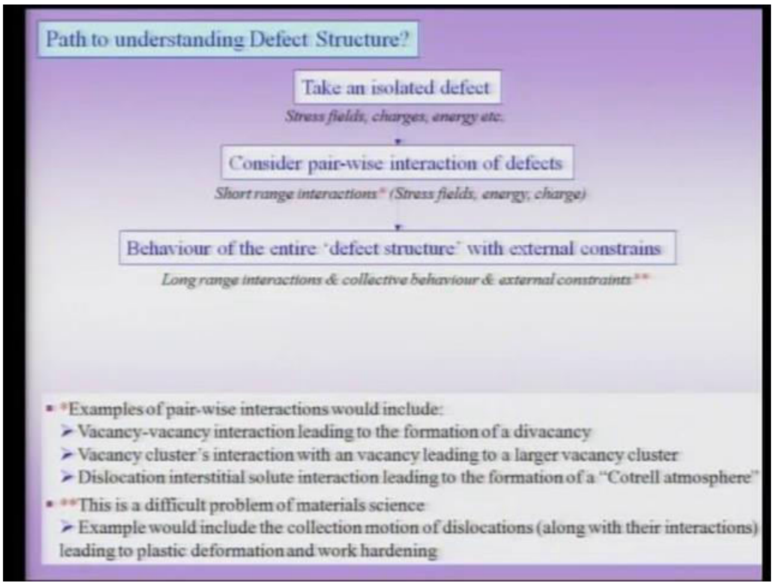
Structure of Materials

Prof. Anandh Subramaniam
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur

Lecture - 22
Defects in Crystals

So, we saw that the term defect structure hides in it a lot of details. If we really want to understand properties of materials, we perhaps have to understand this defect structure. So, what is my path way to understanding this defect structure? As you said the first thing we will do of course, take up isolated defects. These isolated defects could be vacancies, dislocations, they could be stacking faults; another kind of defects which we will take up one by one very soon. We will try to understand their charge associated with them, the stress fields associated with them, the energy of those defects etcetera.

(Refer Slide Time: 01:03)



Path to understanding Defect Structure?

Take an isolated defect

Stress fields, charges, energy etc.

Consider pair-wise interaction of defects

Short range interactions (Stress fields, energy, charge)*

Behaviour of the entire 'defect structure' with external constrains

*Long range interactions & collective behaviour & external constraints***

- *Examples of pair-wise interactions would include:
  - Vacancy-vacancy interaction leading to the formation of a divacancy
  - Vacancy cluster's interaction with an vacancy leading to a larger vacancy cluster
  - Dislocation interstitial solute interaction leading to the formation of a "Cotrell atmosphere"
- **This is a difficult problem of materials science
  - Example would include the collection motion of dislocations (along with their interactions) leading to plastic deformation and work hardening

The next state after taking up an isolated defect would be to take up perhaps a pair-wise interaction. That means, I may take up for instance a two, a vacancy and it is interaction with another vacancy. Of course, even in a pair-wise interaction often, as you shall see very soon that there are certain global considerations especially for instance, if we are talking about would a divacancy form.

Then, for instance, we also have to consider the entropic term. As we all know, entropic entropy is a statistical system wise kind of calculation. That means, I have to see at the global picture as well even in what you might otherwise thing to be a interaction between two vacancies. Of course, then, we can consider an interaction between for instance a vacancy and a vacancy cluster. They could have vacancy cluster having lot of vacancies. I can talk about its interaction with an isolated vacancy.

So, for instance, this vacancy cluster could grow. Actually, it can emit vacancies and it can shrink. So, there are these various possibilities. But I need to now, then, talk about an individual vacancy with a vacancy cluster. An important other for an example of an for instance, a pair-wise interaction between two kind of defects would be for instance a dislocation interstitial solute interaction. We will see later for instance, this can lead to important phenomena known as the end point phenomena, when you are talking about stress strain diagram for mild steam. What you might otherwise called an uniaxial tension experiment for mild steam.

So, we start first of all with an isolated defect, a vacancy, a stacking fault or a dislocation. Try to understand its stress fields, its energetics, its charge associated with them etcetera. Then, we talk about pair-wise interaction. This pair-wise interaction would perhaps lead me to a larger assemblage of defects. We had seen that while talking about that. We not only have to talk about interaction but association of these defects. Disassociation can lead to a larger cluster of defects; for instance, defect structure, which is slightly more complicated or has many other defects associated with each other.

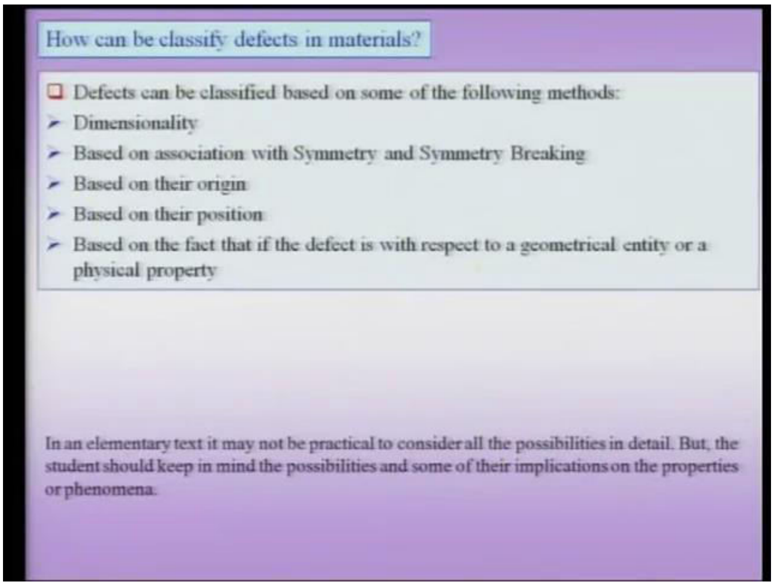
Then, when I am talking about this pair-wise interaction again, I obviously worry about the stress fields, energy and charge etcetera. Then, once I am done with this task, I can now proceed to a larger global picture. I am talking about behavior of an entire defect structure with external constraints. That means, I have to worry about for instance, suppose, I am applying stress on a material. Then, I have to understand how this stress can affect a motion of a single dislocation.

I need to worry about the collective motion of large number of dislocations. I need to worry how these dislocations interact with each other. What other kind of other defects or other kind of structural changes in the dislocation line can be brought about by these interactions? So but, as we shall note, this is actually a very difficult problem in material science. This is not a very easy problem. There are good attempts going on at the various length scales now. But this is definitely not a solved problem on material science.

I said one of the important problems now being considered is a collective motion of dislocations. The thing we would worry about when I talking about collective motion of dislocations is obviously plastic deformation and also work hardening. So, when I am talking about this collective motion and external constraints, I could external constraints could be forces. They could be electromagnetic fields, any other thing, which could affect my dislocation structure in the material. I am worrying about long range interactions in that case.

I am also worrying about collective behavior. So, there are two important things, which I need to worry about; when I am talking about this large scale problem of defect structure especially, the behavior of the defect structure under external constraints. So, this is my global thought process I would undertake, when I am going to understand this problem of defect structures. But as I said, we shall start with the simpler understanding, wherein we consider isolated defects and more often than not. Some of these considerations are more than enough for understanding certain kind of phenomena. So, the next thing we take up is that how can we classify defects in materials.

(Refer Slide Time: 05:07)



How can be classify defects in materials?

☐ Defects can be classified based on some of the following methods:

- Dimensionality
- Based on association with Symmetry and Symmetry Breaking
- Based on their origin
- Based on their position
- Based on the fact that if the defect is with respect to a geometrical entity or a physical property

In an elementary text it may not be practical to consider all the possibilities in detail. But, the student should keep in mind the possibilities and some of their implications on the properties or phenomena.

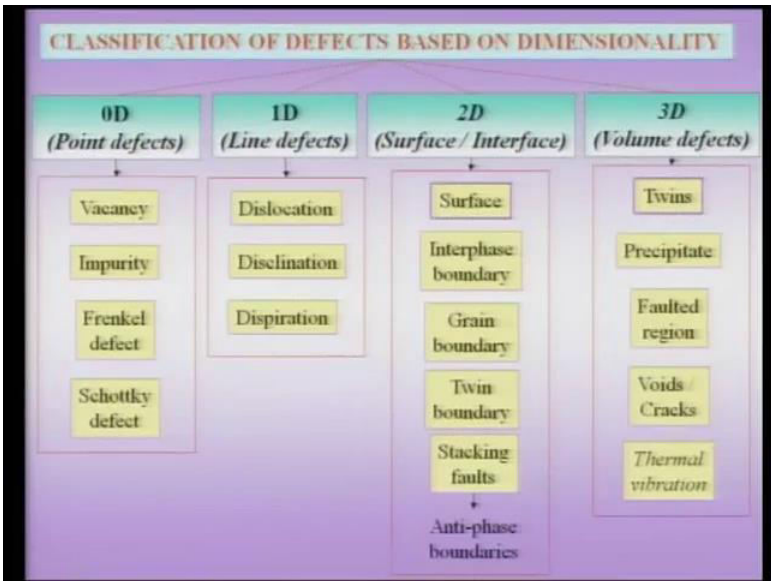
There are very many ways of attacking this problem, very many perspectives towards understanding defects in materials. Each of them perhaps throws slighter wings to focus certain aspect of the defect. Of course, we will start with something known as the dimensionality of the defect. As we shall see, this is an sort of an ideal geometrical definition.

We can talk about them with their association with symmetry and symmetry breaking. How certain defects lead to symmetry breaking? How they are associated with certain kinds of symmetry? We can talk about them based on their origin. Of course, this or word origin here is defined as slightly different since, the initial sense. You will see in what sense we are talking about the base on the origin. We can talk about based on their position. Of course, when we defined a crystal, we said, whenever I talking about a crystal, we always talk about a crystal if the motif is actually a geometrical entity, a physical property or a combination of both.

Similarly, with the defect, we have to worry about this is a defect with respect to physical property or is it something related only to a geometrical entity. So, these are the questions I would ask myself. I would classify my defects based on these very many criteria. Of course, we have known that this is a sort of an elementary, introductory course on this subject of structure of materials. Therefore, we will not consider all the possibilities in detail. But it is very important that the broad overview is in focus or kept in mind when you are studying the details later on.

So, even though some of the concepts we are introducing in his next few slides are what you might call a broad umbrella kind of description of the subject. That means there are lots of definitions, which we will not consider in detail. But please do keep in mind some of these definitions even though we may not consider them in detail in this course. So, let us start by sort of classifying defects based on dimensionality.

(Refer Slide Time: 06:54)



CLASSIFICATION OF DEFECTS BASED ON DIMENSIONALITY

0D *(Point defects)*
- Vacancy
- Impurity
- Frenkel defect
- Schottky defect

1D *(Line defects)*
- Dislocation
- Disclination
- Dispiration

2D *(Surface / Interface)*
- Surface
- Interphase boundary
- Grain boundary
- Twin boundary
- Stacking faults
  - Anti-phase boundaries

3D *(Volume defects)*
- Twins
- Precipitate
- Faulted region
- Voids / Cracks
- *Thermal vibration*

So, we could have zero dimensional defects, one dimensional defects, two dimensional defects and three dimensional defects. Again, as we know dimension is a freely speaking a geometrical kind of a definition. In other words, when I am saying 0 D, I do not really mean zero dimensional. What I mean is point like and when I am saying one dimensional, what I mean essentially for instance, suppose, I am talking about displacement fields associated with the defect.

Then, I would think that the displacements fields are line like. Similarly, when I am talking about a two dimensional defect, I do not really mean, it is a exact geometrical two dimensional surface. But what I mean is that it is almost two dimensional. So, that is what we mean by this, these lower ordered dimensionality of defects. This kind of a classification is very important because that throws in view most of the kind of defects. We will normally deal with in material science.

Zero dimensional defects could be for instance, a vacancy. It could be one of those alloying element atoms we have seen before like a substitutional element or a interstitial element. Then, in charge systems, you will see there are additional defects like frenkel and schottky defects. So, these are so, there are possibilities which are only possible in charge materials, which is frenkel and schottky defects, one dimensional line defects. They are very important as far as material behavior goes. There are three important ones the dislocation, the disclination and the dispiration.

In this set of slides and in this course especially, we will focus basically on the dislocations. But, we need to remember that there are other possibilities like disclinations and dispirations surface defects. When I mean surface sometimes I may use the term loosely surfaced. What I mean is an interface defect and surface being a special of an interface between a material and vacuum or material and air typically. That I call a surface but we have to remember when I am saying surface, it is actually a many times just I am talking about a interface.

So, and we had already noted that for instance, the surface is an inevitable defect in a material. So, there is always going to be a surface in any real practical material. Then, there is a possibility of an interface between one material and other material, which we call an interface material. For instance, on one side of the boundary, a flat two dimensional boundary, I could have copper other side. I could have aluminum and that would be an interface boundary.

Then, there could be a boundary between two materials with the same kind. That means there could be one crystal on one side with respect to another crystal on other side. It is misoriented with respect to the other. Two crystals are misoriented by some angle. Therefore, that I call a grain boundary. Then, if the two materials have a special kind of a symmetry relation on each side of the boundary then, I call it a twin boundary. Typical twins would say for instance, be mirror related twins.

Then, there are additional defects, which are stacking faults which come up in the order of stacking. There are special other kind of boundaries, special class of the stacking fault which are known as anti-phase boundaries. When you are talking about three dimensional or volume defects, we are already seen that one kind is which is unavoidable. It is thermal motion or thermal vibration. So, one kind of three dimensional defect is always present in a material. Whenever I am talking even about a lattice or a crystal, I am actually defining a crystal with respect to an average position of atoms. Therefore, thermal vibration is definitely going to distort your that ideal crystal with respect to those lattice positions.

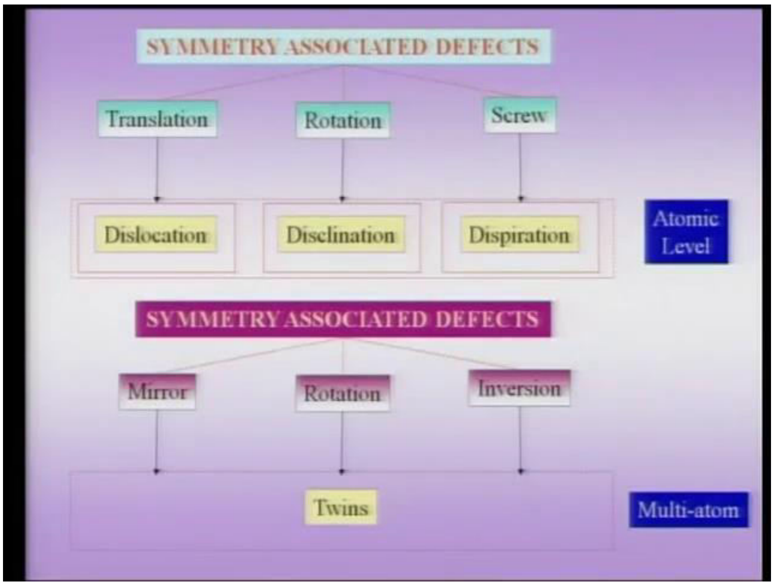
The entire volume of a twin within another material can be a defect, which I call a twin the boundary itself. We saw is a two dimensional version, which is called a twin boundary. But, the entire twin which is present with in another material is called which itself could be defect. Then, a precipitate for instance, a second phase within a larger matrix could be a defect in the crystalline order of the matrix; the faulted region for instance when I talked about the stacking fault. The faulted region could be a 3 D volume defect voids and cracks are 3D volume defects. Therefore, there are many possible defects based on dimensionality. Sowmya has a question.

