Diffusion in Multicomponent Solids
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Lecture 37
Correlation Effects in BCC and Diamond Cubic for Vacancy Mechanism

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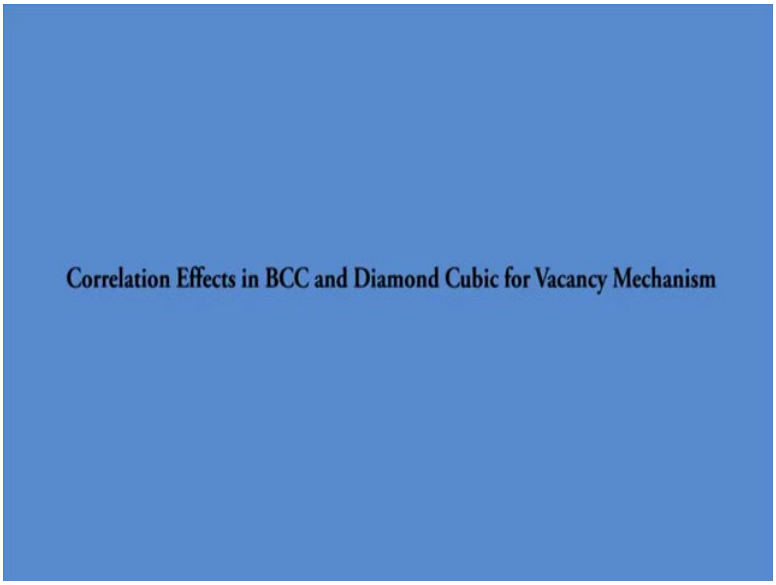

Welcome to the 37th lecture of the open course on Diffusion in Multicomponent Solids. In this lecture I have illustrated the jump frequency models for Diamond Cubic Structure and BCC crystal for the diffusion by vacancy mechanism and as proposed by manning.

These models can be used for determining correlation factors for impurity atom diffusion by vacancy mechanism in diamond cubic and in BCC structures. We will not go in depth of calculating the correlation factors. But, this treatment should give an idea about how the jump probabilities of a tagged atom and vacancy are affected by different coordination of these structures.

Welcome back. In the last class we derived the expression for correlation factor in FCC lattice which was for diffusion of a substitutional atom by vacancy mechanism. Today, we will look into correlation factor of BCC and diamond cubic lattices. We will not go in depth of the derivation of correlation factor but we are just interested in knowing how the jump frequencies of vacancy and the substitutional atom are placed in diamond cubic and BCC lattices and how they give rise to the correlation effect.

The detail derivation was presented by Manning and I will just give a brief of what this model looks like. Let us first consider the Diamond Cubic lattice.

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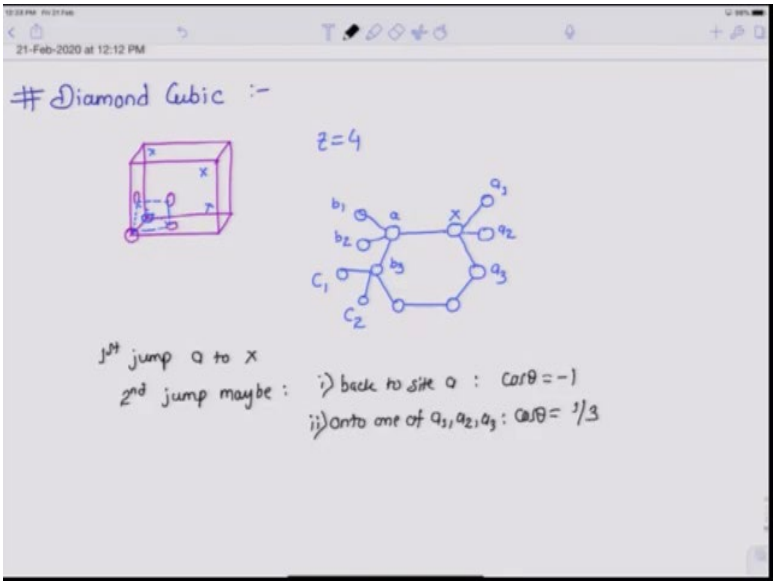

