INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
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NPTEL ONLINE CERTIFICATION COURSE
Structural Analysis of Nanomaterials
LECTURE – 03
Imperfection in Structure of Materials
With
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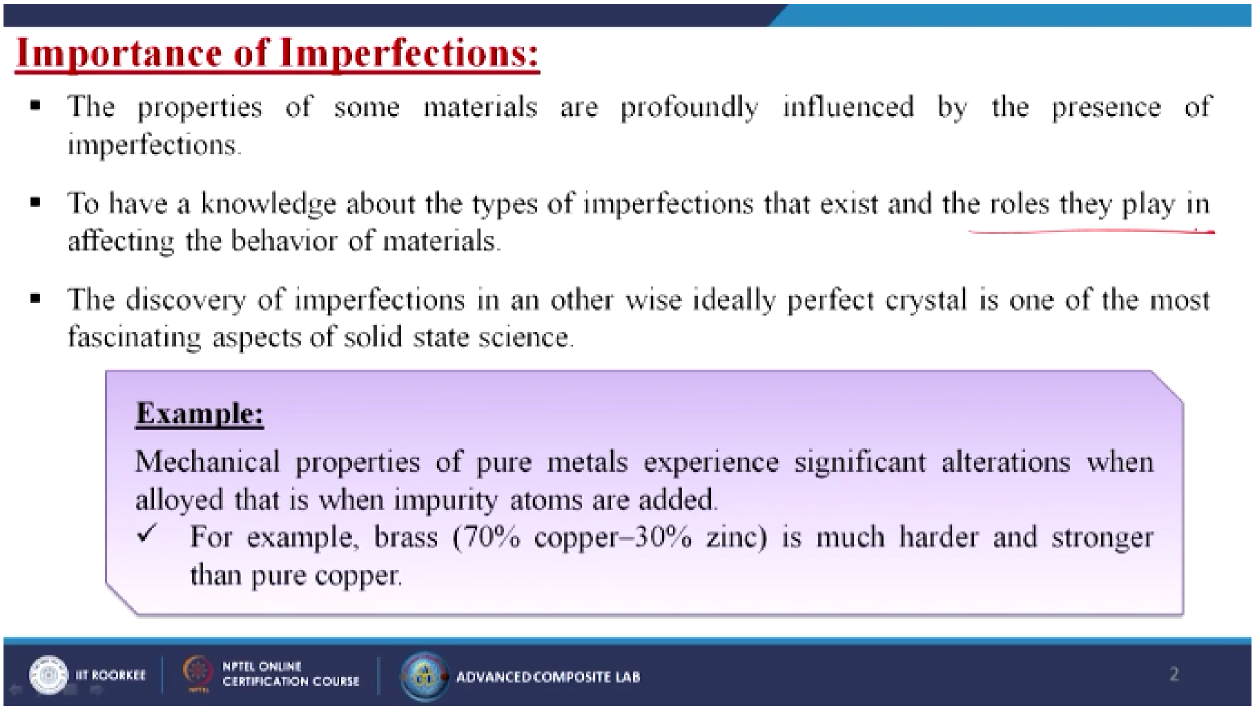
Hello, today our lecture topic is that Imperfections in Structure of Materials. In our last lectures we have already discussed about the atomic bonding and the crystal structure of different materials, so before going to start just let us know what is the importance of imperfections, because sometimes it is required for getting the material properties or maybe the betterment of the material properties.



Importance of Imperfections:

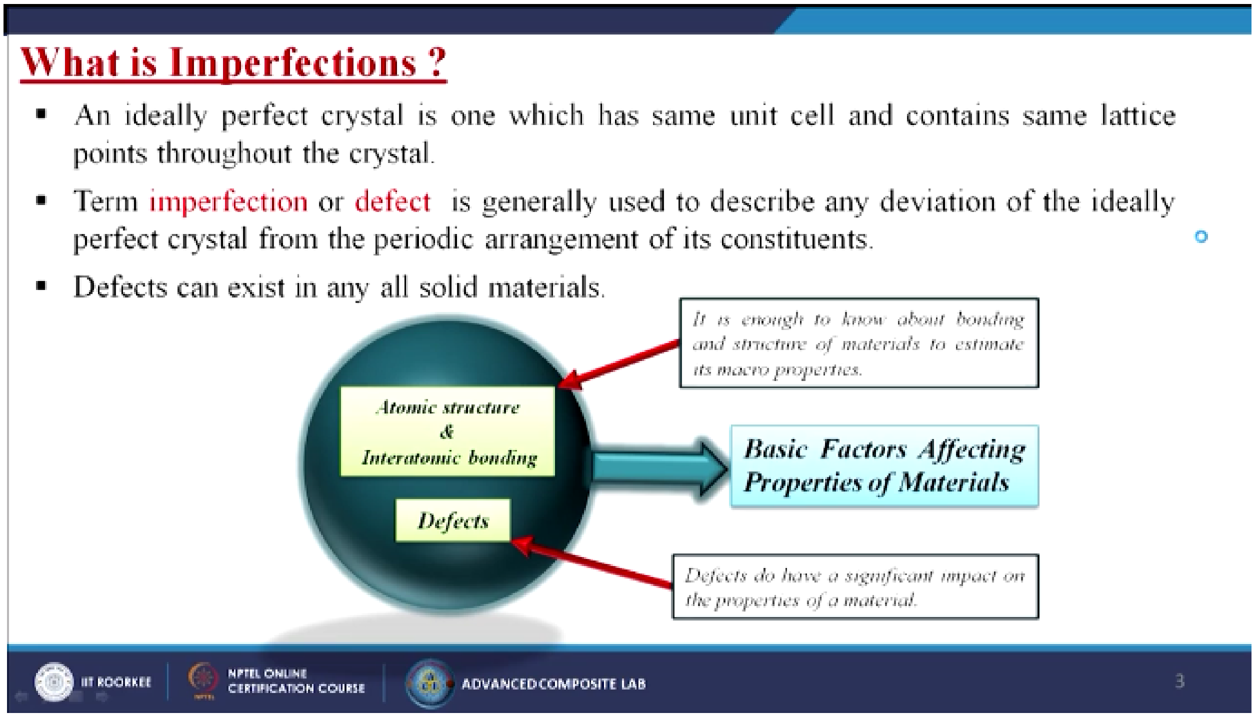
- The properties of some materials are profoundly influenced by the presence of imperfections.
- To have a knowledge about the types of imperfections that exist and the roles they play in affecting the behavior of materials.
- The discovery of imperfections in an other wise ideally perfect crystal is one of the most fascinating aspects of solid state science.

Example:

Mechanical properties of pure metals experience significant alterations when alloyed that is when impurity atoms are added.

✓ For example, brass (70% copper–30% zinc) is much harder and stronger than pure copper.

So the properties of some materials are profoundly influenced by the presence of the imperfections, yes of course sometimes we desired that imperfections should be there so that we can modify the materials or maybe we can enhance some kind of mechanical properties, to have a knowledge about the types of imperfections that exist and the roles they play in effecting the behavior of materials, so that discovery of the imperfections in an otherwise ideally in a perfect crystal is one of the most fascinating aspects of solid state science, so say if I give an example, if I give an example of a brass, so brass is made of the copper and the zinc, so if you compare the properties of the brass in compare with to the copper we can found that the brass properties are better than the pure copper.



What is Imperfections ?

- An ideally perfect crystal is one which has same unit cell and contains same lattice points throughout the crystal.
- Term imperfection or defect is generally used to describe any deviation of the ideally perfect crystal from the periodic arrangement of its constituents.
- Defects can exist in any all solid materials.

Atomic structure & Interatomic bonding

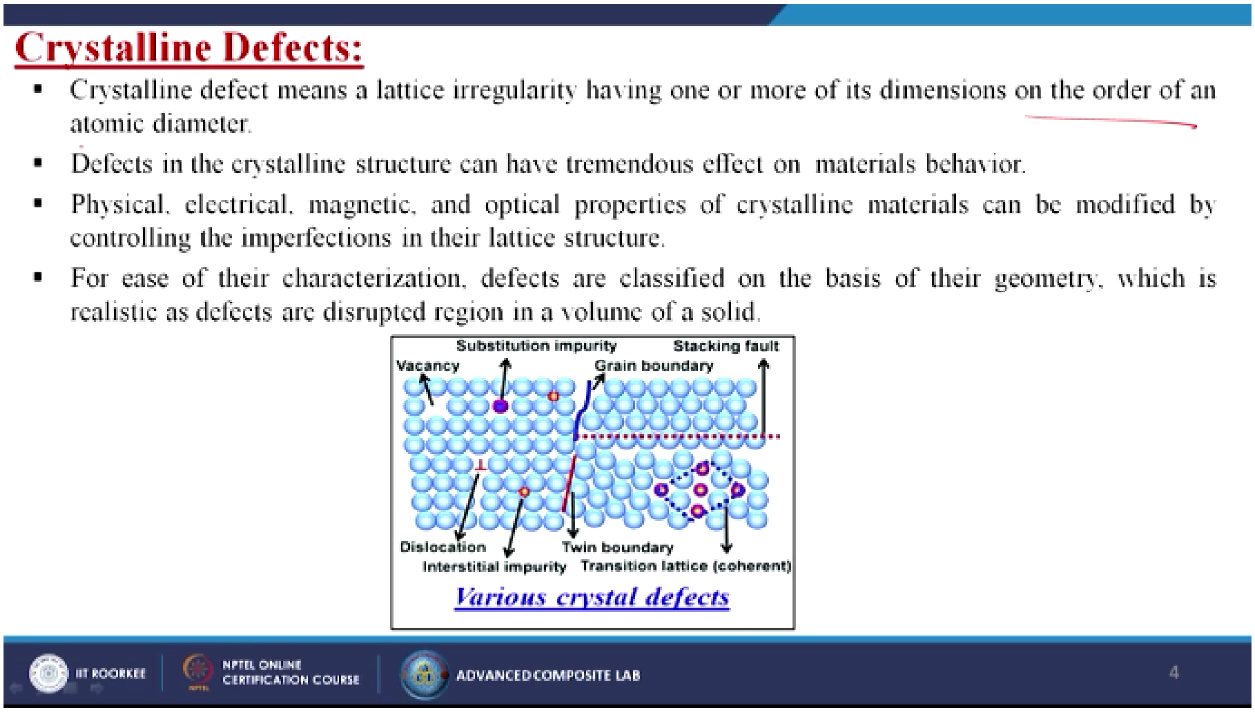
Defects

Basic Factors Affecting Properties of Materials

It is enough to know about bonding and structure of materials to estimate its macro properties.

Defects do have a significant impact on the properties of a material.

So now we have to know that what is imperfections, so an ideally perfect crystal in one which has some unit cells and contain some lattice point throughout the crystals already we have read this points, term imperfections or maybe sometimes we are calling it as a defect is generally used to describe the any diffusions means any kind of little bit diffusions of the ideally perfect crystals means there is some problems in the crystal structure. From the periodic arrangements of its constituents, defects can exist in any all solid materials, so there are some basic factors generally which affecting the properties of materials, so first one is the atomic structure and the interatomic bonding, it is enough to know about the bonding and structure of materials to estimate its micro properties and another one is defects, so defects to have a significant impact on the properties of a material.

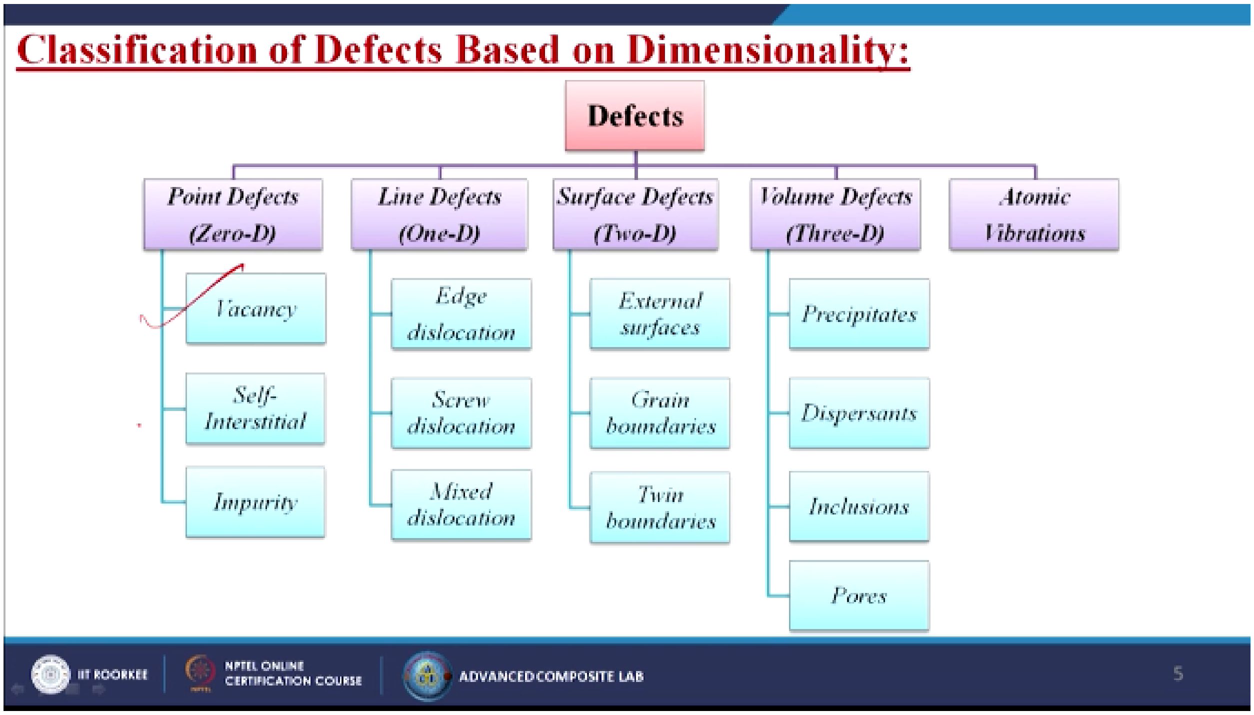


Crystalline Defects:

- Crystalline defect means a lattice irregularity having one or more of its dimensions on the order of an atomic diameter.
- Defects in the crystalline structure can have tremendous effect on materials behavior.
- Physical, electrical, magnetic, and optical properties of crystalline materials can be modified by controlling the imperfections in their lattice structure.
- For ease of their characterization, defects are classified on the basis of their geometry, which is realistic as defects are disrupted region in a volume of a solid.

Various crystal defects

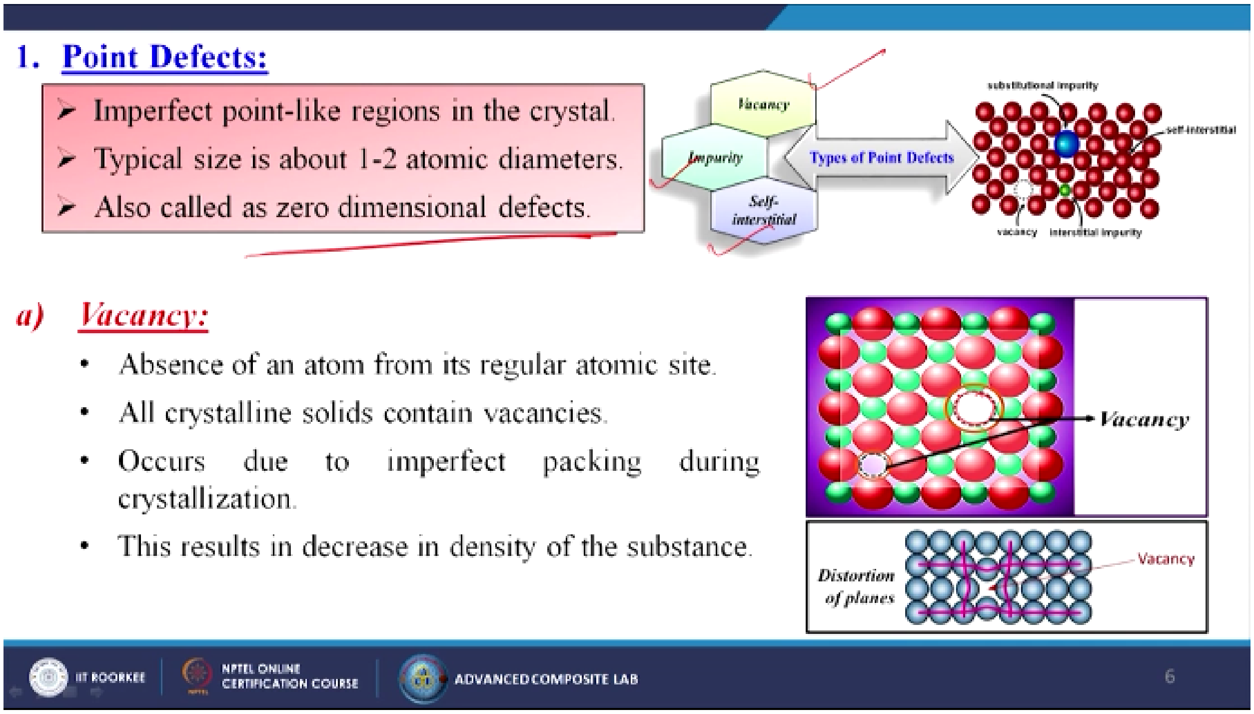
So first we have to know what is crystalline defects, so generally the crystalline defects means a lattice irregularity having one or more of its dimensions on the order of an atomic diameter, so generally a crystal or maybe materials this is having a specific crystal structure, in that crystal structure we can see some kind of vacancy, some kind of defects, so these all are known as the crystalline defects of that particular material, defects in the crystalline structure can have tremendous effect on material behavior because we can change or maybe substitute some host atoms or maybe we can put some kind of new atoms inside that host atoms like this way we can change the material properties, physical, electrical, magnetic and the optical properties of crystalline materials can be modified by controlling the imperfections in there lattice structure, for ease of their characterizations defects are classified on the basis of their geometry, maybe types which is realistic as defects are disrupted region in a volume of solids, so from this image we can see that there are so many types of defects like vacancy, like dislocations, then some kind of impurity like substitution impurity or maybe that interstitial impurity, some kind of two in boundary problems, some kind of grain boundary or maybe the stacking fault, so there are so many types of defects which we are going to discuss one by one in the subsequent slide.



