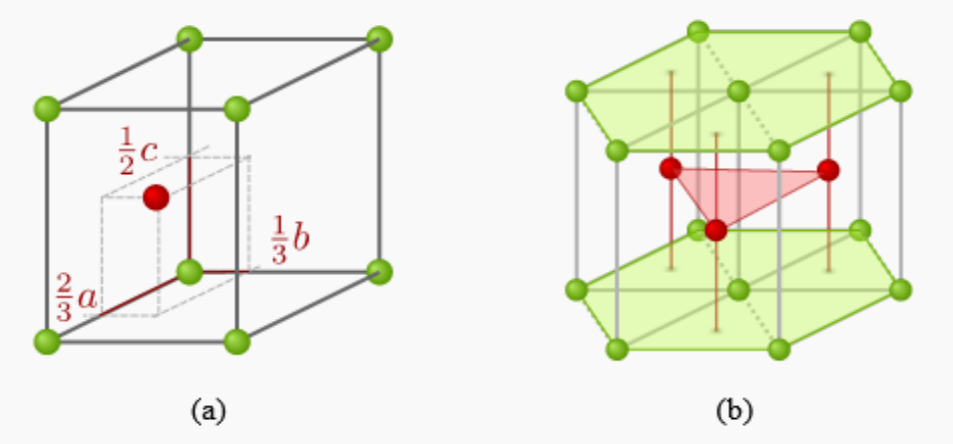
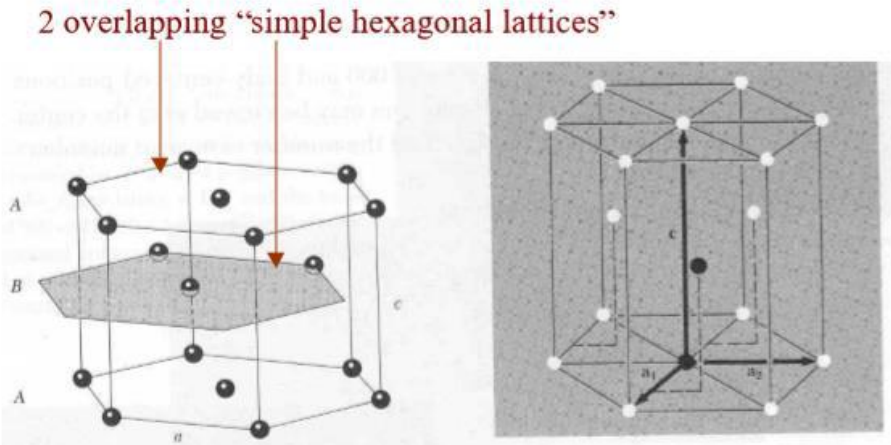
Tutorial 2

1. The hcp structure

Identify: primitive vectors; primitive cell; total number of atoms per unit cell; atom packing factor and the coordination number.

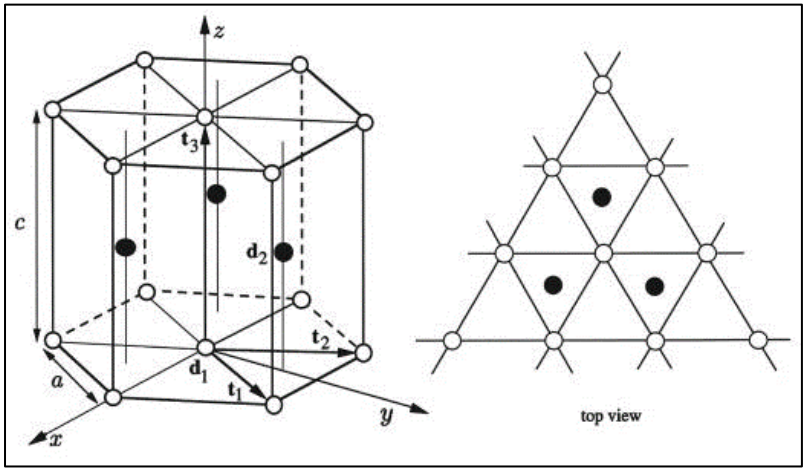




- The hcp structure is characterized by two interleaved hexagonal lattices shifted by the vector 2/3, 1/3, 1/2) (in the conventional unit cell basis) shifted with respect to each other.
- The underlying lattice is not a Bravais lattice because the individual lattice points are not equivalent.

