Quantum electronics

1

Geometry of solid state

IFM PAN

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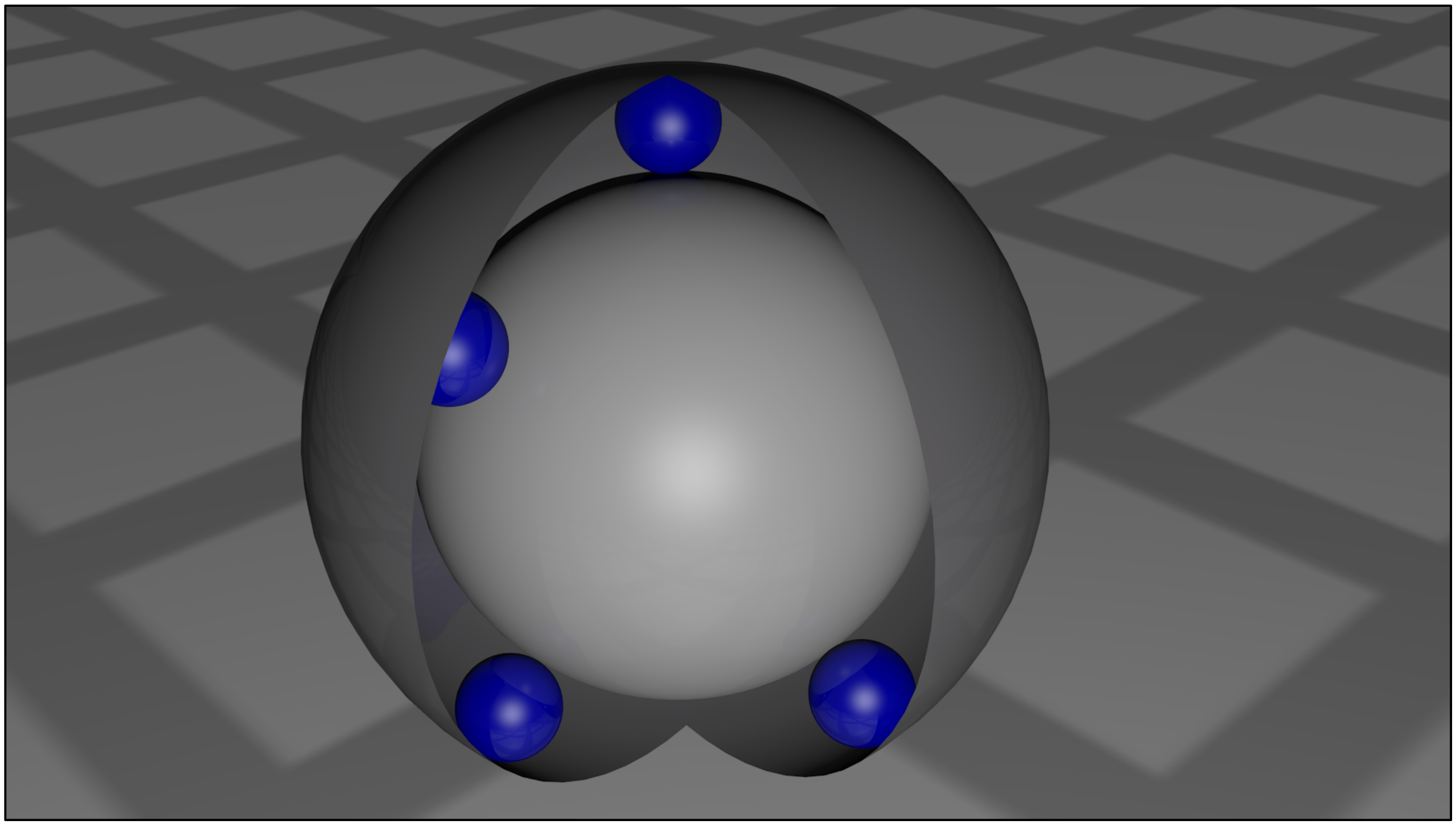
Politechnika Poznańska 2017

Geometry of solid state

- Constraints and order
- Symmetry properties of crystals

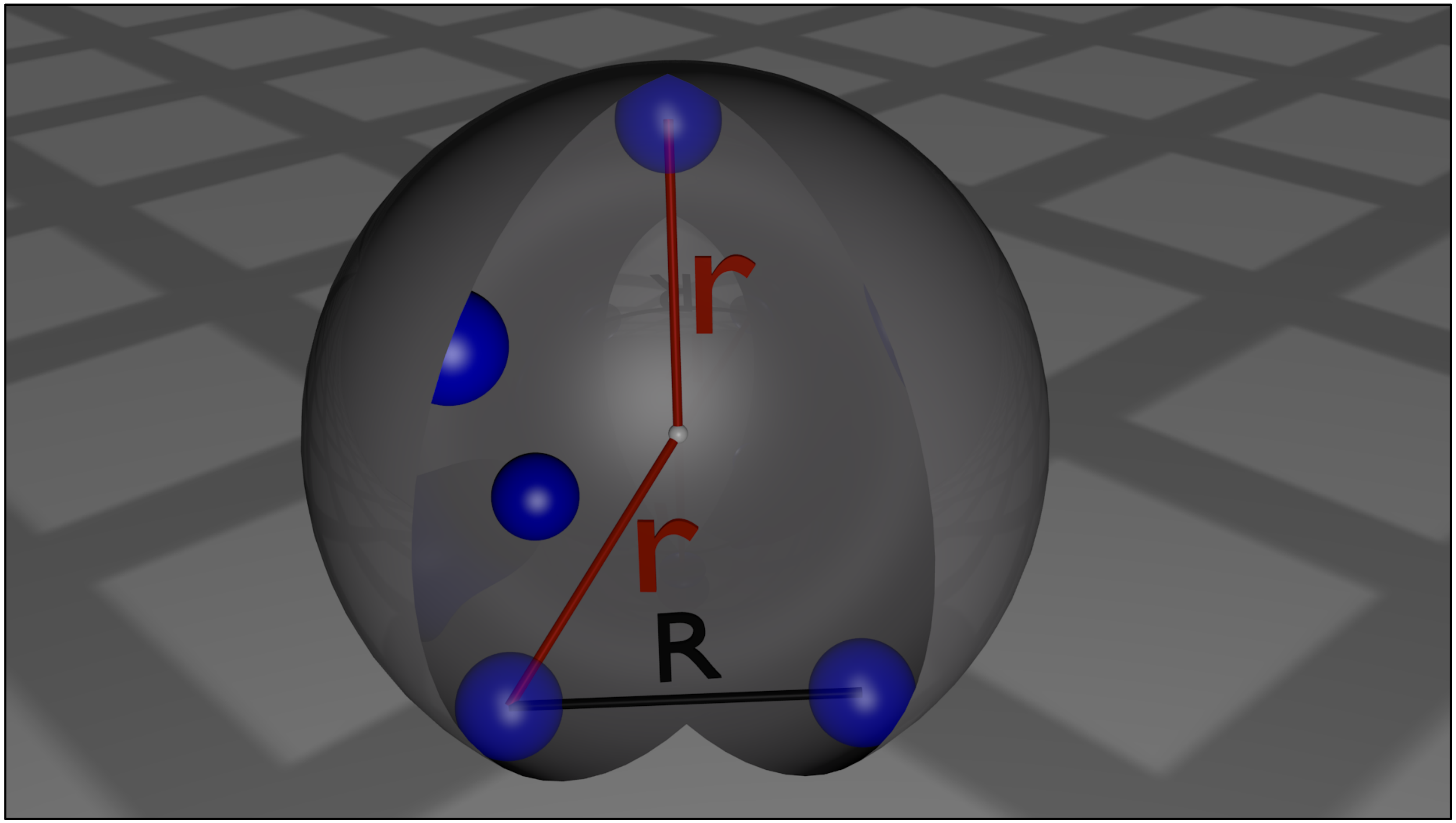
- Minimum electrostatic energy configuration for n electrons constrained to a surface of a sphere
- **Electrons** interact (repel each other) according to Coulomb's law



$$F \propto \frac{1}{R^2}$$

- The problem is related to the early (“pre quantum”) investigations of electrons in atoms [1]

- Minimum electrostatic energy configuration for n electrons constrained to a surface of a sphere
- **Electrons** interact (repel each other) according to Coulomb's law



$$F \propto \frac{1}{R^2}$$

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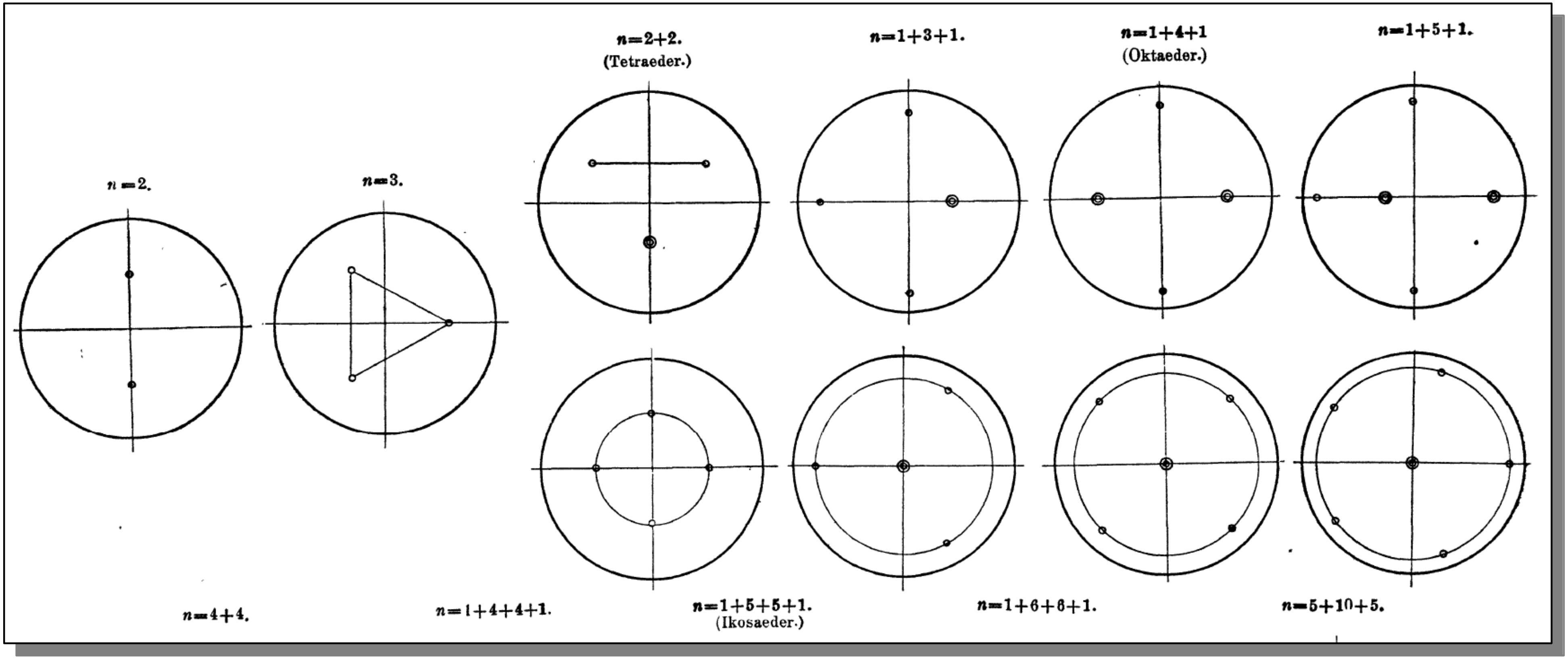
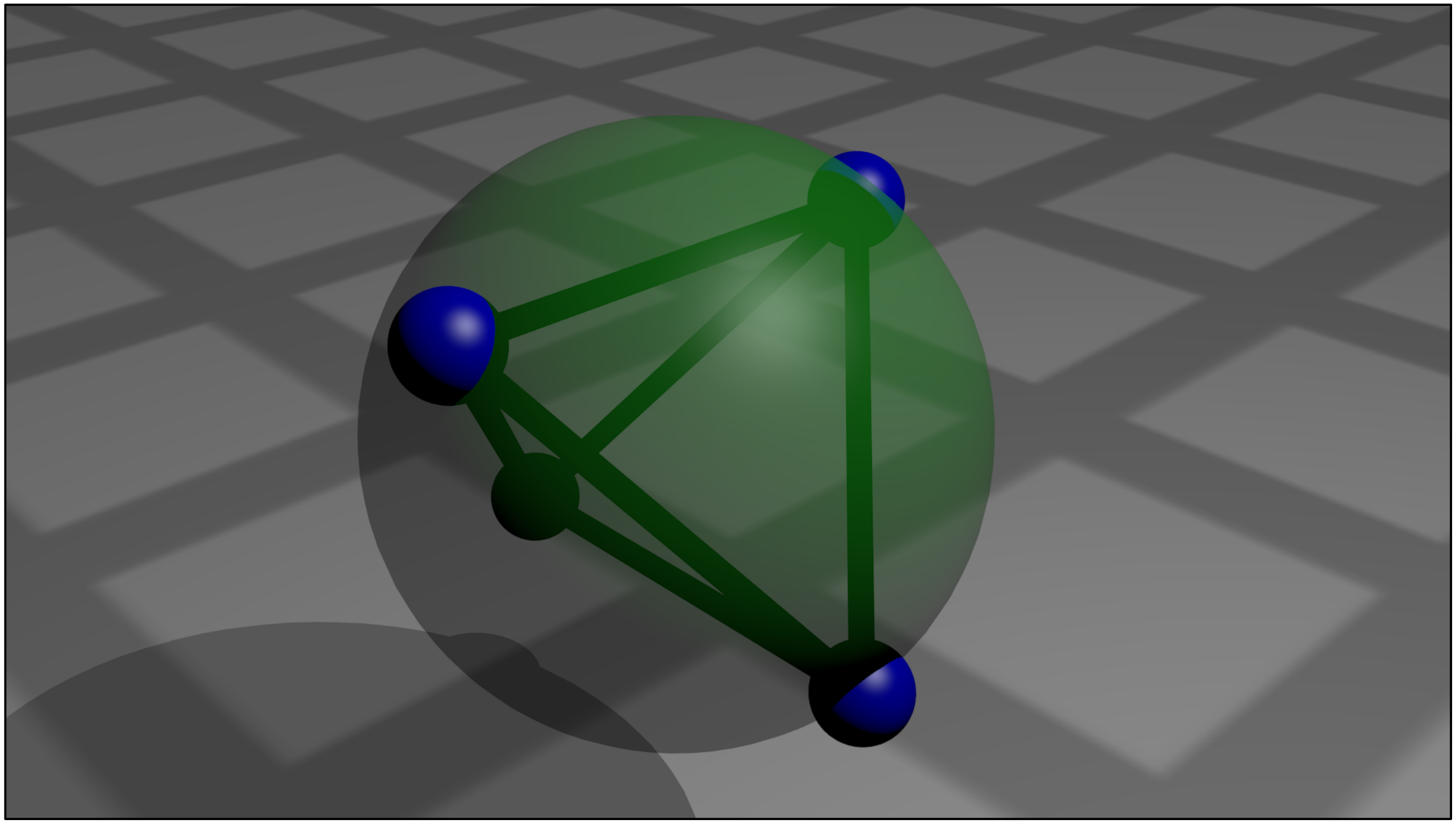


Image source: L. Föppl, Journal für die reine und angewandte Mathematik 141, 251 (1912) [6]

- The drawing shows stable configurations of electrons as determined by L. Föpll [1]

- Minimum electrostatic energy configuration for n electrons constrained to a surface of a sphere
- **Electrons** interact (repel each other) according to Coulomb's law



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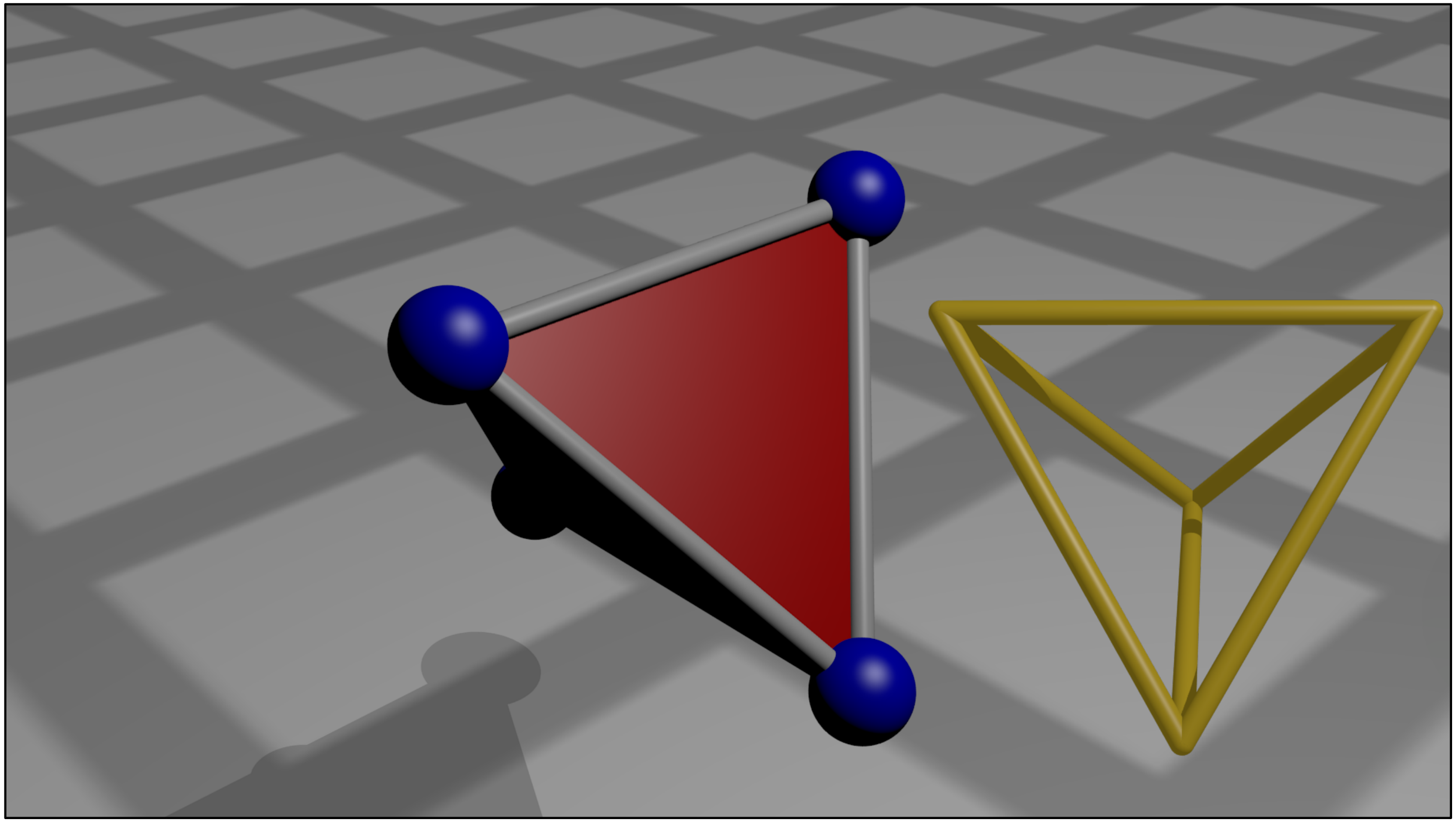
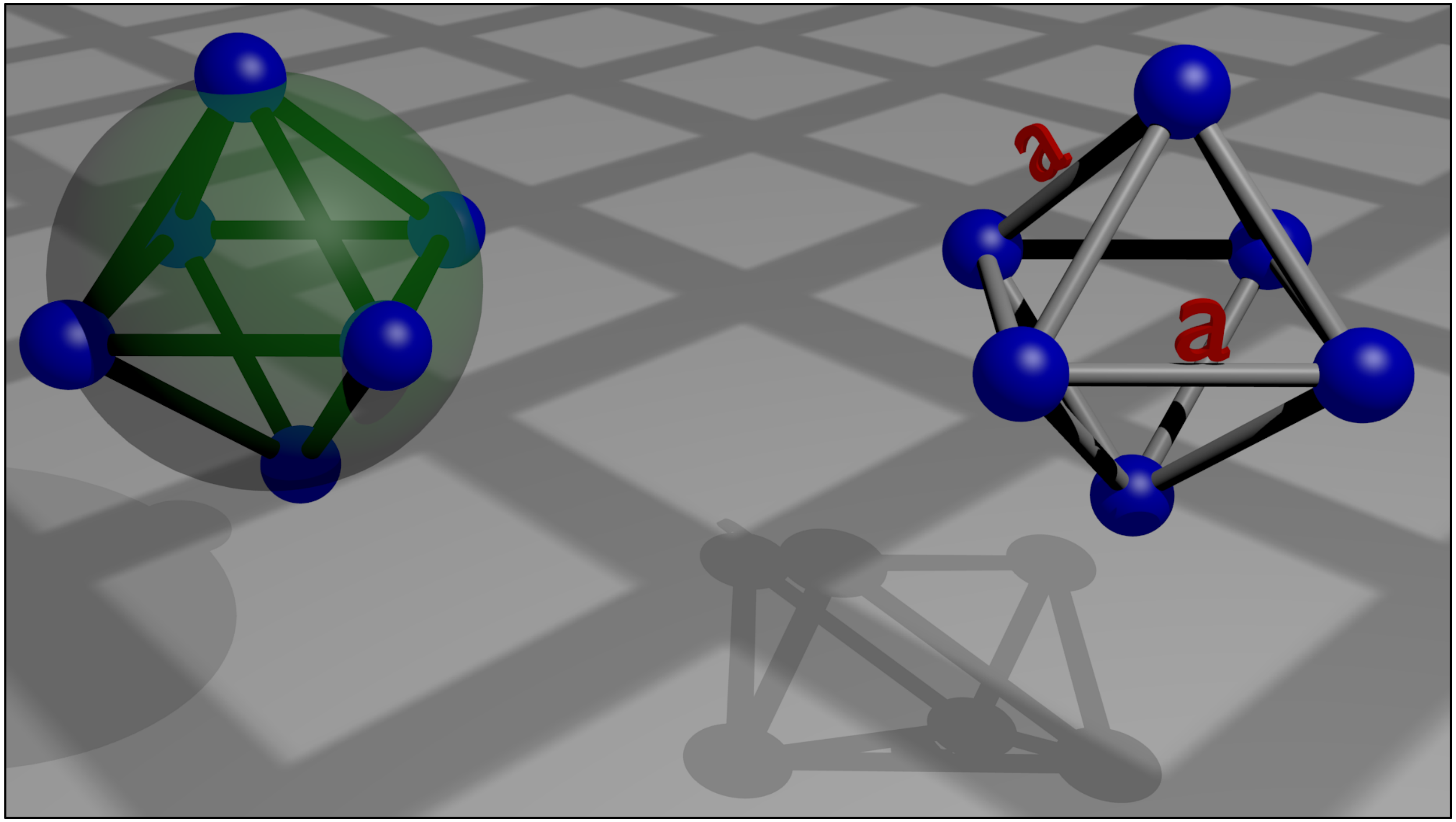


