



# 5. I Need More Structure in My Life

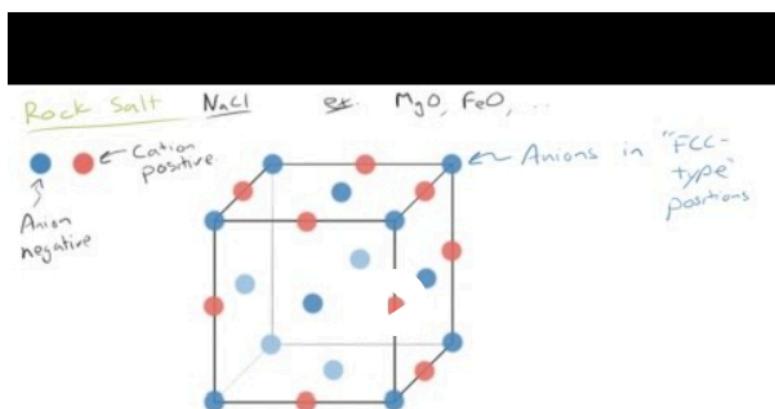
## Learning Objectives

1. Calculate the theoretical density of a rock salt type ceramic given the atomic weights, and atomic radii
2. Calculate the theoretical density of a BCC metal given the atomic weight, crystal structure and atomic radius
3. Demonstrate that the coordination number for BCC is 8
4. Demonstrate that the coordination number for FCC is 12
5. Show that the atomic packing factor (APF) for BCC is 0.68
6. Calculate the geometrically ideal interstitial site size for the following interstitial sites: octahedral, simple cubic
7. Using the hexagonal close packed crystal structure, illustrate how the theoretical density of a polycrystalline metal can be calculated from knowledge of the crystal structure, atomic radius, and atomic weight
8. Calculate the theoretical density of an HCP metal given the atomic weight, crystal structure and atomic radius
9. Demonstrate that the coordination number for HCP is 12
10. Demonstrate how the FCC and HCP crystal structures may be formed from stacking close packed planes in an ABCABC or an ABAB pattern



## A Common Ceramic Crystal Structure - Rock Salt

At this point, you have a fairly good handle on the FCC crystal structure. That's great, since it can be used as a conceptual framework for understanding so many other crystal structures: diamond cubic, zinc blende, even aspects of calcium fluoride ( $\text{CaF}_2$ ), to name a few.



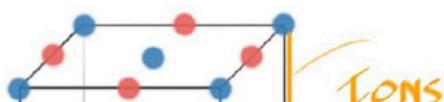
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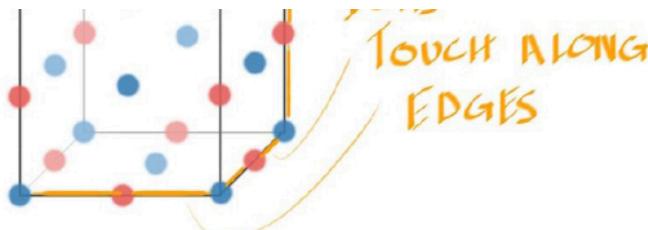
## But Why Do I Care About NaCl?

At this point, it is worth discussing briefly the naming of crystal structures. If you think back to our first (and only at this point) metallic crystal structure, FCC, you may realize that the name was general. That is, it was not associated with a specific element. Aluminum forms the FCC crystal structure; gold also forms the FCC crystal structure, yet we didn't call the structure, "The Gold Structure!" We simply described the symmetry and the atom positions concisely in a three-word name: *face centred cubic*. Why then do we call Rock Salt *Rock Salt* or *NaCl*? These names seem very specific. In fact, it seems to be referring specifically to one particular ionic compound.

The reason for this is that it is very difficult to concisely describe the positions of two atom types in a tidy little name. For example, "*The Structure Formed From an FCC-Type Lattice of Anions With Cations Occupying All Octahedral Interstitial Sites*," doesn't really roll off the tongue, does it? I mean, it's accurate, but way too long. Maybe we could take the first letter of each word in that description and call it *TSFFAFTLOAWCOAOIS*. Hmm, no, that doesn't really work. So, let's pick the most common ceramic that has that particular spatial arrangement of anions and cations. We could use magnesium oxide MgO, or iron(II) oxide FeO, or many others, but table salt is pretty common so we use it.

Let's dive right into the rock salt structure then. With ceramic structures involving more than one atom type, you'll frequently see structures depicted apparently differently, but actually only viewed from a different perspective. You see, the symmetry is cubic and we could start off by positioning our negative ions or *anions* at the cube corners, or we could start by placing the positive ions or *cations* at the corners. Provided we appropriately place the second ion type within the first, we can accurately describe the structure either way. Most frequently, you'll see the anions placed in the cube corners. I think this is because the anions are typically larger and it is easier for our human brains to visualize placing the large things first and then squeezing the small things in between the large ones. So, let's start by placing the anions into the corner positions and while we're at it also into the face-centred positions to make a structure that appears to be FCC. (Can you picture it? If not, flip back earlier in these notes!)





**Figure 1:** Anions represented as blue dots in the traditional FCC-type positions, with cations in the edge centre positions. Cations touch their nearest neighbour anions along the cube edges. Note: this is not yet Rock Salt - there is something missing.

