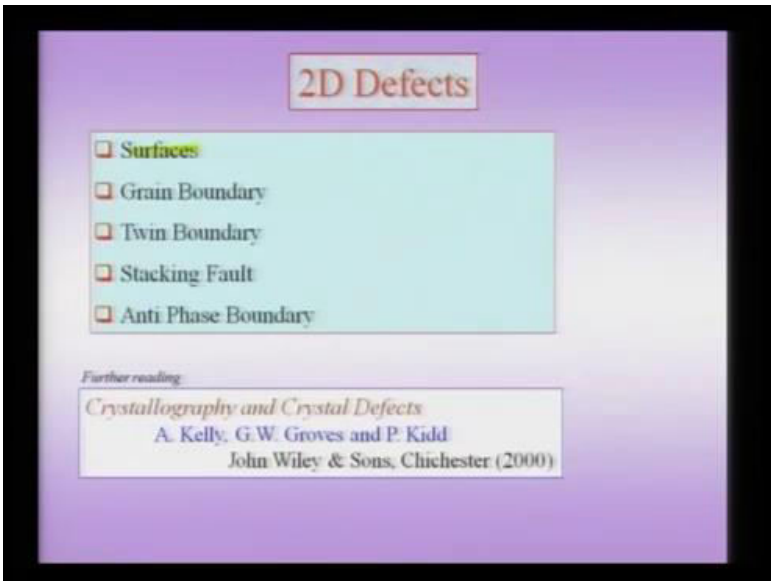
# Structure of Materials
**Prof. Anandh Subramaniam**
**Department of Material Science and Engineering**
**Indian Institute of Technology, Kanpur**

## Lecture - 28
## Chapter-05
## Defects in Crystals

After, considering the dislocation, which is the one dimensional defect.

(Refer Slide Time: 00:36)



2D Defects

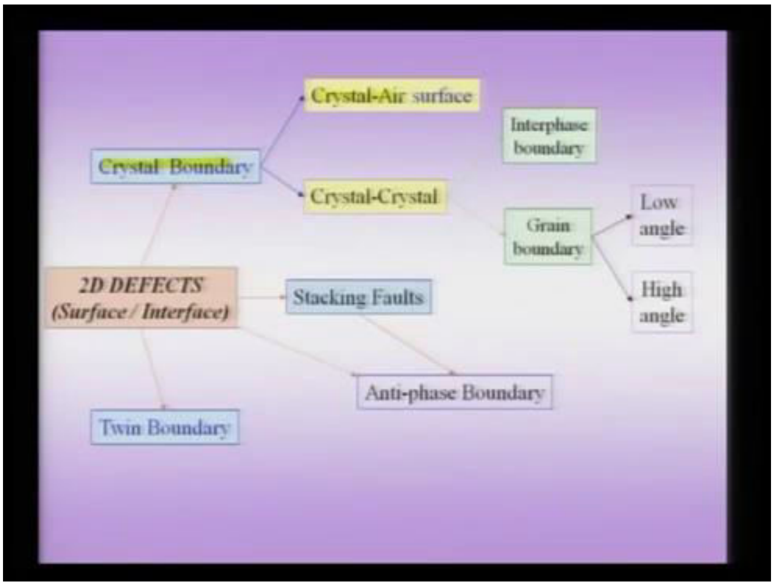
- ☐ Surfaces
- ☐ Grain Boundary
- ☐ Twin Boundary
- ☐ Stacking Fault
- ☐ Anti Phase Boundary

*Further reading*

*Crystallography and Crystal Defects*
A. Kelly, G.W. Groves and P. Kidd
John Wiley & Sons, Chichester (2000)

Let us now, proceed to two dimensional defect and we have already describe inhabitable one, which is the surface in any practical crystal. We will also consider the green boundary, the twine boundary and the stacking fault, apart from the anti face boundary when we discuss the two dimensional defects. For those who are interest in taking the advance training they can considering the book by Kelly and Groves on crystallography and the crystal defect.

(Refer Slide Time: 01:00)



Crystal-Air surface

Interphase boundary

Crystal Boundary

Crystal-Crystal

Grain boundary

Low angle

High angle

*2D DEFECTS*
*(Surface / Interface)*

Stacking Faults

Anti-phase Boundary

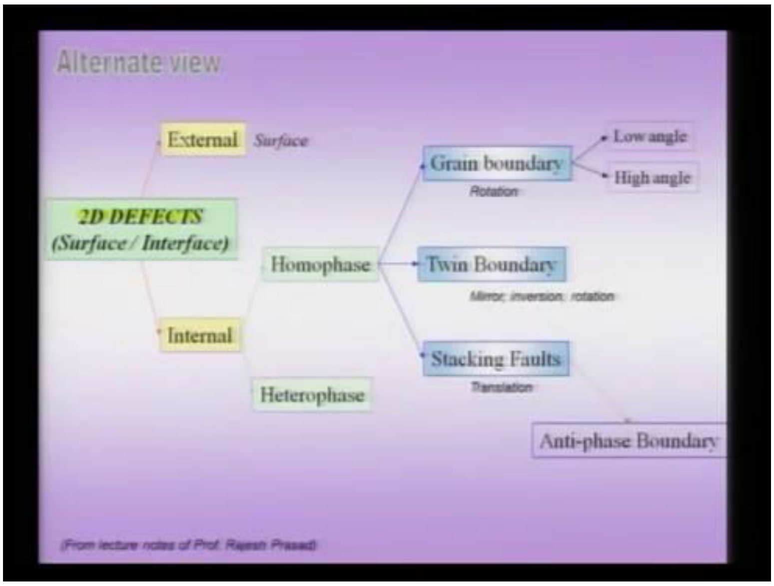
Twin Boundary

Let us start with the broad Oreo of possible two dimensional defects and perhaps more than, one way of classic defining the same. So, if you looking in the two dimensional defect, you can have the crystal boundary and this crystal boundary can be crystal vacuum interface, which we call the surface or it can be the crystal kind of an interface. Apart from this there are stacking fault, which are two dimensional defect and their two boundaries and especial kind of the stacking fault is also called an anti face boundary.

And we will consider, that at the later point we will be doing this lectures, when you are talking about the crystal interface, you can either talk about a crystal homo phase inter phase that means, the material on two size crystal has the identical structure. In which case, you call it the green boundary or it can between two phase in which case it will call and the inter phase boundary.

We will also consider the special case of this green boundary, which we will call the low range boundary and the high angle grain boundary. So, to summarize this line we have various kind of defect, like the crystal boundary, the stacking faults within any crystal and twin boundary, which is the special kind of the interface and amongst the crystal boundary you have the either of the surface or the internal surface. And if I talking about the internal surface, then you can have between two different kind of phases or phases of the same kind.

(Refer Slide Time: 02:19)



Alternate view

**2D DEFECTS**
***(Surface / Interface)***

External *Surface*

Internal

Homophase

Heterophase

Grain boundary
Rotation

Low angle

High angle

Twin Boundary
Mirror, inversion, rotation

Stacking Faults
Translation

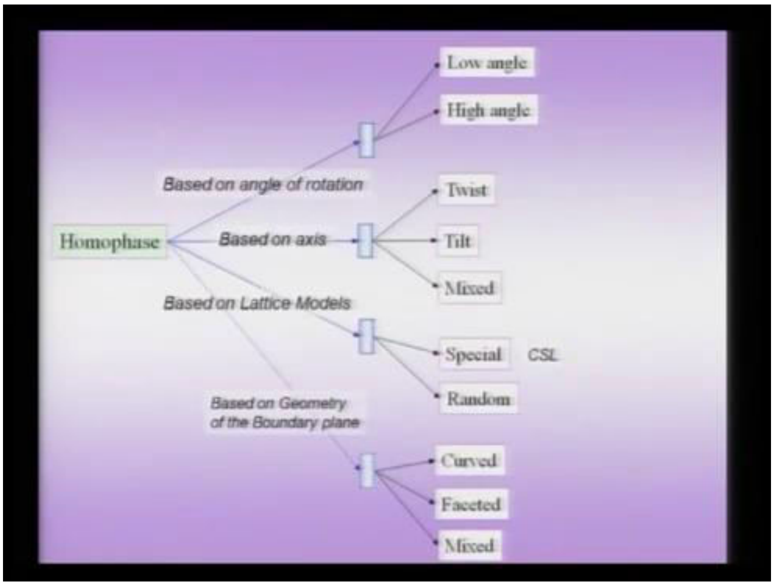
Anti-phase Boundary

(From lecture notes of Prof. Rajesh Prasad)

Let us look at the same classification in the different way, but you have two dimensional defects and they can be the external or the internal, we are talking about the external as I said typically, we consider the surface interface between the crystal and the vacuum or the crystal and layer. And the internal inter face could be the same kind of the face, which we call the homo phase boundary or it can be the hetero phase boundary, in which the phases on the either side of the boundary are of different type.

Homo phase boundary can be grain boundary, twin boundary and stacking fault and there are special thing, which we characterize this kind of boundary, the grain boundary character rotation or twin boundary characterize, by it is association with mirror inversion or the rotation of the symmetry. And the stacking fault is associated with the translation vector, there are special cases of stacking fault which of the antic phase boundaries. Grain boundary themselves has a pointed, out in the low angel or the high angel and the reasons for such, a classification and once it will become very clear, once we discuss the structure of this low angel grain boundaries.

(Refer Slide Time: 03:23)



Homophase

Based on angle of rotation
- Low angle
- High angle

Based on axis
- Twist
- Tilt
- Mixed

Based on Lattice Models
- Special CSL
- Random

Based on Geometry of the Boundary plane
- Curved
- Faceted
- Mixed

Now, the alternate way of looking at some of these or characterizing some of these homo phase boundaries, which we shall contract with hector phase boundary, is the way we look at them from the perspectives. We can look at the homo phase boundary either based on the angel of the rotation, in which case you can have low angel or a high angel and in this case we talking about the value of the angel of the rotation, which case they will have low angel or the high angel homo phase boundaries.