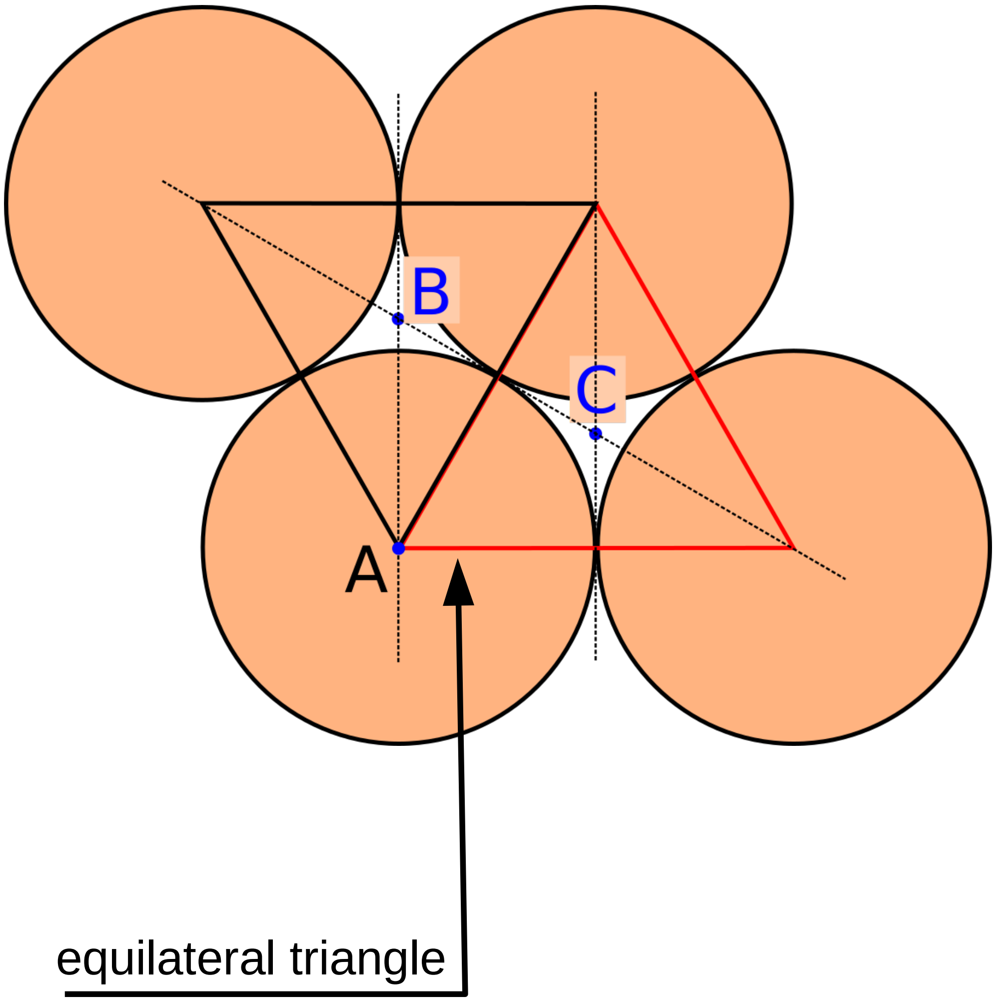
$$F \propto \frac{1}{R^2}$$

- Case of 6 electrons

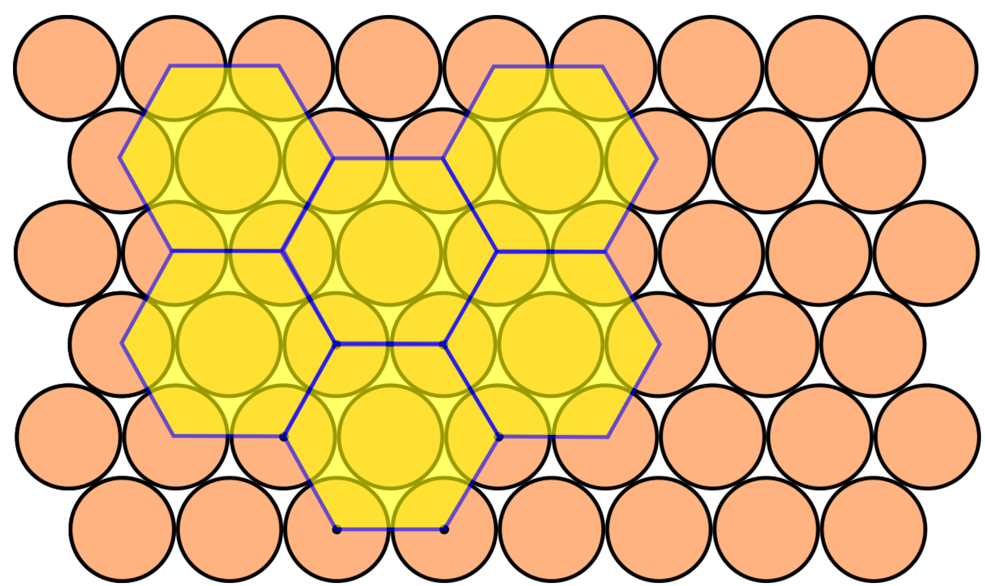


$$F \propto \frac{1}{R^2}$$

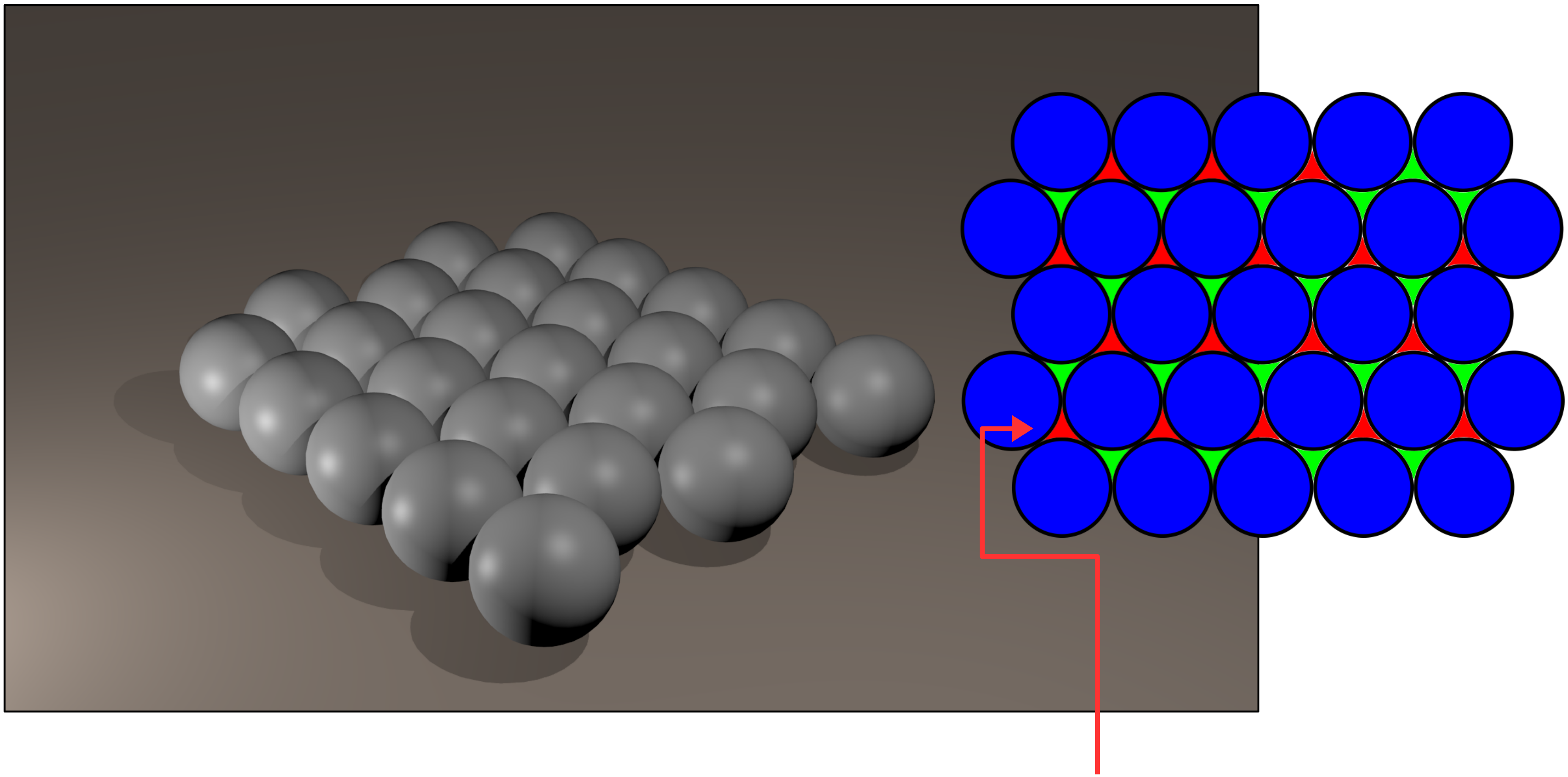
- How to arrange hard spheres to fill the space most effectively (to have as little empty space between them as possible)?
- First try to do this in 2D:



Hexagonal structure



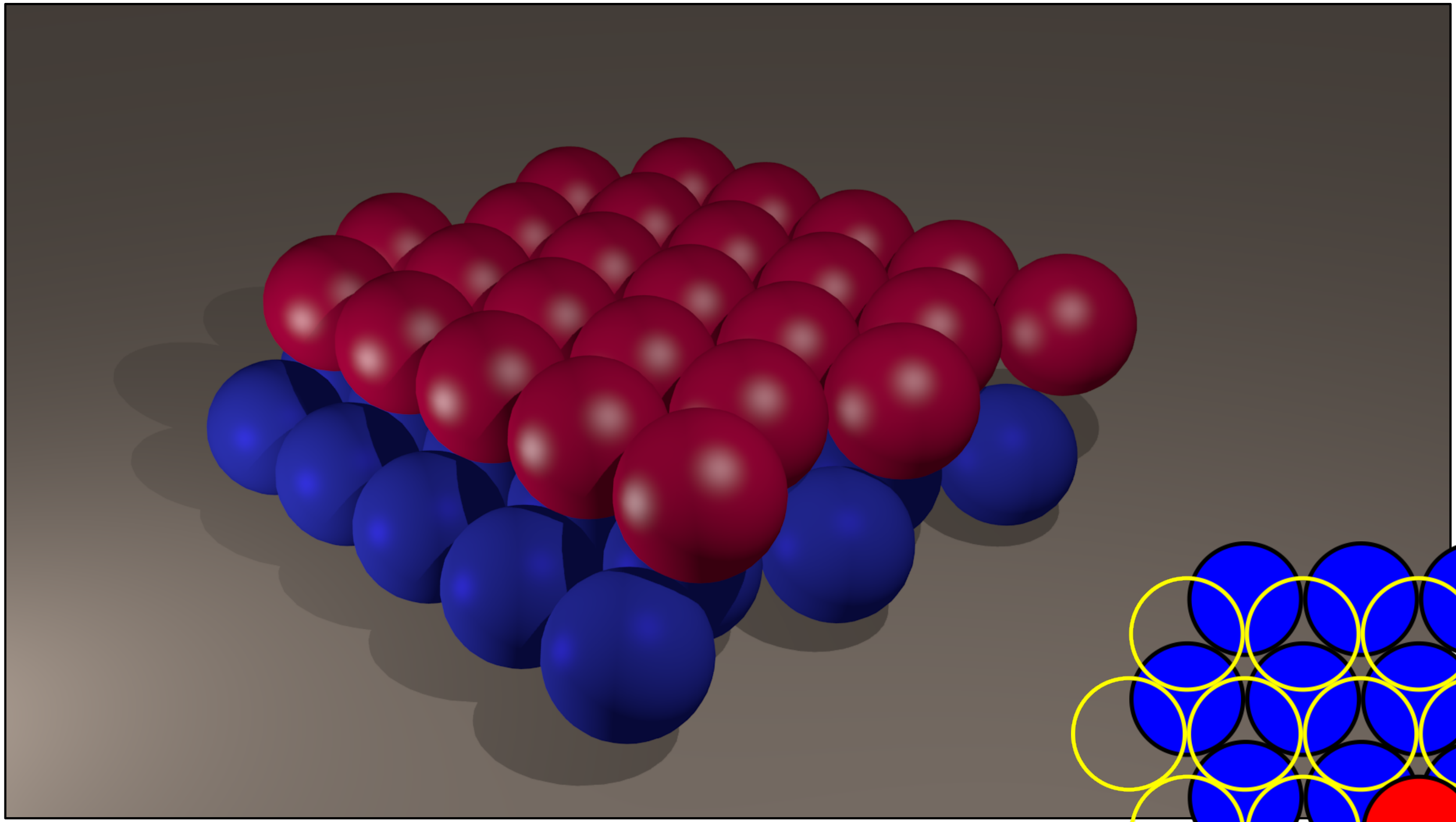
- How to arrange hard spheres to fill the space most effectively (to have as little empty space between them as possible)?
- And in 3D:

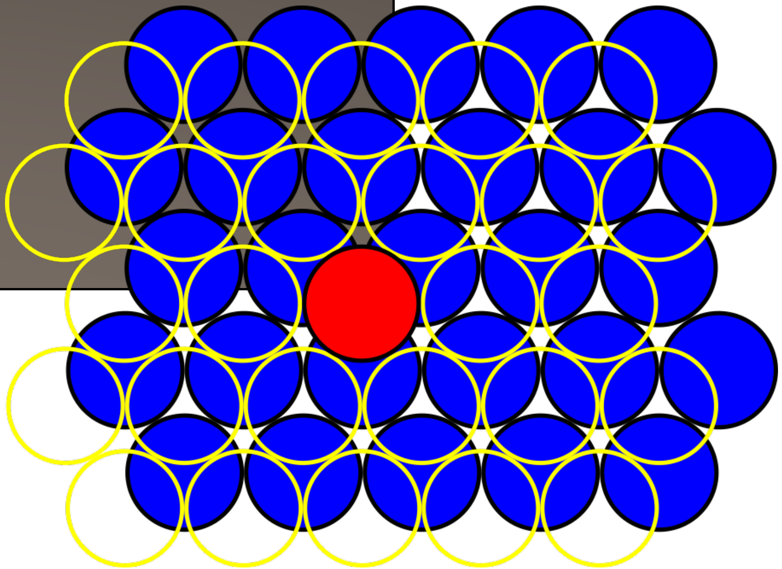


- Single layer of spheres has three times as many interstitials (**B** and **C**) as there are spheres (see schematic on previous page)

Close packing of equal spheres

- How to arrange hard spheres to fill the space most effectively (to have as little empty space between them as possible)?
- And in 3D:

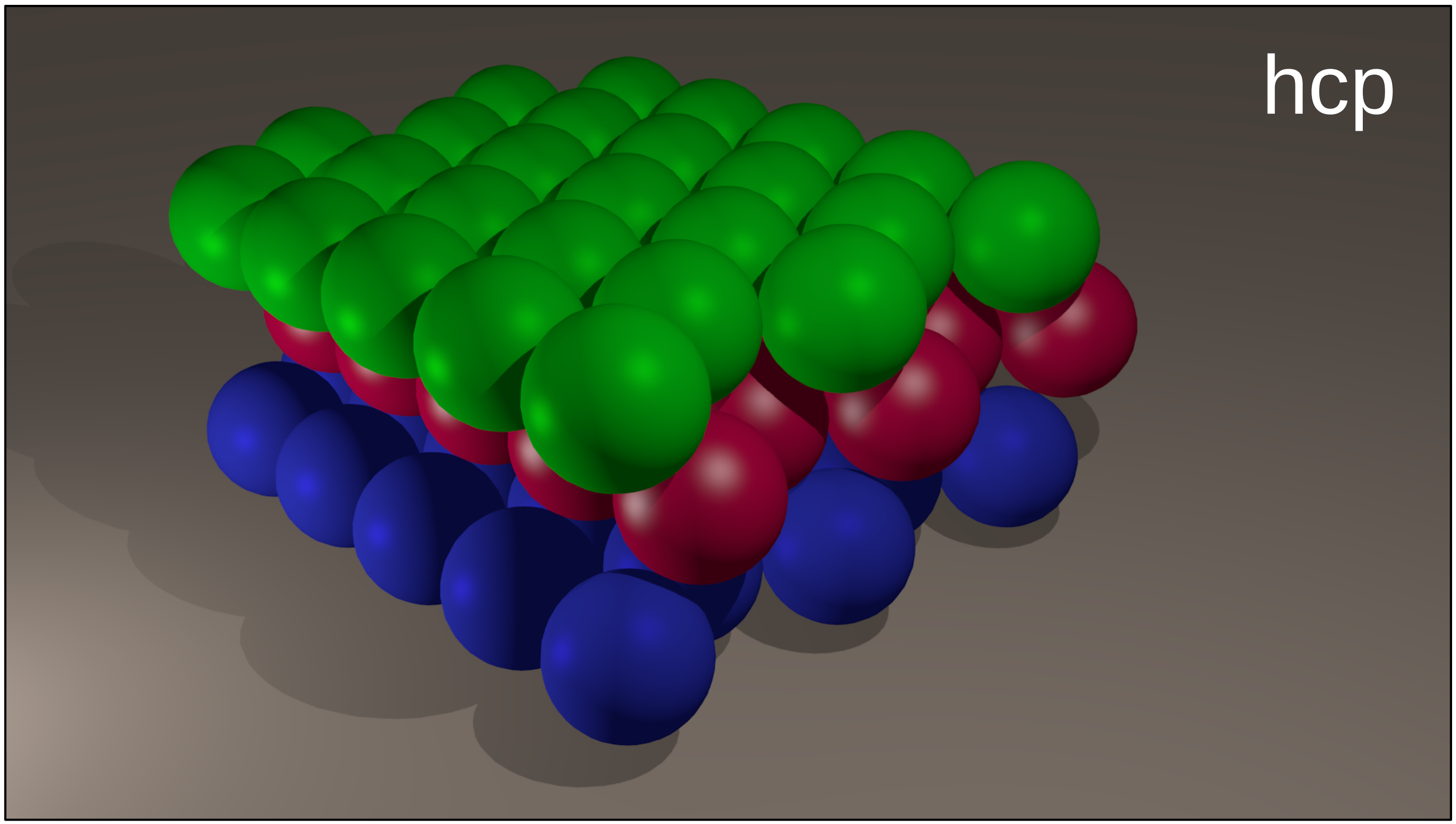




- The next, identical, layer of spheres can be put onto B or C sites

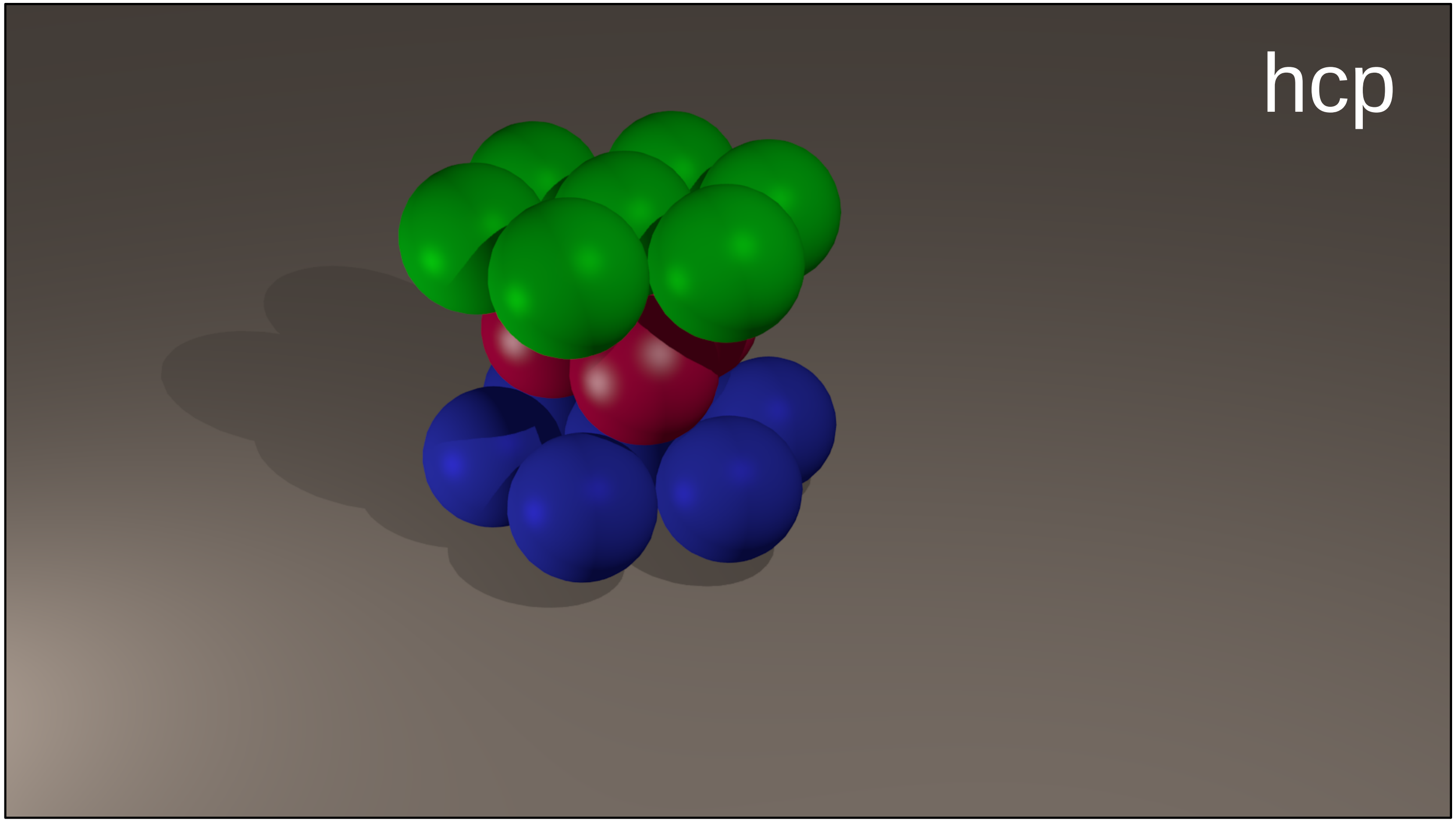
Close packing of equal spheres

- How to arrange hard spheres to fill the space most effectively (to have as little empty space between them as possible)?
- And in 3D:



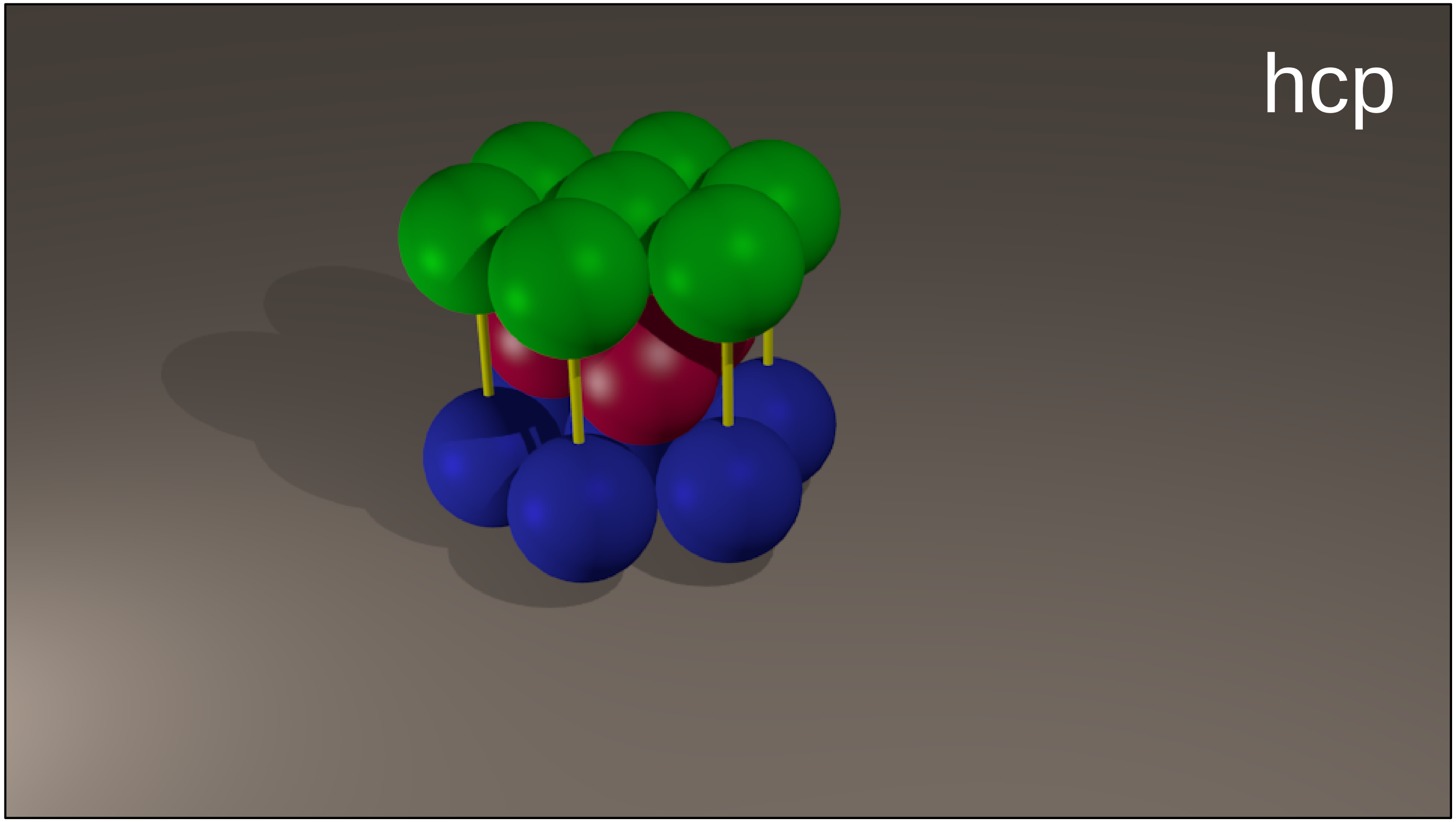
- The third layer of spheres can be put onto B or C sites of the second layer
- For ABAB… sequence the structure is called hexagonal close packed (hcp)
- For ABCABC… sequence the structure is cubic close packed or face centered cubic (see later)

- How to arrange hard spheres to fill the space most effectively (to have as little empty space between them as possible)?
- And in 3D:



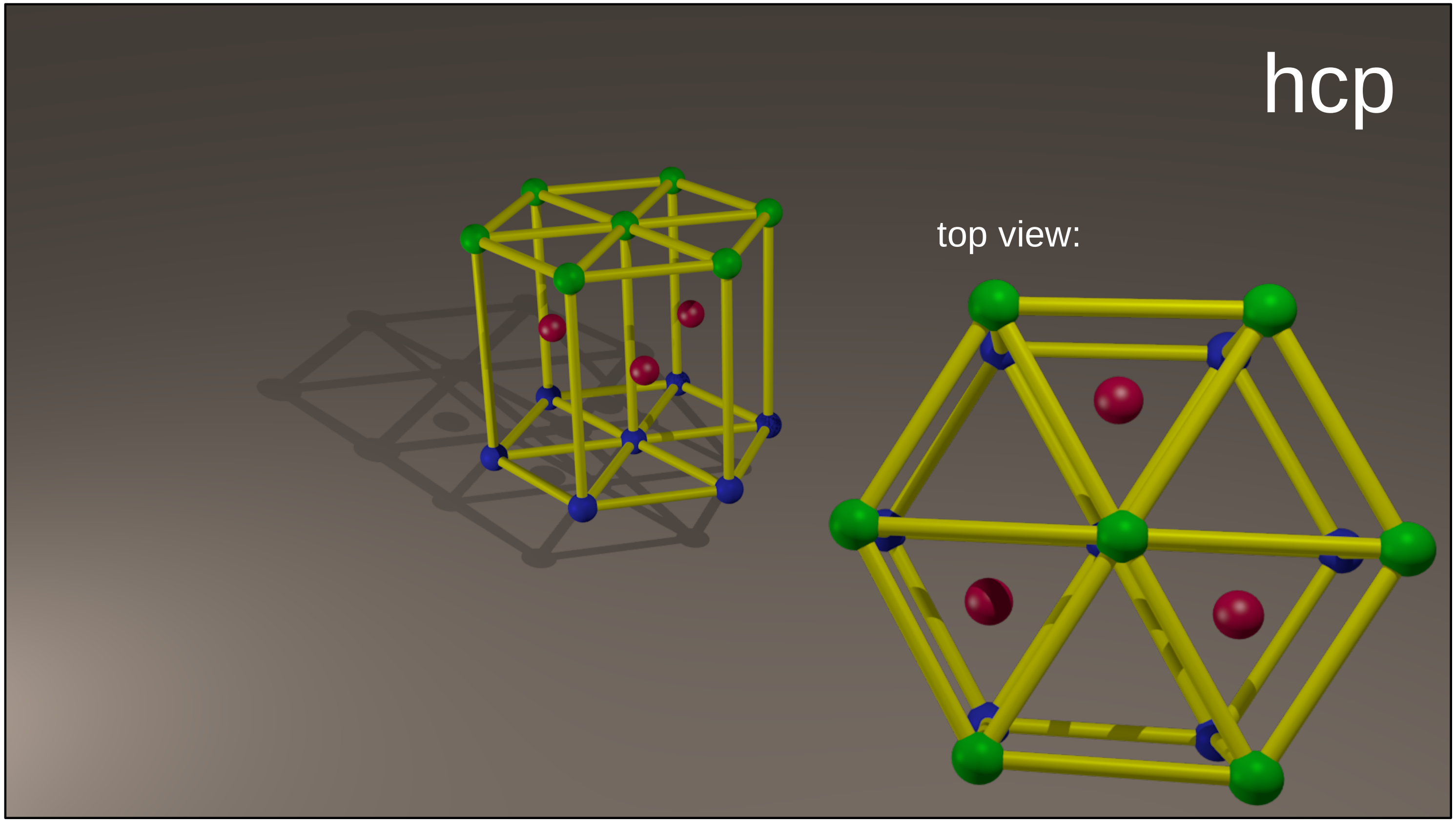
- The third layer of spheres

- How to arrange hard spheres to fill the space most effectively (to have as little empty space between them as possible)?
- And in 3D:



- We add the lines connecting the centers of the spheres

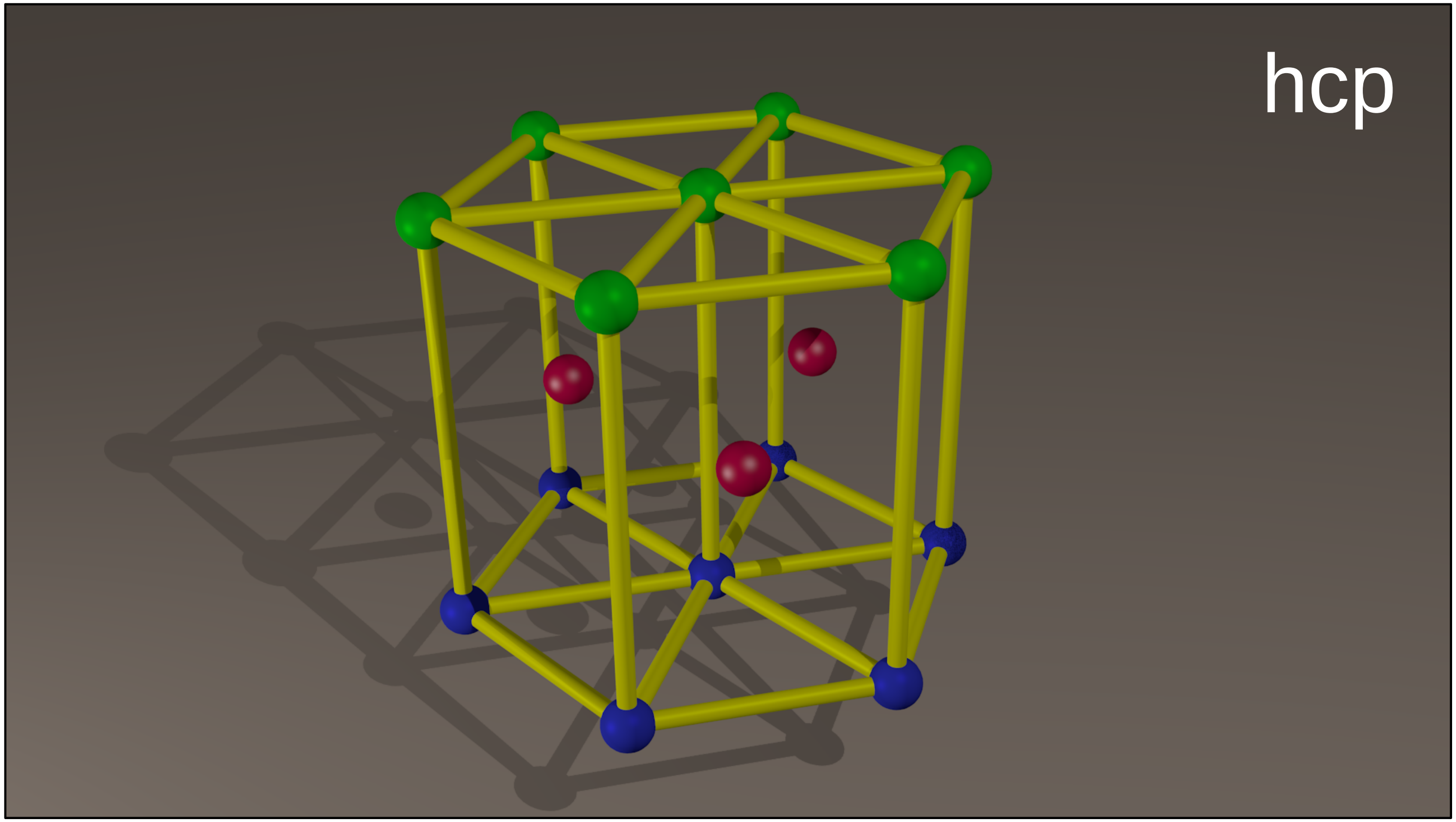
- How to arrange hard spheres to fill the space most effectively (to have as little empty space between them as possible)?
- And in 3D:



Notes that the spheres are deflated but the distances between them are unchanged

- The spheres shrunk

- How to arrange hard spheres to fill the space most effectively (to have as little empty space between them as possible)?
- And in 3D:



Notes that the spheres are deflated but the distances between them are unchanged

- How to arrange hard spheres to fill the space most effectively (to have as little empty space between them as possible)?
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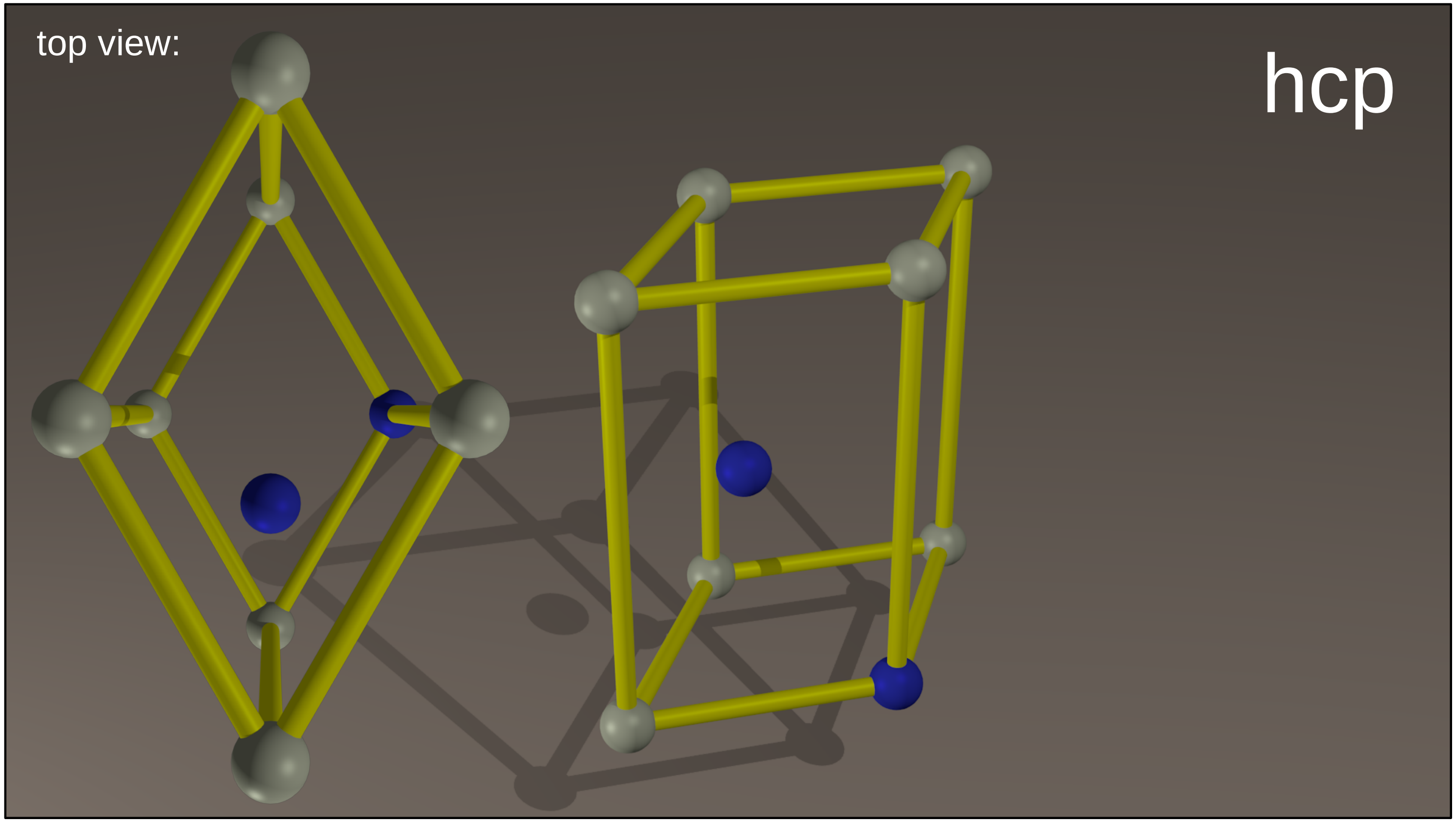
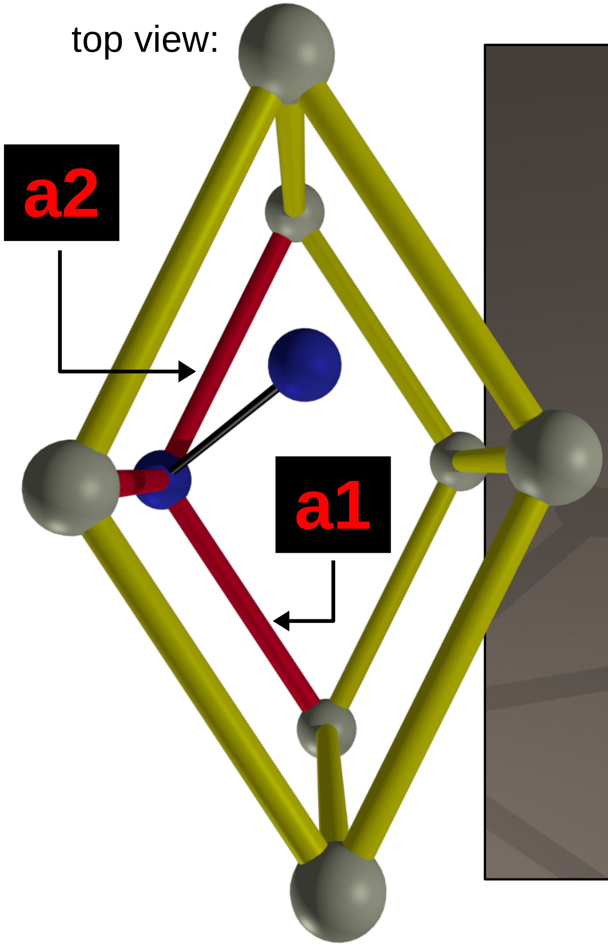


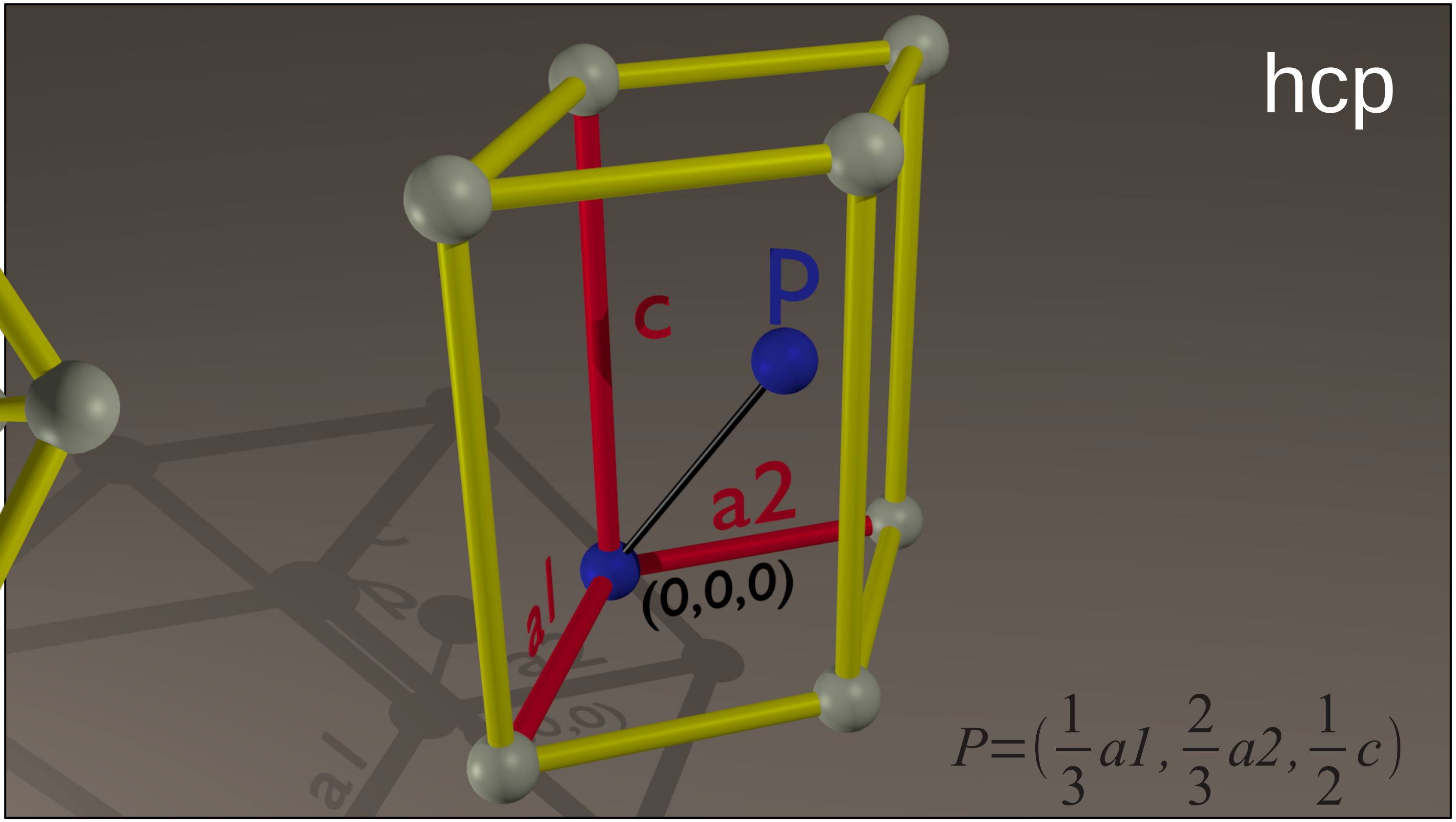
Notes that the spheres are deflated but the distances between them are unchanged

- **Two blue** spheres form the base of ***hcp*** structure – see Bravai's lattice (later on)

- How to arrange hard spheres to fill the space most effectively (to have as little empty space between them as possible)?
- And in 3D:

top view:





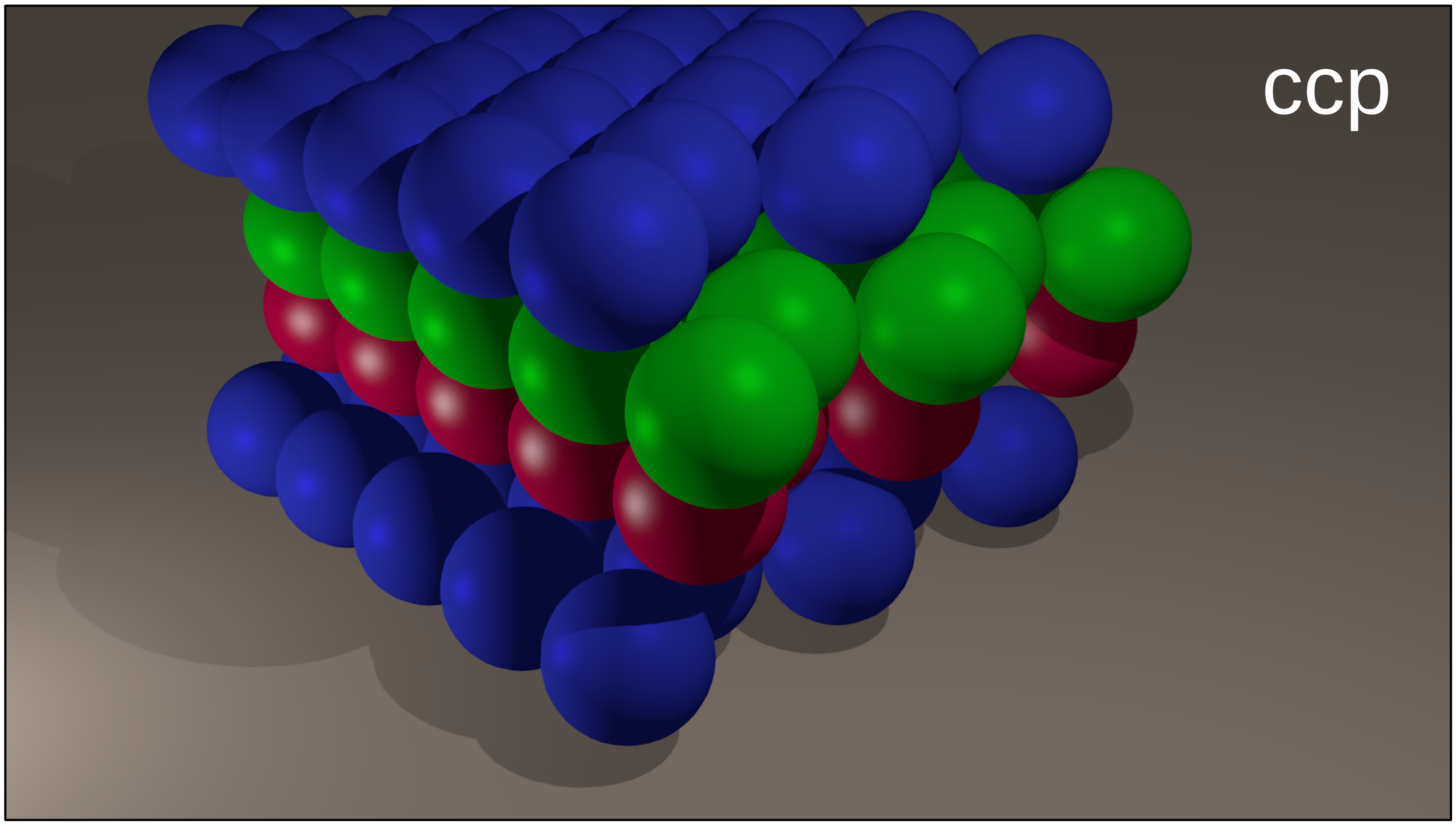
Notes that the spheres are deflated but the distances between them are unchanged

- Edges of the cell: $a1 = a2 = 2 \cdot r$ $\quad r - sphere\ radius$

$$c = 2\frac{\sqrt{6}}{3} \cdot a1 \approx 1.63 \cdot a1$$

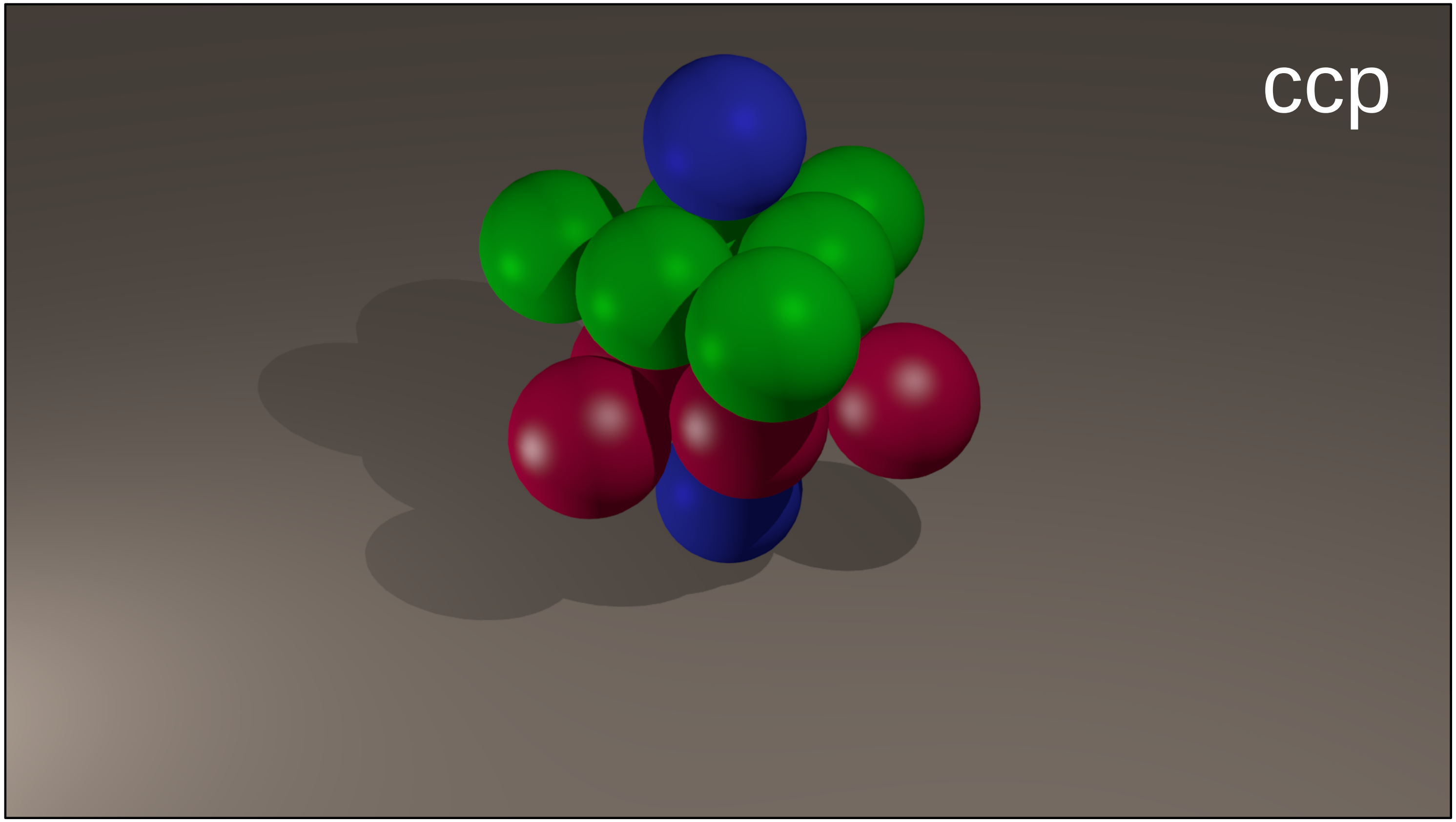
Close packing of equal spheres

- Cubic close packing [2]



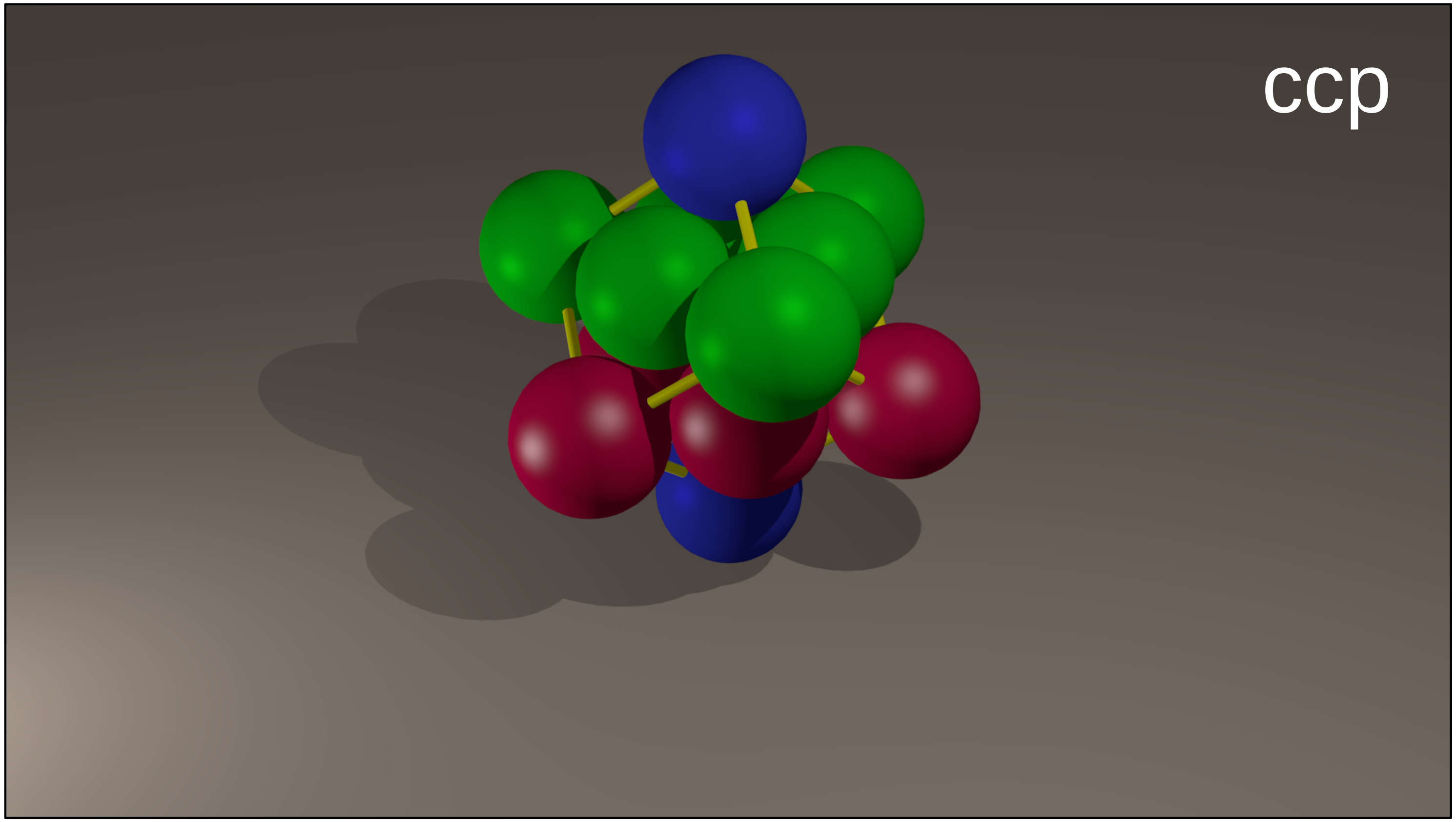
- ABCABC… stacking
- Note that any stacking (without repetition) gives close-packing – so called stacking faults [2]

- Cubic close packing [2]



- ABCABC… stacking

- Cubic close packing [2]