The reason that I am reluctant to call the structure of anions truly FCC is that the cations exist in between the anions and push them apart so that the anions no longer touch one another across the face diagonals of the unit cell. Now, the cations touch the anions along the cube edges, as shown in Figure 1. In a ceramic crystal structure, the cations will always touch their nearest neighbour anions.



## Double Checking the Stoichiometry

You may have noticed something missing from Figure 1. From the chemical name of rock salt, NaCl, we know that there must be a 1:1 ratio of anions to cations. From our knowledge of the FCC crystal structure we know that there are 4 anions within the unit cell, so there must also be 4 cations. Let's count them up. We have  $\frac{1}{4}$  of an atom at each edge position and there are 12 edges on a cube for a total of 3 cations, so we are missing an entire atom. Where is it? Well, if you consider that the cations touch anions along the edges, then there must be a cation in the very centre of the cube touching the front and back face-centred anions, as shown in Figure 2.

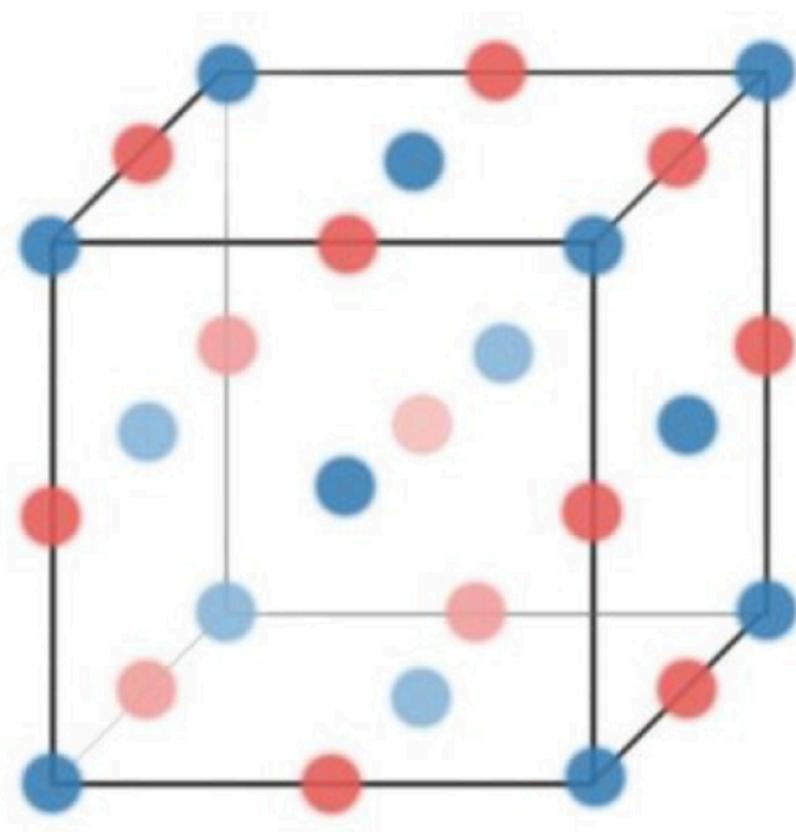


Figure 2: The rock salt ceramic crystal structure.



## EXERCISE YOUR KNOWLEDGE



Q5.1.2  
Review

Mark as: None ▾



How many multiples of a complete Na atom are there within the rock salt crystal structure?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a 1

b 2

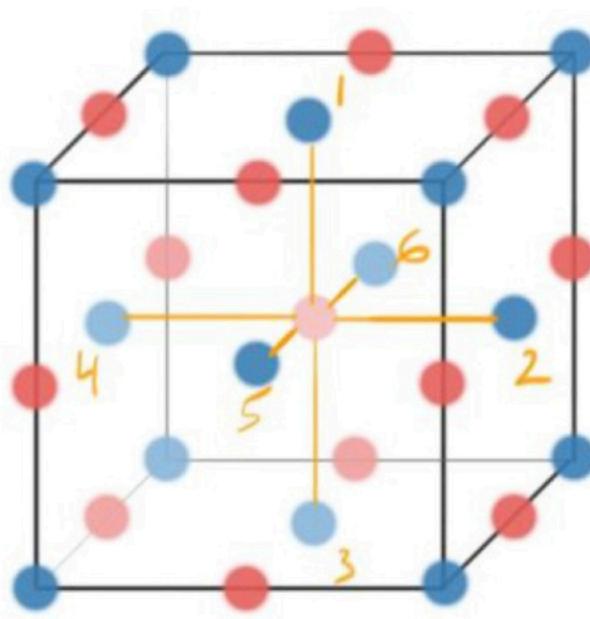
c 4

d 8

### The Coordination Number for Cations in Rock Salt



While we're on the topic of cations making contact with their nearest neighbour anions, we may as well define the *coordination number* which is just that, the number of atoms touching a particular atom.