Classification of Defects Based on Dimensionality:

- Defects
  - Point Defects (Zero-D)
    - Vacancy
    - Self-Interstitial
    - Impurity
  - Line Defects (One-D)
    - Edge dislocation
    - Screw dislocation
    - Mixed dislocation
  - Surface Defects (Two-D)
    - External surfaces
    - Grain boundaries
    - Twin boundaries
  - Volume Defects (Three-D)
    - Precipitates
    - Dispersants
    - Inclusions
    - Pores
  - Atomic Vibrations

So first we have to know what is the broad classifications of defects based on the dimensionality, so defects if we divided into different or maybe rather I can say into five types, first one is called the point defects or maybe the 0D defects like vacancy self-interstitial and the impurity, if we talk about the 1D defects or maybe it is known as line defects also like edge dislocations, screw dislocations and the mixed dislocations, if we talk about the surface defects like 2D, two dimensional in nature that is external surfaces, grain boundaries and the twin boundaries, and when you are talking about the volume defects which is 3D in nature or maybe sometimes it is called the 3D defects is called the precipitates, dispersants, inclusions, and pores and the last one is known as the atomic vibrations.



1. Point Defects:

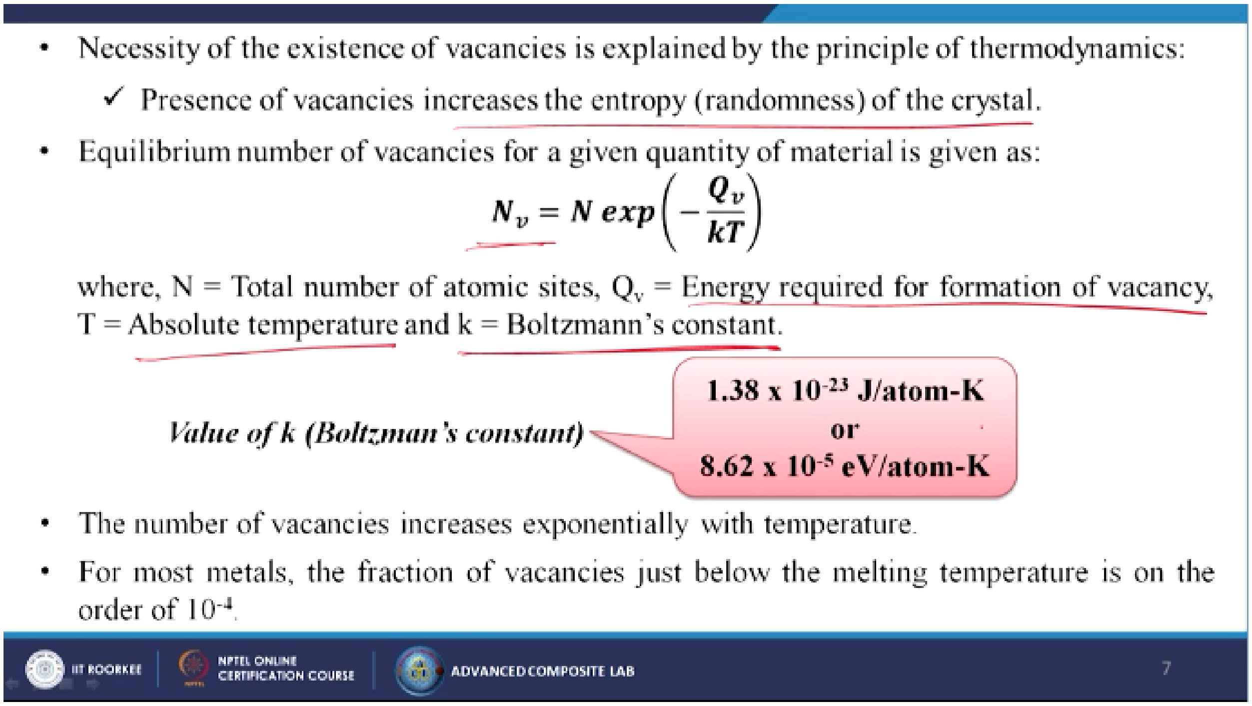
- Imperfect point-like regions in the crystal.
- Typical size is about 1-2 atomic diameters.
- Also called as zero dimensional defects.

a) Vacancy:

- Absence of an atom from its regular atomic site.
- All crystalline solids contain vacancies.
- Occurs due to imperfect packing during crystallization.
- This results in decrease in density of the substance.

So first what is point defects? So point defects means it’s a imperfect point like regions in the crystals, so a single point type of defects in the crystal structure, typical sizes about 1 to 2 atomic diameters also called as the 0 dimensional defects, so there are several types of point defects like vacancy, impurity, and the self-interstitial, so what is vacancy? So vacancy is the absence of an atom from its regular atomic site, so from this particular image you can see that in this particular gap some atom should be present over there but it is not, so some vacant site has been created that is known as the vacancy, all crystalline solid contains vacancies, occurs due to imperfect packing during the crystallizations these result in decrease in density of the substance, yes of course, because generally the crystal structure it is very, very closely packed, if there is gap in between that automatically the density will decrease.

So what is the necessity of the existence of vacancies? So generally it can be proved by the principle of thermodynamics, generally the presence of vacancies increase the entropy or maybe the randomness of the crystal as I told already when there is no vacancy the atoms are very closely packed, but when there is any vacancy or maybe has been any gaps has been generated so automatically the atom will try to move in between those gaps, so equilibrium number of vacancies which is denoted by the NV for a given quantity of material is given by N exponential of –QV/KT, where N is the total number of atomic sites, QV is the energy required for formations of the vacancy, T is the absolute temperature, so if at the time of calculations of the equilibrium number of vacancies if our temperature is in degree centigrade we have to convert it into kelvin and K is known as the Boltzmann’s constant.



- Necessity of the existence of vacancies is explained by the principle of thermodynamics:
  - ✓ Presence of vacancies increases the entropy (randomness) of the crystal.
- Equilibrium number of vacancies for a given quantity of material is given as:

$$N_v = N\,exp\left(-\frac{Q_v}{kT}\right)$$

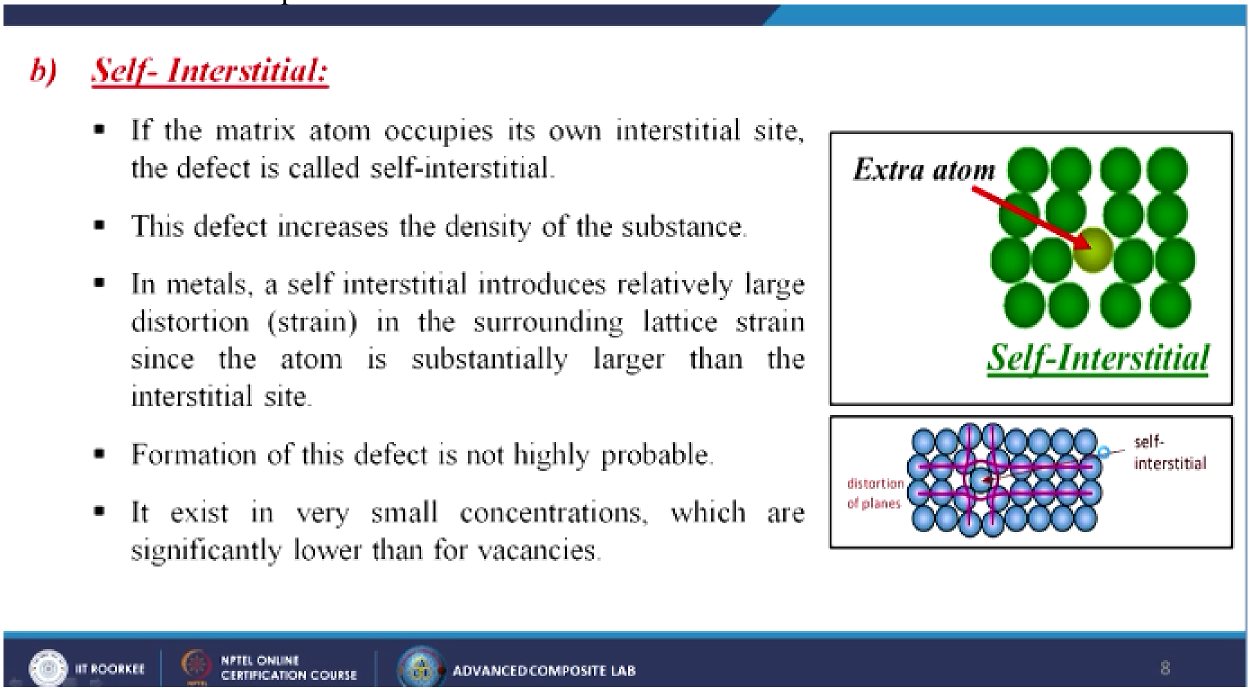
where, N = Total number of atomic sites, Q_v = Energy required for formation of vacancy, T = Absolute temperature and k = Boltzmann's constant.

Value of k (Boltzman's constant)

1.38×10^{-23} J/atom-K
or
8.62×10^{-5} eV/atom-K

- The number of vacancies increases exponentially with temperature.
- For most metals, the fraction of vacancies just below the melting temperature is on the order of 10^{-4}.

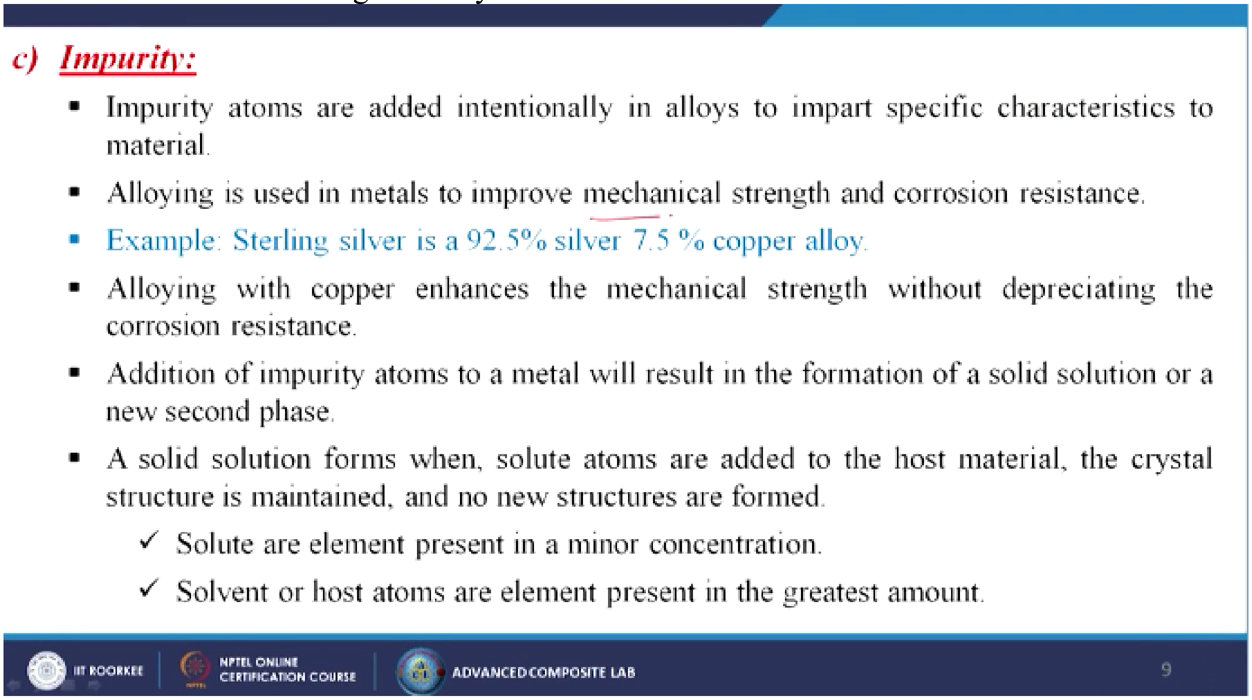
So what is the value of that Boltzmann's constant? So generally if the energy is in joule, so automatically the value of the Boltzmann constant will be 1.38 x 10 to the power -23 joule per atom kelvin, and if the energy is into the electron volt then the value will be 8.62 x 10 to the power -5 electron volt per atom kelvin, so the number of vacancies increases exponentially with temperature for most metals the fraction of vacancies just below the melting temperature is on the order of 10 to the power -4.



b) *Self- Interstitial:*

- If the matrix atom occupies its own interstitial site, the defect is called self-interstitial.
- This defect increases the density of the substance.
- In metals, a self interstitial introduces relatively large distortion (strain) in the surrounding lattice strain since the atom is substantially larger than the interstitial site.
- Formation of this defect is not highly probable.
- It exist in very small concentrations, which are significantly lower than for vacancies.

Now we are going to discuss about the self-interstitial, so if the matrix atom occupies its own interstitial site, because from the name itself we can understand that, that has been done or maybe the created by the host atom itself, the defect is called the self-interstitial, this defect increases the density of the substance, yes of course, because there is no vacant place is left, in metals a self-interstitial introduces relatively large distortions in the surrounding lattice strain since the atom is substantially larger than the interstitial site. So in this particular case you can see that atom has been self-interstitial has been taken place or maybe has been inserted or maybe has taken the place in between the atoms and then it is giving a pressure or maybe the strains to the surrounding atoms. Formation of these defect is not highly probable, it exist and varies small concentrations which are significantly lower than for vacancies.

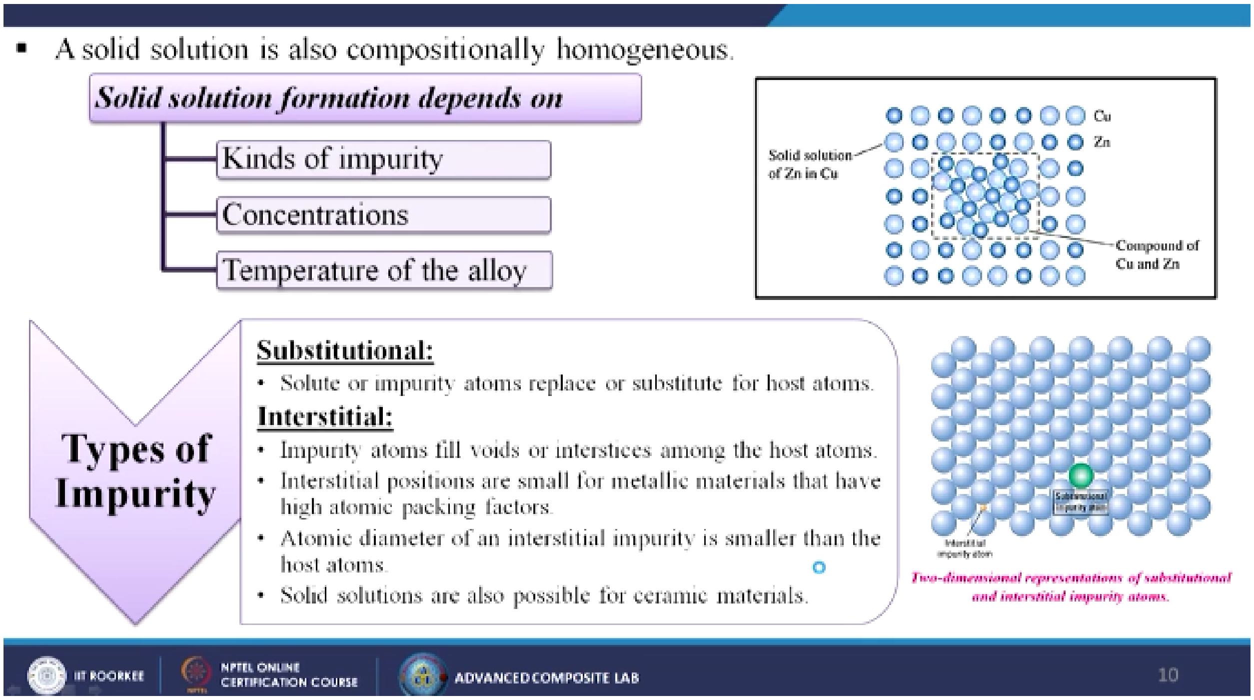


c) *Impurity:*

- Impurity atoms are added intentionally in alloys to impart specific characteristics to material.
- Alloying is used in metals to improve mechanical strength and corrosion resistance.
- Example: Sterling silver is a 92.5% silver 7.5 % copper alloy.
- Alloying with copper enhances the mechanical strength without depreciating the corrosion resistance.
- Addition of impurity atoms to a metal will result in the formation of a solid solution or a new second phase.
- A solid solution forms when, solute atoms are added to the host material, the crystal structure is maintained, and no new structures are formed.
  - ✓ Solute are element present in a minor concentration.
  - ✓ Solvent or host atoms are element present in the greatest amount.

Now we are going to discuss about the impurity, impurity atoms are added intentionally in alloys to impart specific characteristics of the materials, yes of course, sometimes by knowingly or maybe sometimes by unknowingly we are adding the impurities to the systems or maybe the to the matrix or maybe the to the alloys or maybe composites, sometimes we are adding the materials by knowing variations or maybe the by knowing compositions to increase certain properties, sometimes we are preparing the composites we are adding so many constituents, through that constituents also some impurity unknowingly it is coming into the system, alloying is used in metals to improve the mechanical strength and corrosion resistance, so if I give an example of the standing silver it is made of 92.5% silver with 7.5% copper alloy, if I give an example of the gold ornaments generally we are not using the 100% gold over there, because otherwise it will not be malleable, to make the gold into the malleable format we are adding some kind of materials into it, so that it can be malleable.

