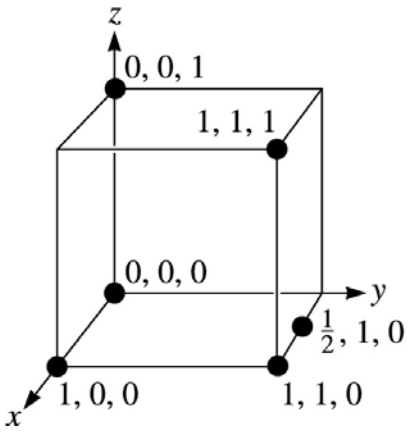
Navigating the Crystal

Need to know:

- Positions within the crystal
- Directions in the crystal
- And planes of the crystal

We need a coordinate system centered in a corner of the crystal and where the unit corresponds to the lattice parameter *regardless* of its magnitude



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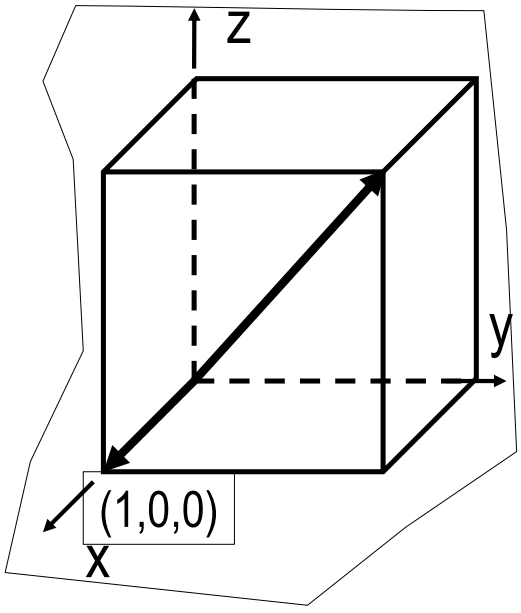
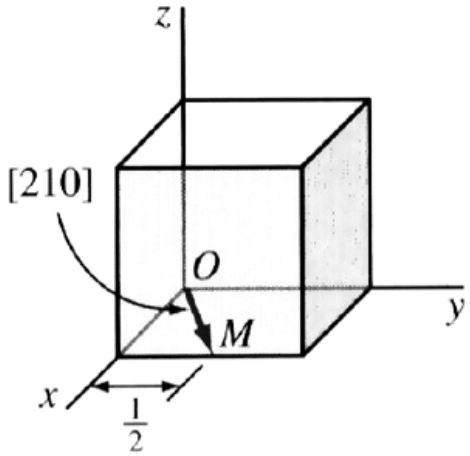
Miller Indices of Crystallographic Directions

- To calculate the indicated direction:
- Verify the initial and end points of the vector
- Subtract the *the head minus the tail*: (1,0,0) – (0,0,0) = 1,0,0
- Eliminate fractions if necessary (by multiplying by common denominators)
- Designate the direction as a set of three numbers without commas enclosed by brackets.
- The red direction would be: [100]
- *Do the same for the blue direction*

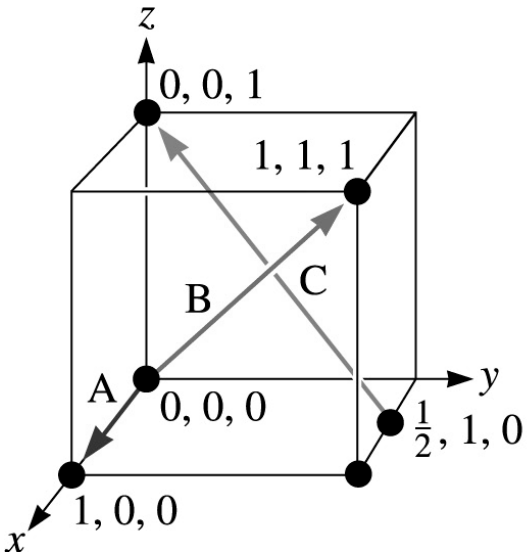


Miller Indices of Crystallographic Directions (cont.)



First, write down the coordinates of the head and then the tail of the vector. Then subtract them.

