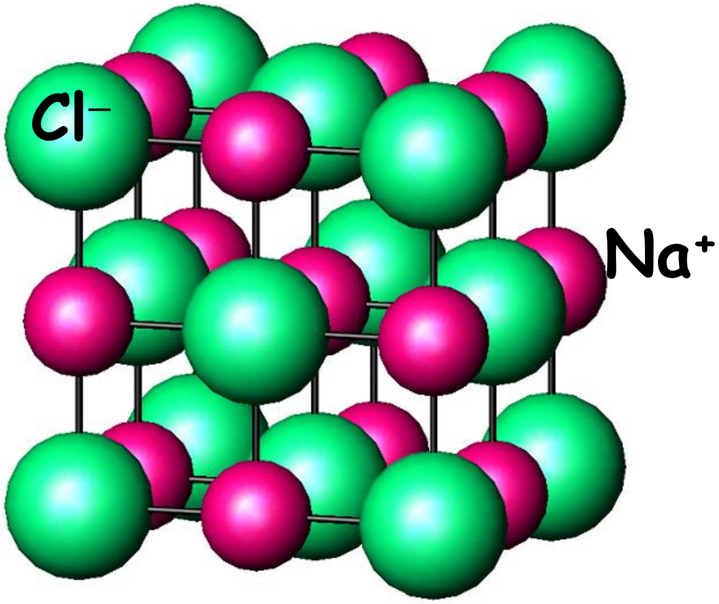
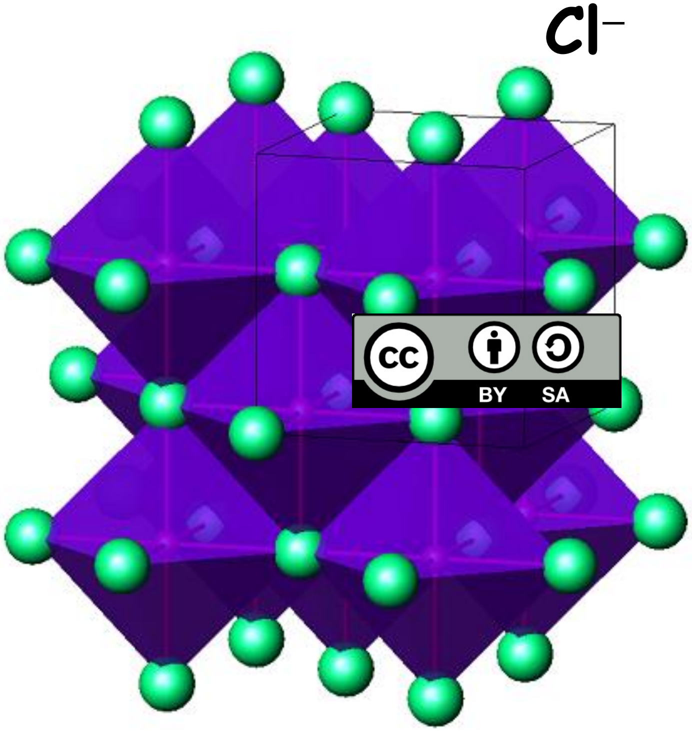
Compounds with the structure of CCP

NaCl (halite) - stoichiometry AB



Sphere model



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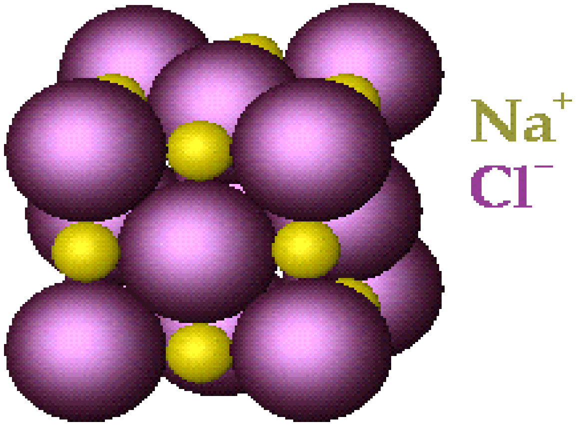
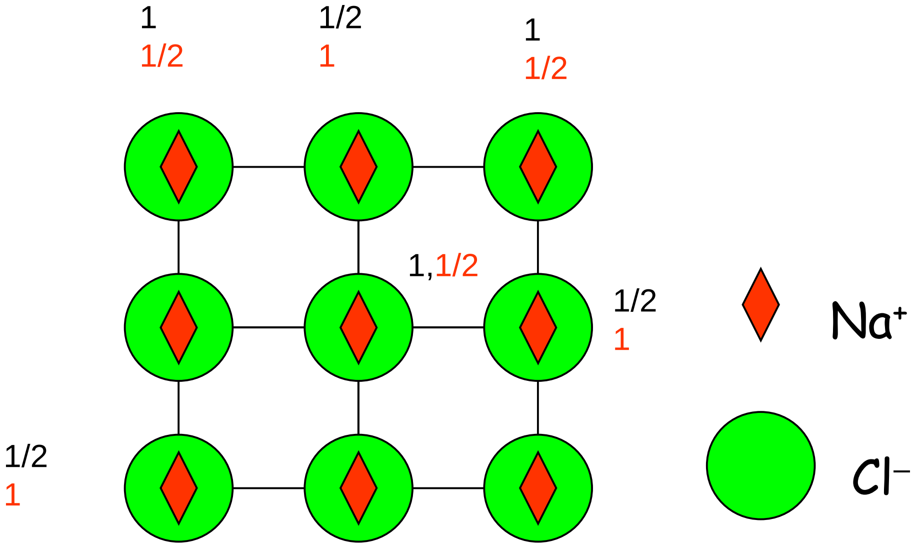
Polyhedral model



Representation filling space



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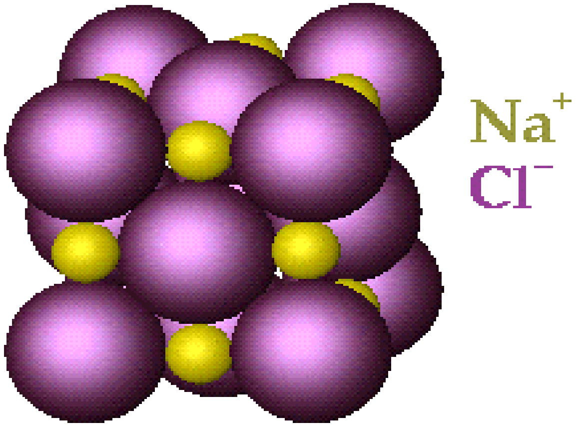
2D projection

- CCP structure of Cl^- anions with Na^+ cations occupying all octahedral positions
- n balls and n octahedral cavities on the elementary cell. Stoichiometry of the cation: anion = 1: 1
- CN (cation) = 6 (octahedral); CN (anion) = 6 (octahedral)
- Fractional coordinates of Cl (0,0,0); Na (1 / 2,0,0)

Crystal structure of NaCl

Calculation of density

The theoretical density of crystalline materials can be calculated from elementary cell parameters
In the case of NaCl, $a = 2r + + 2r-$.



Ionic radii (Shannon-Prewitt):
r (Na^+) = 1.16 Å and r (Cl^-)
$a = 2\,(1.16) + 2\,(1.67) =$
$a = 5.66 \times 10^{-8}$ cm

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$$Density = \frac{m}{v} = \frac{\dfrac{4(22.99)+4(35.45)}{6.022\times10^{23}}g}{(5.66\times10^{-8})^3 cm^3} = 2.14 g/cm^3$$

The real density is 2.165 g/cm^3
The ratio of radii 1.16/1.67 = 0.69
corresponds to the octahedral
coordination of cations

AB: NaCl

Representative	The ratio of the NaCl radius
NaCl, CaO, MgO, FeO	0.56

Coordination number of Na^+	Coordinating polyhedron	Radius of the cation (Å)
6	Octahedral	1.02

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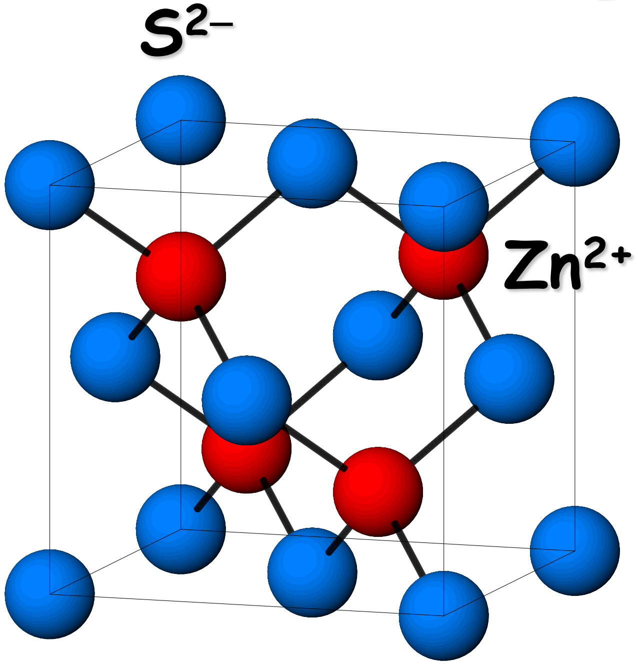
Coordination number of Cl^-	Coordinating polyhedron	Radius of the anion (Å)
6	Octahedral	1.82

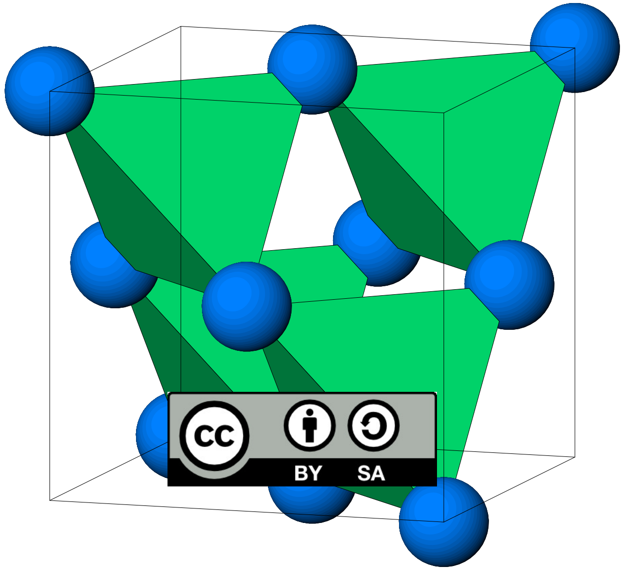
- The most common structural type (includes "ion", "covalent" and "intermetallic" compounds)
- Most alkaline halides (except CsCl, CsBr, CsI)
- Most alkaline earth metal oxides / chalkogenides
- Many nitrides, carbides, hydrides (e.g., ZrN, TiC, NaH)

