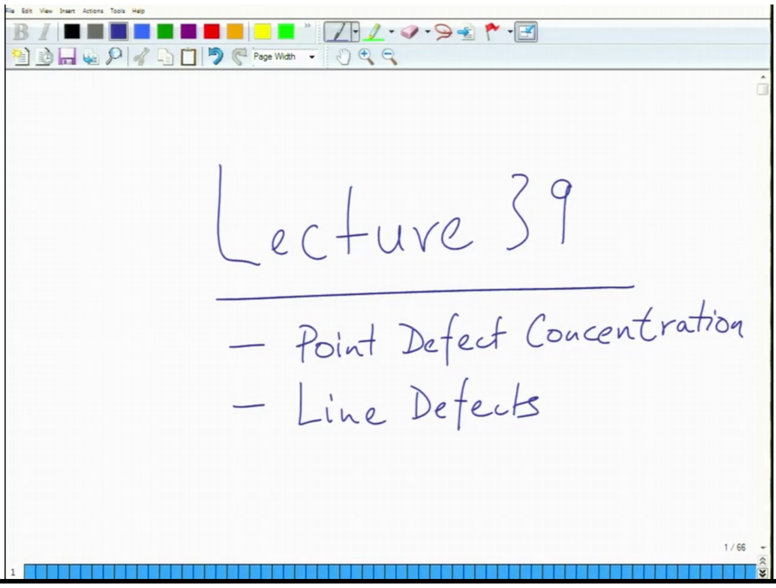
An Introduction to Materials: Nature and Properties
(Part 1: Structure of Materials)

Prof. Ashish Garg
Department of Material Science and Engineering
Indian Institute of Technology, Kanpur

Lecture - 39
Point Defect Concentration
Line Defects

(Refer Slide Time: 00:16)

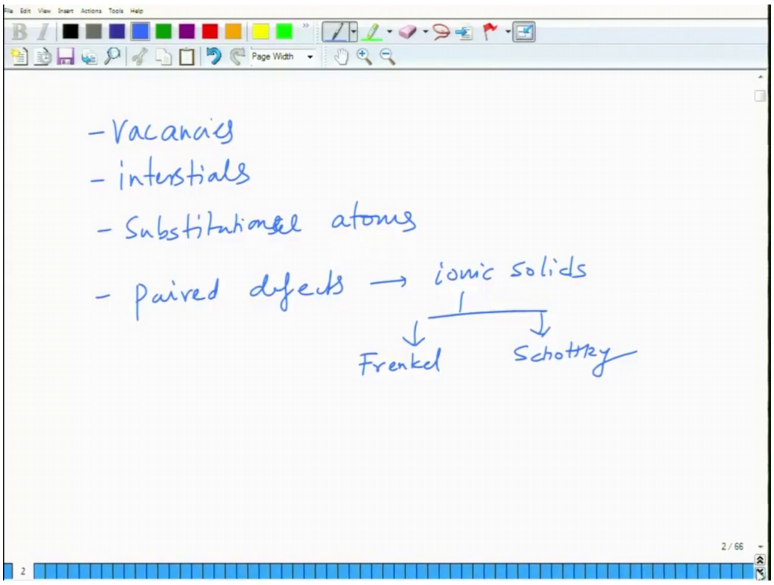


Lecture 39

- Point Defect Concentration
- Line Defects

So we begin lecture 39 now in which we will talk about point defect concentration and the line defects. So, what we talked in the last lecture was about that materials in reality they have various defects and depending upon the nature of defect they can be classified in three categories; point defects which are zero dimensional defects, line defects which we have not talked about yet and the two dimensional defects which are line defects are one dimensional defects and two dimensional defects are a surfaces basically grain boundaries, twin boundaries which you will talk in perhaps this lecture next lecture.

(Refer Slide Time: 00:53)



- Vacancies
- interstitials
- Substitutional atoms
- paired defects → ionic solids

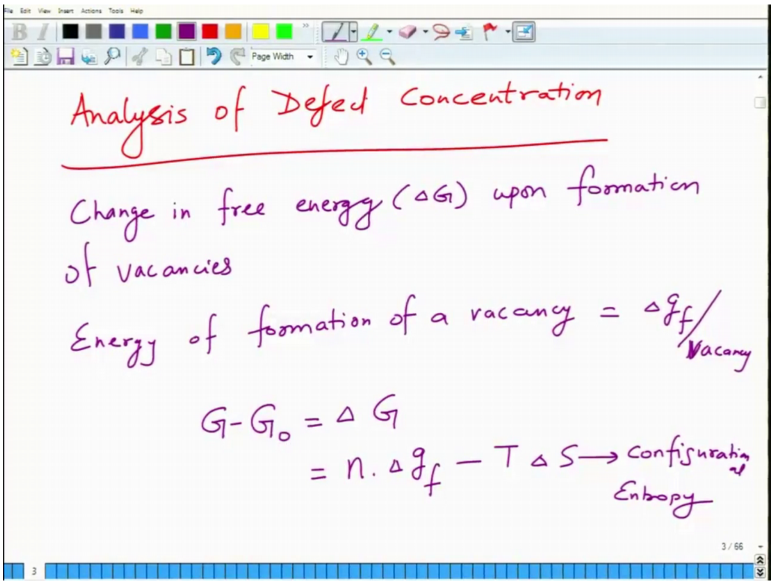
Frenkel

Schottky

So, what we will do is that now we will we have seen that there are point defects such as you have vacancies, you have interstitials, you have so, this could be substitutional you and you can have substitutional impurities; sorry interstitial cannot be substitutional. So, you can have interstitial, so you can have substitution atoms, you can have paired defects typically in ionic solids such as Frenkel and Schottky.