Alloying with copper enhances the mechanical strength without depreciating the corrosion resistance in case of the sterling silver, additions of impurity atoms to a metal will result in the formation of the solid solutions or maybe new second phase, so generally in a systems I am having the host atom and then from outside I am adding another third party atom, so a solid solution forms when the solid atoms are added to the host material, so a solute atoms is the third party materials, the crystal structure is maintained and no new structures are formed, so generally there are two ends solute are element present in a minor concentrations, so whatever the impurity I am adding that concentrations or maybe quantity is very very less.



- A solid solution is also compositionally homogeneous.

Solid solution formation depends on

- Kinds of impurity
- Concentrations
- Temperature of the alloy

Types of Impurity

Substitutional:

- Solute or impurity atoms replace or substitute for host atoms.

Interstitial:

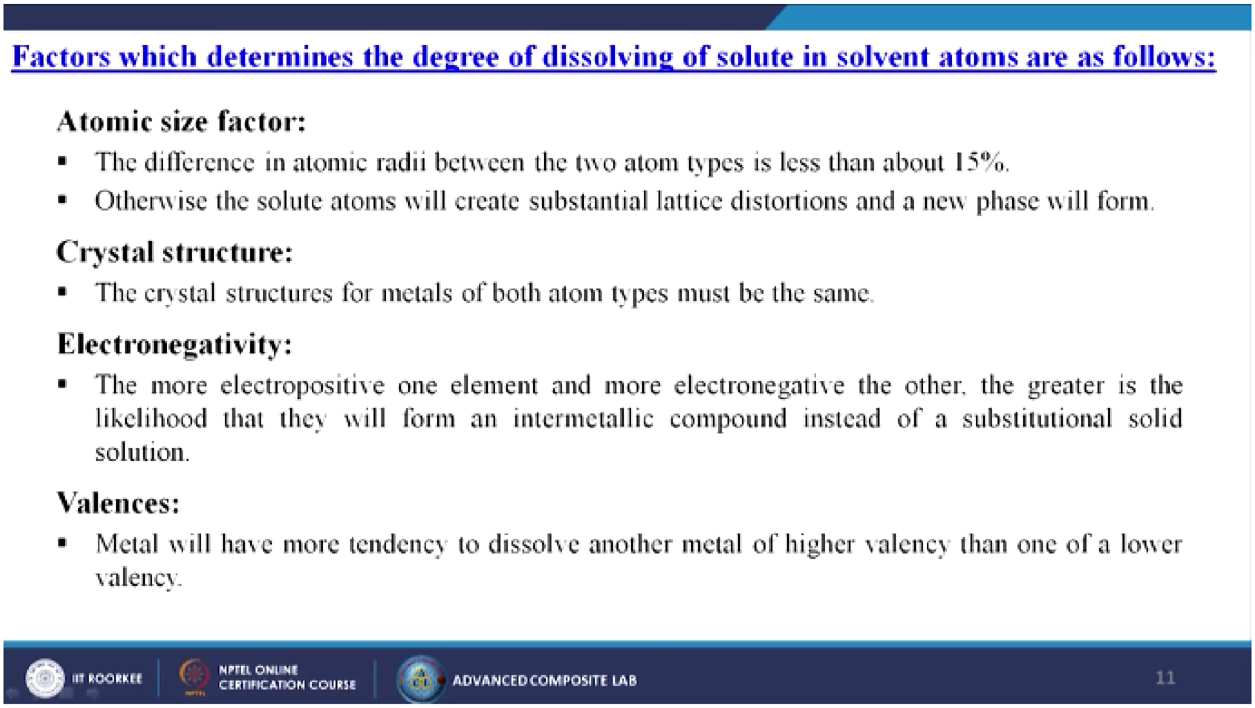
- Impurity atoms fill voids or interstices among the host atoms.
- Interstitial positions are small for metallic materials that have high atomic packing factors.
- Atomic diameter of an interstitial impurity is smaller than the host atoms.
- Solid solutions are also possible for ceramic materials.

Two-dimensional representations of substitutional and interstitial impurity atoms.

Another one solvent or host atoms of course there numbers are in very large or maybe the greatest amount, so a solid solutions is also compositionally homogeneous, so solid solution formations generally it depends on three characteristics, one is called the kinds of impurity, then concentrations and the temperature of the alloy, right hand side you can see that when we are talking about the solid solution of the zinc in copper so you can see they are perfectly in order, but when we are talking about the compounds, the atoms are very closely packed but they are not in order, so that is the basic difference in between the solid solutions and the compound.

Now if see about the impurity, there are two types of impurity, one is called the substitutional, another is called the interstitial, so from the name itself for substitutional we can understand that it is substituting some atom, so solute or impurity atoms replace or substitute for host atoms, so simple there is some host atoms but the impurity atoms it is substituting the host atoms inside the crystal structure, and when you are talking about the interstitial so impurity atoms feel voids or interstices among the host atoms, so here you can see there is certain gap, in between that gap the impurity atom is taking place or maybe it is taking that area.

Interstitial positions are small for metallic materials that have high atomic packing factors because they are very closely packed, so in between the atoms the gaps are or maybe the places are very very small, atomic diameter of an interstitial impurity is smaller than the host atoms, solid solutions are also possible for ceramic materials.



Factors which determines the degree of dissolving of solute in solvent atoms are as follows:

Atomic size factor:

- The difference in atomic radii between the two atom types is less than about 15%.
- Otherwise the solute atoms will create substantial lattice distortions and a new phase will form.

Crystal structure:

- The crystal structures for metals of both atom types must be the same.

Electronegativity:

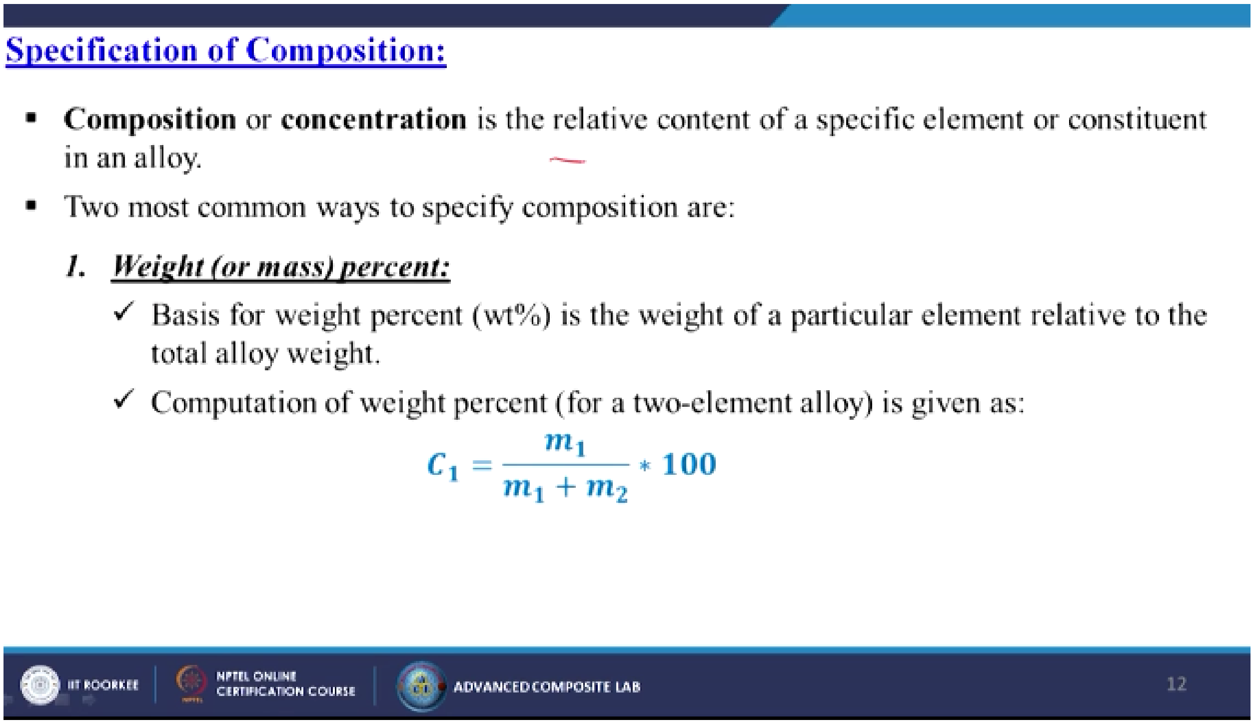
- The more electropositive one element and more electronegative the other, the greater is the likelihood that they will form an intermetallic compound instead of a substitutional solid solution.

Valences:

- Metal will have more tendency to dissolve another metal of higher valency than one of a lower valency.

Now what are the factors which determines the degree of dissolving of solute in solvent atoms are as follows, first is called the atomic size factor, the difference in atomic radii between the two atoms types is less than about 15%, otherwise the solute atoms will create substantial lattice distortions and a new phase will form but this is only valid for the substitutional impurity not the interstitial one.

Then crystal structure, the crystal structure for metals of both atoms types must be the same, then electronegativity, the more electropositive one element and more electronegative the other, the greater is the likelihood that they will form an intermetallic compound instead of a substitutional solid solutions, then valances, metal will have more tendency to dissolve another metal of higher valency than one of a lower valency, so these all are the important parameters, suppose when we are trying to make any kind of new composites or maybe trying to do the doping or maybe some kind of insertions of the impurities into some waste metals, so generally these all are the factors which we are, we need to look and then based on that we have to choose the proper materials and or maybe the impurities and we have to insert them into the host material.



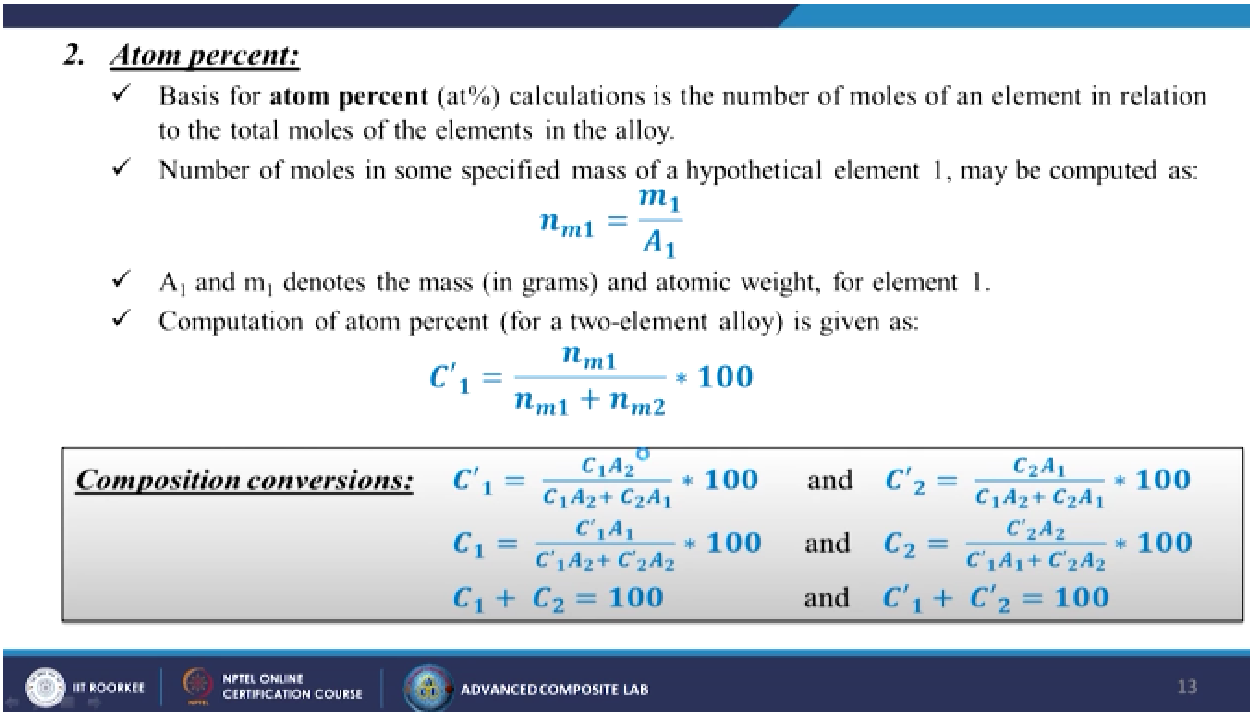
Specification of Composition:

- **Composition** or **concentration** is the relative content of a specific element or constituent in an alloy.
- Two most common ways to specify composition are:

1. ***Weight (or mass) percent:***
   - ✓ Basis for weight percent (wt%) is the weight of a particular element relative to the total alloy weight.
   - ✓ Computation of weight percent (for a two-element alloy) is given as:

$$C_1 = \frac{m_1}{m_1 + m_2} * 100$$

So now what is the specification of the compositions, so what is compositions? So compositions or concentrations is the relative content of a specific element or constituent in an alloy, there are two most common ways to specify the compositions, one is called the weight percent, another one is called the atom percent, so what is weight percent? Basis for weight percent is the weight of a particular element relative to the total alloy weight, computation of weight percent for a two element alloy is given as C1 = M1/M1+M2 x 100, however M1 is for the one element and M2 for the second element.



2. ***Atom percent:***
   - ✓ Basis for **atom percent** (at%) calculations is the number of moles of an element in relation to the total moles of the elements in the alloy.
   - ✓ Number of moles in some specified mass of a hypothetical element 1, may be computed as:

$$n_{m1} = \frac{m_1}{A_1}$$

   - ✓ A_1 and m_1 denotes the mass (in grams) and atomic weight, for element 1.
   - ✓ Computation of atom percent (for a two-element alloy) is given as:

$$C'_1 = \frac{n_{m1}}{n_{m1} + n_{m2}} * 100$$

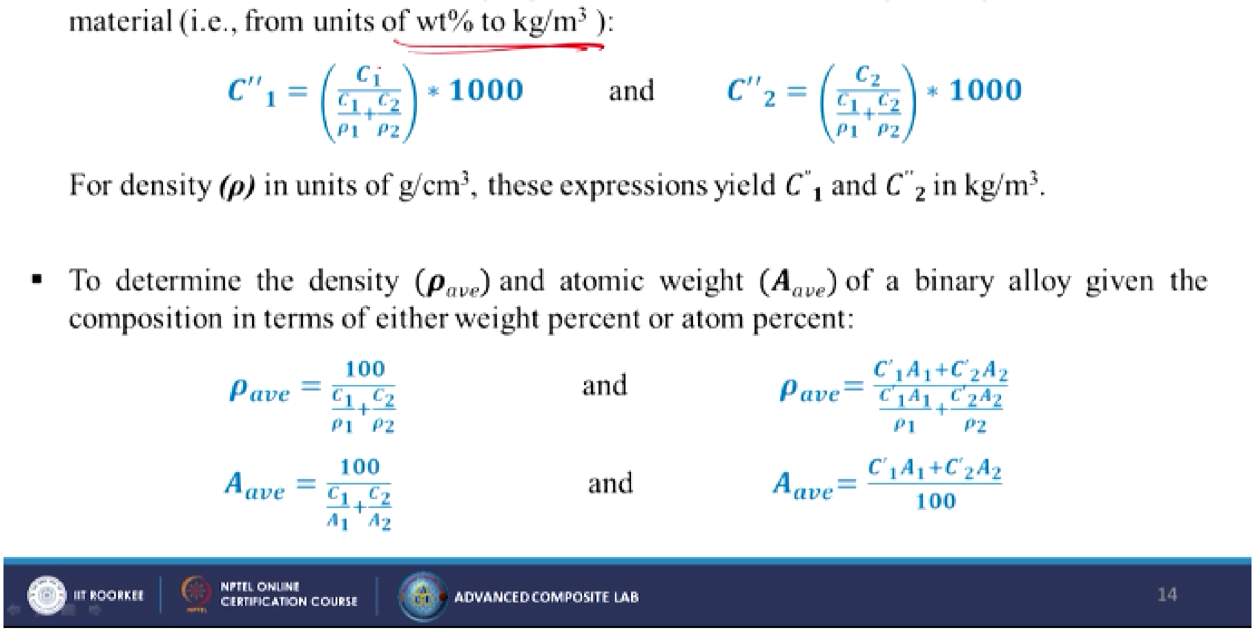
Composition conversions:

$$C'_1 = \frac{C_1A_2}{C_1A_2 + C_2A_1} * 100 \quad \text{and} \quad C'_2 = \frac{C_2A_1}{C_1A_2 + C_2A_1} * 100$$

$$C_1 = \frac{C'_1A_1}{C'_1A_2 + C'_2A_2} * 100 \quad \text{and} \quad C_2 = \frac{C'_2A_2}{C'_1A_1 + C'_2A_2} * 100$$

$$C_1 + C_2 = 100 \quad \text{and} \quad C'_1 + C'_2 = 100$$

And now when we are talking about the atom percent, so the basis for atom percent calculation is the number of moles of an element in relation to the total moles of the elements in the alloy itself, so number of moles in some specified mass of a hypothetical element one maybe computed as NM1 = M1/A1, so here A1 and M1 denotes the mass in grams and atomic weight for element 1, so computation of atom percent for a two element alloy is given as C1 prime = NM1/NM1 + NM2 x 100, so if we are going to calculate the percentage, weight percentage of different element or maybe the atom percent of different element so we can get like C1 prime = C1 A2/ C1 A2 + C2 A1 x 100 and C1 = C1 prime x A1/C1 prime A2 + C2 prime A2 x 100, but any of the cases C1 + C2 because total composition constituent is 100, so of course C1 + C2 will be 100 or maybe C1 prime + C2 prime will be 100.