Valence has only an indirect impact on the coordination numbers, as evidenced by the $Na^{I}C1$, $Mg^{II}O$, $Sc^{III}N$, $Ti^{I}VC$ *compounds with a rock salt structure, regardless of valence and binding type*

β-ZnS (sphalerite)
Stoichiometry AB



To prevent repulsions, the opposite diagonal positions are alternately filled in this structure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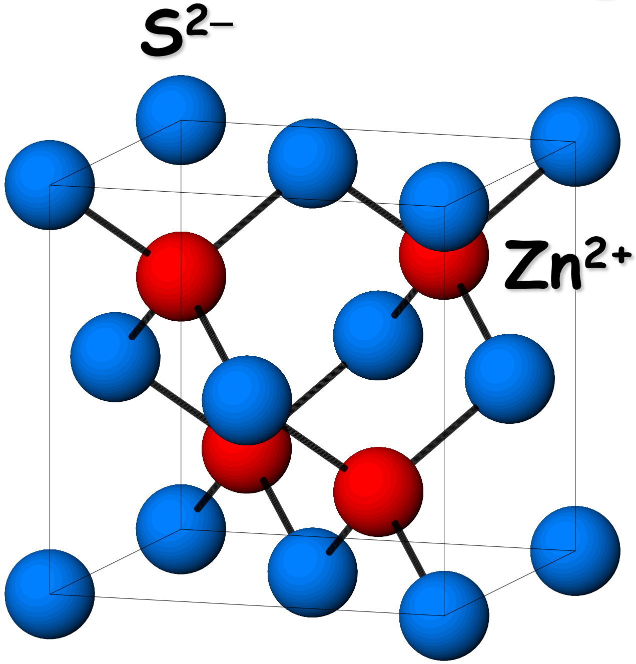
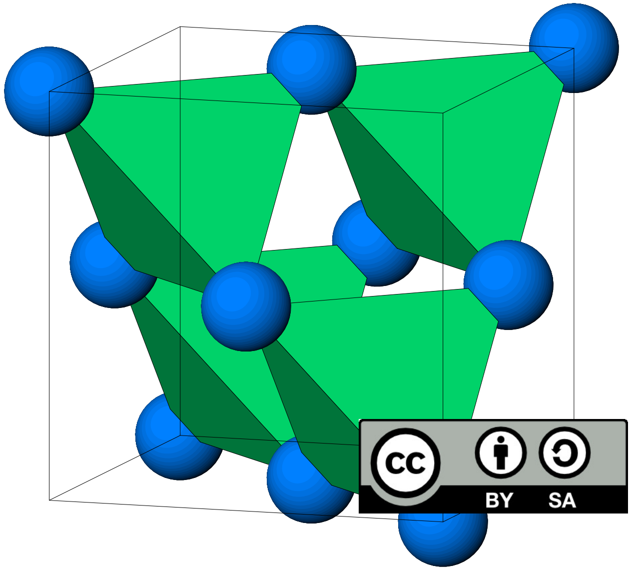
ZnS_4 tetrahedrons

- CCP = FCC S^{2-} anions with Zn^{2+} occupying half the tetrahedral cavities
- The n sphere is $\frac{1}{2}$ of the 2n tetrahedral cavities, therefore the stoichiometry of the cation: anion = 1: 1
- The radius ratio is 0.74 / 1.84 = 0.40 => the upper limit of the tetrahedral coordination
- CN (cation) = 4 (tetrahedral); CN (anion) = 4 (tetrahedral)
- High contribution of covalent bond
- Fractional coordinates: S at (0,0,0); Zn at (1 / 4,1 / 4,1 / 4)
- For example, BeO, ZnO, ZnS, SiC, BN, GaAs

β-ZnS (sphalerite)
Stoichiometry AB





ZnS$_4$ tetrahedrons

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- ❑ Binding in ZnS is more covalent than ionic
- ❑ r_c/r_a = 0.40 => boundaries of tetrahedral and octahedral coordination? sp^3 linkages => tetrahedral coordination
- ❑ found => tetrahedral coordination

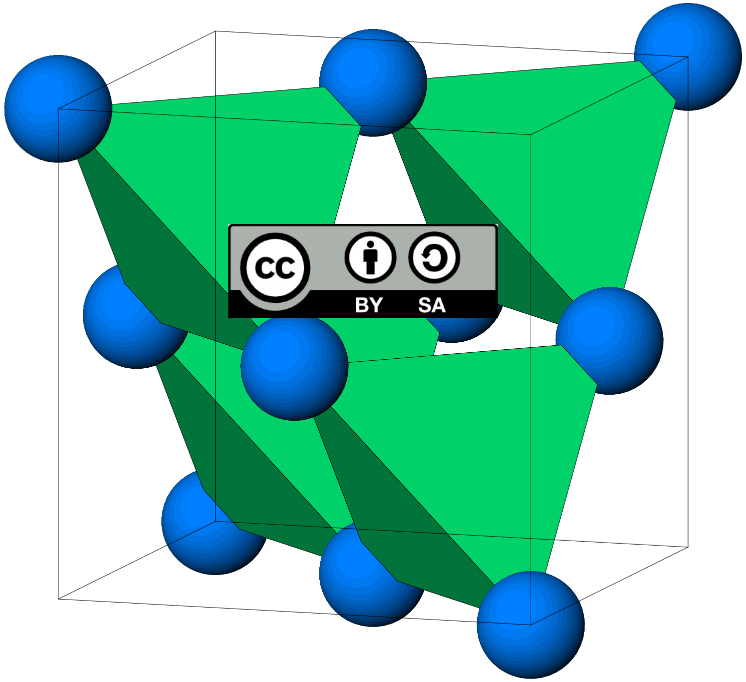
Distances M-X

ZnS (sphalerite)

The unit cell is a cube ($a = 5.43$ Å).

The inter-atomic distance Zn-S and the size of the body diagonal a√3 are interconnected by:

$$d_{Zn-S} = \frac{a\sqrt{3}}{4} = 2,39$$



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Compare ion and covalent radii:

Σionic radii = r (Zn^{2+}) + r (S^{2-}) = 2.65Å

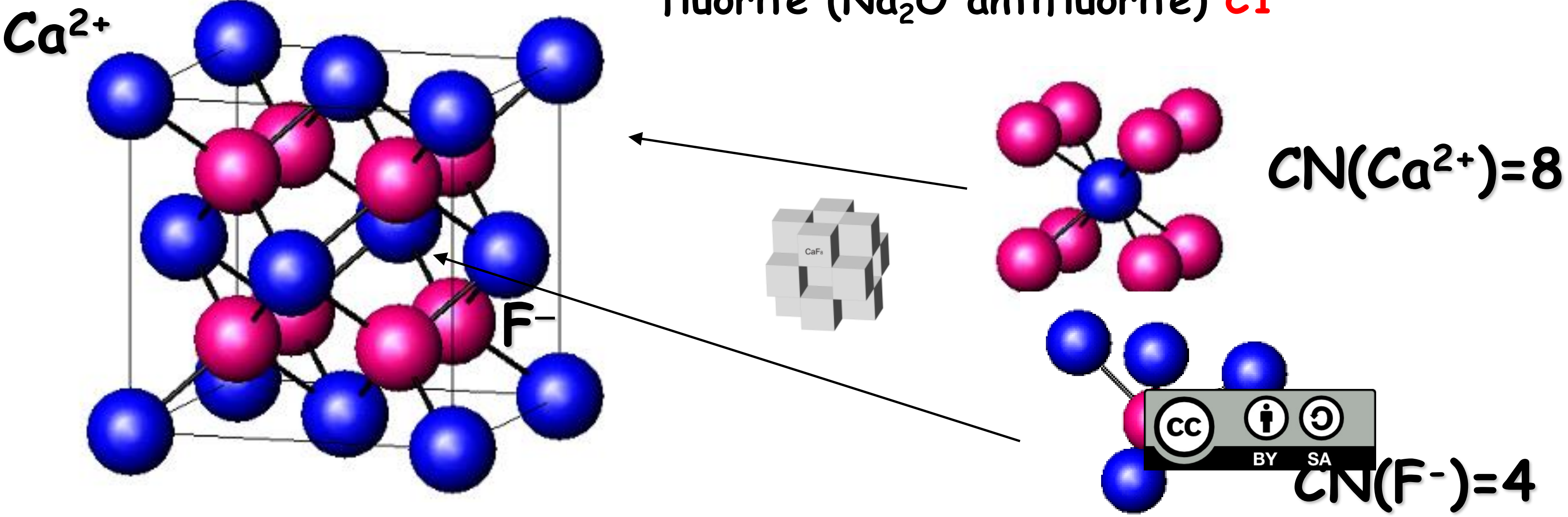
Σcovalent radii. radii = r (Zn) + r (S) = 2.35Å

The latter value is closer to d_{Zn-S}.