So these are some defects that could be present in the vacancies in various materials. Vacancies for example, in metals just the metal vacancy, in case of ionic solids it could be, cation vacancy, it could be anion vacancy, interstitial could be; cation interstitial anion interstitial, substitution again could be cation anion substitutional depending upon what you put in the lattice.

(Refer Slide Time: 02:06)



Analysis of Defect Concentration

Change in free energy (ΔG) upon formation of vacancies

Energy of formation of a vacancy $= \Delta g_f / \text{Vacancy}$

$$G - G_0 = \Delta G$$
$$= n . \Delta g_f - T \Delta S \rightarrow \text{configurational Entropy}$$

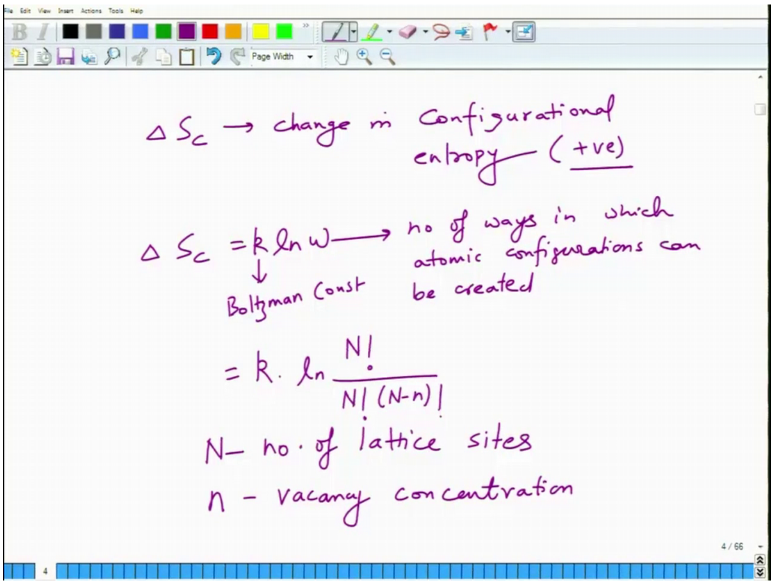
Now, what we will do is that we will do a simple analysis to work out what is the so, analysis of defect concentration all right. So, basically what we do is that when we introduce a vacancy in the system it leads to change in the thermodynamic parameters such as entropy ok; entropy and enthalpy. So, let us first work out what is that change in free energy that is delta G upon formation of vacancies ok.

Now, if you form a vacancy which means it must cost energy because you are removing an atom. Let us say the energy of formation of a vacancy is equal to delta small gf per vacancy ok. Now, the change in the free energy corresponding change in the free energy which is G G minus G naught; G naught is the equilibrium free energy; when you did not have any vacancy.

So, this change in the free energy which is delta G; this can be related to or delta G is equal to delta h minus t delta s; delta h is number of vacancy is multiplied by the heat of formation enthalpy of formation of vacancies which is delta g f minus T delta S and this delta s happens to be change in the configurational entropy.

So, when you introduce vacancies in a material predominantly you are changing the configuration entropy because now you have since you have one vacant place the atoms can be put into various configurations. So, we need to work out what is the configuration entropy that happens upon the change in the configuration entropy that happens upon introducing a vacancy.

(Refer Slide Time: 04:22)



$\Delta S_c \rightarrow$ change in Configurational entropy — $(\underline{+ve})$

$\Delta S_c = k \ln W \longrightarrow$ no of ways in which atomic configurations can be created

$k \downarrow$ Boltzman Const

$$= k \cdot \ln \frac{N!}{N!\,(N-n)!}$$

N– no. of lattice sites

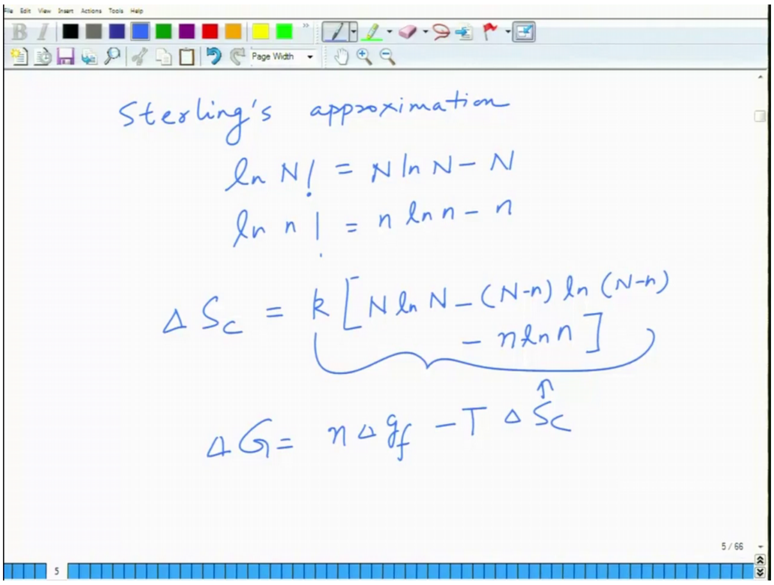
n – vacancy concentration

So, this delta S c is basically change in the entropy and this is basically positive in nature as we will see. So, delta S c is equal to small k ln w; where k is the Boltzmann constant and w is the number of ways in which atoms can now be arranged ok.