Work on the directions indicated



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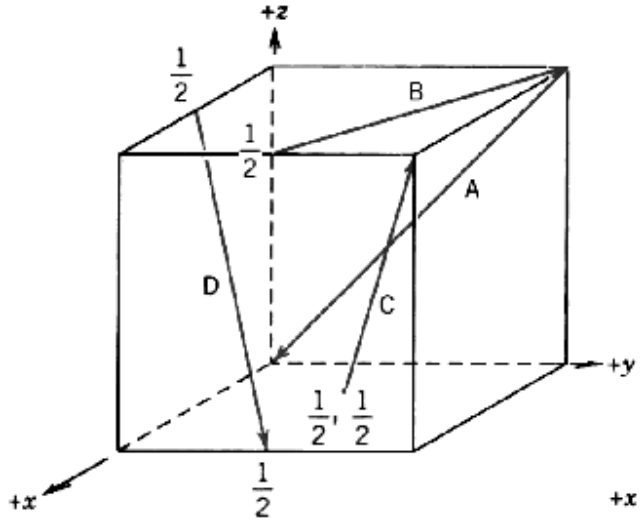
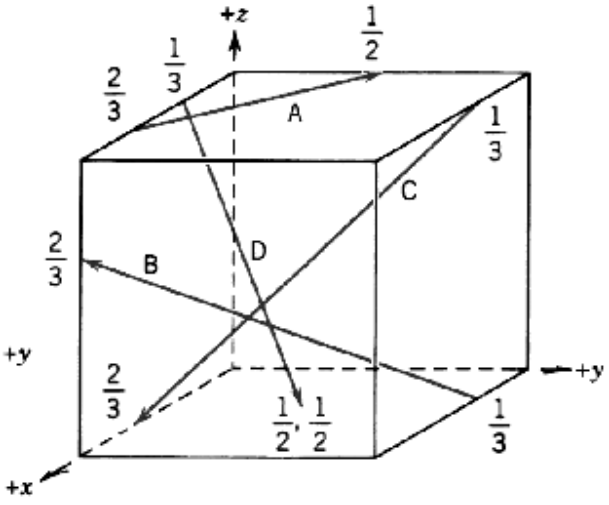
Miller Indices of Crystallographic Directions (cont.)





<u>Always</u> follow the “recipe”!!!

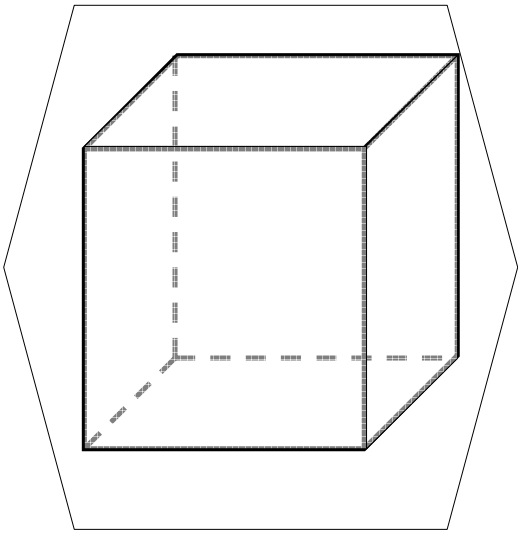
Miller Indices of Crystallographic Planes

- Use the same coordinate system as before
- Find the points where the plane intersects with each axis *(this is the key part)*
- Write down the three-number set and invert it: q,r,s $\Rightarrow$1/q,1/r,1/s
- If there are fractions multiply by the common denominator to get integers
- Assign the following nomenclature: **(*h k l*)**