The model is covalent

Crystal structures AB_2

fluorite (Na_2O antifluorite) C1



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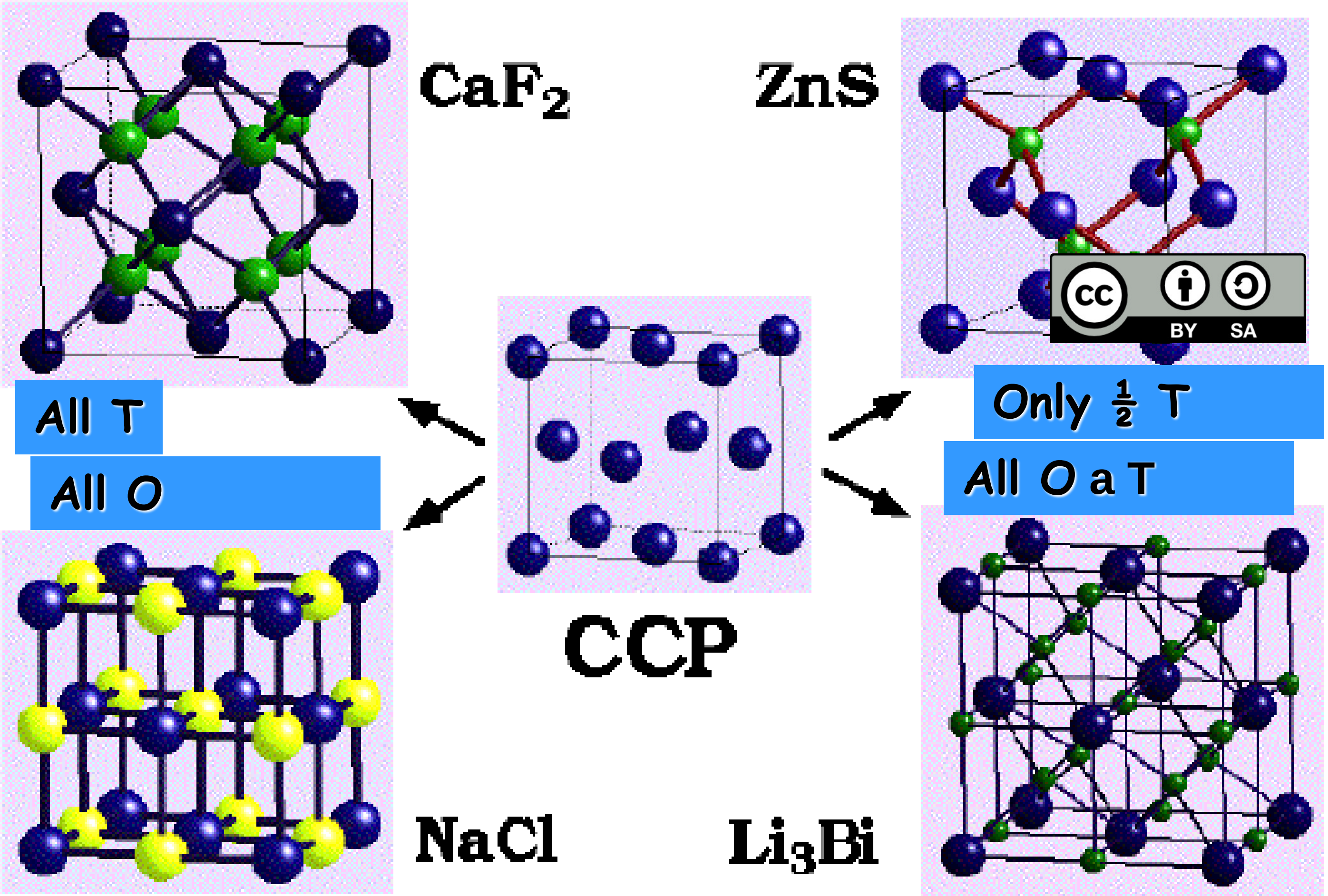
- The structure deviates from the concept of the tightest anion arrangement
- The closest cubic arrangement of Ca^{2+} with F^- in all tetrahedral cavities
- The n-sphere is 2n tetrahedral cavities: the stoichiometry corresponds to a ratio of 2: 1 (the ratio of the ions radii 0.74)
- Fractional coordinates: Ca^{2+} at (0.0.0); 2F - at (1 / 4,1 / 4,1 / 4) & (3 / 4,3 / 4,3 / 4)

SrF_2, BaF_2, CdF_2, HgF_2, UO_2, ThO_2, ZrO_2, CeO_2

- In the structure of antifluorite, the positions of the anions and cations are reversed and hence the stoichiometry corresponds to:
- *CCP O2* - with Na+ in all tetrahedral cavities Oxides, sulphides, alkali metal tellurides - Li_2O,
- K_2O, Li_2S, K_2S, Li_2Se, K_2Se, Li_2Te, K_2Te, Na_2O, Pb_2O, Na_2S, Pb_2S, Na_2Te, Li_2Te
- Larger octahedral cavities are not occupied in this structure - very important for the ions movement in defect structures.

Structures derived from the closest cubic packing



CaF_2

All T

All O

NaCl

CCP

ZnS

Only ½ T

All O a T

Li_3Bi

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Coordination and stechiometry

Coordination equilibrium

The stoichiometry of the substance is not only associated with the number of atoms of each atomic type in the unit cell, but also with the coordination of:

If the compound has the composition M_aX_b and only the M-N bonds exist in the structure, then the relationship is fulfilled independently of the type of chemical bond

(coordination equilibrium):

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$$K(M) \times a = CN(X) \times b \text{ or } CN(M)/CN(X) = b/a$$

Example 1

In SiO_2 Si is tetrahedral coordinated. What is the O CN?

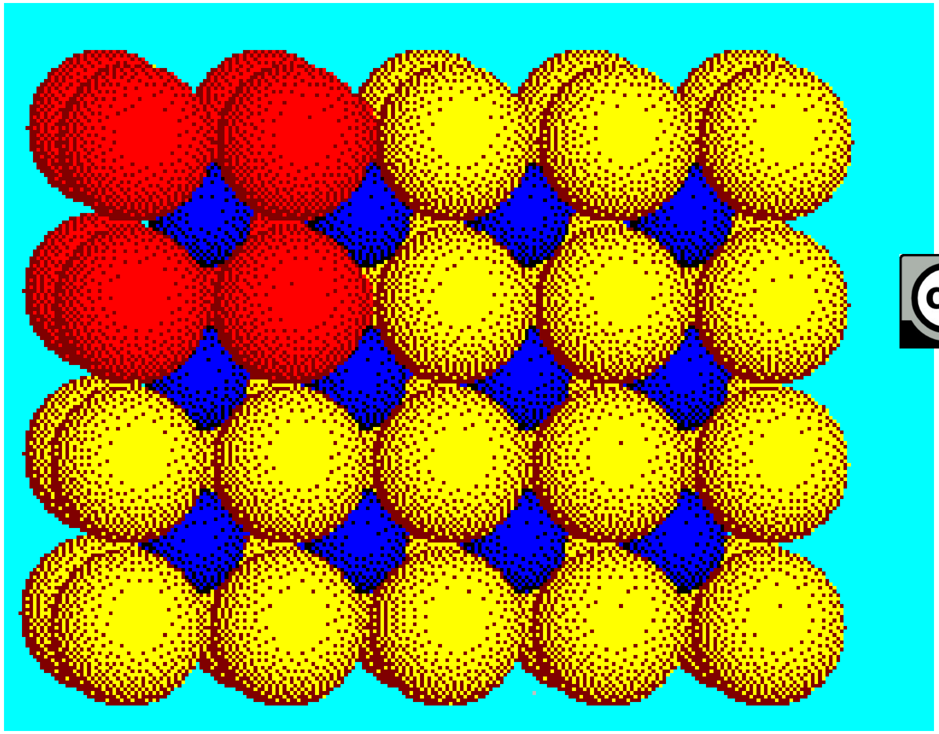
$4 \times 1 = (CN\ O) \times 2 \rightarrow$ Coordination number O = 4/2 = 2

Example 2

In CaF_2, Ca is cubic-coordinated with anions F^-. What is the coordination of F^-?

$8 \times 1 =$ (coordination number F^-)x2 Coordination number $F^- = 4$

Cubic vacancies



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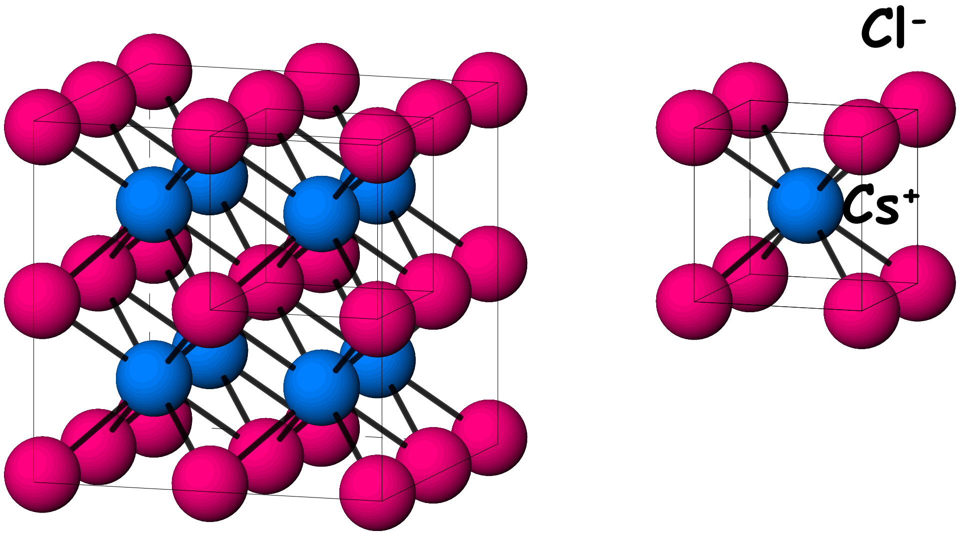
Compounds with structures that do not form the closest packing

CsCl



Stoichiometry of the cation/anion = 1:1, 8 Cs + cations in the cell. It means that all cube centers are occupied