So, number of ways in which atomic configurations can be created after you introduce a vacancy right and this happens to be small k ln N an exclamation mark which is factorial N divided by factorial N into small n minus n factorial; where capital N is the number of lattice sites; not number of atoms number of lattice sites because number of atoms are now reduced and a small n is the vacancy concentration.

So, these are basically, so, capital N is the total number of sides; N minus n is the now number of remaining atoms right because small n is the number of vacancies. So, basically these many number of atoms have now to be configured on the N lattice sites.

(Refer Slide Time: 06:51)



Sterling's approximation

$$\ln N! = N \ln N - N$$

$$\ln n! = n \ln n - n$$

$$\Delta S_c = k\underbrace{\left[N \ln N - (N-n)\ln(N-n) - n \ln n\right]}$$

$$\Delta G = n \Delta g_f - T \Delta S_c$$

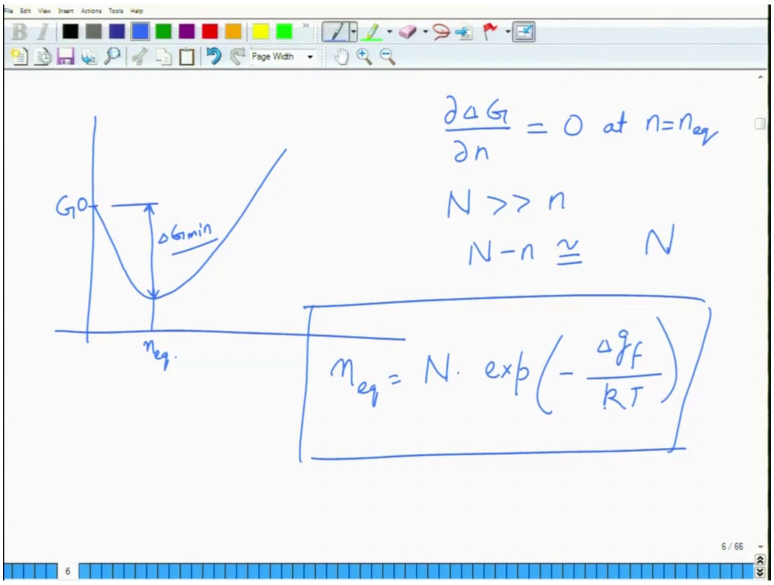
So, to solve this equation we make a approximation which is called as Sterling's approximation; which is called as ln N factorial to be equal to N ln N minus capital N. And likewise you can write a small n is equal to small n ln n minus.

Student: Small n.

Small n; So, if you apply this approximation to the above equation, what you find is that delta S c is equal to small k into capital L ln N minus N minus n ln N minus n minus of small n ln n. This is what you will get after you apply this approximation and then you substitute of course, in delta G; delta G will be equal to n delta g f minus of T delta S c and for delta S c you will introduce this.

Now, if vacancies were equilibrium defect; which means the free energy must become minimum at a certain concentration right

(Refer Slide Time: 08:18)



$$\frac{\partial \Delta G}{\partial n} = 0 \text{ at } n = n_{eq}$$

$$N >> n$$

$$N - n \cong N$$

$$\boxed{n_{eq} = N \cdot \exp\left(-\frac{\Delta g_f}{RT}\right)}$$

So, if you plot the free energy as a function of vacancy concentration; the free energy G, this is let us say 0. The free energy must become minimum at certain concentration. This is concentration n equilibrium and this should show a minima right. This is delta G min; if it is not minimum then it is not a stable defect right.

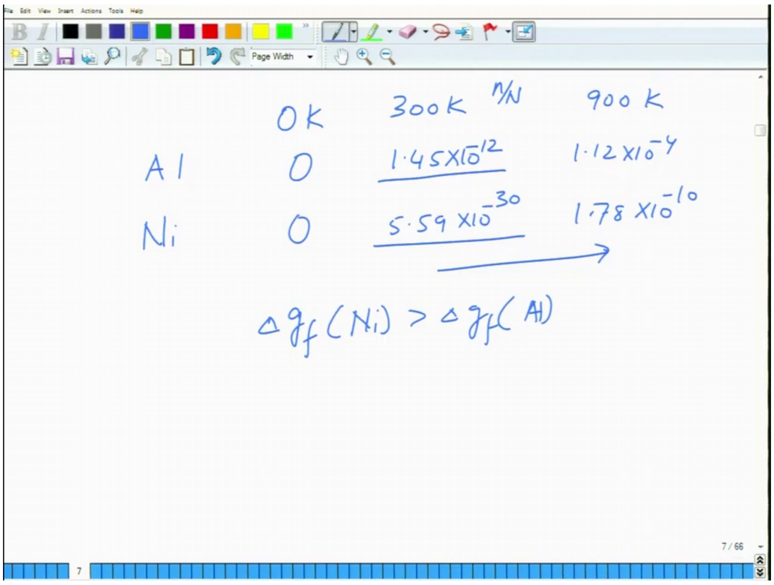
So, when you introduce vacancies and if vacancies are indeed is stable defects; that means, delta G should show a minimum at certain concentration. Which means del of delta G by del n 0 at n is equal to.