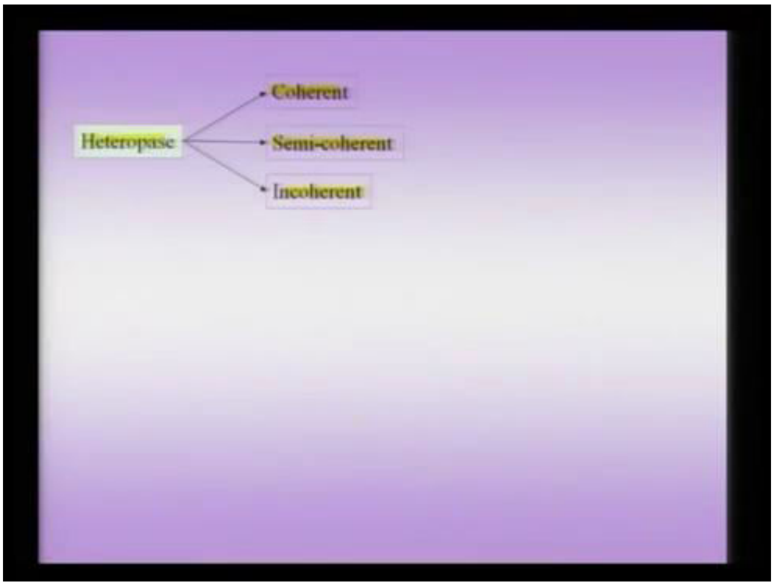
Of course, you could also have under special circumstances, similar kind of definition going to the defining the hector phase boundary, the homo phase boundaries based on the kind of axis. We are talking about can be a twist boundaries, the tilt boundary or a mixed kind of the boundary, the mix boundary will have twist and tilt components both, you will classify the homo phase based on the model, which are used describe them for instants, you can have c s l model describing which is known as a coincident site lattice models describing homo phase boundary.

And in this contest we can call homo phase boundary is special or random, so if you have the low angel, low coincident site lattice number, which is typically given has symbol sigma, then you call them special boundary or otherwise you call them random boundary. You can also classify them these homo phase boundary based geometry of the boundary plane, like you would have the curved boundaries you could have the faceted boundaries. And of course, you have the mixed boundaries in certain section they are curved certain section are faceted

So, to review this slide when I am looking at the homo phase boundary, I can characterize the homo phase boundary based on the various parameters, this parameter can be the angel of the rotation or more prissily the value of the angel rotation, you can be based on the axis. Which defines the rotation or it can be based on the kind of the model, which are used to describe this boundaries and these model also imply that for instant this special boundary typically low surface energy or interface energy value.

And based on the geometry of the bounding plane, like for instance you could have and these geometry also way this boundary behave, under for instance if you trying to course in the grain or you are trying to do one of the process under high temperature, it will depend for instant. if the boundary curved phase or mixed. So, we will consider some of these for instant low angel and the high angle boundary and some other aspect detail, some of the other aspect we will leave for future courses or higher level courses

(Refer Slide Time: 05:50)



Heteropase

Coherent

Semi-coherent

Incoherent

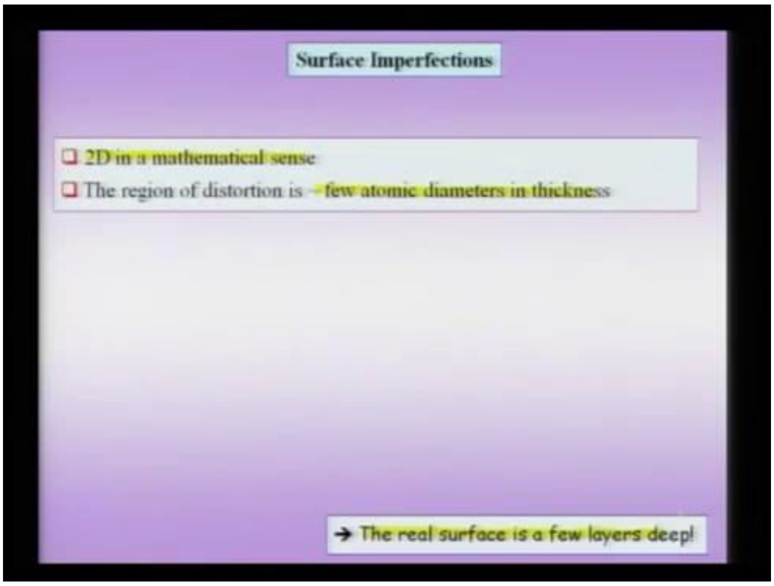
When you are talking about the hector phase boundary, you could have three kind of terminology coming in on the coherent kind of the hector phase, inter phase and in coherent kind of the inter phase or there can be something between which is a semi coherent hetero phase, inter phase. So, we will take up example of these and we will try to understand the structure and in some cases also the stress state of some of these boundaries.

So, going back to this slide we want to classify to dimensional defect and in doing, so we come across certain kind of defect, whose name perhaps many of this kind may be countering for the first time, like the crystal, the grain boundary here write here. The grain boundary or the inter phase boundary or the term like stacking fault, anti phase boundary or the twin boundary.

And we have alternate ways of doing, the same classification and alternative picture which sometime is more useful, in getting the complete picture or multiple percept of the same problem. And also when a talking about the homo phase or hetero phase boundary we come across multiple parameter, which go on to define this boundaries and some of this will be tilt in detail during this set of lectures.

Hetero phase boundaries, which I think very important technology also is very important understanding, the behavior of some of this some of this devices and materials, which are built with this kind of interface can be classified, as the coherent and semi coherent or incoherent.

(Refer Slide Time: 07:14)



Surface Imperfections

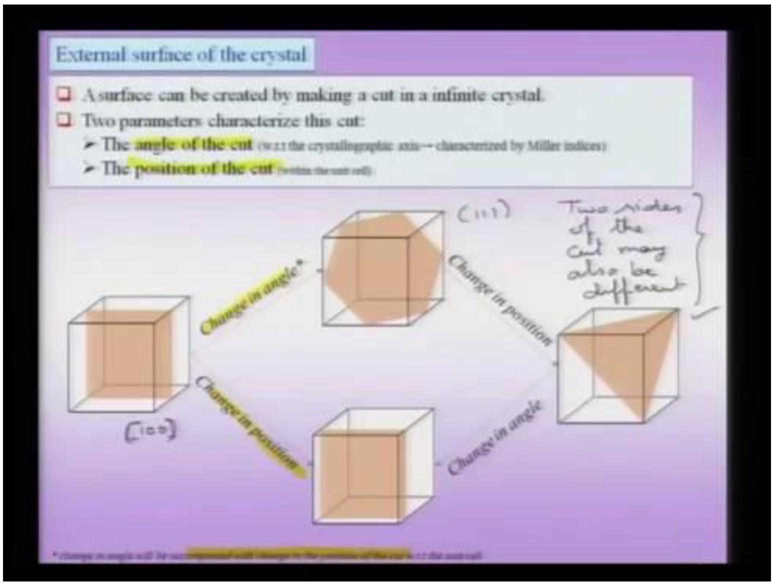
- ☐ 2D in a mathematical sense
- ☐ The region of distortion is ~few atomic diameters in thickness

→ The real surface is a few layers deep!

So, let us start with the most obvious of this inter phases, the surface and as the pointed out that the surface is an interface between the termination bulk with the arrow the vacuum, with even though we call some of this surfaces two dimensional defect. We have to remember as we before as I pointed out before that, this is two dimensional only the mathematical since and typically the region of distorting is the few atomic diameters in thickness.

In fact the real surface is always few layer deep, it is never just few one atomic layer because the disturbance, which is filled in the top layer is always follow to the next layer. And later on we will see, that we will come across the phenomena like reconstruction etcetera, were in the top most layer consist in certain way and the just below the top layer can also get reconstructed, but in the different way. So, it is and even in all cases we always call this surface, even though it is never the two dimensional it extends the few atomic diameter into the bulk.

(Refer Slide Time: 08:15)



External surface of the crystal

- ☐ A surface can be created by making a cut in a infinite crystal.
- ☐ Two parameters characterize this cut:
  - The angle of the cut (w.r.t the crystallographic axis → characterized by Miller indices)
  - The position of the cut (within the unit cell)

So, how do a create surface of the crystal, obviously I need to cut an infinite crystal and for this is an hypothetical experiment and I would cut this crystal and I would get two surfaces. And this cutting process obviously, is going to cutting the bonds and that means, that it is going to cosmic energy to actually create the cut. So, what are the parameter which would characterize such a cut obviously, it is going to be the angle of cut.

And now I am talking about the angel with respect to the crystallography access and be taken characterize, the miller indices and the second thing is the position of the cut within the unit cell. So, this is the another thing which I need to keep in mind, so whenever I am making, the cut of a crystal to create the surface I need to characterize the cut by angel, of the cut with respect to the crystallography axis.

And the position of the cut as well for instant, now suppose I have a crystal on the left hand side, which is shown on the unit cell of the crystal and I make the cut as I shown here, I can change the angle of the cut. And of course, along with this complete change in the position of the cut as well as with respect the unit cell, so we changing angel on the cut.

Now, I can cut the crystal in the different, as you can see the area of this plane is changing and obviously, the kind of bond, which I broken also will change with this. We will soon make some calculation of the energy, which is caused to make such cuts, but it is essential to the number that angel of the cut has to be changed. Alternately I can move this plane within the unit cell and changes the position of the cut.

So, in this case cut instant it is the 1 0 0 kind of the plane, but the 1 0 0 has been positioned differently, the cut which is shown here on the top this one is, so this is my 1 0 0 kind of a cut. But, now the same 1 0 0 as has positioned differently, now sorry I have to draw the plane here, so this the 1 0 0 cut. And this would be typically the 1 1 1 kind of the cut.

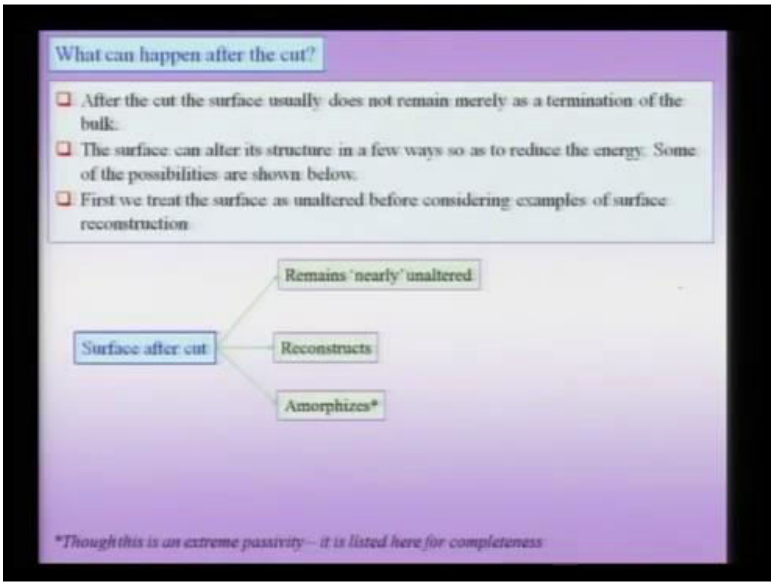
But, I can change the position of the is 1 1 1 plane and take a alternate 1 1 1 cut also within the crystal, the change in the such a position obviously, is going to alter the kind of the surface, I am going to expose could this may not be true for all kind of the crystal, but this and all kind of the plane. But, suppose I am visualizing for instant sodium chloride crystal, if I now change the orient the position within the crystal.