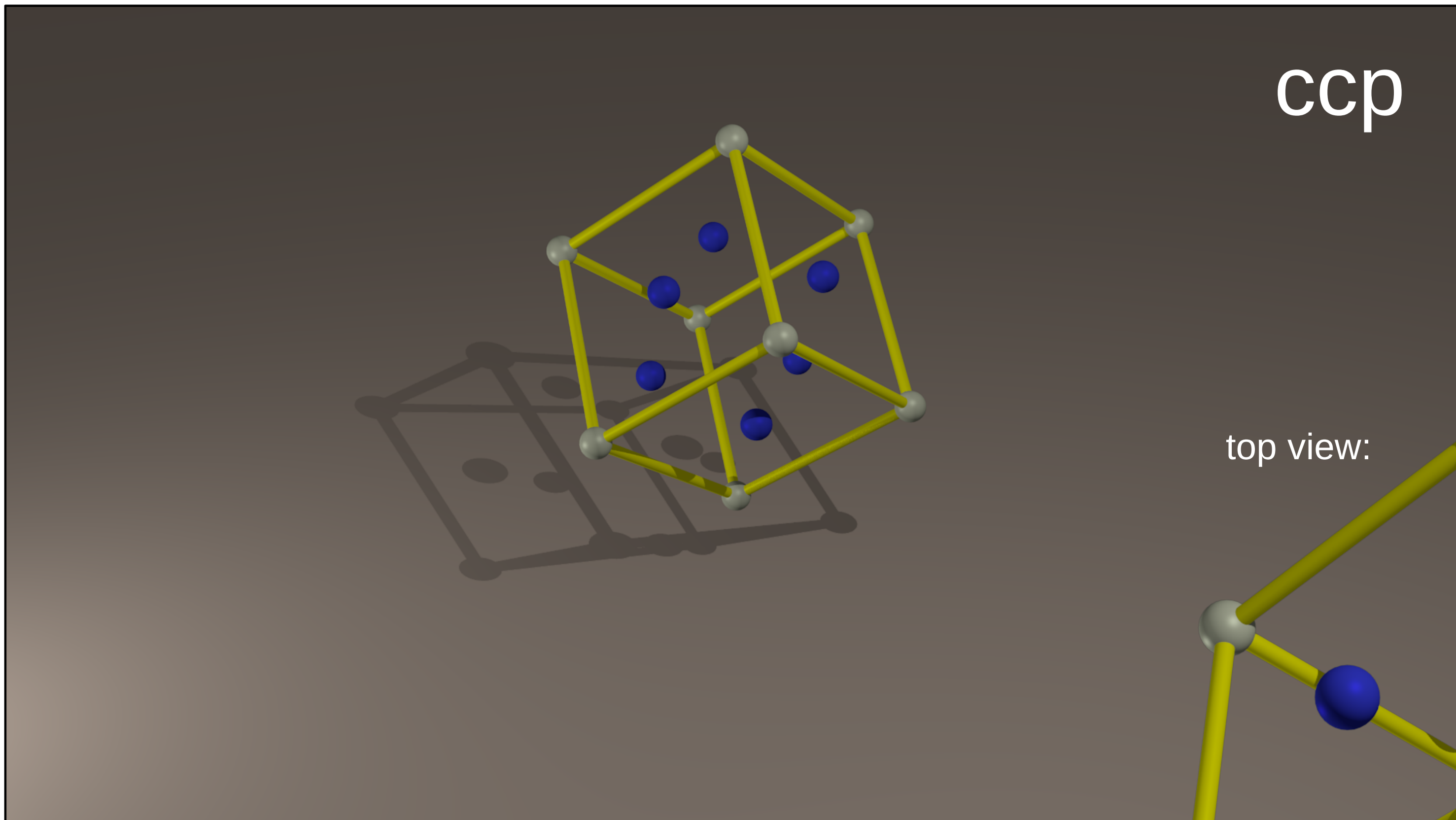


- ABCABC… stacking
- We add the lines connecting the centers of the spheres

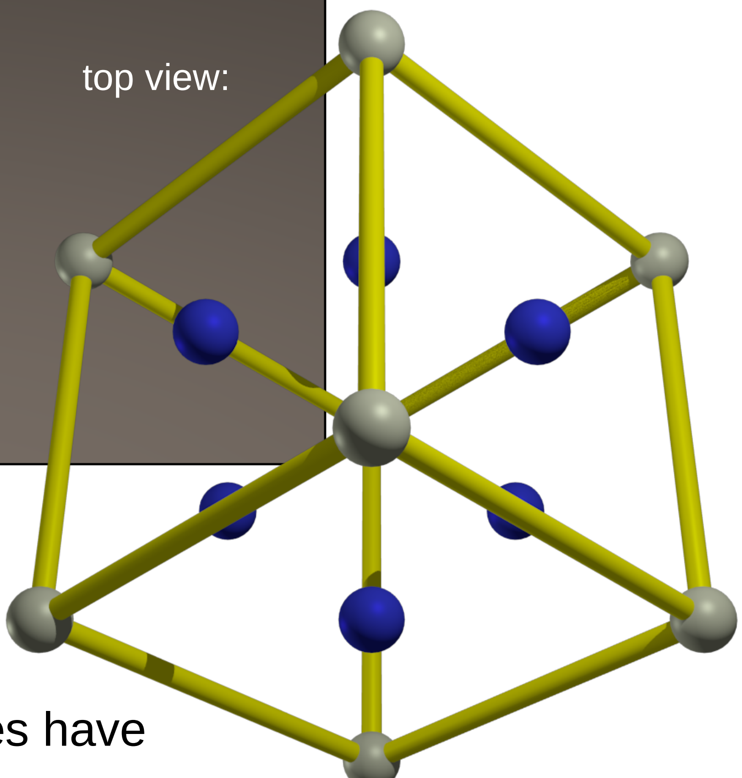
Close packing of equal spheres

- Cubic close packing [2]

Notes that the spheres are deflated but the distances between them are unchanged



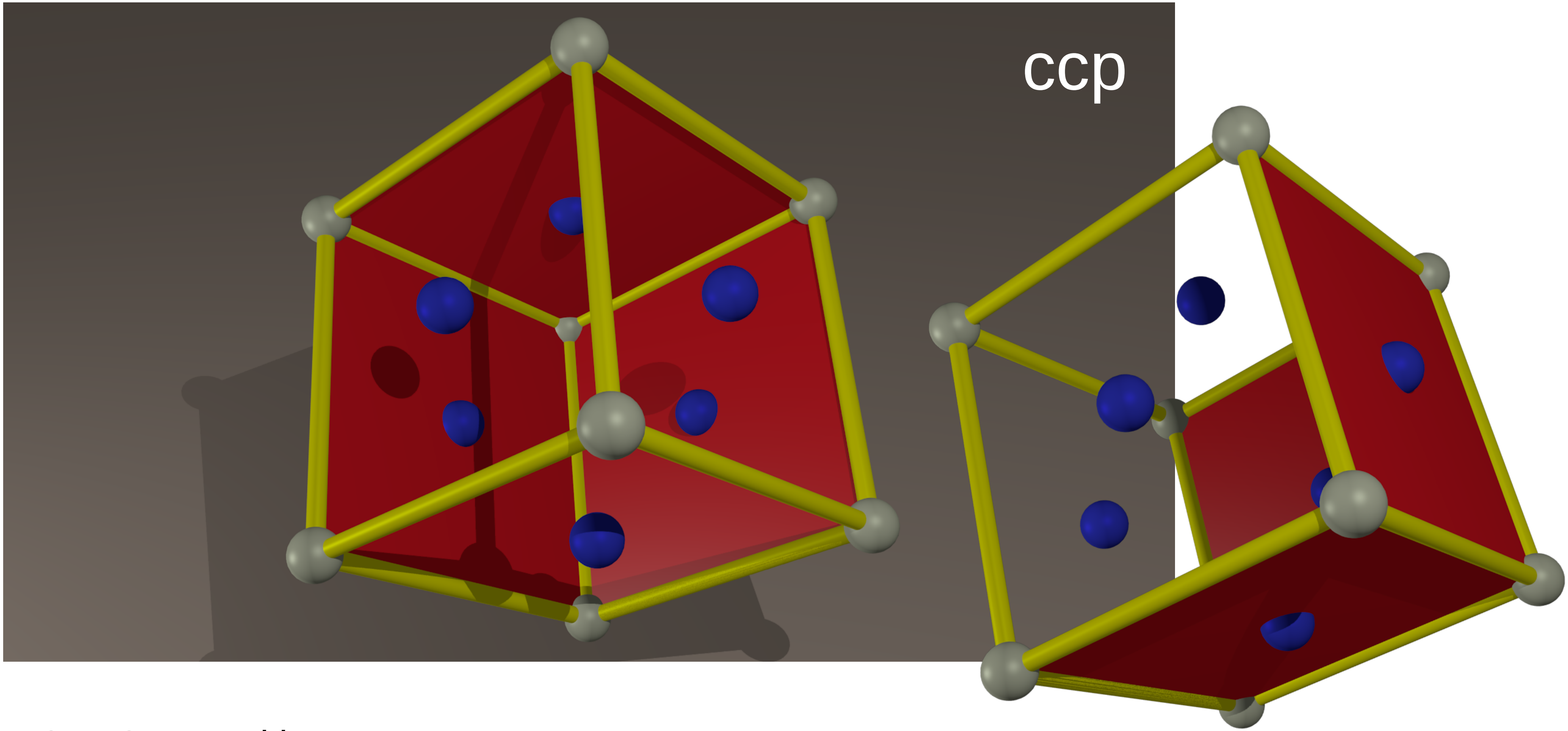
top view:



- ABCABC… stacking
- diagonal of the cube is perpendicular to hexagonal planes
- From previous considerations we know that these planes have densest packing

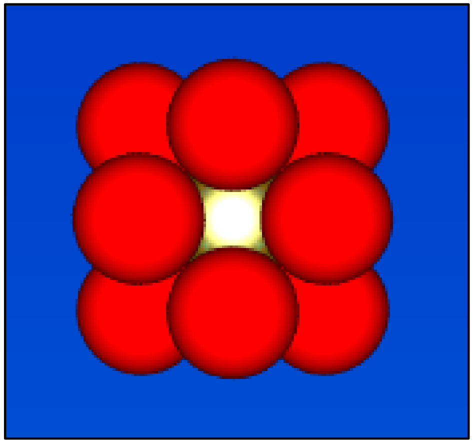
- Cubic close packing [2] = **face-centred cubic**

Notes that the spheres are deflated but the distances between them are unchanged

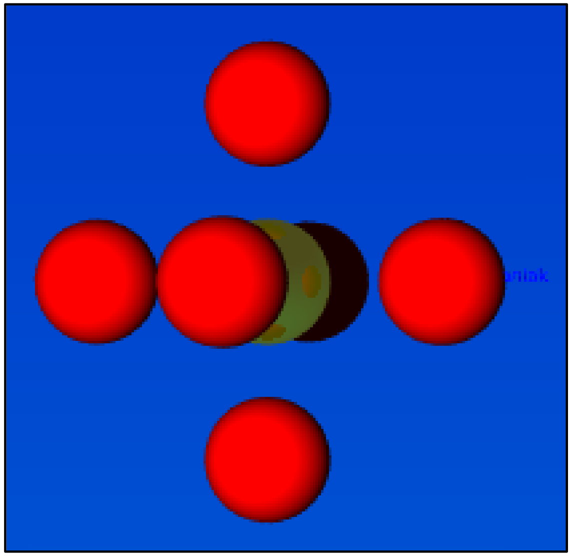


- ABCABC… stacking
- Center of each face of the cube is occupied by a **sphere** (atom)
- The cube contains 4 atoms (8•⅛ corner atom+6• ½ face atom)

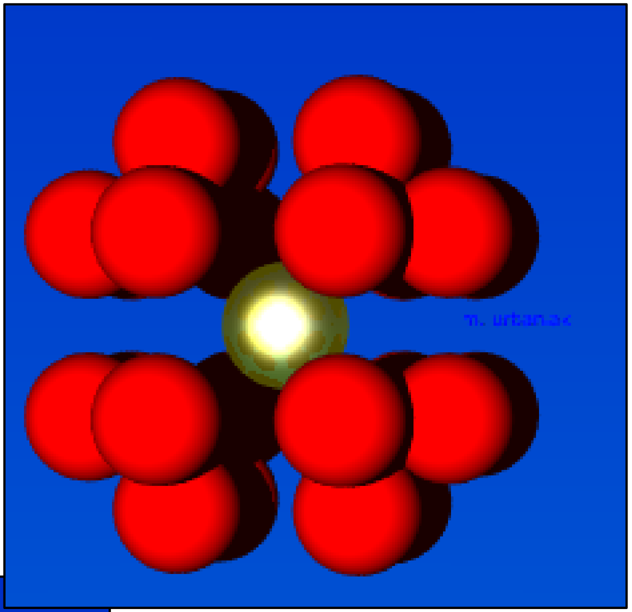
- Coordination layers in **fcc** structure – number of nearest neighbors, second nearest neighbors (snn),...



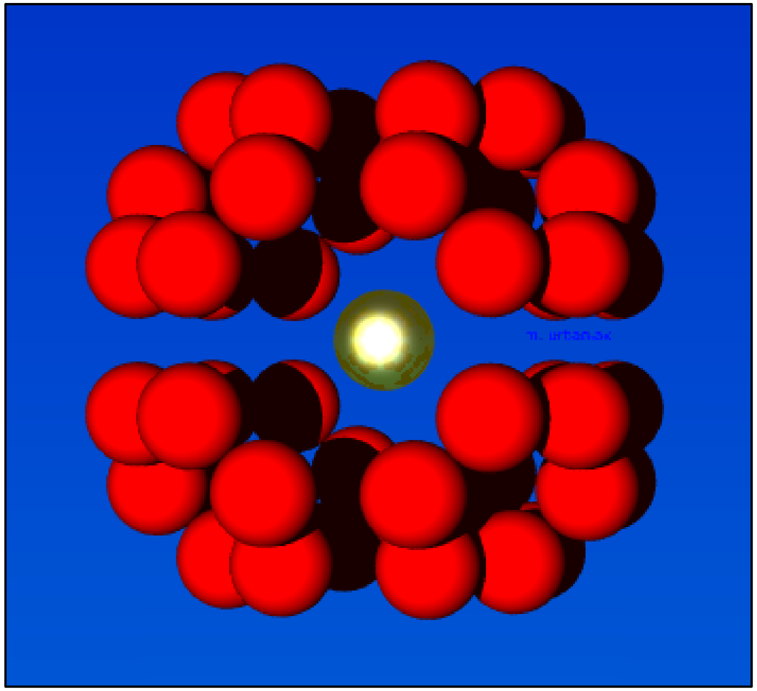
first layer



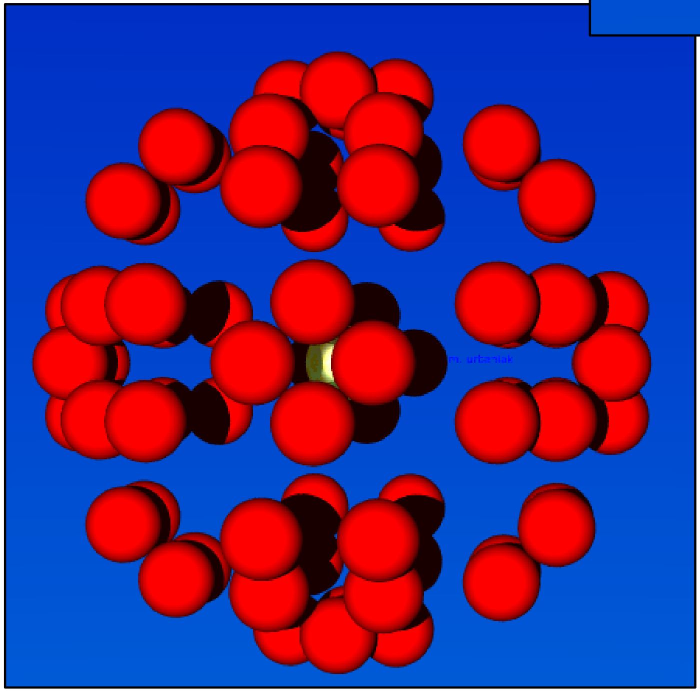
second layer



third layer



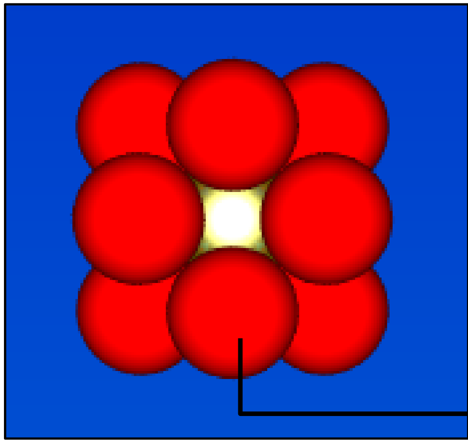
7^{th} layer – 24 neighbors



13^{th} layer – 72 neighbors

Close packing of equal spheres

- Coordination layers in **fcc** structure – number of nearest neighbors, second nearest neighbors (snn),...

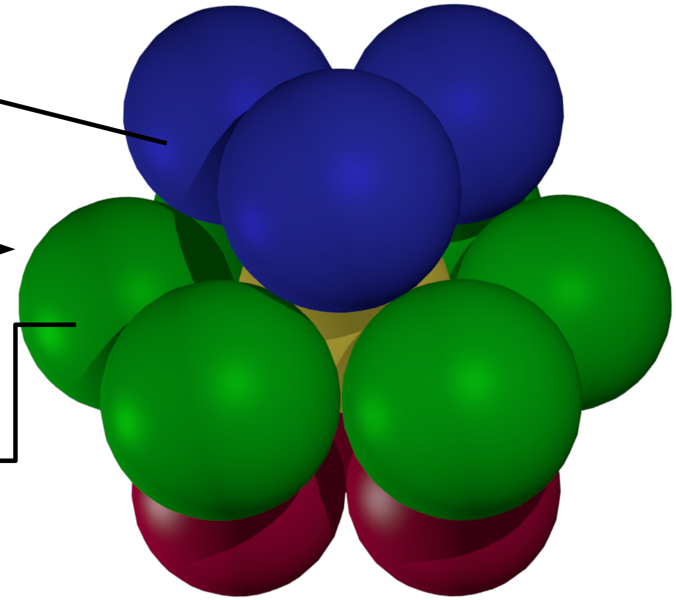


first layer – 12 neighbors

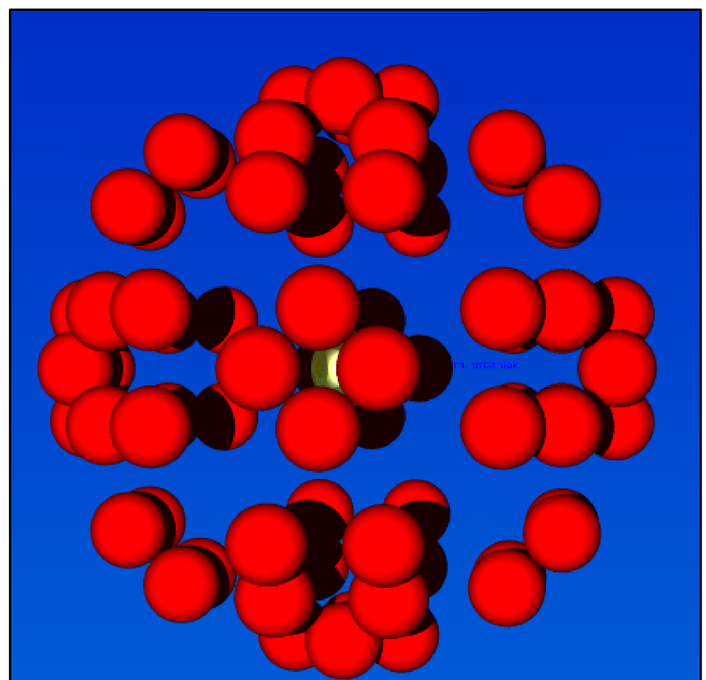
3 neighbors in lower and upper layers

alternative view (stacking)

6 neighbors in “own” close-packed layer



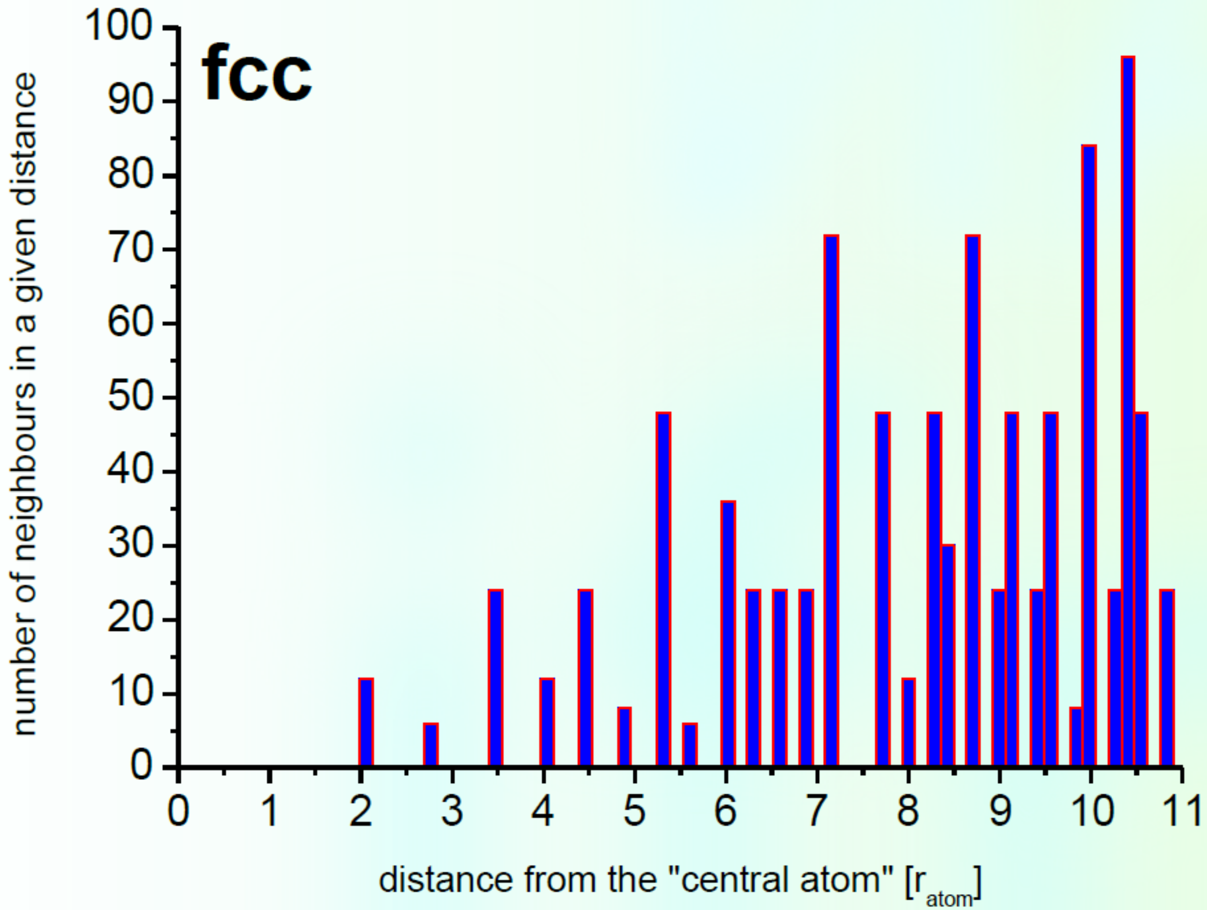
One is usually not interested in neighbors farther than in the second layer*



13th layer – 72 neighbors

*structural investigations may be exception

- Coordination layers in **fcc** structure – number of nearest neighbors, second nearest neighbors (snn),...



Fcc structure:

nn 12

nnn 6

snnn 24

....

- Amorphous substances – radial distribution function

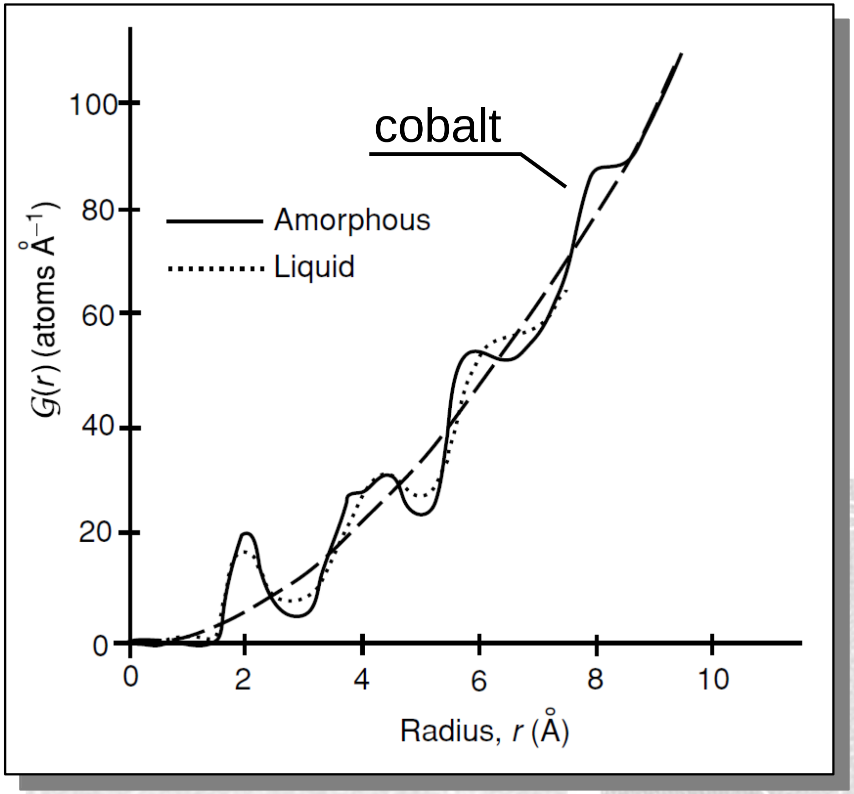


Image source: J. M. D. COEY, Magnetism and Magnetic Materials, Cambridge University Press 2009 [6]

- Amorphous solids have no crystal lattice*
- The metallic amorphous alloys are usually produced by quenching (very fast cooling) from liquid or vapor