Student: N equilibrium.

N equilibrium and since N is much larger than a small n, I can say N minus n is equal to capital N. So, if I do this now differentiate the above equation which I have showed earlier and apply this condition what we will get is n equilibrium is equal to capital N multiplied by exponential minus of delta g f divided by small k T.

This is the equilibrium concentration of vacancies that we calculate which means now, what this eq expression shows that higher the energy of formation of vacancy smaller will be the vacancy concentration; higher the temperature is larger the vacancy concentration will be; lower the temperature is smaller the vacancy concentration will be.

(Refer Slide Time: 10:03)



	0K	300K n/N	900K
Al	0	1.45×10^{-12}	1.12×10^{-4}
Ni	0	5.59×10^{-30}	1.78×10^{-10}

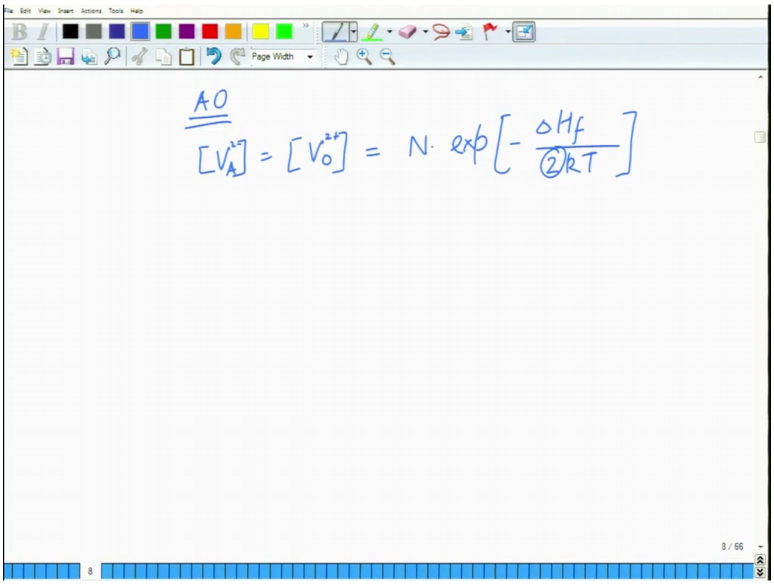
$$\Delta g_f(Ni) > \Delta g_f(Al)$$

And that is why different materials show different vacancy concentration. For example, if you calculate difference between Aluminum and Nickel at 0 Kelvin of course, both of them will have 0 ok. At 300 Kelvin aluminum will show you 1.45 into 10 to power minus 12, fraction of vacancies ok. So, this is basically n divided by N and this happens to be 5.59 into 10 to power minus 30 and at 900 Kelvin, this happens to be 1.12 into 10 to power minus 4; this happens to be 1.78 10 to power minus 10.

So, you can see that as the temperature is increasing there is exponential increase, but there is a difference between aluminum and nickel. Aluminum has a vacancy concentration which is far higher as compared to nickel because nickel is a high temperature material, aluminum is a low temperature material; the bond energy of nickel is higher as compared to aluminum.

As a result the energy which is required to form a vacancy in aluminum is lower as compared to energy that is required to form a vacancy in nickel. So, delta g f for nickel would be larger than delta g f for aluminum which is depending upon the bond energy of the two materials. So, this is basically the equilibrium vacancy concentration calculation.

(Refer Slide Time: 11:44)



AO

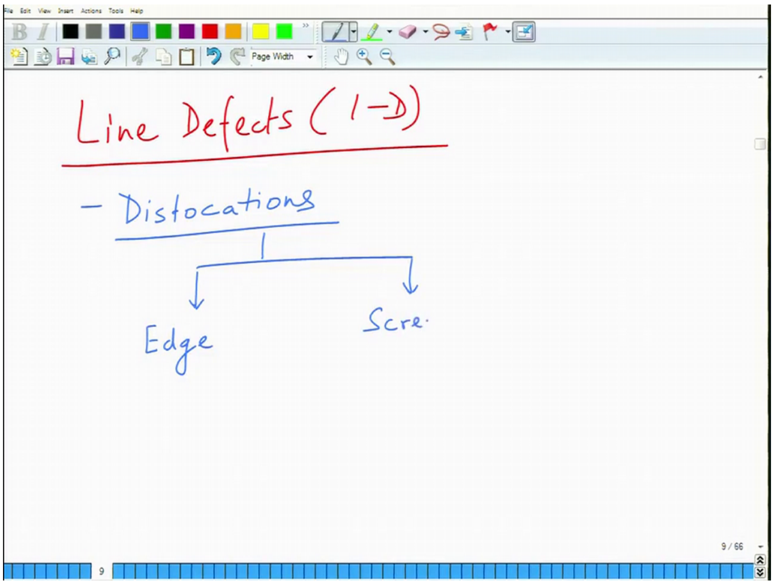
$$[V_A^{2-}] = [V_O^{2+}] = N \cdot \exp\left[-\frac{\Delta H_f}{\textcircled{2} kT}\right]$$

For Schottky defects ionic defects the equation will change a little bit. So, since you have vacancy so, delta V let us say vacancy of a is equal to vacancy of o; let us say for a AO solid ok. So, this would be 2 minus, this would be 2 plus and this is basically total number of sides N, exponential of minus delta Hf which is the free energy which is the enthalpy of formation of vacancy divided by 2 kT.