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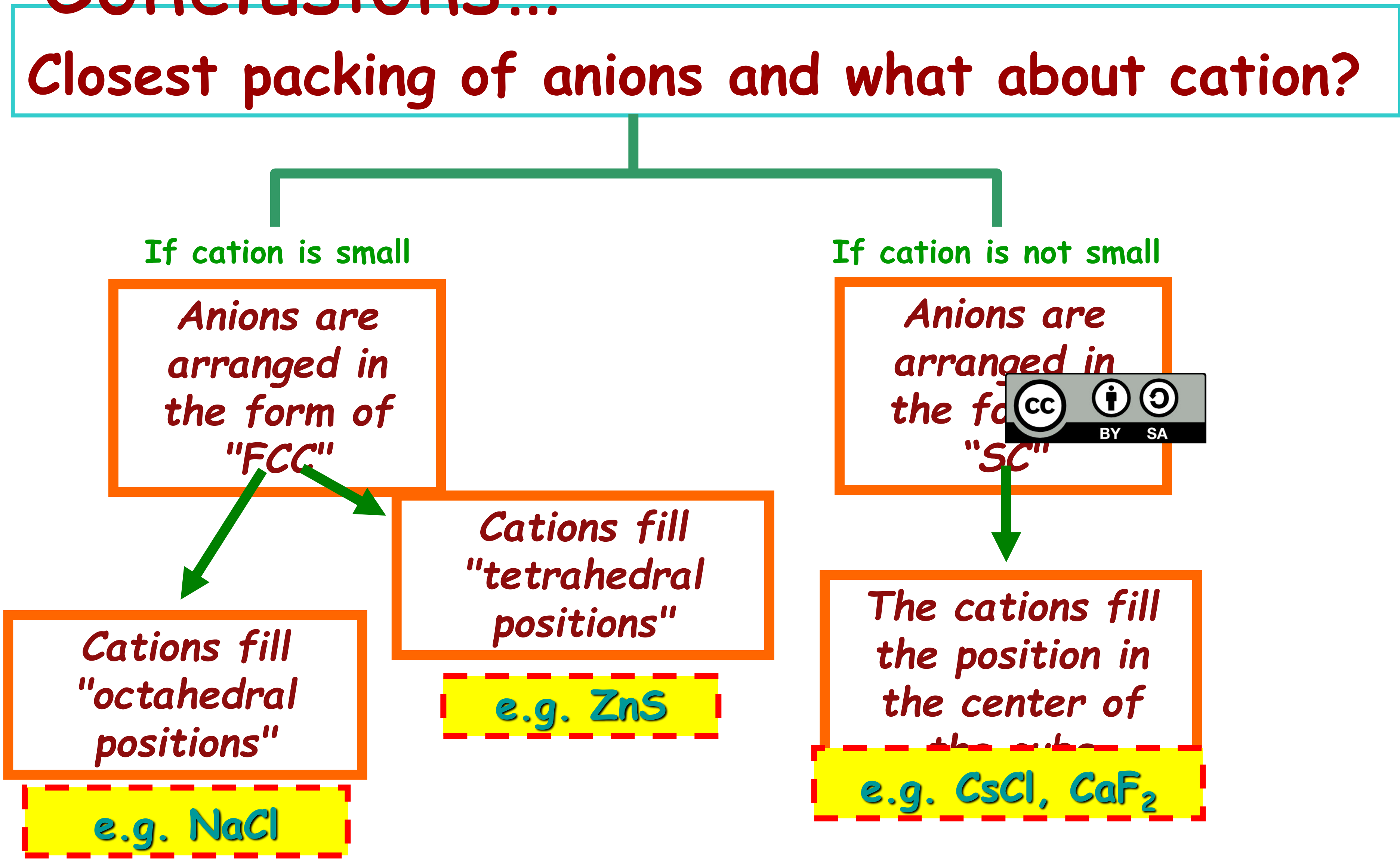
- Cubic unit cell (primitive - not body-centered)
- CN (Cs) = 8 (cubic); CN (Cl) = 8 (cubic)
- Fractional coordinates: Cl (0,0,0); Cs (1 / 2.1 / 2.1 / 2)
- For example, CsBr, CsI, TlBr, TlI, TlCl, NH_4Cl, NH_4Br, CsCN

Conclusions…



Closest packing of anions and what about cation?

If cation is small

Anions are arranged in the form of "FCC"

Cations fill "octahedral positions"

e.g. NaCl

Cations fill "tetrahedral positions"

e.g. ZnS

If cation is not small

Anions are arranged in the fo "SC"

The cations fill the position in the center of the cube

e.g. CsCl, CaF_2

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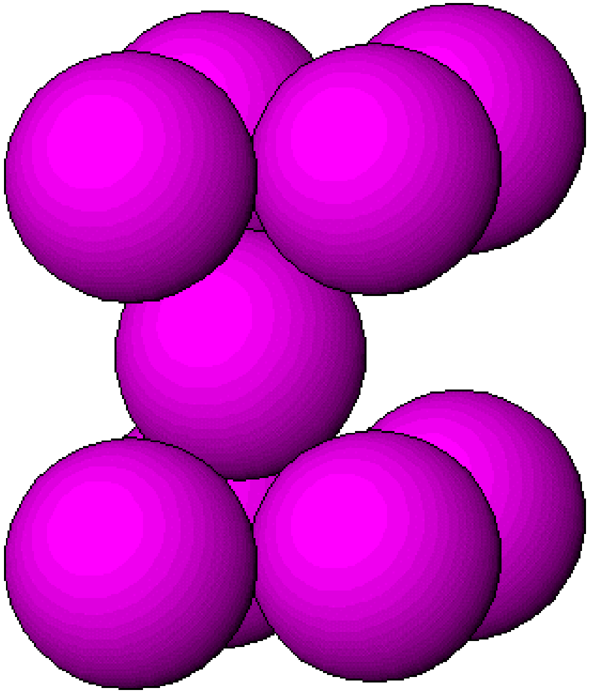
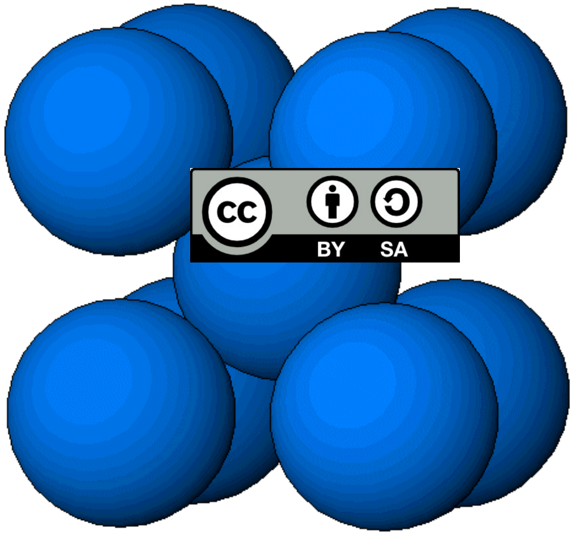
Hexagonal closest packing (hcp)





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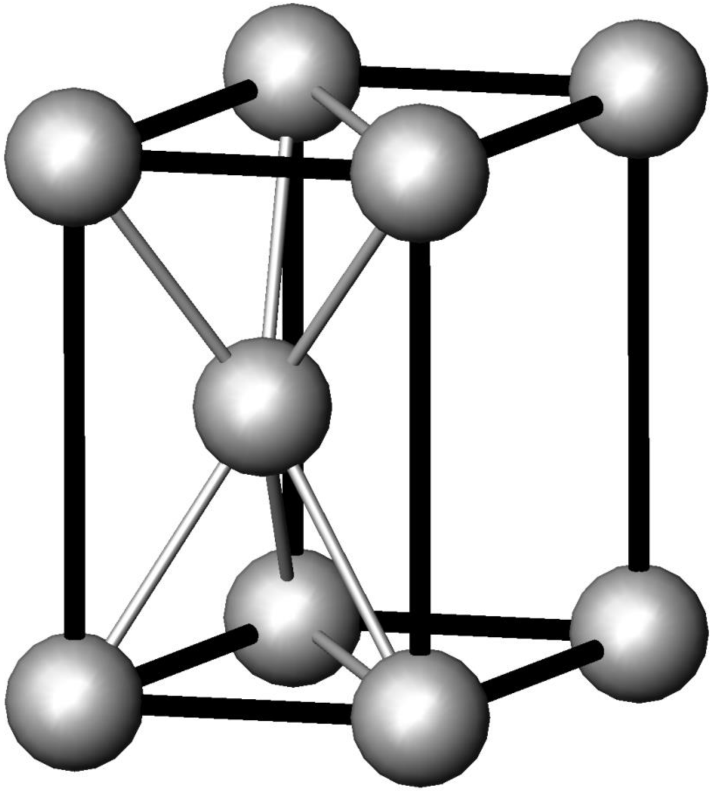
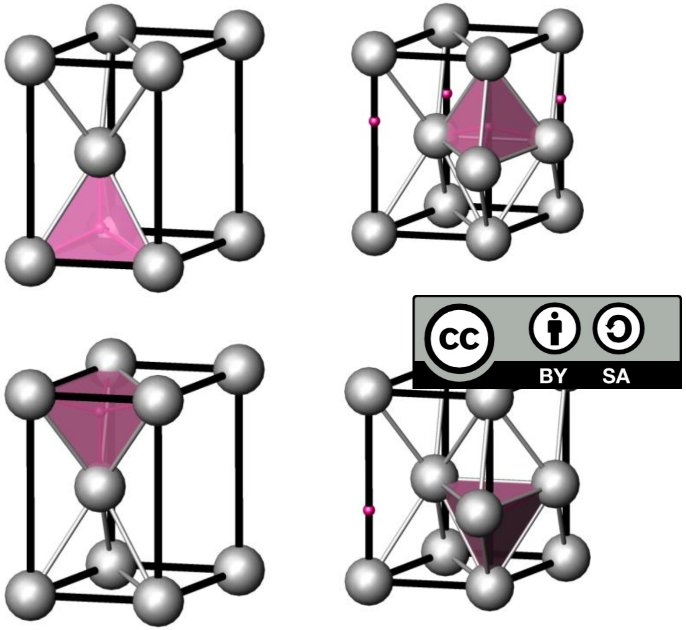
hcp ≠ bcc