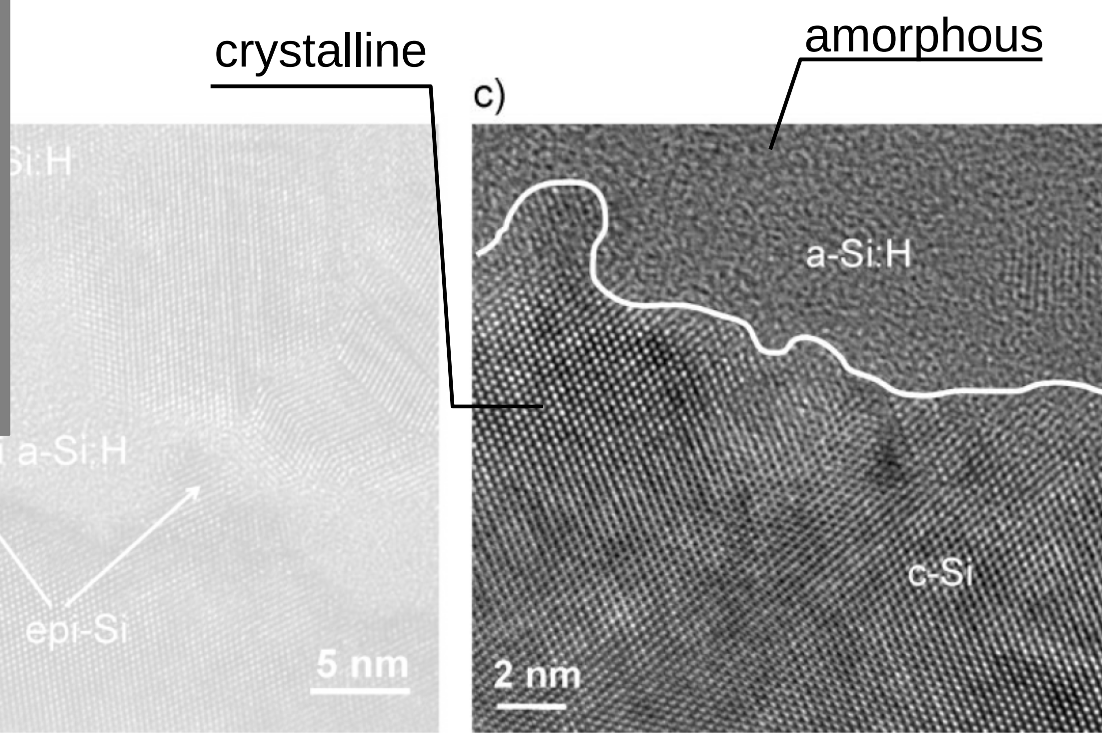
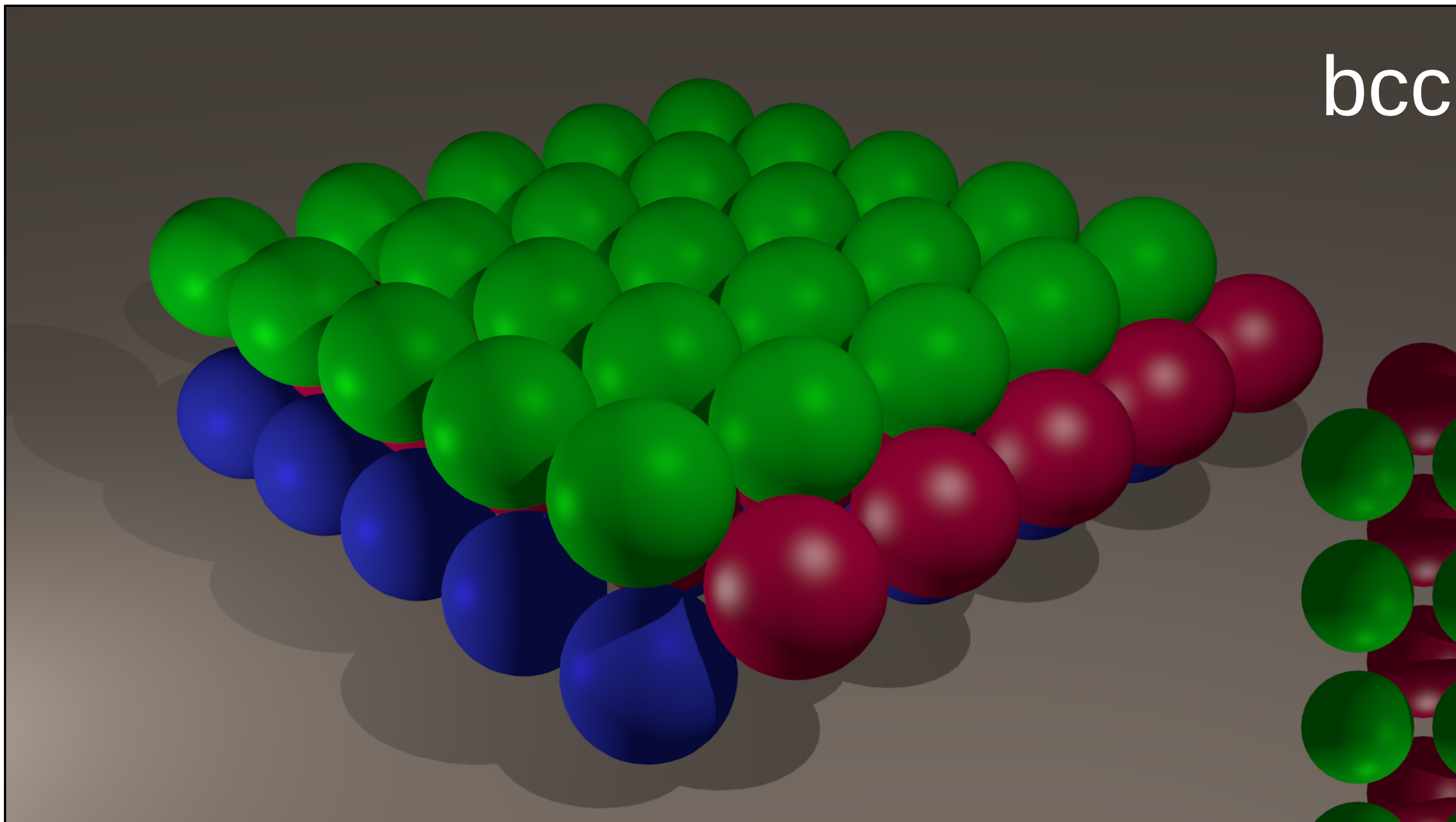


Figure 8 HR-TEM micrographs showing (a) abrupt flat crystallographic c-Si/a-Si:H/μc-Si:H interfaces of Si HJ solar cells, (b) an epitaxially connected *i* a-Si:H interface passivation layer in the pyramidal groove of a textured Si HJ solar cell, and (c) a rough a-Si:H/c-Si interface, also of a textured Si HJ solar cell.

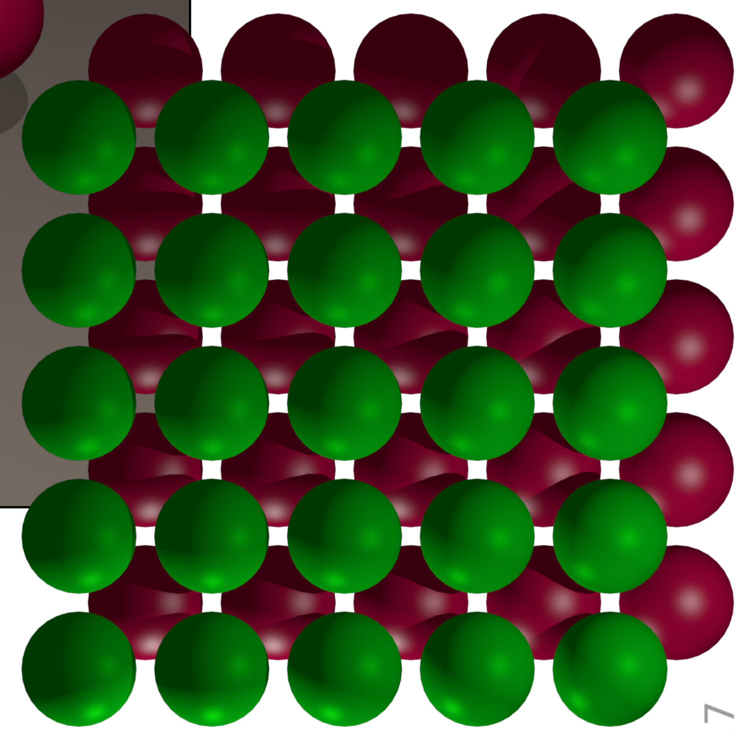
Image source: S. Olibet et al., Phys. Status Solidi A, 1–6 (2010) / DOI 10.1002/pssa.200982845

*see later in this lecture

- Body centred cubic (bcc)

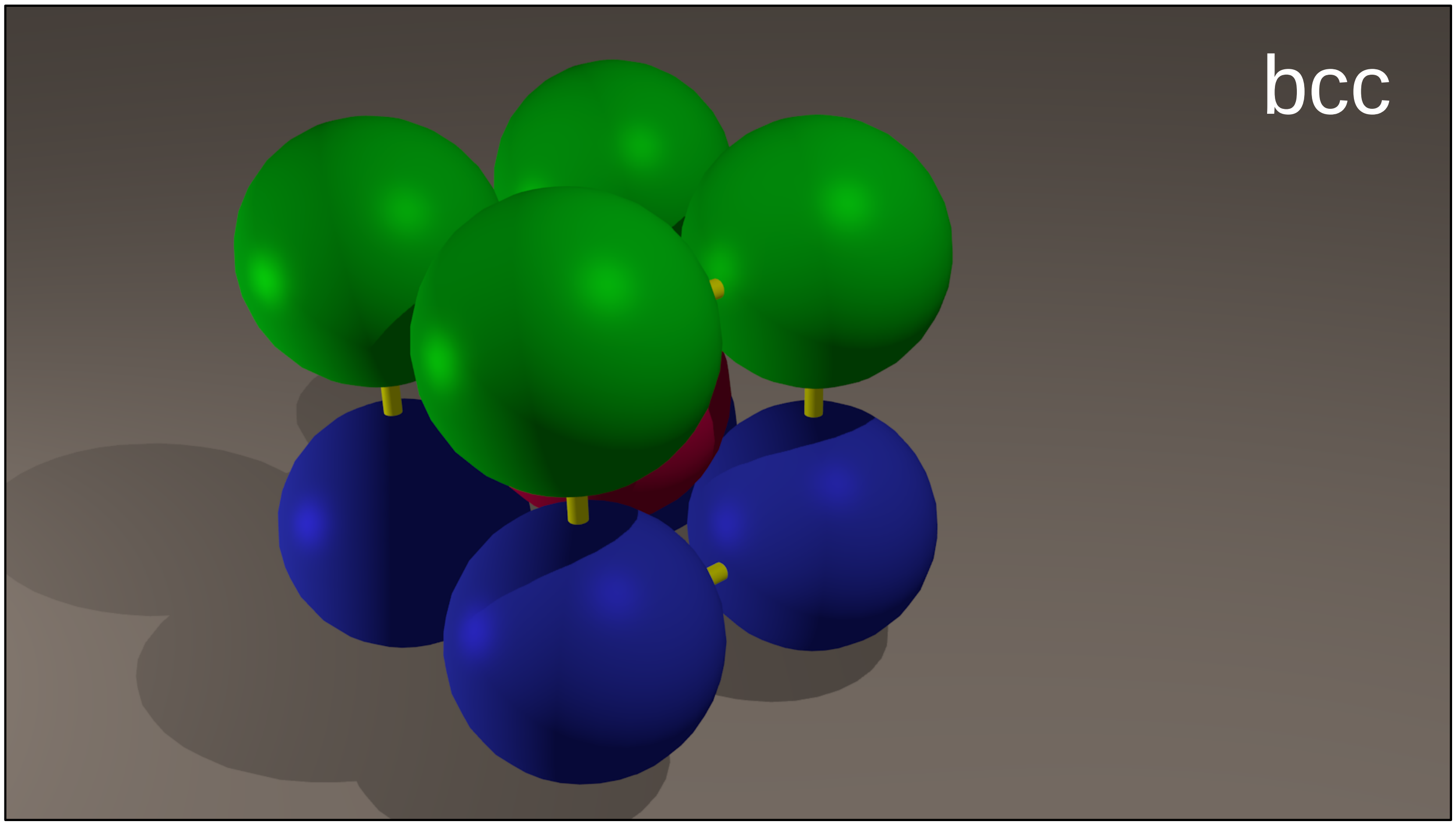


top view, orthographic:



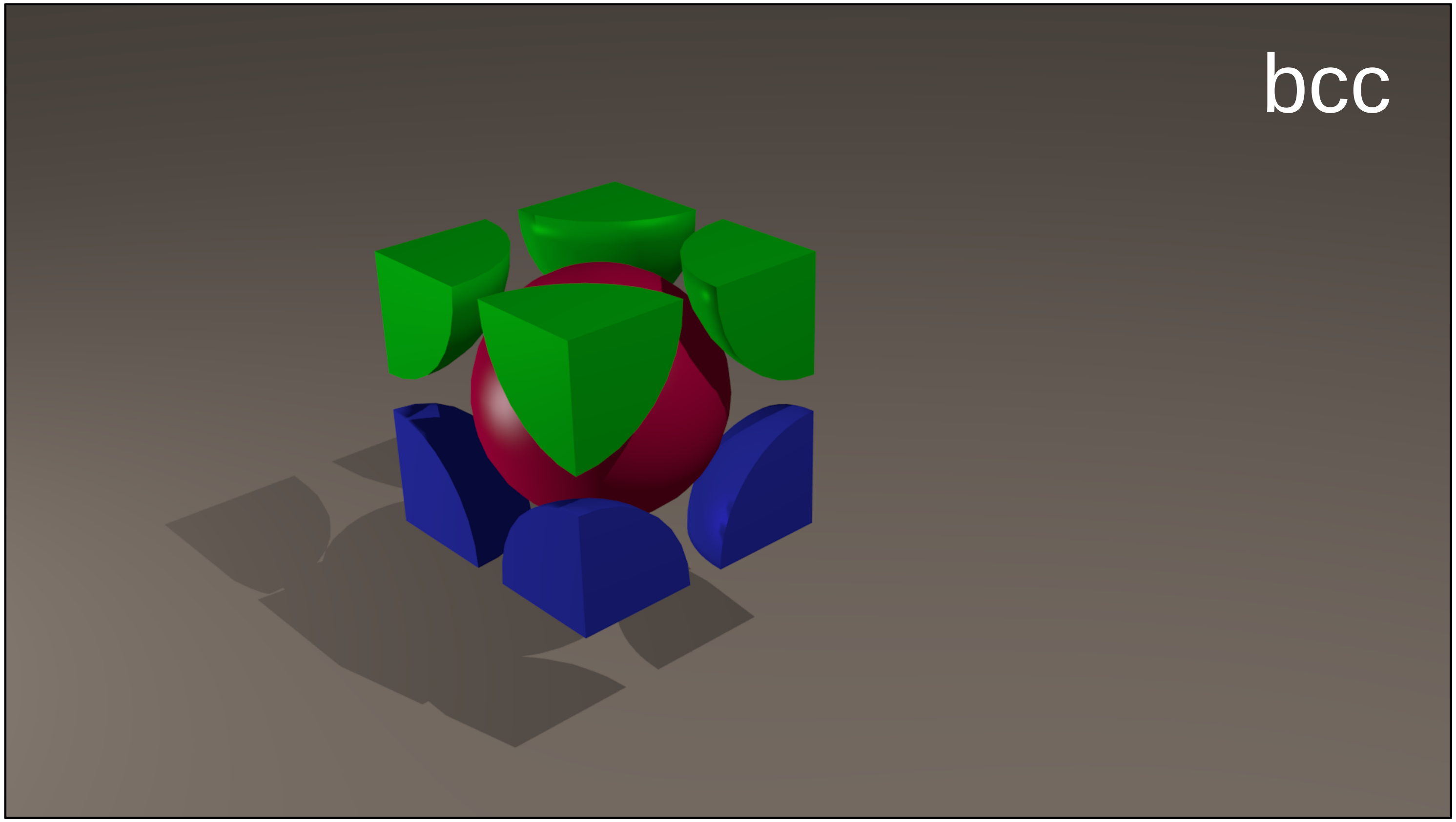
- The **bcc** structure is **not close-packed**!

- Body centred cubic (bcc)



- The **bcc** structure is **not close-packed**!
- Unit cell contains two atoms

- Body centred cubic (bcc)



- The **bcc** structure is **not close-packed**!
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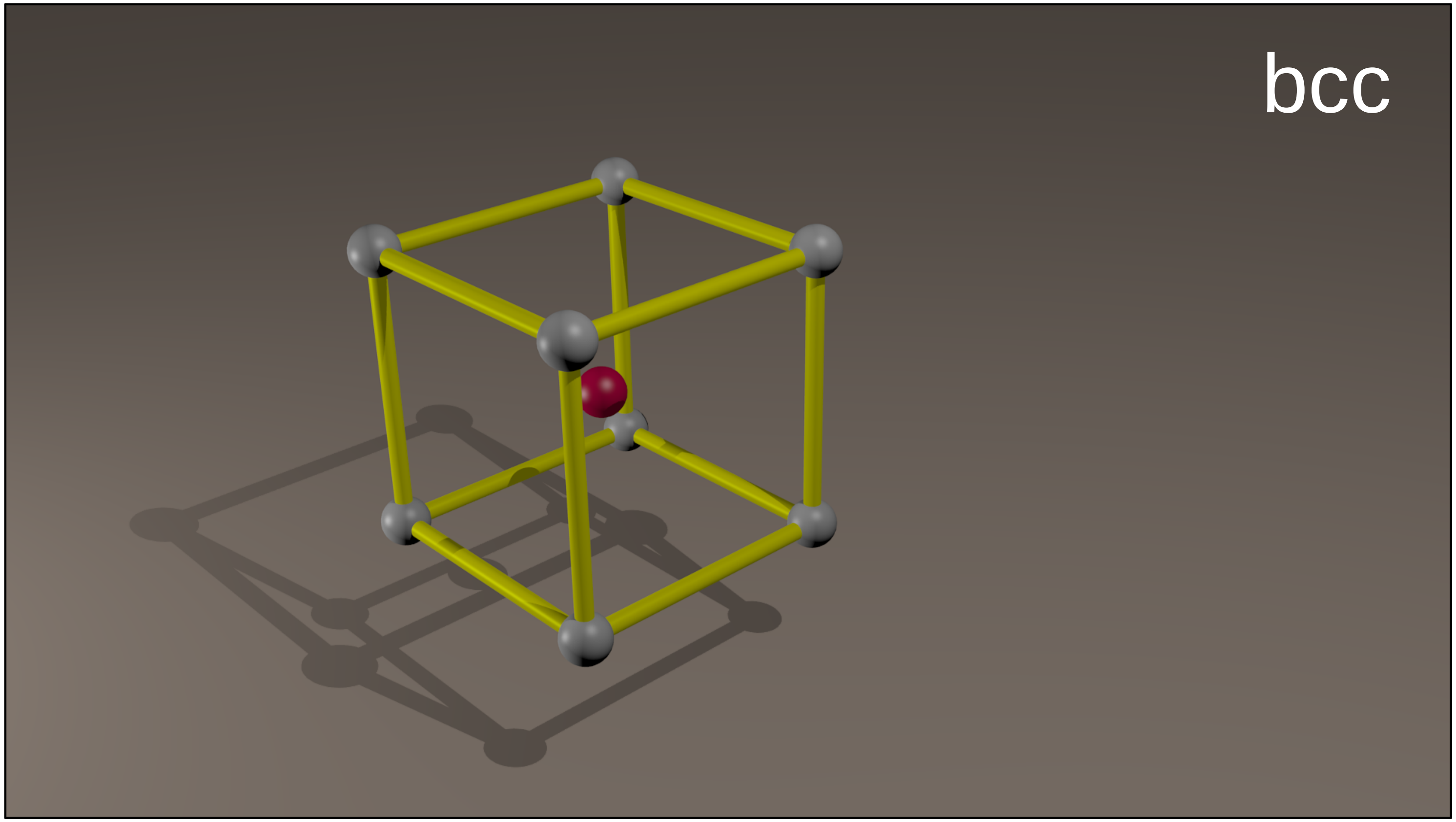
- Body centred cubic (bcc)

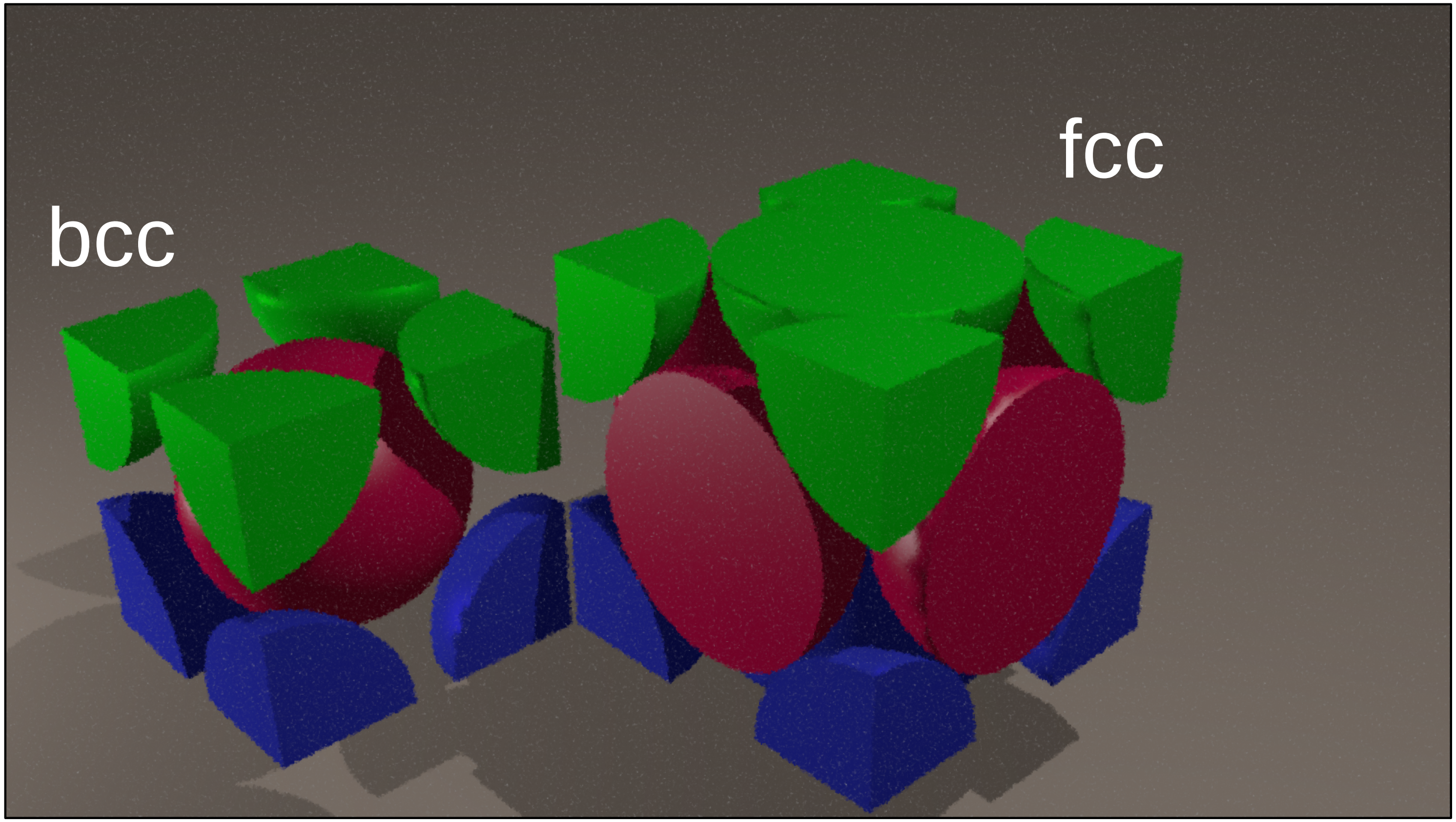
Notes that the spheres are deflated but the distances between them are unchanged



- The **bcc** structure is **not close-packed**!
- Unit cell contains two atoms

- For same size of spheres **bcc** cell is smaller than **fcc** cell

Both cubes in the image are drawn in the same scale



$$bcc: a = \frac{4r}{\sqrt{3}}$$

$$fcc: a = \frac{4r}{\sqrt{2}}$$

$$\frac{a_{fcc}}{a_{bcc}} = \frac{\sqrt{3}}{\sqrt{2}} \approx 1.23$$

- For same size of spheres **bcc** cell is smaller than **fcc** cell

bcc structure	fcc structure
2 atoms in a unit cell	4 atoms in a unit cell
Fraction of space occupied by the spheres: $f_{packing}=\frac{2(4/3\pi r^3)}{(4r/\sqrt{3})^3}=\frac{\sqrt{3}\pi}{8}\approx 0.68$	Fraction of space occupied by the spheres: $f_{packing}=\frac{4(4/3\pi r^3)}{(4r/\sqrt{2})^3}=\frac{\sqrt{8}\pi}{12}\approx 0.741$
Coordination number*: 8	Coordination number*: 12

$$bcc: a=\frac{4r}{\sqrt{3}}$$

$$fcc: a=\frac{4r}{\sqrt{2}}$$

$$\frac{a_{fcc}}{a_{bcc}}=\frac{\sqrt{3}}{\sqrt{2}}\approx 1.23$$

*number of nearest neighbors

- In real crystal structures the ratio between the lengths of cell edges ***a*** (i.e., ion/sphere diameter) to a spacing between successive close-packed layers always differs from the predictions of purely geometrical model described previously [2]

Table 1

Material	h/a	Material	h/a
Cd	0.943	AgI	0.815
Zn	0.928	BeO	0.815
He	0.8165	CdSe	0.815
Co	0.814	ZnO	0.800
Mg	0.812	AlN	0.800
Sc	0.797	CdS	0.810

For ideal close-packed structures the (stacking faults can be present) ***h/a*** ratio is approx. 0.8165

- In fabrication of thin films one can obtain, using molecular beam epitaxy (MBE), structures which are ideal over hundreds of interatomic distances

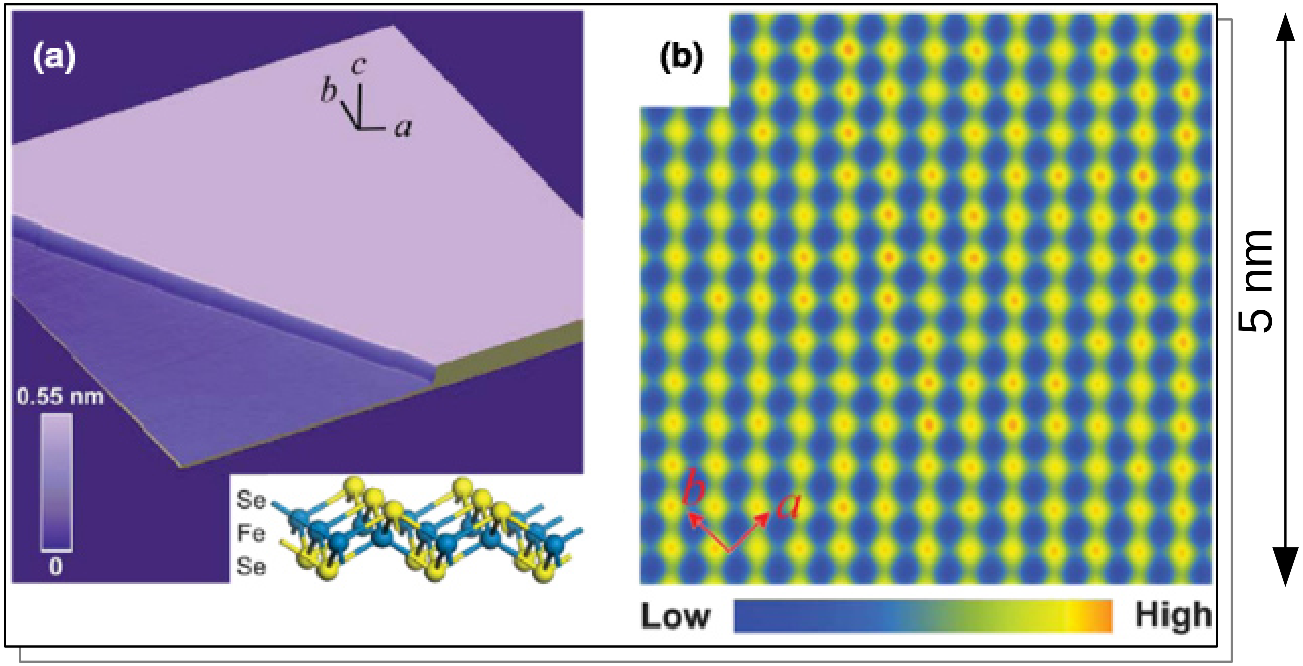


Figure 10. STM characterization of the as-grown FeSe films. (*a*) Topographic image (2.5 V, 0.1 nA, 200 × 200 nm^2) of a FeSe film (about 30 unit cells thick). The step height is 5.5 Å. Inset shows the crystal structure. (*b*) Atomic resolution STM topography (10 mV, 0.1 nA, 5 × 5 nm^2) of the FeSe film. The bright spots correspond to the Se atoms in the top layer. *a* and *b* correspond to either of the Fe–Fe bond directions. The same convention is used for *a*- and *b*-axes throughout the paper. (*c*) Temperature dependence of differential conductance spectra (setpoint: 10 mV, 0.1 nA). (*d*) Schematic of the unfolded Brillouin zone and the Fermi surface (green ellipse). The nodal lines for $\cos k_x \cos k_y$ and $(\cos k_x + \cos k_y)$ gap functions are indicated by black and red dashed lines, respectively. The size of all pockets is exaggerated for clarity. The black arrow shows the direction of nesting (from [73]).