- Convert concentration from weight percent to mass of one component per unit volume of material (i.e., from units of wt% to kg/m³):

$$C''_1 = \left(\frac{C_1}{\frac{C_1}{\rho_1}+\frac{C_2}{\rho_2}}\right) * 1000 \qquad \text{and} \qquad C''_2 = \left(\frac{C_2}{\frac{C_1}{\rho_1}+\frac{C_2}{\rho_2}}\right) * 1000$$

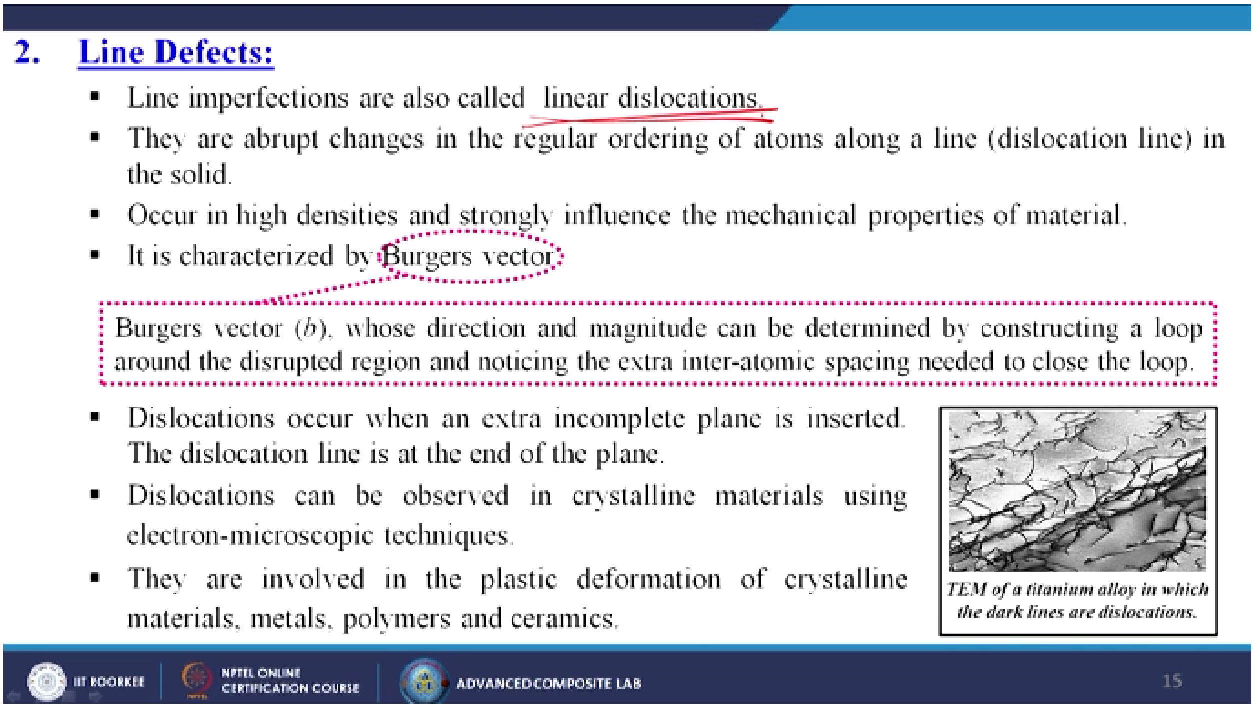
For density ***(ρ)*** in units of g/cm³, these expressions yield C''_1 and C''_2 in kg/m³.

- To determine the density (ρ_{ave}) and atomic weight (A_{ave}) of a binary alloy given the composition in terms of either weight percent or atom percent:

$$\rho_{ave} = \frac{100}{\frac{C_1}{\rho_1}+\frac{C_2}{\rho_2}} \qquad \text{and} \qquad \rho_{ave} = \frac{C'_1A_1+C'_2A_2}{\frac{C'_1A_1}{\rho_1}+\frac{C'_2A_2}{\rho_2}}$$

$$A_{ave} = \frac{100}{\frac{C_1}{A_1}+\frac{C_2}{A_2}} \qquad \text{and} \qquad A_{ave} = \frac{C'_1A_1+C'_2A_2}{100}$$

Now convert that concentrations from weight percent to mass of one component per unit volume of material, so from units of weight percent to the KG per meter cube, the conversions is C1 double prime = C1/C1/rho 1 + C2/rho 2 x 1000 and C2 double prime = C2/C1/rho 1 + C2/rho 2 x 1000, so for density rho in units of grams per centimeter cube this expressions yield C1 double prime and C2 double prime in KG per meter cube, so like this way we can calculate the average means rho average, density average and the atomic weight average of that particular atoms or maybe the constituents.



2. Line Defects:

- Line imperfections are also called linear dislocations.
- They are abrupt changes in the regular ordering of atoms along a line (dislocation line) in the solid.
- Occur in high densities and strongly influence the mechanical properties of material.
- It is characterized by Burgers vector.

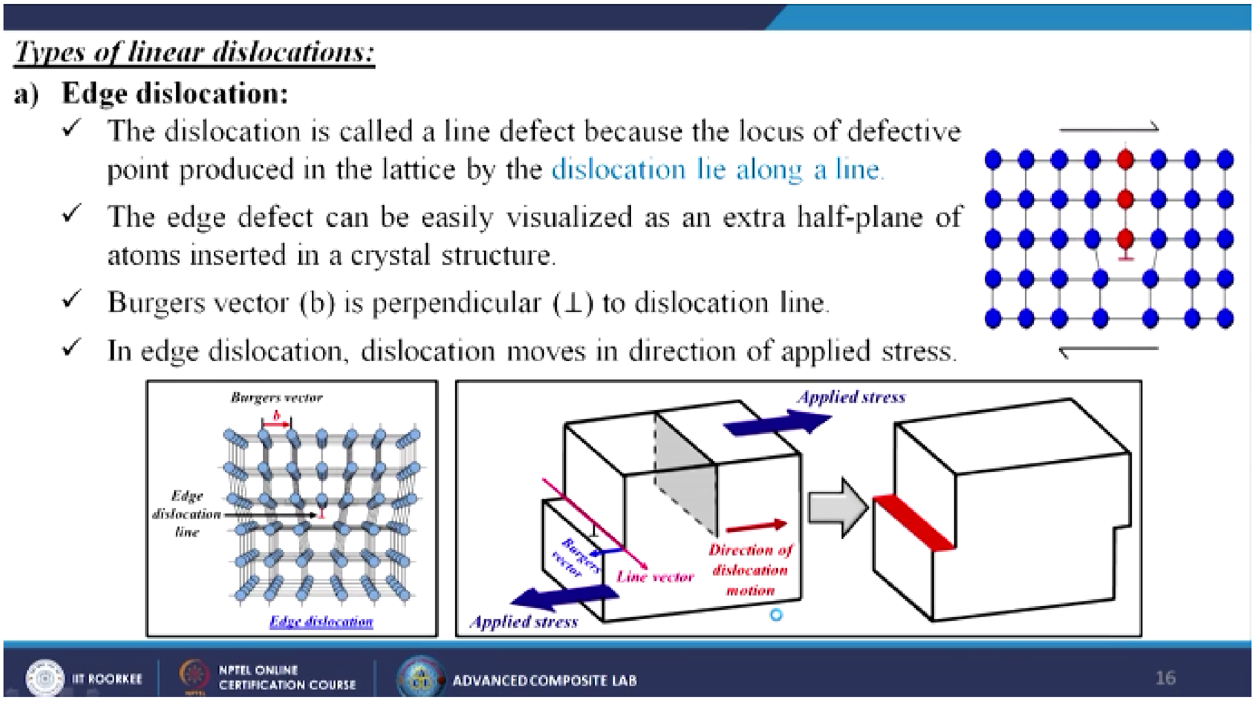
Burgers vector (b), whose direction and magnitude can be determined by constructing a loop around the disrupted region and noticing the extra inter-atomic spacing needed to close the loop.

- Dislocations occur when an extra incomplete plane is inserted. The dislocation line is at the end of the plane.
- Dislocations can be observed in crystalline materials using electron-microscopic techniques.
- They are involved in the plastic deformation of crystalline materials, metals, polymers and ceramics.

TEM of a titanium alloy in which the dark lines are dislocations.

Now we are going to discuss about the line defects, so generally from the name itself we can understand the defects will take place along a line or maybe it looks like a line inside the crystal structure, so line imperfections are also called the linear dislocations, they are abrupt changes in the regular ordering of atoms along a line or maybe the dislocation line in the solids, occur in high densities and strongly influence the mechanical properties of materials, it is characterized by the Burgers vector, the name of the scientist is Burgers who has invented this one, so what is the Burgers vector? Burgers vector tell us that whose directions and magnitude can be determined by constructing a loop around the disrupted region and noticing the extra interatomic spacing needed to close the loop.

Dislocations occur when an extra incomplete plane is inserted, the dislocation line is at the end of the plane itself, so this can be proved by the transmission electron microscope image of the titanium alloy where we can find that there is some black color, dark black color lines are present which is known as the dislocations of that particular alloy. So dislocations can be observed in crystalline materials using the electron-microscopy techniques like edge or tem, or maybe the tem, or maybe the scanning electron microscopy, or maybe that find FEACM, they are involved in the plastic deformations of crystalline materials, metals, polymers, and the ceramics.

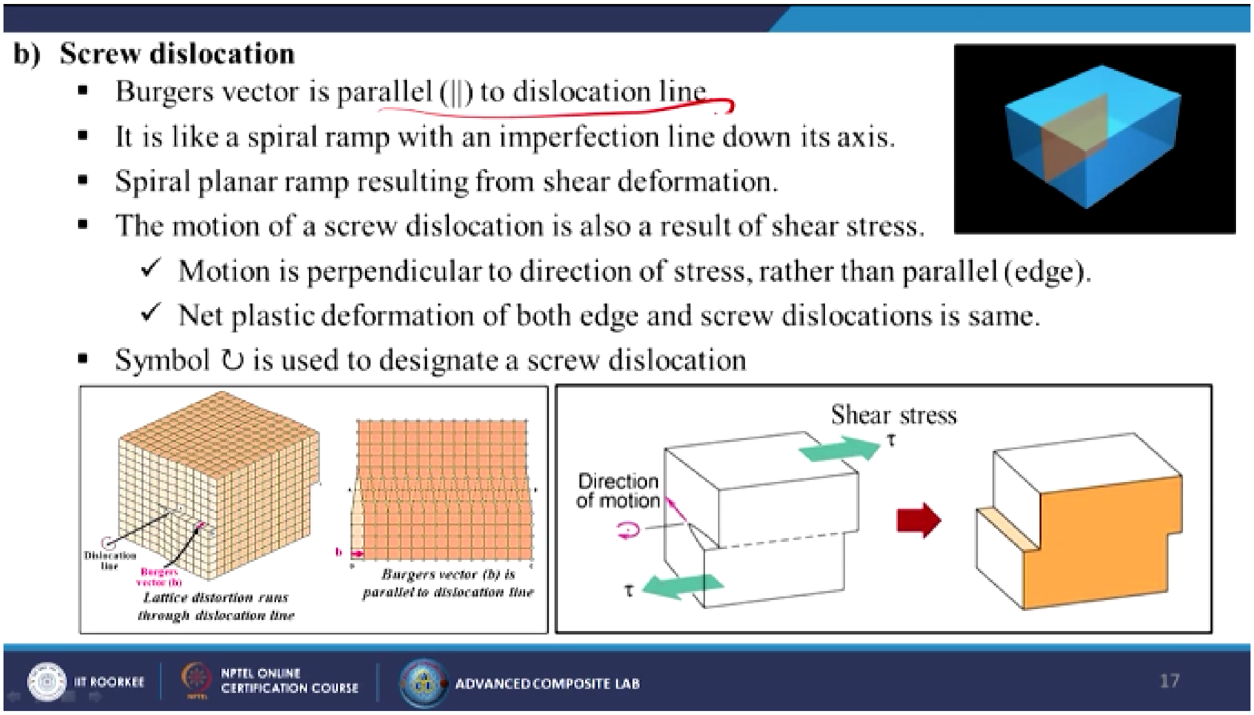


Types of linear dislocations:

a) Edge dislocation:

- ✓ The dislocation is called a line defect because the locus of defective point produced in the lattice by the dislocation lie along a line.
- ✓ The edge defect can be easily visualized as an extra half-plane of atoms inserted in a crystal structure.
- ✓ Burgers vector (b) is perpendicular (⊥) to dislocation line.
- ✓ In edge dislocation, dislocation moves in direction of applied stress.

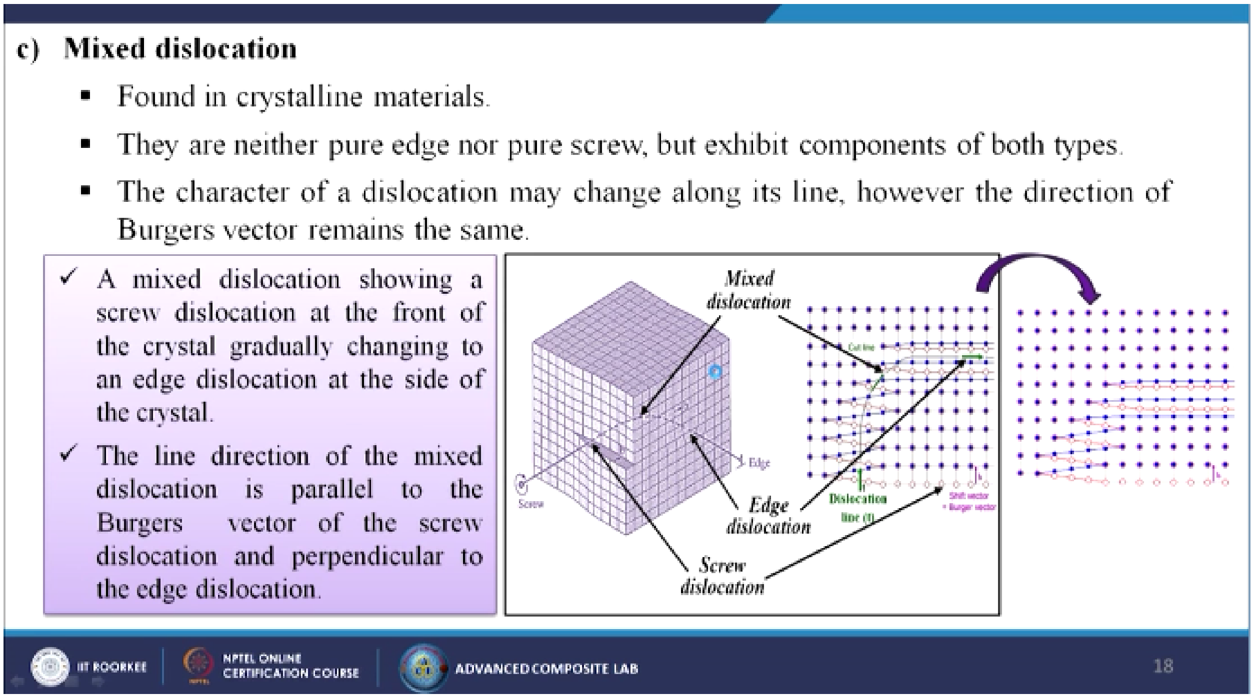
Now there are several types of that linear dislocations, so first is called the edge dislocations, so what is edge dislocations? The dislocations is called the line defect because the locus of defective point produced in the lattice by the dislocation lie along a line itself, so here you can see that dislocation it’s in a line and it has been shifted, so anywhere it can be presented inside the material. The edge defect can be easily visualized as an extra half-plane of atoms inserted in a crystal structure, so extra half-plane you can see that red in color and it is shifting. Burger vector which is denoted by the small b is perpendicular to dislocations line, so in this particular case so this is your line vector and burger vector is here which is exactly the perpendicular to that line vector.



b) Screw dislocation

- Burgers vector is parallel (||) to dislocation line
- It is like a spiral ramp with an imperfection line down its axis.
- Spiral planar ramp resulting from shear deformation.
- The motion of a screw dislocation is also a result of shear stress.
  - ✓ Motion is perpendicular to direction of stress, rather than parallel (edge).
  - ✓ Net plastic deformation of both edge and screw dislocations is same.
- Symbol ↻ is used to designate a screw dislocation

So now second is the screw dislocations, so Burgers vectors in this case is parallel to the dislocation line, so in this case the dislocation lines if you see the dislocations line over here and Burger vector is here, so almost it is parallel to the dislocations line, it is like a spiral ramp with an imperfection line down its axis, so in this case you can see that two surface it is like, so it’s a spring type of arrangement is taking place, so a first is a plane is created and then after that it is divided into two parts, the motion of a screw dislocations is also called a result of shear stress, how? The motion is perpendicular to direction of stress rather than parallel edge, net plastic deformation of both edge and screw dislocations is same, so symbol, by this symbol generally it is used to designate a screw dislocation.



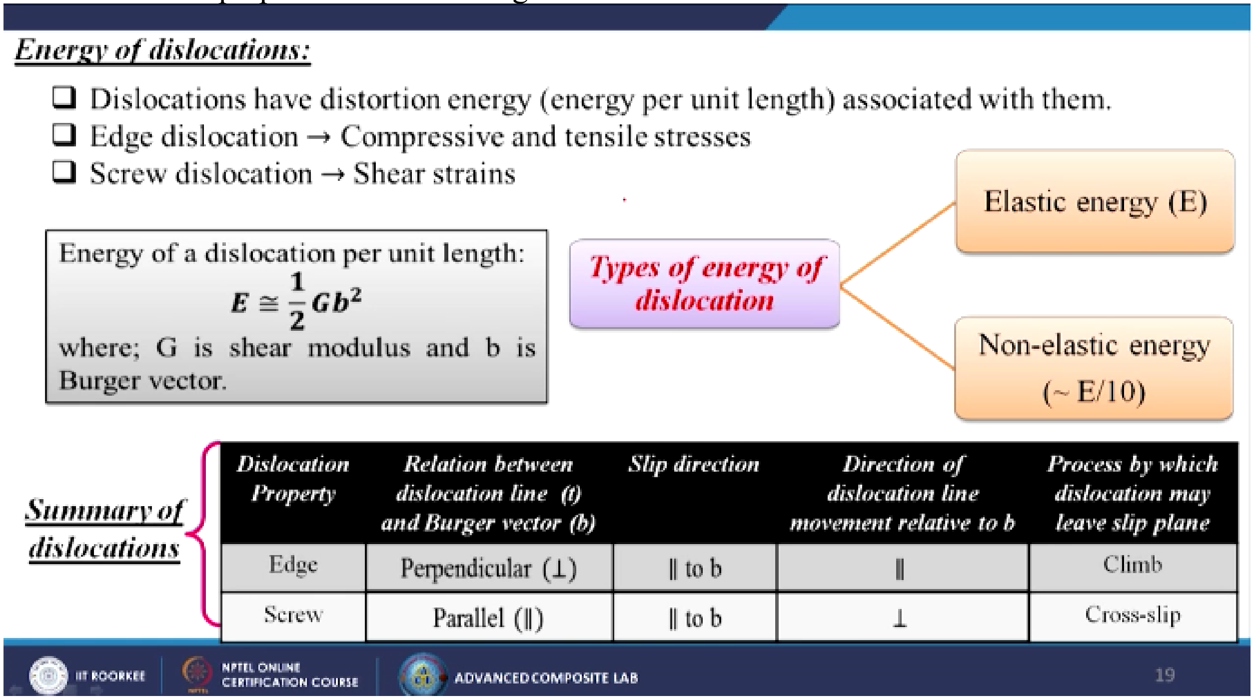
c) Mixed dislocation

- Found in crystalline materials.
- They are neither pure edge nor pure screw, but exhibit components of both types.
- The character of a dislocation may change along its line, however the direction of Burgers vector remains the same.