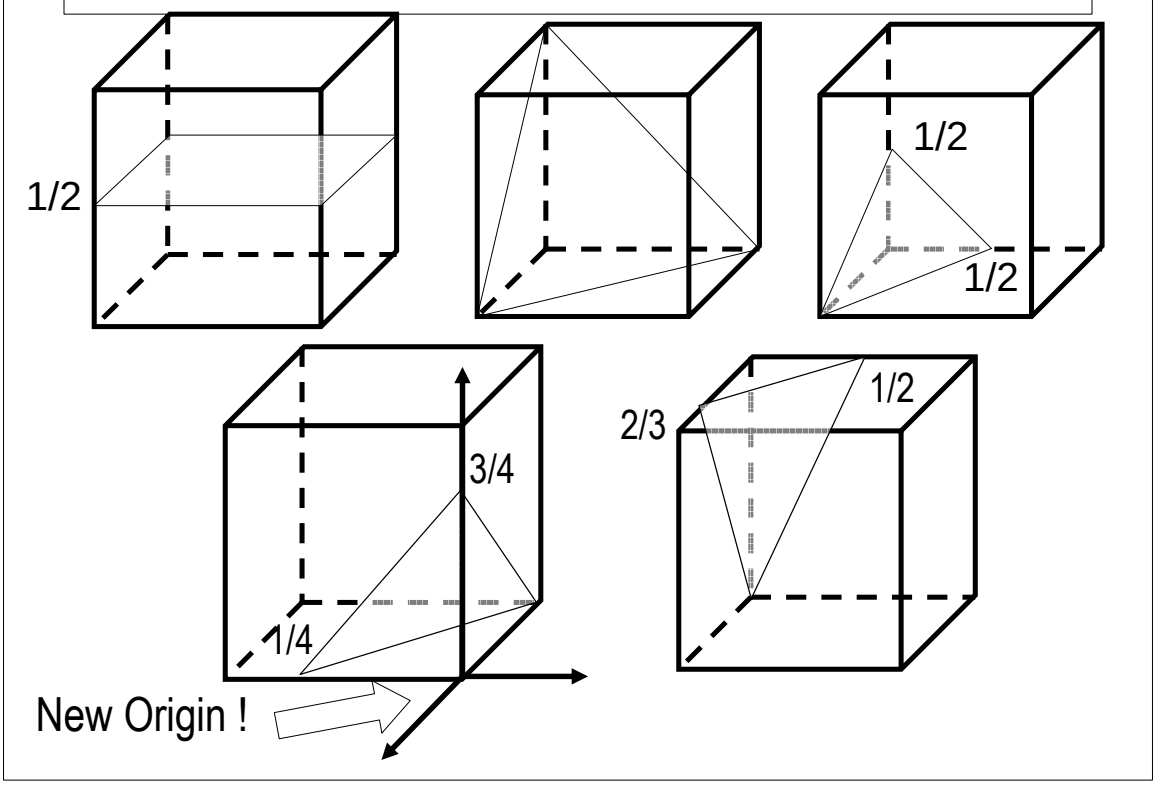
Miller Indices of Planes (cont.)

Let's practice by finding the Miller indices of the three planes (green, blue and red) indicated.

Always follow the recipe given before.