So, I may have the crystal with surface, which consist of only sodium atoms or I could have the crystal, which as only potassium chlorine atom on the surface. So, that would just be nearly by changing the position of the cut within the unit cell, so suppose I had the I make the cut like this in the position, I could land up in the one kind of the surface and I change the position, I could land up the other kind of the surface.

And the two side of the surface could also be different, suppose if have like this then the crystal on the top side could be different on the crystal, on the bottom side this is something which we have to remember, so we just write this down. So, this is something we have to remember and therefore, even though I may given the single plane of cut for instant 1 kind of a miller index, I have to remember, that if I move the plane within the unit cell, then I may actually we creating very many different kind of the surface depending of course, of the complex of the crystal structure and consider.

So, the essential to parameter remain, the angel of the cut the position of the cut and of course, once have may having may have a cut, I have to differentiate the two kind of the crystal, the two surface it make and they may not equaling. Because, the kind of the bond below the surface can be different on the one side compared to the other side, so this is something we have to keep in mind.

(Refer Slide Time: 11:56)



What can happen after the cut?

- ☐ After the cut the surface usually does not remain merely as a termination of the bulk.
- ☐ The surface can alter its structure in a few ways so as to reduce the energy. Some of the possibilities are shown below.
- ☐ First we treat the surface as unaltered before considering examples of surface reconstruction

Surface after cut

Remains 'nearly' unaltered

Reconstructs

Amorphizes*

*Though this is an extreme passivity – it is listed here for completeness

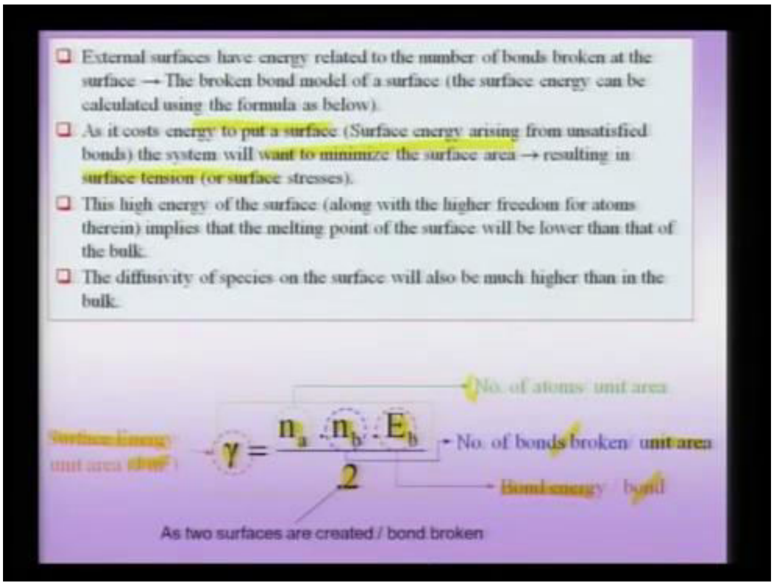
Now, the question we are asking is that after having the had cut after and having the two surfaces and we already mentioned, this two surfaces could actually different then what can happened to the surface, will the surface remain un halted or will it change, its change in certain way. So, the of course, the simple possibility is that it remain essentially un halted, so this is my simplest available alternate.

But, there are interesting possibility, which happened to the crystal like for instant surface can actually reconstruct that means, the surface crystal structure can become different from the bulk crystal structure and therefore, the surface is no longer merely a termination of the bulk. So, this is something which very important and we will take up may be some examples during the later part of this lectures.

So, what I am trying to tell in this case is that, when I am making the cut I create a surface, which is nothing, but the termination of the bulk. But, it is surface need not remain nearly the termination of the bulk and can alter, it structure respect to the bulk and this alteration obviously, takes place. So, that the energy of the surface can be reduce, because now the cutting it involves increase in the energy of the system.

Because, now you have broken the bonds and this reconstructions can actually, lead to the reduction in the surface energy in extreme circumstances we can also be visualize, this surface may actually become less order with respect to the bulk, but this is an extreme possibility and we will not consider this further.

(Refer Slide Time: 13:27)



❑ External surfaces have energy related to the number of bonds broken at the surface → The broken bond model of a surface (the surface energy can be calculated using the formula as below).

❑ As it costs energy to put a surface (Surface energy arising from unsatisfied bonds) the system will want to minimize the surface area → resulting in surface tension (or surface stresses).

❑ This high energy of the surface (along with the higher freedom for atoms therein) implies that the melting point of the surface will be lower than that of the bulk.

❑ The diffusivity of species on the surface will also be much higher than in the bulk.

$$\gamma = \frac{n_a \cdot n_b \cdot E_b}{2}$$

Now, what is the simplest way I can calculate the energy of the surface, so the simplest assumption I can make is that after making the cut, this surface remain un alter and it is exactly the same as the bulk, it is the termination of the bulk. So, in this case I can go had and make the calculation of the energy based on the number of the bonds it is broken.

So, I can see that the energy to put the surface, the system I want to minimize the surface area and this will result in surface structure. So, before I go into surface structure let us try to calculate the energy and what are the terms, going to be calculation of the energy.

So, the surface energy which is joule per meter square, because now the two dimensional ((Refer Time: 14:09)) per meter square denominator, is usually designated by the value gamma.

And initially we are considering just the mean surface, what you might call the energy of the surface, additionally we can also define terms like surface free energy like the surface free energy. But, we are not doing, so in this case that means, we are ignoring isotropic in this energy, now what is the value of the surface energy is first thing to know is there are number of the atoms on the surface, then I need to know that numbers of bond broken, when I acutely take the cut then I need to know the bond energy per bond.

And of course, I will divide this whole function by 2, because now the two surface being created half the energy would one side of the one surface, on the other half of the energy, because of the breaking of the bonds will any other surface. So, if you calculate the unit of this diagram or the units of the function, you will see that it is number of atoms per area, which is n a and if you multiple that by number of bonds broken per unit area.

So, this is the second term and this is bond energy per bond, so you will get that multiplication of the three units will give you energy per unit area. So, you will have this energy per unit area, while this bond terms will cancel with bond terms here, this function in this number of atoms the terms will cancel with. So, you will land up with this is the number of atom per unit area, so you get this area from there.

So, what does it mean to have a surface energy when I make, this cut it means that the surface will always want to be reducing its area. And we will try to pull upon itself this is an important thing that means, that the crystal does not want to have the large surface area it will try to minimize this surface area, atoms on the surface area want to come towards each other. And this implies the surface is in a state of tension, which is known as the surface tension.

As you can see later the term surface tension is better used in the contest of liquid and the terms surface stresses is better used in the contest of solids and we will state the reasons why, but never the less the origin of the surface tension is coming from the energy, which is expanded, when i am trying to put a surface. Now, we will make the calculation, showing how the formula can be used in the calculation of the surface energy.

But, we have to remember this is what is called the broken bond model, in other words that I do not incorporate any other effect, like surface relaxation after the cut is made or any kind of reconstruction effects and therefore, this is the simplest kind of formula, I can deal. Now, the another important effect of the surface energy is that, the given the surface as an is the state of high energy and also the fact, that the surface has higher freedom compared to the bulk the atoms in the surface can vibrate higher degree of freedom.

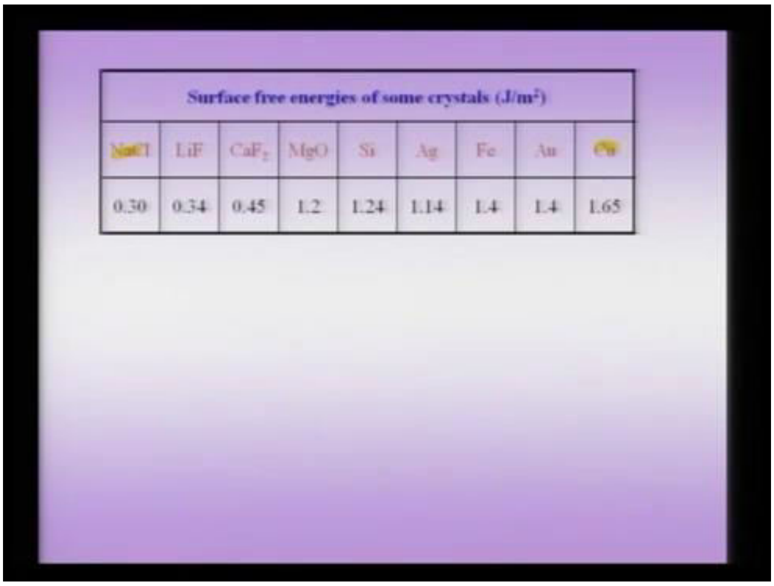
As compare to the atoms in the bulk, then the melting point of the surface is lower than the melting point of the bulk that means, the surface would melt at lower temperature as compared to the bulk, additionally the surface is the region were diffusivity of spices also we much higher as compared to the bulk. So, wherever I have a diffusivity issues there are lot of the surfaces, in the system then the atomic species will rather be transported though the surface, even though cross section available through the surface may be small.

But, it will be transported on the surface as compared to the bulk, a good example would be suppose I had the material, polycrystalline material here. And we had a vertical boundary a green boundary, so what will happen is the suppose if I heat such the material then due to surface tension balance you will see small glow will form. And typically this glow tent to form and this is purely in this effect of temperature.

So, I have the boundary which is deeply, now in this case ((Refer Time: 18:07)) mass transport has to occur from the region, here were there was material to the surface. And this can take place either to the bulk or it can take this surface were essential, it absorb in such problems it is a surface diffusion is playing the dominate role. Because, there is the defect to get the surface, because of the available freedom of the atoms to be present there is much higher than the bulk diffusion.