HCP: tetrahedral sites





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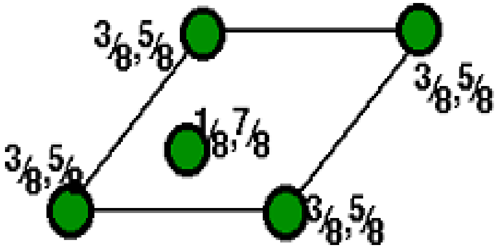
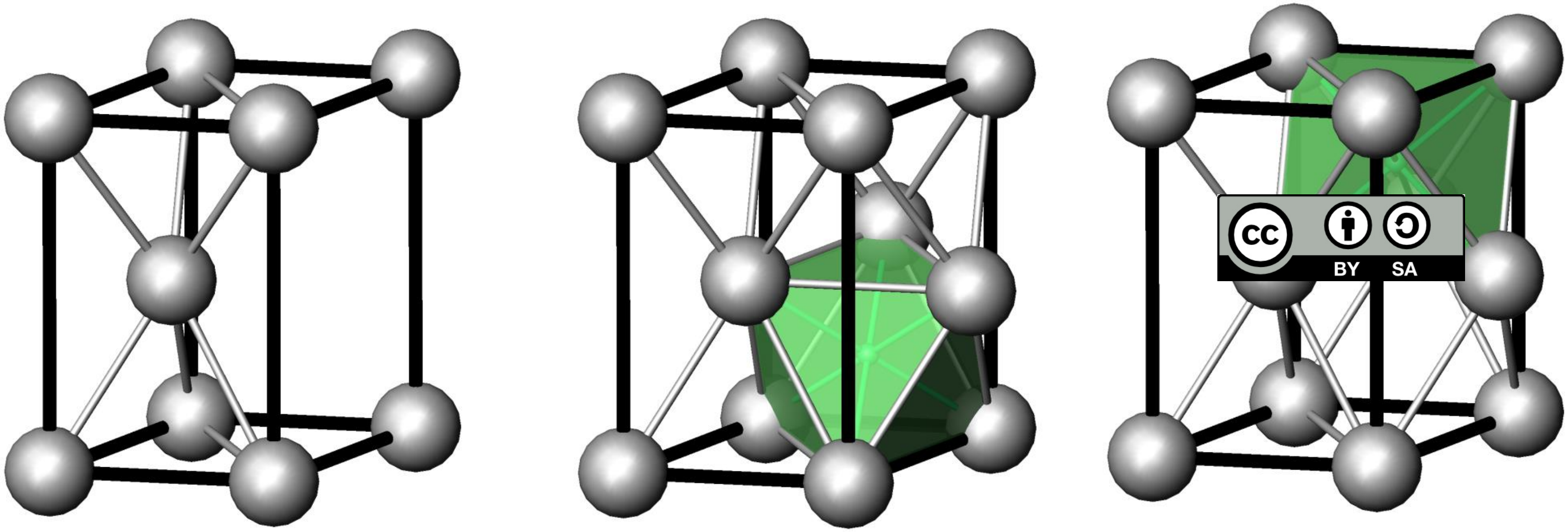


4 sites/unit cell
2 sites/closely packed atom

HCP: octahedral sites



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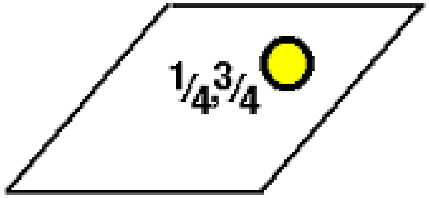
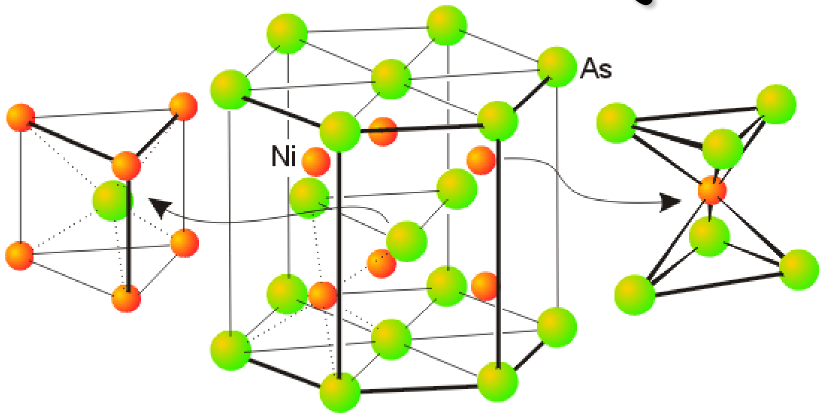
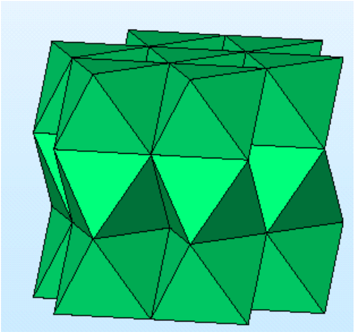
2 sites/unit cell
1 site/closely packed atom

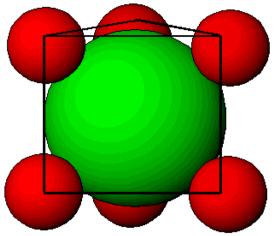


HCP variant of NaCl –NiAs (nickeline)

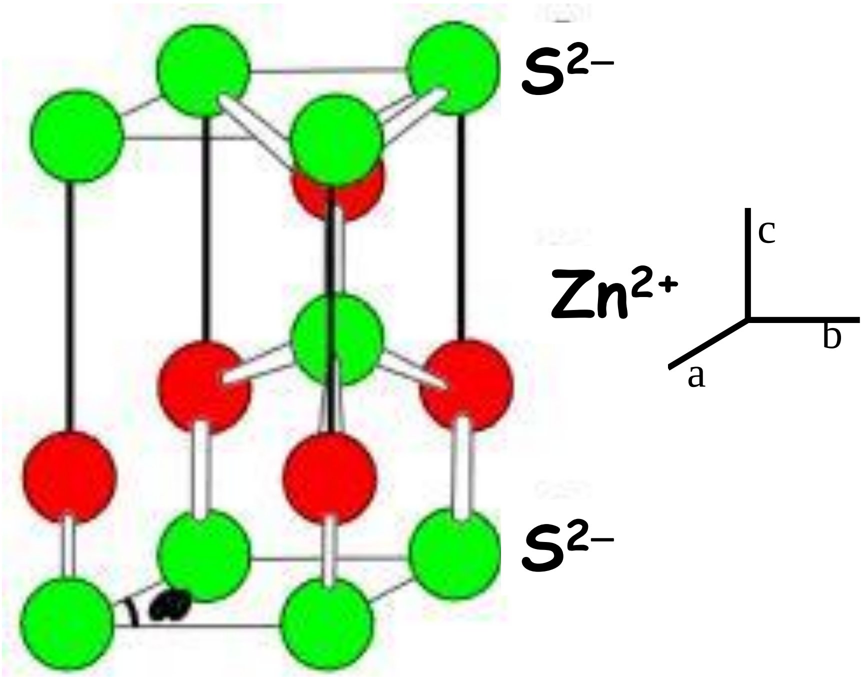




- *The HCP packing of cation and anions occupy all (2) Oh positions*
- *The cationic layers are superimposed*
- *CN = 6.6*
- *In the direction of the c-axis, the Ni-Ni distance is shortened. Overlapping orbitals lead to metal bonding*
- *The structure of NiAs is common for metallic compounds consisting of (a) transition metals with (b) elements which are occupied by the orbitals of As, Sb, Bi, S, Se. For example: NiS, FeS, CoS, PtSn ... ..*



ZnS wurtzite



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- HCP of S^{2-} with Zn^{2+} in the middle of tetrahedral cavities (T + {or T-})
- Stoichiometry of the cation: anion = 1: 1
- CN (Zn) = 4 (tetrahedral); CN (S) = 4 (tetrahedral)
- ZnS bleach and wurtzite are polymorphic modifications. Zn wurtzite is a high temperature ZnS
- Fractional coordinates: S (0,0,0) & (2/3,1/3,1/2); Zn (2/3,1/3,7/8) & (0,0,3/8)
- α-ZnS, α-CdS, α-SiC (semiconductors - crystallize in both polymorphic forms), AlN, BeO, ZnO.

Is there an HCP analogue of fluorite (CaF_2)?

- The structure of HCP with all filled tetrahedral positions (T + and T-) is not known (i.e., there is no HCP analog of fluorite or anti-fluorite structures).

- T+ and T-interstitial positions above and below the layer of tightly arranged spheres in HCP are too close to each other to allow Coulomb repulsive inte to be tolerated.

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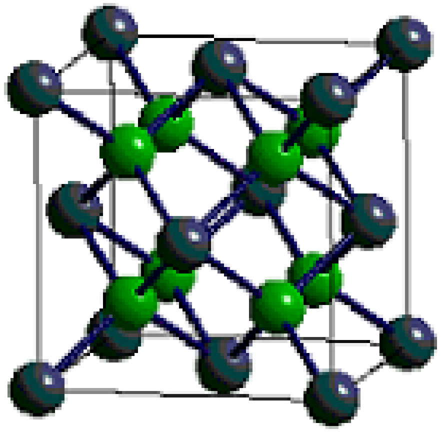
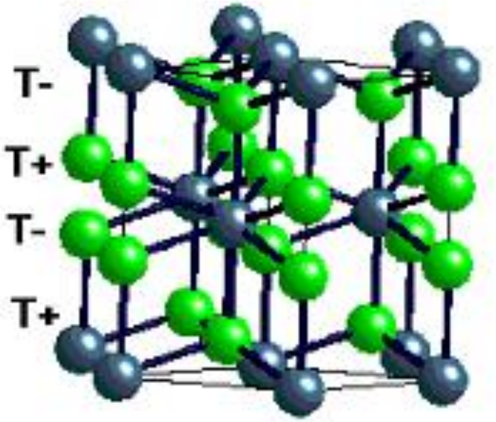
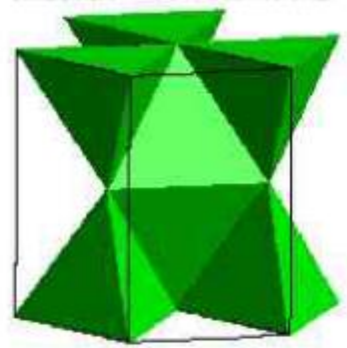


Fluorite





Unknown analog of fluorite of the HCP type

Summary

Anion	T_+	T_-	O	Structure
ccp	-	-	full	Halite, NaCl
ccp	full	-	-	Sphalerite, ZnS
ccp	full	full	-	Antifluorite, Na_2O
ccp	-	-	1/2	$CdCl_2$
hcp	-	-	full	
hcp	full	-	-	Wurtzite, ZnS
hcp	-	-	1/2	CdI_2
ccp	1/16	1/16	1/2	Spinel, $MgAl_2O_4$
hcp	1/8	1/8	1/2	Mg_2SiO_4
hcp	-	-	2/3	Corundum, Al_2O_3
ccp AO_3 ccp (only $\frac{3}{4}$)	- -	- -	1/4 1/4	Perovskite $CaTiO_3$ RhO_3

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Oxidic structures and networks

metal oxides are the most important solid inorganic substances

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AB_2: TiO_2

Representative	Radius of the ions TiO_2
TiO_2, PbO_2, GeO_2	0.52

Coordination number Ti^{4+}	Coordinating polyhedron	Radius of the cation (Å)
6	Octahedral	0.68