✓ A mixed dislocation showing a screw dislocation at the front of the crystal gradually changing to an edge dislocation at the side of the crystal.

✓ The line direction of the mixed dislocation is parallel to the Burgers vector of the screw dislocation and perpendicular to the edge dislocation.

Now the third one is called the mixed dislocations where we can found the both, so found in crystalline materials, they are neither pure edge nor pure screw, but exhibit components of both types over there, the character of a dislocation may change along its line, however the direction of Burger vector remains the same, so in a mixed dislocations when your screw dislocation at the front of the crystal gradually changing to an edge dislocation at the side of the crystal itself, so from screw it is starting and then at the last it is showing the edge dislocations over there, so that the line directions of the mixed dislocation is parallel to the Burger vector of the screw dislocations and perpendicular to the edge dislocation.



Energy of dislocations:

- ☐ Dislocations have distortion energy (energy per unit length) associated with them.
- ☐ Edge dislocation → Compressive and tensile stresses
- ☐ Screw dislocation → Shear strains

Energy of a dislocation per unit length:

$$E \cong \frac{1}{2}Gb^2$$

where; G is shear modulus and b is Burger vector.

Types of energy of dislocation

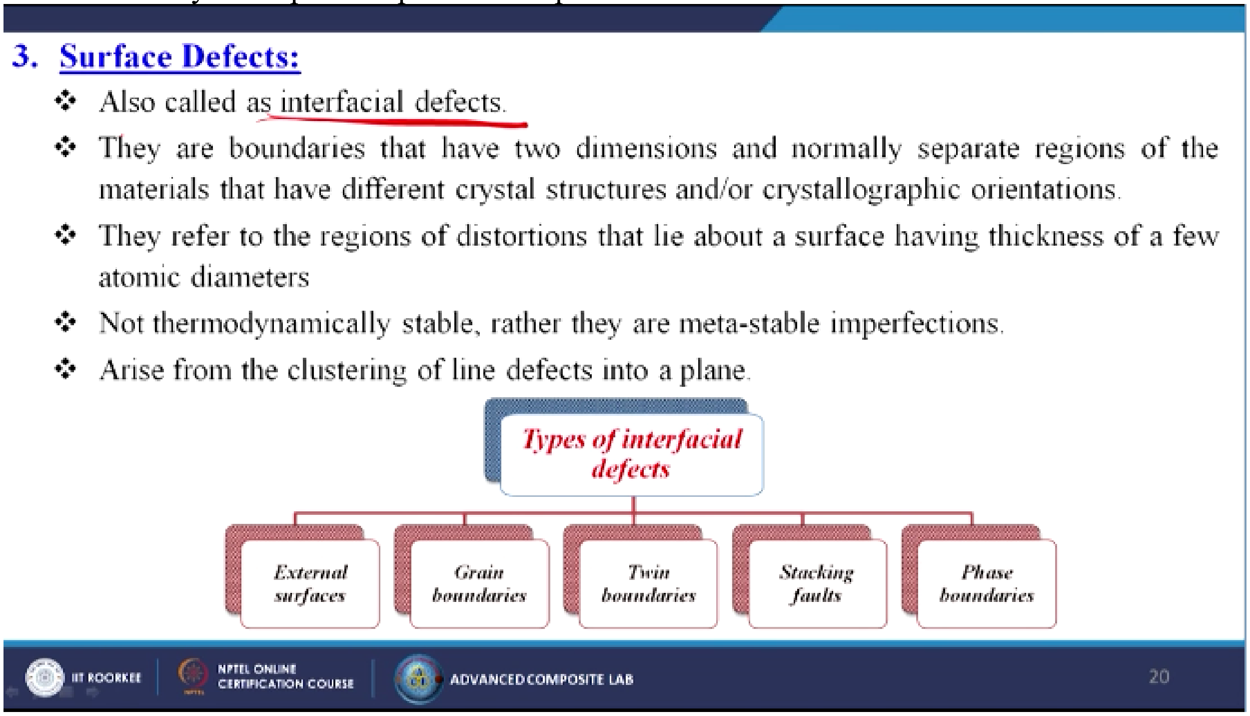
Elastic energy (E)

Non-elastic energy (~ E/10)

Summary of dislocations

Dislocation Property	*Relation between dislocation line (t) and Burger vector (b)*	*Slip direction*	*Direction of dislocation line movement relative to b*	*Process by which dislocation may leave slip plane*
Edge	Perpendicular (⊥)	‖ to b	‖	Climb
Screw	Parallel (‖)	‖ to b	⊥	Cross-slip

Next energy of dislocations, so dislocations have distortion energy, energy per unit length associated with them. So generally edge dislocations which is in compressive and the tensile stresses and screw dislocations is mainly for the shear strains, so energy of a dislocations per unit length E is more or less equal to 1/2 GB square, so what is G? G is a shear modulus and B is the Burger vector, so there are two types of generally energy for the dislocations, one is called the elastic energy, another one is called the non-elastic energy which is more or less E divided by tem, so summary of the dislocations if we go through which I have already told you, so if we go for the edge it is perpendicular because the dislocations line and the Burger vector or the perpendicular slip directions is parallel to Burger vector, direction of dislocation line movement related to B is parallel, process by which dislocation may leave slip plane is climb, and screw it is parallel, then parallel to B it is perpendicular in nature and the process by which the dislocation may leave plane slip is cross slip.



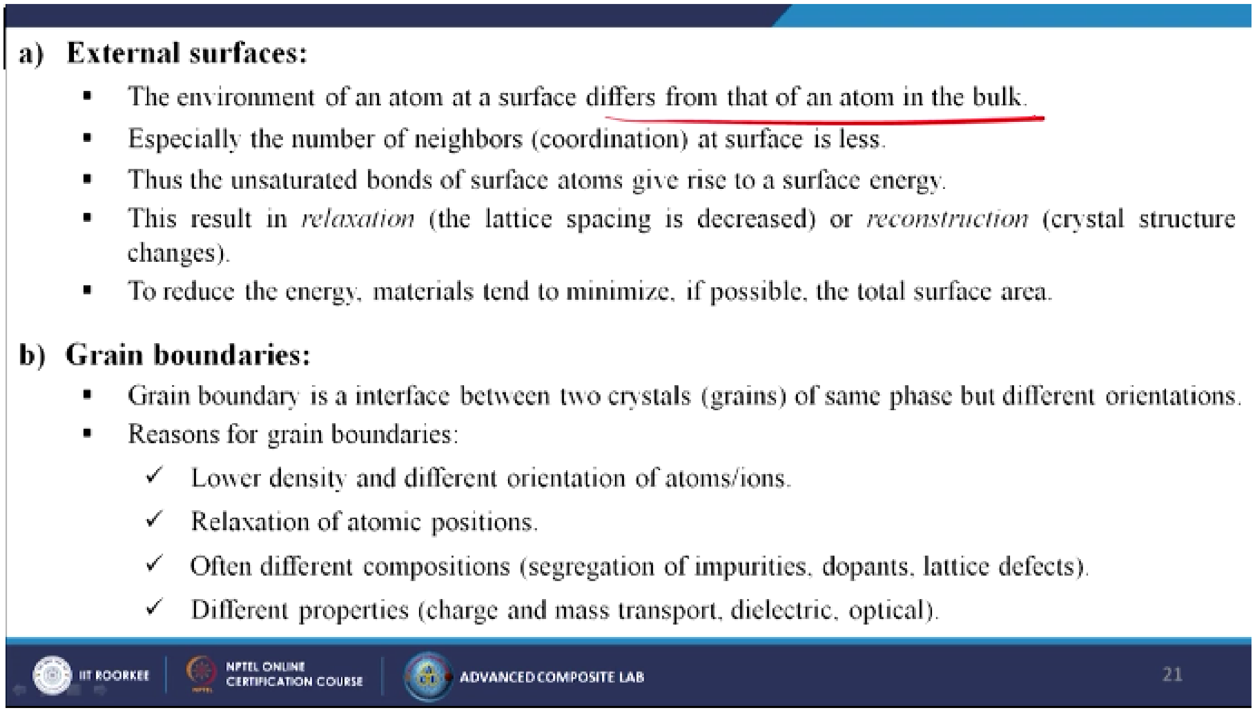
3. Surface Defects:

- Also called as interfacial defects.
- They are boundaries that have two dimensions and normally separate regions of the materials that have different crystal structures and/or crystallographic orientations.
- They refer to the regions of distortions that lie about a surface having thickness of a few atomic diameters
- Not thermodynamically stable, rather they are meta-stable imperfections.
- Arise from the clustering of line defects into a plane.

Types of interfacial defects

- *External surfaces*
- *Grain boundaries*
- *Twin boundaries*
- *Stacking faults*
- *Phase boundaries*

Now we are going to discuss about the surface defects, so generally also called as the interfacial defects, surface defects is also sometimes known as interfacial defects, they are boundaries that have two dimensions and normally separate regions of the materials that have different crystal structures and/or crystallographic orientations, they refer to the regions of distortions that lie about a surface having thickness of a few atomic diameters, not thermodynamically stable, rather they are meta-stable imperfections, arise from the clustering of line defects into a plane, so there are several types of interfacial defects are present, so first one is called the external surfaces, then grain boundaries, then twin boundaries, then stacking faults and last one is called the phase boundaries.



a) External surfaces:

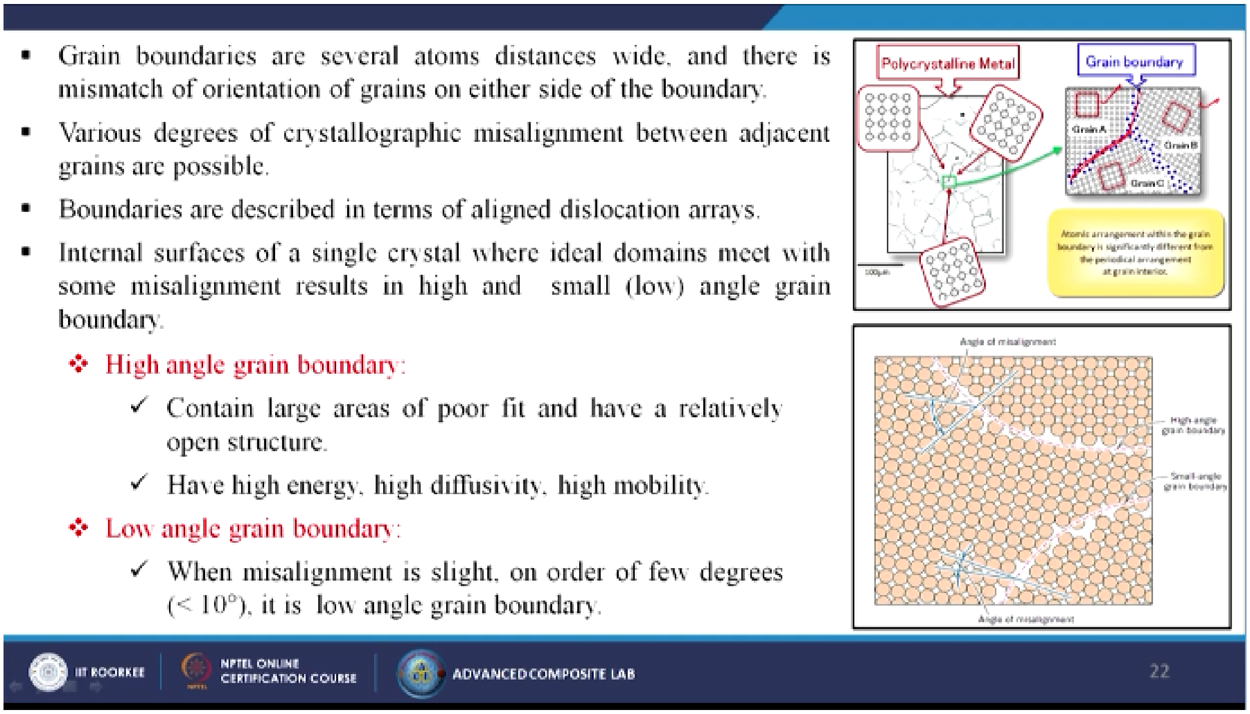
- The environment of an atom at a surface differs from that of an atom in the bulk.
- Especially the number of neighbors (coordination) at surface is less.
- Thus the unsaturated bonds of surface atoms give rise to a surface energy.
- This result in *relaxation* (the lattice spacing is decreased) or *reconstruction* (crystal structure changes).
- To reduce the energy, materials tend to minimize, if possible, the total surface area.

b) Grain boundaries:

- Grain boundary is a interface between two crystals (grains) of same phase but different orientations.
- Reasons for grain boundaries:
  - ✓ Lower density and different orientation of atoms/ions.
  - ✓ Relaxation of atomic positions.
  - ✓ Often different compositions (segregation of impurities, dopants, lattice defects).
  - ✓ Different properties (charge and mass transport, dielectric, optical).

So what is external surfaces? The environment of an atom at a surface defers from that of an atom in the bulk itself, especially the number of neighbors coordination at surface is less, thus the unsaturated bonds of surface atoms give rise to a surface energy, this results in relaxation, the lattice spacing is decreased or reconstructions crystal structure changes, to reduce the energy materials tend to minimize if possible the total surface area.

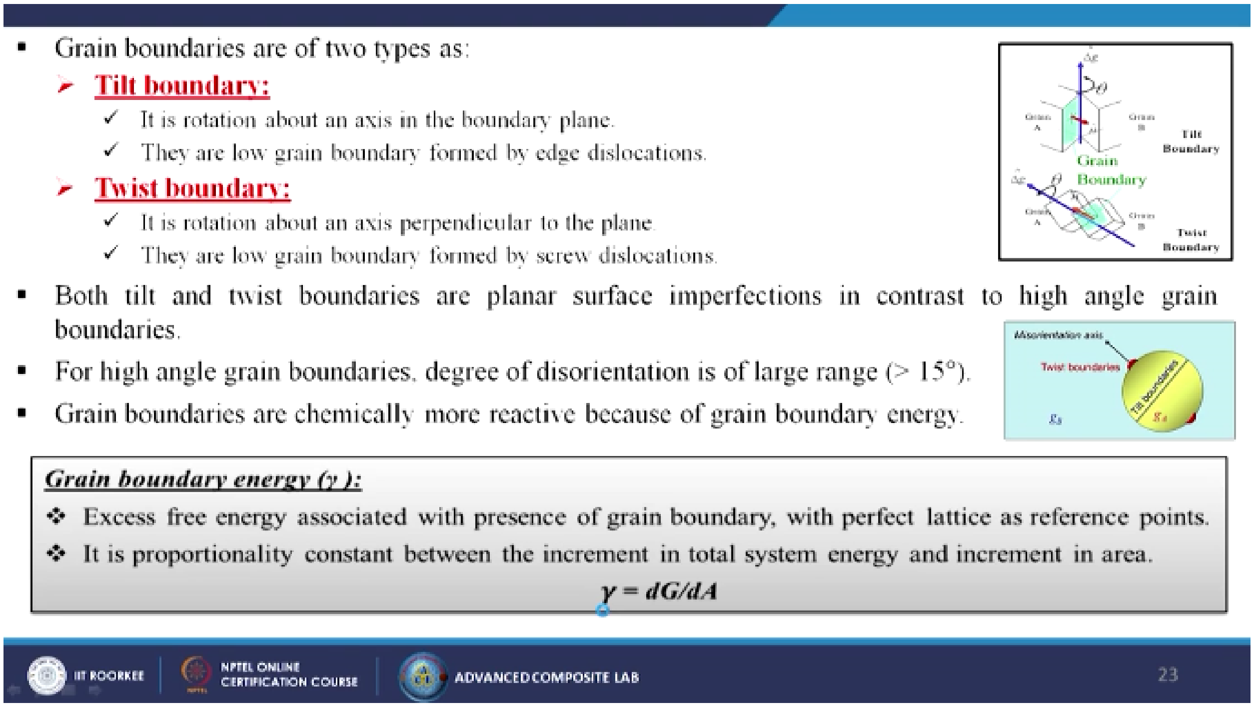
Next grain boundaries, so grain boundaries is a interface between two crystals or maybe the grains of same phase, but different orientations, means that is a one kind of boundary wall in between the two different grains, reasons for grain boundaries, lower density and different orientations of atoms or maybe the ions, relaxation of atomic positions, often different compositions that means segregations of the impurities, dopants, or maybe the lattice defects, and different properties like charge and mass transport or maybe the dielectric or maybe the optical. So grain boundaries in this particular case you can see that there are three types of grain boundaries, grains are present or rather I can say that grain A, grain B, grain C and these is known as the grain boundary because the characteristics of these three grains, the structure or maybe the properties are different.