So, we have the formula for the energy and this formula has three terms to it, the number of atoms per unit area, the number of the bond broken per unit area in the bond energy per bond.

(Refer Slide Time: 18:48)

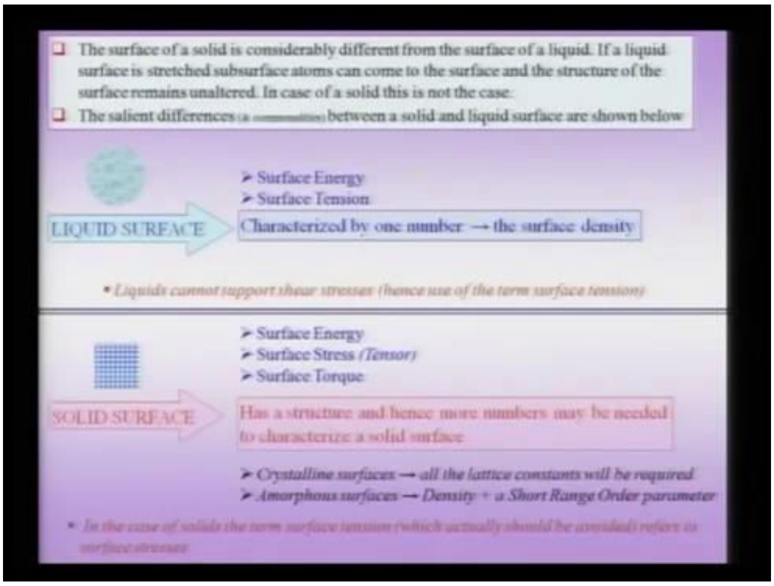


| Surface free energies of some crystals (J/m$^2$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| NaCl | LiF | CaF$_2$ | MgO | Si | Ag | Fe | Au | Cu |
| 0.30 | 0.34 | 0.45 | 1.2 | 1.24 | 1.14 | 1.4 | 1.4 | 1.65 |

If you look at the surface free energy of some crystal listed here, you would notice that some of the iron nickel sodium chloride etc have a lower surface energy as compared to the copper. And of course, in the sodium chloride we have to worry about the kind of the surface, we are talking about and we will come to the detail of the kind of surface very soon.

Because, typically surface energy is not isotropic and that is the reasons suppose if you have equilibrium crystal will notice that the surface is never ((Refer Time: 19:13)) you have equilibrate the crystal for a long time, it will be notice that it is actually polyhedron surface that, the crystal would put out. Now, so but you can see the order out surface energy is about, the order about joule per meter square of the surface.

(Refer Slide Time: 19:30)



- ❑ The surface of a solid is considerably different from the surface of a liquid. If a liquid surface is stretched subsurface atoms can come to the surface and the structure of the surface remains unaltered. In case of a solid this is not the case.
- ❑ The salient differences ([illegible]) between a solid and liquid surface are shown below

LIQUID SURFACE

- ➢ Surface Energy
- ➢ Surface Tension

Characterized by one number → the surface density

- *Liquids cannot support shear stresses (hence use of the term surface tension)*

SOLID SURFACE

- ➢ Surface Energy
- ➢ Surface Stress *(Tensor)*
- ➢ Surface Torque

Has a structure and hence more numbers may be needed to characterize a solid surface

- ➢ *Crystalline surfaces → all the lattice constants will be required*
- ➢ *Amorphous surfaces → Density + a Short Range Order parameter*

- *In the case of solids the term surface tension (which actually should be avoided) refers to surface stresses*

Now, I had mentioned that a surface of a solid is considerably different from the surface of a liquid and they have be differentiate and not only that, the number of the parameter which go into the definition itself is very different. Suppose I had the liquid surface the essential difference come, suppose the stretch liquid surface. So, what it happen is that the surface area is increasing by stretching, suppose I take the soap fill for instants has a example I would take the soap fill between two slider.

Now, I am looking at the soap filling from the side, if you look from the top slider like this and I have the soap this is my slide view here, this one and i am stretching this. So, I am stretching this soap fill across the this sliders, so what would happen is that as the film is stretch the surface area is increasing. But, then the atoms is the sub surface can acutely can come and sit on the surface atom belong can come and sit on the surface.

And to accommodate with stretch, in other words my surface stretch remains an alter with respect to the stretching, as I keep on stretching more and more atoms come to the surface and the surface structure remains unaltered as I am stretching the material for this soap fill. But I am suppose, I am stretching the solid obviously, this is not true at least at the normal temperature, whether the deficient rate is very small this is not true.

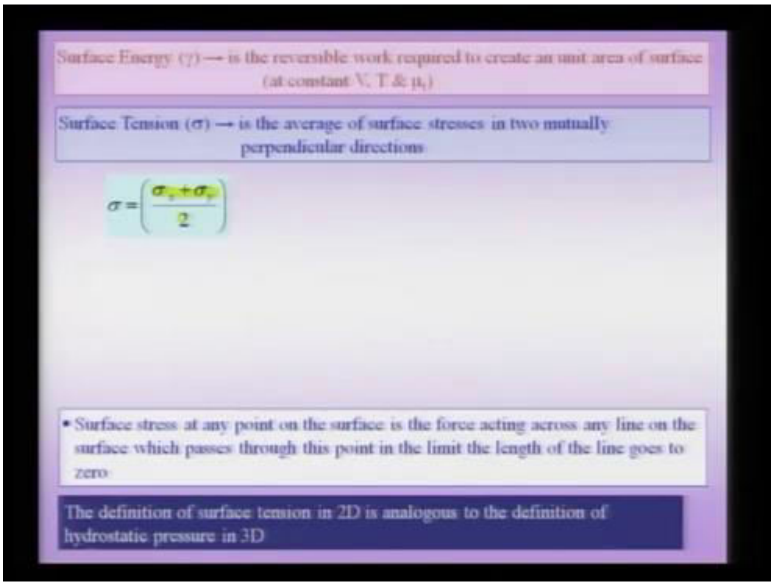
Now, this make the liquid surface considerably different from the solid surface, let us look at the some of the terms which are used defend in solid and liquid surface obviously, both of them are associated with the surface energy, which is coming from unsatisfied coordination. In the case of the liquid surface, a term like surface tension will be used while in the case of solid, the appropriate term surface s stress, which is actually the stress.

And the difference between the two molecule when you go to the next slide and in the case of, if I want to characterize a liquid surface I need to characterize just by one number, which is the surface density of the atoms. And more importantly liquid surface cannot support sphere s stress, they can support normal s stress, but not share stress a solid surface apart from being characterize by actually ((Refer Time: 21:40)) surface in the surface tension.

Of course, we could always calculate surface tension based on the surface stress, but we will see that this is not sufficient and actually the surface stress is the better term to define the solid surface. But, additionally the surface also say that something known as the surface torque, the origin of the surface torque we will consider very soon, but more importantly let us first consider the term surface stress and its different between the liquid and the solid.

And suppose I want to characterize the solid surface, we have to remember that is why I am talking about crystalline surface, then all the lattice surface will be required to characterize my crystalline surface, amorous surface can be characterize by the density and sort a short rage parameter. So, what is the surface tension and why is the and different from the surface stress.

(Refer Slide Time: 22:28)



Surface Energy ($\gamma$) → is the reversible work required to create an unit area of surface (at constant V, T & $\mu_i$)

Surface Tension ($\sigma$) → is the average of surface stresses in two mutually perpendicular directions

$$\sigma = \left(\frac{\sigma_x + \sigma_y}{2}\right)$$

- Surface stress at any point on the surface is the force acting across any line on the surface which passes through this point in the limit the length of the line goes to zero

The definition of surface tension in 2D is analogous to the definition of hydrostatic pressure in 3D

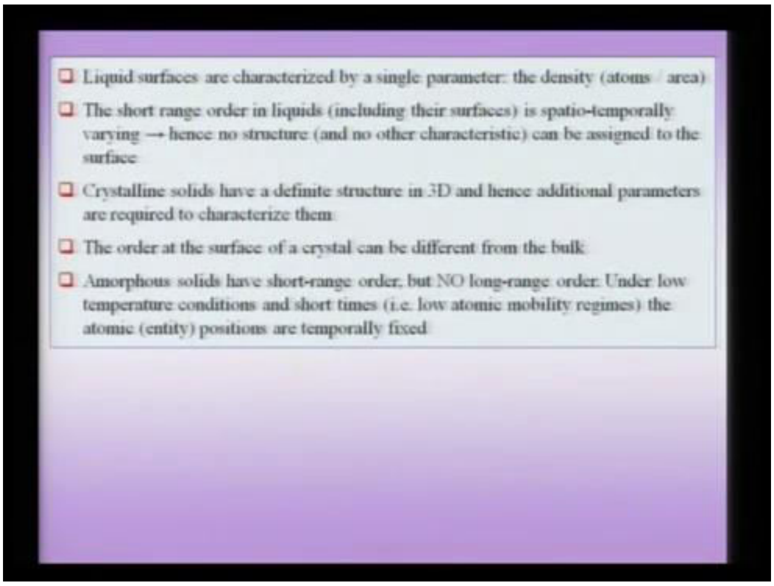
Suppose I have surface obviously, two dimensional defect and therefore, I will have a four component to my surface, I can define the surface tension as the average of this stress into to orthogonal direction, so that is my surface tension. But, now because if I am talking about the solid, I need all the four of course, it is symmetry tensile and i will have three independent component to this and we will also have the sphere stress component which of course, the liquid surface cannot support.

Therefore, I have to remember the surface terms is the better term to describe solid surfaces and I can calculate of course, the average of the two orthogonal stress. Which is nothing, but which is analogist to the definition of the hydro static pressure in three dimension, this kind of the average is nothing, but analogues to the two dimensional version of the three dimensional hydro static stress.

So, when I am looking with the liquid surface, I can use the some surface tension, but I will never working solid surface, I need to use the surface stress as the describing quantity. The surface energy can alternately can be define, as the reversible work done to the create a unit surface, so this is an alternate way which is based on energy, which is input acutely to create the surface. And this kind of the definition would beautifully when i of course, the kind of experiment I am talking about were in you have the slider pulling soap bubble or a soap sorry.