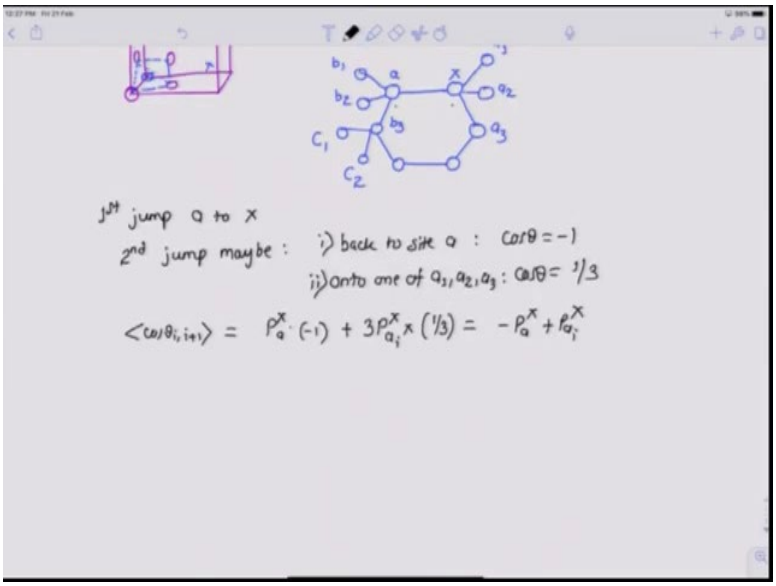

We can visualize the diamond cubic lattice something like this. Imagine a cubic cell with 3 face centre positions and the corner position that is adjacent to these 3 face centred position. We can draw a tetrahedron by joining these 4 lattice site and then at the centre of this tetrahedron there is one atom placed and this is how diamond cubic structure looks like.

This looks like a tetrahedral void in an FCC lattice but this is not a void, this is a regular atomic position. Also this is not an FCC unit cell but this is a diamond cubic structure. Now, there are 8 such positions inside this one cube, but only alternate positions are filled with

atoms. And the 4 positions inside this cube would be alternate corners as shown by cross in figure.

We can see the coordination in a diamond cubic is 4 that means each atom has 4 nearest neighbours and the nearest neighbour form a tetrahedron. If we draw the projection of this on a plane it will be something like this. So, we consider the tagged atom as x here which has jumped from a position denoted as a.

Each atom has 4 nearest neighbour. For x, one of the nearest neighbour is this site at a and there will be 3 more denoted as a_1, a_2 and a_3. Similarly, there will be 3 nearest neighbour for a, which are actually the second nearest neighbour for x and this continues. The second nearest neighbour of x, we can denote by b_1, b_2 and b_3 and then, there will be third, fourth nearest neighbour and on. Third nearest neighbour we denote as c_1, c_2 etc.

If the first jump of the tagged atom was from a to x then the second jump maybe:

$$2^{nd}\ jump\ may\ be:\ \ 1)\ back\ to\ site\ a\ :\ \cos\theta_{i,i+1} = \cos\theta = -1$$

$$2)\ onto\ one\ of\ a_1, a_2, a_3\ :\ \cos\theta = \frac{1}{3}$$

There would be one jump which would make a cosine of -1 and three jumps which would make a $\cos\theta$ of $\frac{1}{3}$ with the first jump vector $\overrightarrow{ax}$. The average of $\cos\theta_{i,i+1}$ would be given by the probability that the second jump of x would be into site a, which we denote as P_a^x times $\cos\theta$ corresponding to this and there is one such site plus the probability that atom jumps onto either a_1, a_2, a_3 denoted by $P_{a_i}^x$ and there are three such sites:

$$\langle\cos\theta_{i,i+1}\rangle = P_a^x.(-1) + 3P_{a_i}^x.\left(\frac{1}{3}\right) = -P_a^x + P_{a_i}^x$$