- Grain boundaries are several atoms distances wide, and there is mismatch of orientation of grains on either side of the boundary.
- Various degrees of crystallographic misalignment between adjacent grains are possible.
- Boundaries are described in terms of aligned dislocation arrays.
- Internal surfaces of a single crystal where ideal domains meet with some misalignment results in high and small (low) angle grain boundary.
  - ❖ High angle grain boundary:
    - ✓ Contain large areas of poor fit and have a relatively open structure.
    - ✓ Have high energy, high diffusivity, high mobility.
  - ❖ Low angle grain boundary:
    - ✓ When misalignment is slight, on order of few degrees (< 10°), it is low angle grain boundary.

Grain boundaries are several atoms distance wide, and there is mismatch of orientation of grains on either side of the boundary itself, various degrees of crystallographic misalignment between adjacent grains are possible, boundaries are described in terms of aligned dislocations arrays, internal surfaces of a single crystal where ideal domains meet with some misalignment results in high and small angle grain boundary, so there are generally two types of grain boundary, one is called the small angle grain boundary or maybe the low angle grain boundary, another one is called the high angle grain boundary, so when you are talking about the high angle grain boundary, so in this image you can see that this is known as the high angle grain boundary, and this is the small angle grain boundary, how? High angle grain boundary contain large areas of poor fit and have a relatively open structure, so in this case the angle of misalignment is more, so that’s why it is called the high angle grain boundary, and in this case the angle of misalignment is less, so that’s why it is called the low angle grain boundary.

Then high angle grain boundary have high energy, high diffusivity and high mobility, and for the low angle grain boundary when misalignment is slight on order of few degrees less than 10 degree means area of misalignment it is low angle grain boundary.



- Grain boundaries are of two types as:
  - **Tilt boundary:**
    - ✓ It is rotation about an axis in the boundary plane.
    - ✓ They are low grain boundary formed by edge dislocations.
  - **Twist boundary:**
    - ✓ It is rotation about an axis perpendicular to the plane.
    - ✓ They are low grain boundary formed by screw dislocations.
- Both tilt and twist boundaries are planar surface imperfections in contrast to high angle grain boundaries.
- For high angle grain boundaries, degree of disorientation is of large range (> 15°).
- Grain boundaries are chemically more reactive because of grain boundary energy.

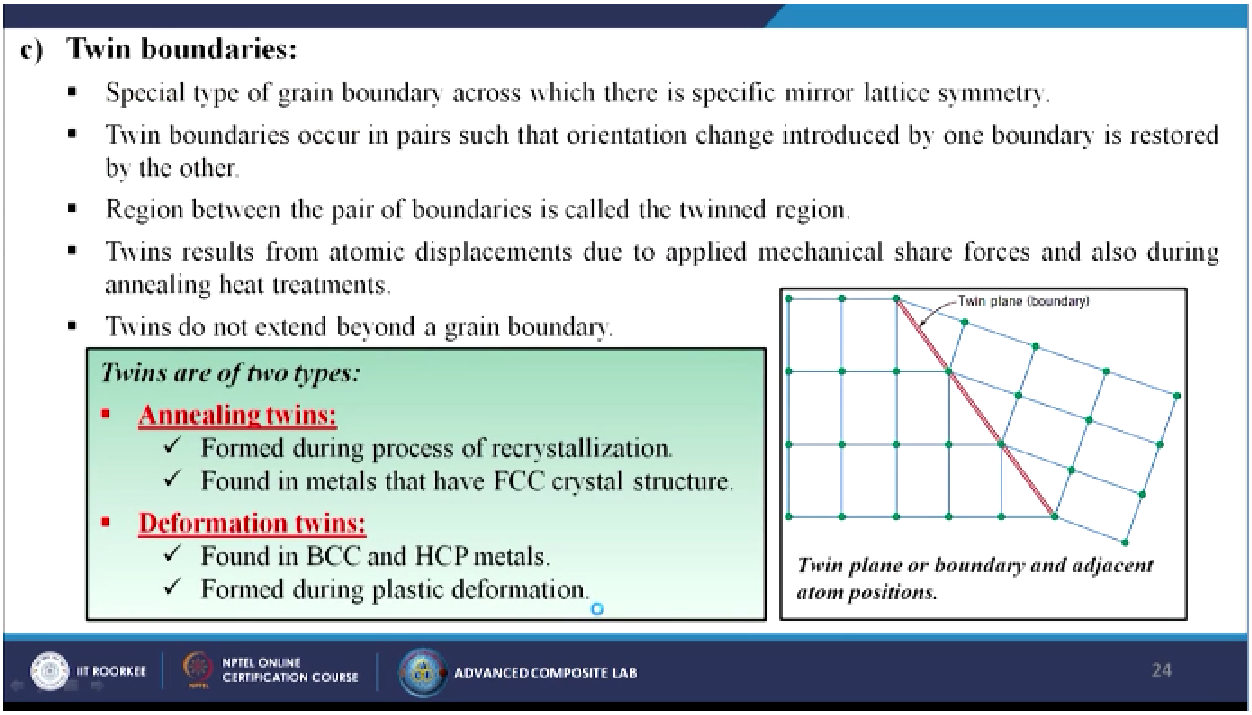
Grain boundary energy (γ):

- ❖ Excess free energy associated with presence of grain boundary, with perfect lattice as reference points.
- ❖ It is proportionality constant between the increment in total system energy and increment in area.

$$\gamma = dG/dA$$

Now there are grain boundaries that is also for two types as tilt boundary, another one is called the twist boundary, so in the tilt boundary you can see that the grain boundary it has been tilted with some angle, and twisted means there is certain kind of rotations in between the grain boundaries, so when we are talking about the tilt boundary it is rotations about an axis in the boundary plane, so this is the axis and through which the rotation is taking place, they are low grain boundary formed by the edge dislocations, and when you are talking about the twist boundary, so it is rotation about an axis perpendicular to the plane, so this axis is totally perpendicular to the plane itself, they are low grain boundary formed by screw dislocations, both tilt and twist boundaries are planar surface imperfections in contrast to high angle grain boundaries, for high angle grain boundaries degree of disorientations is of large range that is more than 15 degree.

Grain boundaries are chemically more reactive because of grain boundary energy, and what is grain boundary energy? Generally it is denoted by the gamma, so excess free energy associated with the presence of grain boundary with perfect lattice as reference points, it is proportionality constant between the increment in total system energy and increment in area, so gamma = DG/DA.



c) Twin boundaries:

- Special type of grain boundary across which there is specific mirror lattice symmetry.
- Twin boundaries occur in pairs such that orientation change introduced by one boundary is restored by the other.
- Region between the pair of boundaries is called the twinned region.
- Twins results from atomic displacements due to applied mechanical share forces and also during annealing heat treatments.
- Twins do not extend beyond a grain boundary.

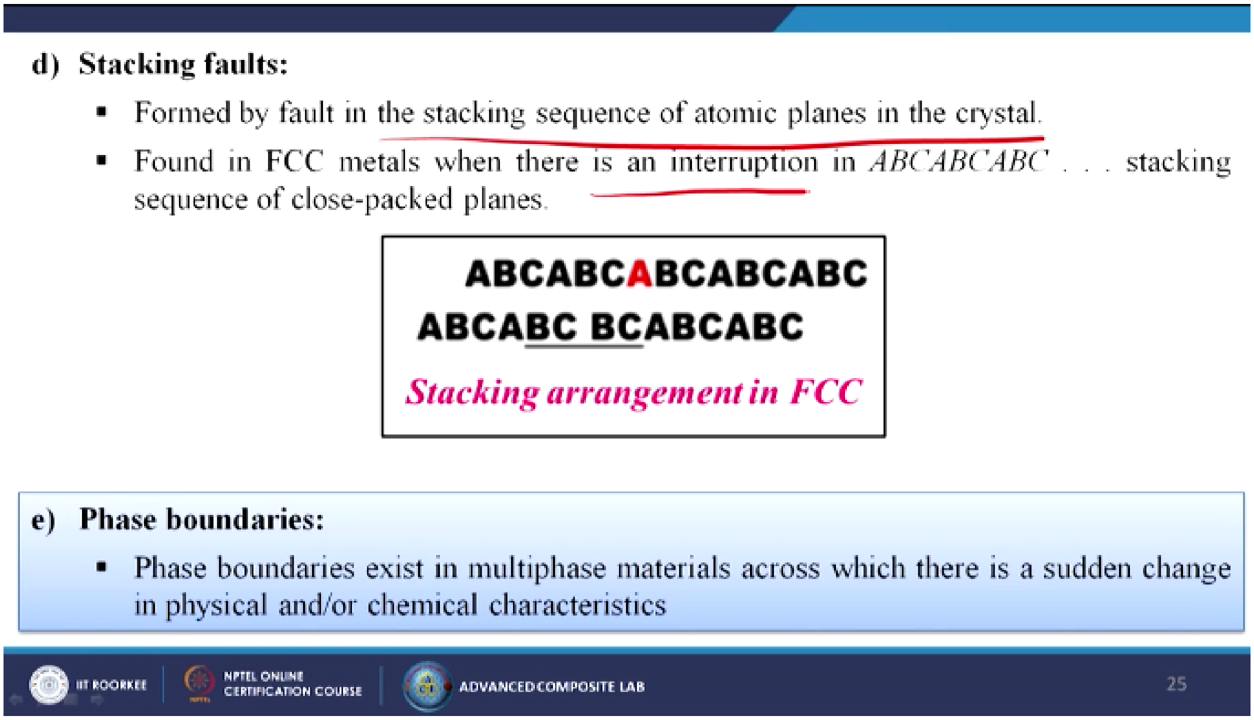
Twins are of two types:

- **Annealing twins:**
  - ✓ Formed during process of recrystallization.
  - ✓ Found in metals that have FCC crystal structure.
- **Deformation twins:**
  - ✓ Found in BCC and HCP metals.
  - ✓ Formed during plastic deformation.

Twin plane or boundary and adjacent atom positions.

Now we are going to discuss about the twin boundaries, so special type of grain boundary across which there is specific mirror lattice symmetry, so in this case this is known as the twin plane of that boundary, so mirror like image is taking place into the opposite side. Twin boundaries occur in pairs such that orientation change introduced by one boundary is restored by the other. Region between the pair of boundaries is called the twin region, so mirror image.

Twins results from atomic displacement due to applied mechanical share force and also during annealing heat treatment. Twin do not extend beyond a grain boundary, so twin are also two types, one is called the annealing twins and another one is called the deformation twins, so what is annealing twins? Formed during process of recrystallizations, found in metals that have FCC, face centered cubic crystal structure. Deformation twins found in the body centered cubic and HCP metals, and formed during the plastic deformation.



d) Stacking faults:

- Formed by fault in the stacking sequence of atomic planes in the crystal.
- Found in FCC metals when there is an interruption in *ABCABCABC . . .* stacking sequence of close-packed planes.

ABCABCABCABCABC
ABCABC BCABCABC

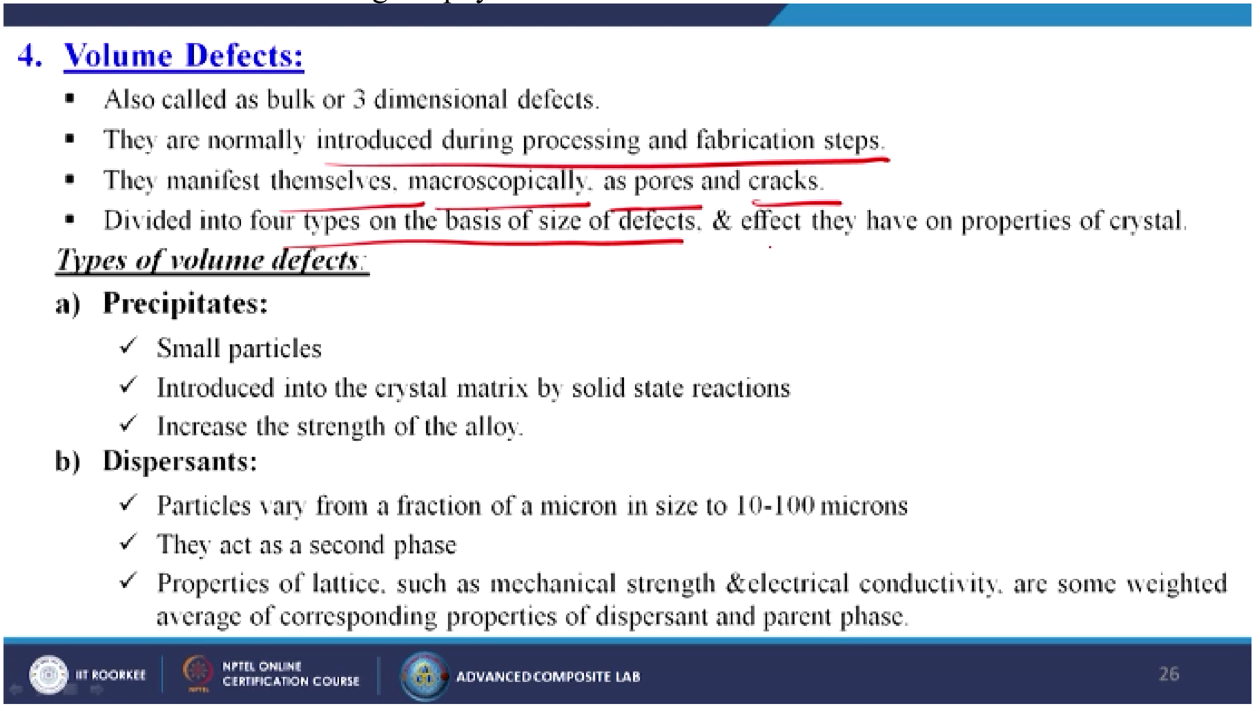
Stacking arrangement in FCC

e) Phase boundaries:

- Phase boundaries exist in multiphase materials across which there is a sudden change in physical and/or chemical characteristics

Next is called the stacking fault, so formed by fault in the stacking sequence of atomic planes in the crystal itself, found in FCC metals when there is an interruptions in ABC, ABC, ABC and so on, stacking sequence of close packed planes, so here you can see ABC, ABC, then this A is missing then BC, again ABC, ABC so this is known as the stacking faults, so generally the stacking arrangements of the FCC structure.

Then next is called the phase boundaries, phase boundaries exist in multiphase materials across which there is a sudden change in physical or chemical characteristics of the materials itself.



4. Volume Defects:

- Also called as bulk or 3 dimensional defects.
- They are normally introduced during processing and fabrication steps.
- They manifest themselves, macroscopically, as pores and cracks.
- Divided into four types on the basis of size of defects. & effect they have on properties of crystal.

Types of volume defects:

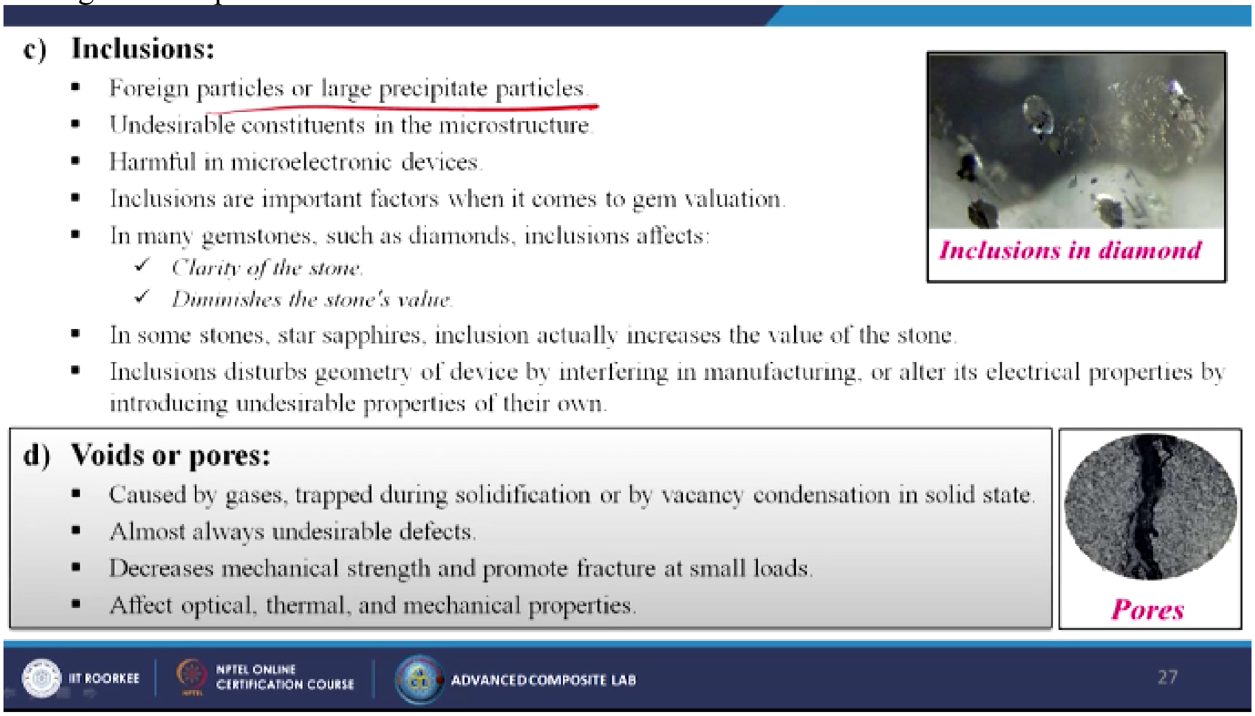
a) Precipitates:

- ✓ Small particles
- ✓ Introduced into the crystal matrix by solid state reactions
- ✓ Increase the strength of the alloy.

b) Dispersants:

- ✓ Particles vary from a fraction of a micron in size to 10-100 microns
- ✓ They act as a second phase
- ✓ Properties of lattice, such as mechanical strength &electrical conductivity, are some weighted average of corresponding properties of dispersant and parent phase.