Student: What is meant by dispiration and disclination?

What we will do this is just a broad overview of picture. Here, I am trying to show that actually defects can be classified based on dimensionality. We have considered some names. For now, we have not even defined what is a vacancy though we have seen what an impurity is. We also note the surface for instance from common experience. But, we were not defined most of these things. So, we will take them one by one up. But, with regard to your special question of what is a disclination or dispiration, we will define them very soon when we talk about line defects.

But more importantly, we will not go into detail of dispirations and disclinations, while we will take up dislocations in detail. So, we will take up those definitions very soon. So but, this is the broad understanding overview of the possible defects and a way of classifying them based on dimensionality. Of course, if you want to a specific answer for now, a disclination is a defect associated with the rotational symmetry of the crystal associated is the word. Dispiration is a symmetry associated with the screwed symmetry of a crystal.

(Refer Slide Time: 11:58)



SYMMETRY ASSOCIATED DEFECTS

Translation → Dislocation

Rotation → Disclination

Screw → Dispiration

Atomic Level

SYMMETRY ASSOCIATED DEFECTS

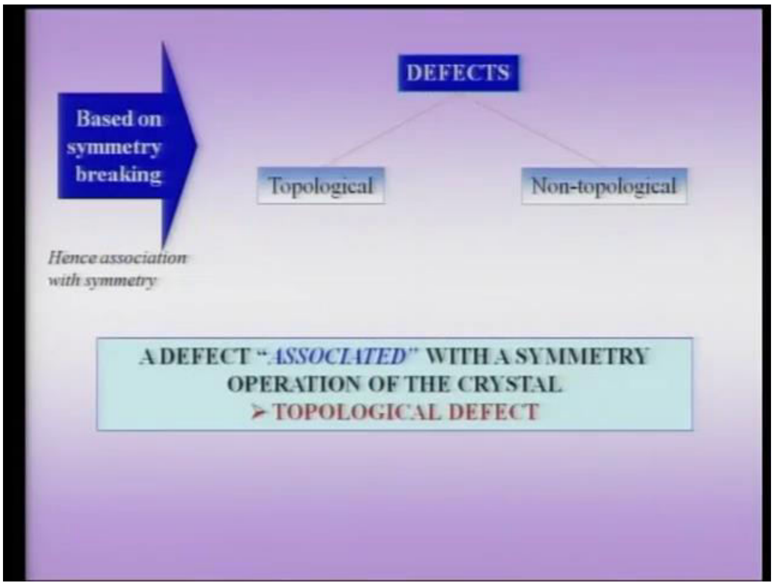
Mirror, Rotation, Inversion → Twins

Multi-atom

Now so, I perhaps, the next slide answers your question much better. Here, so, we can classify some of these defects based on their association with certain symmetries of the crystal. So, the dislocation is a defect associated with translational symmetry. Disclination is a defect associated with the rotational symmetry. Dispiration is a defect associated with screw symmetry. I am talking about these symmetries. I am talking about the atomic level or the symmetries at the crystallographic level but essentially, the atomic level.

But I could also have symmetry associate defects, which are rather multi atom or exactly a larger picture or larger length scale. We could have twins, which are mirror symmetry related twins. We could have rotation symmetry related twins. We could have inversion twins though often the most common kind which the material science will deal with is the mirror twin. But we should not forget, if there are two regions in a crystal because usually in typical typically in contact and if they are related by a symmetry operation then, that is two variants can be called twins. So, the symmetry operation relating the two crystals could be inversion or a rotation or a mirror. So, we will consider some of these in detail later on.

(Refer Slide Time: 13:15)



DEFECTS

Based on symmetry breaking

Topological

Non-topological

Hence association with symmetry

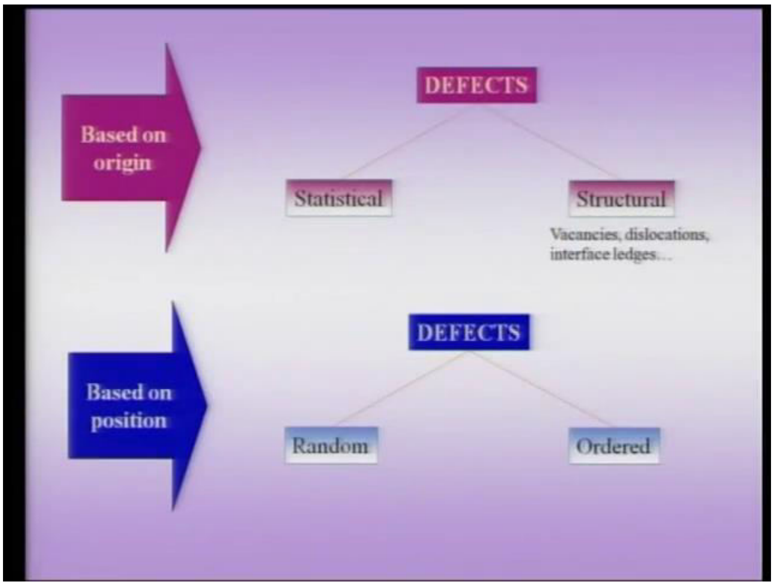
A DEFECT "*ASSOCIATED*" WITH A SYMMETRY OPERATION OF THE CRYSTAL

➢ TOPOLOGICAL DEFECT

This is something again we will not talk about detail. But, just as maybe a slide in the passing so that we at least know that there are certain kinds of defects based on what is known as symmetry breaking. So, there are defects known as topological defects and there are non-topological defects. A defect associated with the symmetry operation of the crystal is called a topological defect. So, this is just a definition. Perhaps, mostly in this course, we will not further use many of these terms.

But, just to note that when I am talking about, when you come across literature, whether I talking about a topological defect; they typically mean it is a defect associated with symmetry of the crystal.

(Refer Slide Time: 13:54)



This slide is an actually important slide. We will take up some examples of some of these. When we go to the individual defects for instance, defects can be based on origin, we can define them or based on position, we can define them. So, we had said this before when you are talking about based on origin. Of course, I do not mean, origin means how they came a word to be in the material. But, there were you will understand what I mean by the word origin here.

So, defects can be what you might call statistically stored defects or they could be structural defects. Now, there is an important distinction here because and of course, there is a very closely related term to structural defects. Sometimes, the term uses geometrically necessary defects especially, with regard to dislocations, a term is used called geometrically necessary dislocations. But I would like to distinguish geometrically necessary defects from structural defects. I will call these structural defects clearly to distinguish or user distinguishing name. For instance, I am talking about vacancies.

Now, vacancies could be statistically stored. As you know their origin in the crystal could be because of thermodynamics, the entropic stabilization they can provide. We will soon when we talk about vacancies, we will see how we can calculate the equilibrium concentration of vacancies in the material. So, at finite temperature, you will have certain concentration of vacancies. These vacancies arise purely because of thermodynamic requirement or in other words the configurational richness. In other words, entropy increases.

So, at every finite temperature, you will have a certain concentration of vacancies. These vacancies are typically randomly present in the crystal. So, they could, they are statistically stored. They could be present anywhere in any of the lattice points. For instance, at a given temperature, they may also move around. Now, a structural vacancy on the other hand is not present because of thermodynamics of the system. It is because for instance, we will take up examples that maybe present because of off stoichiometry.

That means if I have a compound like for instance, a typical example nickel Ni Al. I do not have a perfect fifty fifty composition. I have an off stoichiometry composition. This off stoichiometry is accommodated by the presence of vacancies. Those vacancies are typically localized to a sub lattice. Therefore, they have a different origin. Their role in diffusion is for instance, very different from the statistically stored vacancies.

Therefore, when I am looking at properties, I have to distinguish. I have to make distinguish between a structural and a statistically stored dislocation or defect. A good example would be dislocations for instance, when I grow a crystal typically, it will never be perfect. For instance, I grow, I solidify, I melt of aluminum, I would find that it has lot of dislocations.

Typically, we will see the density of these dislocations could be about 10 power 3meter per meter cube or 10 power 4 meter per meter cube or in that range of values. Now, apart from these kind of statistically because these dislocations could be present anywhere in the crystal these, I could call a statistically stored dislocation. But, if you see dislocation could have a totally different origin for instance, if I have a misorientation between two grains of a crystal. What will I call a misorientation typically less than about 10 degrees? This misorientation can be accommodated by an array of dislocations.

But, these array of dislocations are localized to the interface between these two crystals. Therefore, this dislocation is performing a structural role in the material. It is accommodating the misorientation. It could also accommodate mis-fades. We shall see soon, other kind of rotations.

Now, these dislocations are not the statistically stored dislocation. They can be clearly seen that suppose, I am talking about the role of these dislocations in plasticity. Then, this dislocation wall; which is now the low angle grain boundary would be very different in behavior as compared to the statistically stored dislocation, in terms of their effect on plastic deformation. So, even simple externally applied shear stress at which statistically stored dislocation may move it. It could be very different from a dislocation, which is present in a dislocation wall.

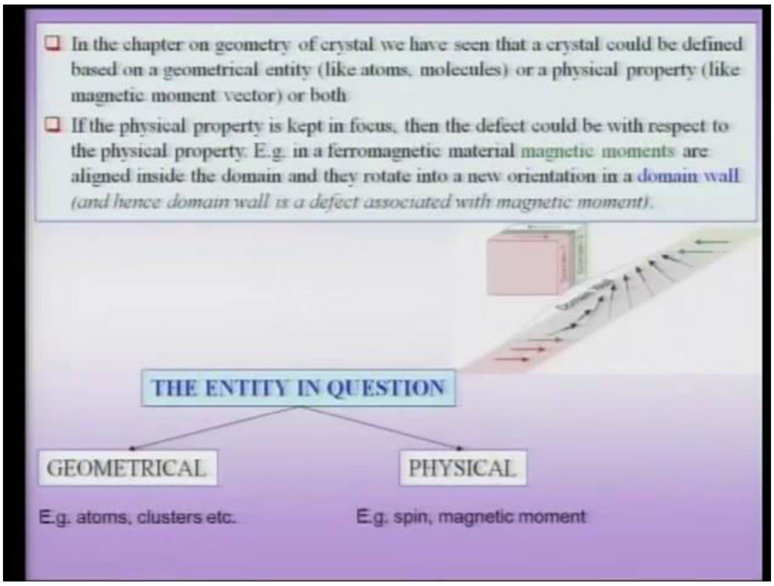
So, we could have statistically dislocations and structural dislocations or statistically stored defects and structural defects. We need to differentiate them because of their role they playing material behavior. Now, again based on position, in some sense these two are very closed related. But, we will try to differentiate the two that based on position. Again, defects could be random or ordered. Now, for instance, so both had vacancies.

Now, vacancies, as I said could normally be present in a random fashion. But, suppose, it could happen that in a sudden system and typical examples are vanadium carbine systems. These vacancies could get actually ordered. That means the vacancy would have a sub lattice for itself. Therefore, in the process of this ordering obviously, you know the symmetry of the structure would change. It could lead to a change in the crystal structure. For instance, beautiful examples, we will consider later of defect ordering would be stacking fault ordering, which could again alter the crystal structure.

But, we have to remember that this is now based on the position. When once a defect gets ordered, it cannot be treated like an ordinary random defect because it is now going to change your entire crystal structure. If the crystal structure is changing obviously, the properties are going to change. So, for instance, give a nice example. As I said the vacancy ordering phenomena, wherein and they vacancy ordered phase are apart from vanadium carbide. Also for, I mean aluminum, copper, nickel kind of systems. You would notice that once vacancies have got ordered, they have a sub lattice. I can now even talk about a hierarchy of defects.

In other words, first of all, of course, I have a vacancy which is got ordered. Now, I have a sub lattice for the vacancies. Now, there can be a vacancy in the vacancy sub lattice. It would actually be an atom. So, I can now talk about a hierarchy of these kinds of defects. But, I need to remember. Now, once the vacancies have got ordered, they have a profound influence not only in the crystal structure and therefore, on the behavior of the material.

(Refer Slide Time: 20:16)



- ☐ In the chapter on geometry of crystal we have seen that a crystal could be defined based on a geometrical entity (like atoms, molecules) or a physical property (like magnetic moment vector) or both
- ☐ If the physical property is kept in focus, then the defect could be with respect to the physical property. E.g. in a ferromagnetic material magnetic moments are aligned inside the domain and they rotate into a new orientation in a domain wall *(and hence domain wall is a defect associated with magnetic moment).*

THE ENTITY IN QUESTION

GEOMETRICAL

E.g. atoms, clusters etc.

PHYSICAL

E.g. spin, magnetic moment

This next slide relates to the way these defects are defined. We have seen that we have been talking that we can actually define a crystal. Hence, for instance, the motif which contributes the formation of crystal could be actually a physical property. So, we have seen the crystal could be defined based on a geometrical entity or a physical property. When I am talking about if the crystal is with defined with respect to physical property then, the defect in that crystal will also would be with respect to that physical property and not with respect to a geometrical entity.

Of course, if the crystal is defined with respect to both the geometrical and the physical property then, geometrical entity and the physical property. Then, the defect also would be a combined kind of a defect. But let me take up an example, wherein I am talking about a defect with respect to a physical property. A good example of this would be the domain wall in a ferromagnetic material. You know in a ferromagnetic material, there are regions, wherein all the magnetization vectors are aligned.