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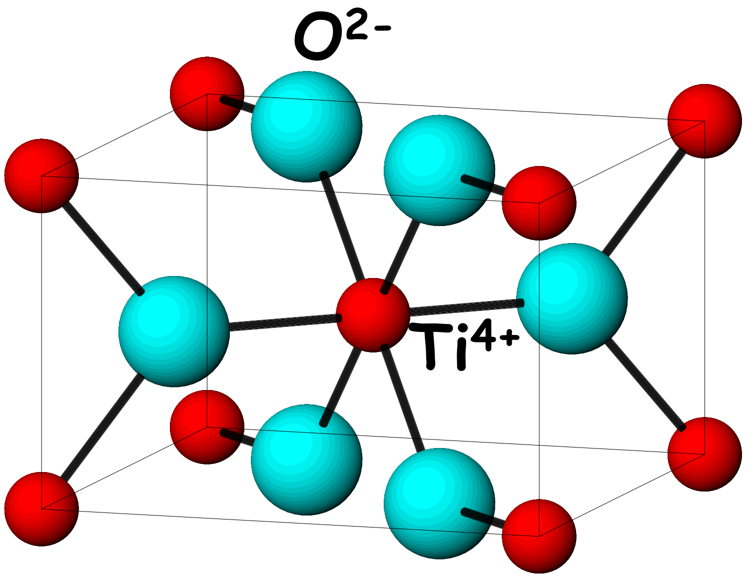
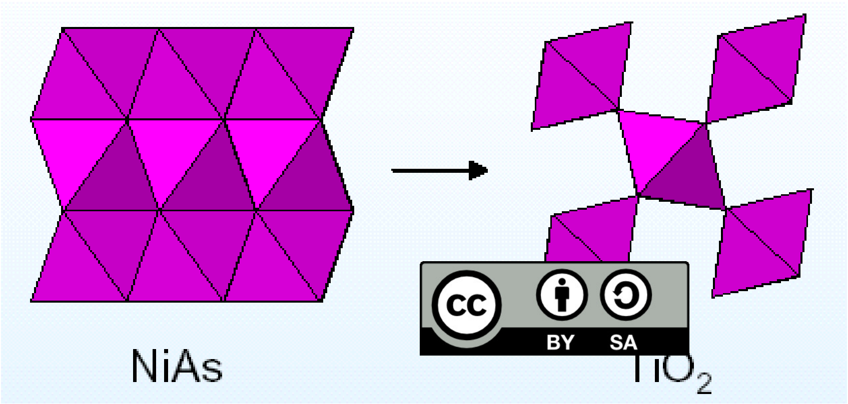
Coordination number O^{2-}	Coordinating polyhedron	Radius of the cation (Å)
3	triangle	1.32

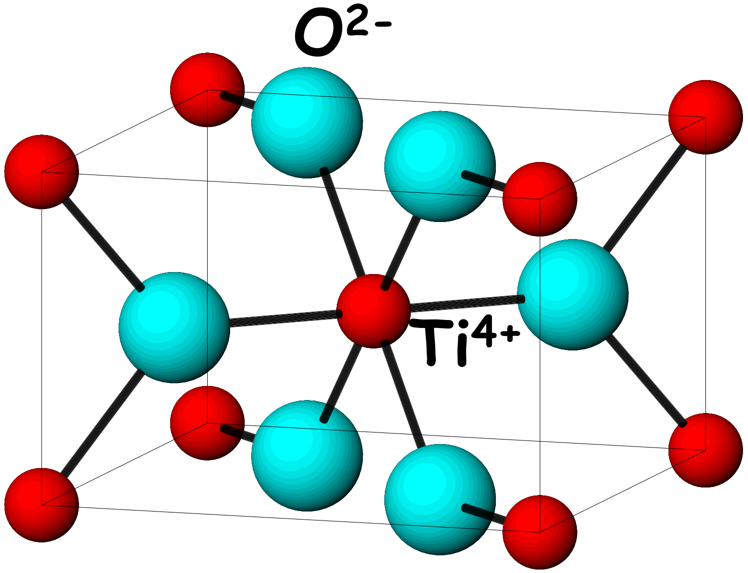
Rutile TiO_2 stoichiometry AB_2

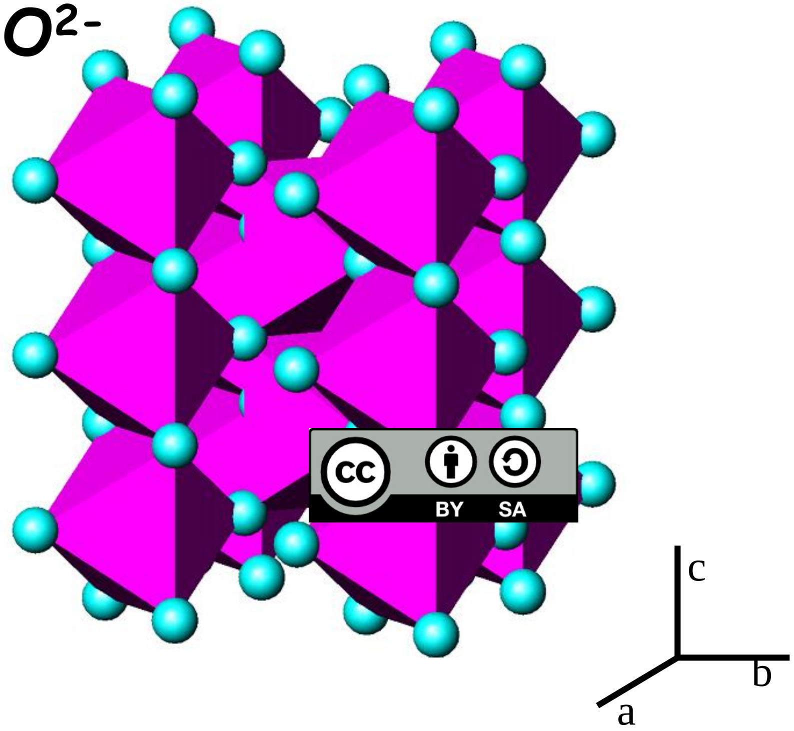




- ·The radii ratio radii TiO_2 = 0.59 assumes CN=6. This is not the closest packing
- ·Distorted HCP O^{2-} with Ti in 1/2 of the octahedral positions
- ·Tetragonal unit cell ($a = b \neq c$)
- ·CN (Ti) = 6; CN (O) = 3
- ·Edge-shared Ti-O octahedron strings

Rutile TiO_2 stoichiometry AB_2





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Spinel

- Oxides with magnetic properties
- AB_2O_4 ($MgAl_2O_4$) - a structural combination of NaCl and ZnS
- The oxygen atoms form the FCC
- Normal spinel - $[A]_{tetr}$ $[B_2]_{oct}O_4$
- There are different charge combinations (ratio cation:anion = 3:4)
- The repulsion between the cations leads to the fact that adjacent tetrahedral and octahedral positions are not occupied simultaneously

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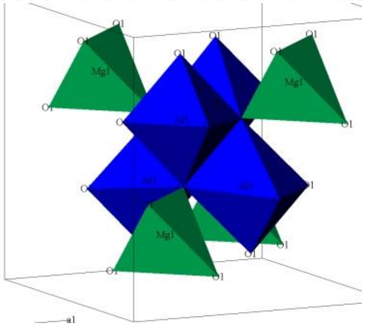


What is the O coordination in the spinel structure?

$4 \times 1 = (\text{CN of } O_{Mg}) \times 4$

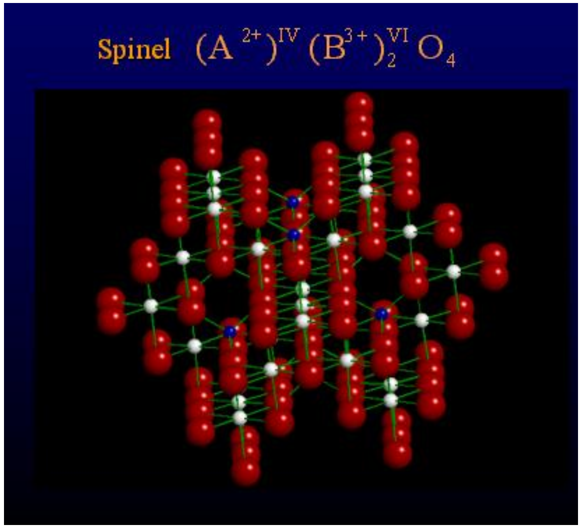
$\text{CN of } O_{Mg} = 1$

$6 \times 2 = (\text{CN of } O_{Al}) \times 4$

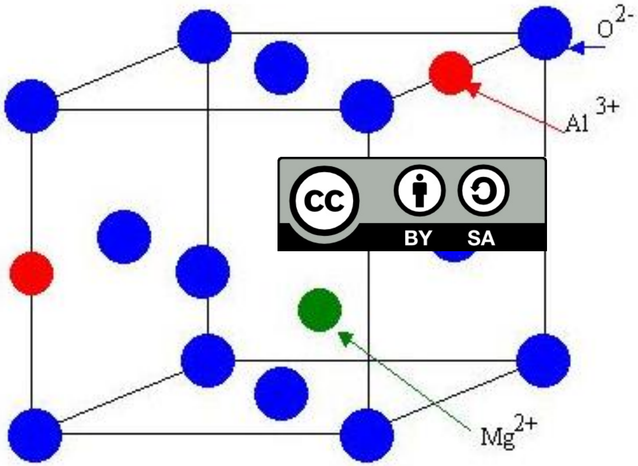
$\text{CN of } O_{Al} = 3$

In one form of the spinel unit there are 4 oxygen atoms. In the closest packing, there are two tetrahedral and one octahedral positions per anion. In theory, 8 tetrahedral and 4 octahedral positions should be possible in the spinel:

Mg fills 1/8 of all possible tetrahedral positions
Al fills 1/2 of all possible octetric positions



Structurel of common spinel ($MgAl_2O_{4.}$)



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Cut out of the spinel structure ($MgAl_2O_{4.}$)

In one form of the spinel unit there are 4 oxygen atoms. In the closest packing, there are two tetrahedral and one octahedral positions per anion. In theory, 8 tetrahedral and 4 octahedral positions should be possible in the spinel:

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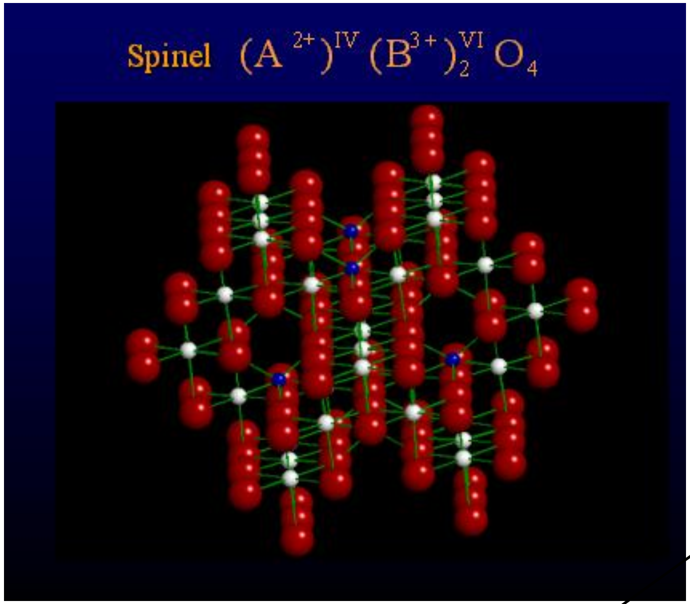
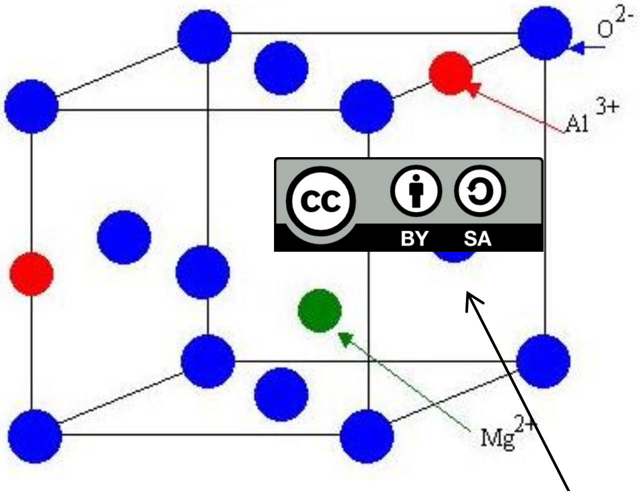


Structure of common spinel ($MgAl_2O_4$.)



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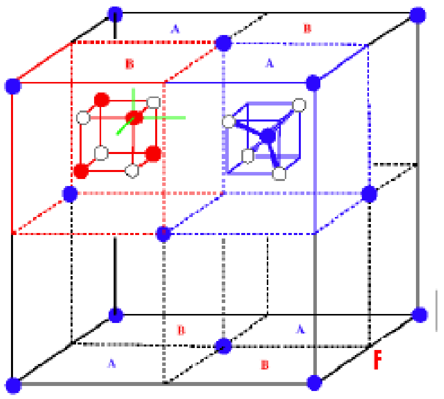
Cut out of the spinel structure ($MgAl_2O_4$.)

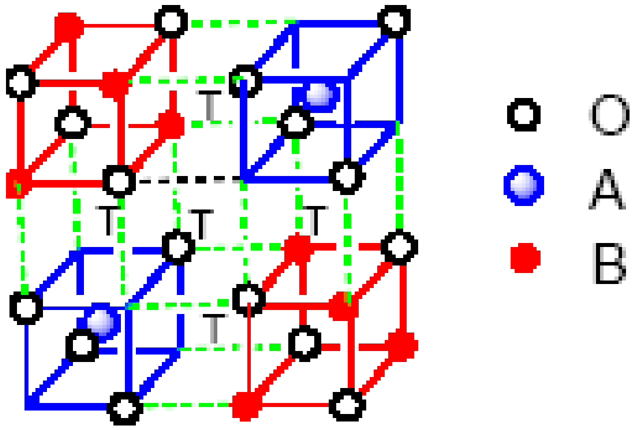
NaCl Structural combination ZnS

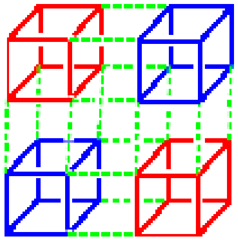
The complete unit cell requires the presence of 32 atoms of O, 16 atoms of Al, and 8 atoms of Mg

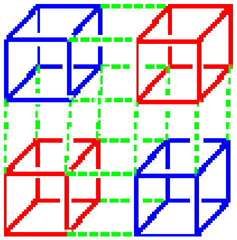
Crystal structure of the spinel AB_2O_4

1. The basis of the cube structure based on ccp ion A and its distribution into eight small cubes.






Front


Back side

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The complete elementary cell requires the presence of 32 atoms of O, 16 atoms of Al, and 8 atoms of Mg

2. Paste cubes of B_4O_4 into half T_d, it means $A_{1/2}B_4O_4$
3. To the second half of T_d add AO_4 cubes, *it is* $A_{3/2}O_4$

4. STOICHIOMETRY = $A_{1/2}B_4O_4 + A_{3/2}O_4 = A_2B_4O_8 = AB_2O_4$

ABX_3: Perovskite

Representative	Radius of the ions
$CaTiO_3$, $BaTiO_3$	$Ca^{2+}:O^{2-}$= 0.75, $Ti^{4+}:O^{2-}$=0.52

Coordination number Ca^{2+}	Coordinating polyhedron	Radius of the cation (Å)
12	Cubic-octahedral	0.9

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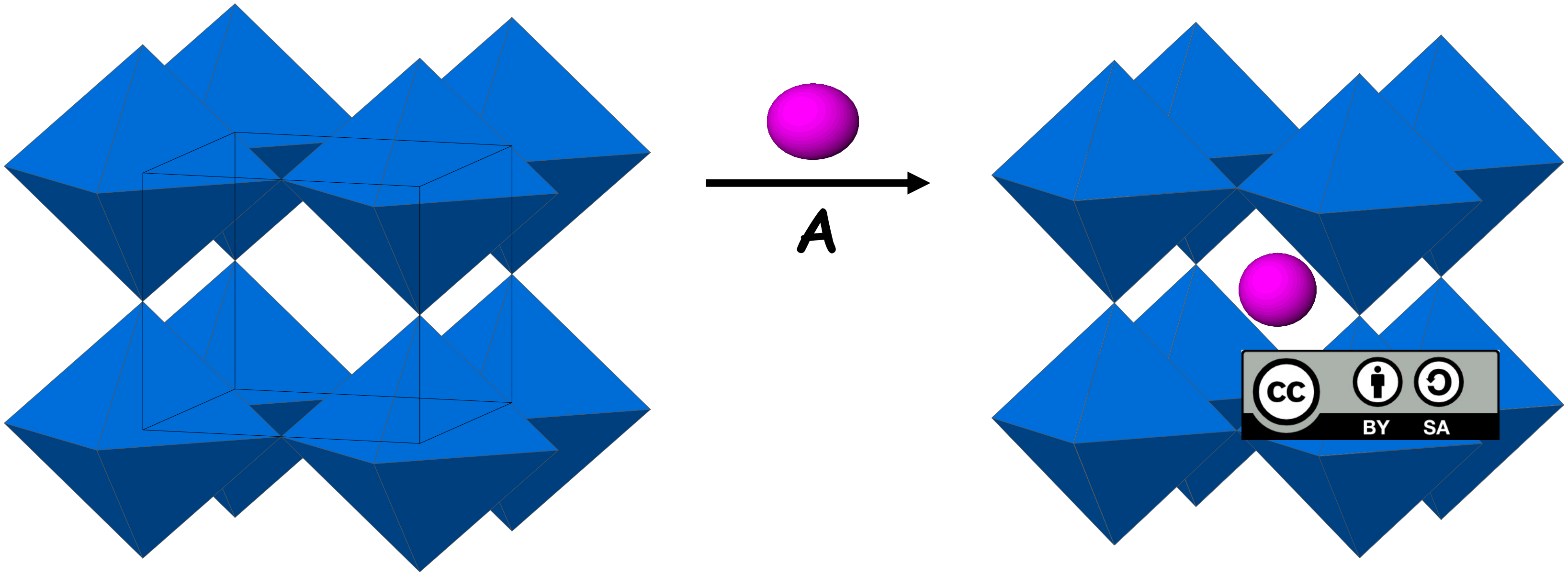
Coordination number Ti^{4+}	Coordinating polyhedron	Radius of the cation (Å)
6	Octahedral	0.68

Coordination number O^{2-}	Coordinating polyhedron	Radius of the cation (Å)
4	Square	1.32

Ternary compounds

Structure of perovskite ABX_3



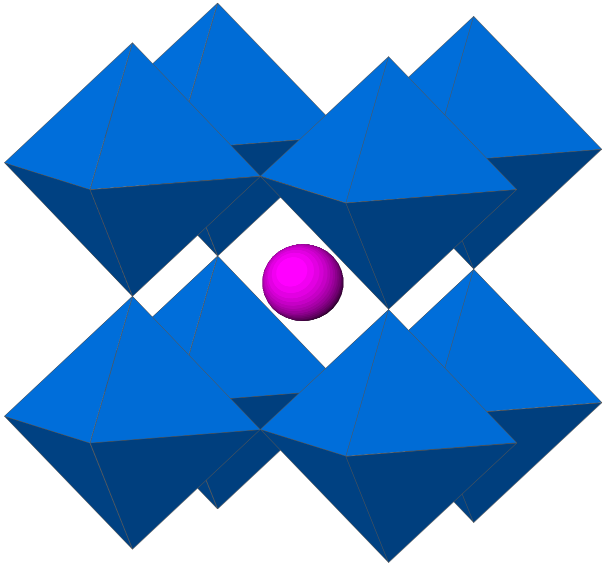
ReO_3 (BX_3)

$CaTiO_3$ (ABX_3)

