

**Physics of Functional Materials and Devices**  
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**Lecture – 12, Week 3**  
**Crystal imperfections**

Welcome to the third lecture of week 3. Till now you have seen the importance of synthesis routes. As you move from one synthesis route to the other, you can make different types of crystals. We have also discussed about the types of crystals in two dimension and three dimensional crystals. In the previous lecture, I discussed about the Bravais lattice and about the Miller indices. If you look in this discussion, we are considering that the crystals are ideal.

What do we mean by that? We consider that the crystals which are forming have the conditions that all the atoms will be occupying the designated lattice site. But as we know, it is a very rare case that you can achieve an ideal condition because there are various parameters which can contribute towards taking the situation from an ideal type to a non-ideal type. What do I mean? I mean that it is very rare that you get an ideal crystal. Crystals which you get or the materials which you are going to investigate that have crystalline nature always tend to have imperfections.

And therefore, it is very critical to understand the different types of imperfections which can stabilize in a crystal or a material and how does a given imperfection modify the properties of those materials. Today's lecture will focus on some of the common imperfections which you will encounter when you make materials. These include crystal imperfections, point defects, line defects and how do you actually quantify these defects? They are done by defining a vector which is called Burger vector. And as we near the end of this today's lecture, I will also give you a brief description about the interfacial defects. So, let us start.

What are imperfections? As all of us know imperfect situation means that you consider a given situation but what you see is not exactly superimposing on that situation which you thought but it is slightly different and this different situation is then termed as an imperfect situation to what you had envisaged. This is the broad layman language to describe imperfections. But in terms of crystals, how do you define defects? A crystalline defect refers to the lattice irregularity. So, there is irregularity in the lattice. In a perfect crystal, we had considered that the lattice would be such that the definition of the lattice would lead to conditions such as translational symmetry as well as rotational symmetry and you will have periodicity extending throughout the lattice.

But if you have imperfect conditions, there would be certain regions where you will see the loss of this periodicity and that is what we are indicating by the term irregularity. So, crystalline defects refers to lattice irregularities having one or more of its dimensions of the order of atomic diameter. So, the irregularity can extend in one dimension or it can extend in two dimension or it can extend in three dimension also. So, what is the need of understanding these imperfections? As I said till now we have considered ideal cases but very rarely do we get materials which have ideal structure. You will have certain disorder or imperfections in those materials.

All these materials contain a large number of defects of or imperfections and these defects or imperfections actually have significant influence on the properties of these materials and therefore, it is important to understand about these defects and how do you control these defects if you want to and what are the consequences which the extent of defects in crystals can have on a property or properties of a material. That is the importance of this understanding. The defects in crystals can be of various types. For example, you can have point defects as just even if you do not understand the details, point defects means this defect is localized at one point and if I then move to line defect, what do you expect? These defects will be extending in a line or you will have a line along which you will see imperfections. It is not localized at one point and the third is interfacial defect which means you will see modification of the lattice in a way that you start seeing some defects at sites which the lattice did not recommend.

That means you have some interfacial positions where you are seeing some kind of defects or manipulation taking place and those are called as interfacial defects. The point defects can be of various types. Some of the common ones are the vacancy defects, the interstitial defect or substitutional defects. Similarly, the line defects can be edge dislocation or screw dislocation and finally, the interfacial defects can be of stacking fault type or you can see these interfacial defects along the grain boundaries or twin boundaries and hence these names. Let us start with the first that is point defects and their types.

Point defects as I said are local, so they are localized in one region of the lattice or the material which you are considering. They concern just a few atoms close to a defect. So, if you have a large material and then you have a lattice which is forming that material, if you have a point defect then within this region there will be a small region where you will see this defect and the effect of this defect will be felt by the atoms near these defects. It is not that it will start immediately impacting at large the whole lattice. Vacancies are defined as a missing atom in a lattice site.

So, you have a case where you consider a lattice. This is an ideal lattice, but if you have a case where at say one of these sites the atoms are missing that means you have a vacant site those cases will be called as a vacancy and this is the simplest point defect. The necessity of this existence of these point effects is that they increase the entropy of the

crystal and helps in the arrangement of the atoms in desired form because entropy or increase in entropy is beneficial when you are trying to have certain growth of a crystal or a lattice. Vacancy defects also include impurity atoms that occur in crystal lattice and causes distortion. These impurity atoms are the ones which are not occupying the desired lattice site or if you consider in terms of unit cell they are not occupying the Wyckoff position.