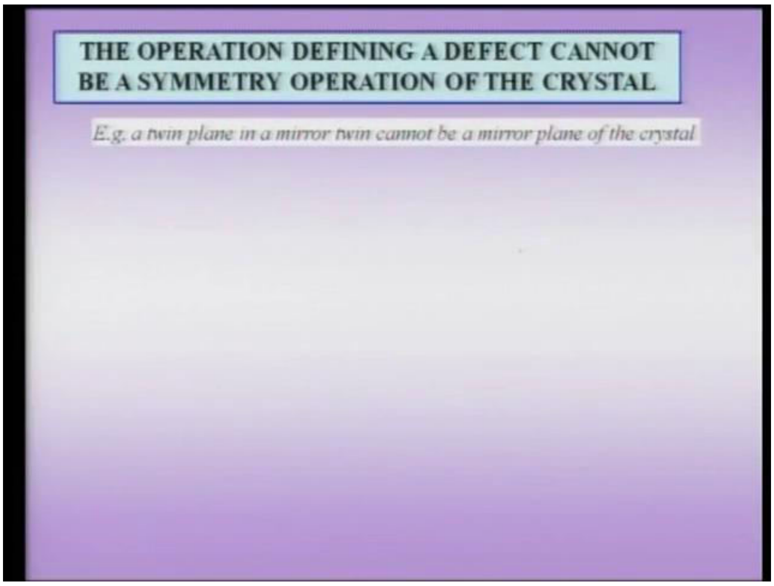
So, for instance, you see the figure below on the left hand side, which I call domain 1. You can see the domain 1. You can see that all the magnetization vectors are in the right hand direction to point to the right. There could be a different domain which is the one which is marked in green which I call domain 2. Here, the magnetization vector is pointing in the opposite direction. Now, the region in between, which has been shown in gray region here; so you can see this gray region here.

This is a transition region which is shown in projection here. So, this is my transition region. In the transition region, my magnetic moment vectors go from this pointing direction to the opposite pointing direction. Now, clearly this crystal, the way it has been defined the ferromagnetic ordering, this is the respect to the spin vectors or the magnetization vectors. Therefore, it is a physical property. Now, what happens in between this transition?

Typically, the vector rotates and it rotates of the plane. If the rotation is of the plane, it is called a block wall. When the rotation is in plane actually, it is called a neil wall. So, you see that there is a block wall, which is forming here. It is a domain wall and you clearly this is a defect with respect to the perfect ordering either with respect to domain 1 or domain 2. The ordering in the domain wall is not perfect. It is actually changing its orientation from position to position. So, this defect, the domain wall is clearly a defect not with respect to the geometrical entity. It is with respect to the physical property, which is now the magnetization vector or the spin vector.

Therefore, I can also talk about the effects with respect to either the geometrical entity or the physical property. So, this also has to be kept in mind. Though we shall not consider very many examples of these kind of defects in this course, but it has to be kept in mind. If my definition of the crystal itself involves a physical property then, there could be defects with respect to that physical property. A very good example here is this domain wall.

(Refer Slide Time: 23:15)



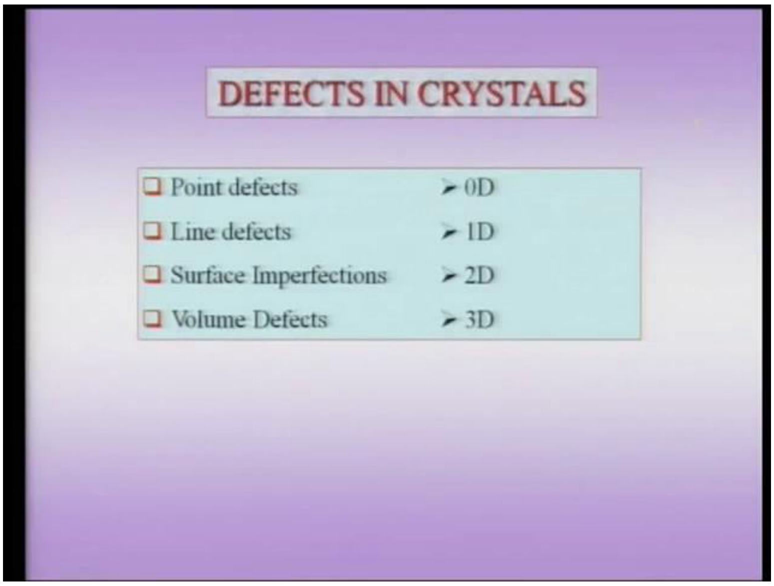
THE OPERATION DEFINING A DEFECT CANNOT BE A SYMMETRY OPERATION OF THE CRYSTAL

E.g. a twin plane in a mirror twin cannot be a mirror plane of the crystal

This is something, a word of caution perhaps that whenever I am talking about a symmetry, which is going on to define a defect. Then, the operation defining a defect cannot be a symmetry operation of the crystal. So, this point has to be kept in mind for instance, a twin plane in a mirror, twin cannot be a mirror plane of the crystal. So, this is perhaps somewhat obvious. But, it has to be stated at the beginning so that property of which is closely related to the symmetry of the crystal.

So, to repeat this note is that the operation defining a defect cannot be a symmetry operation of the crystal. In other words, for instance, a twin plane in a mirror; twin cannot be a mirror plane of the crystal. So, this point has to be kept in mind. So, with this, we come to the end of the broad interaction of what you might call defects in crystals.

(Refer Slide Time: 24:02)

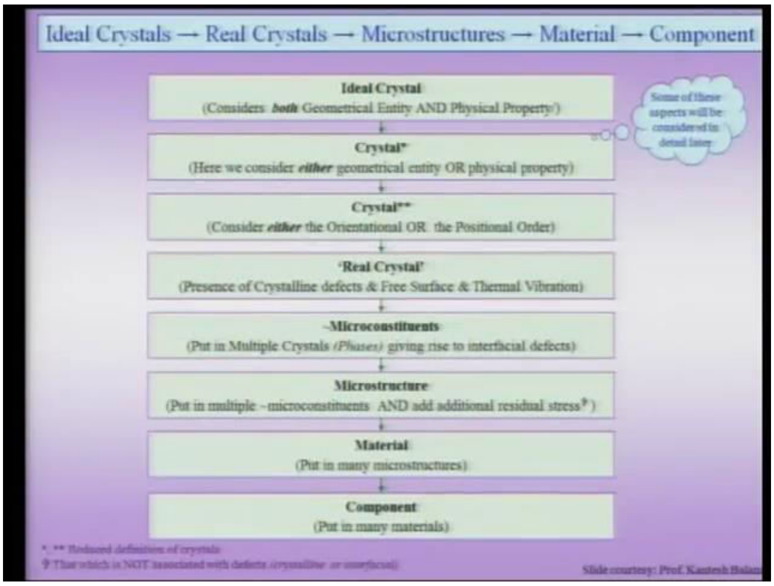


DEFECTS IN CRYSTALS

- ☐ Point defects ➢ 0D
- ☐ Line defects ➢ 1D
- ☐ Surface Imperfections ➢ 2D
- ☐ Volume Defects ➢ 3D

So, we have taken up a broad overview. But since, we are dealing with so many concepts in this very classification, let me briefly revise the various concepts.

(Refer Slide Time: 24:15)



Ideal Crystals → Real Crystals → Microstructures → Material → Component

Ideal Crystal
(Considers *both* Geometrical Entity AND Physical Property)

Crystal*
(Here we consider *either* geometrical entity OR physical property)

Crystal**
(Consider *either* the Orientational OR the Positional Order)

'Real Crystal'
(Presence of Crystalline defects & Free Surface & Thermal Vibration)

~Microconstituents
(Put in Multiple Crystals *(Phases)* giving rise to interfacial defects)

Microstructure
(Put in multiple ~microconstituents AND add additional residual stress†)

Material
(Put in many microstructures)

Component
(Put in many materials)

Some of these aspects will be considered in detail later

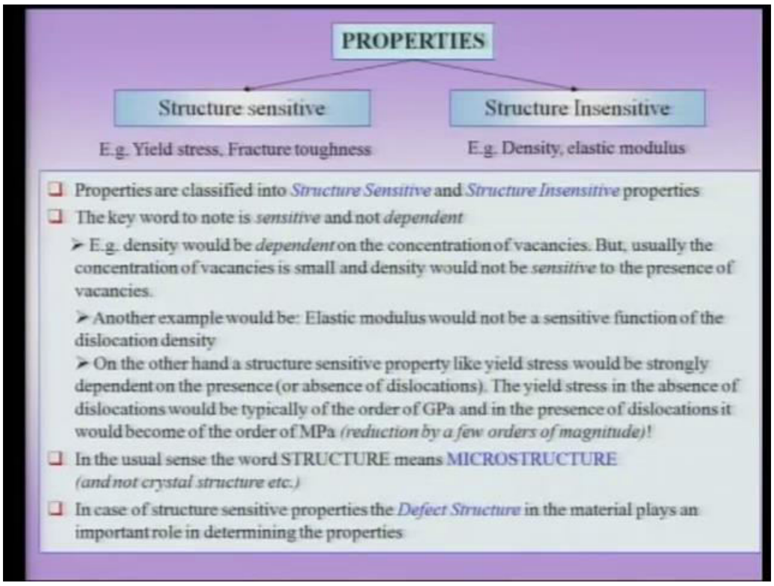
*, ** Reduced definition of crystals
† That which is NOT associated with defects *(crystalline or interfacial)*

Slide courtesy: Prof. Kantesh Balan

Try to see that how this forms the basis for some other important discussions we take up later. So, thing we started off in this chapter of the discussion of point defects was that we can go from an ideal crystal to a real crystal, which means that I have to introduce defects in the crystal. Then, I go to the concept of micro constituents and micro structure.

So, the important intermediate step is the formation of the real crystal, which is a defected crystal.

(Refer Slide Time: 24:45)



PROPERTIES

Structure sensitive

E.g. Yield stress, Fracture toughness

Structure Insensitive

E.g. Density, elastic modulus

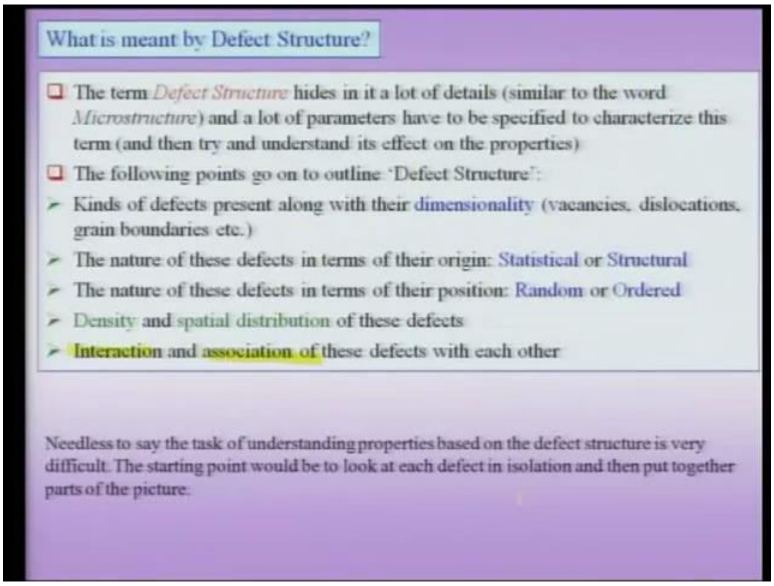
- ❑ Properties are classified into *Structure Sensitive* and *Structure Insensitive* properties
- ❑ The key word to note is *sensitive* and not *dependent*
  - ➢ E.g. density would be *dependent* on the concentration of vacancies. But, usually the concentration of vacancies is small and density would not be *sensitive* to the presence of vacancies.
  - ➢ Another example would be: Elastic modulus would not be a sensitive function of the dislocation density
  - ➢ On the other hand a structure sensitive property like yield stress would be strongly dependent on the presence (or absence of dislocations). The yield stress in the absence of dislocations would be typically of the order of GPa and in the presence of dislocations it would become of the order of MPa *(reduction by a few orders of magnitude)*!
- ❑ In the usual sense the word STRUCTURE means MICROSTRUCTURE *(and not crystal structure etc.)*
- ❑ In case of structure sensitive properties the *Defect Structure* in the material plays an important role in determining the properties

The need for us to consider these defects in crystal is its importance with respect to many properties and especially, those properties which we call the structure sensitive properties. In this context, I had pointed out. When I mean a structure, I typically mean a micro structure. When I am talking about defects, we said, we also pointed out that. Let us emphasize the point for instance, the importance of defects in a material. We had seen that for instance, suppose, I am talking about yield stress in a material. In the absence of dislocations, the yield stress could be of the order of Giga Pascals. But, when you have dislocations of material, the yield stress could reduce.

It could be of the order of Mega Pascals. Therefore, there could be a large change in the properties. Of course, the question may be a more philosophical kind of question. We can ask is that these defects good or bad. It depends on the context. For instance, suppose, I am talking about forming of component by plastic deformation; then, I want the crystal to be weak so that I can use, press, which is of lower tonnage. Suppose, I am talking about forging a crystal, I would use a lower capacity machine. That means, I need to have a lesser investment on the capital cost.

The operating cost also will be lower. Therefore, in this context, actually dislocations are good because it gives me an easy plastic deformation. So, if defects are good or bad in a material that actually depends on the context. It is not good to actually comment on that without actually considering the context. But, we can clearly see that some of these defects play a very important role in the properties. Then, we also talked about the important thing called defect structure.

(Refer Slide Time: 26:21)



What is meant by Defect Structure?

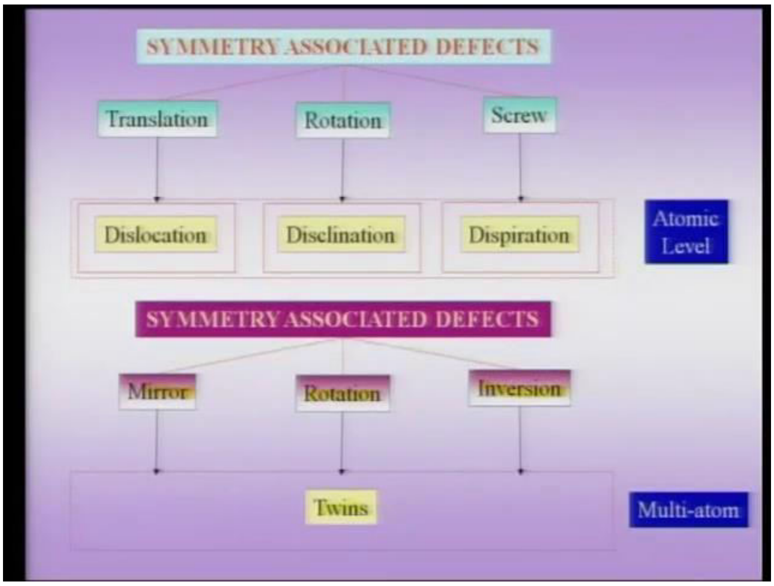
- ☐ The term *Defect Structure* hides in it a lot of details (similar to the word *Microstructure*) and a lot of parameters have to be specified to characterize this term (and then try and understand its effect on the properties)
- ☐ The following points go on to outline 'Defect Structure':
- ➢ Kinds of defects present along with their dimensionality (vacancies, dislocations, grain boundaries etc.)
- ➢ The nature of these defects in terms of their origin: Statistical or Structural
- ➢ The nature of these defects in terms of their position: Random or Ordered
- ➢ Density and spatial distribution of these defects
- ➢ Interaction and association of these defects with each other

Needless to say the task of understanding properties based on the defect structure is very difficult. The starting point would be to look at each defect in isolation and then put together parts of the picture.