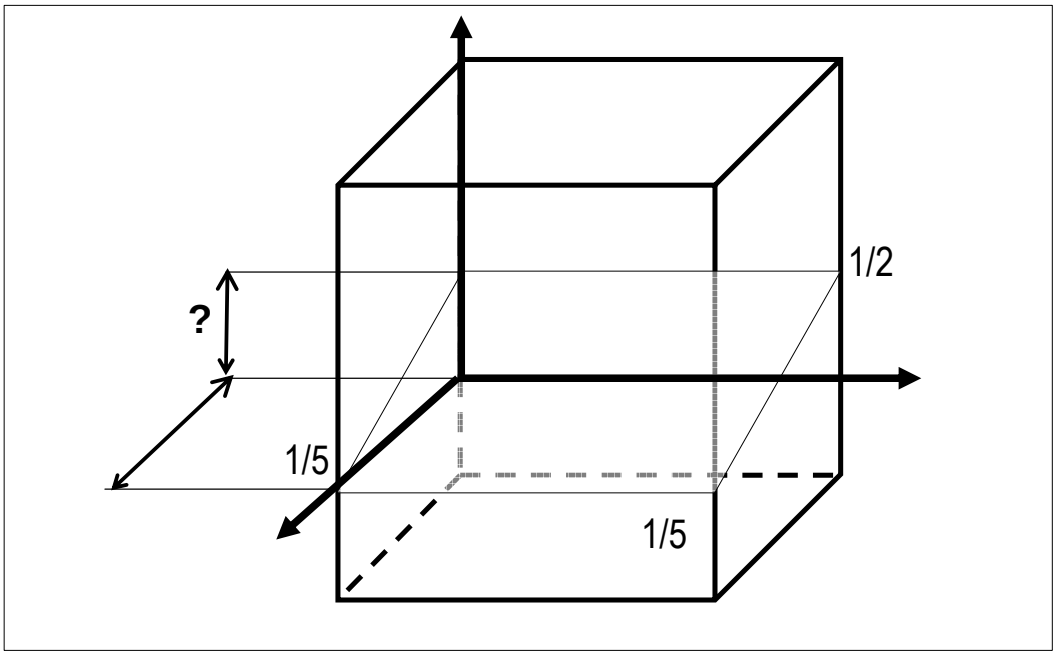


More Miller Indices



More Miller Indices (cont.)

There are four ways of solving this problem, resulting in two different sets of Miller indices.

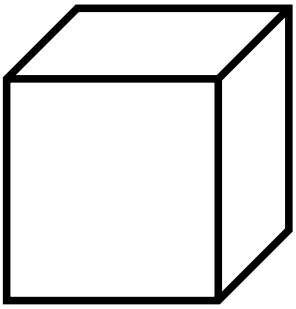


Got it? Now let's do it the reverse way

Draw the (222) plane of this cubic unit cell:

Now draw the (130) plane and [210] direction.

Easy? Now try this $(3\bar{1}0)$ and this $(\bar{2}0\bar{3})$

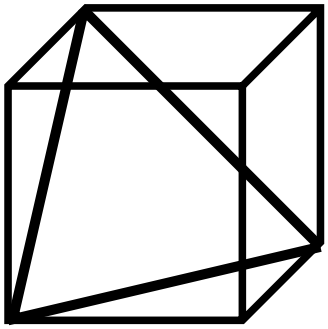


Homework

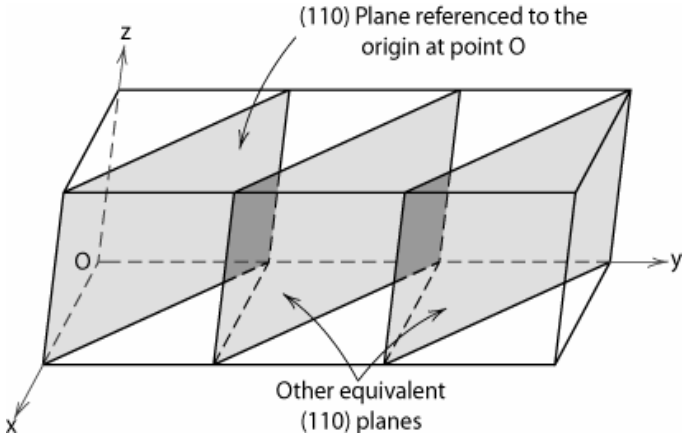
Demonstrate that the (111) plane does not pass through the central point of a cubic crystal. You need to do this numerically (geometrically).

Hint: Draw the [111] direction and work on it.

Now do the same for the $(\bar{1}\,\bar{1}\,\bar{1})$ plane and calculate the distance between both planes (111) and $(\bar{1}\,\bar{1}\,\bar{1})$



Distance Between Equivalent Planes



d_{hkl}: Distance between planes with Miller indices *h k l*

For the most general case, i.e. orthorhombic crystals the relation is:

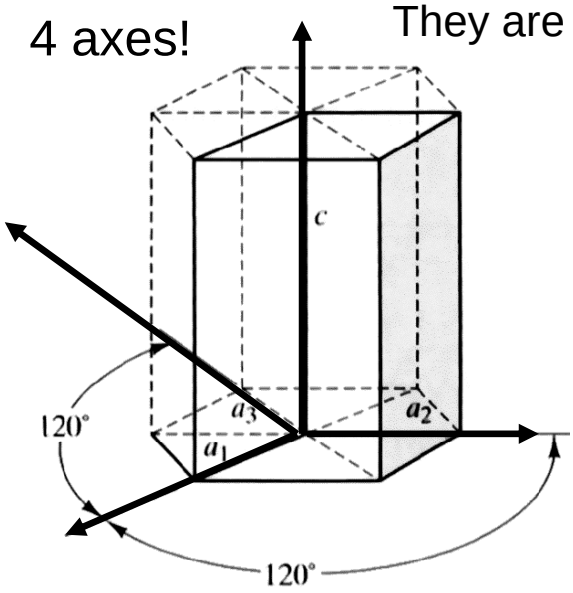
$$\left(\frac{1}{d_{hkl}}\right)^2 = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

For cubic crystals this becomes:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Crystallographic planes and directions in hexagonal unit cells

4 axes!