So, it is now clear that I am talking about the solid surface, which can now support the sphere stress I need to be little careful in the way I characterize the solid surface. And the important point to note is, that I am pulling the surface the solid surface can will actually alternate the structure, the bonds on the surface will be longer and it will no longer maintain original structure, before the stretching process begin. Which is what the assume in the case of the liquid surfaces and addition as said, there is the additional terms which we need to worry about surface torque, the origin which we will take up soon.

(Refer Slide Time: 24:31)



- Liquid surfaces are characterized by a single parameter: the density (atoms / area)
- The short range order in liquids (including their surfaces) is spatio-temporally varying → hence no structure (and no other characteristic) can be assigned to the surface
- Crystalline solids have a definite structure in 3D and hence additional parameters are required to characterize them
- The order at the surface of a crystal can be different from the bulk
- Amorphous solids have short-range order, but NO long-range order. Under low temperature conditions and short times (i.e. low atomic mobility regimes) the atomic (entity) positions are temporally fixed

So, to summarize the liquid surface is the characterize by the single parameter density which is atoms per unit area, there is short range order liquids, but this order is bearing in time. And therefore I can describe any further structure to this liquid surface, the crystalline solid have the definition structure in the 3 d additional parameters are it is required to characterize, the surface of this crystalline solid and more importantly the order of the surface of the crystal can be different from the order in the bulk.

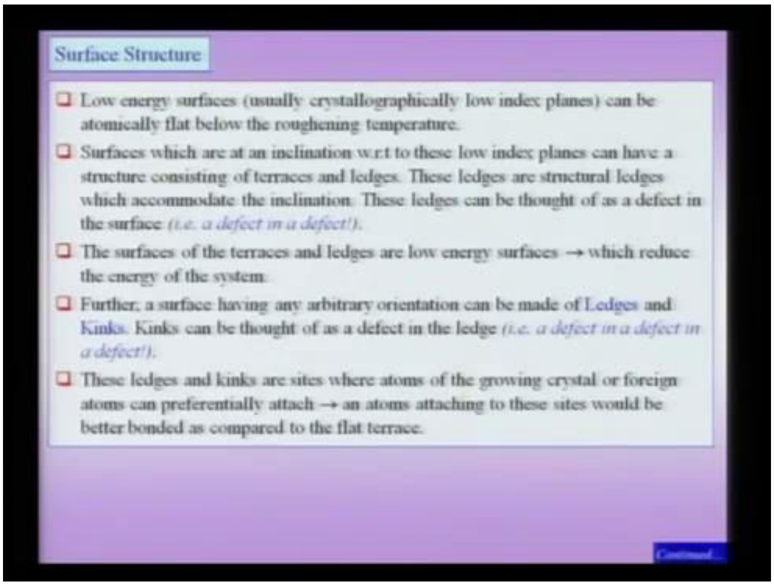
So, that is why the surface can have an independent entity or existence or description compared to the bulk of the system, so this is very important to note and amorous solid have only short range order, but no long range order, And so this is why the enormous surface would have to be characterize very differently from the crystalline kind of the surface.

So, how what is the structure of the surface, that we are talking about typically it is obvious, that if I have the crystal we create and I inhale the for long times, this crystal like to put up the lower energy surfaces, the system cost to the energy is small what kind of the construction we will briefly argue. So, we know how to arrive this kind of equilibrium the surface construction, though we will not go into detail, but we will at least tell the methodology, which is involves in understanding how the surface is what kind of the surface the crystal put out.

But, never the less, it is clear that there are this low energy planes and this low energy planes and these energy plains typically are the cryptographic low index planes. So, the crystal suppose puts out the low energy plane, this can atomically smooth below the roughing temperature. So, the roughing temperature is the temperature above which actually the surface, becomes very rough and there is no longer actually nice to talk about this flat atomic planes.

But, essentially suppose I am talking about a crystal at low temperatures that means, that I can talk about this low crystallographic index plane, which are low energy planes and they are atomically smooth. Now, if I go of this low angel that means, I do not no longer work with low index plane, but I am of the angel in which this instillation of this low index planes.

(Refer Slide Time: 26:43)



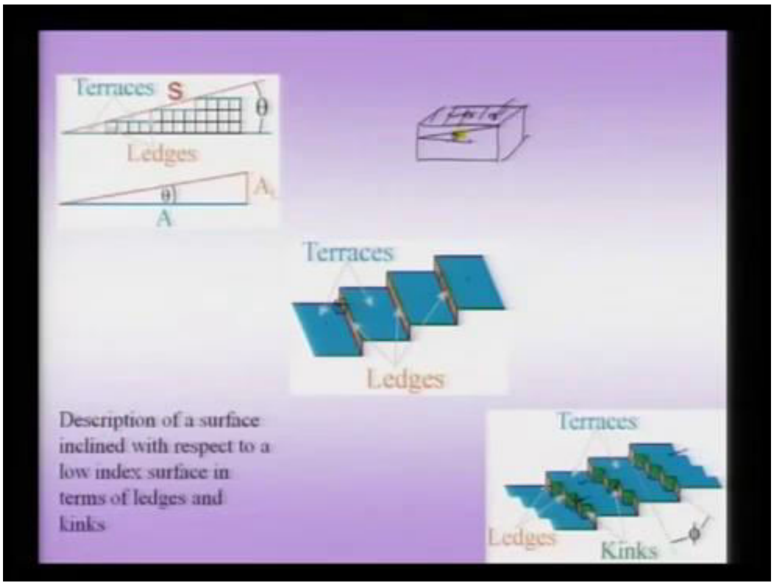
Surface Structure

- ☐ Low energy surfaces (usually crystallographically low index planes) can be atomically flat below the roughening temperature.
- ☐ Surfaces which are at an inclination w.r.t to these low index planes can have a structure consisting of terraces and ledges. These ledges are structural ledges which accommodate the inclination. These ledges can be thought of as a defect in the surface *(i.e. a defect in a defect!)*.
- ☐ The surfaces of the terraces and ledges are low energy surfaces → which reduce the energy of the system.
- ☐ Further, a surface having any arbitrary orientation can be made of Ledges and Kinks. Kinks can be thought of as a defect in the ledge *(i.e. a defect in a defect in a defect!)*.
- ☐ These ledges and kinks are sites where atoms of the growing crystal or foreign atoms can preferentially attach → an atoms attaching to these sites would be better bonded as compared to the flat terrace.

Then this structure of these kind of planes can be described, by terraces terrace and ledges and we will see the picture in very next slide, these ledges which I am talking about a structural ledges. So, this is very important, because these ledges are not random ledges they are structural ledges they are accommodate the inclination. So, like we talked about the dislocation are accommodating inclination, between two grains.

And which we will consider in this chapter, were we will talk about low angel grain boundary, which go on to accommodating inclination between two grains. Similarly, an in inclination of the surface is accommodate by this structural ledges, which forms on the surface and we will and this is how they look.

(Refer Slide Time: 27:20)



Description of a surface inclined with respect to a low index surface in terms of ledges and kinks

Suppose I have a low index plain to star with demo this low index plane, so suppose I have the low index plane like this, now in the crystal then I make a cut, which is at the inclination to this low index plane for instance as shown, here at the angel theta for instance, then this low index plane is not a plane which is continuous. But, it is accommodated by the presence of terraces like this blue mark region, which are terraces terrace and ledges.

And as I pointed out this ledger are structural ledges and in principle this ledger would repeal each other and therefore, there will be tent to be as equally spaced as possible. So, now when I am going of this low index plane to into high energy configuration, the surface breaks up into two components, one is the surface a terraces terrace and ledges.

Such that, both of this correspond to low energy and therefore, the system energy is minimize by putting out not some arbitrary inclined surface.

But, the surface which is low energy inclination which planes which are bounded by plane, which are low energy, so this a very important point and this ledges interesting can be classified as a defect in a defect. Because, surface itself is the defect which, now the termination of the bulk in some sense and these ledges are the defect in the surface and therefore, they can be thought of defect in a defect.

Now suppose and this defect arise, because now had inclined my surface in one direction with respect to the original free surface, now I can cause inclination in the other surface as well that means, I have further incrimination not one angel theta, but the other direction as well. As in that case you would notice that the surface accommodate not only by the presence of these ledges and terraces, but also by kink in the ledge and interestingly consider in this figure which is the bottom, I am showing here figure the bottom, that these are the kink.

So, originally you had just a terraces, which is the free surface here which we can call it terrace it can broke down into ledges here and the terrace and the ledges, again had a orientation which was a low index plane, low energy surface. Further the second inclination was accommodate by the presence of kinks in the ledges and the kinks obviously, again put out the low energy surface.

Now, the total energy of the system can be calculated the energy of the terrace plus the energy of the kink plus the energy of the ledges and interestingly if you want to understand this ledges again this are structural ledges, sorry this kinks are structural and more interestingly I can understand this kinks as a defect unit. So, this is a second order defect, because surface was the first defect the ledges was defect in the surface therefore, I called them in a defecting the kinks are defect in the ledges therefore, there are defect in the defect.

And this kinks and ledges are very important role, when we are talking about crystal growth and for instance suppose I have an a growing crystal. Suppose, I had a flat surface like this then attachment of atoms to this surface will involve nucleation problems, that means, that this atoms this side would be no more to ((Refer Time:

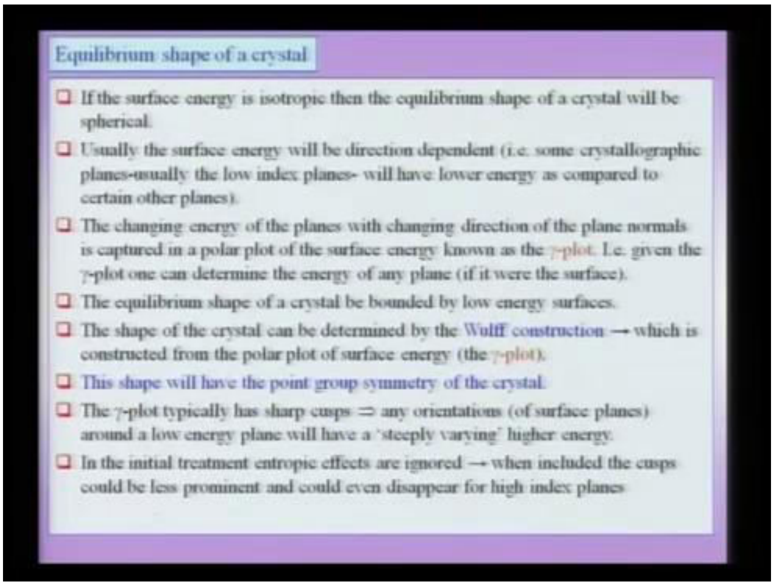
30:47)) then some other sides on the surface and the atoms actually diffuse around analyses, the a critical mass which is called a nuclei the crystal surface would not grow.