**Figure 3:** The rock salt ceramic crystal structure.

For cations in rock salt, it is fairly easy to determine by looking carefully at the unit cell, focusing on the central cation, as shown in Figure 3. The central cation touches each of the face centred anions, for a coordination number of 6. **Cation Coordination Number<sub>RockSalt</sub> = 6** (1)

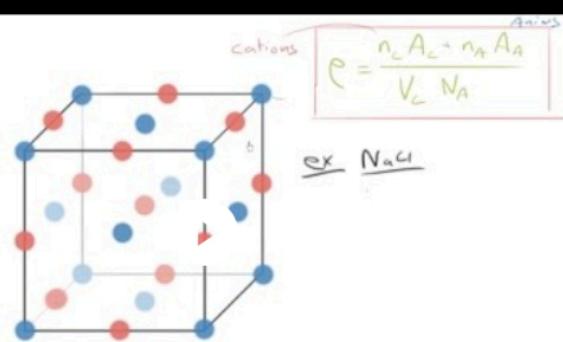


## EXERCISE YOUR KNOWLEDGE



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## Theoretical Density of Ceramics



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Remember how we were able to calculate the theoretical density of a metal from knowledge of its crystal structure? Well, I imagine that you can see that we can also do that for ceramic structures. There are two differences to keep in mind. First, there is more than one atom type present, and if we restrict our discussion to ceramics having only two elements, we must then account for the molar mass of both the anions and the cations. Secondly, we must be careful to correctly calculate the unit cell volume  $a^3$  by being careful to determine the lattice parameter  $a$  using both the anion and cation radii, keeping in mind that the cations will always touch their nearest neighbour anions. With this in mind, we can slightly modify our ceramic density equation to account for two atom types and write the theoretical density of a ceramic as:

$$\rho = \frac{n_C A_C + n_A A_A}{V_C N_A} \quad (2)$$

where  $\rho$  is the Greek letter *rho*, used for density,  $n_C$  and  $n_A$  are the number of cations and anions within

the unit cell, respectively,  $A_C$  and  $A_A$  are the molar masses of the cation and anion, respectively,  $V_C$  is the volume of the unit cell, and  $N_A$  is Avogadro's Number.



## EXERCISE YOUR KNOWLEDGE



Q5.1.3  
Review

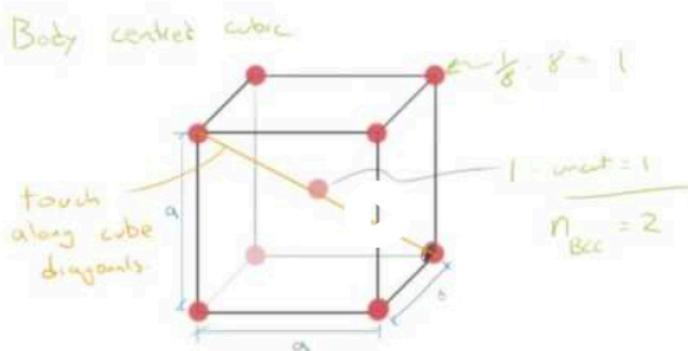
Mark as: None ▾

Cadmium oxide CdO has the rock salt crystal structure. The ionic radii of cadmium and oxygen are 109 pm and 126 pm, respectively. Calculate the theoretical density of CdO in  $\frac{\text{g}}{\text{cm}^3}$ . Note:  $1\text{pm} = 1 \times 10^{-12}\text{m}$

Type your numeric answer and submit

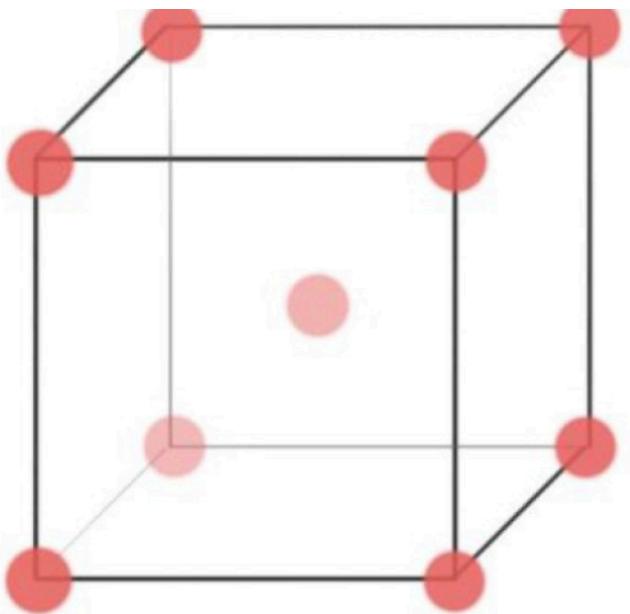


## The Body Centred Cubic Crystal (BCC) Structure



[Link to this video on U of T servers.](#)

I'd like to introduce another metallic crystal structure at this point. This is quite a common structure - it is the structure of most steel alloys. As with FCC, the name BCC is fairly descriptive.



**Figure 4:** The body centred cubic crystal structure.

We start with atoms in each of the corner positions, again, each corner position only containing  $\frac{1}{8}$  of an atom within the unit cell. Then we position a final atom exactly in the centre of the unit cell, as shown in Figure 4. This gives us a total of 2 atoms within the BCC unit cell:  $n_{BCC} =$

2 (3)