So, here you have this factor of 2 that comes in the denominator for ionic solids, but the relations are similar all right. So, this is about the point defects discussion that you have point defects such as vacancies interstitials. And point defects are basically stable defects, they are equilibrium defects and free energy is minimum at a certain concentration at a given temperature and that their concentration increases as a function of temperature.

So, as you increase the temperature they become more in number exponentially ok.

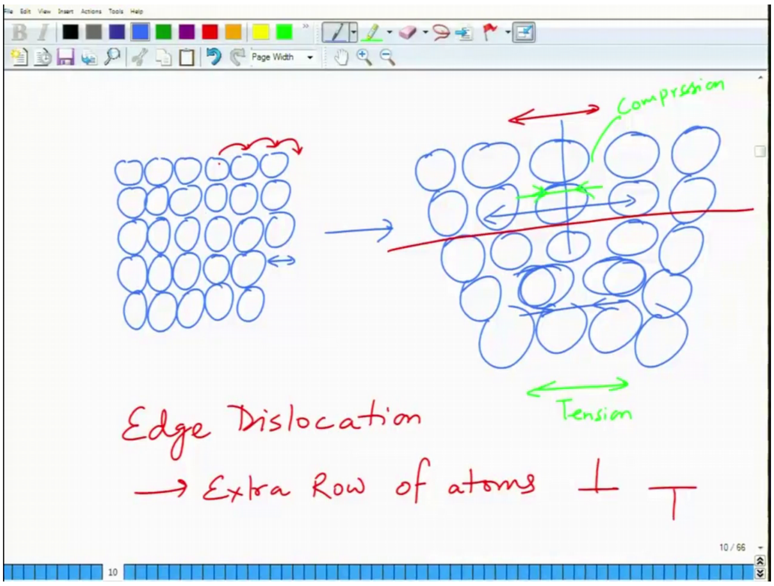
(Refer Slide Time: 13:02)



So, now let us discuss the second category of defects which is called as line defects or 1-D defects. Now, these are in our in the language of material scientists, these are called as dislocations ok.

There are two kinds of dislocations that we find in materials; primarily first is called as edge dislocation, second is called as screw dislocation.

(Refer Slide Time: 13:39)



Edge dislocation essentially is an extra row of atoms in the material. So, you have a structure like this which is the perfect structure ok. Now, what we do here is we remove some of the atoms. So, we remove these two atoms, these three these atoms let us say. So, what happens in this case now this structure will now slightly because you have created an extra row of atoms in between which does not completely go through the material.

As a result, it will create some distortion. So, you will have you will have distortion like this and then in between you will have these atoms. So, this is an extra row of atom. So, this extra row of atoms has created a strain on the lattice. This part has expanded and this part has contracted.

As a result this part will be under tension and this part will be under compression. Resultant stress will be compression and this kind of dislocation is called as edge dislocations. This we call as so, this edge basically an extra row of atoms. So, if you have a row, if you have a extra row present on the top plane it is called as.

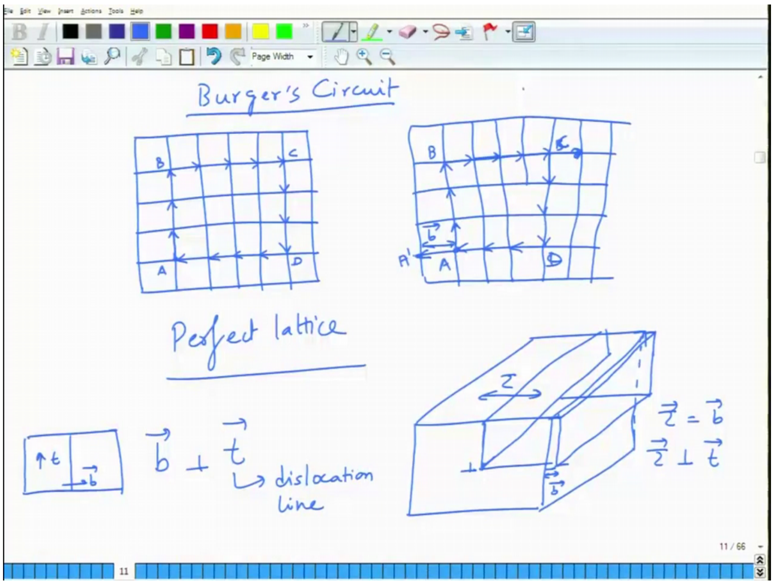
Student: Positive edge.

