Nanostructures and Nanomaterials: Characterization and Properties

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Lecture – 3
Introduction to Nanomaterials (CI)
Overview of fundamental concepts (continued)
Details of defect structure and classification of defects in materials (0D, 1D and 2D defects)

In understanding the distribution of phases implicitly, we have introduced one kind of a defect which is the interface between the phase a and the phase b.

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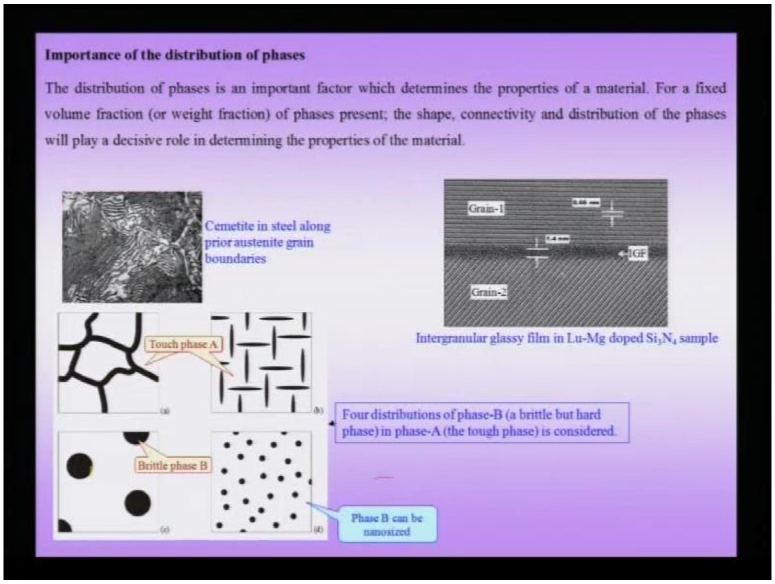

Importance of the distribution of phases

The distribution of phases is an important factor which determines the properties of a material. For a fixed volume fraction (or weight fraction) of phases present; the shape, connectivity and distribution of the phases will play a decisive role in determining the properties of the material.

Cemetite in steel along prior austenite grain boundaries

Intergranular glassy film in Lu-Mg doped Si_3N_4 sample

Four distributions of phase-B (a brittle but hard phase) in phase-A (the tough phase) is considered.

Phase B can be nanosized

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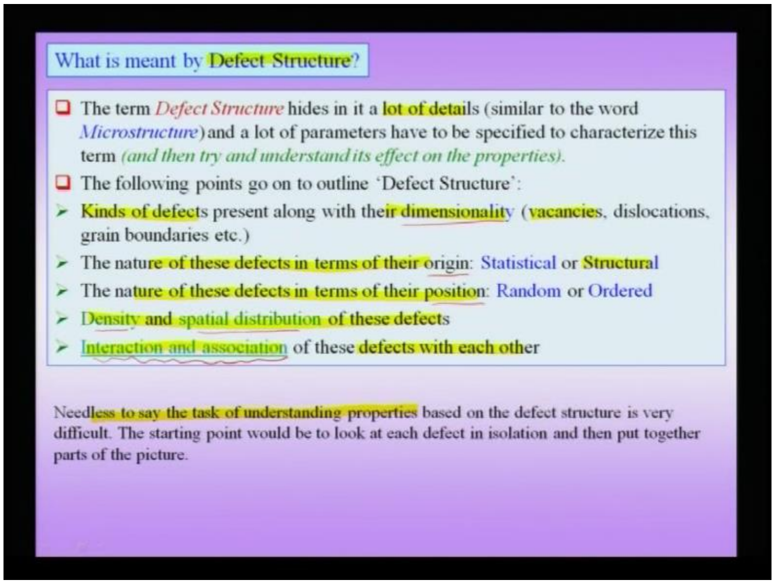

What is meant by Defect Structure?

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

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

To understand the properties of materials we have to understand not only one kind of a defect but what is called the entire defect structure in the material. So, last after the question, what is meant by the defect structure? Actually, the definition, the small term of the phrase defect structure hides in it lot of details. It is actually a very, what you call, involved term, wherein you have to use lot of parameters in order to characterize the defect structure. And more further, we have to take it to the stage where the defect structure can be understood in terms of its influence on the properties of the material.

