Diffusion in Multicomponent Solids
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Lecture 31
Point Defects in Intermetallics and Ionic Compounds

Welcome to the 31st class of this open course on Diffusion in Multicomponent Solids. In this lecture, we will discuss point defects in intermetallics and ionic compounds. I have first explained the nature of B_2 and L_{12} types of structures and then discussed various defects with respect to these structures. The defects that are discussed include Schottky defects, Frenkel defects, antisites and triple defects.

Now that we have gone through the point defects and diffusion mechanisms in metallic alloys, next couple of classes I would like to go over the Point Defects and Diffusion Mechanism in ordered structures. Ordered structures means there is a site preference, for example, in ionic compounds or intermetallics. If you have a metallic alloy of say component A and B, there is no site preference, the alloying is random. Which means B is randomly distributed in A or A is randomly distributed in B. However, in ordered structures, there is a site preference. In ionic compounds different types of ions would like to bond with each other and in intermetallics, the enthalpy of mixing is highly negative such that an order is established.

Every A atom would like to have B as its neighbour or every B atom would like to have A as its neighbour. Depending upon this stoichiometry, the type of the crystal structure will be different and obviously it will be different from either pure A or pure B. First let us take a look at couple of important ordered structures.

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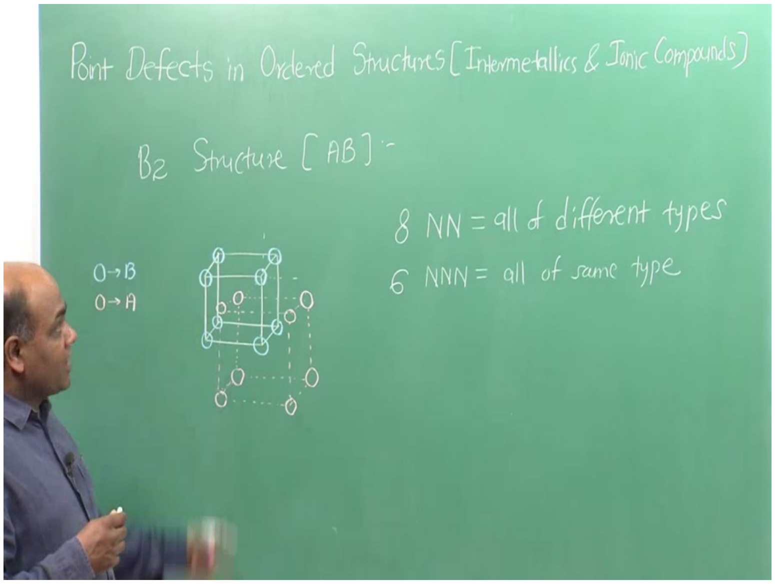

Point Defects in Ordered Structures [Intermetallics & Ionic Compounds]

B_2 Structure [AB] -

8 NN = all of different types

6 NNN = all of same type

The first one of it is called a B_2 structure and the intermetallics or compounds with the stoichiometry of the form AB exhibit this type of crystal structure. B_2 structure basically can be looked at as an interpenetration of two simple cubic sub lattices. One for type A atoms and the other for type B atoms. If we draw a single cubic cell, it resembles a BCC unit cell with all the corner sites occupied by 1 type of atom and the body center occupied by the other type of atom.

In this case, I am denoting type A atom which is located at the body center with this red color and the blue color on the corners are the type B atoms. Each of the A and B form their own sub lattices, which is of the type of simple cubic. In this particular cube it is very easy to see the simple cubic sub-lattice of type B because all the corner atoms are occupied by type B.