In order to find this probability we need to know the probability that vacancy after itself making $n-1$ jumps comes to one of the nearest neighbour site of that particular site either a or a_1, a_2, a_3. Now you can see that in diamond cubic structure, there is no common nearest neighbour site for $a\ and\ x$. In other words, there is no common nearest neighbour site for the tagged atom and the vacancy. The vacancy has to leave the coordination shell and come back to the nearest neighbour coordination shell of x. Manning defined 4 types of frequencies for diamond cubic structure.

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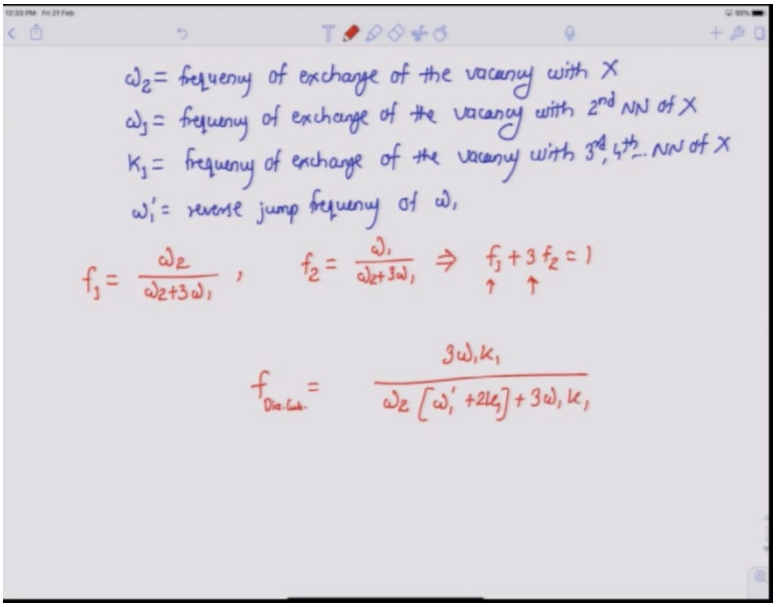

$$\omega_2 = frequency\ of\ exchange\ of\ the\ vacancy\ with\ tagged\ atom\ \ X$$

$$\omega_1 = frequency\ of\ exchange\ of\ the\ vacancy\ with\ 2^{nd}\ NN\ of\ X$$

$$k_1 = frequency\ of\ exchange\ of\ the\ vacancy\ with\ 3^{rd}, 4^{th}\ \ NN\ of\ X$$

$$\omega_1' = reverse\ jump\ frequency\ of\ \omega_1$$

The vacancy at a it can either exchange with x or it can exchange with either b_1, b_2 or b_3 all three of them are the second nearest neighbour of x. When vacancy is a nearest neighbour of x there is a binding between vacancy and impurity if x happens to be an impurity atom. And as the vacancy makes ω_1 jump it is leaving the nearest neighbour or first coordination shell of and the frequency of exchange from a to one of the b sites will be different from the reverse jump that is from one of the b sites to a.

This way we defined 4 frequencies and obviously the probability that at any time a vacancy will exchange with x in this particular situation denoted as f_1 would be given by:

$$f_1 = \frac{\omega_2}{\omega_2 + 3\omega_1}$$

and the probability that a vacancy will make ω_1 type of jump would be:

$$f_2 = \frac{\omega_1}{\omega_2 + 3\omega_1}$$

Because the vacancy at a can make 1 ω_2 type of jump and 3 ω_1 type jumps:

$$f_1 + 3f_2 = 1$$

With this manning derived the expression for correlation factor for diffusion of a tagged atom by vacancy mechanism in a diamond cubic lattice as:

$$f_{Dia.\ cubic} = \frac{3\omega_1 k_1}{\omega_2[\omega_1' + 2k_1] + 3\omega_1 k_1}$$

So, this was the model for diamond cubic. Next we will look into the model for BCC.