So, we have to worry about the kinds of defects present along with their dimensionality when you want to understand the defect structure in a material. We need to understand the nature of these defects, and in terms of their origin for instance, or this defects statistical in nature or the structural in nature? Some of these terms maybe new to you like what is meant by structural defect or a statistically stored defect, we will briefly take up these terms in the coming slides to understand these kind of classification of defects.

We need to understand the nature of these defects in terms of their position. In other words, or this defects random or they ordered, and how would be the difference in properties with respect to a single defect. Let me take an example of a vacancy, how a random vacancy would be differed different from an ordered vacancy. I need to know the density of these defects and their special distribution.

Not only that, I need to know the, what we might call, we have been discussing before the spatial temporal revolution of these defects. In other words, if I am putting a component to service or a material to service, or I am doing a processing in order to engineer the material to have a decide defect structure, then how the defect structure evolves with time and in the defect structure how is the spatial distribution, and terms like this density and location, etcetera, can be used to understand the spatial distribution of these defects.

Last but not the least, I need to understand the interaction and association of these defects with each other. It is not sufficient that I talk about one kind of a defect let it be a vacancy, or an industrial, or a dislocation, or maybe a segregated region among the green boundary. I need to understand that how one kind of a defect interacts with the other kind of a defect, and how these kinds of a interaction may lead to what you may call the association of these difference. This is going to be the theme of the understanding which we will take up in the coming slides.

Needless to say, this kind of an endeavor is extremely complicated, and some of this is badly being undertaken today. Because, when I am talking about these defects like a vacancy or a precipitate, these represent not only single lens scale but multiple lens scales. And, not only that, a single defect like a dislocation could have its expression in multiple lens scales. And therefore, for instance, at the, receiving the dislocation level, the effective stress field of a dislocation can be taught of us pervading about few tens of nanometers.

But, when I am talking about the dislocation shell structure or dislocation sitting along the green boundaries, then I am talking about the different lens scale associated with these dislocations. Therefore, I am actually talking about a really difficult problem of material science wherein a time to understand the defect structure across multiple lens scales, in other word the sapatio temporal evolution of the defect structure. And, this problem as I pointed out is going to be one of the key steps in understanding how our material behavior is dependent on the micro structure.

Now, it is worthwhile for me to now be free revise like because lot of new terminologies has been introduced here, and but essentially what we are talking about is defects in the material, and what I would like to do in the coming slides is to understand these defects in terms of their dimensionality, in terms of their origin, in terms of their positional origin, in terms of the density, in terms of their spatial distribution, last but not least in terms of their interaction and association.

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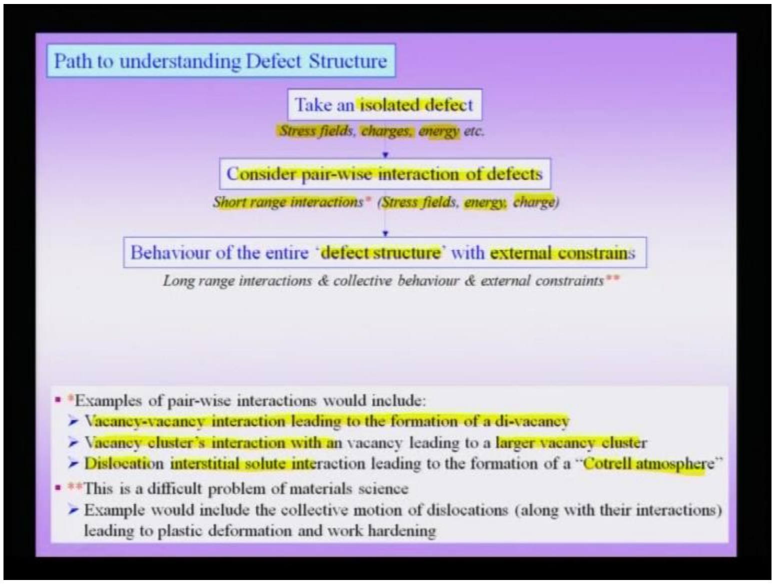

Path to understanding Defect Structure

Take an isolated defect

Stress fields, charges, energy etc.

Consider pair-wise interaction of defects

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

Behaviour of the entire 'defect structure' with external constrains

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

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

So, how can I simplify this problem of understanding defects? What I can do is that, initially of course, I just can takeup an isolated defect. And, of course, when I am talking about an isolated defect, I could be talking about a single interstitial atom, I could be talking about a single edge dislocation, I could be talking about a single precipitate in a crystal. I could also associate with these defects certain quantities which are very, very important like the stress field associated with the defect, if there are any charges associated with these defects, what is the energy of these defect, etcetera.