That means that I cannot just consider defects in isolation or considered defect and forget about its overall role in terms of its interaction with other defects etcetera. So, the quantities for instance, I needed to consider was the density and spatial distribution of defects. I needed to consider its interaction with the other defects and its association with defects of the other kinds and its own kind. I need to consider for instance, its dimensionality. I need to worry about is it a random defect or a structural ordered defect or it is a statistically stored defect or it is a structural defect.

When I have answers to all these questions, I also consider what you might known as the collective behavior of dislocations especially, collective or collective behavior of defects. These can be especially, under the influence of external constraints or external influences like magnetic fields and stresses. Then, I have a handle on the properties of the material. Therefore, I not only have to consider defects in isolation but I also need to consider defect structure of the material. Then, we went on to classify defects based on dimensionality, based on their association of symmetry.

(Refer Slide Time: 27:25)



SYMMETRY ASSOCIATED DEFECTS

Translation | Rotation | Screw

Dislocation | Disclination | Dispiration

Atomic Level

SYMMETRY ASSOCIATED DEFECTS

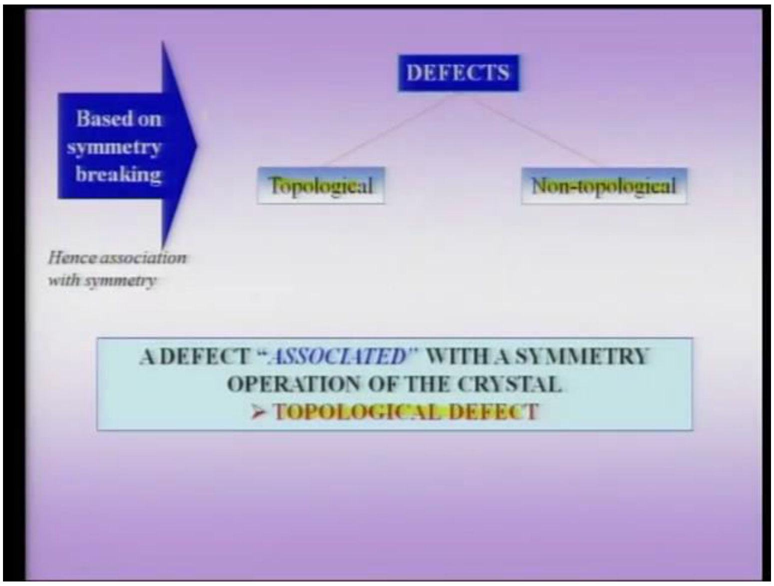
Mirror | Rotation | Inversion

Twins

Multi-atom

We said that for instance, a dislocation can be thought of as an defect associated with the translational symmetry of the crystal. Similarly, we also saw that twins can be inversion twins, mirror twins or even rotation twins.

(Refer Slide Time: 27:44)



Based on symmetry breaking

Hence association with symmetry

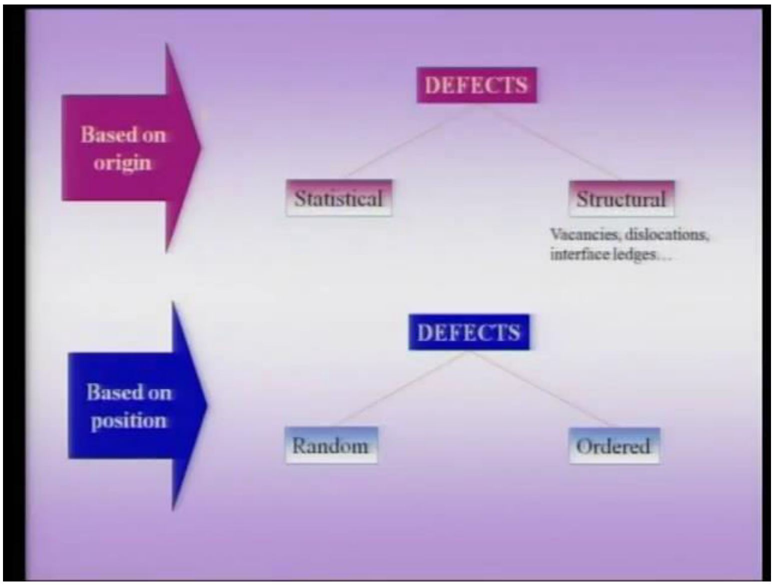
DEFECTS

Topological | Non-topological

A DEFECT "*ASSOCIATED*" WITH A SYMMETRY OPERATION OF THE CRYSTAL
➢ TOPOLOGICAL DEFECT

We also saw that defects are sometime classified as either topological or non topological defects.

(Refer Slide Time: 27:46)



Based on origin

DEFECTS

Statistical

Structural

Vacancies, dislocations, interface ledges…

Based on position

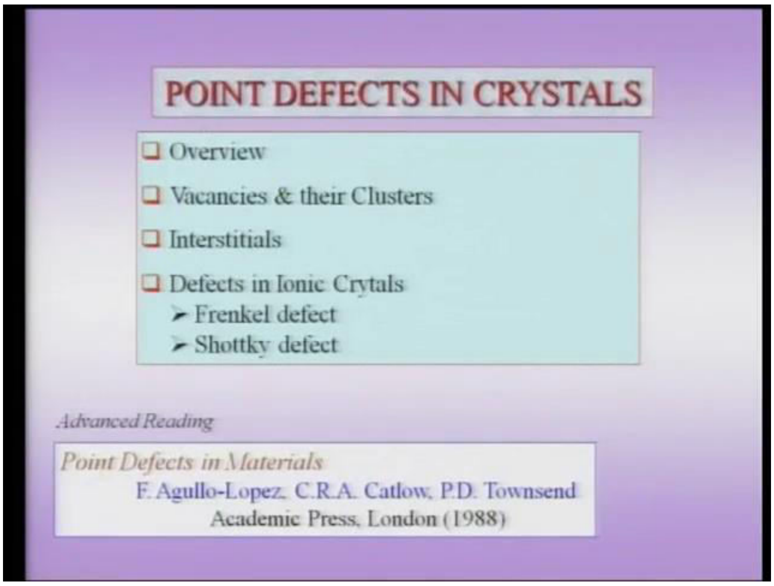
DEFECTS

Random

Ordered

You also consider the important aspect that when I am talking about defects, if I ignore their origin or for instance, if I am talking or their order in the material then, I am making a serious mistake. In other words, a structural vacancy can play a very different role in the properties of material as compared to a statistically stored vacancy. Similarly, this ordered defect has a very profound influence on the crystal structure of the material. Then, you also said that whenever like in the definition of a crystal structure, we also need to worry if the defect is defined based on the geometrical entity or the physical property.With that, we come to a sort of a broad understanding of the overview of classification of defects in materials. Then, now, we will slowly take up one by one all the defects. We will start with point defects. So, let us first take up point defects in crystal, which we might say ordered zero dimensional defects in crystals.

(Refer Slide Time: 28:48)



POINT DEFECTS IN CRYSTALS

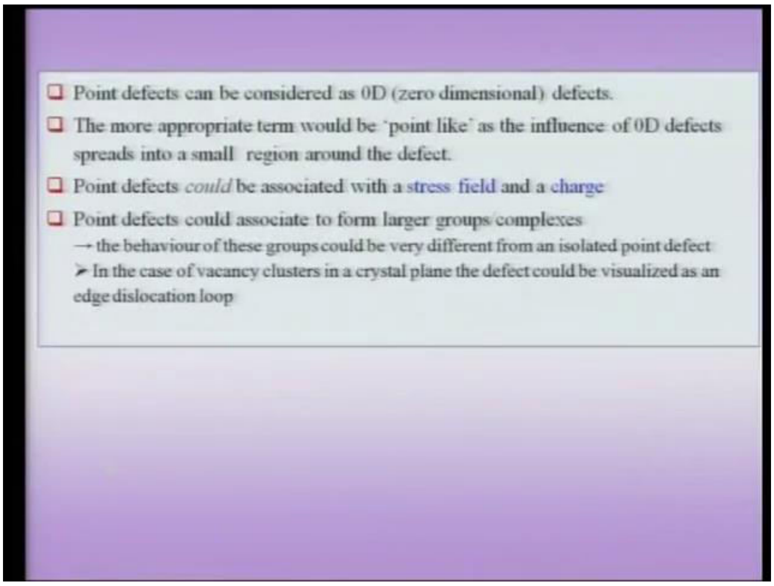
- ☐ Overview
- ☐ Vacancies & their Clusters
- ☐ Interstitials
- ☐ Defects in Ionic Crytals
  - ➢ Frenkel defect
  - ➢ Shottky defect

Advanced Reading

Point Defects in Materials
F. Agullo-Lopez, C.R.A. Catlow, P.D. Townsend
Academic Press, London (1988)

So, we will start with the overview. Then, we will talk a little about vacancies and their clusters interstitials and other kind of defects in charge materials like the Frenkel defect and the Shottky defect. Through this particular treatment, we are dealing with here is a very elementary treatment for those who are interested in doing advanced reading in this subject. They can go refer to a say, the advanced texts like the one by Lopez and co workers, which is the point defects in materials.

(Refer Slide Time: 29:148)



- ☐ Point defects can be considered as 0D (zero dimensional) defects.
- ☐ The more appropriate term would be 'point like' as the influence of 0D defects spreads into a small region around the defect.
- ☐ Point defects *could* be associated with a stress field and a charge
- ☐ Point defects could associate to form larger groups/complexes
  → the behaviour of these groups could be very different from an isolated point defect
  ➢ In the case of vacancy clusters in a crystal plane the defect could be visualized as an edge dislocation loop

So, we have already seen that point defects are mathematically zero dimensional defects. The more appropriate term is the term, which we can call that these defects are point like. In other words, the influence fear of these defects spreads into only a very small region around the point typically not more than a few lattice spacing s around the single atom for instance. Therefore, we can still classify them as point defects. We will later on also, when we are defining defect space from dimensionality, we have to notice that.

Suppose, I am calling a dislocation of one dimensional dislocations. Often, this fear of influence of dislocation as usually for instance, in the stress field could be very long distance. In other words, the stress field of a distance is a long range interaction and definitely not constrained to a line. So, the line in that case, what we will mean is perhaps to what if as I am talking about a edge dislocation. If the line, where perhaps the half plane of atoms end or a missing half plane ends so, this is what you might call a working mathematical definition rather in a very real definition.

But, often you can see that this definition gives us a good handle on the classification, if not always on the understanding of the properties of the defect. So, when we say a line defect or a point defect, we mean it is point like or line like. In other words, the essence of the defect can be understood in that dimensionality. We shall see that point defects could be associated with the stress field and a charge. This is very important for instance, like in the case of charge, we will see that there is something known as f centers. It can impart color to a crystal.

A stress field is a very another important thing, which a point defect could be associated with. For instance, a vacancy and it can interact with other defects in the material through this stress field. This stress field obviously, could be long ranged. It need not be confined to a few lattice parameters or so. This long range interaction can actually lead to revolution of the defect structure.

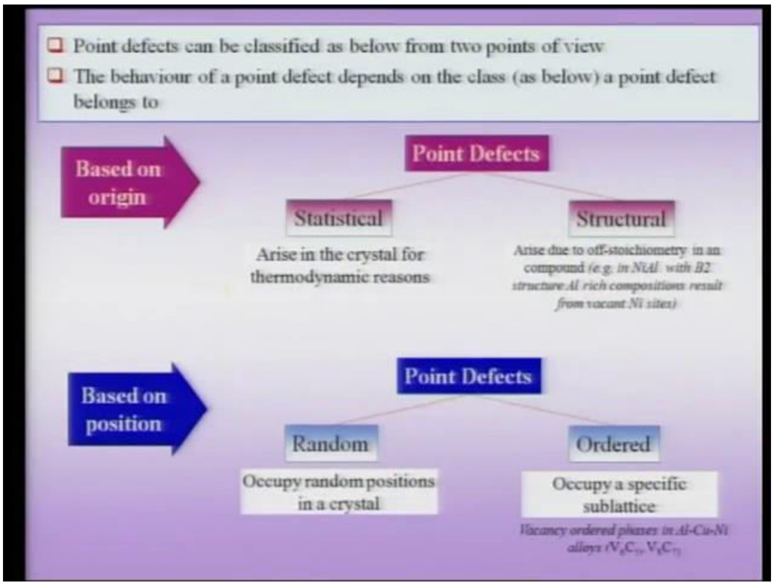
So, when I am talking about point defects, I have to worry about the stress feed associated with the point defect and at times also with the charge associated with the point defect. The other important point which I mention when I was talking about point defects and other defects is that these could associate to form larger groups and complexes. This is something very important because the behavior of these groups could be very different from the associated point defects.

Suppose, I have a single vacancy. These are a cluster of vacancies. Obviously, a cluster vacancy is no longer 0 D. It is going to have a perhaps, a some sort of a two dimensional nature if it is confined to a plane. It could even get into a three dimensional if it is more like a spherical association of vacancies. Therefore, the properties of the defect are considerably altered, when they start to aggregate or they start to associate with each other. This point is absolutely to be kept in mind that I am talking about an isolated defect.

For instance, the point defect, I am talking about an association of these point defects or any other kind of defect. The other important thing is that often when these defects associate, they can be even, the language for their description can even change. For instance, vacancy clusters in a crystal plane. We shall take up this actually in detail later when we talk about dislocations. Now, we visualized not as just merely a vacancy cluster but also, as a edge dislocation loop.

We shall see in FCC crystal for instance, this edge dislocation loop is something known as the frank partial dislocation loop. So, when I am talking about dislocations, I need to worry about the stress field. I need to worry about the charge associated with them. I also need to know how they are associated with other point defects and other kind of defects in the material. More importantly, sometimes the language used to describe these clusters changes. The nice example for that could be the vacancy cluster on a crystal close packed crystal plane in FCC crystal. It can be visualized as a frank partial dislocation loop which would be what you might call a disc of vacancies.