Positive edge dislocation; if it is present in the other side it is called as a negative edge dislocation. Now this edge dislocation moves as a function of stress in the material. So, when you apply stress, the dislocation can move in this or this direction ok. So, the way it happens is that this is the plane on which it moves and it can move.

So, this can eventually, so this row will eventually move out to this point and to this point; then to this point. So, eventually what will happen is that these atoms will come here and the one on the side will disappear.

So, it will create a step on the surface and this is how basically deformation in materials happens by movement of dislocations in material that is how they deform. So, when you apply stress it will move to right or left side depending upon that stress and it will create deformation in the materials.

(Refer Slide Time: 16:50)



So, you can represent this material this edge dislocation by a grid kind of factor and quantify it. So, let us say this is the perfect grid of a material; 2, 3, 4 and 5. 1, 2 this is a perfect grid ok; your atoms sitting at the corners there. So, let us say you start from this point, this is point A ok; go one step up there, another step, another step; you go one step here, one step here, one step here, one step here; this is A, B, C; three steps down D and then three steps left; four steps left you go to again A.

There is a perfect lattice if you have a edge dislocation what will happen is that; you will have slight distortion ok. So, you have one. So, let us say somewhere in between you have one row there ok. So, I had 5, 6 columns there; 1, 2, 3, 4; 1, 2, 3, 4, 5. So, let us say I have created one extra one there; let us get rid of this and then we have this thing here; 1, 2.

So, now if we again do this circuit, this is called a Burger's circuit ok. So, we start from this point. So, this is called Burger's circuit. So, this is Perfect lattice. In n imperfect lattice you again start from point A, go one step up; another step; another step; reach point B; one step, two step, three step, four step; you have to go to this point now. This is the point B let us say, you had four steps right.

So, let us and then you come to three steps down to point C and then you reach this point to reach point. So, this is A, A, B sorry C, D and you do not reach a rather you reach another point A prime. This is one extra step; this is called as.

Student: Burger’s circuit.

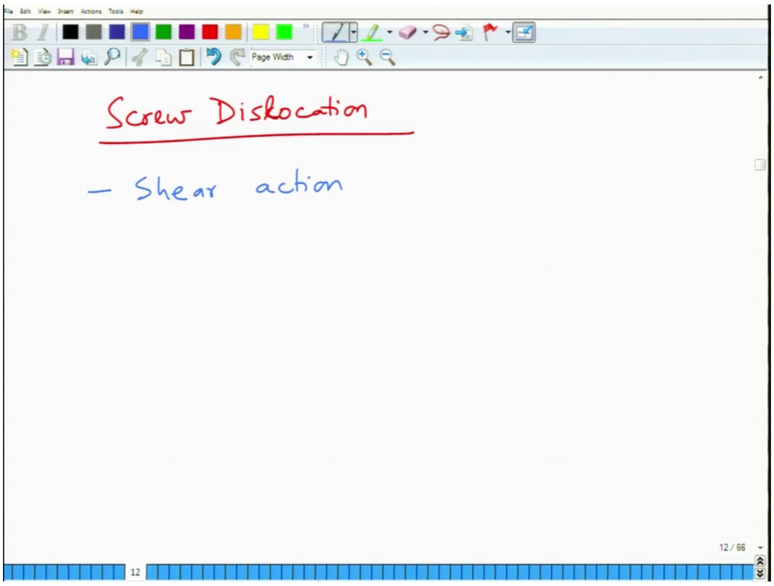
The Burger’s vector of our edge dislocation alright and this Burger’s vector is perpendicular to the; so this is your dislocation. So, the so, if you if you look at this location now if I draw the 3-D diagram. So, this is your 3-D diagram. So, this is your extra step that has formed somewhere here ok. This is your extra step and this will be your otherwise backside of the crystal ok.

So, this extra step is the Burger’s vector and your dislocation line is somewhere running like this in this direction ok. So, this is your dislocation line which is running in like this. So, this is your extra plane of atoms. So, this is; so, so basically Burger’s vector is perpendicular to that dislocation line in case of.

Student: Stress dislocation.

Stress dislocation ok. So, this is positive edge dislocation, this is the Burger’s factor. So, b is perpendicular to t which is called as dislocation line. So, if you draw the plane, the planar view is like this. If you look at the top view, this is dislocation line t and this is the Burger’s vector b ok.

(Refer Slide Time: 21:39)

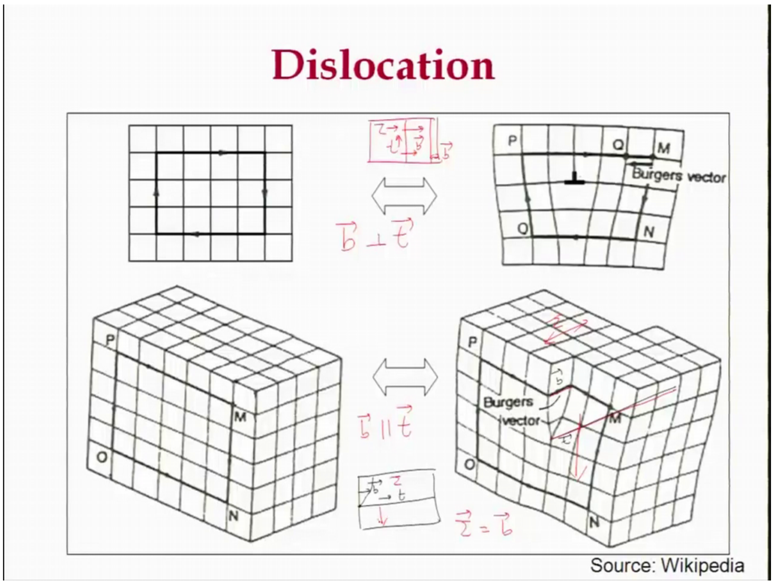


Screw Dislocation

- Shear action

The second dislocation which is present in materials is called as screw dislocation. And this is basically formed by shearing ok. So, this is formed by shear action as if you have a shear action in the material. So, for this I need to take help of illustration.