The impurity atoms occur either as an interstitial atom that means you have an atom which is occupying a site which is in the middle of the lattice positions and you had not defined this position while drawing this lattice. So, you were not expecting any atom to be occupying that position. That is an interstitial site. An interstitial atom is the atom which is occupying that site and mostly it is considered as an atom between the ordinary lattice sites. A substitutional atom what the word substitutional is coming in from substitute.

So, you have substituted one of the atoms. So, if you look into the violet large size ball and the pink shaded ball which is smaller than the violet colored ball, you find that the violet colored ball has substituted one of the pink balls, but because of its size it has probably induced a case that either the electro positivity or electronegativity has increased. And to compensate this charge increase you have to simulate a condition that you have to take the pink ball out so that again you reach the condition of charge neutrality. So, this is why you induce these kind of interstitials and such substitutional atoms are actually occupying the ordinary site, but because of their charge they enforce a condition where one of the original atoms is kicked out from this site so that the overall charge neutrality condition is obtained. So, you can see a simple vacancy defect means a vacant site.

Interstitial defect you have an atom at the interstitial site and then you can have self-interstitial defect or Frenkel defect. What are those? The self interstitial defects are the one which occur when the atom of the same crystalline solid occupies the interstitial position by leaving its original lattice site. So, you have not brought any foreign atom or a subsequent to occupy a interstitial site. What has happened? One of the atoms which was occupying the original lattice site leaves that site and sits in the interstitial position. That is called self-interstitial defect.

What is the difference between self interstitial and interstitial? Self interstitial defects occur when atoms of the same crystalline solid occupies the interstitial position leaving its original lattice site. So, it moves from the original site to the interstitial position. Whereas in the case of interstitial defect a foreign atom occupies the interstitial site. So, you have a foreign atom which comes and sits at the interstitial site. The Frenkel defect is the defect which forms when an atom or a smaller ion usually cations leaves its place in the lattice and if it leaves its place in the lattice what will be left behind? A vacancy and this atom or smaller ion becomes an interstitial by lodging itself in a nearby location.

So, it goes and becomes an interstitial by lodging itself in a nearby location and goes and sits at somewhere in the vicinity from the place where it left. Please note no ions are missing from the crystal lattice as a whole in Frenkel defect. Thus, the density of solid and its chemical properties remain mostly unchanged as well as the crystal as a whole remains electrically neutral. So, you are not sending in any foreign atom, you are not extracting an atom, the total number of atoms are remaining the same and if the material was initially stable with those number of atoms it will remain stable in the case even if you induce Frenkel defect because no new atom has gone in or no atom has been extracted out of the lattice. The next is the line defects and what are their types? As the name suggests dislocations are line defects in crystal lattice.

They are created when there is a deviation from an ideal crystal. So, please remember whenever we talk about defects we are talking about a condition where we deviate from ideal crystal and in dislocations this deviation is along a plane or a line of atoms resulting in irregularity in a complete line of crystalline solid. These defects can have significant impact on the properties of materials, which type of properties such as mechanical strength, the electrical conductivity, the thermal conductivity, the diffusivity. They can also affect the behavior of other defects in the material such as point defects or grain boundaries and based on the nature of this deviation line the line defects are characterized under two broad headings, but the third one is also possible. The two broad headings are edge dislocations or screw dislocations or you can have mixed dislocations.

You can have edge and screw dislocations coexisting. An edge dislocation what do you imagine if there is a defect in the edge? This is basically an extra portion of a plane of atoms or half plane whose edge terminates within the crystal. This is sometimes termed as dislocation line. So if you consider the hand then this is an ideal case, but if I move half of it you can see that the other plane came in, but it stopped at half the plane and you have the other half remaining vacant. So you have this whole plane where you expected something to be filled, but it is not filled because the other plane which came in only went up to the half of the area which you were expecting it to cover.

So you have the other dislocation line or plane which is formed. The screw dislocation is the case where the defect occurs when the plane of atoms in the crystal lattice trace a helical path around a dislocation line. So if there is a dislocation line for example if the dislocation is along the pen I am holding on the palm then the screw defect will form a helical path around this dislocation line and I hope you understand what would be the mix dislocations you will have both edge and screw dislocations coexisting. Before we learn the types of defects in detail we must understand how do we quantify the defects and how much defect is there in a given lattice or material. Somebody will say you have very high defects, you have somebody will say you will have low concentration of defects.