Then volume defects, it is also called as a three dimensional defects or maybe the bulk defects, they are normally introduced during processing and fabrication steps, they manifest themselves microscopically as pores and cracks, divided into four types of the basis of size of defects and effect they have on properties of the crystal itself. So types of volume defects, first one is called the precipitates, what is that? Small particles, introduced into the crystal matrix by solid state reactions, increase the strength of the alloy. Then second one is called the dispersants, so particles vary from a fraction of a micron in size to 10 to 100 microns, they act as a second phase, the properties of lattice such as mechanical strength, electrical conductivity are some weighted average of corresponding properties of dispersant and parent phase, so that is the mixing both the phases.



c) Inclusions:

- Foreign particles or large precipitate particles.
- Undesirable constituents in the microstructure.
- Harmful in microelectronic devices.
- Inclusions are important factors when it comes to gem valuation.
- In many gemstones, such as diamonds, inclusions affects:
  - ✓ *Clarity of the stone.*
  - ✓ *Diminishes the stone's value.*
- In some stones, star sapphires, inclusion actually increases the value of the stone.
- Inclusions disturbs geometry of device by interfering in manufacturing, or alter its electrical properties by introducing undesirable properties of their own.

Inclusions in diamond

d) Voids or pores:

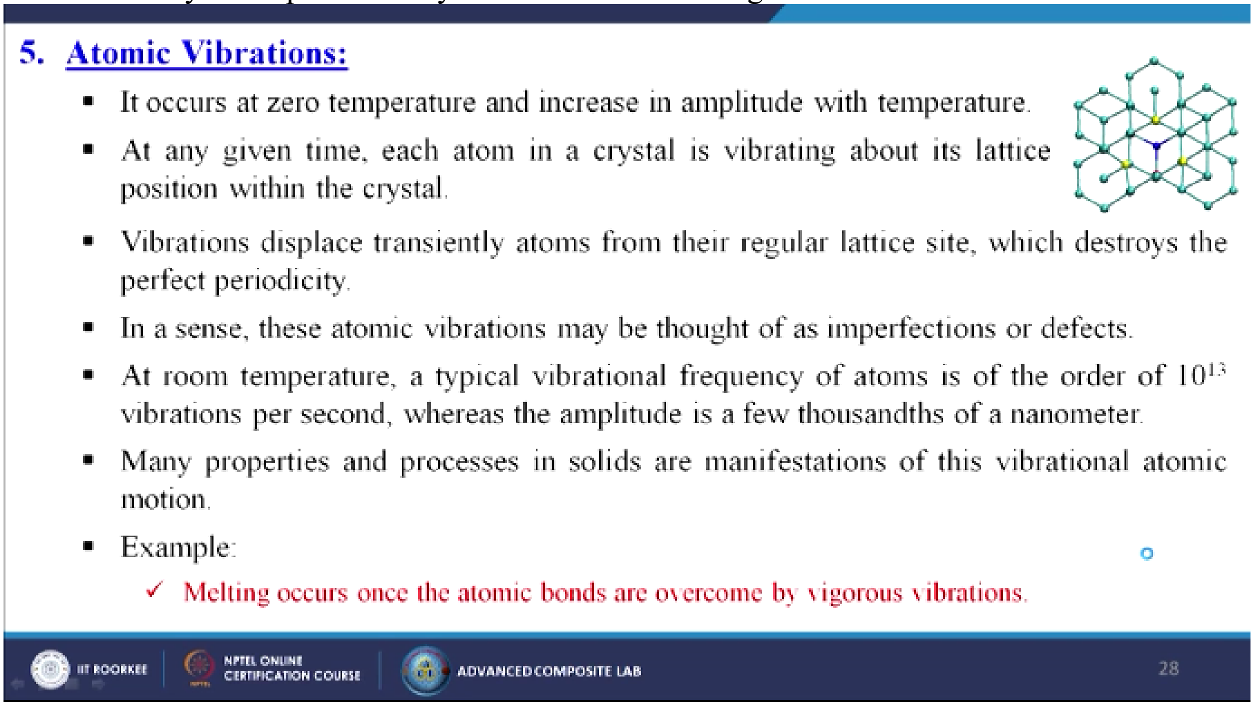
- Caused by gases, trapped during solidification or by vacancy condensation in solid state.
- Almost always undesirable defects.
- Decreases mechanical strength and promote fracture at small loads.
- Affect optical, thermal, and mechanical properties.

Pores

Then inclusions, from the name itself you can understand that inclusions means introducing something inside the matrix, so in this case foreign particles or maybe the large precipitate particles are included, undesirable constituents in the microstructure, harmful in microelectronic devices, inclusions are important factors when it comes to gem valuations, so inclusions inside the diamond so some kind of unwanted materials has been inserted into the diamond, in many gem stones such as diamonds inclusions affects, clarity of the stone, diminishes the stones value, yes of course, because it is reducing the cost because some kind of third party element which is cheaper in nature has been incorporated or maybe it is already present inside the diamond itself, so cost of the diamond will reduce, and the clarity of the stone or maybe the glittering property of that particular stone has been increased.

In some stones star sapphires inclusion actually increase the value of the stone itself, inclusion disturbs geometry of device by interfering in manufacturing or alter it electrical properties by introducing the undesirable properties of their own.

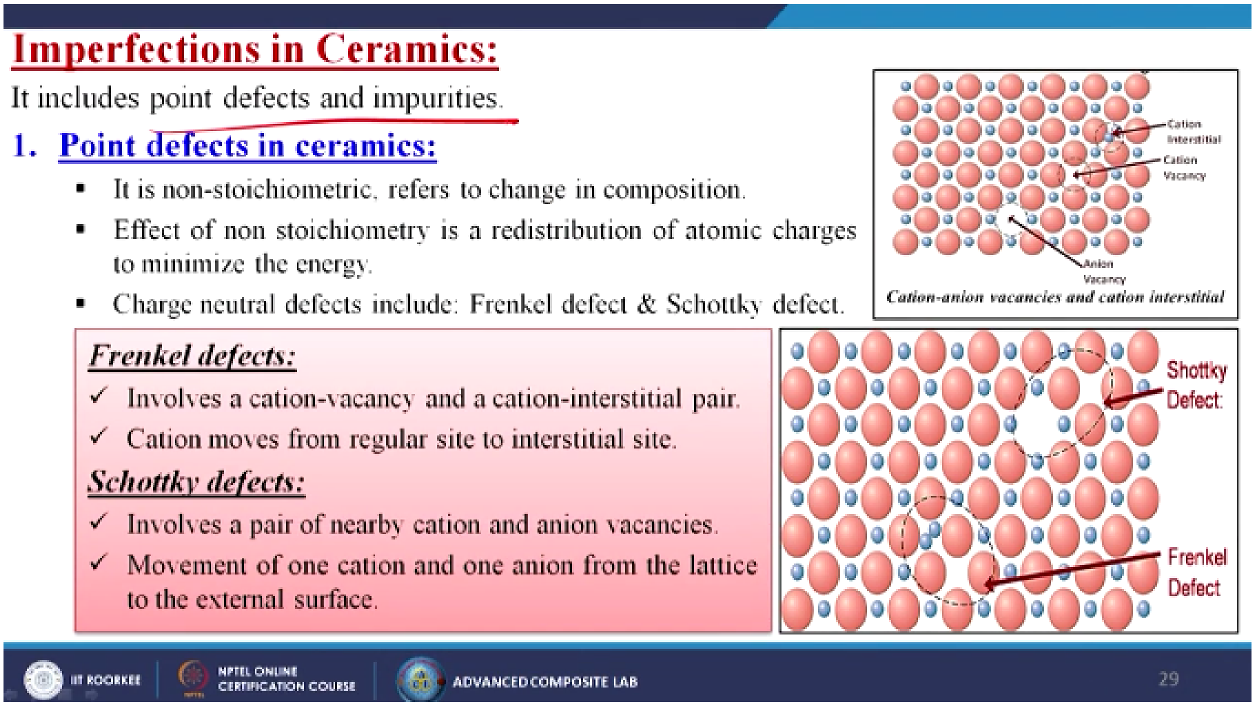
Then next one is that voids or maybe the pores, so caused by gases trapped during the solidification or by vacancy condensation in the solid state, yes of course because when we are heating that materials then the materials is changing its phase from solid to liquid and then when it is liquid, the liquid metal is having the affinity that it can absorb the moisture or maybe the oxygen or maybe the hydrant gas from the environment itself, and that will be trapped inside the molten metal, and then at the time of solidifications that trap gas by increasing the volume it will make a crack and it will come out and it will create a hollow space inside it which is known as the pores or maybe the voids, almost always undesirable defects decreases mechanical strength and promote the fracture at small loads, affect optical, thermal and mechanical properties, so in this particular image you can see through that if you see this type of image that void has been cracked or maybe the pores or maybe the cracks has been generated.



5. Atomic Vibrations:

- It occurs at zero temperature and increase in amplitude with temperature.
- At any given time, each atom in a crystal is vibrating about its lattice position within the crystal.
- Vibrations displace transiently atoms from their regular lattice site, which destroys the perfect periodicity.
- In a sense, these atomic vibrations may be thought of as imperfections or defects.
- At room temperature, a typical vibrational frequency of atoms is of the order of 10^{13} vibrations per second, whereas the amplitude is a few thousandths of a nanometer.
- Many properties and processes in solids are manifestations of this vibrational atomic motion.
- Example:
  - ✓ Melting occurs once the atomic bonds are overcome by vigorous vibrations.

Then atomic vibrations, so it occurs at zero temperature and increase in amplitude with temperature itself, at any given time each atom in a crystal is vibrating about its lattice positions within the crystal itself, so from this image you can see that vibrations is taking place inside the crystal structure, so vibrations displace transiently atoms from their regular lattice site, which destroys the perfect periodicity, due to that vibrations some atoms maybe shifted from their original place, in a sense these atomic vibrations maybe thought of as imperfections or defects, at room temperature a typical vibrational frequency of atoms is of the order of 10 to the power 13 vibrations per second, whereas the amplitude is a few thousands of nanometer, many properties and process in solids are manifestations of this vibrational atomic motions, what is the examples? Melting occurs once the atomic bonds are overcome by the vigorous vibrations, so when we are heating that materials so vibrations has started in between the atoms due to that the melting occurs of the metal itself.



Imperfections in Ceramics:

It includes point defects and impurities.

1. Point defects in ceramics:

- It is non-stoichiometric, refers to change in composition.
- Effect of non stoichiometry is a redistribution of atomic charges to minimize the energy.
- Charge neutral defects include: Frenkel defect & Schottky defect.

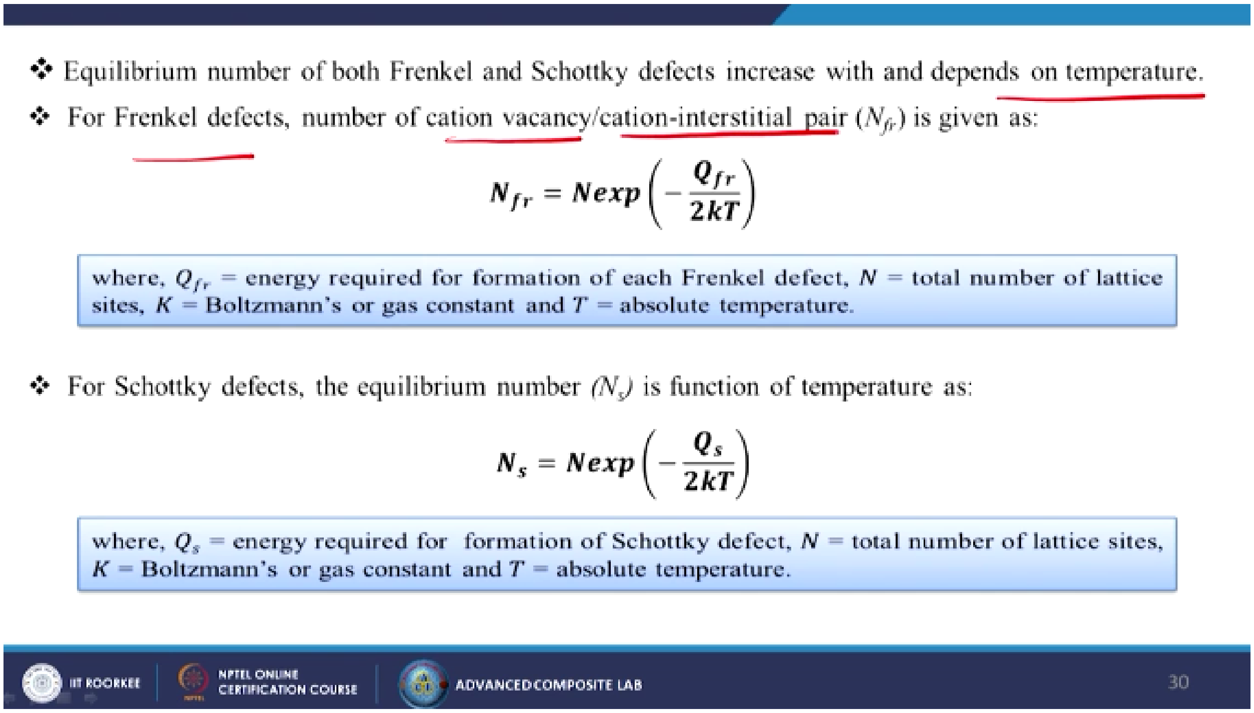
Frenkel defects:

- ✓ Involves a cation-vacancy and a cation-interstitial pair.
- ✓ Cation moves from regular site to interstitial site.

Schottky defects:

- ✓ Involves a pair of nearby cation and anion vacancies.
- ✓ Movement of one cation and one anion from the lattice to the external surface.

Then we are going to discuss about the imperfections in ceramics, so generally it includes the point defects and the impurities, so what is the point defects in ceramics? So it is non-stoichiometric refers to change in compositions, effect of non-stoichiometry is a redistribution of atomic charges to minimize the energy, charge neutral defects include Frenkel defect and the Schottky defect, so what is Frenkel defects? So involves a cation vacancy and a cation interstitial pair itself, so the vacancy has been created over here. Cation moves from regular side to the interstitial side so from here it has been moved from here to here, and what is Schottky defects? Involves a pair of nearby cations and anions vacancy, so in this particular zone both cations and anions has been shifted, movement of one cation and one anion from the lattice to the external surface, so that is known as the Schottky defect.



- Equilibrium number of both Frenkel and Schottky defects increase with and depends on temperature.
- For Frenkel defects, number of cation vacancy/cation-interstitial pair (N_{fr}) is given as:

$$N_{fr} = Nexp\left(-\frac{Q_{fr}}{2kT}\right)$$

where, Q_{fr} = energy required for formation of each Frenkel defect, N = total number of lattice sites, K = Boltzmann's or gas constant and T = absolute temperature.

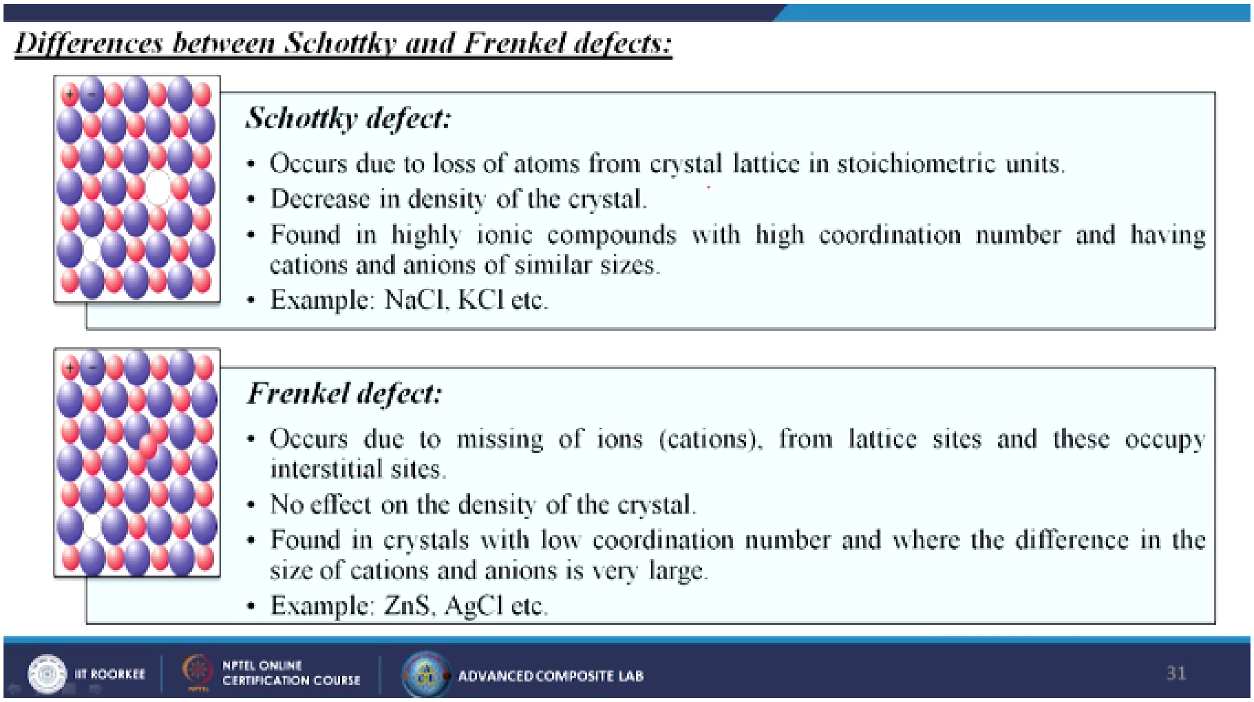
- For Schottky defects, the equilibrium number (N_s) is function of temperature as:

$$N_s = Nexp\left(-\frac{Q_s}{2kT}\right)$$

where, Q_s = energy required for formation of Schottky defect, N = total number of lattice sites, K = Boltzmann's or gas constant and T = absolute temperature.

So equilibrium number of both Frenkel and Schottky defects increase with and depends on the temperature itself, for Frenkel defects number of cation vacancy or maybe the cation interstitial pair which is known as the Nfr is given as Nfr = N exponential (-Qfr/2kT), so where Qfr is energy required for formations of each Frenkel defects, N is the total number of lattice sides, K is known as the Boltzmann's or maybe the gas constant, and T is the absolute temperature.