(Refer Slide Time: 22:03)



Dislocation

Source: Wikipedia

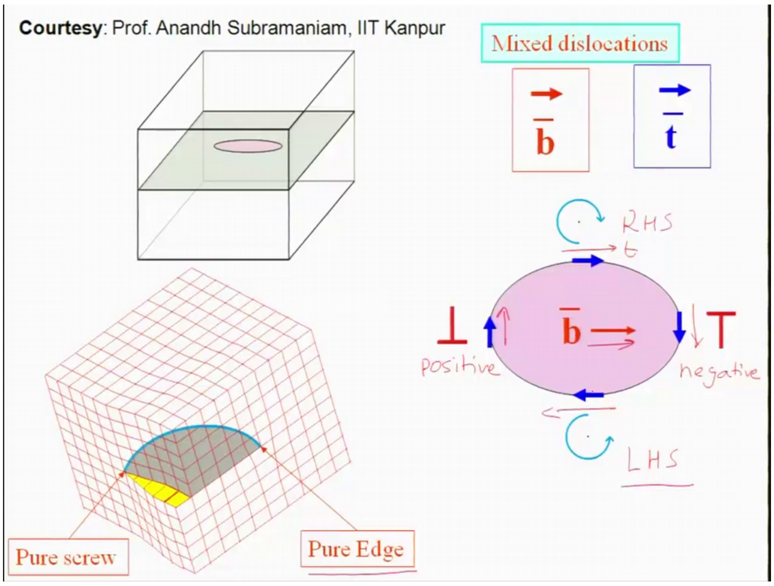
So, this was the edge dislocation, we had a Burger’s circuit which showed extra step in the in the in the Burger’s in the in the in the circuit. The screw dislocation you have two parts of the crystal sheared in this fashion. And now when you make this circuit, let us say from MNOP. So, you start from M to N four steps; N to O four steps and you have P to M you take an extra step here.

This is an extra step and this is sheared with respect to this point. So, this point if you if you if you now draw this point somewhere within the crystal. So, somewhere parallely you will have a line like that. So, here this is b vector; this is t vector. So, b and t are now parallel to each other. So, in this case what you had was b and t were perpendicular to each other. In this case if you draw the top view, top view would be like this.

If I draw the side view for example, this is the side view. This is the point of dislocation line this is t and your b will be in this direction as well; this is your b ok. So, the sheared region is the, so this is the step that you create; this is the line that you have. Both of them are parallel to each other. So, in this case b is perpendicular to t because t is perpendicular to the board ok.

So, this is t; this is b. If you look at the top view, the top view would be like this; t and b this is an extra step b, this is b. So, this is b vector. Here it would be parallel. So, b is parallel to t and these are the two kinds of dislocations that we have present in the materials and but in real life they do not exist. You know you do not have pure edge or pure screw.

(Refer Slide Time: 24:17)



Courtesy: Prof. Anandh Subramaniam, IIT Kanpur

Mixed dislocations

What happens in real life is what you press, what you have is a dislocation structure in which you have a mixed dislocation. So, mixed dislocation what happens is that for example, this is the part of the crystal. So, you can see on the right face of the crystal you have an extra row of atoms here.

So, this is the edge dislocation. So, this is pure edge. On the left side you can say there is a bit of shearing right. So, this is the extra step that you form here. This is the screw dislocation and since dislocations cannot end freely, they since they do not, they do not they have to close the circuit.

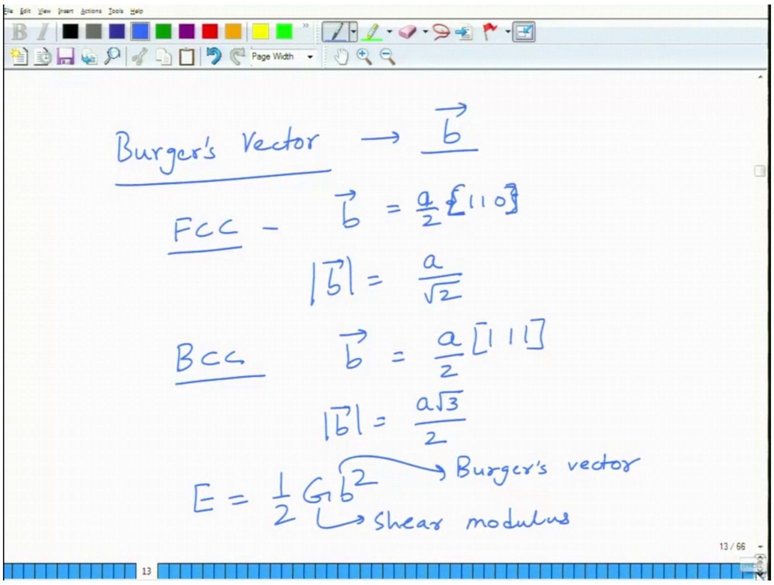
So, to close the circuit they exist like these dislocation loops inside the material. So, in the materials real materials you will have dislocation loops. So, depending upon whether it is a right handed screw or left hand. So, it screws are defined edges are just described as, so here for example, it is a positive edge right.