(Refer Slide Time: 33:36)



- ❑ Point defects can be classified as below from two points of view
- ❑ The behaviour of a point defect depends on the class (as below) a point defect belongs to

Based on origin

Point Defects

Statistical

Arise in the crystal for thermodynamic reasons

Structural

Arise due to off-stoichiometry in an compound *(e.g. in NiAl with B2 structure Al rich compositions result from vacant Ni sites)*

Based on position

Point Defects

Random

Occupy random positions in a crystal

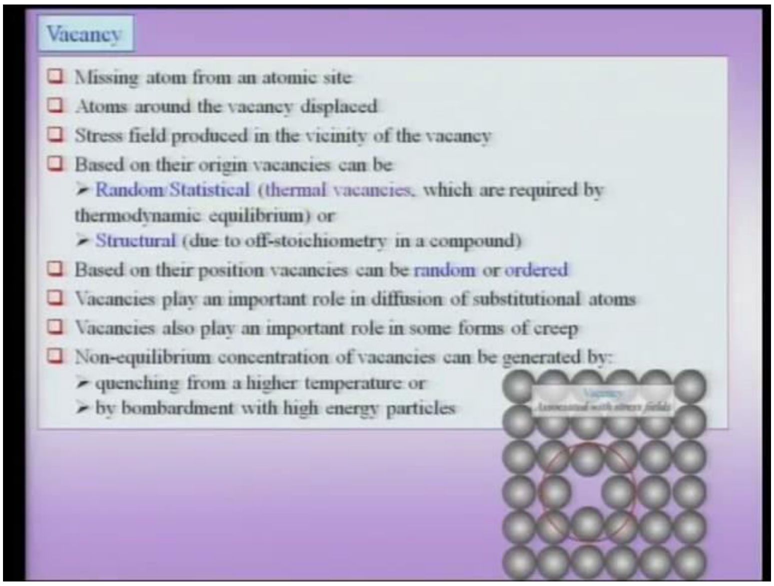
Ordered

Occupy a specific sublattice

Vacancy ordered phases in Al-Cu-Ni alloys (V_6C_{11}, V_4C_7)

So, we already have seen this slide. But, now we will take up examples and consider little more detail about for instance, structural and statistical vacancies or structural and statistical defects. We had already of course, we have seen this aspect. So, just to, this is perhaps a revision. But, we have a nice example here in the case of a structural vacancy. Now, for instance, as I said, suppose I am talking about a point defect and one of the point defects, let me may be consider that point defect first.

(Refer Slide Time: 34:04)



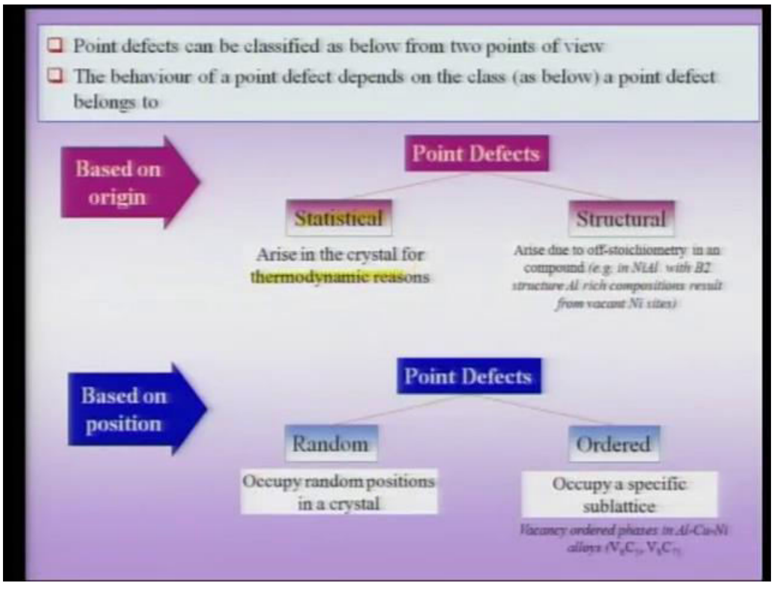
Vacancy

- ❑ Missing atom from an atomic site
- ❑ Atoms around the vacancy displaced
- ❑ Stress field produced in the vicinity of the vacancy
- ❑ Based on their origin vacancies can be
  - ➢ Random/Statistical (thermal vacancies, which are required by thermodynamic equilibrium) or
  - ➢ Structural (due to off-stoichiometry in a compound)
- ❑ Based on their position vacancies can be random or ordered
- ❑ Vacancies play an important role in diffusion of substitutional atoms
- ❑ Vacancies also play an important role in some forms of creep
- ❑ Non-equilibrium concentration of vacancies can be generated by:
  - ➢ quenching from a higher temperature or
  - ➢ by bombardment with high energy particles

So, the most important point defect would be perhaps will start with could be a vacancy a. For instance, an atom missing from a side; so, you can see the figure below that the region here when atom is missing. It is a vacancy. Whenever I create, remove an atom from the lattice position then, obviously the atom surrounded would not remain in their equilibrium position. They would also move and this would create a certain kind of a displacement feed around the vacancy.

Now, so with basic definition of vacancy, let me go back to the classification of point defects based on origin. Now, we already have seen that the statistical origin is because of thermodynamic reasons. For instance, you could talk about of course, in case of vacancy, there are thermodynamic vacancies. These are created purely because of Gibb's energy minimization. But of course, you could have an alloying element. For an interstitial alloying element could again go and sit in a random position. Now, a structural vacancy for instance, is as I pointed out can arise because of off stoichiometry.

(Refer Slide Time: 35:07)



- ☐ Point defects can be classified as below from two points of view
- ☐ The behaviour of a point defect depends on the class (as below) a point defect belongs to

Based on origin

Point Defects

Statistical

Arise in the crystal for thermodynamic reasons

Structural

Arise due to off-stoichiometry in an compound *(e.g. in NiAl with B2 structure Al rich compositions result from vacant Ni sites)*

Based on position

Point Defects

Random

Occupy random positions in a crystal

Ordered

Occupy a specific sublattice

Vacancy ordered phases in Al-Cu-Ni alloys (V[illegible]C[illegible], V[illegible]C[illegible])

That means suppose, I take an Ni Al compound, which is AB 2 structure. That means it has got an ordered CSEL structure which we know is two interrupt iterating simple cubic lattices. One with the origin at 0 0 0 and one with an origin at half half half. So, in other words, it is an ordered BCC ordering of a disordered BCC structure. It becomes simple cubic then, in a Ni Al kind of structure, you can have it is not a purely a stoichiometry compound. That means, it is not a lien compound. It can accommodate considerable off stoichiometry.

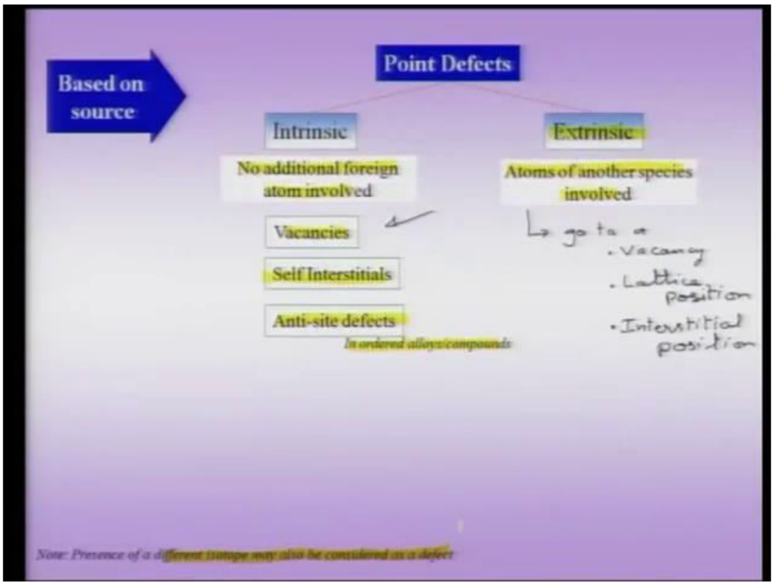
That means it can get Ni rich or it can get aluminum rich. The aluminum rich compositions are noticed a result from vacant nickel sites. Suppose, I want to make aluminum rich composition. There are two possibilities for me. Either I can start putting aluminum in nickel sites, which would give me a richness of aluminum or I can start removing atoms from the nickel side, which will also make it stoichiometrically aluminum rich.

But, in the case of nickel aluminum, there is of course, an asymmetry with respect to aluminum rich compositions and nickel rich compositions the want. They are accommodated, the aluminum rich compositions are accommodated by vacant nickel sites. So, this is found energetically favorable. Therefore, you have vacant nickel sites. Now, these vacant nickel sites are not coming because of thermodynamic reason, not because they give rise to an increase in entropy. But they are coming because of the off stoichiometry.

Therefore, they will be localized to the nickel sub lattice. Of course, they could be disorderedly present anywhere in the nickel sub lattice. So, they are in that sense random within the nickel sub lattice. But their origin is purely because of the off stoichiometry. Now, that means that suppose I am talking about diffusion.

Therefore, this vacancy cannot jump to the aluminum site. A jump to the aluminum site would be energetically unfavorable. Now, similarly, when I am talking about vacancies, as I pointed out, it will get ordered. Typical examples of these vacancy ordered phases are aluminum, copper, nickel alloys. There are specific compound like V 6 C 5 and V 8 C 7. So, whatever I told in general was true for classification of defects. In general, it should also true for point defects.

(Refer Slide Time: 37:26)



Based on source

Point Defects

Intrinsic

No additional foreign atom involved

Vacancies

Self Interstitials

Anti-site defects

In ordered alloys/compounds

Extrinsic

Atoms of another species involved

↳ go to a
- Vacancy
- Lattice position
- Interstitial position

Note: Presence of a different isotope may also be considered as a defect

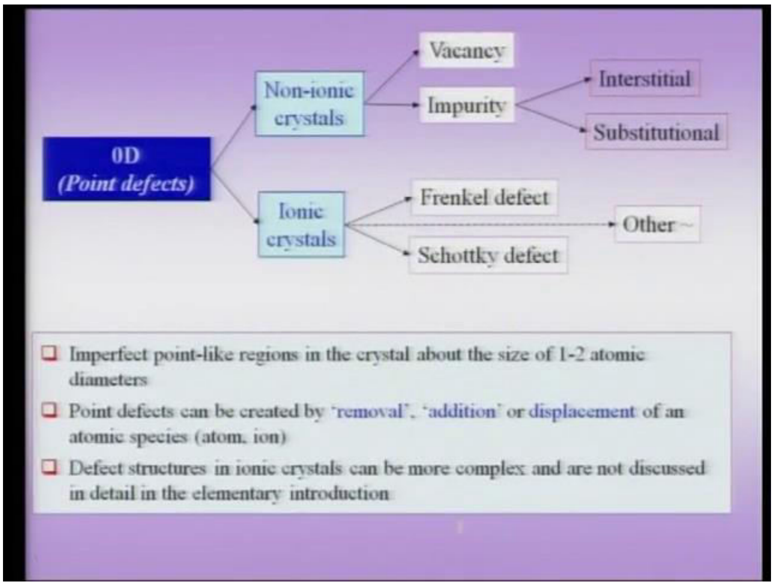
Now, point defects could have intrinsic or extrinsic source. In other words, this is additional thing we need to consider when I am talking about classification of point defects. Now, if I am talking about an intrinsic defect like a vacancy then, no additional atoms involved. So, they could these intrinsic defect could be vacancies. They could be self interstitial. In other words, what is a self interstitial atom? It is supposed to sit in the lattice position has been displaced and it sits in the interstitial position. So, this does not involve an addition of an additional atom. This would be called a self interstitial atom.

So, this is an example of an intrinsic point defect. Anti-site defect is also an intrinsic point defect. This is found only in ordered alloys or compounds. For instance, suppose I am talking about this Ni Al, which I saw in the previous slide. So, I have a specific sub lattice, a simple cubic sub lattice for nickel. There is a specific aluminum sub lattice for aluminum. Suppose, nickel goes and sits in the aluminum sub lattice. Those would be called an anti-site defect and obviously like all the vacancies and self interstitial, they caused energy to the system.

They are unfavorable that means if I take the system to a global energy minima then, self interstitials and anti-site defects would be annulated vacancies. This we shall calculate to an equilibrium concentration would persist because they are thermodynamically favorable defects. Extrinsic defects on the other hand, involve atoms from other species. That means that say for instance, you could have an impurity atom or a atom of which you can call a dopant or any other element or a impurity, which can now of course, go and sit in a pre-existing vacancy.

It can go if the impurity atom, which I have added can go and sit in a vacancy. It can go and sit in for instance, interstitial position. It could replace one of the existing atoms. So, all three possibilities exist. So, let me write down these possibilities. So, all these possibilities exist when I add an extrinsic kind of an element. That means which does not belong to the system existing in the larger perspective presence of a different isotrope of a material. For instance, let me go back. The presence of a different isotrope of a material may also be considered as a defect. So, this thing has to also be considered. This can be actually beneficially used in many circumstances as trays are in diffusion for instance. So, let us come to a different way of looking.

(Refer Slide Time: 40:17)

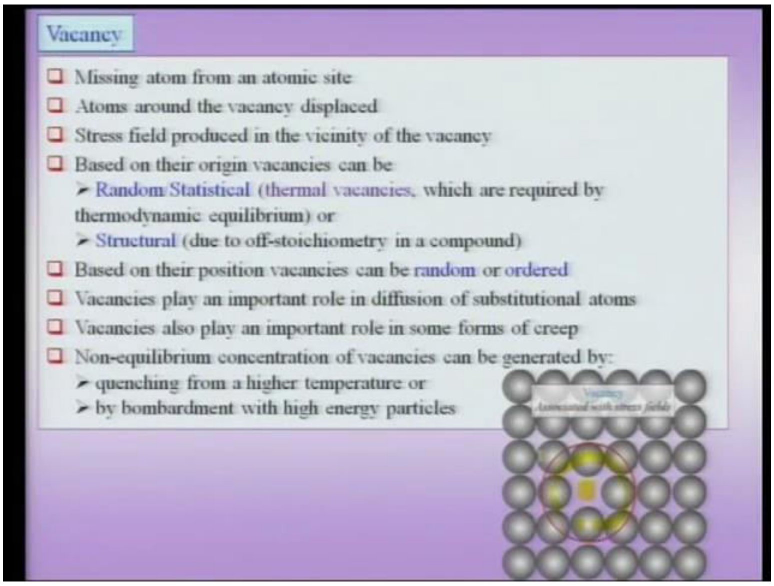


- ❑ Imperfect point-like regions in the crystal about the size of 1-2 atomic diameters
- ❑ Point defects can be created by 'removal', 'addition' or displacement of an atomic species (atom, ion)
- ❑ Defect structures in ionic crystals can be more complex and are not discussed in detail in the elementary introduction

A different way of looking at point 0 D or point defects in ionic crystals for instance, we have frenkel defects, schottky defects and other kind of defects. They are possible in non ionic crystals. We could have vacancy or an impurity. This way impurity we already seen can be an interstitial or a substitutional kind of impurity. So, we should basically start with the impurities in non ionic crystals. Then, proceed to defects in ionic crystals. Point defects can be created by removal addition or displacement of an atomic species.