But, we are talking about the presence of ledger, then this sides are high energy size to come and sit here, you can see can actually put an atoms here much most easily compare to the interest. So, you have preferential sides, now, on the crystal surface for crystal to grow, now we already seen that we talking about this can preferential sides this ledges is very simple to the kind of which provide screw dislocation comes minting on the surface. We saw constructed the role of dislocation and crystal grow and that surface the role was similar to the ledge providing crystal growth.

Now kinks again even higher preferred better side for at atoms to common attach at you can, now comes and attach here, so this is the most preferred sides next preferred side will be the here and third less would be the proffered terrace. So, the kinks sides higher performance ledges of slidely lowers preference and terrace and even lower presence when it comes to atoms attaching to the presence of this kinks and ledges which are defects from the surface, actually help in crystal growth.

So, in this case we consider them as to be arising out of necessity of the accumulating inclination on the surface, so this is coming from the fact the I am inclining to my surface with respect of to the low index planes. And this inclination is the accumulate as not smooth cut, but as break up into ledges this kinks, because this now that in the case of crystal only putting out the post and surfaces, which have a low energy, so this is the description of the surface in terms of ledges and kinks.

(Refer Slide Time: 32:44)



## Equilibrium shape of a crystal

- ☐ If the surface energy is isotropic then the equilibrium shape of a crystal will be spherical.
- ☐ Usually the surface energy will be direction dependent (i.e. some crystallographic planes-usually the low index planes- will have lower energy as compared to certain other planes).
- ☐ The changing energy of the planes with changing direction of the plane normals is captured in a polar plot of the surface energy known as the $\gamma$-plot. I.e. given the $\gamma$-plot one can determine the energy of any plane (if it were the surface).
- ☐ The equilibrium shape of a crystal be bounded by low energy surfaces.
- ☐ The shape of the crystal can be determined by the Wulff construction → which is constructed from the polar plot of surface energy (the $\gamma$-plot).
- ☐ This shape will have the point group symmetry of the crystal.
- ☐ The $\gamma$-plot typically has sharp cusps $\Rightarrow$ any orientations (of surface planes) around a low energy plane will have a 'steeply varying' higher energy.
- ☐ In the initial treatment entropic effects are ignored → when included the cusps could be less prominent and could even disappear for high index planes

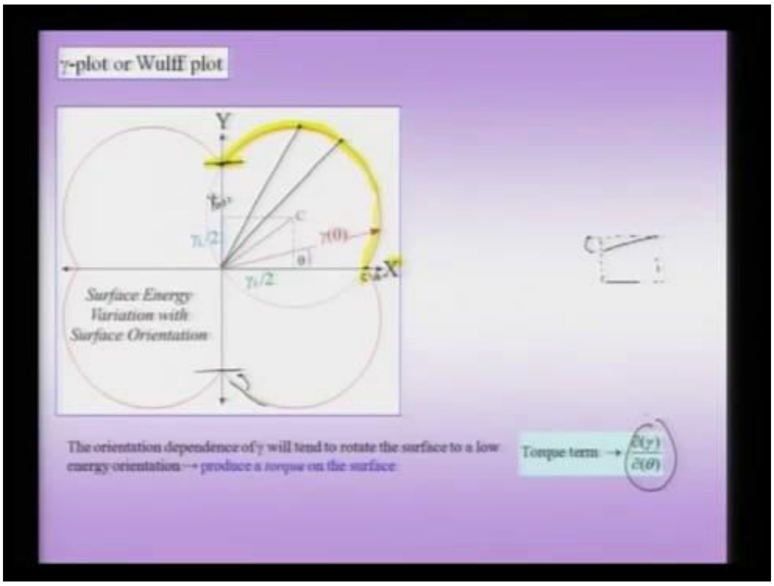
Next, we go the another important topics, which is the equilibrium shape of the crystal now if the surface energy isotropic, I should another words surface energy does not depend o n the directions, in which I am looking for or equivalently the plane of the cut then equilibrium shape of the crystal is obviously, going to be as sphere. So, the crystal will be theatrical if the surface energy has no preferential direction in other words.

Suppose I make cut in the crystallography become 1 0 0 or 1 1 1 or even 42 3 4 hundred 32 and that kind of index plane, it would not make a difference and therefore, the equilibrium shape of the crystal would the spherical, the equilibrium shape of the crystal will always be different associated with respect to the growth shape of the crystal. Because, the growth shape of crystal becomes the fat of growing planes exhaust themselves like growing fast and the crystal would be left out the planes, which are the slow growing planes and that is clearly difference from the equilibrium the shape of the crystal.

Now, the equilibrium shape of the crystal means that I am talking about crystal is only putting the low surfaces, which are low in energy. So, this is clearly the difference between equilibrium shape and the grow shape of the crystal, now to obtain the equilibrium shape of course, the crystal has to be yield, normally for long times and crystal gas go to slowly, which is the list and for the system.

But, normally individual crystals the surface of energy are non isotropic that means, going to be depended or it is going to depend on the kind of plane and I putting out the kind of cut time, making out the surface it going to tell me, what is the energy of the system. Therefore, the certain place of the lower energy compare to the certain other planes which have not higher energy. So, this point has to be kept in mind, now this energy variation of plane with the respect of directions, is captured is polar plot of surface energy, which is known as the gamma plot.

(Refer Slide Time: 34:43)



$\gamma$-plot or Wulff plot

The orientation dependence of $\gamma$ will tend to rotate the surface to a low energy orientation → produce a torque on the surface

Torque term → $\frac{\partial(\gamma)}{\partial(\theta)}$

And let me show the gamma plots like gamma plots look like something this another words, suppose I have the coordinates this sill of equator plot. So, what I am drawing here is that, suppose if I am looking out this direction and this my surface energy for this planes ((Refer Time: 34:55)) I am working some other arbitrary direction for instance my surface energy actually increases. So, this distance is proportional to my surface energy the gamma.

So, here surface energy gamma has the certain value, so this is for instance suppose this plane is correspond to the 0 1 plane and this is arbitrary plane and therefore, the surface energy increased, you go further away from this is increase even further and then again it reduce the and I go to a crystallography equivalent like 1 0. Therefore, in typically in crystal surface energy will varies with respect to the angle of the cotter.

Now, if I already have a gamma plot that means, and I can determined energy of any given plane or from the gamma plot of the initially the gamma plot has to be itself, it has to be determined knowing the kind of surface the crystal has got. Now the equilibrium the shape of crystal will be bounded by, this low energy surfaces and we will determined the crystal shape by something, known as the wolf constructions and which we construct from the polar are surface energy the gamma plot you will see that.

So, having the gamma plot we can use the wolf construction to determined the equilibrium shape of the crystal and the important thing, about this equilibrium shape is that it will have the point groups symmetry of the crystal. So, another words the whole mathematical concept of point group and a which are know, what I mind call physical bases or comparison with real crystals, which are derived truly mathematically, they converse with the concept of real crystal, when actually talking about the external equilibrium shape, which will correspond to another point group of symmetries of the crystals.

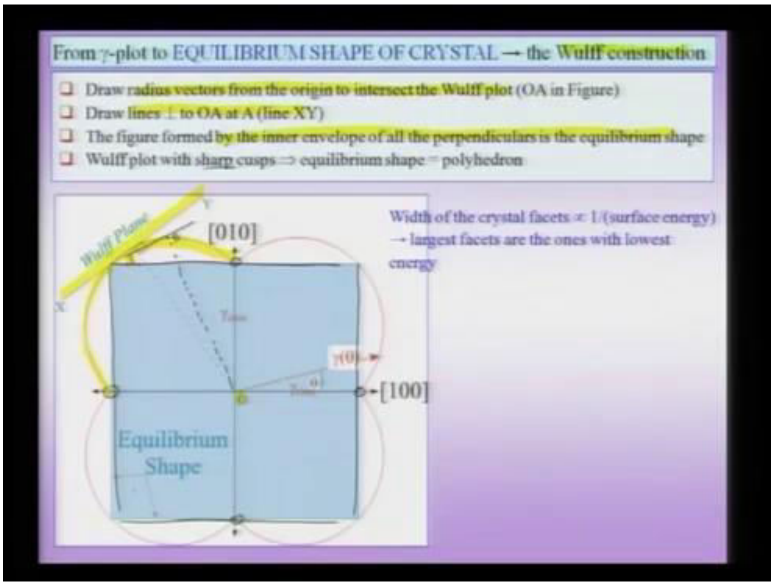
Now, to the point group symmetry of the crystal, now important point noted about this gamma plotted that typically has sharp cusp and any orientation or any plane around this will low energy plane, will have with stably very the higher ledges that means, the crystal. If the gamma plot has sharp cusps, then the crystal to throughout those planes which corresponds on to this directions, initial treatment we will elastic ignore then to the epics and just try to understand physically, that how a crystal can have actually allowing next plane as surface.

So, we already seen gamma plot you seen that the energy of the surface, where is the respect of two directions and it goes through, maximize number between a certain angles but they are sharp cusp in the gamma plot, which correspond to certain lowing index planes. Now, what is this imply that means, that suppose I have a crystal having this kind of surface see for the instance, this surface or compare to the surface which are this surface system.

So, now, I have un making crystal and this is my low energy surface this is, now I am making the crystal surface which has a cut something like this obviously, this surface will not like to be a orientation. And it want to rotate itself to low energy orientation then other this surface would like one to go to an orientation, like this and this is origin of the surface tall in another words.

The surface energy and isotropy or the variation of the energy in surface directions, once to rotate the surface to low energy surface and this is something like a tark. And then therefore, this origin for the surface tark, this is why this initial surface in trophy is energy makes surface, crystalline surface to different to in way living of significant various different from the liquid surfaces, the they will be no such effect of surface tark. So, this is something in a at list the concept of surface talk, directly comes out of the study of this from a plots, wherein the witch. So, the variation of the energy with direction.