So, when I am talking about an isolated defect it simplifies my problem of understanding the larger picture of the defect structure; and have to approach this isolated defect, given all its what you might call, all the facets of the problem. For instance, now if this isolated defect can talk to other defects where the long line stress fields with which it is associated. If this defect is going to cost the crystal energy, then such a defect could be in a metastable state. And, when you amine the crystal, the defect is going to be the crystal.

In other words, this energy associated with the defect is going to dictate whether stable or metastable or how much of energy is associated, of course, at the code of the defect and also around it. If there are any charges associated with these defects then this could affect the properties of the defect.

For instance, we will see, soon see that surfaces in ionic crystal like sodium chloride can be polar, such as surface could have because their charges associated with them, the kind of segregation which occurs of these surfaces, the kind of energies of these surfaces is going to be different from a surface for instance, in a copper crystal which is non polar in nature.

Then, once I am having a reasonable handle on the isolated defect, then I can consider a pair-wise interaction of these defects. This pair-wise interaction would essentially imply that I am talking about short range interactions. Some examples of these pair wise interactions could be a vacancy-vacancy interaction leading to the formation of a di-vacancy.

The vacancy's interaction with the cluster of vacancies leading to the formation of a larger cluster, vacancy cluster. It could be the interaction between a dislocation and an interstitial solute which finally leads to the segregation of these solids along the core of the dislocation, typically edge dislocation which is called the Cotrell atmosphere. And, of course, how this association of these interactions lead to finally change in properties; that is the goal, of course.

So, when I am considering pair wise interaction of defects, again I worry about some of the quantities we worried at the stage when we talking about an isolated defect like, I could worry about this stress fields of this combined or the paired defect. I need to know about the energy of this paired defect; has there been a lowering of energy, has there been increasing energy of the system because of now we are having 2 of this defects. I need to know the same kind of an effect, on the charge is the overall charge reduced; is there a redistribution of the spatial charge because of this interaction of these defects.

And therefore, I need to worry about all these issues. And, this becomes an important goal or an intermediate step in understanding the larger picture which is now considering the entire defect structure along with the external constraints. Now, why do I have to take the external constraints into effect, is because now the presence of this internal defects could influence each other. In addition, the external influence also is going to play an important role, and how these defects are going to behave.

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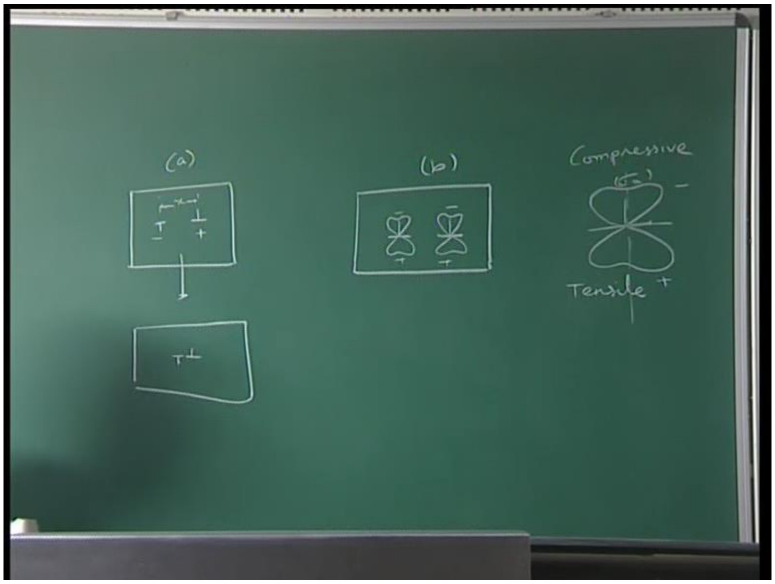

So, let me take an example, for instance. Suppose I have an edge dislocation in a material, and now suppose I apply shear stress on this material, then there is a tendency for this dislocation to move, and therefore finally of course this dislocation would come out of the crystal and create the surface step of magnitude, b. In other words, I have an internal defect which is a dislocation which is an edge dislocation I have considered. The external stresses interact with the stress field of the dislocation, trying to get to the surface.

On the other hand, if I am considering 2 dislocations in the material, I have couple of possibilities here - the configuration a, and the configuration b. In configuration a, the 2 dislocations are in position in such a way that they would attract each other; in configuration b, their position in such a way that they repel each other. What is the agency by which the interaction is mediated? It is obviously the long range stress fields of the dislocation.