On the other side it would be negative edge. Here it is right handed screw and here it would be left handed screw and you can see that the dislocation line in this case is in this direction and your b is in this direction. So, b and t are perpendicular in both the configurations.

In these cases this is your t this is the b in this case this is the t this is b. Here this is t, this is b; here this is t and the one in the center is the b. So, you can see that there is a relationship that the relationship between b and t is honored ok.

So, this is the these are the dislocations in the materials which are called as line locations and the energy of these dislocations are characterized by a parameter called as, so dislocations are characterized by parameter called as Burger's vector which is b. Basically it is related to lattice parameters ok.

(Refer Slide Time: 26:23)



Burger's Vector $\rightarrow \vec{b}$

FCC – $\vec{b} = \frac{a}{2}\{110\}$

$|\vec{b}| = \frac{a}{\sqrt{2}}$

BCC $\vec{b} = \frac{a}{2}[111]$

$|\vec{b}| = \frac{a\sqrt{3}}{2}$

$E = \frac{1}{2} G b^2$

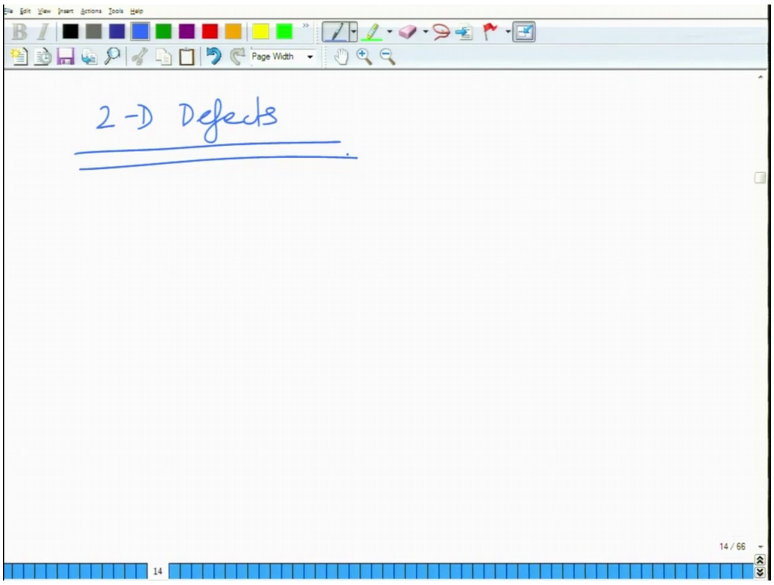
$b \rightarrow$ Burger's vector

$G \rightarrow$ Shear modulus

So, for example, in an FCC material b is equal to half of 110 or you can say half of 110 type of direction; a by 2 110. So, the length of b would be equal to a divided by root 2. For a FCC, for a BCC material it would be a divided by a 111 divided by 2 ok. So, this would be equal to a root 3 divided by 2 ok. So, this is how you calculate the Burger's vector lengths that these dislocations have energy as well.

So, energy of dislocations in is called as is characterize is expressed as half of G b square. So, G is the shear modulus and b is the magnitude of the Burger's vector ok. So, this is how you can you analyze dislocations in the material these are all 1-D defects.

(Refer Slide Time: 28:02)



2 -D Defects

And now, in the next class what we will do is that we look at the dislocation. We will look at the third category of defects which are called as 2-D defects which are basically surfaces ok. So, this we will discuss in the next lecture which is the final lecture of this course. And these dislocations let me tell you these dislocations in the materials they move out of the crystal when you apply stress.

So, for example, in this case when you apply stress in this direction tau, they set extra row of atoms will move out the, so the movement that the stress will look at the relation between stress line vector in the Burger's vector; tau is parallel to b and tau is perpendicular to t. If you look at the screw dislocation case, it is other way round. In case of a screw dislocation, if you want to now apply the shear stress, now to make so, that stress has to be applied in this direction. This is the stress axis.

So, stress is parallel to Burger's vector and the stress is perpendicular to the it is also parallel to the dislocation line. So, as you keep as you keep, as you apply the stress this direction will move in this; this line will move to the edge of the crystal. So, that it will create a complete step at the end of it. So, at the end of it you will have all the bonds broken and you will have complete step created.

So, the movement of dislocation line will happen in the direction perpendicular to the applied stress. Whereas, in this case the movement of dislocation line will in case of edge dislocation the so, this as you apply stress tau, the line will also move in the same direction. In this case as you apply stress the line will move in this direction ok. So, the movements are opposite in case of agenda screw dislocation with respect to the applied stress direction.

So, with this I think this is enough for this course we will discuss now the surface defects in the next lecture.