image source: Jin-Feng Jia et al., J. Phys. D: Appl. Phys. **44**, 464007 (2001)

- “*The STM topographic images (figures 10(a) and (b)) revealed atomically flat and defect-free Se-terminated (0 0 1) surfaces with large terraces.*” [3]
- layer-by-layer growth on SiC(0 0 0 1) substrate

Metallic bonds – bonds between atoms of low electronegativity that contain **low number of electrons in outer shell** [12]:

- the metallic bond is not directional
- the bond is weaker than covalent bond
- metal may be viewed as a set of positive ions immersed in electronic cluod

Characteristic features of metal structures [12]:

- they form high symmetry structures, regular or hexagonal
- due to the dense packing or packing close to dense they have high density**
- high coordination numbers (about 12) and relatively high bonding energies result in relatively high melting temperatures
- the metals are mallable***

Metals that are most important for electronics:
- Al, Cu, Au
- Fe,Co,Ni

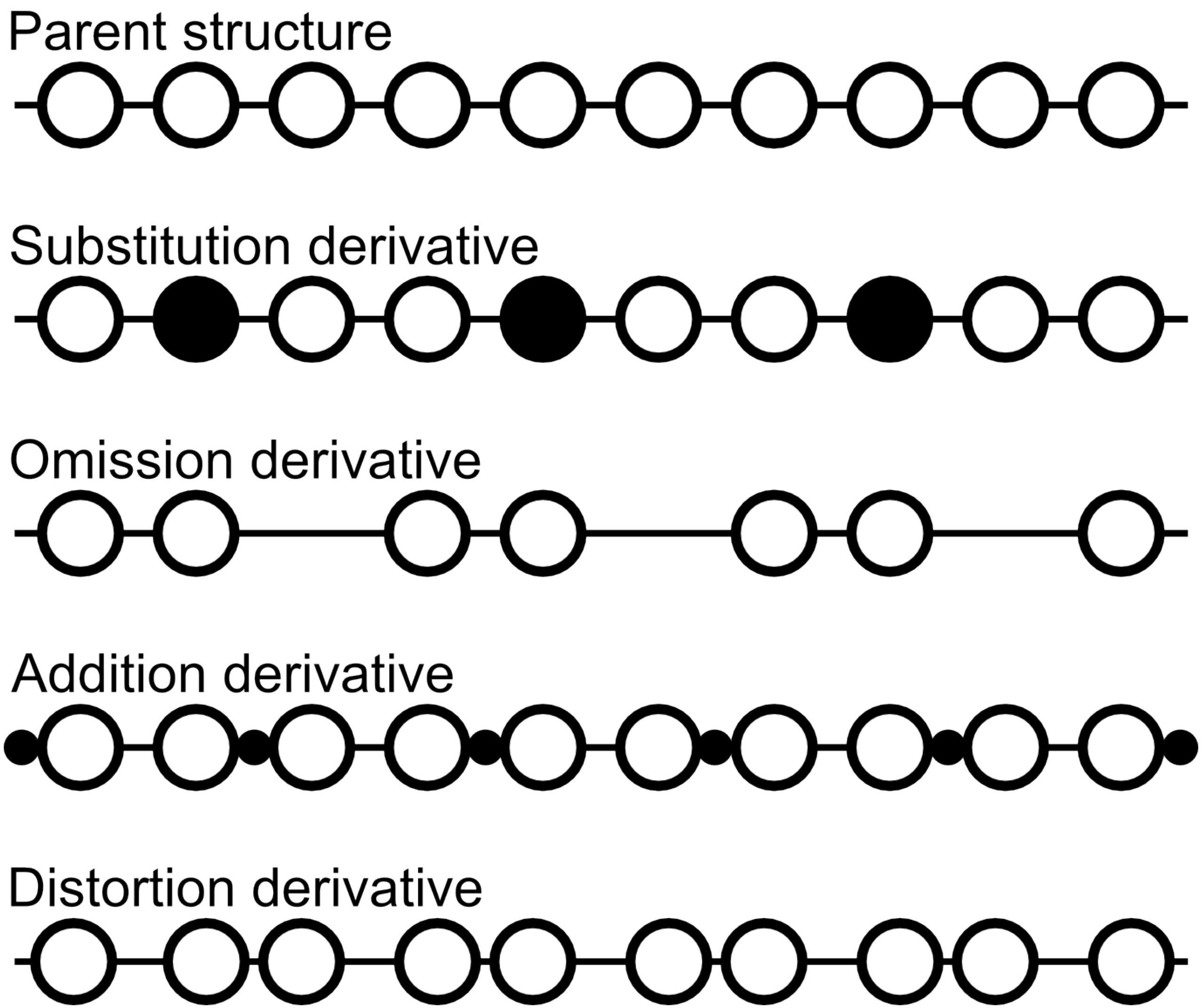
$_{13}$**Al** $1s^2\,2s^2 2p^6\,3s^2 3p^1$

$_{29}$**Cu** $1s^2\,2s^2 2p^6\,3s^2 3p^6 3d^{10}\,4s^1$

* the power of an atom to attract electrons to itself [13]. The higher the electronegativity the higher the tendency to attract electrons.
**in fact in every period of the Mendeleyev's periodic table the metals are the elements with the highest density (bor is a half-metal) [14]
***able to be hammered or pressed into shape without breaking or cracking (google dictionary)

Derivative structures

- More complicated structures can be obtained from simpler ones by operations removing some symmetries present in the initial structure – the idea introduced by M. Buerger [4]
- One dimensional example*:

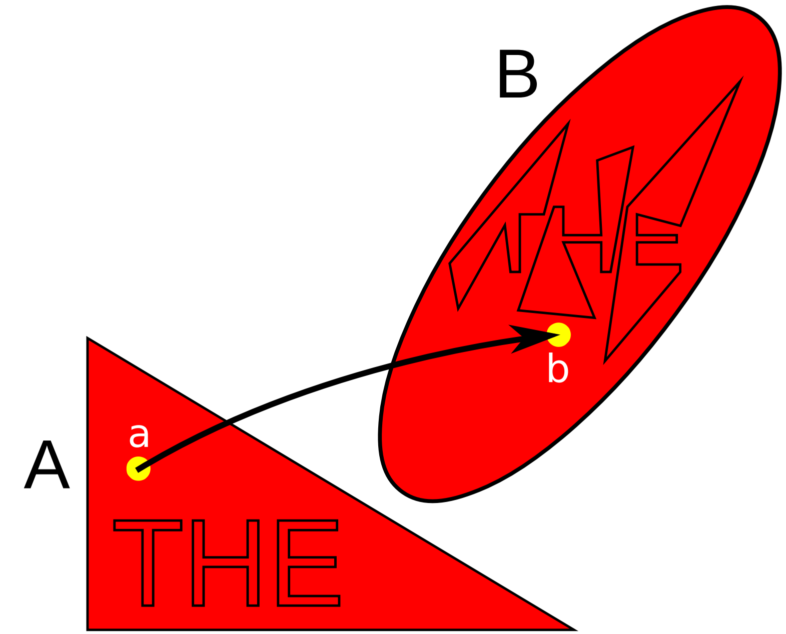


The translational periodicity of the derivatives is higher than that of the parent

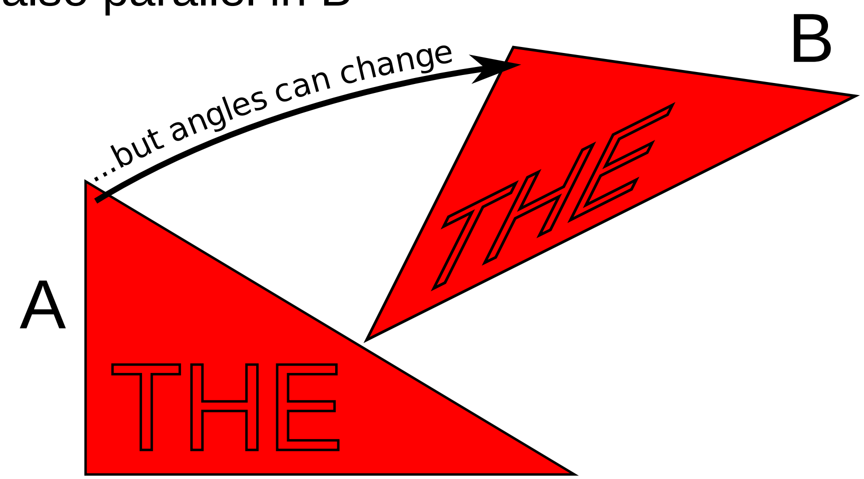
superstructures

*taken from crystallography lectures by Prof. Bernhardt Wuensch – MIT,USA, 2005 [4]

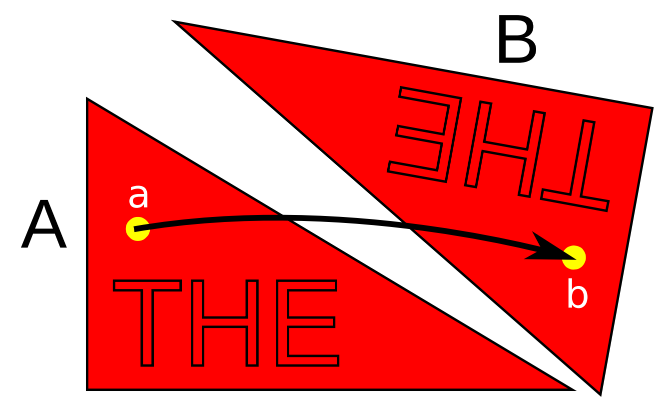
- **A mapping** of a set A into a set B is a relation such that for each element $a \in$ A there is a *unique* element $b \in$ B which is assigned to a. The element b is called the image of a.



- **An affine mapping** – lines parallel in A are also parallel in B



- **An isometry** - affine mapping that leaves all distances between points (and thus angles between lines) invariant

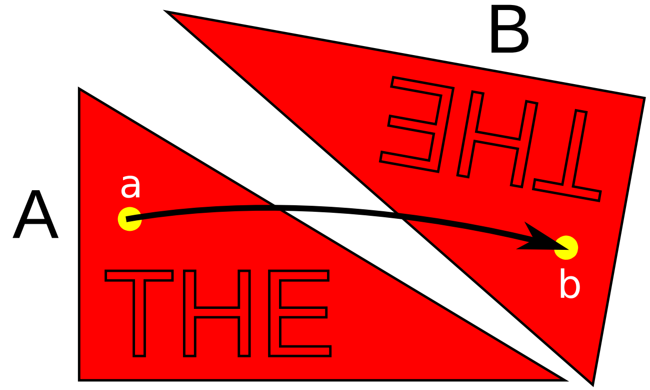


*taken mostly from H. Wondratschek, Matrices, *Mappings and Crystallographic Symmetry*, 2002 [5]

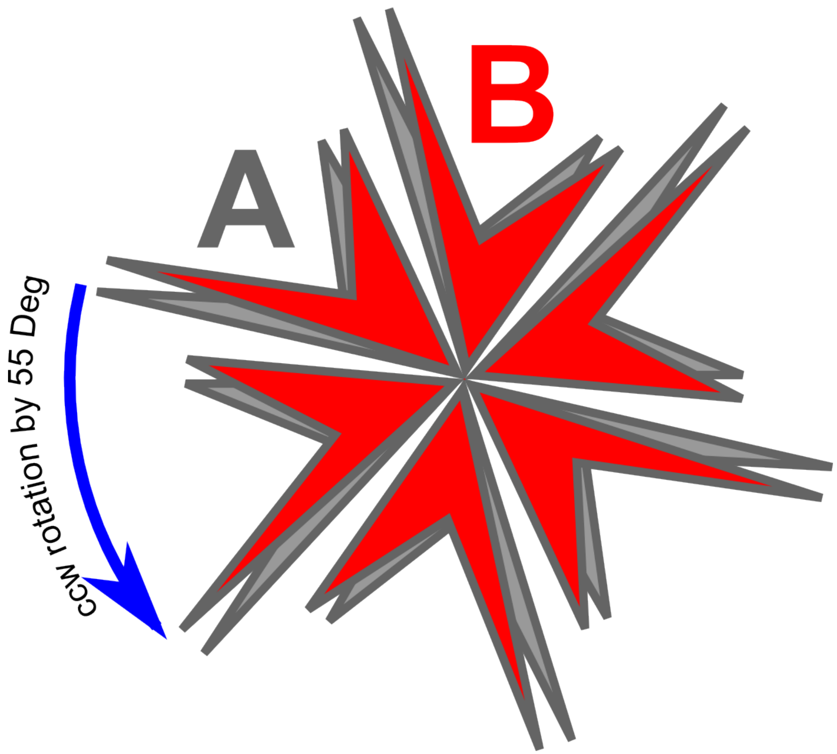
Some facts about crystal symmetries*

Quantum electronics

- **An isometry** - affine mapping that leaves all distances between points (and thus angles between lines) invariant



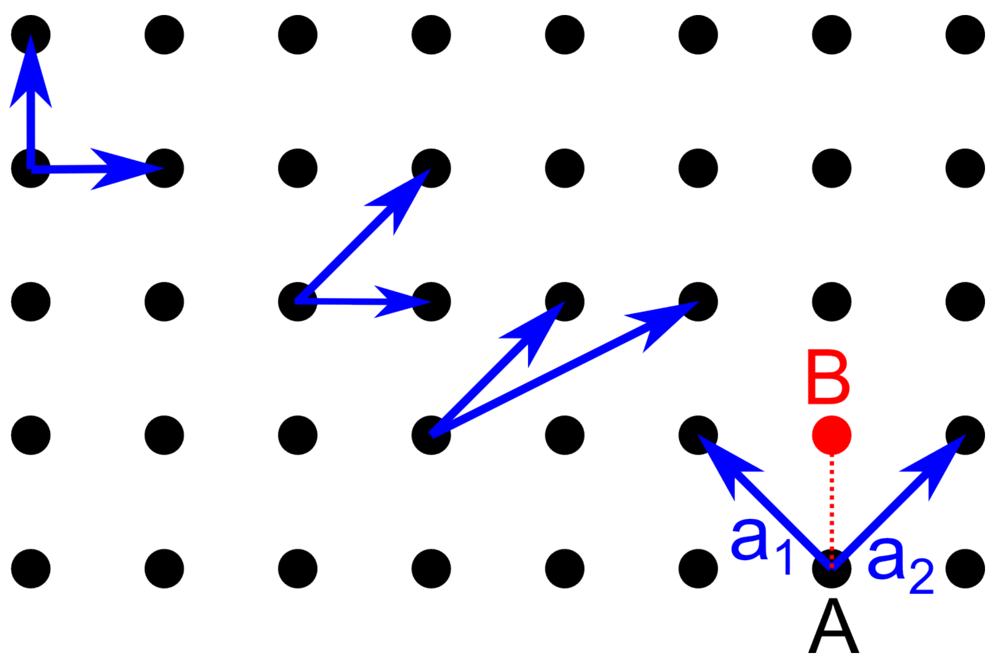
- **Symmetry operations** of an object – "*isometries which map the object onto itself such that the mapped object cannot be distinguished from the object in the original state*" [5]



Rotation by 60 Deg (cw or ccw) brings **A** into Itself (**B**=**A**)

*taken mostly from H. Wondratschek, Matrices, *Mappings and Crystallographic Symmetry*, 2002 [5]

- **crystal patterns** - idealization of real crystals in the physical space by 3–dimensional periodic sets of points representing, e. g., the centres of the atoms of the crystal [5].
- The set of all translation vectors belonging to symmetry translations of a crystal pattern is called the **vector lattice** of the crystal pattern (and of the real crystal). Its vectors are called **lattice vectors**.
- A basis of three (two in 3-dimmensional patterns) linearly independent lattice vectors is called a *lattice basis*. If all lattice vectors are integer linear combinations of the basis vectors, then the basis is called a **primitive basis**.

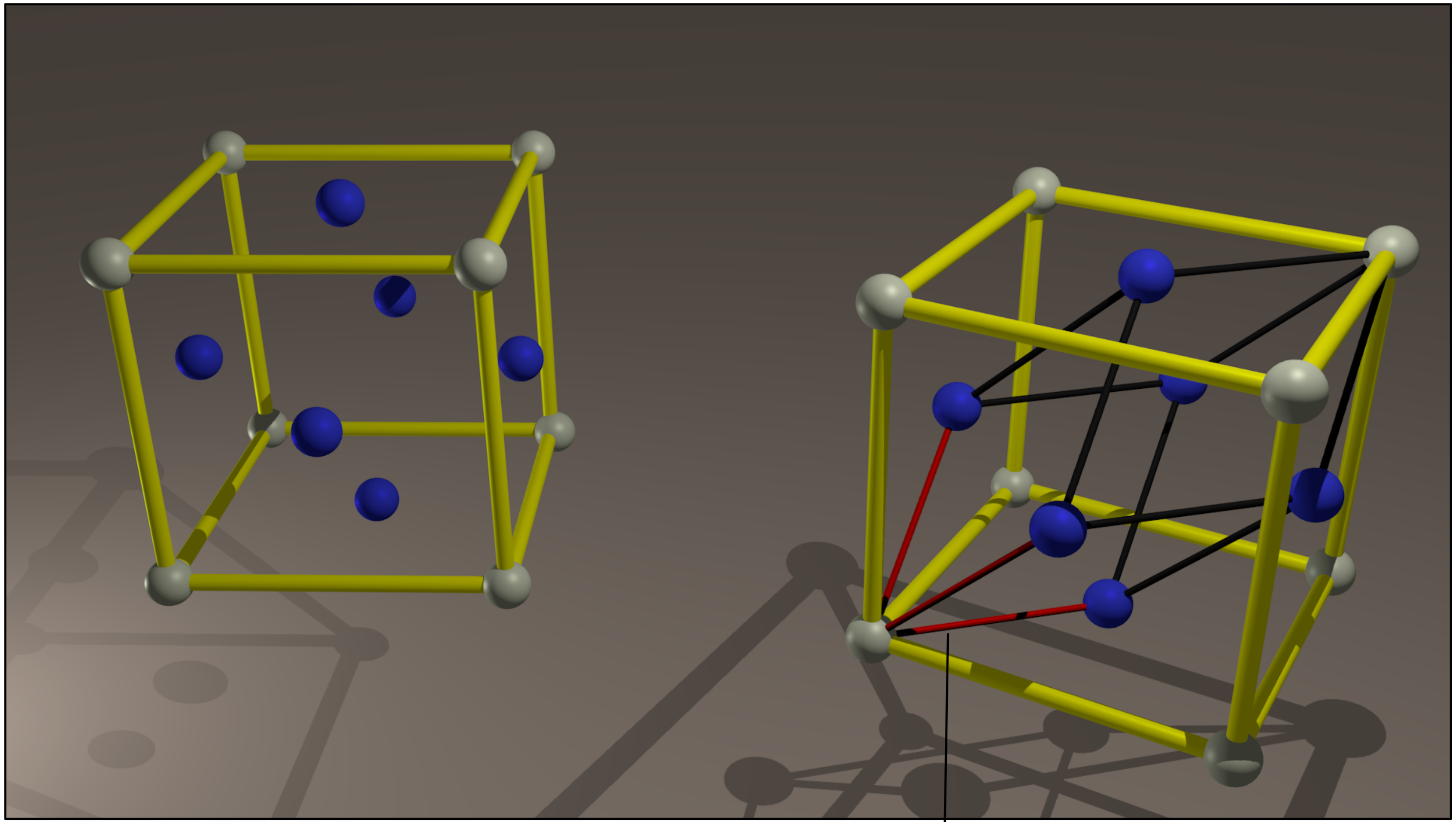


For each lattice there exists an infinite number of primitive bases

Basis (a_1,a_2) is not a primitive basis: one can not reach **B** from **A** by translation with integer multiplies of a_1 and a_2

*taken mostly from H. Wondratschek, Matrices, *Mappings and Crystallographic Symmetry*, 2002 [5]

- Example of primitive basis for 3-dimensional lattice – **fcc** structure

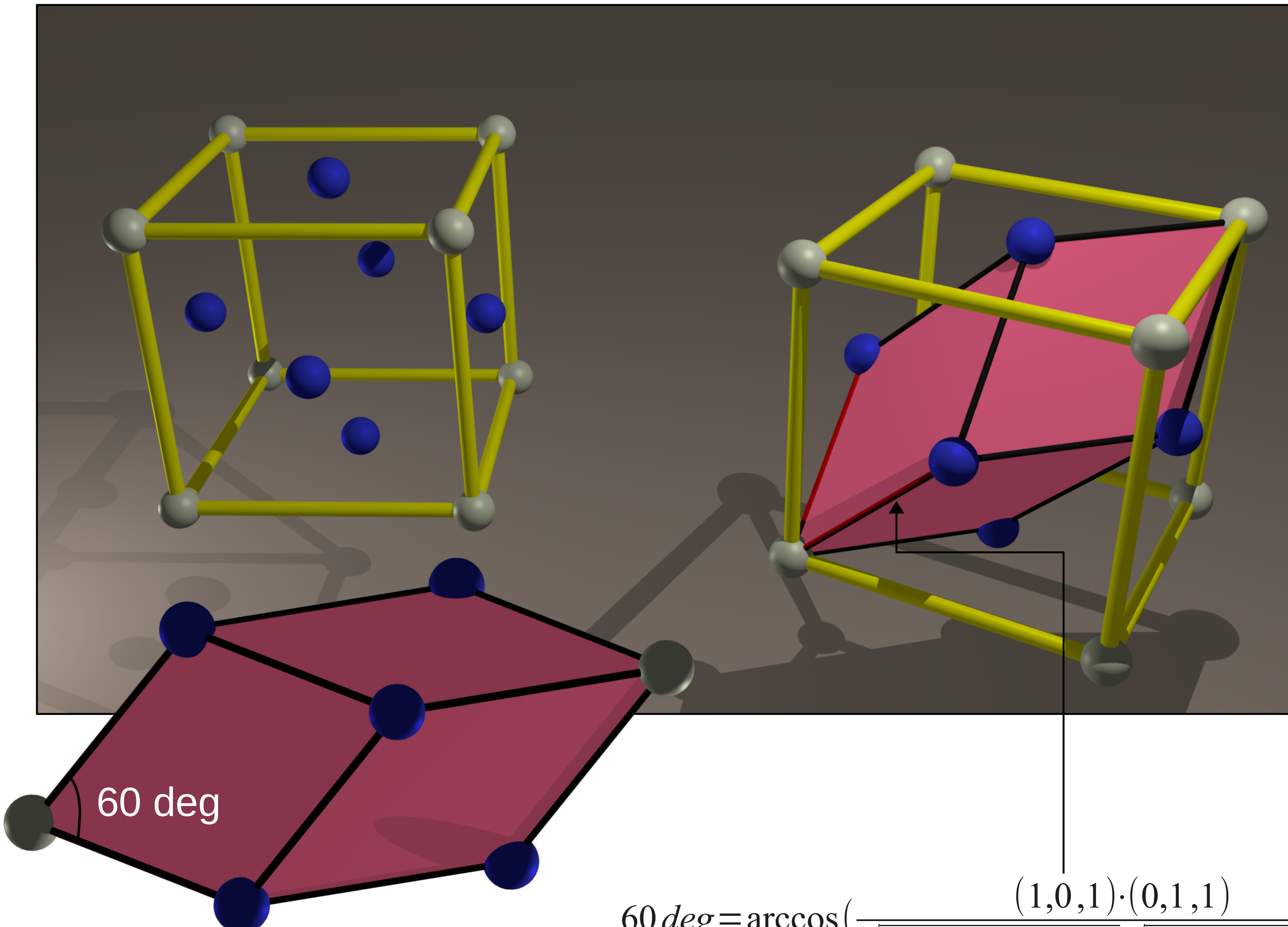


primitive basis (red rods)

*taken mostly from H. Wondratschek, Matrices, *Mappings and Crystallographic Symmetry*, 2002 [5]

Primitive (lattice) basis*

- Example of primitive basis for 3-dimensional lattice – **fcc** structure



$$60\,deg=\arccos\left(\frac{(1,0,1)\cdot(0,1,1)}{\sqrt{((1,0,1)\cdot(1,0,1))}\sqrt{((0,1,1)\cdot(0,1,1))}}\right)$$

*taken mostly from H. Wondratschek, Matrices, *Mappings and Crystallographic Symmetry*, 2002 [5]

Bravais lattice:

- an **infinite** arrangements of points in space ("*A **lattice** is an infinite array of points in space, in which each point has identical surroundings to all others*" [8])
- the lattice can be generated from one point using the translation operators:

$$t_{n_1, n_2, n_3} = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}, \qquad n_{1,} n_{2,} n_3 - integers$$

- the lattice points are given by the end points of the vectors ***t*** (vectors ***a***,***b***,***c*** are linearly independent*)
- vectors ***a***,***b***,***c*** have the same origin; no matter which lattice point is chosen as an origin, the array always looks the same when viewed from it [8]
- forming the parallelpiped from ***a***,***b***,***c*** vectors one obtains a **unit cell**
- unit cells fill the entire space
- The only rotations that are symmetry elements of crystals are n-fold rotations with n=1,2,3,4,6 (proper or improper) – it is not possible to fill the space with uniformly shaped unit cells of other symmetries (without gaps and overlapping)

- One can fill the space with cells of other rotational symmetries using two or more kinds of cells – **quasi-crystals** [8,9]

*it is not possible to get zero vector summing integer multiples of ***a***,***b***,***c***

Bravais lattice:

- an infinite array of points in space ... f points in space
- ... has identical su...
- th... d from one point
- th... by the end point ... in...
- ve... he origin; no mat... origin, the array always looks the same wh...
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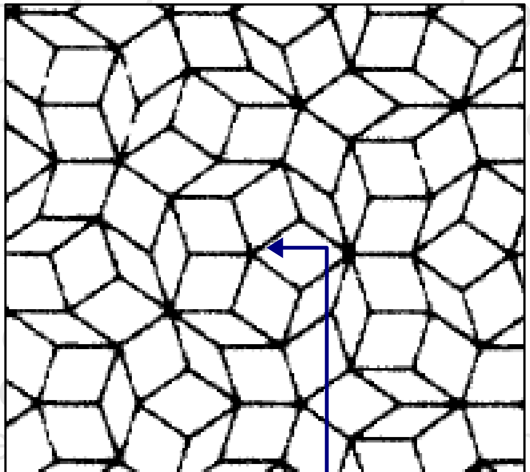

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  Penrose tiling example – 5 fold and 10-fold symmetry

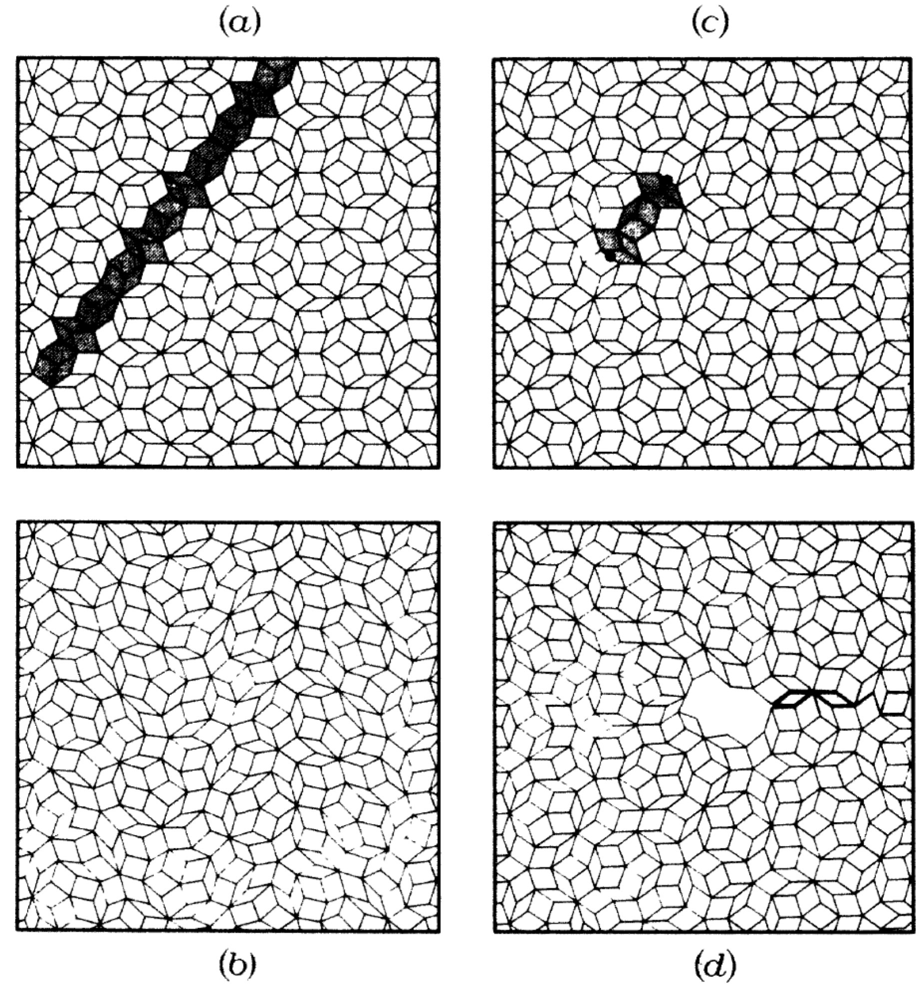
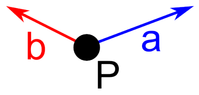


FIG. 3. Penrose tilings. (a) A portion of a perfect Penrose tiling. The shaded unit cells compose a segment of a "worm." (b) A distortion of the tiling of (a) corresponding to variations in the phonon degree of freedom $\mathbf{u}_t$. The unit-cell shapes are distorted, but their arrangement is the same as in (a). (c) A tiling

Image source : J. E. S. Socolar, T. C. Lubensky, P. J. Steinhardt, Phys. Rev. B **34**, 3345 (1986) [10]

*it is not possible to get zero vector summing integer multiples of ***a***,***b***,***c***

- There are 14 Bravais lattices in 3D
- Thera are 5 Bravais type lattices in 2D: oblique, rectangular, centered rectangular, hexagonal and square



We start with an arbitrary point P in a plane and arbitrary vectors **a** and **b**

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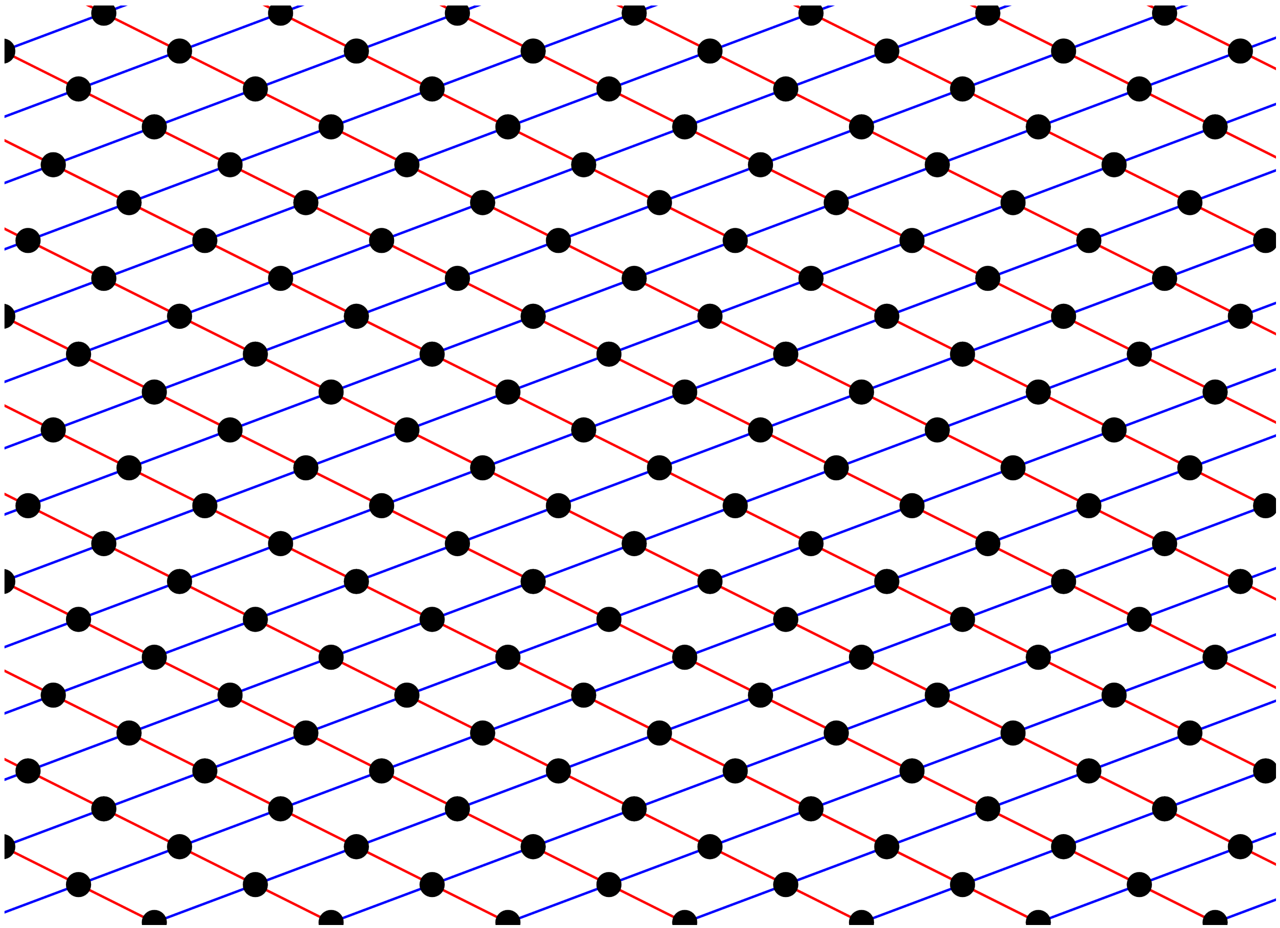

For arbitrary base vectors identity** may be the only symmetry of the structure

We start with an arbitrary point P in a plane and arbitrary vectors **a** and **b**
...and “orbit“* with translations $t_{n_1, n_2, n_3} = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}$

*”The infinite set of symmetry-related points is known as a **crystallographic orbit**” [8]
**denoted usually with 1 or E

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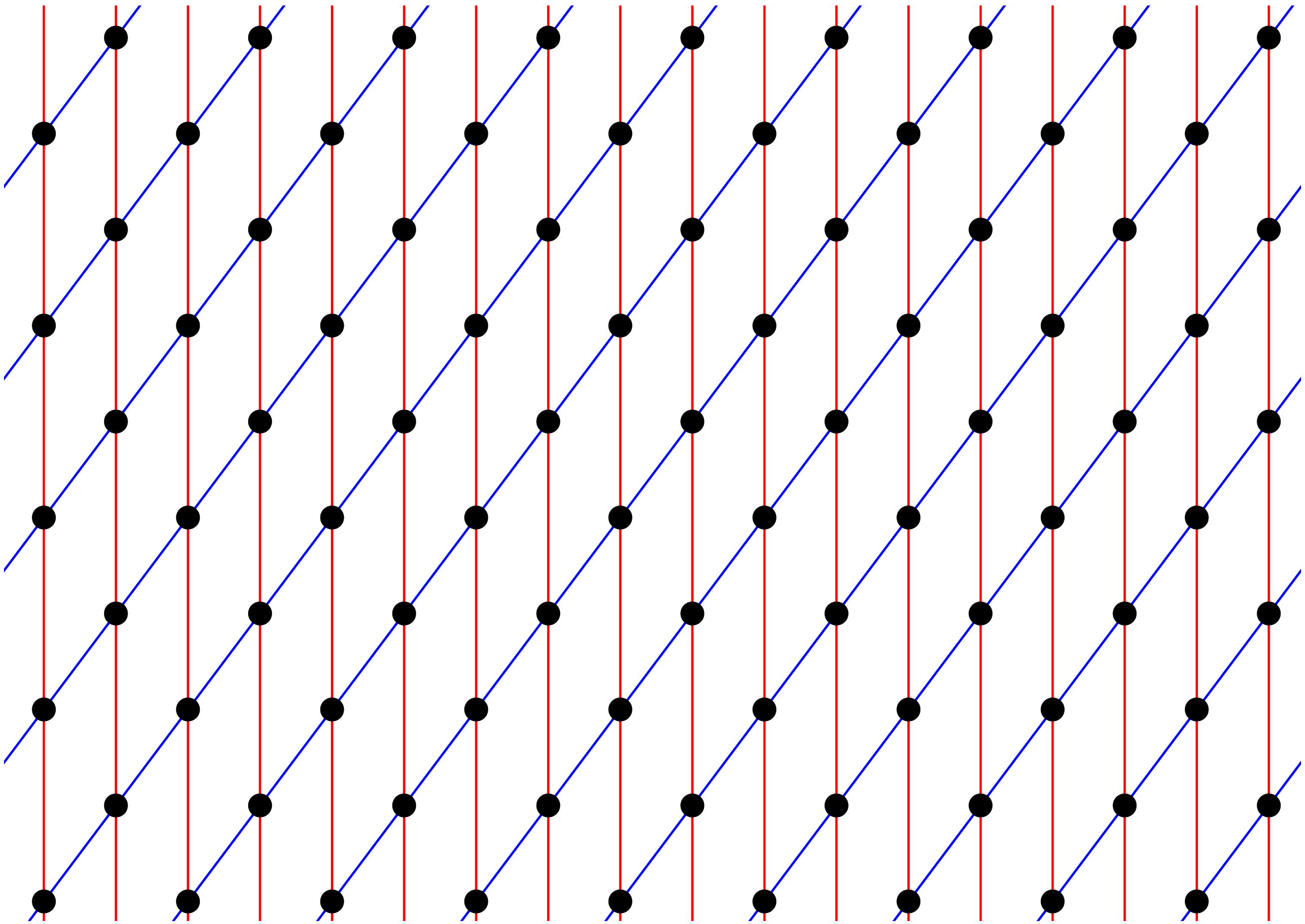

$$\vec{a}_y = \frac{1}{2} \vec{b}_y$$

For some special relations between vectors **a** and **b** it is customary to use unit cell that is different from the primitive cell [11]

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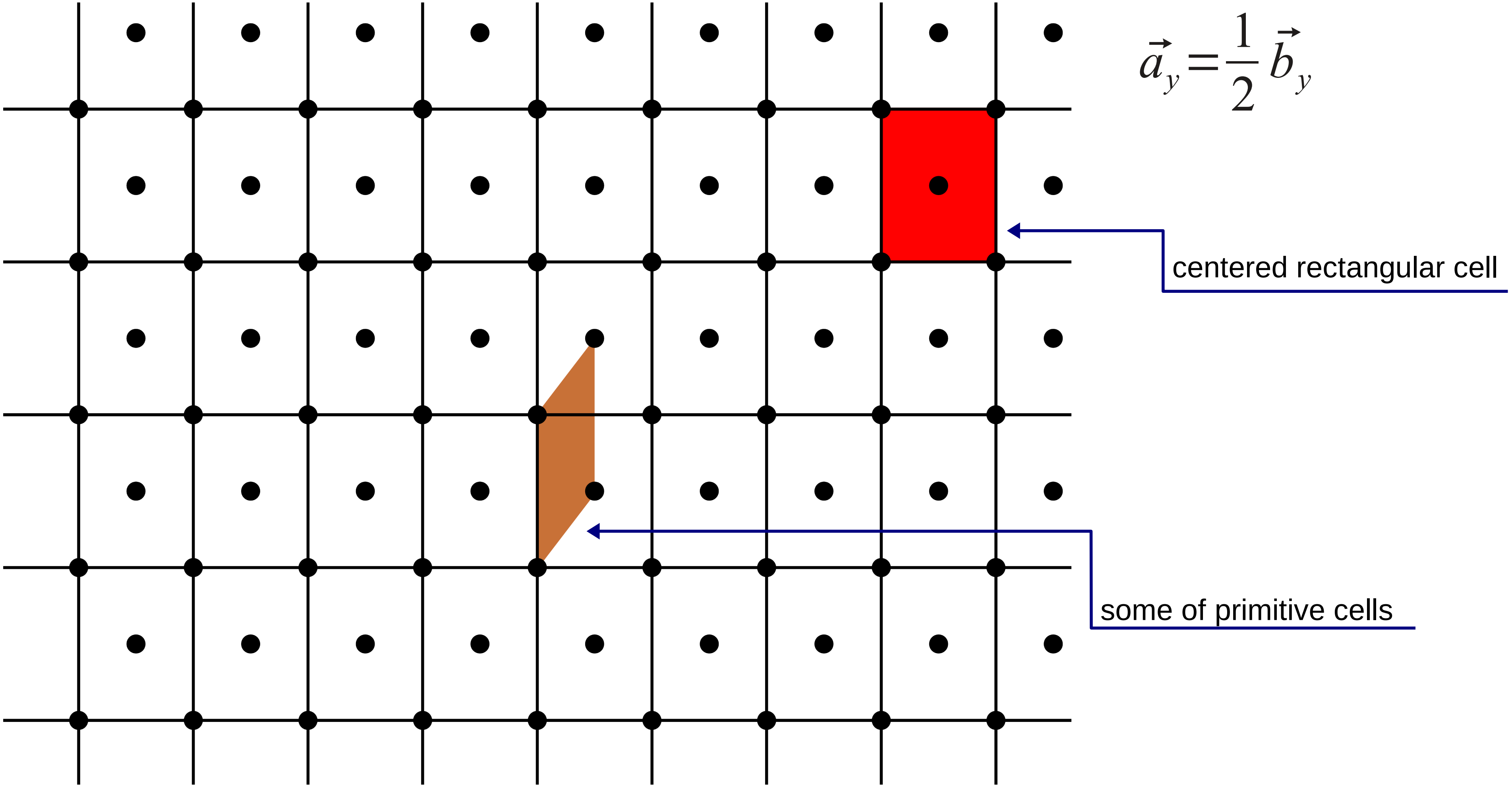


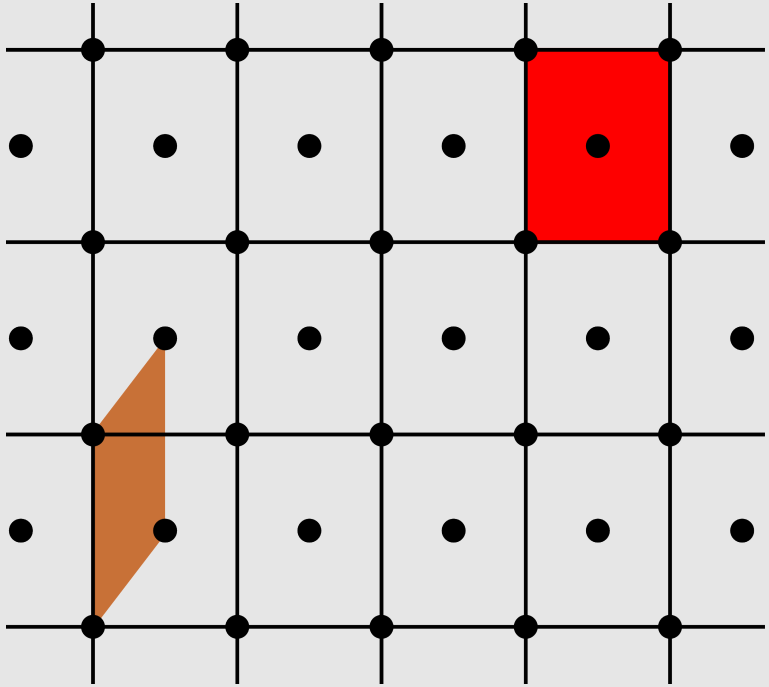
$$\vec{a}_y = \frac{1}{2}\vec{b}_y$$

For some special relations between vectors **a** and **b** it is customary to use unit cell that is different from the primitive cell [11]

The choice of the Bravais unit cell for a given basis is made using the following conditions* [11]:

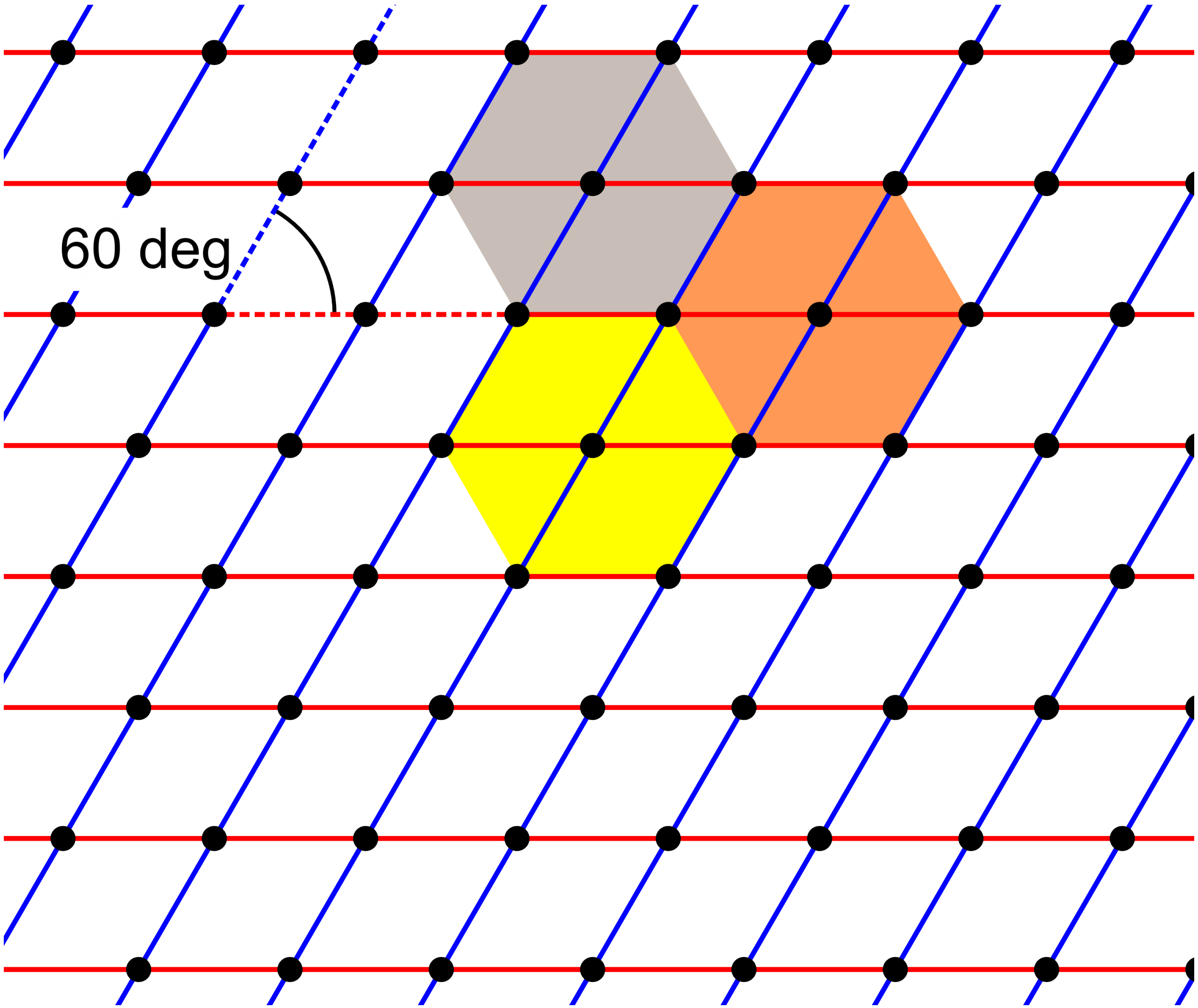
1. The symmetry of the unit cell should correspond to the symmetry of the crystal (lattice). Edges of the cell should be lattice vectors
2. The unit cell should contain maximum possible number of right angles (between edges) or equal angles and equal edges
3. The unit cell should have minimum volume

- The primitive cell to the right has minimum volume
- The cell has no right angles
- The cell (*its symmetry operations*) has no planes of symmetry present in the symmetry of the lattice



*the conditions should be fulfilled consequtively: the first condition is more important than the second

For special relation between basis vectors **a** and **b** one (equal length, in-between angle of 60 deg) one obtains lattice with 6-fold rotational symmetry consistent with close packing of spheres in a plane (*hexagonal lattice*)



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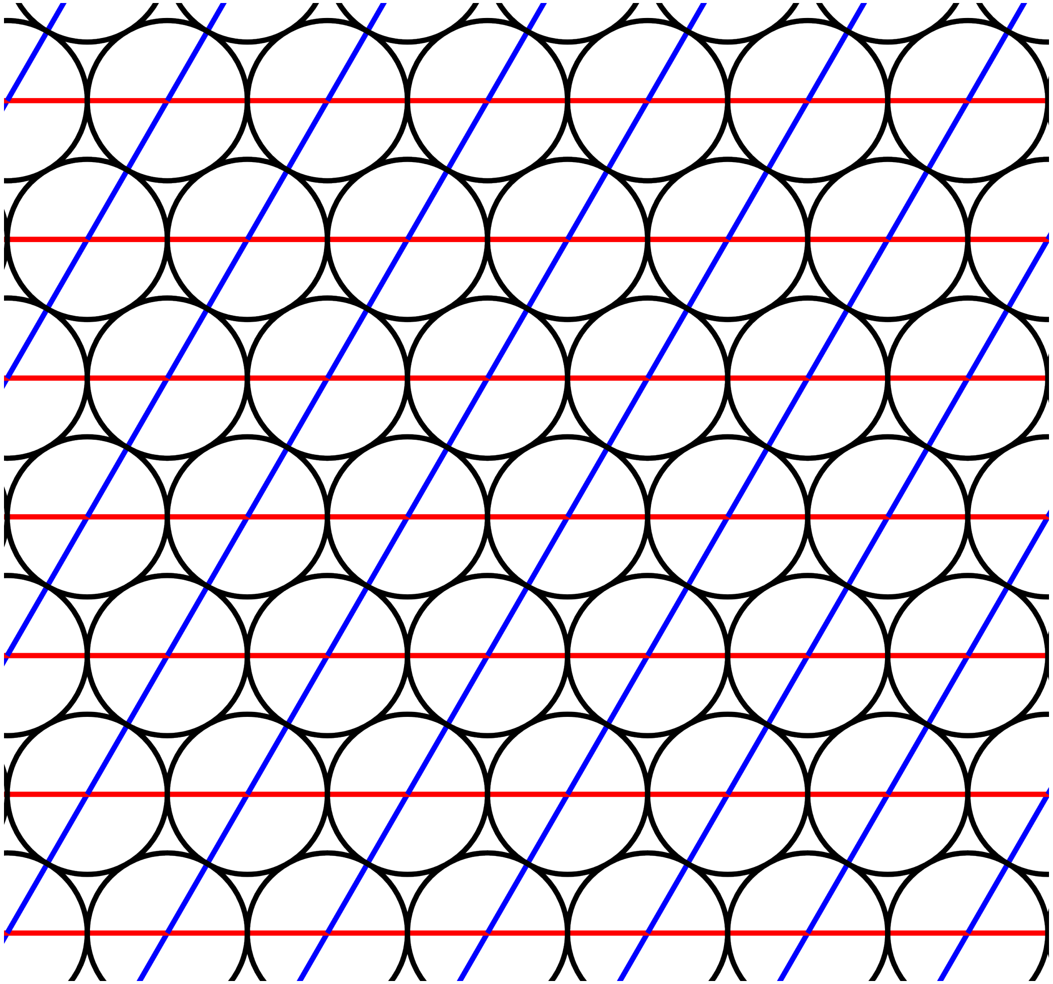
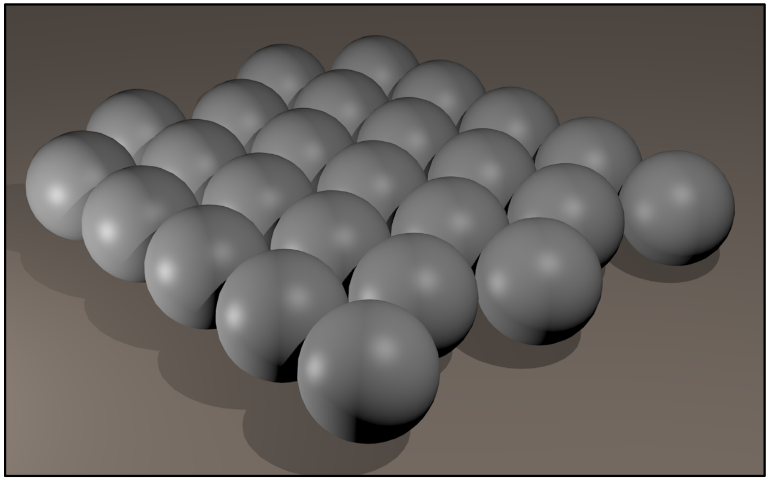