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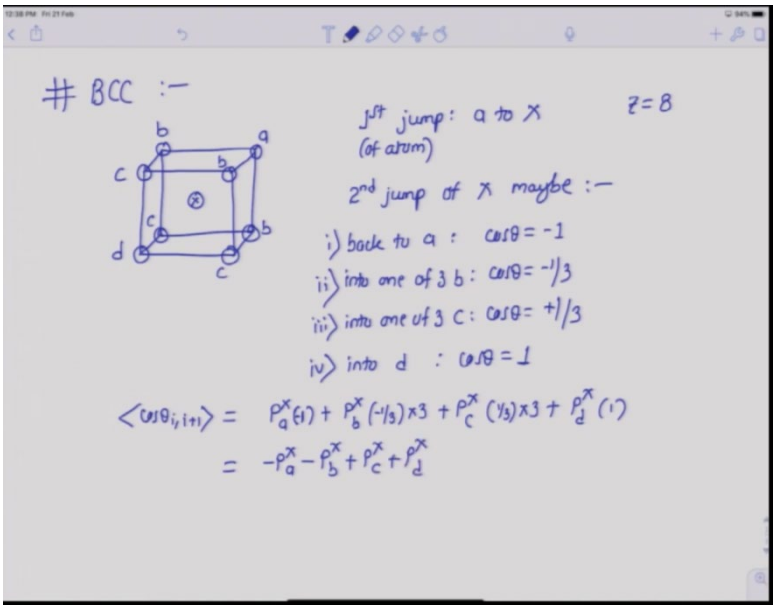

Let us consider a BCC unit cell as shown here in this figure. Let us say the first jump of the tagged atom was from this site a to x. The tagged atom is now at x and the vacancy is at a. Now the coordination number for BCC is 8, so each atom has 8 nearest neighbour. It can jump onto one of the 8 nearest neighbour sites.

In this case:

$$1^{st}\ jump\ of\ atom:\ a\ to\ x$$

$$2^{nd}\ jump of\ X\ \ may\ be:$$

$$1)\ back\ to\ site\ a\ :\cos\theta = -1$$

$$2)\ onto\ one\ of\ 3\ b\ :\cos\theta = -\frac{1}{3}$$

$$3)\ onto\ one\ of\ 3\ c\ :\cos\theta = +\frac{1}{3}$$

$$4)\ into\ d\ :\cos\theta = 1$$

To find out the average $\cos\theta$, we need the probabilities that the atom x makes its second jump either into $a\ or\ b\ or\ c\ or\ d$:

$$\langle\cos\theta_{i,i+1}\rangle = P_a^x(-1) + P_b^x\left(-\frac{1}{3}\right)\times 3 + P_c^x\left(-\frac{1}{3}\right)\times 3 + P_d^x(1)$$

This should be:

$$\langle\cos\theta_{i,i+1}\rangle = -P_a^x - P_b^x + P_c^x + P_d^x$$

Again, to get to these probabilities we need the probabilities that the vacancy after itself making n jumps comes to one of the nearest neighbour sites. Now, just like in diamond cubi, there are no common nearest neighbour sites for x and a in BCC. Manning defined 6 types of frequencies for BCC. To look into this frequency let us redraw the BCC cell again.