## EXERCISE YOUR KNOWLEDGE



Q5.2.1  
Review

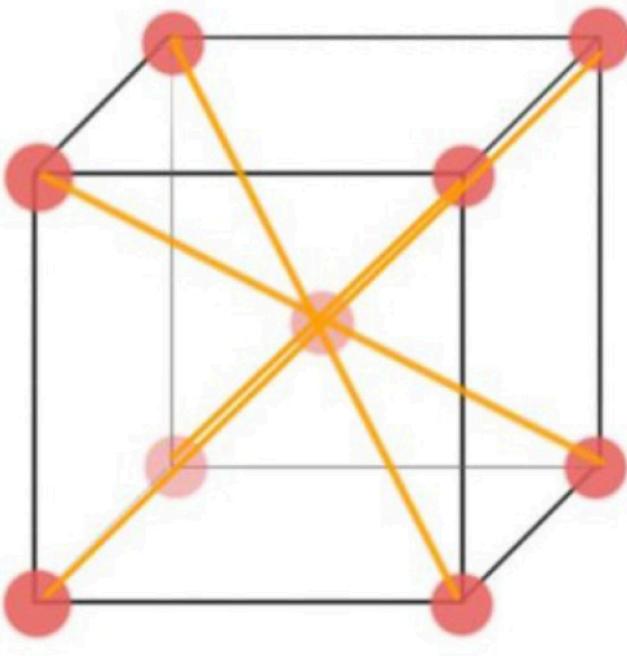
Mark as: None ▾

Iron at room temperature exists in the BCC crystal structure and has an atomic radius of  $124 \times 10^{-12}\text{m}$ . Calculate the theoretical density of iron in  $\frac{\text{g}}{\text{cm}^3}$ .

Type your numeric answer and submit

## The Coordination Number for BCC

I like to introduce the coordination number for BCC before the coordination number for FCC because it is significantly easier to visualize the coordination number in BCC.



**Figure 5:** The body centred cubic crystal structure, showing the direction of contact across the cube diagonals and the coordination number of eight.

This is because we can look at the central atom and see all of the nearest neighbour atoms without needing to leave a single unit cell. The central atom touches each of the eight corner atoms as shown in Figure 5.

And so we can confidently state: Coordination Number<sub>BCC</sub> =

$$8 \quad (4)$$

It is also apparent from Figure 5 that the direction of contact between atoms is across the cube diagonals. Recall for FCC that the direction of contact was along the face diagonals.



### EXERCISE YOUR KNOWLEDGE



Q5.2.2  
Review

Mark as: None ▾

Which of the following is the most accurate description of the direction that atoms within the BCC crystal structure touch one another?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a Along the face diagonals

b Along the cube diagonals

c Along the cube edges

d None of the above



Q5.3.1  
Review

Mark as: [None ▾](#)

The number of atoms touching an atom in the BCC crystal structure is:

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a 8

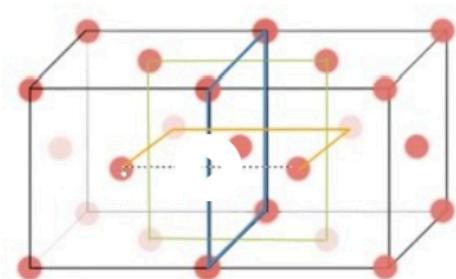
b 4

c 6

d 12

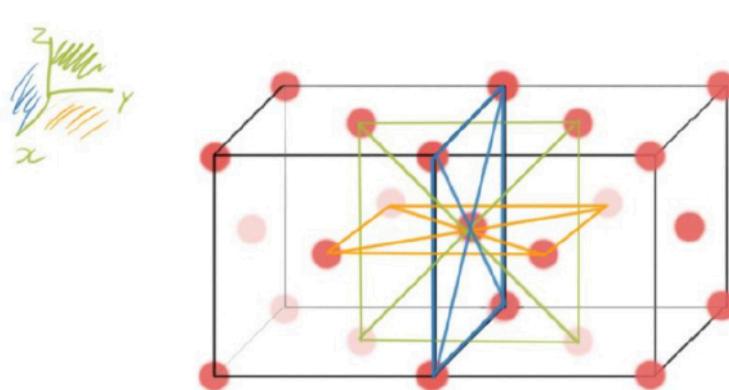


## The Coordination Number of FCC



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Hopefully you're feeling pretty good about the FCC crystal structure at this point and hopefully you also understood the coordination number for BCC. If so, I think you are ready to take a look at the *coordination number* for atoms in the FCC crystal structure. The reason I didn't introduce this with our initial discussion of FCC was that it is a tad challenging to picture the coordination number in FCC.



**Figure 6:** The coordination number for atoms in FCC. The right side face-centred atom makes contact with four atoms in the right side plane, with four atoms in the face-centred positions in the original unit cell, and with four atoms in the face-centred positions in the unit cell to the right.

There is no atom that has all of its nearest neighbour atoms within a single unit cell. From my own experience, I find it is easiest to count coordination number from the right side face-centred atom, as shown in Figure 5. The right side face-centred atom makes contact with four atoms in the right side plane, with four atoms in the face-centred positions in the original unit cell, and with four atoms in the face-centred positions in the unit cell to the right.

And so, the coordination number for FCC is twelve:

$$\text{Coordination Number}_{FCC} = 12 \quad (5)$$

## The Atomic Packing Factor for BCC

Let's put some of this new knowledge into practice and calculate the atomic packing factor for BCC, as we did for FCC.

$$APF_{BCC} = \frac{\text{Volume}_{\text{spheres}}}{\text{Volume}_{\text{Unit Cell}}} \quad (6)$$

or,

$$APF_{BCC} = \frac{\frac{4}{3}\pi R^3}{n \cdot \frac{a^3}{6}} \quad (7)$$

and, specifically for BCC

$$\frac{4}{2} \cdot \pi R^3$$

$$\text{APF}_{\text{BCC}} = \frac{3}{a^3} \quad (8)$$

Once again, we have this issue of  $R$  in the numerator and  $a$  in the denominator. Let's express  $a$  in terms of  $R$ . Since the atoms in BCC touch along the cube diagonal we need to apply the Pythagorean theorem twice:

$$\begin{aligned} a^2 + a^2 + a^2 &= (4R)^2 \\ 3a^2 &= 16R^2 \end{aligned} \quad (9)$$

$$a_{\text{BCC}} = \frac{4}{\sqrt{3}}R \quad (10)$$

Which we can substitute back into our APF equation to give

$$\text{APF}_{\text{BCC}} = \frac{\frac{4}{3}\pi R^3}{\left(\frac{4}{\sqrt{3}}R\right)^3} \quad (11)$$

$$\text{APF}_{\text{BCC}} = 0.68 \quad (12)$$

Which we see is less than the APF for FCC.