Bravais lattices in 3D

Quantum electronics

primitive | base centered | body centered | face centered

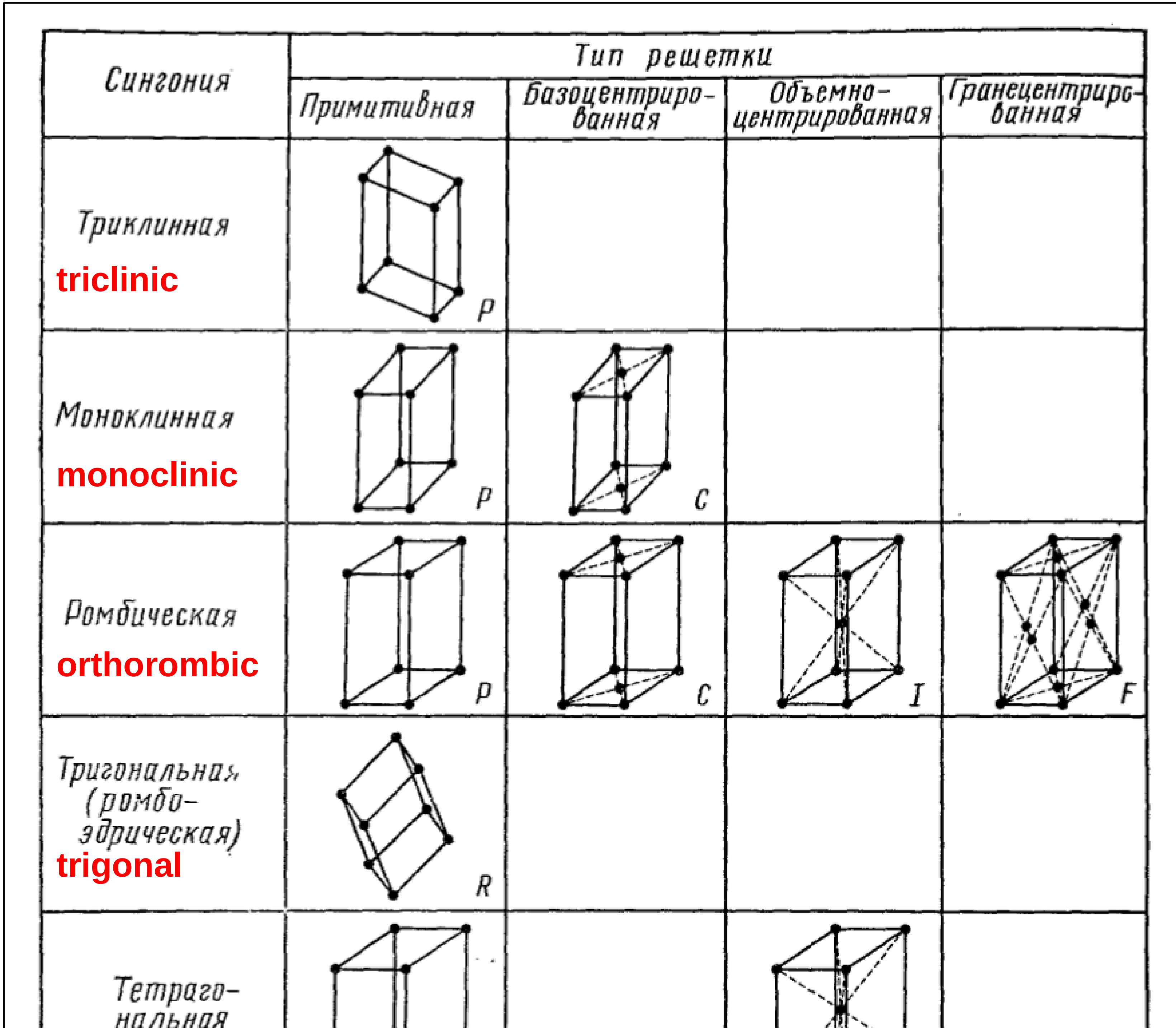
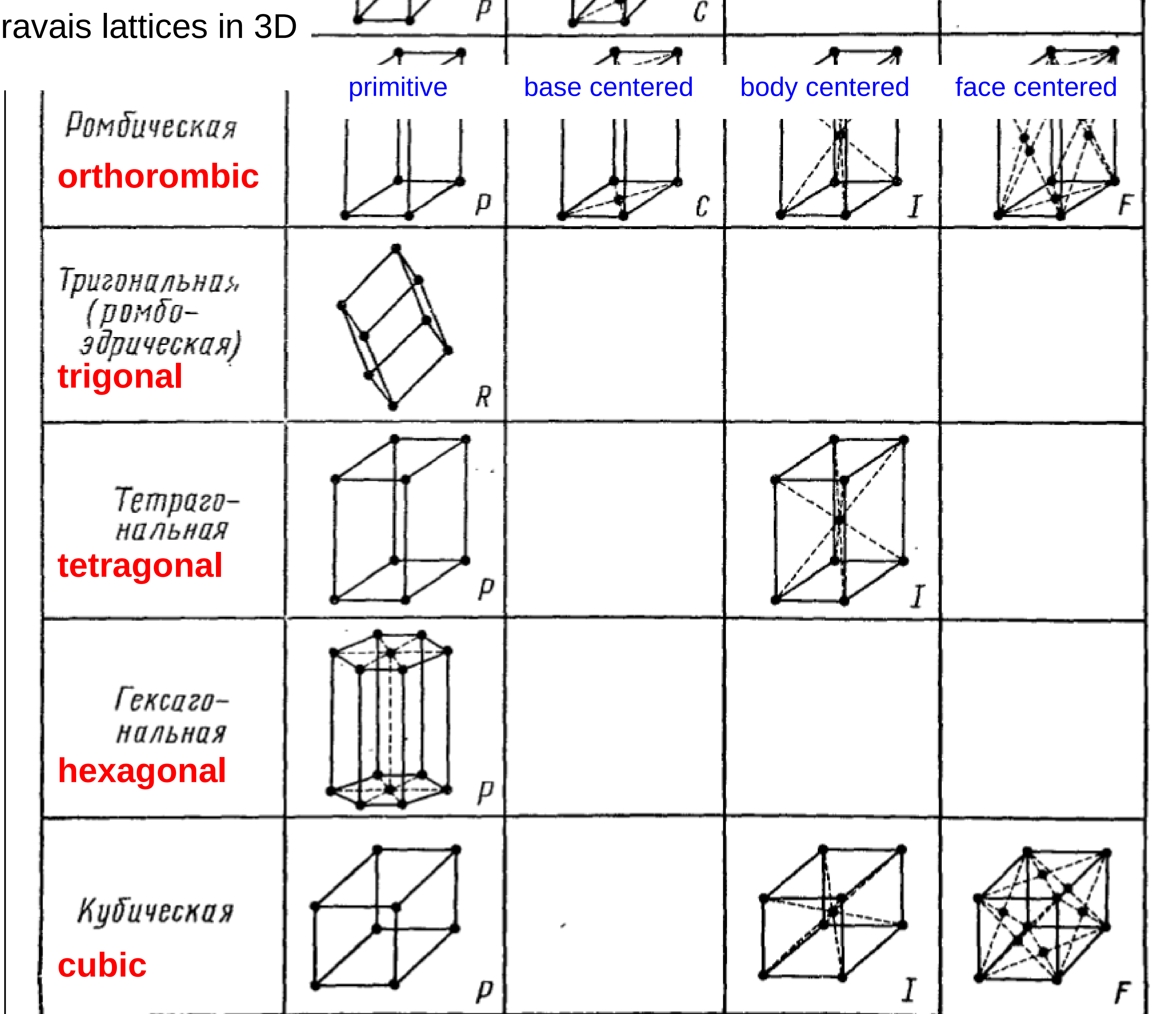


Image source : М.П. Шаскольская, Кристаллография, Москба, “Высшая Школа”, 1984, Fig.92

Bravais lattices in 3D



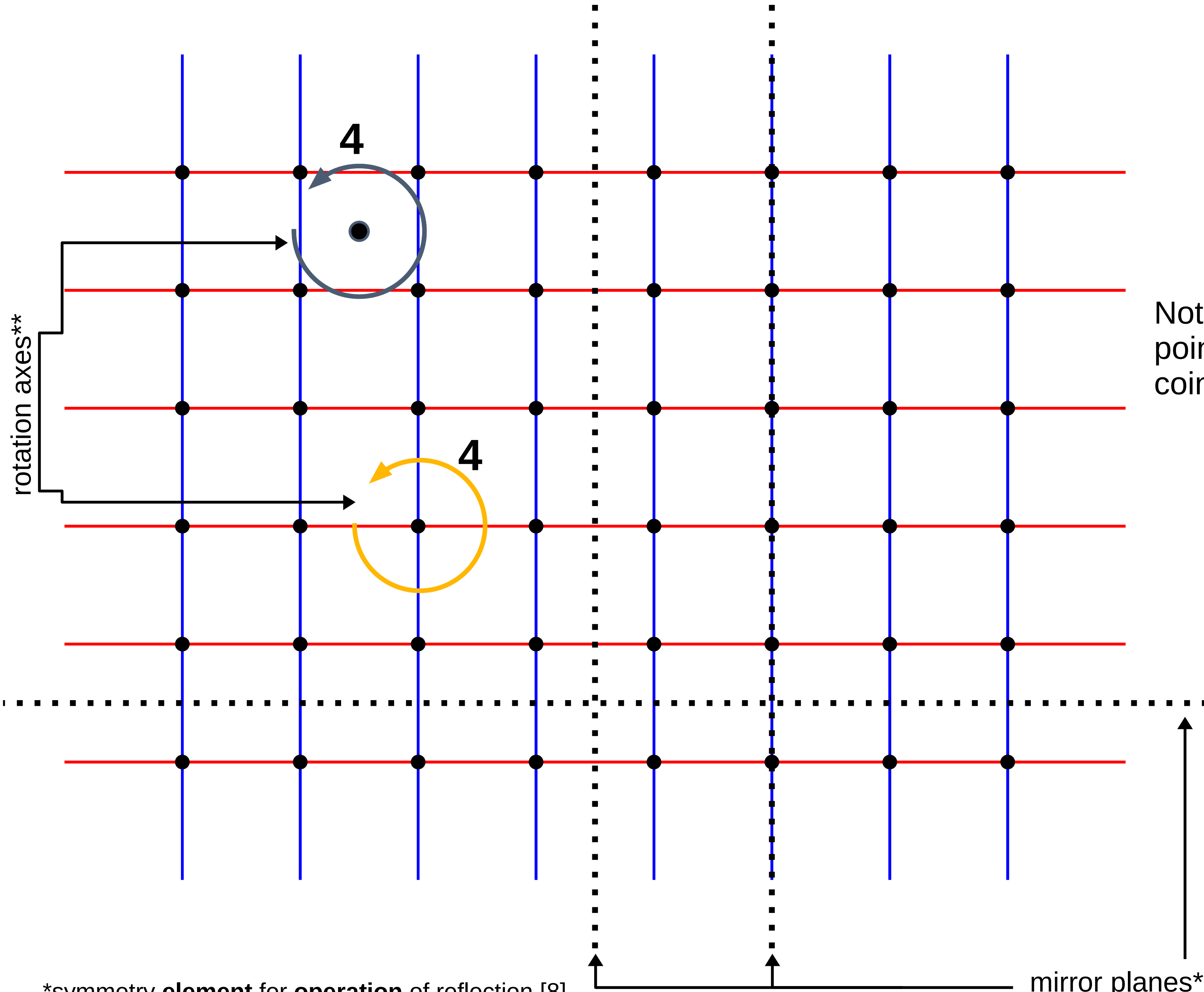
92.
14 решеток Бравэ

Image source : М.П. Шаскольская, Кристаллография, Москба, "Высшая Школа", 1984, Fig.92

- **Point group** – all the symmetry operations that leave one point fixed; this point is called the origin [8].
- "the point group which has the symmetry of the lattice is called the **holohedral point group**, and as such it possesses the largest number of symmetry operations" [8]
- There are several methods to develop (find) point groups; one of them is to:
  1. start with five point groups defined by rotations 1, 2, 3, 4 ,and 6*
  2. add 2-fold rotations perpendicular to these axes
  3. add reflections perpendicular to, or containing the cyclic axis
  4. substitute improper** for proper rotation
- One arrives then at 32 **crystallographic point groups** (allowed in normal crystals – filling all space)
- Point groups characterize macroscopic crystals
- "*most of the macroscopic symmetry aspects of the physical properties of solids are related to the point group, as given by the so-called Neumann principle*" [8]

*in *international notation* the ***n*** symbo denotes symmetry axis (*cyclic axis of symmetry*) with rotation by 2π/n radians
**rotation followed with inversion; symbol $\bar{n}$

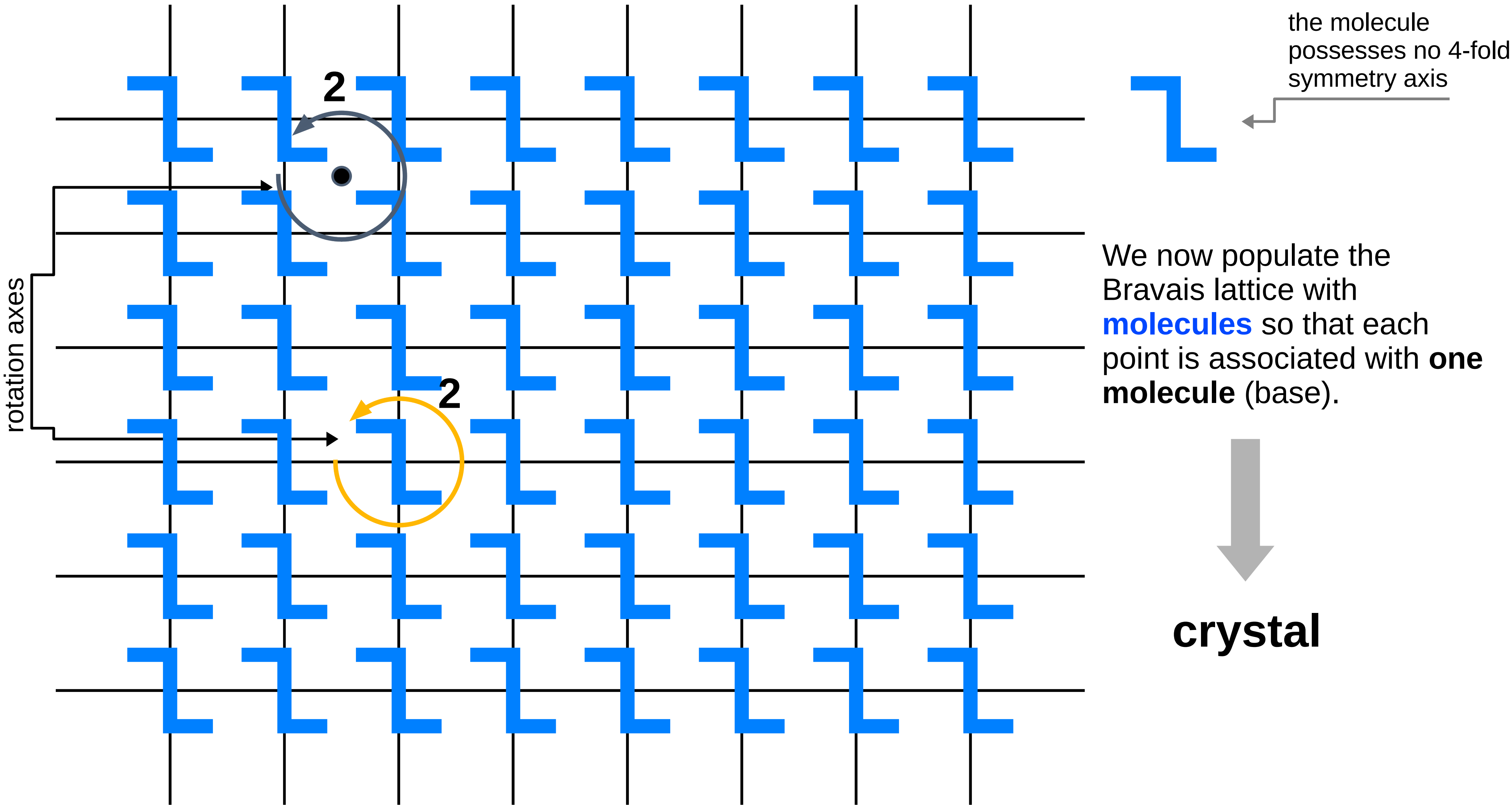
Consider some 2D Bravais lattice*** (rectangular, equal length of basis vectors)



Note that Bravais lattice points do not necessarily coincide with atoms

*symmetry **element** for **operation** of reflection [8]
it is customary to talk about counter-clockwise rotations, * 2D lattice is called **a net**

Consider some 2D Bravais lattice (rectangular, equal length of basis vectors)



We now populate the Bravais lattice with **molecules** so that each point is associated with **one molecule** (base).

crystal

The new structure (crystal) has **no mirror planes** and only 2-fold axes of rotation (previously 4-fold). **The translational symmetry is preserved.**

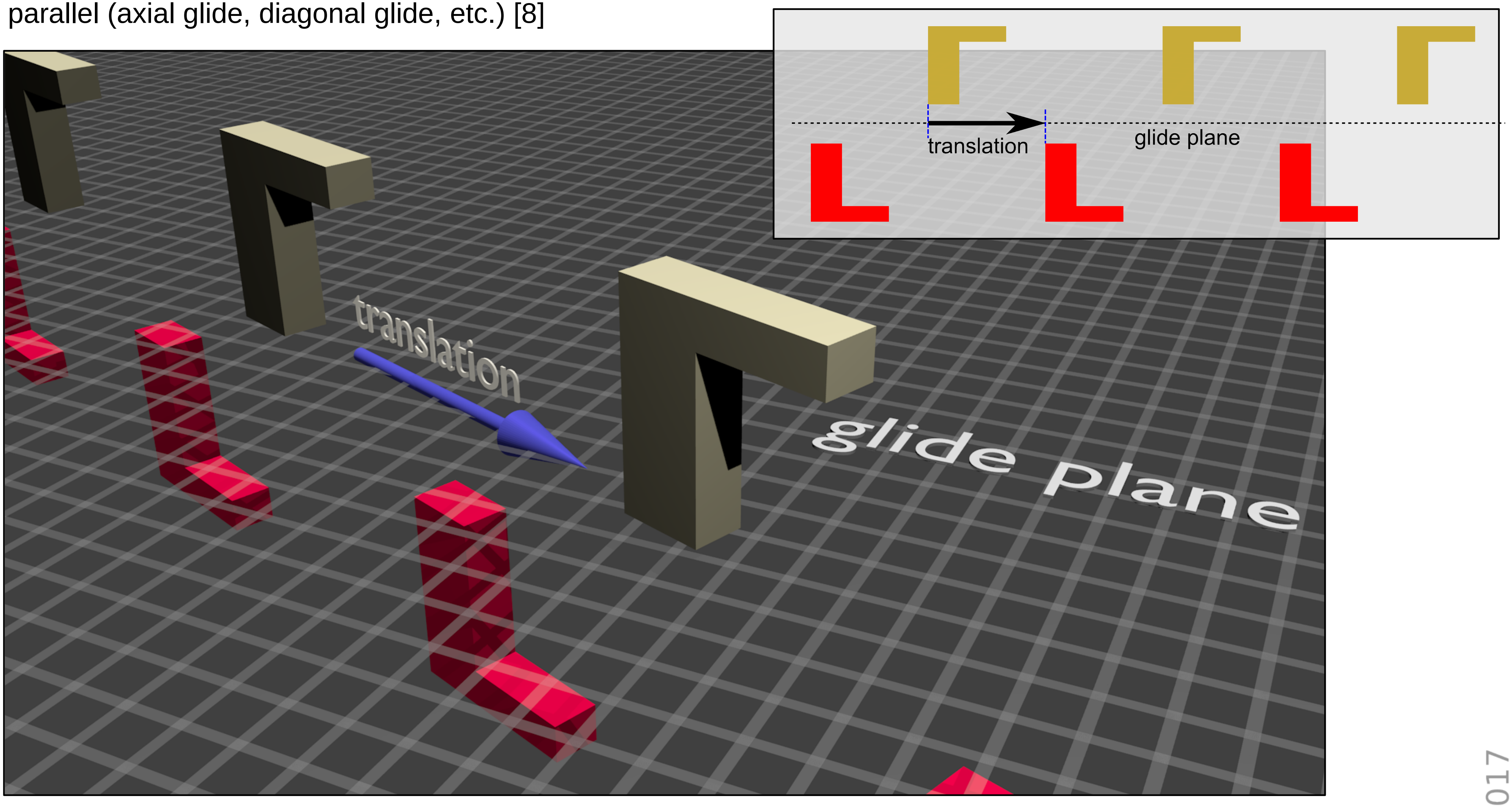
- **Space group** - the set of geometrical symmetry operations that take a three-dimensional periodic object (a crystal) into itself [8]
- The operations belonging to the space group must form a **group** in the mathematical sense.
- Space groups are obtained combining translational symmetry (Bravais lattice) with point symmetry (point groups) together with two additional symmetry operations:
  -glide reflection
  -screw rotation
- Both these operations may involve translation **τ** smaller than a primitive lattice translation
- Simple combination of 32 point groups with 14 Bravais lattice gives 73 out of 230 space groups (so called *symmorphic groups***)

Group [16]:
- the product of any two elements in the group must be an element of the group (square of each of them too)
- one element of he group must commute with all others and leave them unchanged (identity element)
- the associative law of multiplication holds:
  A(BC)=(AB)C
- every element must have a reciprocal within the group

*taken largely from G. Burns and A.M. Glazer, *Space Groups for Solid State Scientists* [8]
**screw and glide operations can be symmetry operations but they can be obtained by combining other operations

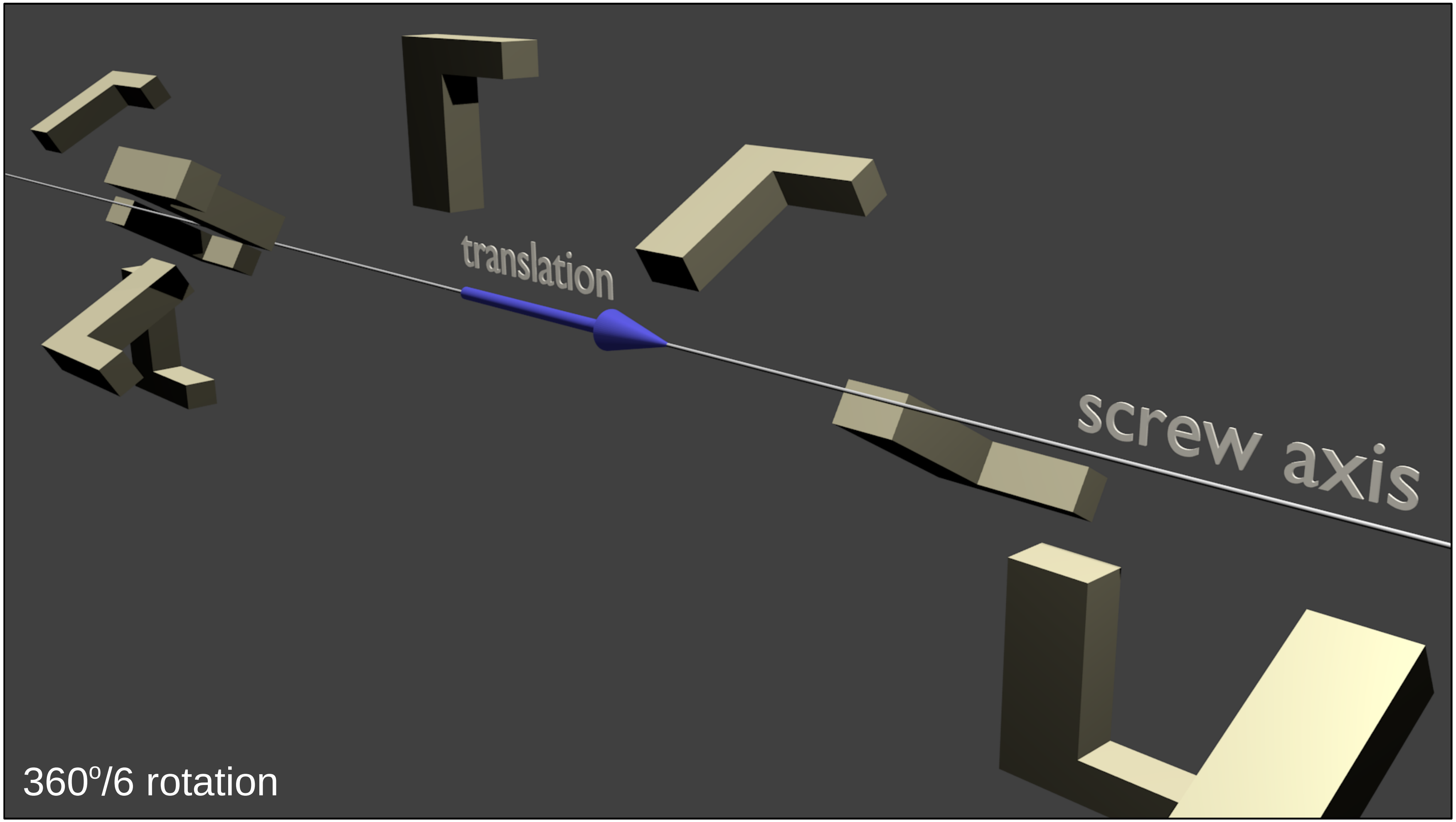
- Space groups are obtained combining translational symmetry (Bravais lattice) with point symmetry (point groups) together with two additional symmetry operations:
  -**glide reflection**: reflection through glide plane followed by translation
  -screw rotation

Note that translations can have various orientations relative to basis vectors, i.e., not necessarily parallel (axial glide, diagonal glide, etc.) [8]



- Space groups are obtained combining translational symmetry (Bravais lattice) with point symmetry (point groups) together with two additional symmetry operations:
  -glide reflection: reflection through glide plane followed by translation
  -**screw rotation**: rotation by 360°/n followed by a translation

Note that "..., the amount of translation is (1/n) th of one or more unit repeat distances" [8] ← Performing n screw rotations results in multiples of unit vector translation



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