Answer:

1. Understanding structure by construction:



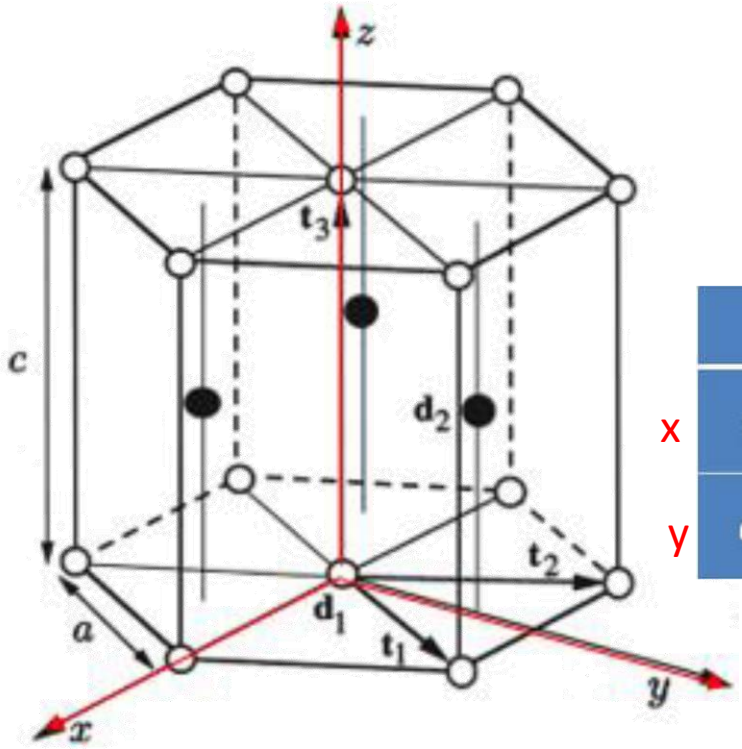
- To describe this structure, consider a two-dimensional arrangement of equilateral triangles (or regular hexagons including their centers) of the edge, as shown in the figure. Then, along the axis, stack a second plane of equilateral triangles over the centers of the other triangles, as shown in figure.
- Then repeat the sequence of planes ABABAB..., the third plane is directly above the first, the fourth plane is direclty above the second and so on. The hexagonal close-packed structure can be represented as it is formed by two interpenetrating simple hexagonal Bravais simple hexagonal Bravais lattices which are primitive translation vectors and the two basis vectors of the hcp structure.
- According to our image, we can say that the **primitive translation vectors are t_1, t_2, t_3,** and the **two basis vectors of the hcp structure are d_1 and d_2**.

- We write their coordinates like following:

$$\mathbf{t}_1 = a\left(\frac{1}{2}, \frac{\sqrt{3}}{2}, 0\right), \quad \mathbf{t}_2 = a\left(-\frac{1}{2}, \frac{\sqrt{3}}{2}, 0\right), \quad \mathbf{t}_3 = c(0, 0, 1)$$

$$\mathbf{d}_1 = 0, \quad \mathbf{d}_2 = \left(0, a\frac{\sqrt{3}}{3}, \frac{c}{2}\right)$$

WHY?