Now, if I plot this sigma x, stress field of a dislocation, I am sorry, in this one, I would have iso stress contours, so this will be my compressive region, and this is my tensile region, and I would have a tensile stress; of course, this plot would display a some kind of mirror symmetry now in the middle. Now, if I have 2 dislocations in this configuration, the compressive region of this dislocation would repel the compressive region of this dislocation, similarly the tensile stress fields would repel each other, and therefore this dislocation would repel each other.

On the other hand, such a configuration would meet, but my compressive region is in connection with the tensile region and therefore and there is some other from the top, and therefore they would attract each other, where there will be long stress fields. And, if the dislocations in a future picture go towards each other, that means they come closer each other, then this being the separation of the dislocations, then the energy of the system comes down, and therefore there is a natural tendency for the system to go from here to here.

This, of course, could happen even in the absence of the external stresses, if the attractive force between the dislocations is greater than the Paul's force which is the inherent lattice friction. In other words, if my; then these dislocations can spontaneously move towards each other and anal each other.

Similarly, if the repulsive force is larger than the Paul's force or the Paul's stress then automatically the dislocations can move further apart till of course the value of the stress is about repulsive stress becomes lower than that of the Paul's stress. Therefore, when I am considering the pair-wise interactions, I, these defects can talk to each other while having the long line stress fields.

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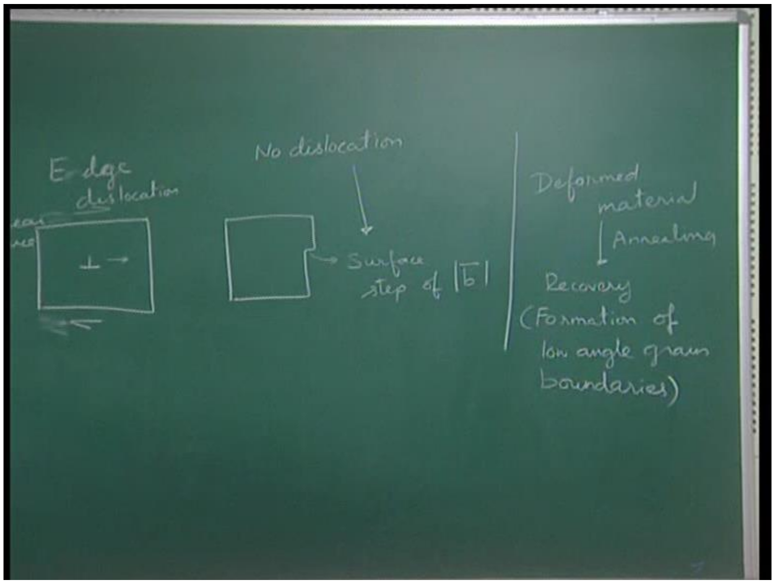

And additionally, we have to also worry about the external stresses or external constraints which have been imposed on the system and its effect on the evolution of the defect structure. In other words, in this clear cut example you can see that this is now an edge dislocation, and here there is no dislocation but only a surface step. And, the long range stress field associated with the dislocation has vanished; then the surface step forms.

Therefore, it would clearly seen, one defect is evolved into another defect, and in the process the energy of the system has been lowered. And, this is being mediated by an externally applied shear stress tau. Of course, externally what you may call an externally applied force because it is caused typically what you can apply a constraints on the surface, what evolves inside the system is a stress field. So, stresses are typically inside the material and what you apply outside we can call of the shear force. In other words, we cannot apply shear stresses, but we need to apply shear forces.

Now, when I am trying to understand this in this example, I can take an isolated defect, I can see its interaction with the external constraints of the forces I am applying, then I can take a pair of defects, then I can understand how this system is going to evolve, given these pair of defects. And, the parameters I would like to prang during this is obviously the combined stress field.

In other words, in this case, of course, this stress, overall stress region decreases because of the cancellation of the compressive and tensile regions, the energy as the dislocation structure evolves, and of course in some cases as I told you there may be charges also involved which I need to track.

And finally, I have to talk not only about this one, or 2 dislocations, but entire gamete of dislocations. And, many of these dislocations will be lying in multiple slip planes, they could have defects within this dislocations which we will consider briefly later. In other words, I have a very complicated structure which is evolving under the external constraint. And, I have to track how this evolution of structure gives rise to what we might call the properties of the material.