They are called Miller-Bravais indices:

[*h k i l*]

(*h k i l*)

The unique symmetry of the hexagonal structure requires a special set of indices created having 3 axis in the "a" direction. The first three integers in the designation correspond to the a_1, a_2, a_3 intercepts.

Miller-Bravais indices of directions

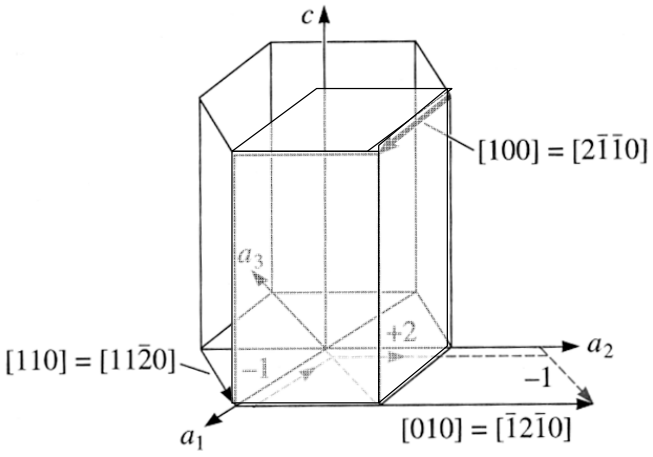
- The directions are obtained better by assuming first only three axis: a_1, a_2 and c. We obtain then: *h' k' l'*
- Then we do this:

$$h = \frac{1}{3}(2h' - k')$$

$$k = \frac{1}{3}(2k' - h')$$

$$i = -\frac{1}{3}(h' + k')$$

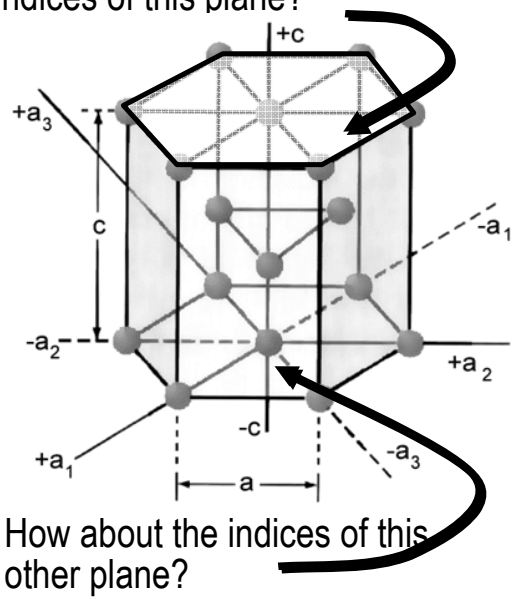
$$l = l'$$



- The values of *h, k, i* and *l* may require clearing of the fractions or reducing to lowest integers.

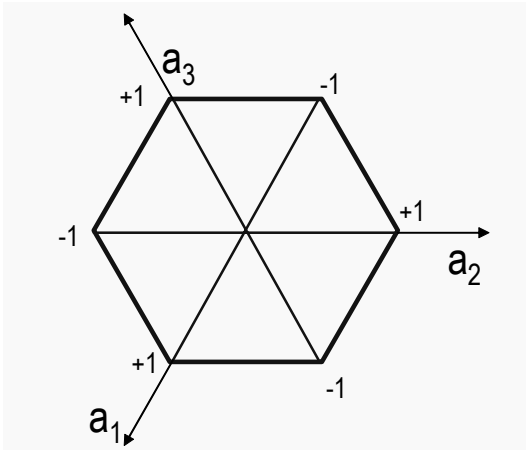
Miller Bravais Indices of Planes in HCPs

So, what are the Miller Bravais indices of this plane?