(Refer Slide Time: 38:46)



From $\gamma$-plot to EQUILIBRIUM SHAPE OF CRYSTAL → the Wulff construction

- ☐ Draw radius vectors from the origin to intersect the Wulff plot (OA in Figure)
- ☐ Draw lines ⊥ to OA at A (line XY)
- ☐ The figure formed by the inner envelope of all the perpendiculars is the equilibrium shape
- ☐ Wulff plot with sharp cusps ⇒ equilibrium shape = polyhedron

Width of the crystal facets ∝ 1/(surface energy)
→ largest facets are the ones with lowest energy

Now, how to get the equilibrium shape of the crystal from the gamma plot as we set the something known as the good constructions, which briefly go around go over here. But, I am sure a advance task there can be more detail describes of the same, so what we derive we do does that of course, we have we gamma plot start with. So, this my gamma plot lines.

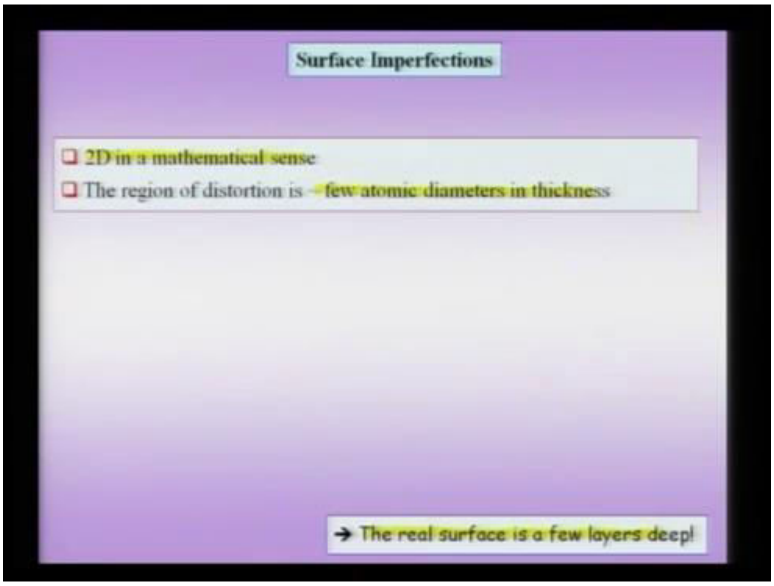
And then I draw origin vectors from the vectors take the wolf plot, for instance draw this line like o a just shown here o a which intersect the gamma plot, I draw a tangent lines perpendicular to o a like lines x y here. And now the figure form the inner all the perpendiculars with the equilibrium shape of the crystal. So, I draw a 1 point here at plane o a then I consider another point o, d here, then I draw my line joining the 2 then I draw perpendicular here to this line, then I calculate inner this is point b for instance I calculate inner envelope the all this point.

And that will give me my equilibrium shape of the crystal, because this plot shown in a gamma plot has dark as points like this points, now the inner envelope, now actually consist of planes which are shown here which is nothing, but this plate planes here. And therefore, now my equilibrium shape of the crystal, this crystal into 2 dimensions square and therefore, any kind of a gamma plot or any crystal having gamma plot very ((Refer Time: 40:27)) to have a poly hydrant outer shape.

Of course, if I enter the extra takes in the account, some of this phase maintain to get more smooth then as compare to strict poly hydrant, but in the ideal case when we interface of ignore, then you will see that this crystal is bound by faces, which form of poly hydrant. And width of this faces inversely proportional to the surface energy that means, the largest face are the once within lower energy, which is obviously, given fact that take always like to put maximum area for those surfaces which is have a lower energy.

So, given the gamma plot I can make a wolf constructions to determined the equilibrium shape of the crystal. So, that is revise some others concept here come across during the concentration surfaces and some of this terminology may be new to us when we decide discuss surfaces.

(Refer Slide Time: 41:21)



Surface Imperfections

- ❑ 2D in a mathematical sense
- ❑ The region of distortion is ~few atomic diameters in thickness

→ The real surface is a few layers deep!

So, important thing we started with even that we call it as the surface, it is actually extends of few players and often the inertial layers of also have a performed equivalents on the properties of the surface. Now, for instance and we create the second things saw that the surface can be created by angle of cut and the position of the cut. And when I create us a cut the two size of the two surfaces, which I create using the cut may actually have different, may be actually different kind of surfaces and this is very important.

And when we do cut we can start with the simplest models, which is known as the broken bone model, we are in when we understand the surface as I said termination of the balk kind, I need to bother in calculate of the energy another kind of aspects during the crystal surface. But, typically or in many cases there could be a approaches, which is known as construction and therefore, my surface would be alternate structure with respect of to the bulk.

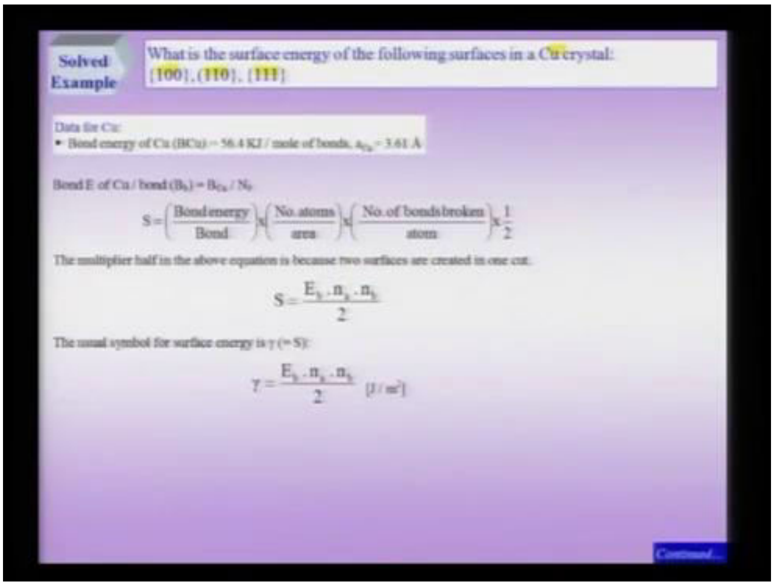
When I write down the surface energy, I can see that I need to worry about the numbers of atoms per unit on the surface, which is going to change obviously, the respect of inclination of surface, I need to worry the number of bonds program on when I make this cut and I need to worry about the energy for bond. Of course, initially we can start with a simple metals like copper vary, we can a assume that the bond energy keeper bond does not depend only angle of the cut, then we try to differential lead could surface is from solid surface and the essential point be mention, was the liquid surfaces when i am stressing the surface remains alternate structure.

But, (42,55)the solid surface can actually stress the solid surface is require can be better describe by surface stresses or other surface tension and additionally, there is a point quantity like surface, which come into picture and I am describing solid surface. Now, the surface of the solid inclined any arbitrary inclined of surfaces can be describe in crystal can be describe by terraces ledges and kinks.

And I can make and actually calculation of the energy based on the density of this like ledges and terraces in a material. And reason that the surface like to put out this kinks and adjusting having smooth surface are inclined, because it will like to keep those low energy expose to another than the higher energy ones, we can also saw the typically that surfaces are finally tropical energy and that implies, that the equilibrium shape of crystal is never going to theatrical, it is going to have certain poly hydrant shape as specially leave in the surface and energy was orientation plot, which is known as the gamma plot there are sharp cusp.

And we use something known as a the wolf constructions to take us from y the gamma plot, what to the equilibrium shape of the crystal. So, let us do one example to calculate how to use broken bond model, to calculate surface energy of a crystal.

(Refer Slide Time: 44:28)



**Solved Example**

What is the surface energy of the following surfaces in a Cu crystal: {100}, {110}, {111}

Data for Cu:
- Bond energy of Cu (BCu) = 56.4 KJ / mole of bonds, $a_{Cu}$ = 3.61 Å

Bond E of Cu / bond ($B_b$) = $B_{Cu} / N_A$

$$S = \left(\frac{\text{Bond energy}}{\text{Bond}}\right) x \left(\frac{\text{No. atoms}}{\text{area}}\right) x \left(\frac{\text{No. of bonds broken}}{\text{atom}}\right) x \frac{1}{2}$$

The multiplier half in the above equation is because two surfaces are created in one cut.

$$S = \frac{E_b . n_s . n_b}{2}$$

The usual symbol for surface energy is γ (= S):

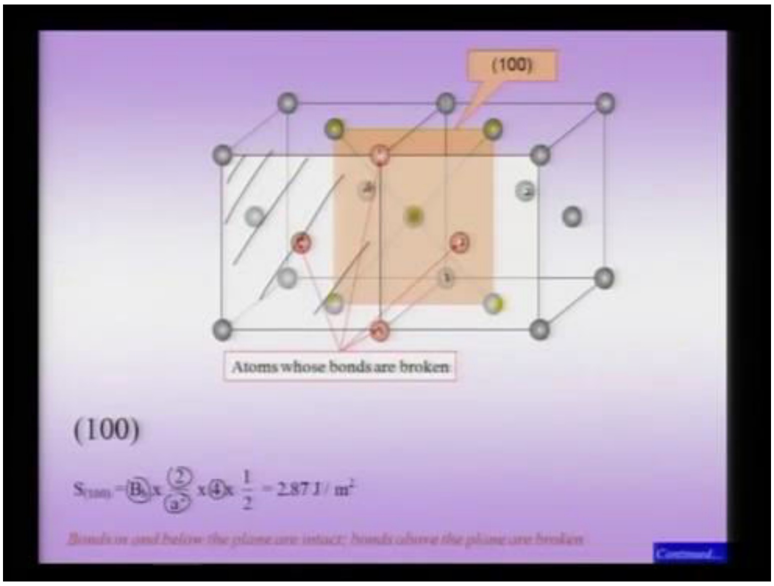
$$\gamma = \frac{E_b . n_s . n_b}{2} \quad [J/m^2]$$

Continued...

So, let us try to calculate it is some other surface energy of copper crystal it, start with some simple low intense plane like 1 0 0 plane, you 1 1 0 plane for 1 1 plane for common crystal and try to calculate, the surface energy of this three surfaces. Now, data will be require this things born per born and this is b subscript see you, this is 36 point kilo per mole a born atomic that is parameter for 3 point 6 1.

So, I was use formula as before which is says, that says surface energy now judge per square meter is born energy, per bond multiplied numbers of atom per unit area and numbers of bond broken or atom. So, the difficult term in this calculation is the number of bond broken per atom. Because, this require it will be visualization that actually making a cut and how the numbers of atoms, number of bonds, which are actually broken the term half as come fact, that each dimensions make a correct surface and half of the energy this expected recycle, one surface on the half face of the to be other surface.