This aspect we already seen in the previous slide; for instance, we have already seen that removal, they constitutes, a vacancy displacement constitutes a self-interstitial and addition consist of an extrinsic kind of a point defect. So, we already have seen this aspect. We will also take up later on, certain more complex kind of defect, point defect structures.

(Refer Slide Time: 41:07)



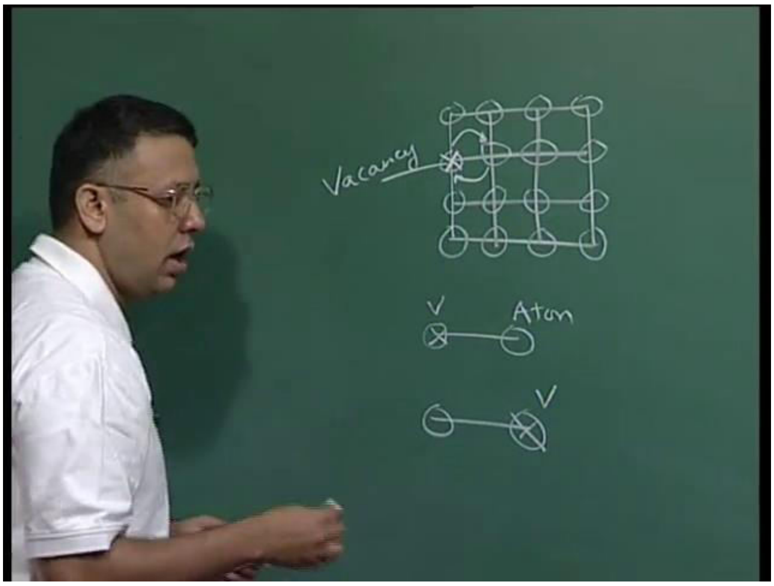
Vacancy

- Missing atom from an atomic site
- Atoms around the vacancy displaced
- Stress field produced in the vicinity of the vacancy
- Based on their origin vacancies can be
  - Random/Statistical (thermal vacancies, which are required by thermodynamic equilibrium) or
  - Structural (due to off-stoichiometry in a compound)
- Based on their position vacancies can be random or ordered
- Vacancies play an important role in diffusion of substitutional atoms
- Vacancies also play an important role in some forms of creep
- Non-equilibrium concentration of vacancies can be generated by:
  - quenching from a higher temperature or
  - by bombardment with high energy particles

So, we basically briefly consider this slide before wherein we defined what is a vacancy. We had noticed that the atoms around a vacance lattice side are displaced with respect to their equilibrium position. This displacement field could exist predominantly. The displacement field would be a small region around the vacancy. But, could the effect exist a little longer distance through via this long range stress fields? So, of these things we already seen, I need to revise that the vacancies can be; as I said, random or statistical or structural. We have seen this aspect. So, I need not go over them. The important thing role of vacancies is in diffusion of substitutional atoms.

This is very important for instance, suppose I need to dope for instance, silicon with some dopant to make it a p type or n type semiconductor. Then, often this or this diffusion of this spacious into silicon will take place through vacancy migration. That means if I jump from vacancy from one side to the other, it can be considered as an opposite jump for the atom. So, let me show this on the board.

(Refer Slide Time: 42:15)



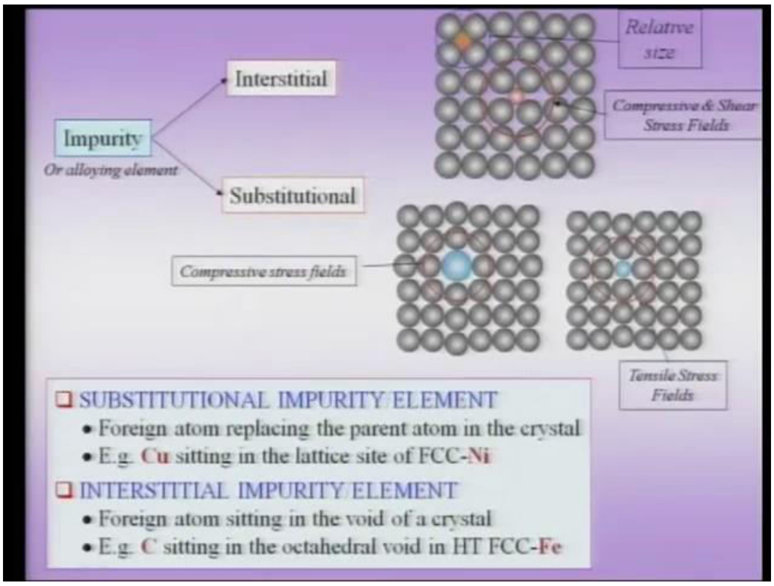
So, it is my perfect crystal and say for instance, one of these sites is vacant. So, this is my vacancy. Now, my jump of a vacancy from here to here can be considered as a jump of an atom from here to here. So, this is something. So, after this jump has taken place, I can now redraw the picture because now, I had considered these two atoms here. So, this is my initial configuration with a vacancy and an atom. After the jump has taken place, the atom would be on the left hand position. The vacancy would be here. So, by this kind of successive jumps of the vacancy, I can consider diffusion to be taking place. Vacancies also play a important role in various forms of creep.

This is something which has to be noted. Not only can there be equilibrium concentration of vacancies that means vacancies can be present in the right concentration. This can minimize the Gibb's free energy. But, they can also be present in a higher concentration than dictated by thermodynamic equilibrium for a given temperature. This can be obtained for instance, by quenching from higher temperature. That means I take my material to higher temperature, where my equilibrium demands are higher concentration of vacancies.

Then, I quench it to a lower temperature. But then, of course, all the vacancies may not be quenched in. Some, many of the vacancies may quenched in. But, this concentration of vacancies can be much higher than the one which is present at high temperature. Now, this obviously would mean that the diffusivity of the material, which has higher concentration of vacancies would be much much higher then. Now, I am talking about the diffusion of substitutional atoms to be much higher than the one, which has just an equilibrium concentration of vacancies.

But, bombardment of high energy particles can actually lead to an enhanced concentration of vacancies. This is very important especially, when we are talking about materials which are involved in nuclear reactors etcetera. So, we can have an equilibrium concentration of vacancies or an higher than equilibrium concentration of vacancies. I have just outlined two methods by which we can produce an higher than concentration of vacancies. Now, some of these aspects we have considered before.

(Refer Slide Time: 44:44)



Impurity

Or alloying element

Interstitial

Substitutional

❑ SUBSTITUTIONAL IMPURITY ELEMENT
- Foreign atom replacing the parent atom in the crystal
- E.g. Cu sitting in the lattice site of FCC-Ni

❑ INTERSTITIAL IMPURITY ELEMENT
- Foreign atom sitting in the void of a crystal
- E.g. C sitting in the octahedral void in HT FCC-Fe

The important thing known as interstitial alloying element, we have also seen. What kind of sites for instance, they would set in a FCC crystal or a cubic close packed crystal or a BCC crystal or a HCP crystal. We have actually calculated the number of voids per atom etcetera previously for instance. Now, if I try and we have seen that when I will try to put an interstitial atom so, let me show the interstitial atom sitting at the top here in this picture. So, I have an interstitial atom here. We can see that it is typically larger in the lattice position. Therefore, they cause stress fields and displacement around the position in which they sit.

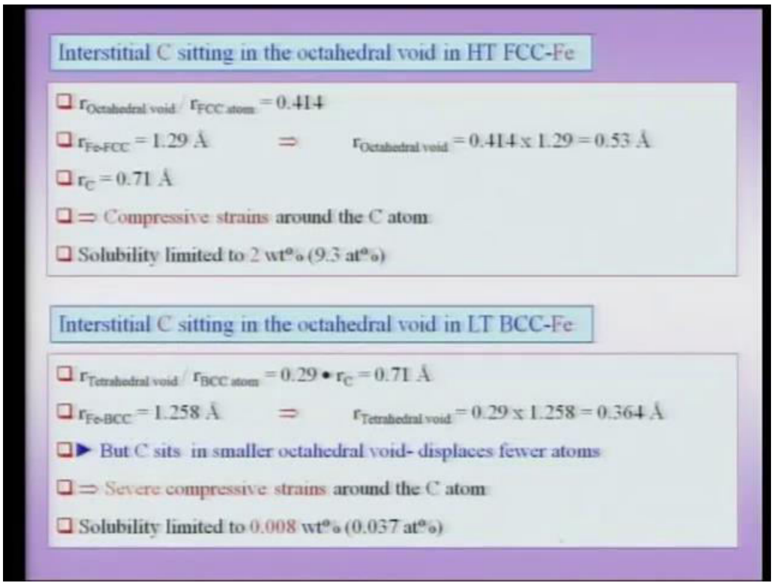
In this, as we shall see later on, this is a very important effect especially, when I am talking about for instance, carbon and steel. I am talking about the interaction of these carbon atoms with a dislocation course. So, this would be an important thing, we will consider later. This is coming from the long range stress fields of the dislocation, which is interacting with the stress field of the interstitial atom. This stress field of a interstitial atom typically has higher shear component as compared to a stress field, which is around a substitutional atom.

It is somewhat rather hydrostatic. A substitutional atom could be larger in the atom parent host atom. It could be smaller leading to compressive or tensile stress fields. It does make a difference to us if it is compressive or tensile. Of course, in isolation, both of them would cost energy to an equal extent. But, when I am talking about larger picture of interaction between defects, it will now make a difference that where would this for instance, substitutional atoms segregate with respect to a dislocation line.

Would it go into the compressive region of a dislocation or would it go into a tensile region of dislocation would be determined by the relative size with respect to the parent atom. Now, examples of substitutional atoms we know for instance, are copper sitting in the lattice site of an FCC nickel. So, this would be an example of substitutional impurity element, interstitial element. We have considered in detail before like for instance, carbon sitting in the octahedral void of high temperature FCC ion.

So, we already dealt with these. So, we do not have to, just this is a revision as before. So, when I am talking about an impurity atom, I need to know where it sits. Additionally, what is its relative size with respect to the position, where it is sitting. Hence, the kind of stress fields it associated with, so this is something which we need to consider. There are three specific cases, wherein an atom and this specific example would be for instance, boron and steel. That atom can occupy both the lattice position and interstitial position. So, there is a competition between its distribution between the interstitial and lattice positions. These are of course, rare examples wherein for instance, this boron is one such example.

(Refer Slide Time: 47:27)



Interstitial C sitting in the octahedral void in HT FCC-Fe

- ☐ $r_{\text{Octahedral void}} / r_{\text{FCC atom}} = 0.414$
- ☐ $r_{\text{Fe-FCC}} = 1.29$ Å $\Rightarrow$ $r_{\text{Octahedral void}} = 0.414 \times 1.29 = 0.53$ Å
- ☐ $r_C = 0.71$ Å
- ☐ $\Rightarrow$ Compressive strains around the C atom
- ☐ Solubility limited to 2 wt% (9.3 at%)

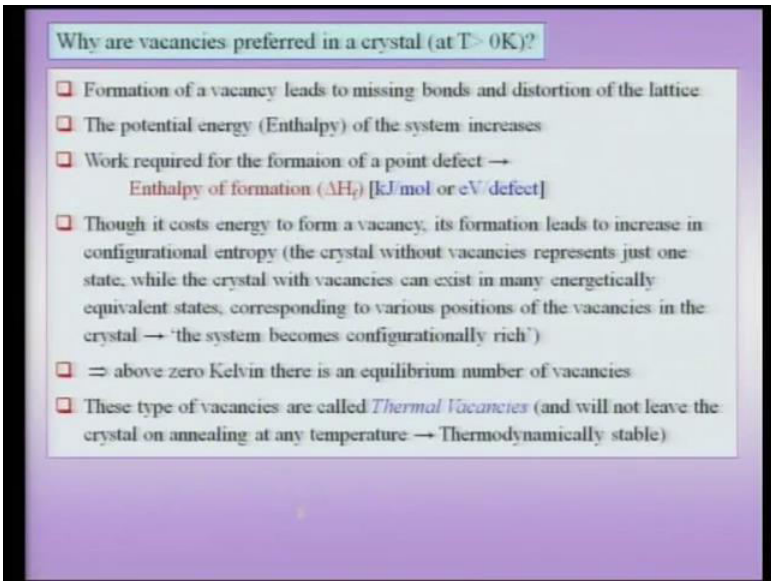
Interstitial C sitting in the octahedral void in LT BCC-Fe

- ☐ $r_{\text{Tetrahedral void}} / r_{\text{BCC atom}} = 0.29$ • $r_C = 0.71$ Å
- ☐ $r_{\text{Fe-BCC}} = 1.258$ Å $\Rightarrow$ $r_{\text{Tetrahedral void}} = 0.29 \times 1.258 = 0.364$ Å
- ☐► But C sits in smaller octahedral void- displaces fewer atoms
- ☐ $\Rightarrow$ Severe compressive strains around the C atom
- ☐ Solubility limited to 0.008 wt% (0.037 at%)

This slide perhaps is just a revision of the previous slides. But now, since we are talking about this slide in the context of point defects, it is worthwhile to revise this slide. Note the important point that when I am talking about for instance, carbon sitting in an octahedral void in a high temperature FCC ion. There are these compressive strains because the carbon atom is much larger than the void. This we would we have seen that its limit is solubility to about 2 weight percent. So, this is something which we need to note.

In BCC ion, the same strains are responsible for even lower solubility in iron. So, carbon is very less soluble in alpha ion, which is the BCC form of iron. So, understanding the relative sizes and understanding the kind of stresses and strains they produce. In other words, understanding the energy cost of the system to accommodate this point defect can tell me sort of this solubility of the system. When I am talking about this solubility, I am perhaps some time constraint much more solubility than what is simply entropically benefit because we have seen that vacancies. Similar interstitials etcetera can be entrophically stabilized. Solubility is very much fixed by the thermodynamic equilibrium.

(Refer Slide Time: 48:42)



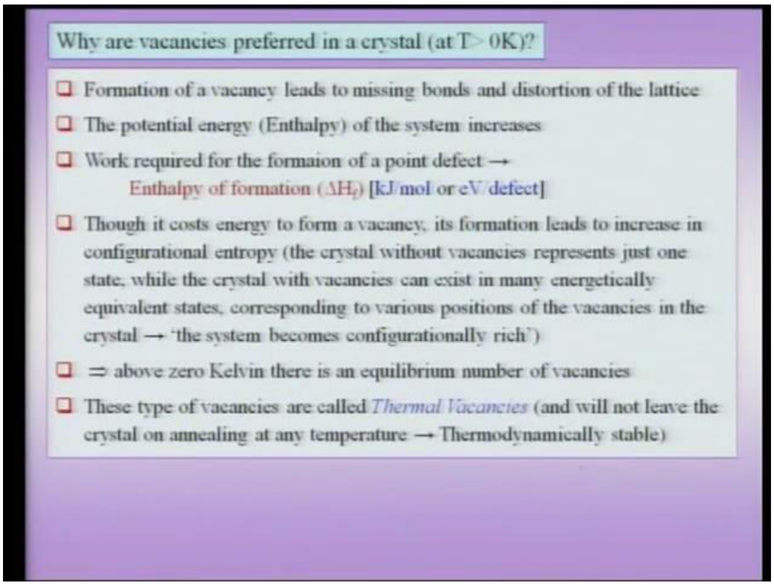
Why are vacancies preferred in a crystal (at $T > 0K$)?