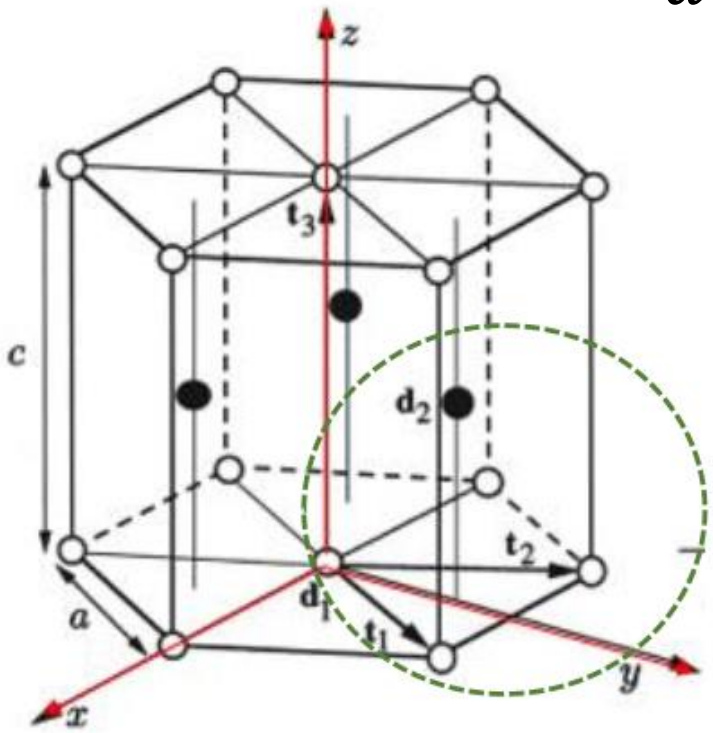


- The angle between t_1 and t_2 is 60°; the y-axis forms an 30° angle with t_1 and t_2; t_1 forms an angle of 60° with x-axis ...and...

		0°	30°	45°	60°	90°
x	sin θ	0	$\frac{1}{2}$	$\frac{1}{\sqrt{2}}$	$\frac{\sqrt{3}}{2}$	1
y	cos θ	1	$\frac{\sqrt{3}}{2}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2}$	0

- How do we think about the d_1 and d_2?
- Using our knowledge of triangles and the Pythagorean theorem, if *a* and *b* are the lengths of the sides at the right angle, the cathetus, and *h* is the length of the side opposite the right angle, the hypotenuse, then the theorem is expressed as an equation.