## EXERCISE YOUR KNOWLEDGE



Q5.4.1  
Review

Mark as: [None](#) ▾

A large room is filled with spherical helium balloons in a BCC arrangement. If the volume of the room is 6000  $\text{m}^3$  what will the volume of air (not helium) in the room be in  $\text{m}^3$ ? Express your final answer with three significant figures and do not include units in your final answer.

Type your numeric answer and submit



Q5.9.1  
Review

Mark as: [None](#) ▾

Determine the atomic packing factor for atoms in the FCC crystal structure. Express your final answer with two significant figures.

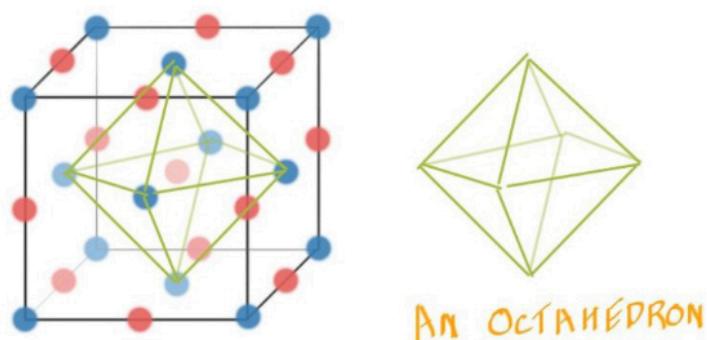
Type your numeric answer and submit

## Interstitial Sites



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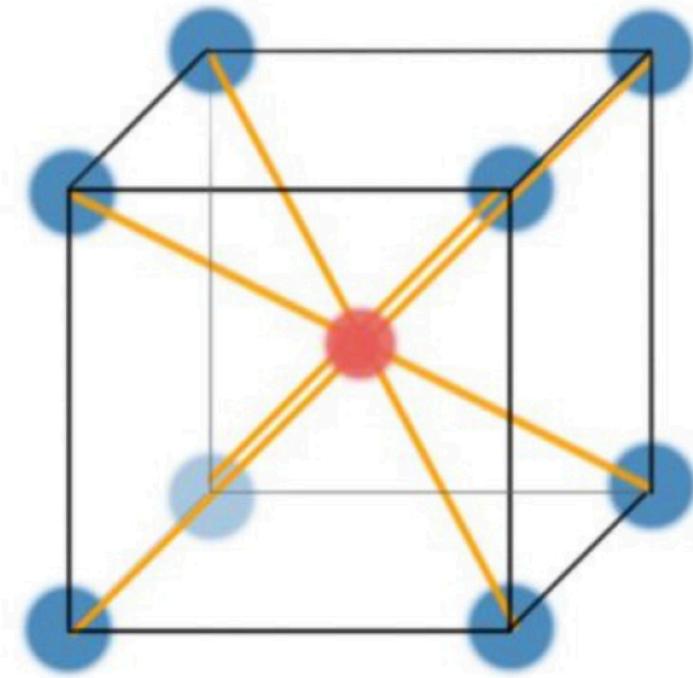
Want to know a secret? You already know about interstitial sites. Yes, an *interstitial site* is just a space between other atoms. This space may contain another atom, like when we put cations into the spaces between anions in the rock salt crystal structure, or these spaces could be empty, like those same positions are in the FCC metallic crystal structure. So, let's study the *interstitial sites* that the cations exist in for the rock salt crystal structure. By convention, we name interstitial sites according to the solid geometry that they create.



**Figure 7:** The octahedral interstitial site. Note that all cations, not just the central one, occupy octahedral interstitial sites within rock salt.

So, the interstitial site with a coordination number of 6, which is the site that the cations exist in within rock salt is called the *octahedral interstitial site*. This is illustrated in Figure 7.

Another interstitial site that you are generally familiar with at this point is the simple cubic interstitial site, shown in Figure 8.



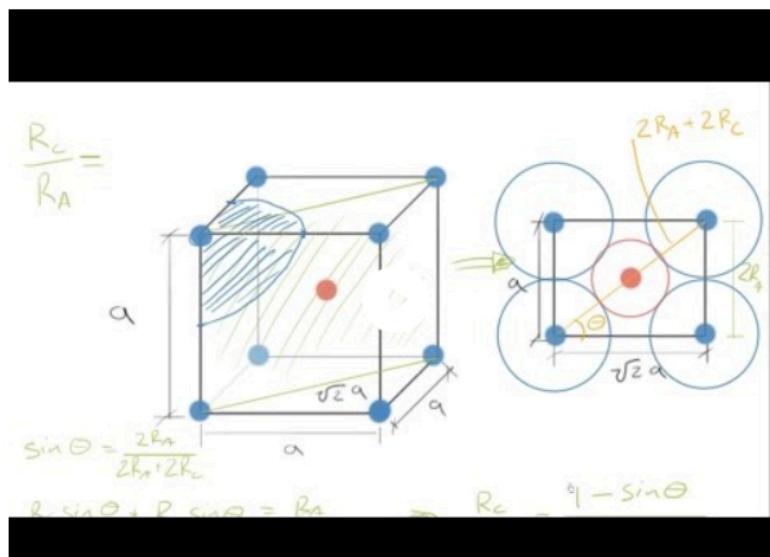
**Figure 8:** The simple cubic interstitial site.