How about the indices of this other plane?

One good way to determine intercepts is by drawing the basal plane and work on it



Determine the indices of all *lateral* vertical planes of the unit cell

Note that the third Miller Bravais index *i* is such that: $h + k = -i$. *This is true for all planes in hexagonal crystals*

Volume Density

$$\text{Volume Density} = \rho_v = \frac{\text{mass / unit cell}}{\text{volume / unit cell}}$$

Also known as *Theoretical Density*. Please find out <u>why</u> this is called *theoretical* density.

First the mass in <u>one</u> unit cell:

$$\text{mass} = \#\,\text{atoms} \cdot \text{one atom mass}$$

Depends on crystal structure

Estimate using N_A

$$\text{one atom mass} = (\text{atomic weight}) \cdot \frac{1}{N_A}$$

$$\left[\frac{g}{\text{atom}}\right] = \left[\frac{g}{\text{mol}}\right] \cdot \frac{1}{\frac{\text{atoms}}{\text{mol}}}$$

Theoretical Density (cont.)

$$\rho_v = \frac{\#\ \text{atoms} \cdot (\text{atomic weight}) \cdot \frac{1}{N_A}}{\text{volume of one unit cell}}$$

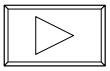
Units? In g/cm^3 or kg/m^3 please!

- Calculate the volume density of copper (FCC) at room temperature

What data do you need?

$A_{Cu} = 63.546$

$R_{Cu} = 0.1278$ nm

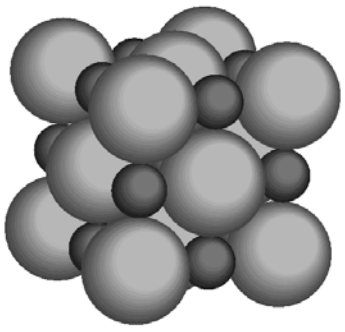


Density of Ceramic Compounds

$$\rho_v = \frac{n_1 \cdot A_1 + n_2 \cdot A_2}{(\text{unit cell vol.}) \cdot N_A}$$

A_1 and A_2 are the atomic weight of the elements conforming the compound

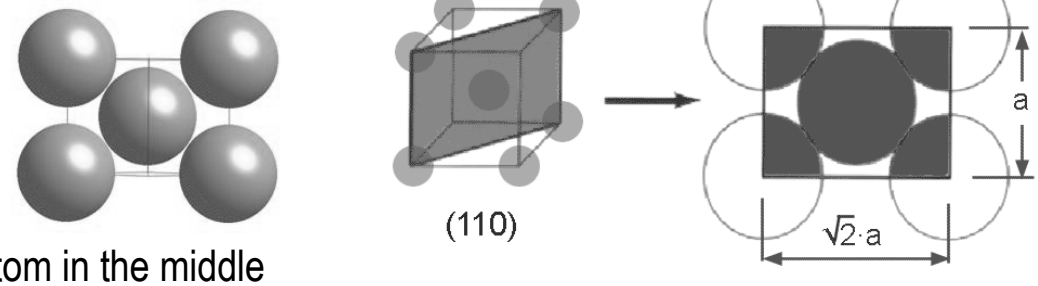
- Homework: LiF is an ionic solid commonly used in sensors. Calculate its theoretical density. The image on the right will help you. Li^+ cations are the red balls and F^- anions are the green ones. You will need information about ionic radius data. Then compare your calculation with data from the literature.



Planar Atomic Density

$$\rho_p = \frac{\#\text{ atoms with centers intersected}}{\text{selected area}}$$

Consider the (110) plane in a BCC unit cell. How many atoms intersected by the plane?

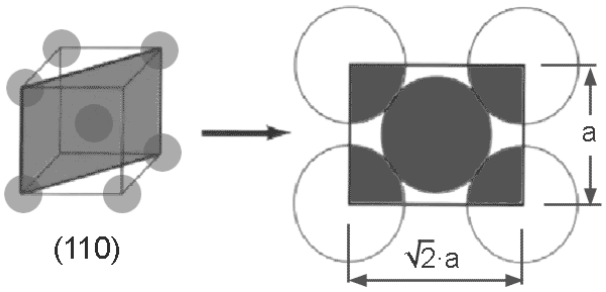


1 atom in the middle

4 atoms in the corners that contribute ¼ $\rightarrow$ 4 · ¼=1

Total: 1 + 1 = 2 atoms intersected

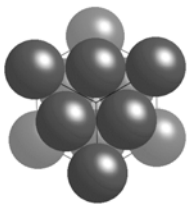
Planar Atomic Density (cont.)

