9.1 Example: The Size of the Tetrahedral Interstitial Site

LEARNING GOALS

Learning Objectives

1. Calculate and describe the geometrically ideal interstitial site size for the tetrahedral interstitial site

Calculating the Geometrically Ideal Size of the Tetrahedral Interstitial Site

The tetrahedral interstitial site tends to cause the most anxiety for students out of all of the interstitial sites, so don't be hard on yourself if you are feeling a little unsure about it. Let's get right into it.

You've seen it before, so in Figure 1 I've went ahead and added in some dimensions and relationships. There is quite a lot in the Figure to take in so give yourself some time to look it over and be sure that you understand and agree with all of the values I've written in green. I've explained them here, in no particular order.

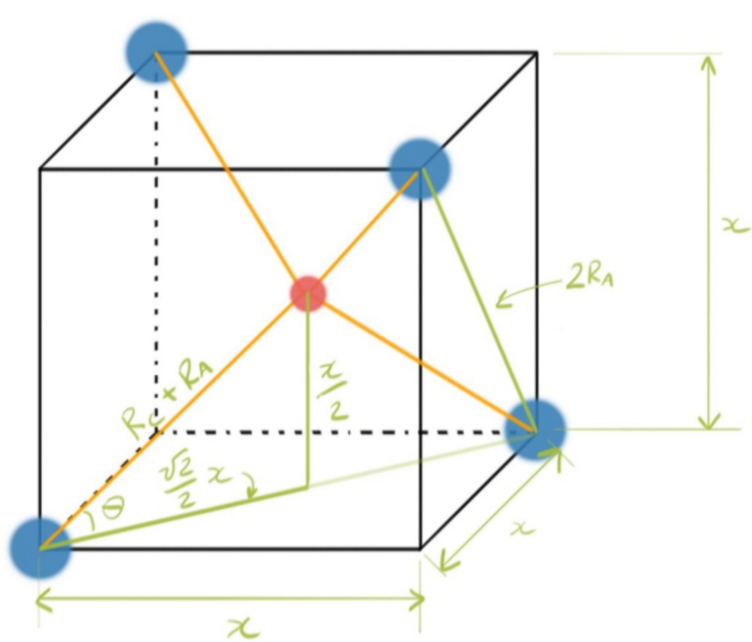

Figure 1. An excellent way to visualize the tetrahedral interstitial site is to

picture the four anions at corners of a cube with the interstitial site at the centre, as illustrated here.

$R_C + R_A$ - This distance, half of the $[\bar{1}11]$ direction within this cube, sketched in orange in the figure can be thought of as the bond length, or the centre-to-centre distance between the anion and the cation. Since we know that cations will always touch their nearest neighbour anions we know that this must be exactly equal to an anion radius plus a cation radius.

$\frac{\sqrt{2}}{2}x$ - This distance is half of the $[\bar{1}10]$ direction, or half of a face diagonal. Since I've defined the edge lengths of this cube as x the face diagonal would be calculated with some help from good old Pythagoras as:

$$x^2 + x^2 = (\text{Face Diagonal})^2$$

$$\text{Face Diagonal} = \sqrt{2x}$$

$$\text{Half of Face Diagonal} = \frac{\sqrt{2}}{2}x$$

$\frac{x}{2}$ - Well, if you understand that the interstitial site is exactly in the centre of this cube and the cube edge length is x then hopefully it follows clearly that the height from the bottom of the cube to the red cation, in the interstitial site, is $\frac{x}{2}$. Any trouble you might be having is undoubtedly due to my sketch.

$2R_A$ - This distance is one complete face diagonal, or the $[101]$ direction. Since we are considering the *geometrically* ideal situation here, where the cation perfectly fits into the interstitial site without pushing the anions apart, the anions are still touching as they would in FCC, so the distance is two anion radii. (Remember the ZnS structure? We had cations occupying half of the tetrahedral interstitial sites with anions in *"FCC-type"* positions.) The trick that we can do here, which is not so much a trick as it is applying the Pythagorean Theorem, is to use this distance to relate x to R_A.

$$x^2 + x^2 = (2R_A)^2$$

$$x^2 = \frac{(2R_A)^2}{2}$$

$$x = \frac{2R_A}{\sqrt{2}} \qquad \textbf{(Equation 1.)}$$

θ - I have defined the angle between the base of the cube and the orange cube diagonal as θ.

Now that we understand Figure 1 we can get down to the business of calculating the size of the tetrahedral interstitial site.

First, let's calculate the value of θ.

$$\theta = \arctan(\frac{\frac{x}{2}}{\frac{\sqrt{2}}{2}x}) = 35.26^\circ$$

And now we can proceed as we have done already for the octahedral and simple cubic sites.

$$\sin\theta = \frac{\frac{x}{2}}{R_C+R_A}$$

And substituting Equation 1 in for x we can write:

$$\sin\theta = \frac{\frac{\frac{2R_A}{\sqrt{2}}}{2}}{R_C+R_A}$$

$$= \frac{1}{\sqrt{2}}\frac{R_A}{R_C+R_A}$$

Multiplying both sides by $R_C + R_A$ and doing a little *massaging* of the math gives:

$$R_C\sin\theta + R_A\sin\theta = \frac{1}{\sqrt{2}}R_A$$

$$\frac{R_C}{R_A}\sin\theta + \frac{R_A}{R_A}\sin\theta = \frac{1}{\sqrt{2}}\frac{R_A}{R_A}$$

$$\frac{R_C}{R_A}\sin\theta + \sin\theta = \frac{1}{\sqrt{2}}$$

$$\frac{R_C}{R_A}\sin\theta = \frac{1}{\sqrt{2}} - \sin\theta$$

$$\frac{R_C}{R_A} = \frac{\frac{1}{\sqrt{2}}-\sin\theta}{\sin\theta}$$

$$\frac{R_C}{R_A} = 0.225$$

Keep in mind that there are other ways to solve this. I personally just like working through the angle and using $\sin\theta$, as we did here.