And for Schottky defects the equilibrium number NS is function of temperature like NS = N exponential (-Qs/2kT), here Q is the energy required for formations of that Schottky defect, N is the total number of lattice side, K is the Boltzmann's constant or maybe the gas constant, and T is the absolute temperature.



Differences between Schottky and Frenkel defects:

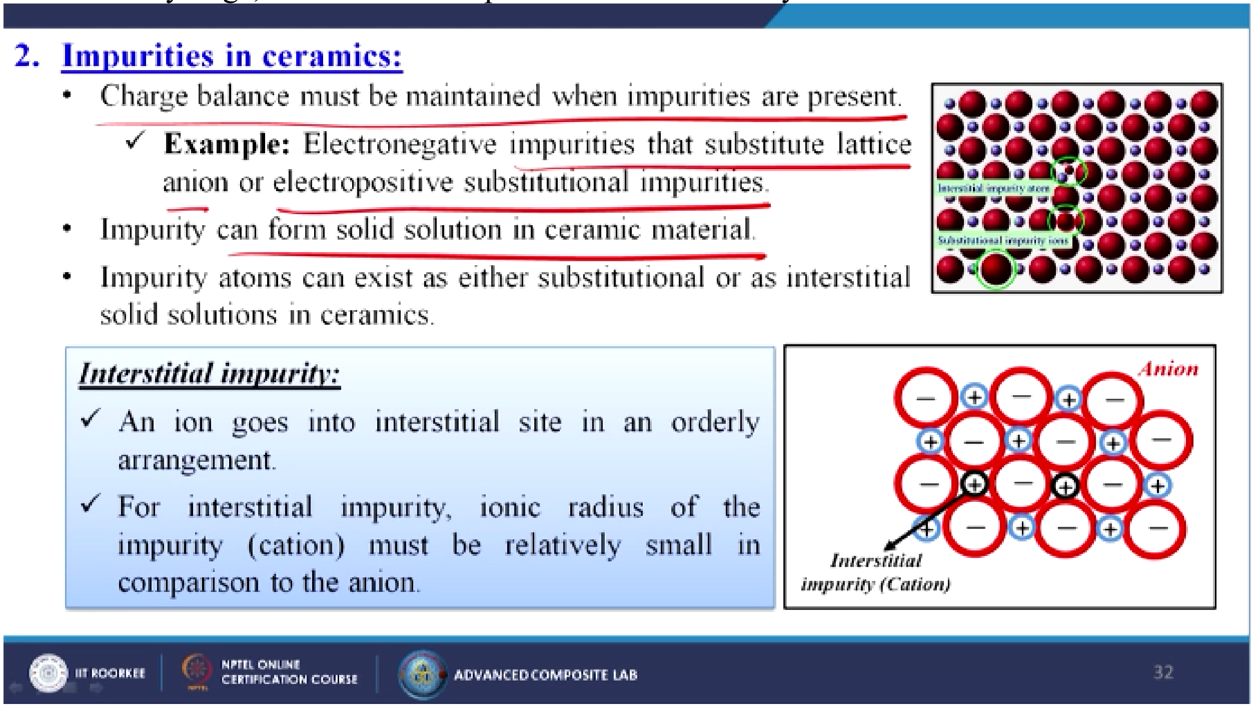
Schottky defect:

- Occurs due to loss of atoms from crystal lattice in stoichiometric units.
- Decrease in density of the crystal.
- Found in highly ionic compounds with high coordination number and having cations and anions of similar sizes.
- Example: NaCl, KCl etc.

Frenkel defect:

- Occurs due to missing of ions (cations), from lattice sites and these occupy interstitial sites.
- No effect on the density of the crystal.
- Found in crystals with low coordination number and where the difference in the size of cations and anions is very large.
- Example: ZnS, AgCl etc.

Now what is the difference between Schottky and the Frenkel defects? So first Schottky defects, its occurred due to loss of atoms from crystal lattice in stoichiometric units, it decrease in density of the crystal, found in highly ionic compounds with high coordination number and having cations and anions of similar sizes, what is the examples? Sodium chloride NaCl, potassium chloride KCl etcetera, and what is Frenkel defect? So occurs due to missing of ions, I mean cations from lattice sites and these occupy interstitial sites, no effect on the density of the crystal, found in crystal with low coordination number and where the difference in the size of cations and anions is very large, what is the example? Zinc sulfide or maybe the silver chloride etcetera.



2. Impurities in ceramics:

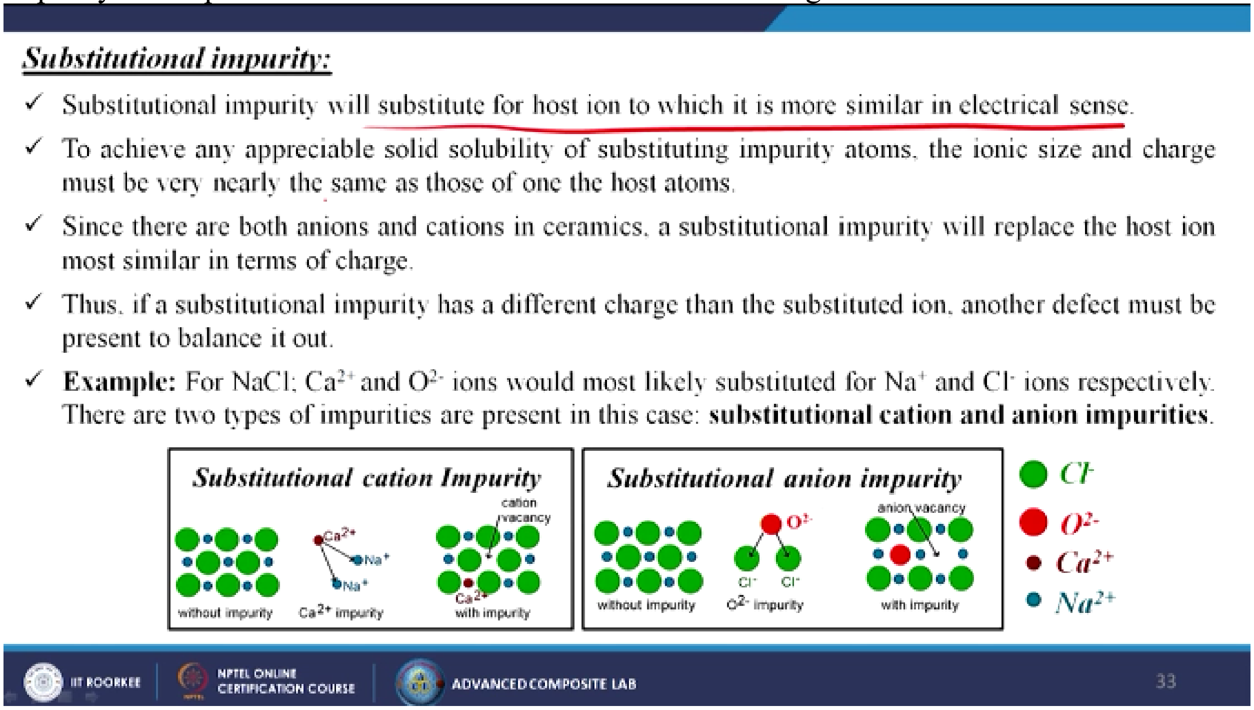
- Charge balance must be maintained when impurities are present.
  - ✓ **Example:** Electronegative impurities that substitute lattice anion or electropositive substitutional impurities.
- Impurity can form solid solution in ceramic material.
- Impurity atoms can exist as either substitutional or as interstitial solid solutions in ceramics.

Interstitial impurity:

- ✓ An ion goes into interstitial site in an orderly arrangement.
- ✓ For interstitial impurity, ionic radius of the impurity (cation) must be relatively small in comparison to the anion.

Now there are impurities also presence in the ceramics that also creates symptom kind of defects inside the ceramics structure, so how? Charge balance must be maintained when impurities are present, example electronegative impurities that substitute lattice anion or maybe the electropositive substitutional impurities, impurity can form solid solutions in the ceramic materials, so in this particular case you can see some kind of substitutional impurity ion is taking place and in this case the interstitial impurity atom is going inside it, so impurities atoms can exist at either substitutional or as interstitial solid solutions in ceramics.

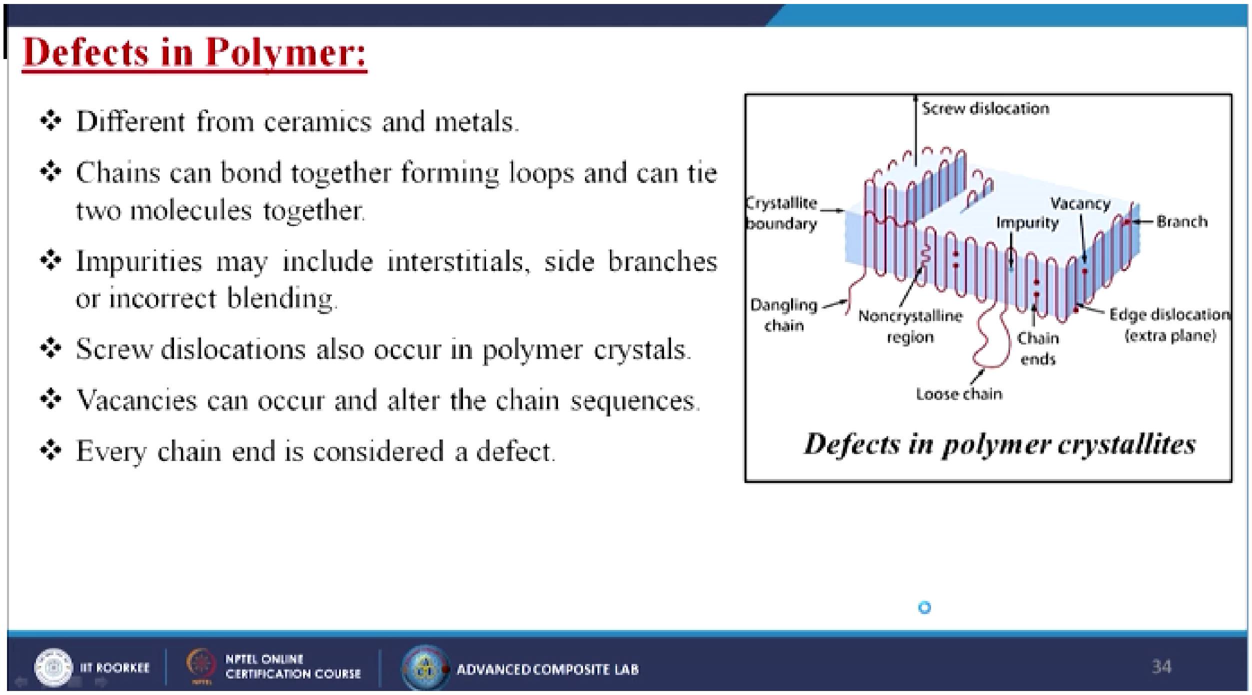
What is interstitial impurity? An ion goes into interstitial site in an orderly arrangement, for interstitial impurity, ionic radius of the impurity cation must be relatively small in comparison to the anion itself, so here the interstitial impurity cation is taking place, so just it is replacing, and when we are talking about the substitutional impurity, substitutional impurity will substitute for host ion to which it is more similar in electrical sense, to achieve any appreciable solid solubility of substituting impurity atoms, the ionic size and charge must be very nearly the same as those of one of the host atoms, since there are both anions and cations in ceramics a substitutional impurity will replace the host ion most similar in terms of charge.



Substitutional impurity:

- ✓ Substitutional impurity will substitute for host ion to which it is more similar in electrical sense.
- ✓ To achieve any appreciable solid solubility of substituting impurity atoms, the ionic size and charge must be very nearly the same as those of one the host atoms.
- ✓ Since there are both anions and cations in ceramics, a substitutional impurity will replace the host ion most similar in terms of charge.
- ✓ Thus, if a substitutional impurity has a different charge than the substituted ion, another defect must be present to balance it out.
- ✓ **Example:** For NaCl; Ca^{2+} and O^{2-} ions would most likely substituted for Na^+ and Cl^- ions respectively. There are two types of impurities are present in this case: **substitutional cation and anion impurities**.

Thus if a substitutional impurity has a different charge than the substituted ion another defect must be present to balance it out, yes of course, because plus and minus, if it is plus plus then automatically there should be a minus to balance it out, for example for sodium chloride Ca2+ and O2- would most likely substituted for sodium Na+ and Cl- ion respectively, there are two types of impurities are present in this case, substitutional cation and the anion impurities, so in this case this is without the impurity and here Ca2+ is the impurity, so in this case the cation vacancy is taking place in this particular case, and when you are talking about the substitutional anion impurity, so like in this case this is without impurity, so we are having two Cl- which is stacker with O2-, so here O2- is the impurity and the O2 is taking place in this particular zone and anion vacancy is taking place in this particular zone which is called the substitutional anion impurity.

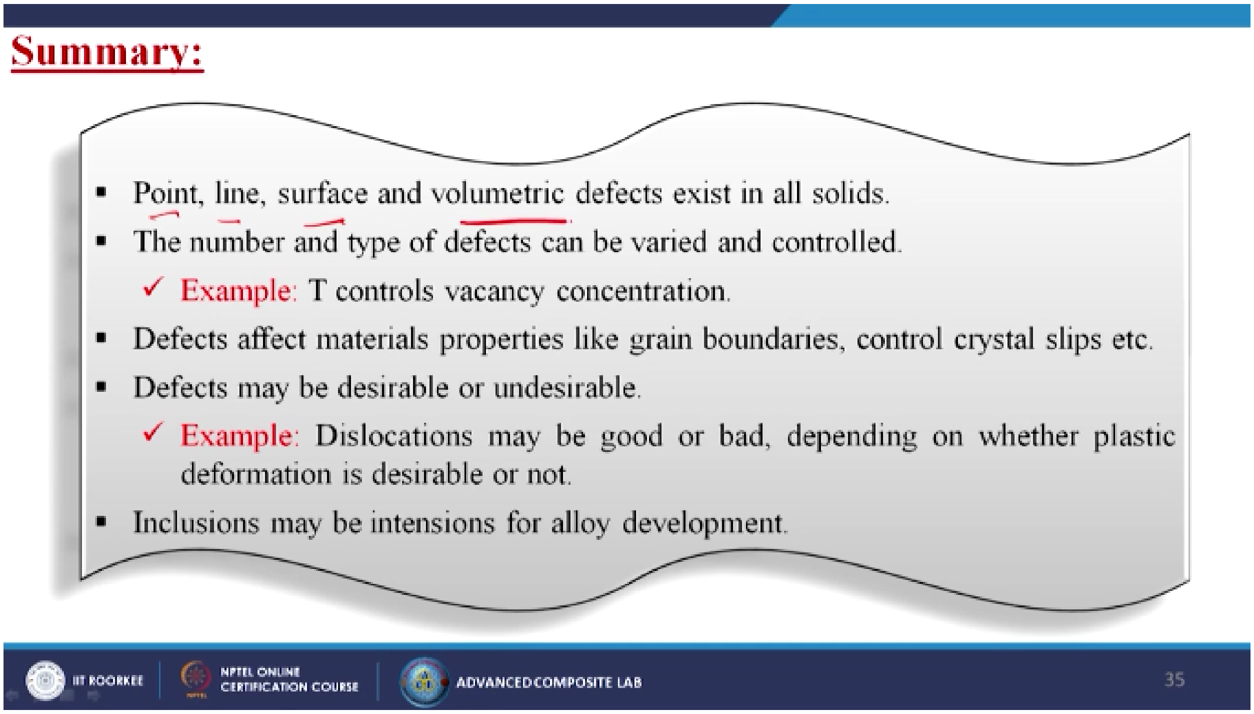


Defects in Polymer:

- Different from ceramics and metals.
- Chains can bond together forming loops and can tie two molecules together.
- Impurities may include interstitials, side branches or incorrect blending.
- Screw dislocations also occur in polymer crystals.
- Vacancies can occur and alter the chain sequences.
- Every chain end is considered a defect.

Defects in polymer crystallites

Now the last one that is defects in polymer, it is very very critical one, it is also very very difficult to measure, so different from ceramics and metals, chains can bond together forming loops and can tie two molecules together, impurities may include interstitials, side branches or maybe the incorrect blending, screw dislocations also occur in polymer crystals, vacancies can occur and alter the chain sequences, every chain end is considered a defect, so in this case the screw dislocation is taking place in this particular zone, impurity has been added or maybe has taken place some chain ends is taking place, vacancy is looks like this or maybe some kind of branching is taking place, here this one is the non-crystalline region that or maybe some kind of dangling chain is taking place, so these are maybe the loose chain, so there are several types of defects but it is very very difficult to understand the defects inside the polymer.



Summary:

- Point, line, surface and volumetric defects exist in all solids.
- The number and type of defects can be varied and controlled.
  - ✓ Example: T controls vacancy concentration.
- Defects affect materials properties like grain boundaries, control crystal slips etc.
- Defects may be desirable or undesirable.
  - ✓ Example: Dislocations may be good or bad, depending on whether plastic deformation is desirable or not.
- Inclusions may be intensions for alloy development.

So now we have come to the end of this particular lecture, so we have to summarize, so in this particular lecture we have discussed about the point line surface and volumetric defects in, which is exist in all solids, the number and type of defects can be varied and controlled, like example temperature controls the vacancy concentrations, defects affects the material properties like grain boundaries control crystal slips, so it can control the crystal slips also, defects maybe desirable or maybe sometimes it is undesirable, sometimes it can improve the material properties by inserting some materials or maybe sometimes it may reduce the material properties also, example dislocations maybe good or bad depending on whether the plastic deformation is desirable or not, inclusions maybe intensions for alloy development sometimes it is intentionally, sometimes it is unintentionally also. Thank you.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Acknowledgement
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