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

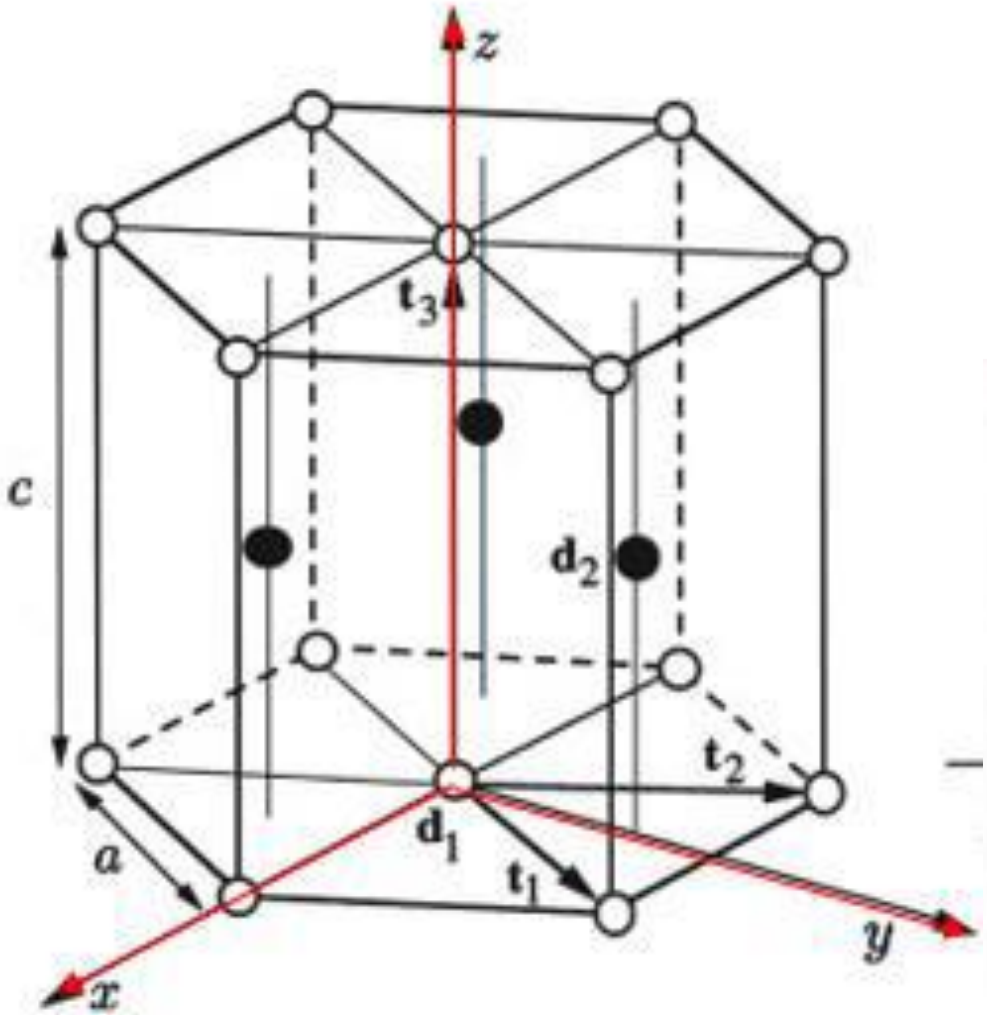


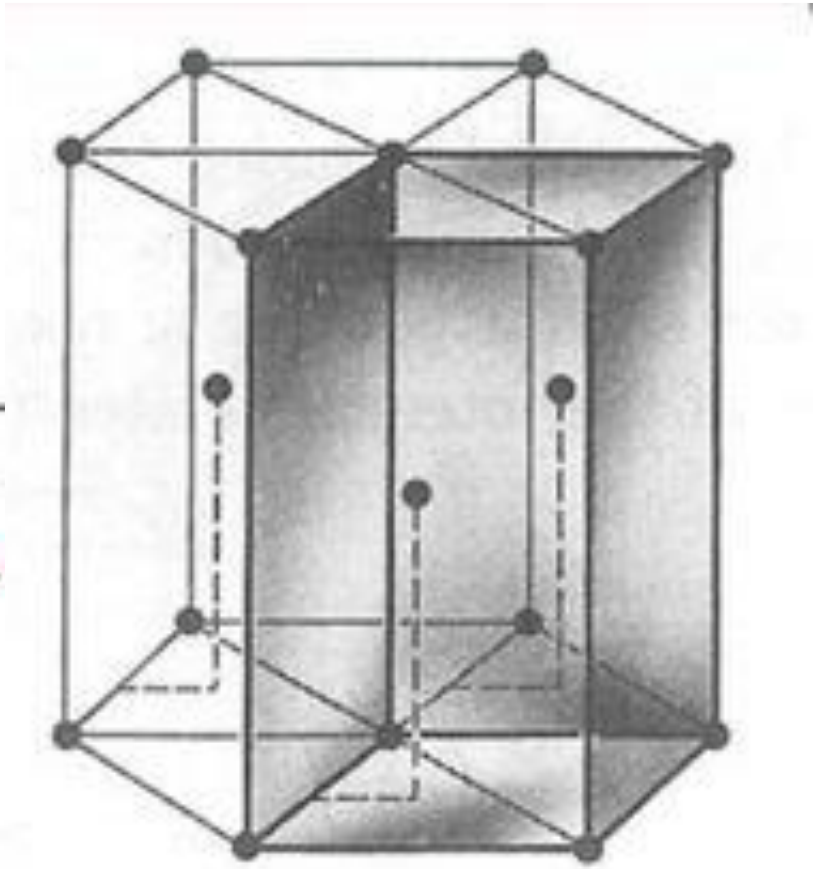
In our situation are:

- a=a/2, c=a and b=?
- a is the lattice constant

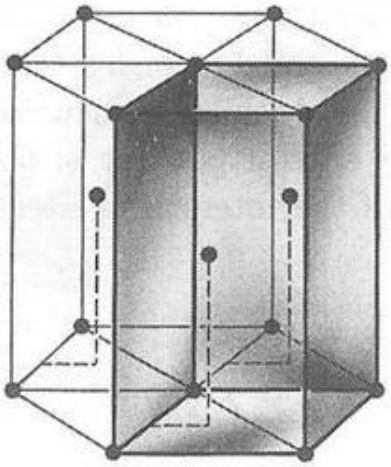
- $(a/2)^2 + b^2 = a^2 \rightarrow \mathrm{b} = \frac{\sqrt{3}}{2}$
- $y_{d2} = \left(\frac{2}{3}\right) * b \Rightarrow y_{d2} = \frac{\sqrt{3}}{3} * a$
- $z_{d2} = \left(\frac{1}{2}\right) * c$
- $x_{d2} = 0$

Primitive Cell

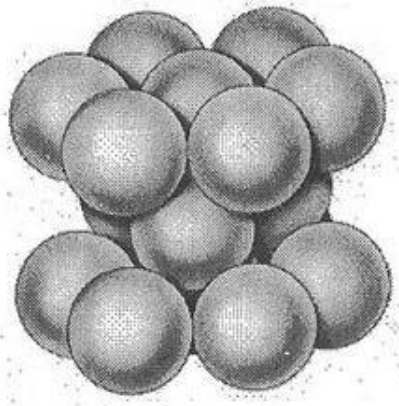




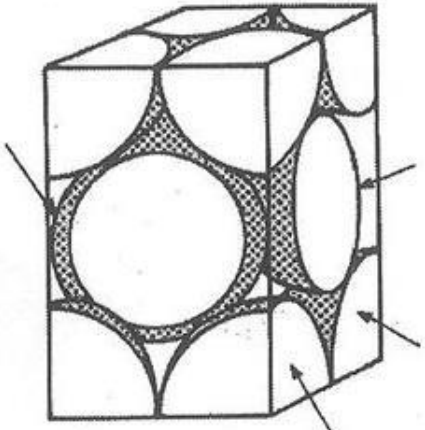
Number of atoms in a primitive cell



(a)