In order to see the sub-lattice of type A atoms, we can visualize 8 cubes placed side by side and one below the other. So, all the body centers are occupied by A atoms and if you connect those you will be able to see simple cubic unit cell of type A sub lattice. If we can imagine one cube on the right side of blue simple cubic lattice, type A atom will be at the body center of it. One cube below the first one and the one cube below the cube which was on the right side. So the A atoms will lie at the body center of all the four cubes. Then you can imagine similar four cubes placed in front and see the body centers of those. All the body centers of eight cubes will constitute another sub lattice of type A atoms. You can see two inter-penetrating simple cubic sub lattices and at the body center of the sub lattice of A, you have a B atom. At the body center of sub lattice of B, you have an A atom. So, this is the B_2 type of structure, you can see in B_2 structure there are 8 nearest neighbors to any atom. If you consider this atom A located at the body center of this cube, you can see 8 B atoms at the corners, which are the nearest neighbor of A. All the nearest neighbors are of different type. 8 nearest neighbor atom, let us denote nearest neighbor as NN, are of different types and each atom has 6 second nearest neighbors. If you consider any corner atom, for example you can see the 3 next nearest neighbor within this cube itself and 3 you can imagine, one on right, one on top and one in the cube in front. There are 6 second nearest neighbor or what we call as next nearest neighbor. Let us denote it by NNN, 6 NNN and all of same type. You can see all next nearest neighbor of any B atom are B atoms, all next nearest neighbors of any A atom are A atoms. This is important to understand next nearest neighbors and nearest neighbors. Because it will help us in understand the diffusion mechanism.

For example, any jump onto the nearest neighbor site will lead to the formation of wrong bonds. Whereas any jump onto the next nearest neighbor site will not cause any disorder in the system. So, we will see that later. Also if you see, each corner atom is shared by 8 cubes. there is only 1 B atom per cube here. Because there are 8 corner atoms divided by 8 and there is one A atom which is lying completely inside at the body center. So, the stoichiometry AB can be maintained by this type of arrangement in the B_2 structure. Now the ionic compounds will be mostly stoichiometry. But in intermetallics, some non-stoichiometry is allowed, that we have seen in the shape of the Gibbs free energy versus composition curve. We can have some miscibility within the intermetallic. The examples of B_2 type of crystal structure are nickel aluminide (NiAl) or iron aluminide (FeAl). Both of them show a wide solubility range on both side of the stoichiometry. Then CsCl is an ionic compound which shows B_2 type of structure.

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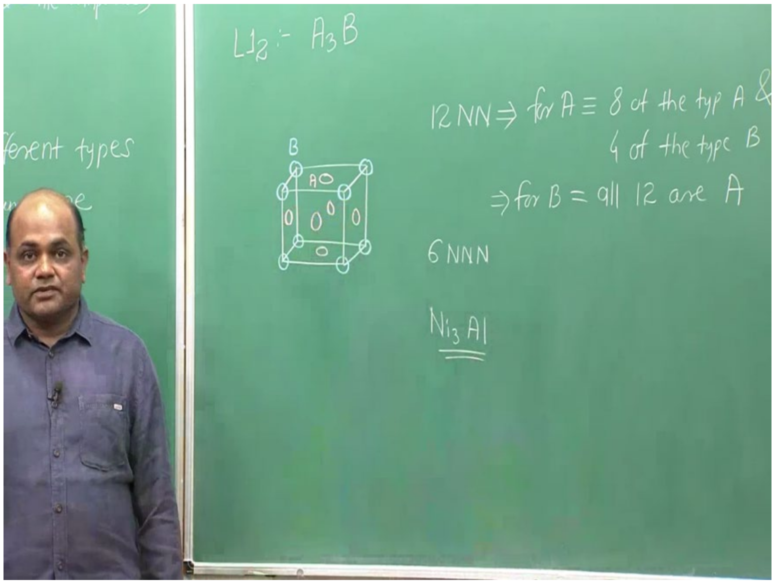

Another important crystal structure in ordered compound is called as L_{12} structure and this occurs in compounds of the stoichiometry A_3B: 3 atoms of A per atom of B and this L_{12} structure can be simplistically looked upon as a face centre cube with all B atoms at the corner and all A atoms at the face centres. Pink are A type of atom and the blue circles are B atoms. you can see, each atom in this structure has 12 nearest neighbours. If you consider any A type of atom for example, out of the 12 nearest neighbours, 4 are of different types and the remaining 8 are of the same type. That is, 8 nearest neighbours of any A atom are type A atoms and 4 are B atoms. Whereas for B, all 12 nearest neighbour for any B atom are A atoms. Since each face is shared by 2 cubes and there are 6 faces, so there are total 3 atoms per cube here of type A and each corner again is shared by 8 cubes, so there is only 1 B atom per cube. The stoichiometry of A_3B type is maintained by this type of structure.