This is spatially similar to the place that the body centred atom in BCC occupies. The cation in the simple cubic interstitial site touches each of the corner anions, meaning that the coordination number for this interstitial site is eight:

$$\text{Coordination Number}_{\text{SimpleCubic}} =$$

8

(13)



[Link to this video on U of T servers.](#)



## EXERCISE YOUR KNOWLEDGE



Q5.5.1

Review

Mark as: [None ▾](#)

Which of the following is the correct coordination number for the octahedral interstitial site?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a 6

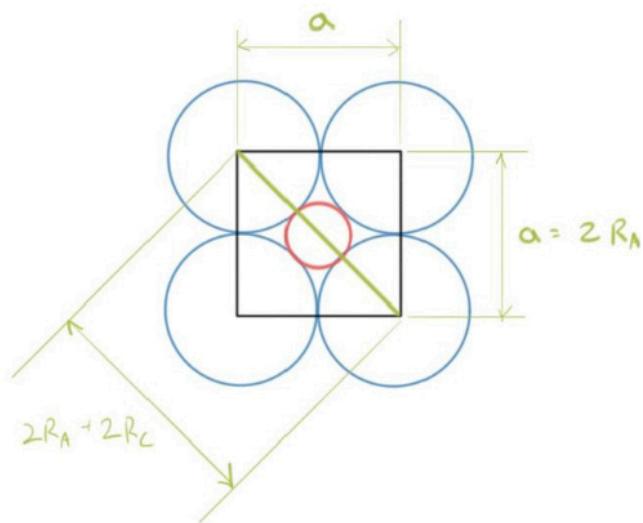
b 8

c 4

d 12

## The Size of Interstitial Sites

As mentioned earlier, cations will always touch their nearest neighbour anions. This means that a cation will not occupy an interstitial site if it is not at least big enough to touch the nearest neighbour anions when they are as close to one another as possible, that is *touching*.



**Figure 9:** A 2D slice through the octahedral interstitial site at the geometrically ideal radius ratio when the anions are touching one another and the cation is just big enough to fit into the site without pushing the anions apart.

Let's take a look at the octahedral site as an example. Figure 9 shows this situation.

I think that the simplest way to approach this problem is to apply a little trigonometry.

$$\begin{aligned} \sin 45 &= \frac{2R_A}{2R_A + 2R_C} \\ (2R_A + 2R_C) \sin 45 &= 2R_A \\ 2R_A \sin 45 + 2R_C \sin 45 &= 2R_A \\ R_A \sin 45 + R_C \sin 45 &= R_A \\ \frac{R_A}{R_A} \sin 45 + \frac{R_C}{R_A} \sin 45 &= \frac{R_A}{R_A} \\ \sin 45 + \frac{R_C}{R_A} \sin 45 &= 1 \\ \frac{R_C}{R_A} \sin 45 &= 1 - \sin 45 \\ \frac{R_C}{R_A} &= \frac{1 - \sin 45}{\sin 45} \\ \left( \frac{R_C}{R_A} \right)_{CN=6} &= 0.414 \end{aligned} \tag{14}$$



## EXERCISE YOUR KNOWLEDGE



Q5.5.2  
Review

Mark as: None ▾

The coordination number for the cations in the rock salt structure is 8.

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a True

b False

## Hexagonal Close Packed (HCP)



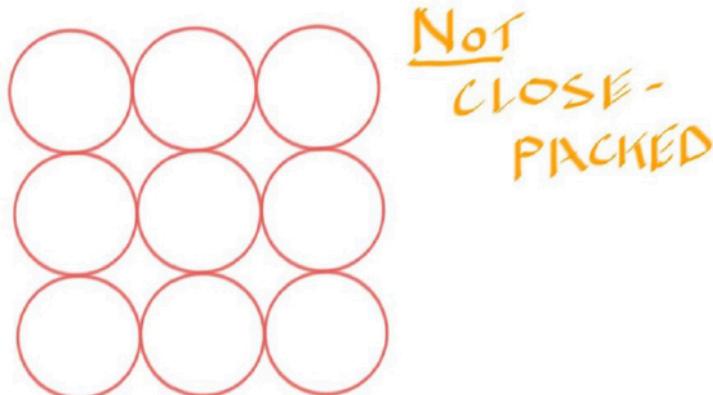
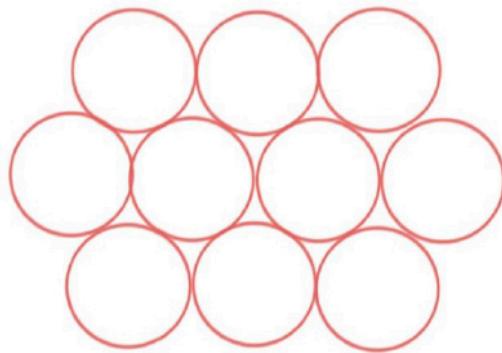


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There is another metallic crystal structure with the same packing fraction as FCC - *hexagonal close packed* or *HCP*. In fact, it is for this reason that you will sometimes see face centred cubic referred to as *cubic close-packed* to differentiate it from hexagonal close packed. This means that the APF for HCP must also be 0.74, which of course it is. With that in mind, we can consider how we might go about making a close-packed structure. It is probably not immediately obvious, but FCC and HCP are very similar.