(b) hexagonal

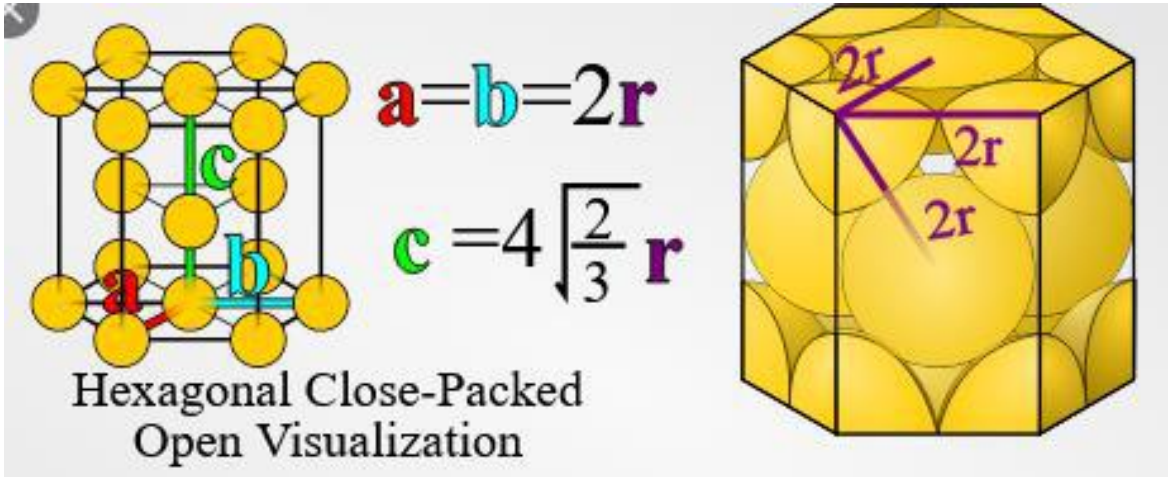


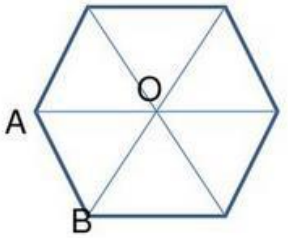
(c)

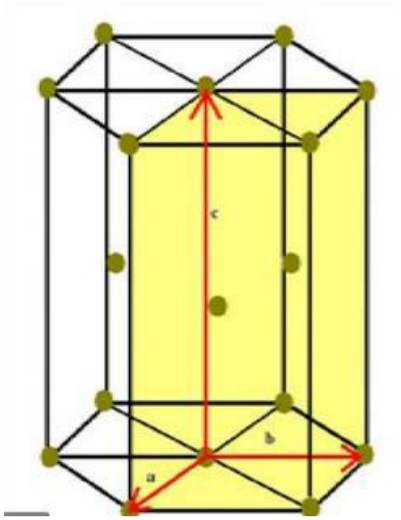
- Each corner atom is divided by 6 neighbouring unit cells, so each corner atom carries (1/6) of an atom, as shown in the model.
- Each surface centre carries 1/2 atom.
- The total number of atoms/unit cells is therefore:
- n= 2*(6×1/6) + 2*(1/2)+3 = 6

APF (atomic packing factor)

$$\varrho = \frac{n \cdot V_{sph}}{V_{uc}}$$

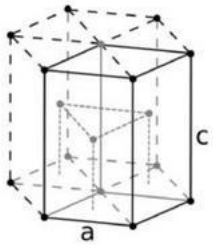






$$a = 2r$$

$$c = \sqrt{\frac{2}{3}}(4r).$$



It is then possible to calculate the APF as follows:

$$\text{APF} = \frac{N_{\text{atoms}} \cdot V_{\text{atom}}}{V_{\text{crystal}}} = \frac{6 \cdot (4/3)\pi r^3}{[(3\sqrt{3})/2](a^2)(c)}$$

$$= \frac{6(4/3)\pi r^3}{[(3\sqrt{3})/2](2r)^2(\sqrt{\frac{2}{3}})(4r)} = \frac{6(4/3)\pi r^3}{[(3\sqrt{3})/2](\sqrt{\frac{2}{3}})(16r^3)}$$