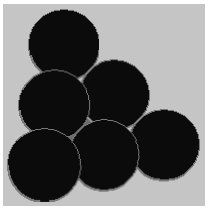


Area of rectangle a^2

$$\rho_p = \frac{2\,\text{atoms intersected}}{\sqrt{2}\,a \cdot a} = \frac{\sqrt{2}}{a^2}$$

Homework: Do the same for the (111) plane in an FCC metal

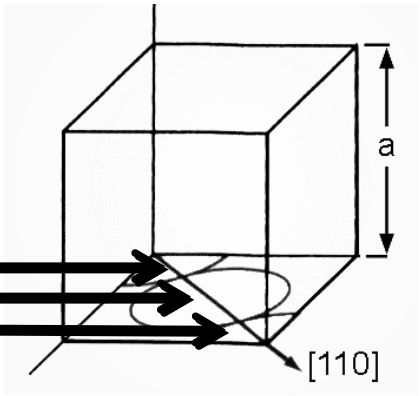




Linear Atomic Density

$$\rho_l = \frac{\#\,\text{atomic diameters intersected}}{\text{selected length of line}}$$

Consider the FCC unit cell and its [110] direction. So how many diameters does [110] cross?

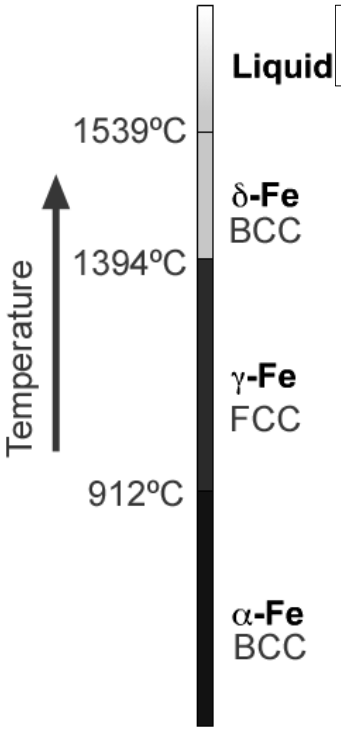


½ diam
1 diam
½ diam

And what is the length? $\rho_l = \frac{2}{\sqrt{2}\,a}$

Polymorphism or Allotropy

Definition | Remember carbon?



Examples:

-Ca *FCC, BCC, HCP*
-Co *FCC, HCP*
-Mn *BCC, FCC*
-Ti *HCP, BCC*
-Y *HCP, BCC*
- Pu has six! → Investigate!!

Also please find three more examples

Polymorphism or Allotropy (cont.)

Volume change ΔV during phase transformation

Exercise:

Find ΔV for an FCC$\rightarrow$BCC phase change. Does the material expand or contract (shrink)?

In BCC $a_{BCC} = \frac{4R}{\sqrt{3}}$ In FCC $a_{FCC} = \frac{4R}{\sqrt{2}}$

Volume *per atom:* $V_{BCC} = \frac{a_{BCC}^3}{2}$ $V_{FCC} = \frac{a_{FCC}^3}{4}$

Change in volume from FCC to BCC:

$$\frac{\Delta V}{V_{FCC}}(\%) = \frac{V_{BCC} - V_{FCC}}{V_{FCC}} \cdot 100$$

Sign?

Polymorphism or Allotropy (cont.)

Upon heating, at about 13ºC, gray tin (α-Sn) undergoes a phase transformation to white tin (β-Sn).

α-Sn has a diamond cubic structure (like C and Si) with lattice parameter: a = 0.649 nm. β-Sn has a body-centered tetragonal structure (BCT) with lattice constants a = 0.583 nm and c = 0.318 nm.

a) Calculate the theoretical density of the two phases.

b) Calculate the volume change upon cooling, i.e. when Sn goes from β to α.