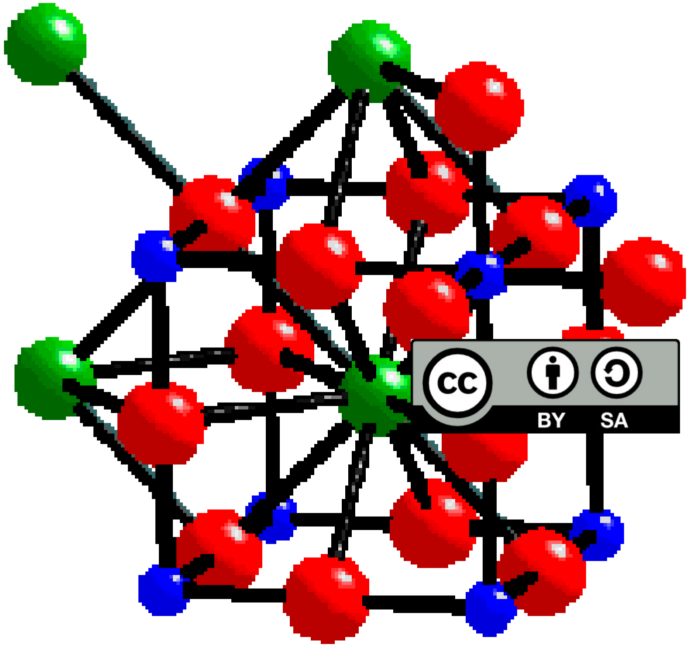
- A is a larger cation than B
- CCP packing of A and O atoms with cation B occupying octahedral cavities CN (B) = 6; CN (A) = 12; CN (O) = 6 (4A + 2B)
- High Tc superconductors are based on the perovskite structure

Ternary compounds

Structure of perovskite ABX_3



$CaTiO_3$ (ABX_3)



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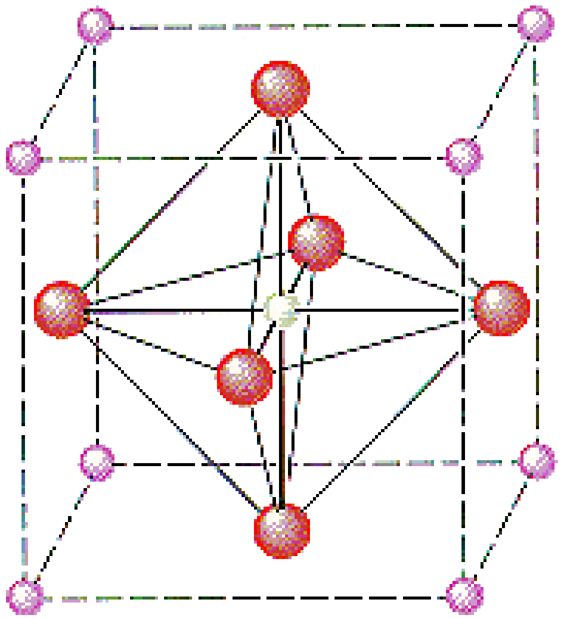
Structure of perovskite



Perovskite ($CaTiO_3$)

○ = Ti^{IV} ○ = Ca^{2+} ● = O^{2-}

- ABO_3
- CCP of the A atoms (larger) in corners
- O atoms in the centers of faces
- smaller atoms B are in the middle of the unit cell (occupy 25% of octahedral sites)

Ca fills the vacant site ccp in ReO$_3$, = CaO$_3$ ccp packing

Materials with perovskite structure are often characterized by interesting electrical properties (eg piezoelectricity, ferroelectricity and high temperature superconductivity).

Coordination and stoichiometry

General coordination balance

In the case of an ionic or covalent compound of more complex composition AaBbCc ... ..Xx - where A, B, C ... are cations and X - anions.
In the existence of only the cation-anion bond, we get a relationship:

$$a.CN(A) + b.CN(B) + c.CN(C) + \ldots = x.CN(X)$$

Specifically for perovskite it is: 1x12 (Ca) + 1x6 (O)

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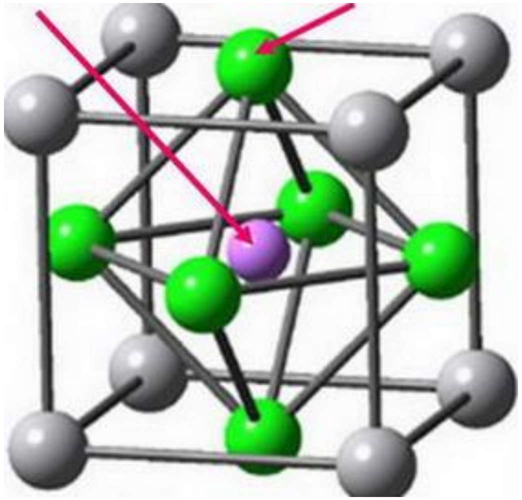

Ti (KČ=8)

O (2Ti + 4Ca)

Ca (CN=12)

Sorting of structures

- Coordination
- Isolated
- Chain-like
- Layered
- Skeletal

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Silicates

Composed mostly from Si a O

Charge equilibrium: $Si^{4+}:O^{2-} = 1:2 \longrightarrow SiO_2$

Radius ratio: $$\frac{R_{Si^{4+}}}{R_{O^{2-}}} = \frac{0.040nm}{0.140nm} = 0.286 \longrightarrow$$ **CN = 4 (Tetrahedral coordination)**

Table 12.3 Ionic Radii for Several Cations and Anions (for a Coordination Number of 6)

Cation	Ionic Radius (nm)	Anion	Ionic Radius (nm)
Al^{3+}	0.053	Br^-	0.196
Ba^{2+}	0.136	Cl^-	0.181
Ca^{2+}	0.100	F^-	0.133
Cs^+	0.170	I^-	0.220
Fe^{2+}	0.077	O^{2-}	0.140
Fe^{3+}	0.069	S^{2-}	0.184
K^+	0.138		
Mg^{2+}	0.072		
Mn^{2+}	0.067		
Na^+	0.102		
Ni^{2+}	0.069		
Si^{4+}	0.040		
Ti^{4+}	0.061		

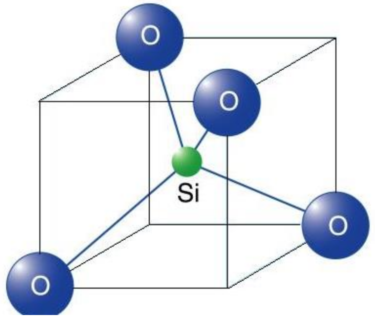
However:

% of ionic character = 51%

(a relatively low [illegible] ionic character, substantial covalent contribution)

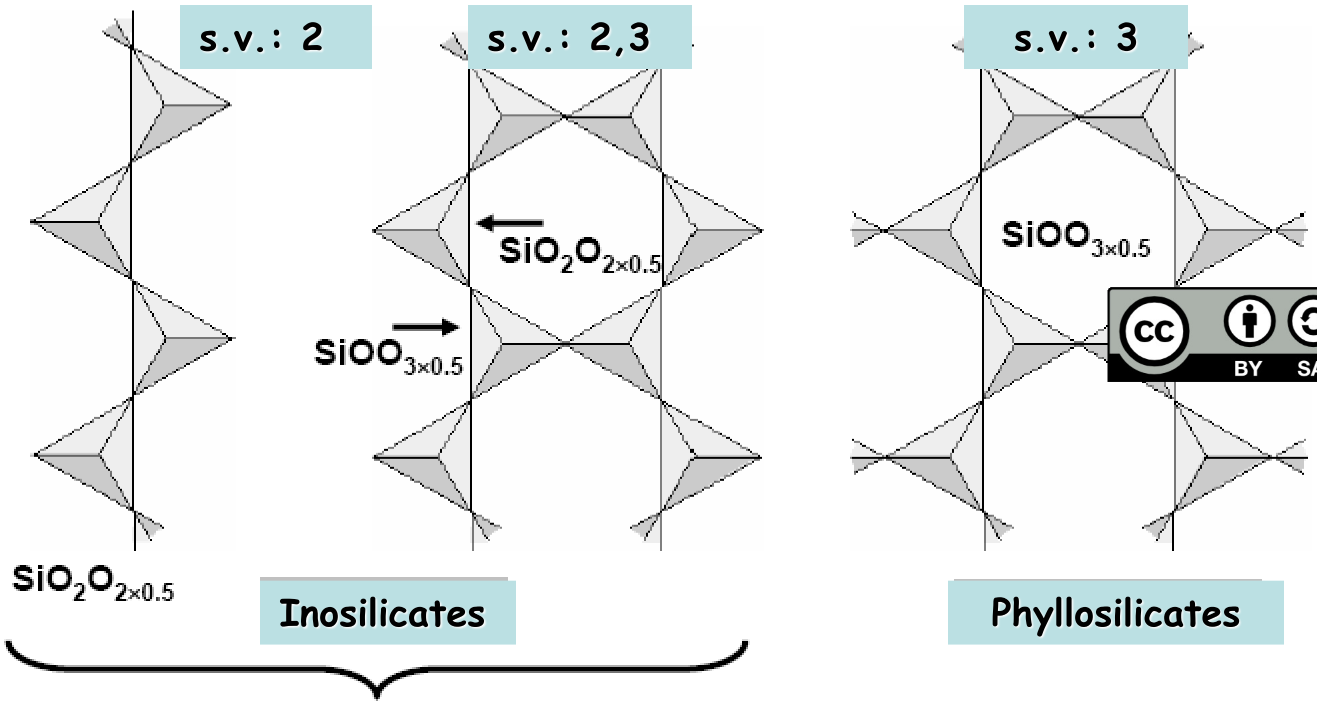
What structures we can expect?

Tetrahedron silicate unit



Structure of silicates

from simple building blocks to complex structures



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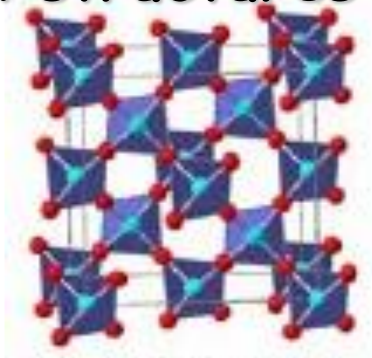
simple chain of SiO_3^{2-}
pyroxene: $(Mg,Fe)SiO_3$

double-chain of $Si_4O_{11}^{6-}$
amphibole:
tremolite $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$

$Si_2O_5^{2-}$ biotite:
$K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$

Structure of silicates

from simple building blocks to complex structures



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Tectosilicates: shared vertexes: 4, SiO_2

Zeolites: Faujasite: $Ca_{28.5}Al_{57}Si_{135}O_{384}$

Pores ↘ $A_{x/n}\underbrace{[Si_{1-x}Al_xO_2]}\cdot mH_2O$ ↙ Pores

T (=Si,Al)O_4-Tetrahedra share all of its vertexes,
isomorphic Si^{4+} exchange, charge cation compensation
copying Al content in the skeleton, charge of the microporous matrix
n: charge of cation A

- Zeolites – aluminosilicates with open cavity channels
- (d <2 nm, "boiling stones")
- Many applications: adsorbents, catalysis ...