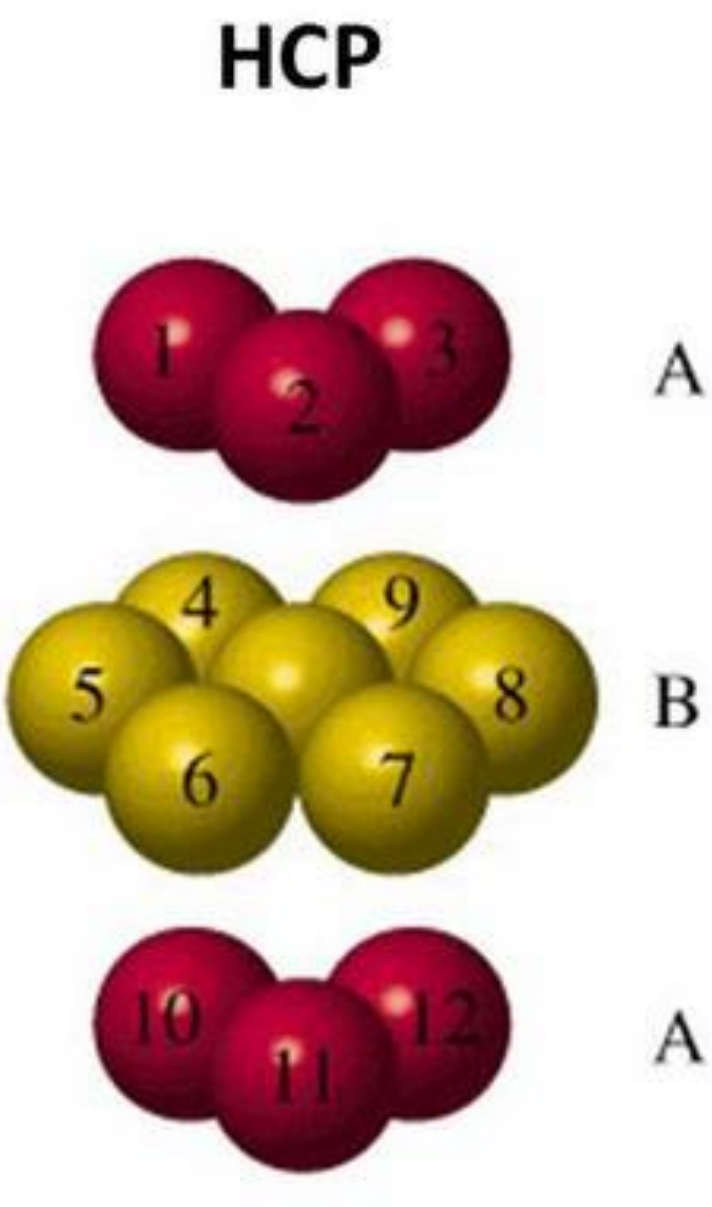
$$= \frac{\pi}{\sqrt{18}} \approx 0.74.$$

$$APF = 6 * \left(\frac{\sqrt{3}}{4}\right) * a^2 * \mathrm{c} = \frac{3\sqrt{3}a^2c}{2}$$

Coordination number

Calculation in connection with the packing process of layers

12



Important hints1

The ideal hexagonal closed structure is obtained when the four given points (t_1 ,t_2 ,d_1 , d_2) form a regular tetrahedron the condition that the lengths of the four edges are all equal gives the condition:

$$\left|\mathbf{d}_2\right| = \left|\mathbf{t}_1\right| \quad \Rightarrow \quad \frac{a^2}{3} + \frac{c^2}{4} = a^2 .$$

The ideal ratio becomes:

$$\frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633;$$

This ratio is only approximately verified in actual hcp crystals The ideal closed hexagonal. Structure occurs when the atoms behave as a hard sphere touching each other.

Important hints2

There is no necessity on connection between the lattice parameters and the ratio is generally different for different materials Several metals have the hcp structure. For example:

$$\mathrm{Be}\ (a = 2.29\mathring{A}; c = 3.58\mathring{A}; c/a = 1.56),$$

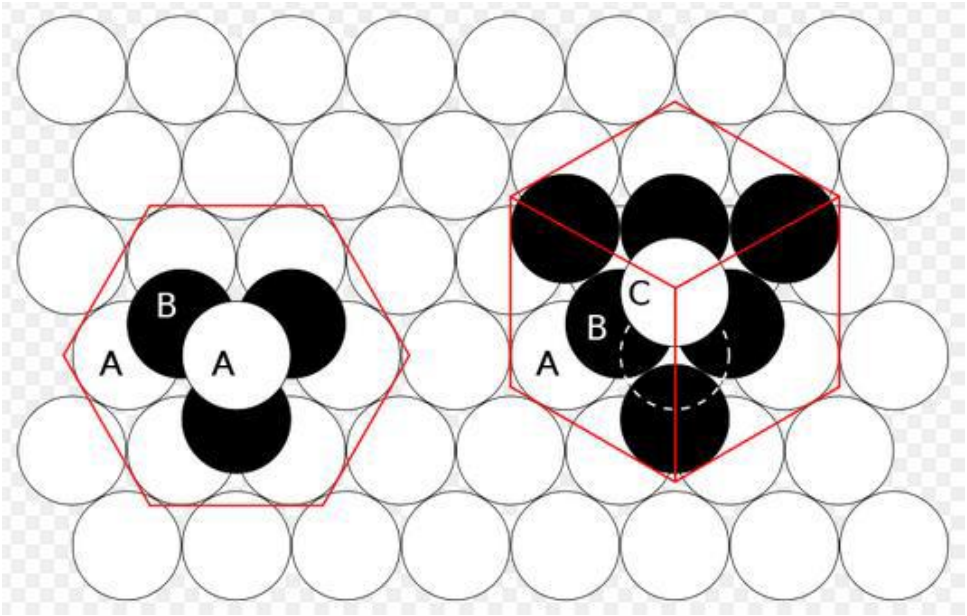
$$\mathrm{Cd}\ (a = 2.98\mathring{A}; c = 5.62\mathring{A}; c/a = 1.88),$$

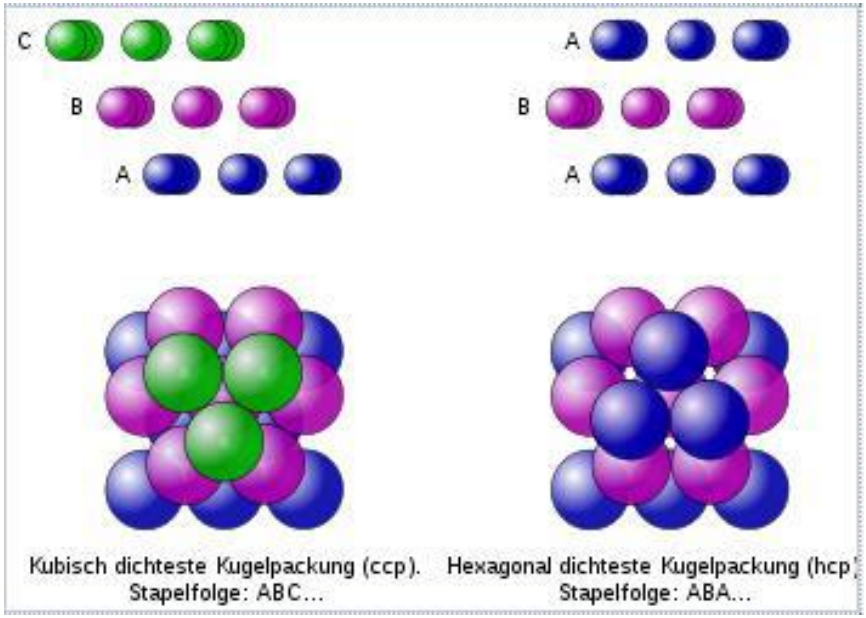
$$\mathrm{Mg}\ (a = 3.21\mathring{A}; c = 5.21\,\mathring{A}; c/a = 1.62)$$

$$\mathrm{Ti}\ (a = 2.95\mathring{A}; c = 4.69\mathring{A}; c/a = 1.59),$$

$$\mathrm{Zn}\ (a = 2.66\mathring{A}; c = 4.95\mathring{A}; c/a = 1.86).$$

There are 2 ideal closest packings. One is the hcp structure we just studied, and the other is the fcc structure the sequence of hexagonal planes in this case is ABC, ABC, etc where C is rotated with respect to the B plane by $2\pi/6$. These closed packed hexagonal planes are orthogonal to the space diagonal of the conventional fcc cube.





Further information see: https://de.wikipedia.org/wiki/Dichteste_Kugelpackung