- ☐ Formation of a vacancy leads to missing bonds and distortion of the lattice
- ☐ The potential energy (Enthalpy) of the system increases
- ☐ Work required for the formaion of a point defect →
  Enthalpy of formation (ΔH_f) [kJ/mol or eV/defect]
- ☐ Though it costs energy to form a vacancy, its formation leads to increase in configurational entropy (the crystal without vacancies represents just one state, while the crystal with vacancies can exist in many energetically equivalent states, corresponding to various positions of the vacancies in the crystal → 'the system becomes configurationally rich')
- ☐ ⇒ above zero Kelvin there is an equilibrium number of vacancies
- ☐ These type of vacancies are called *Thermal Vacancies* (and will not leave the crystal on annealing at any temperature → Thermodynamically stable)

We ask the important question because we have been mentioning this term repeatedly, which is the concentration of vacancies dictated by thermodynamic equilibrium. So, we ask this important question. We did take up this topic somewhat when we dealt with the topic in the context of thermodynamics at the very an early introduction to this course. This is the question we are asking again is that why are vacancies preferred at in a crystal.

The thing we need to understand obviously is that, when I am putting in a vacancy. In other words, removing an atom from the crystal, there are going to be bren bonds. There are going to be distortions of the bonds around the central atom. Suppose, I am removing an atom from this position for instance, the central position. It is now the position of the vacancy. Here, not only are the bonds bren around this, but there is a distortion of the bonds of these atoms because now these atoms around this are going to be moving with respect to the atoms which has been removed. Therefore, the whole system is I mean, it is going to cost me energy and this energy or the enthalpy.

(Refer Slide Time: 49:43)

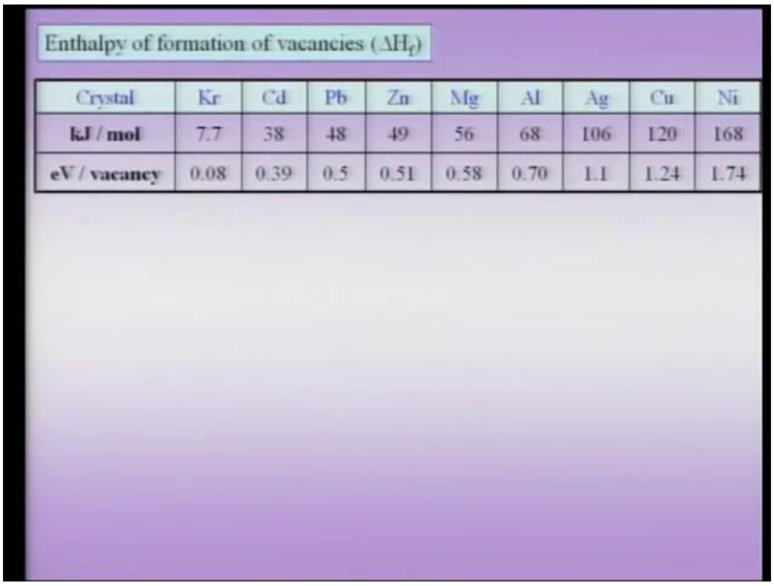


Why are vacancies preferred in a crystal (at T > 0K)?

- ☐ Formation of a vacancy leads to missing bonds and distortion of the lattice
- ☐ The potential energy (Enthalpy) of the system increases
- ☐ Work required for the formaion of a point defect → Enthalpy of formation (ΔH_f) [kJ/mol or eV/defect]
- ☐ Though it costs energy to form a vacancy, its formation leads to increase in configurational entropy (the crystal without vacancies represents just one state, while the crystal with vacancies can exist in many energetically equivalent states, corresponding to various positions of the vacancies in the crystal → 'the system becomes configurationally rich')
- ☐ ⇒ above zero Kelvin there is an equilibrium number of vacancies
- ☐ These type of vacancies are called *Thermal Vacancies* (and will not leave the crystal on annealing at any temperature → Thermodynamically stable)

I call the enthalpy of formation of the vacancy, which I have given a symbol delta H f.

(Refer Slide Time: 49:53)



Enthalpy of formation of vacancies (ΔH_f)

Crystal	Kr	Cd	Pb	Zn	Mg	Al	Ag	Cu	Ni
kJ / mol	7.7	38	48	49	56	68	106	120	168
eV / vacancy	0.08	0.39	0.5	0.51	0.58	0.70	1.1	1.24	1.74

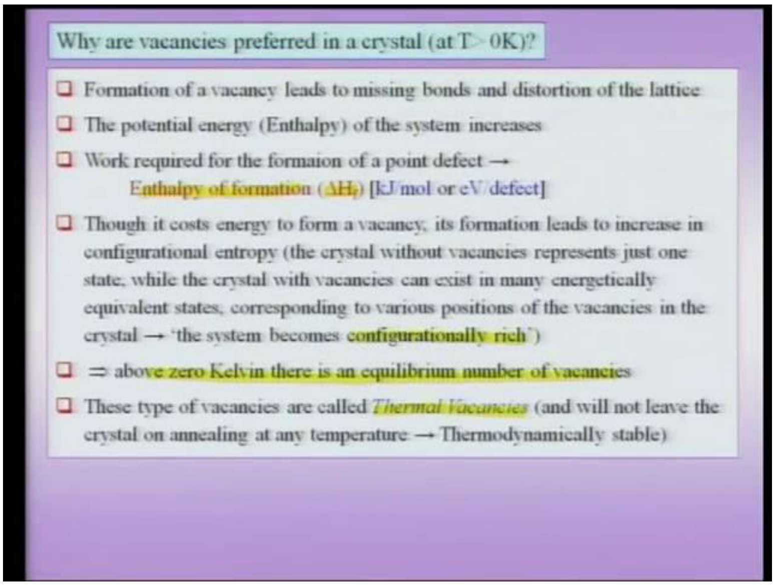
This enthalpy formation typically for various pure metals for instance, is of the order of between about 0.08, as low as 0.08 to about 1.74, which is for nickel electron volt per vacancy. That means of course, it can vary over an order of magnitude of more. Therefore, delta H f can take various values. But nevertheless, what it tells me is that there is a certain cost of putting vacancies in my crystal in terms of its energy. This energy, I am talking of course, in terms of enthalpy. So, you can see that the enthalpy caused is for these are of course, FCC elements.

Here, these two are HCP here and some of these are different crystal structures. So, we can that it varies a lot. Of course, this depends on the strength of the bond in. Now, I am distorting and breaking the bonds. So, if it cost me energy and hence, enthalpy to accommodate vacancies in the crystal. Then, why are vacancies present in the crystal? Now, that means that there must be the other factor, which is now my entropy factor. This entropy factor tells me that above 0 Kelvin, there is an equilibrium concentration of vacancies.

The kinds of vacancies we are talking about here are called the thermal vacancies. Why does this arise? As we said is because of the entropic richness or configurational richness that the system is providing. I take a pure crystal that means the crystal where all lattice points are occupied, a perfect crystal. Calculate the number of configurations possible. That is just 1, which means that if I use Boltzmann's equations equal to k l on omega. Then, l on 1 will be 0.

That means the system does not have any configurational richness. Therefore, its entropy is low. Now, suppose I put in a vacancy into the system. This vacancy could sit in any one of the positions in the lattice positions. All these would be energetically equivalent. Of course, in this case, I am ignoring the surface of the crystal. I am assuming that all positions are configurationally equivalent. That means by introducing a vacancy, the system becomes configurationally rich.

(Refer Slide Time: 52:05)



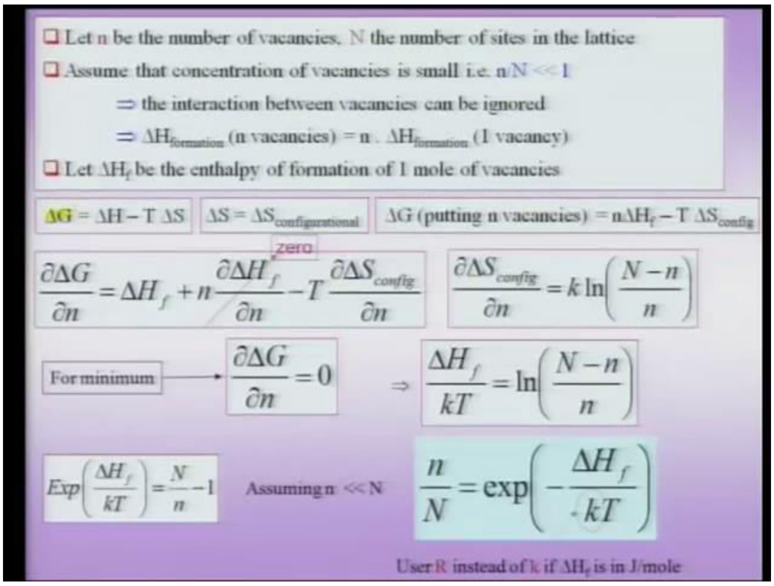
Why are vacancies preferred in a crystal (at T > 0K)?

- ☐ Formation of a vacancy leads to missing bonds and distortion of the lattice
- ☐ The potential energy (Enthalpy) of the system increases
- ☐ Work required for the formaion of a point defect →
  Enthalpy of formation (ΔH_f) [kJ/mol or eV/defect]
- ☐ Though it costs energy to form a vacancy, its formation leads to increase in configurational entropy (the crystal without vacancies represents just one state, while the crystal with vacancies can exist in many energetically equivalent states, corresponding to various positions of the vacancies in the crystal → 'the system becomes configurationally rich')
- ☐ ⇒ above zero Kelvin there is an equilibrium number of vacancies
- ☐ These type of vacancies are called *Thermal Vacancies* (and will not leave the crystal on annealing at any temperature → Thermodynamically stable)

.

In this process, the entropy of the system increases by introducing this vacancy. Since, we know that for a system, when I am talking about if a system is stable or it is unstable, I am talking with respect to the Gibb's free energy. So, the parameter which characterizes the stability of a system is at constant temperature and pressure is the Gibb's free energy. It is applicable to condense matter systems. We would notice that in such a system, it is better for me to accommodate vacancies in spite of the fact that it is energetically going to cost me. So, let us calculate the number of vacancies, which are stabilized any at any temperature T.

(Refer Slide Time: 52:48)



- ☐ Let n be the number of vacancies, N the number of sites in the lattice
- ☐ Assume that concentration of vacancies is small i.e. $n/N << 1$
  - ⇒ the interaction between vacancies can be ignored
  - ⇒ $\Delta H_{formation}$ (n vacancies) = n . $\Delta H_{formation}$ (1 vacancy)
- ☐ Let ΔH_f be the enthalpy of formation of 1 mole of vacancies

$\Delta G = \Delta H - T\,\Delta S$

$\Delta S = \Delta S_{configurational}$

ΔG (putting n vacancies) $= n\Delta H_f - T\,\Delta S_{config}$

$$\frac{\partial \Delta G}{\partial n} = \Delta H_f + n\cancelto{\text{zero}}{\frac{\partial \Delta H_f}{\partial n}} - T\frac{\partial \Delta S_{config}}{\partial n}$$

$$\frac{\partial \Delta S_{config}}{\partial n} = k\ln\left(\frac{N-n}{n}\right)$$

For minimum → $\frac{\partial \Delta G}{\partial n} = 0$ ⇒ $\frac{\Delta H_f}{kT} = \ln\left(\frac{N-n}{n}\right)$

$Exp\left(\frac{\Delta H_f}{kT}\right) = \frac{N}{n} - 1$

Assuming n << N

$$\frac{n}{N} = \exp\left(-\frac{\Delta H_f}{kT}\right)$$

User R instead of k if ΔH_f is in J/mole

So, let n be the number of vacancies. N be the total number of sites in the lattice. We will typically start with configurations, wherein the vacancy concentration is much less than 1. We will also ignore and for such a assumption, we will assume that the vacancies are far apart. Therefore, the interaction between vacancies can be ignored. That means delta H f is not a function of the concentration of vacancies.

If you put the first vacancy, it cost me a certain delta H f. If you put the second vacancy, it costs me the same delta H f because now these vacancies are far away and they do not interact with each other. So, for the third vacancy, the fourth vacancy, all of them, the cost for me would remain identical. That would be delta H f. Delta H for formation of n vacancies. So, the n times delta H for formation of one vacancy. That is the assumption coming from a small concentration of vacancies.

Of course, I could define delta H f for a single vacancy or for a mole of vacancies. So, that possibility I have so, let me calculate what the equilibrium concentration of vacancies is. So, delta G is delta H minus T delta S. In this case, I am talking about delta S being delta S configuration. So, in the chapter on thermodynamics, we had seen that there could be many contributions to the micro states even corresponding to the single macro state. In this case, I am considering a macro state of certain energy.

The micro states could come from electronic, vibrational, rotational or configurational and ignoring that, the other contributions to the entropy, I am purely considering the configurational term, which is the dominant term. So, the delta G for putting n vacancies is n delta H f minus T delta S configurational. Now, to find the minima for the system that the what is my equilibrium concentration of vacancies, I can differentiate this function dou delta G by dou n is delta H f minus n dou delta H f by dou n.

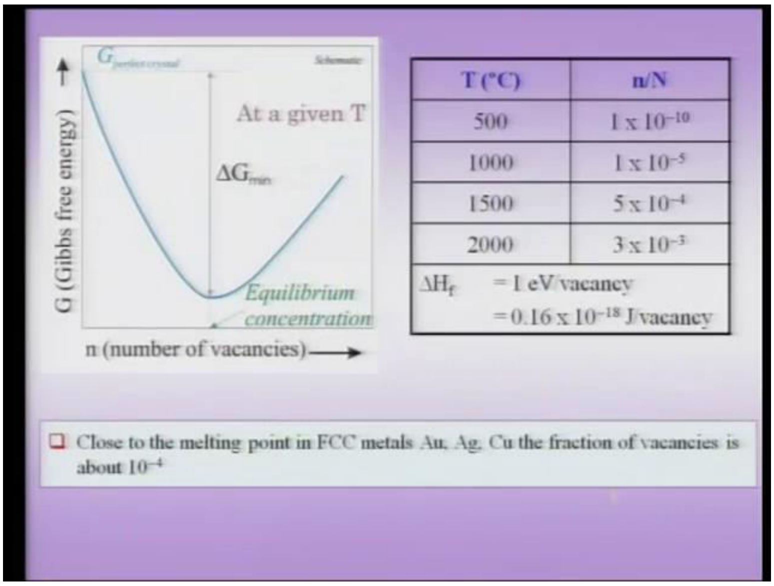
This is what I said. Since, I do not consider dependence of delta H f with respect to n that means, I assume that my energy enthalpy to put the first vacancy is same as the hundredth vacancy. This term goes to 0 and become minus T delta S. Configuration of delta n dou delta S configuration of delta n is k l on N minus n by n. This is coming from Boltzmann’s equation S equal to k l on omega. For minimization, i dou delta j n by dou n equal to 0 gives me delta H f by k T is equal to l on N minus n by n. Assuming that n by n that means n by n is exponential minus delta H f by k T. In other words, n by n is an exponential function of delta H f.