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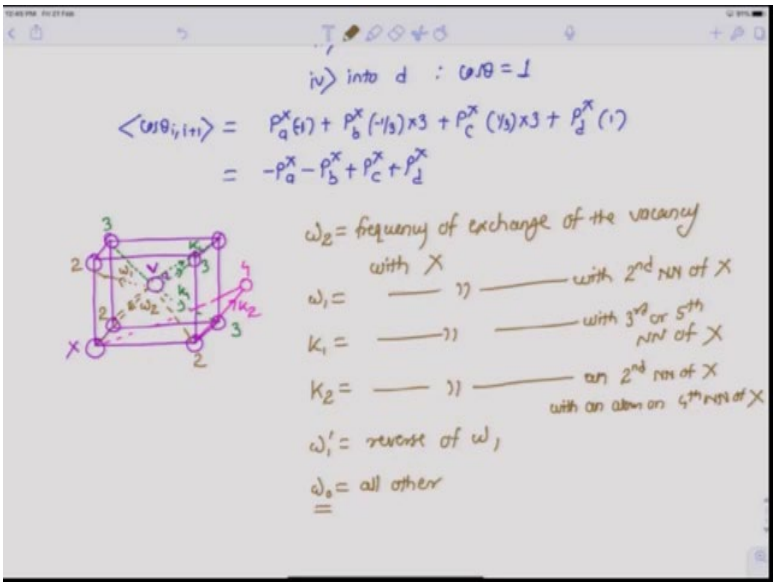

In this BCC cell I am showing the tagged atom x at one of the corners and the vacancy is at the body centre let us call this site as a. Now the vacancy can exchange either with x and the jump frequency for this type of jump is denoted as ω_2 which is the frequency of exchange of the vacancy with the tagged atom x. Or the vacancy can exchange with one of the 3 atoms

which are the next nearest neighbour or second nearest neighbour of x denoted by 2. And that frequency is denoted as ω_1, ω_1 is frequency of exchange of vacancy with second nearest neighbour of x. Or vacancy can exchange with the third nearest neighbour of x. So, which are the third nearest neighbour? Let us denote it as 3 along the face diagonal and the frequency of exchange with the third nearest neighbour is denoted as k_1. There is also one more nearest neighbour of vacancy which is the fifth nearest neighbour of x. That frequency also Manning denoted as k_1.

k_1 is the frequency exchange of the vacancy with third or fifth nearest neighbour of x. k_2 is the fourth frequency Manning defined as the frequency of exchange of the vacancy present on second nearest neighbour of x with atom on fourth nearest neighbour of x. In this case the fourth nearest neighbour basically are the body centre atom of the next cube. Now similar to the diamond cubic, the reverse of ω_1 is denoted as ω_1' obviously because there will be a vacancy impurity binding if x was impurity and ω_1 will not be same as ω_1'. It is because the activation energy for the forward jump and reverse jump in that case will be different. Remember again, we are considering the vacancy impurity binding here, only if they are on the nearest neighbour sites. And all other frequencies he denoted as ω_o.These are basically the frequency of exchange of the vacancies with the solvent atoms outside this coordination shell of x.

$$\omega_2 = frequency\ of\ exchange\ of\ the\ vacancy\ with\ X$$

$$\omega_1 = frequency\ of\ exchange\ of\ the\ vacancy\ with\ 2^{nd}\ NN\ of\ X$$

$$k_1 = frequency\ of\ exchange\ of\ the\ vacancy\ with\ 3^{rd}\ or\ 5^{th}\ \ NN\ of\ X$$

k_2
$= frequency\ of\ exchange\ of\ the\ vacancy\ on\ 2^{nd}\ NN\ of\ X\ with\ an\ atom\ on\ 4^{th}\ NN\ of\ X$

$$\omega_1' = reverse\ of\ \omega_1$$

$$\omega_o = all\ other$$

This is the way Manning defined the frequencies and we can proceed with the similar manner as we did for FCC and can find out the correlation factor for BCC.

We will not go into in depth just like we did for FCC. But, I will leave it to you as an exercise as we went over this just to understand in different cubic lattices, how the jump frequencies

are placed and how the probabilities of exchange are affected by the coordination of the tagged atom and of the vacancy. Alright, we will stop here for today. Thank you.