## CLOSE PACKED



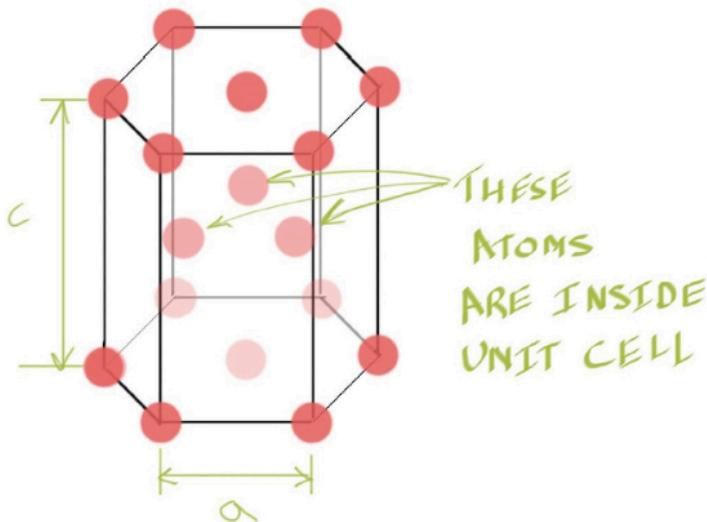
**Figure 10:** A close-packed plane is formed when atoms are packed in two-dimensions as closely as possible. The top plane is part of a close-packed plane, while the lower plane is not close-packed.

One way to think about these two structures is to consider the stacking of *close-packed planes*. A close-

packed plane is a layer of atoms that is placed together as closely as possible, in two-dimensions.

Figure 10 shows a close packed plane, depicted using circles.

As the name hexagonal *close* packed tells us, the atoms, or spheres, must be packed as closely as possible in three dimensions. That is, they must fill the volume as efficiently as possible. You may be able to imagine then that we would not achieve a close-packed structure by placing a second layer of close-packed atoms directly over the first layer. No, there is a more efficient way to stack this second layer. We need to place the second layer into the low spots amongst the atoms of the bottom layer. The difference between FCC and HCP at this point is subtle and lies in the placement of the third close-packed plane. You see, the low spots amongst atoms of a close-packed plane are actually too close together to permit an atom into each location.



**Figure 11:** A hexagonal close packed unit cell. Note that the three atoms in the middle are inside the unit cell and are part of a close packed plane that is identical to the top and bottom planes.

The HCP unit cell is shown in Figure 11. You will notice that the top and bottom planes are exactly in line with each other vertically. That is, the top layer is directly over the bottom layer. Since these planes are close-packed this gives us the ABABAB stacking sequence for HCP.



## EXERCISE YOUR KNOWLEDGE



Q5.6.1  
Review

Mark as: None ▾

Cobalt has the HCP crystal structure and a molar mass of  $58.933 \frac{\text{g}}{\text{mol}}$ . Assuming a radius of  $135 \times 10^{-12} \text{m}$  and that the height of the cobalt unit cell,  $c$ , is  $1.633a$ , where  $a$  is the edge length. The volume of a hexagonal prism is  $V = \frac{3\sqrt{3}}{2}a^2c$ .

Determine the theoretical density of cobalt in  $\frac{\text{g}}{\text{cm}^3}$ . Express your final answer with 3 significant figures and do not include units in your final answer.

Type your numeric answer and submit



Q5.10.2

Review

Mark as: [None ▾](#)

Which of the following best describes the stacking sequence of close-packed planes within the HCP crystal structure?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a There are no close-packed planes in HCP

b ABCABC

c ABAB

d None of the above



## FCC Oranges and Apples

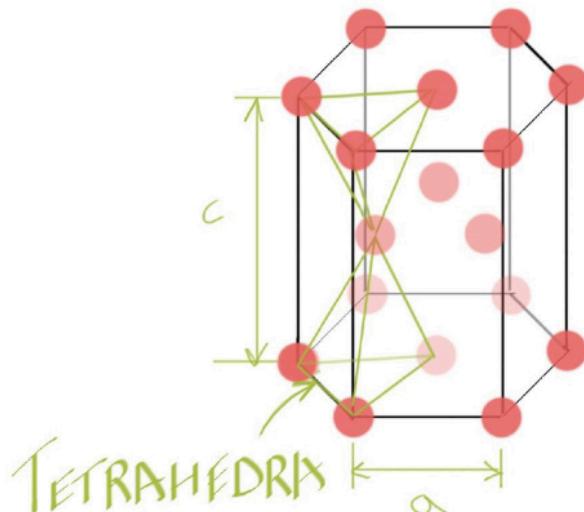
Often, after reading about the formation of FCC and HCP crystal structures by the stacking of close-packed planes, students are left thinking, wrongly, that the only way to create a close-packed structure is by stacking close-packed planes. This is not true and, in fact, it is quite likely that you have seen face centred cubic fruit formed from the stacking of non-close-packed planes, without realizing it. Of course, I can't really blame you for not noticing. Yet. Now that you've read this I expect that you will notice. In fact, I'll be offended if you don't. It's a beautiful thing to behold, FCC fruit. Oh, in case you're wondering, it won't be HCP fruit . You see, at supermarkets where the fruit is carefully stacked, you'll notice that the bottom layer is often placed into divets, or indentations, in a cardboard form that places the fruit into a simple square lattice. This square lattice is actually the front face of an FCC unit cell, as so-called *(001)* planes. The second layer of fruit is then placed into the indentations between the bottom layer