Now if you look at the next nearest neighbours, again there are 6 next nearest neighbours for any atom. We have 6 next nearest neighbours and all of them you can see are of same type. The example of this type of crystal structure is Ni_3Al. It has the stoichiometry of the type A_3B, 3 nickel atom and 1 aluminium atom per unit cube. This is the L_{12} type of structure.

Now let us take a look at some of the point defects that occur in ordered structures. In metallic alloys, there is a metallic bond, which means the positively charged ions are floating in the sea of free electrons. Formation of a vacant site or addition of an impurity does not cause any disturbance of the charge neutrality. However, in ordered structure if you leave one site vacant it leads to disorder in the structure. In ionic compounds, it will cause a local disturbance of the charge neutrality and so the defects in ordered structures most commonly occur in pairs. For example, in an ionic compound, if there is a cation vacancy, then it will be negatively charged. It is because a cation has a positive charge, so cation vacancy implies a missing positive charge hence the vacancy has a negative charge. To balance this extra negative charge, one anion vacancy is created, which has a positive charge and this pair of vacancy on anionic and cationic sites forms one type of defect which is called as Schottky defect.

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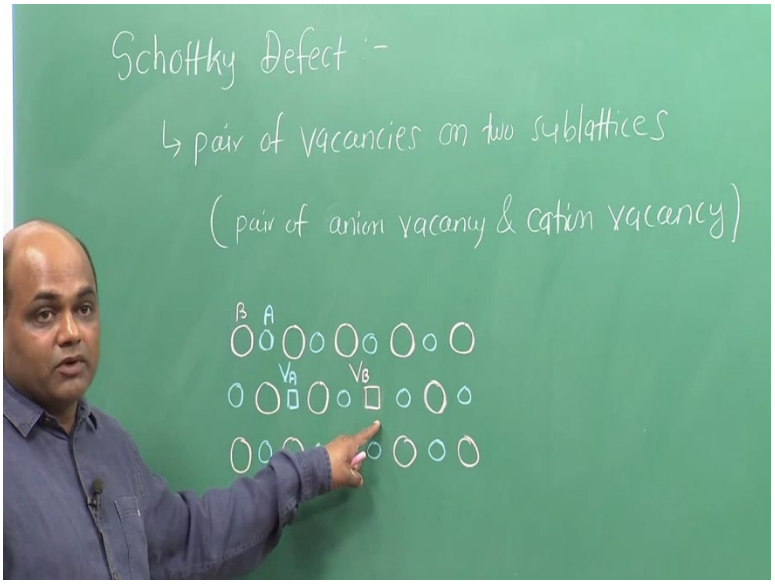

Schottky Defect :-

↳ pair of vacancies on two sublattices

(pair of anion vacancy & cation vacancy)

In case of ionic compounds, it is anion vacancy and cation vacancy. If you consider ordered structure, blue atoms are type A and red atoms are type B. Let us denote a vacancy by a square. Say if we create a vacancy on B sub lattice, this maintain the charge neutrality when a vacancy will be created on A sub lattice. This is denoted as V_A, vacancy on A sub lattice and V_B, vacancy on B sub lattice and this is the Schottky defect. For Schottky defect, you can see the equilibrium concentration of one type of vacancy should be equal to the equilibrium concentration of the other type of vacancy.

Now, if the size difference between A and B is large, then the smaller atom can actually occupy an interstitial position. Once the vacancy is formed by a smaller atom, instead of the bigger atom forming a vacancy, the smaller atom A will go and sit into the interstitial site. In an ionic compound, the smaller ion can fit into the interstices as the energy required to form the anion vacancy may be larger than the energy required to form a cation interstitial and a cation interstitial will accompany a cationic vacancy. The cations are usually small and you will see cation interstitial and cation vacancy pairs. And this is called a Frenkel defect.