(Refer Slide Time: 45:41)



(100)

$S_{(100)} = \textcircled{B_b} \times \frac{\textcircled{2}}{\textcircled{a^2}} \times \textcircled{4} \times \frac{1}{2} = 2.87\ J/m^2$

Bonds in and below the plane are intact; bonds above the plane are broken

Continued...

So, let us try to calculate the try to three surface energy is the 1 0 0 surface and the 1 1 surface and I say pointed out the difficult thing to be show out device, if the numbers of bonds broken per atom. So, now, let us take the 1 0 0 surface and let us consider the suppose have central atom in this fcc copper, this atom sitting on the unit cell between the these two on the face and the center. And making a cut which corresponding corresponds to orange color kind of plane, which of the 1 0 0 plane.

So, each copper atom bonded to 12 atoms. So, I have 12 ((Refer Time: 46:07)) component 1 2 3 4, which is in plane of this board in the pane of this 1 0 0 there are 4 behind the plane, which are this 4, this is 1, and there is 2, and there is 3, and there is 4 and which is behind the plan, And there are this 4 which are in front of the plane, so which I call the 1, the 2, and the 4.

So, 4 in plane 4 behind the plane 4 in front of the plane making 12 bonds per copper atoms, now make this cut obviously, all the bond behind the plane are intact, the bonds in the plane outside that and assume all the bonds in front of the plane or broke. So, another words actually not cutting through the atoms obvious, I cut a little in from of the atoms. So, that I actually create a surface of the 1 0 0 type, now that means, in the case I actually having 4 bonds, which are having 8 of them are in intact and this the number I put here for the 1 0 0 plane, the surface density is 2 atoms for a square area.

So, that is surface density which you can see, because now this is my surface here the 1 0 0 surface, I can clearly see there are 4 contributing 1 and the 1 centers at 2 atoms and area of this is square. So, 2 atoms per a square 4 atoms bonds here broken and the bond energy data, given is a 56 point 4 kilo joule for more and therefore, I get and surface area of 2 point 8 7 other this energy of 2 point 8 7 joule per meter square.

(Refer Slide Time: 47:42)

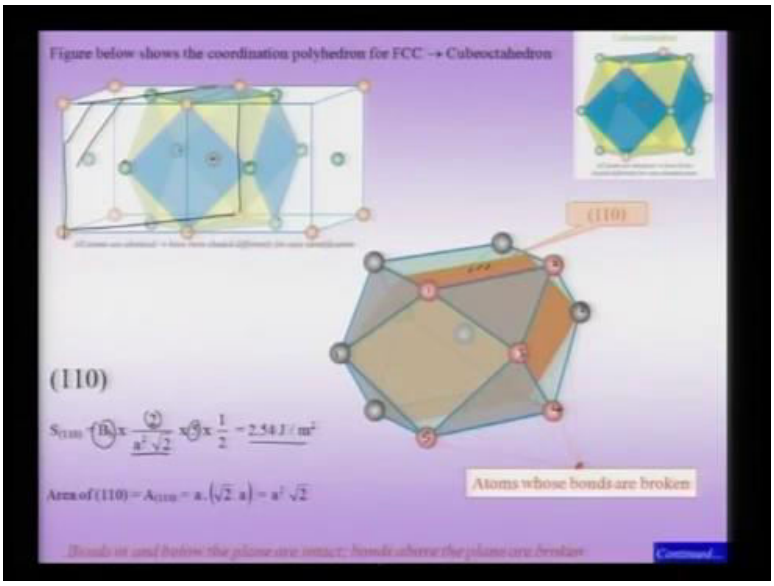


Figure below shows the coordination polyhedron for FCC → Cuboctahedron

(110)

$S_{(110)} = B_E \times \frac{2}{a^2\sqrt{2}} \times 5 \times \frac{1}{2} = 2.54\ J/m^2$

Area of (110) = $A_{(110)} = a.(\sqrt{2}\,a) = a^2\sqrt{2}$

Atoms whose bonds are broken

Bonds in and below the plane are intact; bonds above the plane are broken

Now, let us consider d 1 1 0 surface in this case it is slightly difficult to visualize, show twice and a of course, there are many ways doing the same visualization. But, let us use old tool which is using the cubic ((Refer Time: 47:54)) you see this solid cubic hydrant which is obtain by a cube of equivalently truncating octa hydrant (Refer time: 48:00) line just between the cubic octa hydrant.

Now, in this suppose I create 1 1 0 kind of a cut and so this, central atom its sitting try to the center of this between, the two units cells is bounded to 12 coppers atom surrounded and this 12 can be counted as 1 2 3 4 boundary, 1 2 3 4 in the plane atom. And similarly 1 2 3 4 below all atoms are obviously same, but I been color differently for better visualization. So, each atoms both to 12 atoms and this quad ration poly hydrant is my cubic hydrant for the fcc copper.

Now, when I making a 1 0 0 kind of cut, this my orange plane should be 1 1 0 kind of the, which is shown here when i make this cut obviously and I do not cut to the atom, I cut a little kinds of the atoms, numbers of atoms in the plane of the cut are 1 and 2 the numbers of atoms behind plane the cuts down file and corresponding their files in front, let me count front symmetrical find back 1 2 3 4 5. So, 12 coordination is coming from pie front of the cut, pie behind the cut and 2 the plane of the cuts.

So, they are makes it 12 find in front of the plane are broken bonds and therefore, this numbers files comes here the bond broken for atom, the area of plane can be calculated putting in the normal x units, let me plane here this is my plane ((Refer Time: 49:27)) this is 1 length, of root 2 square atom signing here. If I 2 by 2 2 square and of course, multiply by bond energy of bond get 2 point 5 4 per meter, you can see clearly different from 2 point 7 joule per meter for the 1 1 0 plane, now let us consider.

So, we use need two different methods to be visualize the cuts, through all this have done singular unit self, buts wanted to be using multiple methods like and calculate the numbers bonds for the parameter.

student: ((Refer Time: 50:05))

we will see this is for the one this are the some energy low one suppose you make an arbitrary cut, that will even high energy. So, this will be the.

student: ((Refer Time: 50:16))

which hare here in this one.

student: ((Refer Time: 50:24))

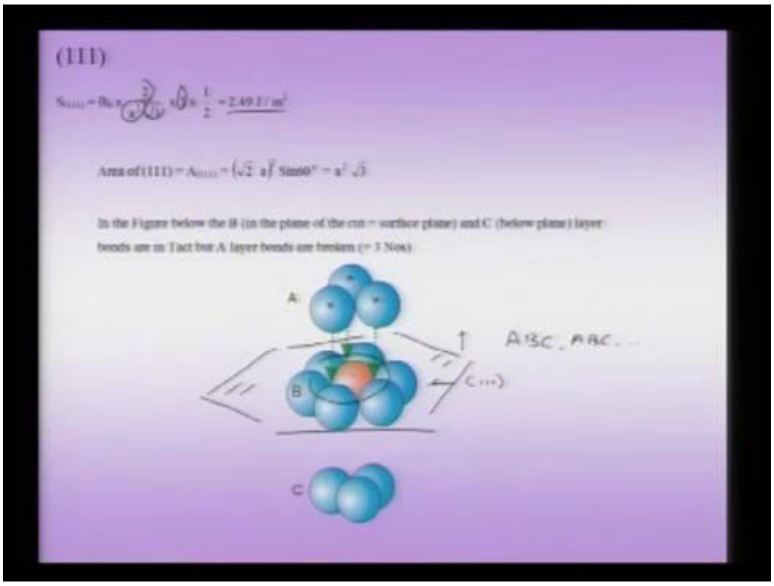
which one, what will be low.

student: ((Refer Time: 50:30))

No, surface energy always higher, so the reference point for surface energy is the bulk we know the reference point for surface energy is not the vacuum. So, this is important point you raise, now this is the surface in a higher state of energy with a respect to safe both consider the isolated atom sitting in vacuum free obviously, the surface energy not that reference states, it is assuming that the crystalline bonds the stage is my reference states and therefore, the surface energy is calculated with the respect to the perfectly bonded line straight.

So, this is very important point to be noted and therefore, this should be, now I am writing any interfaces and want assuming my reference is not d isolated atoms. But, my perfect bonded crystalline estates this are very important point, so that means, we always seen the state of higher energy and therefore, atom and surface wants minimize the area and that is resulting in my, surface substances and always surface stresses and case of code have being, seen that the crystalline surfaces can also have c ((Refer Time: 51:36)).

(Refer Slide Time: 51:44)



(111)

$S_{(111)} = B_b \times \ldots \times \frac{1}{2} = 2.49\ J/m^2$

Area of (111) = $A_{(111)} = (\sqrt{2}\ a)^2 \sin 60° = a^2 \sqrt{3}$

In the Figure below the B (in the plane of the cut = surface plane) and C (below plane) layer bonds are in Tact but A layer bonds are broken (= 3 Nos)

Now, we will take alternate view of finding out my 1 1 surface energy, so to calculate the 1 1 energy let us look at the way 1 1 planes, we constructed them the very first place, we consider the 1 1 plane by considering else central atom. Which six in a close pack layer a rounded, then we construct the a layer putting some atoms in to this very position and then that is a alternative set a voice for form by this and put the c layer. So, we had the a b c a b c, so kind of the packing to form the f c c crystal obviously, of the 1 1 point, each of this plane we had see was the 1 1 plane therefore, I making a cut.

So, this plane is my plane the cut other plane of the cut therefore make a cut again not cutting to the atom I shift my cut, I can see that all the bonds in the plane just six are in fact, 3 below are intact though only 3 bonds are broken. So these 3 atoms are no longer bounded when a face, so numbers of bonds broken is 3, so my prospective the way I am calculating in the bonds broken parameter change.

But, this makes me easy for me to calculate the bond broken parameter, my surface area I can calculate again by simple geometry to be 2 atoms per root 2 square area and my energy surface comes out to be 2 point 4 9 joule per meter square, let us comparison two values it is 2 point 5 4 more and 2 point 8 7 is even here. So, these my least energy surface in proper and non surprise we know it is my surface which shows the close pack.

So, these are the close pack high density plane close fact therefore i except to the lowest energy, so using the example we trying to calculate very simplest equation, the surface energy various kinds of copper of course, I could even lower index plane and try o calculate energy ((Refer Time: 53:40)) three rather low index planes and therefore, we can find which is the lower energy of this three.