called (001) plane. The second layer of fruit is then placed into the low spots between the bottom layer, forming another square lattice of fruit, another (001) plane, which you could think of as being the atoms occupying the face-centred positions if the bottom layer was the front face of an FCC unit cell. A third layer is again stacked into the low spots in the second layer, which happens to be directly over the first layer. You could think of this third layer as the back face of an FCC unit cell. Note, many students will now ask why this is not HCP, since the third layer is directly over the bottom. Remember, however, that these are not close-packed planes. The stacking sequence of FCC and HCP as ABCABCABC and ABABABA respectively only applies to the stacking of close-packed planes. The exciting part about stacking fruit this way is that it exposes a beautiful close-packed plane that slopes back slightly from the bottom to the top and faces customers, making them think, "what a beautiful stack of fruit, I think I'll buy some." Okay, I think some images would help here. I'll try to add them later.



Also shown in Figure 11 is the lattice parameter corresponding to the vertical direction. The letters a, b, and c are used to refer to the lattice parameters in the x, y, and z directions, so for HCP, the height is c.



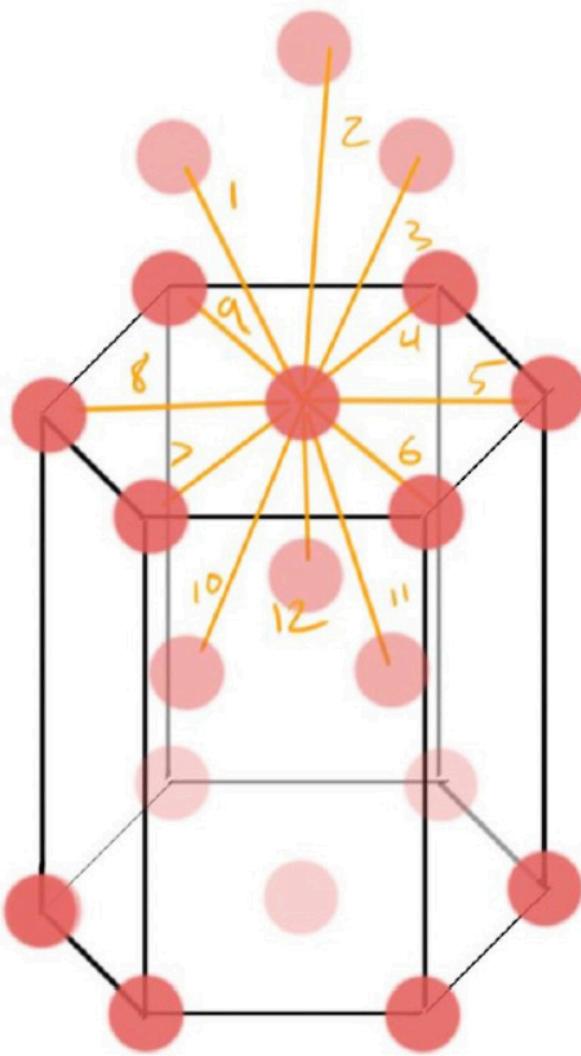
**Figure 12:** A hexagonal close packed unit cell showing the positioning of the three middle atoms nestled into the low spots between three atoms on the bottom plane.

A derivation that we'll likely do later is to prove that the  $c/a$  ratio for HCP, as formed here is 1.633. For the time being, however, we'll leave that as something that I just tell you. Figure 12 shows, a little more clearly hopefully, the positioning of the three middle atoms. They sit on top of the three atoms below them in the lowest spot possible. This creates a tetrahedra, which is repeated with the three atoms above.

## The Coordination Number for HCP

The HCP crystal structure can be a little intimidating sometimes, however, the coordination number is significantly easier to see than for FCC. At least, I think it is. Figure 13 attempts to show the coordination number for HCP using the top face centred atom. This atom touches the three atoms below, the six

atoms in the plane or the top, and the three atoms above, for a total of 12 atoms.



**Figure 13:** A hexagonal close packed unit cell showing the coordination number for the middle face centred atom on the top of the unit cell.



## EXERCISE YOUR KNOWLEDGE



Q5.8.1  
Review

Mark as: None ▾

The coordination number for atoms in the HCP crystal structure is:

Type your numeric answer and submit



Q5.8.2  
Review

Mark as: None ▾

The coordination number for atoms in the HCP crystal structure is the same as that in which of the following crystal structures?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a Simple cubic

b Body centred cubic

c Face centred cubic



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## EXERCISE YOUR KNOWLEDGE



Q5.10.1  
Review

Mark as: None ▾

How many unique close packed planes are there in the FCC crystal structure?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a 2

b 4

c 8

d 12



 Q4.8.1  
Review

Mark as: [None ▾](#)

Which of the following is the best description for why beverage containers are most often made from aluminum, an FCC metal?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a FCC materials contain 4 non-parallel close packed planes

b FCC materials are non-magnetic and allows more efficient material handling

c FCC materials have a higher density than BCC materials and so are less likely to leak

d FCC materials are corrosion resistant



***All images and videos are created by author.***