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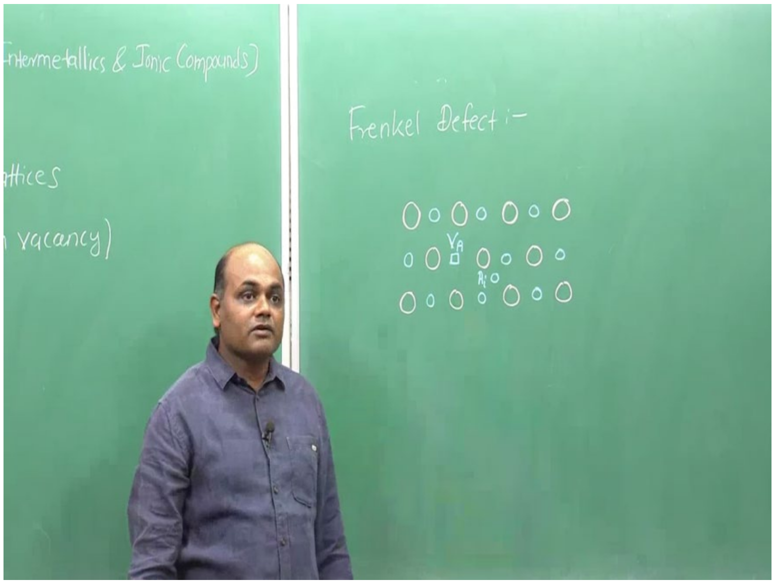

Again, an A atom leaving its site will leave a vacancy behind and A being very small can occupy an interstitial site. This is we call A_i, interstitial of A and this is V_A vacancy on A sub lattice. This is the Frenkel defect. For Frenkel defect the equilibrium concentration of cation interstitial should be equal to the equilibrium concentration of cationic vacancy. Now depending upon the charge difference and the energy required to form anionic vacancy, you can have a mixture of cation vacancies, anion vacancies and the cation interstitials.

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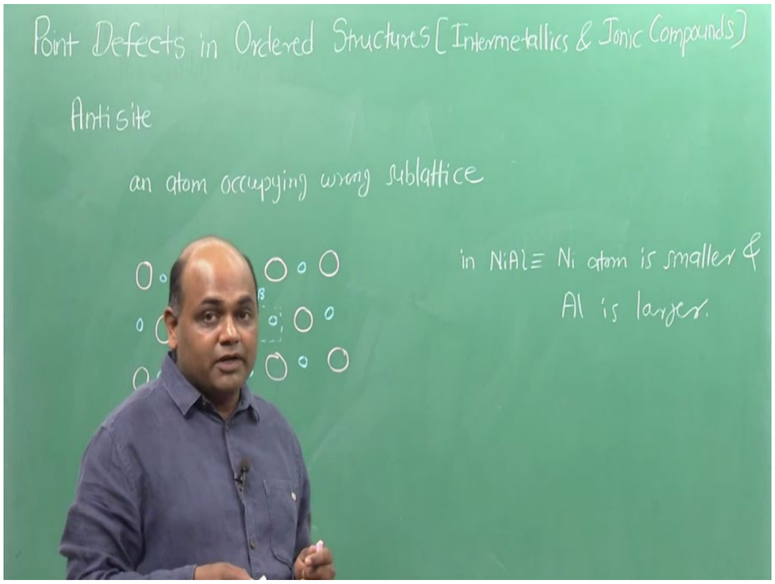