This high and low becomes subjective. Therefore, Burger vectors are used to determine the strength of the dislocation with larger vectors corresponding to stronger dislocations. The directions of the Burger vectors also affect the behavior of the dislocation such as its motion under applied stress. The magnitude and the direction of the lattice distortion associated with the dislocation is therefore expressed in terms of vector  $b$  which is called as Burger vector. The Burger vectors can be either edge or screw type depending upon the type of dislocation.

Even if dislocation changes direction and nature within a crystal the Burger vectors is same at all points along its line. Hence, the Burger vector is perpendicular to the dislocation line for edge dislocation and the Burger vector is parallel to the dislocation line for screw dislocation. Let us discuss what the edge dislocation would be. What would be the edge dislocations? As the name suggests the edge dislocation is the type of linear crystallographic defect. So, you have the linear crystallographic defect where an extra half plane of atoms is inserted between two planes of atoms.

If you see this extra half of atoms has been inserted in between these two planes of atoms, you do not have any atoms here. So, it is not the plane which is expected in a lattice. This results in localized strain because this atom impacts both the sides and hence you have localized strains. The dislocation line is the boundary between the planes of atoms. In this case the Burger vector is perpendicular to the dislocation line and points from the compressed side to the tensile side of the lattice.

The compressed side has a higher atomic density obviously if you have an extra plane you will have a higher atomic density than the tensile side. And the extra half plane of atoms is the dislocation region accommodating this mismatch. In addition, the edge dislocations can be created by various mechanisms such as plastic deformations, thermal stresses or you introduce impurity atoms you put certain number of atoms along a given plane. These dislocations play a critical role in determining the mechanical properties of materials. They decide what would be the strength of the material, what would be the growth mechanism of these materials, what would be the ductility of these materials, how ductile these materials would be.

Similarly, as I expressed the screw dislocation is a type of linear crystallographic defect which is what which is moving in a helical path around the dislocation line. So, the dislocation line is the axis around which the lattice is twisted. Sometimes you use the curvy arrow to designate the screw dislocation. This type of dislocation can be visualized as a spiral staircase. So, as a spiral staircase which you see at various places.

A screw dislocation converts a pile of crystal planes into a single continuous helix. And this helix when it intersects the surface a step is formed. So, when it intersects a surface a step is formed which cannot be eliminated by adding further atoms. So, you have row of

atoms forming a plane and if you have a screw dislocation you have a row and then there is a step and then the other set of atoms. The crystal grows as a never-ending spiral.

So, you have two levels atom here and then atoms here and then the crystal grows as a never-ending spiral. Finally, what are interfacial defects? The interfacial defects are the one that occur at the interface between two materials. So, you have material A and B and when they are brought together to form a solid solution or a single phase material or they have similar matching lattice then there is a boundary that is called as interface. So, these defects are formed when two materials are coming together or they are formed between two regions within the same material that have different crystal structures or two different regions within a given material which have different chemical compositions or two regions within a given material that have different physical properties. These can be stacking faults, grain boundaries or twin dislocations.

The stacking faults are created when there is a deviation from the regular stacking sequence of the planes in the crystal lattice. So, when you are having periodicity you are putting one plane over the other and then you are stacking it. But if you deviate from this stacking sequence then you reach some imperfections and that leads to stacking faults. Stacking faults for example, are not expected in crystals with A B A B sequences. Therefore, it does not occur in a body centered structures as there is no alternative for an A layer resting on a B layer.

Whereas, if you consider the case of a face centered cubic structure you can clearly see that you will have the stacking faults taking place. Similarly, you can have intrinsic stacking fault or an extrinsic stacking fault. An intrinsic stacking fault is the change in sequence resulting from a removal of a layer. So, you just take out one layer that is the time you call it as intrinsic stacking fault. An extrinsic stacking fault is the change in the sequence resulting from an introduction of an extra layer.

So, you introduce an extra layer then you have an extrinsic stacking fault. But if you remove one layer altogether then you have the intrinsic stacking fault. Then you have grain boundaries. So, if you consider crystalline metals these are formed by aggregates of small crystals. So, you have one particle then the other particle then other particle and then you have large number of particles which are coming together.