Now, this delta H f is of course, the energy for formation of vacancy. In other words, it is a barrier for the formation of vacancy. k T is my sort of the measure of the thermal energy of the system at a temperature T. So, this is coming of course, assuming that n by n. That means n is much smaller than n. That means the concentration of vacancies is much smaller than the number of available lattice sites. So, n by n, I can calculate or making this assumption.

Now, that means if I increase my temperature so, this is my reciprocal. This is a negative. So, they cancel each other. Cancel means their effects cancel with respect to the concentration of vacancies. I heat my system, increase the temperature. Then, concentration of vacancies would increase exponentially. This is something, which I need to note. So, we will try to see what kinds of numbers are involved here in terms of this n by n in the next slide. But we note here that this is an exponential function.

Temperature is contributing exponentially to the formation of vacancies. You can see that obviously, these are thermal vacancies. That is why they are called thermal vacancies. Now, if I am talking about naught A delta H f is defined with respect to a single vacancy. Then, I use k in k. If I am talking about A delta H f for the formation of a mole of vacancies then, I use at different temperatures. I am not changing the temperature. Here, I am keeping the temperature constant.

(Refer Slide Time: 56:50)



T (°C)	n/N
500	1×10^{-10}
1000	1×10^{-5}
1500	5×10^{-4}
2000	3×10^{-3}

ΔH_f = 1 eV/vacancy
= 0.16×10^{-18} J/vacancy

☐ Close to the melting point in FCC metals Au, Ag, Cu the fraction of vacancies is about 10^{-4}

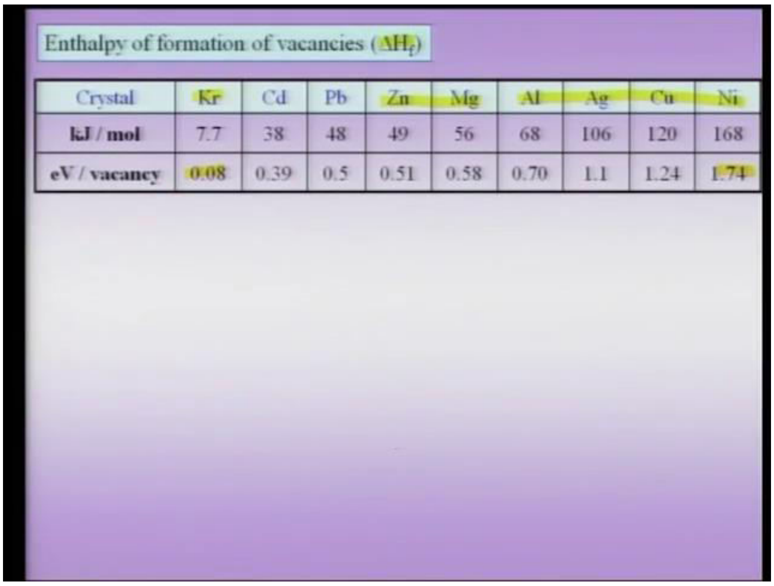
But, what I do is I start with 0 vacancies and slowly, start introducing vacancies in the crystal. That means Ii am starting with 0 here. There will be a 1 vacancy, 2 vacancy. So, forth, I increase the number of vacancies here initially because of the entropic stabilization of the system. That means the system is becoming configurationally rich. My energy of the system, the Gibb's free energy would reduce along this curve. But, after a certain number of concentration of vacancies, it costs me too much energy or too much enthalpy to put vacancies in the system.

Therefore, actually it will lead to an increase in the Gibb's free energy of the system. So, this is now my equilibrium concentration of vacancies. That means at any temperature, there is an equilibrium concentration of vacancies. If there are lower number of vacancies present then, I can accommodate more vacancies and lower the energy of the system. If there are more vacancies present than the equilibrium concentration then, the system is not in thermodynamic equilibrium. Given an opportunity, suppose, you un heal a crystal copper crystal, which has more vacancies.

Suppose, I heat a copper crystal to high temperature. I increase the concentration of vacancies. Then, you can see a table here for instance at 500 degree Celsius. If my concentration of vacancy is 10 power minus 10, that is n by n and if I go to 2,000, it goes to about 1 in 1000. Now, suppose I quench from here. I retain for instance, about 10 power minus 5, concentration of vacancies at 500 degrees Celsius. Then, it is more than the equilibrium concentration. But suppose, I keep it at this temperature for long time then, slowly the vacancies would un heal out.

That means it will leave the crystal and atoms would come back into the original lattice positions. Thus, the energy of the system would go back to its global minima which would correspond to an equilibrium concentration of vacancies. So, let me take a typical example of what kind of concentrations we are talking about. Suppose, I am talking about FCC metals and we already had seen the cost.

(Refer Slide Time: 58:52)



Enthalpy of formation of vacancies (ΔH_f)

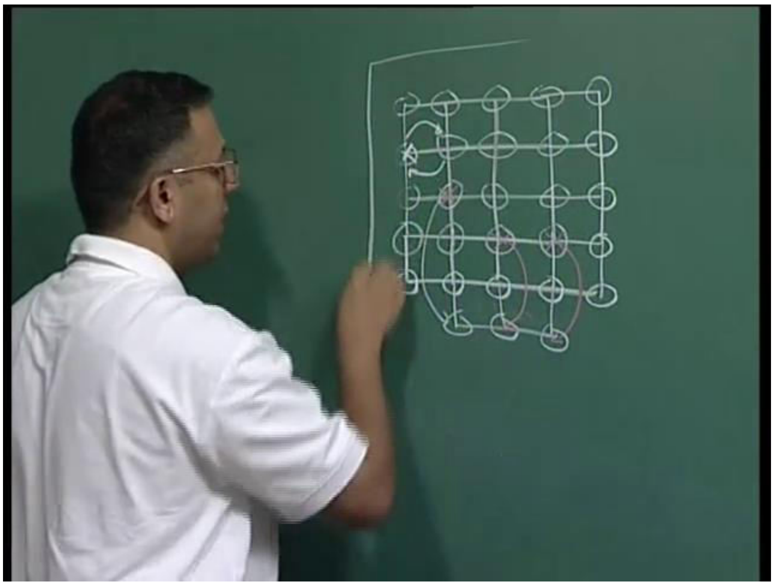
Crystal	Kr	Cd	Pb	Zn	Mg	Al	Ag	Cu	Ni
kJ / mol	7.7	38	48	49	56	68	106	120	168
eV / vacancy	0.08	0.39	0.5	0.51	0.58	0.70	1.1	1.24	1.74

I am having enthalpy cost of putting vacancies in this material. That is pretty large. It is about less than that is 1.74 and about 1.1 electron volt per vacancy. Since, you can also talk in terms of kilo joule per mole, which in terms for nickel terms would be 168 kilo joule per mole of vacancies. Then, this number for about these FCC metals is about 10 power minus 4 at the melting point. That means now, even at the melting point, the fraction of sites which are vacant is still pretty small. It is 1 in about 10,000. So, it is not a very large fraction.

But nevertheless, not a negligible fraction, so this accommodation of vacancies in a crystal actually leads to a very important effect. Suppose I am talking about heating a metal. Then, we know that the metal would expand. Now, the metal would expand because of two reasons. One reason is of course, the fact that the atoms are going to vibrate around their equilibrium lattice spacing. When they are vibrating, you would notice that if I talk about the force displacement curve, the mean position or the energy displacement curve between atoms.

The lowest energy position corresponds to the equilibrium lattice spacing. When you are heating it, this energy displacement curve is asymmetric with respect to the minima. Actually, the mean position shifts to larger lattice parameters. Therefore, when you heat a metal purely of the vibration of the atoms around the lattice position, the metal would expand. So, this is something, which we all know why a metal expands. But, there is a more saddle, an entropic reason, why a metal would expand. This is what we have just now seen. As we heat a metal, more and more vacancies are been accommodated into the material. How are these vacancies accommodated?

(Refer Slide Time: 01:00:41)



The vacancies are accommodated. Now, let me enlarge this crystal a little bit and draw few more atoms. So, as I am heating this crystal, the equilibrium concentration of vacancies has to increase. That means more and more atoms would go and settle on the surface. So, this will become a vacancy. This will go sit on the surface, which will now correspond to a lattice position. So, at even higher temperature, there will be more vacancies which will go and more atoms which will go and sit on the surface.

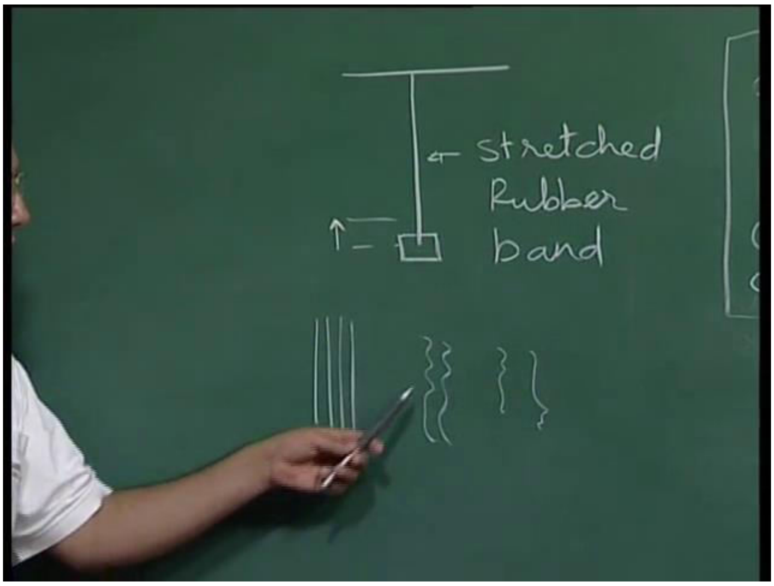
Therefore, I will have vacancy here because I am just drawing because I have a finite diagram. Here, I am drawing next to each other. But in a larger picture, these vacancies would be far away. There could be one more vacancy for instance, which is created somewhere here. This for instance could come and sit here. So, even this screwed schematic, you can see that as I am heating the crystal and as vacancy concentrations increasing, the crystal is increasing in volume.

So, suppose this happened in all three dimensions. Then, I would find that my crystal would become larger with heating though this is as you can see, it is a 1 in a 10,000 effect. With respect to for instance, I have normal thermal expansion. Also, it has a very small fractional contribution. It also remains 1 in 10,000 or that order is still nevertheless purely because of entropy, the system is now expanding. So, there are two reasons why a metal expands when you heat it.

One reason is because of the normal thermal vibration. The second reason being stabilization of vacancies. As you heat the metal so, the material is going to expand as you heat it. This reason is a very settled and very interesting reason that more vacancies are being accommodated in the material expands. It is because of that, there are also theories which talk about melting wherein you discuss melting in terms of a critical concentration of vacancies.

Though we do not consider that here but we need to note that vacancies play a very important role in many other properties like diffusion or as in this case, thermal expansion. Now of course, we should not always conclude that entropically, a material would always expand because of heating a contra intuitive and a contradictory example would be the case of rubber. For instance, you take a rubber band and let me draw the experiment.

(Refer Slide Time: 01:03:07)



I take a simple rubber band and hang a small weight in it. Now, this is my stretched rubber band. There is a small weight here. Now, suppose I heat this system. Then, actually, you will observe to our surprise that the material contracts. So, this is my rubber band and the sort the crude explanation I will give here, which is again related to entropy. There is a fact that suppose have a stretched state of rubber, I can approximate it to sort of the all the polymeric chains being extended.

In the extreme example, would be a straight extended example. When you heat the system, as you know that based on the confirmations of the carbon carbon bond, this can actually take a coiled configuration. In the coiled configuration, you can see that actually there are many permutations of this configuration possible. In other words, it becomes configurationally rich because for instance, suppose, I want to accommodate this curve. This curve could be here or it could be here. Anyone of these configurations would lead to a shortening of the length. So, if I have a starting configuration like this and I heat the material then, the material becomes entropically rich.

Why? Because of the many configurational possibilities or multiplicity of states, which is provided by these coiled molecules and because the molecules coiled up at higher temperature, the rubber band contracts. So, it is possible that a material not only expands because of entropic reasons; but also contracts because of entropic reason, as in the case of rubber. So, we need to note that entropy, even though being a settled phenomenon can actually lead to very interesting results with regard to even physical properties like thermal expansion or thermal contraction, as in the case of rubber.

So, as you can notice, this force which is contracting the rubber is actually a very settled kind of force. This is in a not arising from the typical kind of forces like either gravity or electrochemical forces, which we normally consider in a material. This is coming from the configuration of the entire system. So, this we can write as an entropic force. This is not a force of the normal kind. So, this is in entropic force. It is very different in origin compared to the normal forces you deal with as I said, gravity or electromagnetic forces or even a weak or a strong force.

So, let us me summarize the calculation so far, which is something very important that in spite of the fact that it actually cost me energy to put vacancies in a crystal. This energy or enthalpy increases coming from broken bonds. The fact that Gibb's free energy can actually be reduced by accommodating vacancies implies that I can actually have an increase in vacancy concentration. That means at any temperature, you could have an equilibrium concentration of vacancies.

Therefore, at any temperature, you would actually prefer vacancies, when you are above 0 Kelvin. As we know, 0 Kelvin is un-attainably. In other words, at any positive Kelvin, you will always have a certain concentration of vacancies in a material. Therefore, you can call vacancies as equilibrium thermodynamic defects. This is of course, true that every defect can lead to a configurational richness in a material. Therefore, there will be an entropic contribution by accommodating the defect.

But if you will see as perhaps in the case of dislocations that actually, dislocations cannot be stabilized thermodynamically. It, dislocation cannot be a thermodynamic defect in a material. This is because the temperature at which a dislocation would actually be stabilized in a material would be higher than the melting point of any available material. So, dislocations cannot be equilibrium thermodynamic defects.