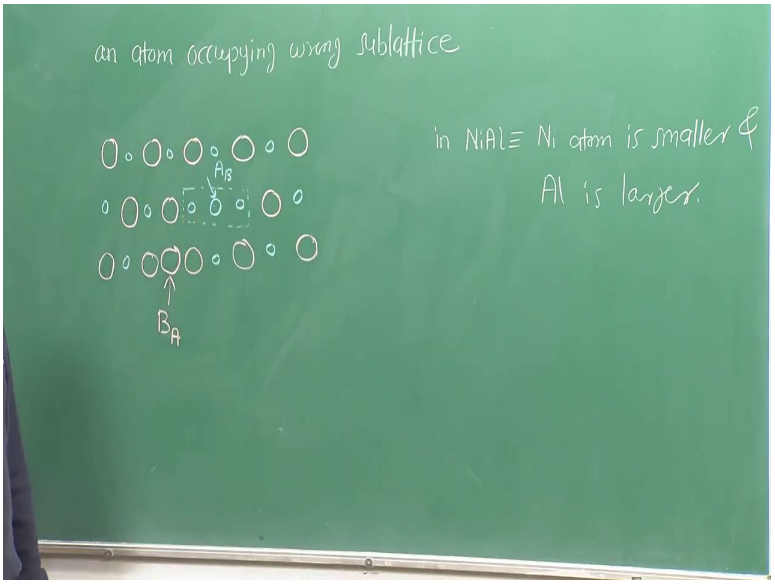

Next type of defect is called an Antisite. As the name suggests, it is an atom, occupying site on a wrong sub lattice. B atom occupying an A sub lattice site or an A atom occupying a B sub lattice site is called an antisite. Here you can see, this is an A atom which is wrongly placed on a B sub lattice. This is an antisite of A on B, we denote it as A_B. If we have a B atom occupying an A sub lattice, like here this is called as antisite of B on A, it is denoted as B_A.

As you can imagine, if the atom size is small, like the size of A atom is much smaller than that of B atom then forming an antisite of A does not require much energy. But since B atom is very large, forming an antisite of B on A requires large amount of energy.

Typically you will see considerable equilibrium fraction of antisite of smaller atoms and this will be especially important when there is a non-stoichiometry. For example in NiAl, nickel atom is smaller and aluminium is larger. If we have nickel rich NiAl, that is, if nickel aluminide is off stoichiometry and has larger amount of nickel than 50 mole percent then it will be accommodated by formation of nickel antisites.

However, on the aluminium rich site, the formation of aluminium antisite is a very high energy event. So, the equilibrium concentration of aluminium antisite will be much lower. The extra aluminium that is the off-stoichiometric aluminium will be accommodated by formation of nickel vacancies. In ionic compounds, the antisite formation is very rare because there is an ionic bond between A and B and forming an antisite leads to formation of wrong bonds again which is a very high energy structure. So, the antisite in ionic compound will almost not be possible.

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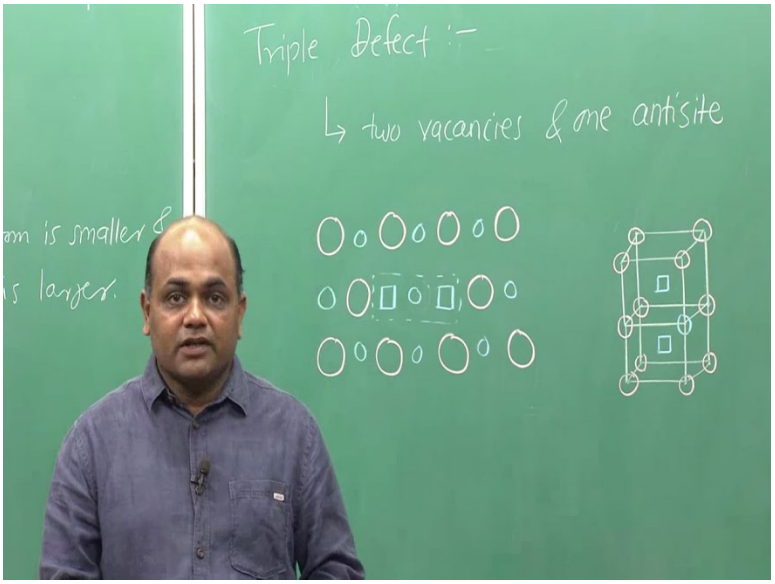

Then the next defect is called Triple defect. As the name suggests, it is a defect complex involving three defects. There are 2 vacancies involved and 1 antisite. So, for example, 1 antisite of A on B sub lattice and 2 vacancies on A sub lattice is a triple defect. This is an important defect that can assist in diffusion of A and B. Particularly A, because A being smaller forms an antisite. We will see that later how it assist the diffusion. In case of B2 structure, to visualize this defect I have shown 2 unit cubes of B2 structure, one above the other, wcan see there is 1 A atom which is occupying the B sub lattice and the 2 body centre sites which are supposed to be occupied by A atom are vacant. So, there are 2 vacancies on A sub lattice, and 1 A antisite and this is how the triple defect would look like in B2 structure. These are some of the important defects which occur in ordered structure. In the next class, we will go over diffusion mechanism in these ordered structure, thank you.