Some of the properties which typically we could see is, for instance, the effective strain hardening. We could be seeing actually what we might call the evolution of structure, but the formation of what is called the low angle grain boundaries which could happen during, after a deformation when you try to do recovery. That is a thermal treatment call recovery which can give rise to lower angle grain boundaries.

So, I can take a material and plastically deform it. So, when I take a deformed material and heat it and call the processor annealing, then the system evolves to a lower energy state in which there is a formation of low angle grain boundaries. Now, this is an important concept, and we will explore it little further later perhaps during the course. But, essentially, we are saying that how the system is evolving during plastic deformation, and how the system is evolving afterwards during the heat treatment. And this, when you talking about system evolution, I am tracking the what you might call the spatio temporal defect structure in the material.

I am just to illustrate the problem involved that is consideration of multiple defects, interactions, their evolution, is actually one of the difficult problems of material science. And, when I am talking about the collective motion of dislocation, as in some example we were talking here, leading to plastic deformation core and work hardening, we need to not only consider millions of dislocations or millions and millions of dislocations but millions and millions of dislocations in a very complicated structure like a cell walls or on the grain boundaries, and their interaction with other defects in the material which makes this problem extremely difficult.

And, this is already only a single phase material and I am talking about multi phase material like example we are considered before, for this is here we talked about 2 phase material. In such a case, in a 2 phase material, things would obviously become much more complicated. But nevertheless, it is extremely important for us to understand the defect structure, in order that can I have an handle on the properties of the material.

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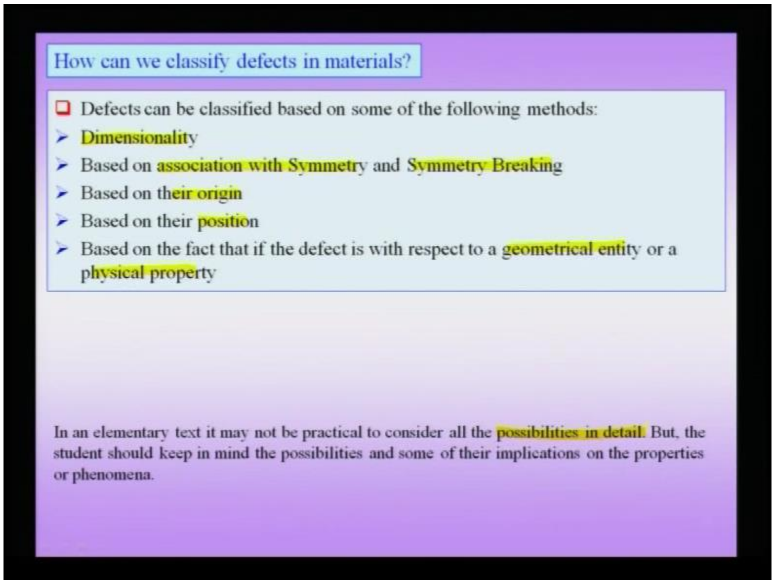

How can we classify defects in materials?

❑ Defects can be classified based on some of the following methods:
➢ Dimensionality
➢ Based on association with Symmetry and Symmetry Breaking
➢ Based on their origin
➢ Based on their position
➢ Based on the fact that if the defect is with respect to a geometrical entity or a physical property

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

Now, we said that it is important to understand the defects in the material, and here in this course since this is the course of nanomaterials and nanoscience and nanotechnology, I am, we will not have the time to go into details of all the aspects of defect structures. But nevertheless, a student can keep in mind the overview of the subject. And, whenever he is faced to the problem or a difficulty on a certain topic, he can go and to refer to some of this terminology, and get more details on the subject from other sources.

Now, why this broad overview is required is because, in nanomaterials often the defect structure is highly altered, and this alteration of defect structure is what, is makes the nanomaterials special in terms of its properties. So, how can I understand and classify what you might call a large number of defects, and what important ways of classification can actually highlight the role of a defect in terms of its property.

So, we can classify defects based on dimensionality, I can classify defects based on association with symmetry and symmetry breaking, I can classify defects based on their origin, you will I will clarify more in a coming slides what do this things mean, I can classify defects based on their position, and I can also classify defects if the defect has been defined with respect to a geometrical entity or a physical property.