When they come together there is a boundary formed here and you can have different sized particles. So, one can be larger the other can be much smaller and then you have different types of boundaries getting formed. And because of this you will have different orientations between these grains. So, these small particles which are formed within the material are called as grains. Within a grain you have the same property, same alignment everything is same but if you move from one grain to the other the arrangements can be different.

Not the chemical formula but you can have different watering, different number of atoms in that grain. So, you have different types of grains which will be formed and you have then the boundaries which are seen. A grain boundary is equivalent to what? It is equivalent to the dense array of static dislocations. It works like a high barrier to moving dislocation. So, if a dislocation is moving let us say if in this plane suddenly when it comes to the boundary the grain boundary you see the nature of the distribution of atoms or arrangement of atoms has changed from this grain to the next.

And therefore, what will happen? The travelling imperfection becomes difficult to propagate further because the nature of the second grain is very different and hence the imperfection does not move so easily into the next grain. Hence the grain boundaries promote hardening because they do not allow the dislocation to propagate throughout the material. The mechanical strength of a crystal is inversely proportional to average grain diameter that we know. The smaller the grains are the better will be the mechanical properties of the material. And if you have smaller grains then what will happen to the boundaries? Can you think? And if the boundaries are getting modified then what will happen to the corresponding travelling dislocation? Have a thought.

If you look into grain boundaries these are often irregular and have higher energy than the ideal lattice. As the arrangement of atoms across the boundary is not perfect. If you have same type of arrangement that means the Gibbs free energy of the whole system is much lower. But suppose I have one grain where all the alignment of smaller particles are in one direction the other grains which where you have the in the other direction you will see you will have entropy change across these two boundaries and hence you will have a higher energy associated with this kind of system and therefore, if you have systems where grain boundaries are getting formed then these materials have higher energy than the ideal lattice. And finally, you will see what are twin crystals? A twin boundary is a special type of grain boundary across which there is specific mirror lattice symmetry.

So, you have mirror lattice symmetry that is atoms on one side of the boundary are located in a mirror image positions of the atoms on the other side. The region of material between these boundaries is called as twin. There are two types of symmetries which you will have to consider the 180 degree rotation about an axis which is called as twin axis or reflection across a plane which is then called as a twin plane. And this can occur during crystal growth. So, when you are growing the crystal suddenly if all the atoms are arranging in one direction when you go beyond a point and if there is some change in the growth parameter suddenly the arrangements may be slightly different and you may start seeing different kind of stacking.

And that leads to mechanical deformations and these are commonly formed in crystals or single crystals when they are growing. Based on today's lecture let me ask you questions. Can you tell me how can you limit defects? The answer lies that if you want to limit defects

have the right synthesis protocol to obtain a given material. What will happen when materials are obtained in different batches? Different batches means what? If they are synthesized in different batches of synthesis. You cannot have hundred kgs of materials produced in one batch.

So, you can produce hundred batches each batch being one kg of material. If there is any difference in synthesis parameters from one batch to the other the properties would be different and the arrangement of atoms would be different. So, if you consider a given case as the ideal case which you want to replicate, but if the synthesis parameters are different in the next cycle then what will happen? The batch of material which is synthesized will have different behavior and it will be called as imperfect with respect to the case which you have defined as perfect. So, it is very important that you maintain similar synthesis parameters and conditions when you make materials batch after batch. If you move from one synthesis route to the other, that means you have different temperatures, different pressures, different vapor pressures, different solid or liquid or gaseous states of reactants you do expect that the materials will have different orders of defects.

It is very important to understand how will you know that there is a defect in the material. So, there are various indirect routes by which you can actually determine the magnitude of concentration of defects in materials which we will discuss bit later. And are the defects always bad? You do not want it. No, there are certain applications like luminescence, photoluminescence, fluorescence, sensing, gas sensing these kinds of applications do need materials with certain defects in them.

So, defects are not always bad as the definition may imply. So, in today's lecture what have we seen? We have seen that crystals which are formed will have deviation from perfect character and those will have different kind of imperfections and those kinds of imperfections were introduced to you in today's class. They include line defects, point defects, interfacial defects and if you want to read more about today's lecture then you can follow the books which I have mentioned. Thank you very much.