It is seen in the definition of a crystal that the very definition of crystal hinges on my consideration of nearly a geometrical entity like an atom or a molecule or a cluster of atoms, etcetera; or if it is based on a physical property. And, we are also see, that the combination of both is also possible. Therefore, similarly here, the defects also in a similar structure is going to be either of geometrical origin or they could have a origin in the physical property.

As just to reiterate once more that in this possibility we are not going into too much detail but we are having a broad overview of the subject understood and can actually go and refer to some detail text when he wants lot of knowledge on this and other allied topics. So, let us see how we can actually classify defects based on these methods, and why is it important to classify these defects because this classification is going to simplify our job. And, when I am talking about a defect I can also understand it from these multiple angles which helps me to straight away pin point its role in terms of a properties of a material.

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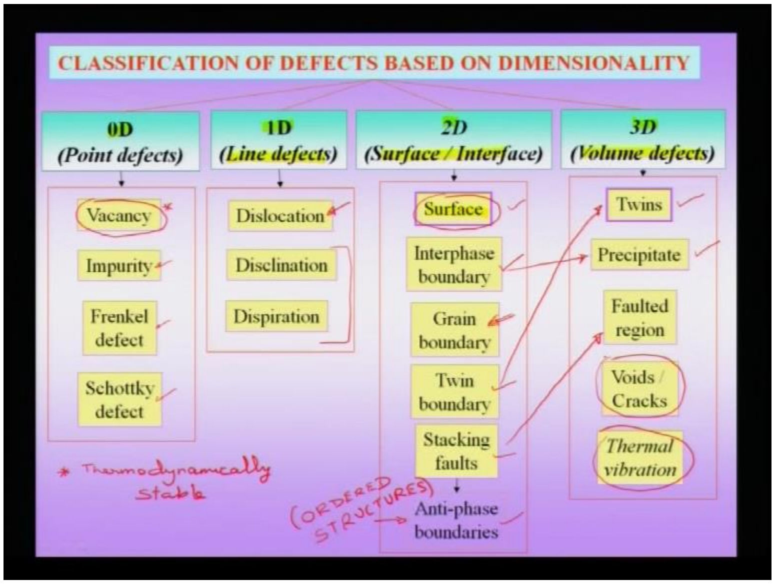

CLASSIFICATION OF DEFECTS BASED ON DIMENSIONALITY

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

* Thermodynamically stable

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

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

(ORDERED STRUCTURES)

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

So, the usual method of classification of defects is based on the dimensionality of the defect. And then, when I am talking about dimensionality, here we mean not in the strict geometrical sense but in a more physical sets. We can have defects which are 0 dimensional, which are otherwise called the point defects, we can have 1 dimensional defects otherwise called the line defects, we can have 2 dimensional defects which are the surface or interface defects, and we can have 3 dimensional defects which are the volume defects.

It must be obvious to any student of material science that is a couple of defects are absolutely unavoidable whenever you have a material. For instance, when you have a material it is going to be finite, it is never going to have any finite material. Therefore, surface is one of the unavoidable defects in a material. So, you need to have a surface if you have any material. The second unavoidable defect is what you might call thermal vibration that is because we always have materials at a finite temperature.

That means that, atoms are vibrating about their mean positions, they are vibrating about their mean lattice positions. And therefore, if I am drawing a picture for lattice here, and it take a snapshot at any point of time, this could be a picture which I might see. In other words, atoms are not located right at their atomic mean positions, and they are actually vibrating around them. So, this is of course a crude schematic, in reality things could be little more ordered. So, therefore, atoms are vibrating along the mean position typically in all 3 dimensions.

Therefore, I can see that this perfect concept of a perfect order or a perfect lattice being a seat of a atom is actually violated. And, because of this, this becomes an unavoidable defect. And, as we know that we always have materials above 0 kelvin, therefore this would be another unavoidable defect in a material.

Now, to have a brief overview, what are the point defects which we need to consider, what are the important line defects which we need to consider, and what are the volume and surface interface defects we need to consider. One other unavoidable defect in the thermodynamics sense is a 0 dimension defect or vacancy. So, what is a vacancy? A vacancy is for instance a missing atoms from a lattice positions, for instance, a copper atom or copper ion could be missing from its lattice position, and this is called a vacancy.

This atom going missing is actually going to cause internal energy in terms of the broken bonds to the material. In other words, the internal energy of the material is going to increase in the presence of a vacancy. But, it is not internal energy which is going to determine my stability of my substance at constant temperature and pressure it is usually giffs free energy.

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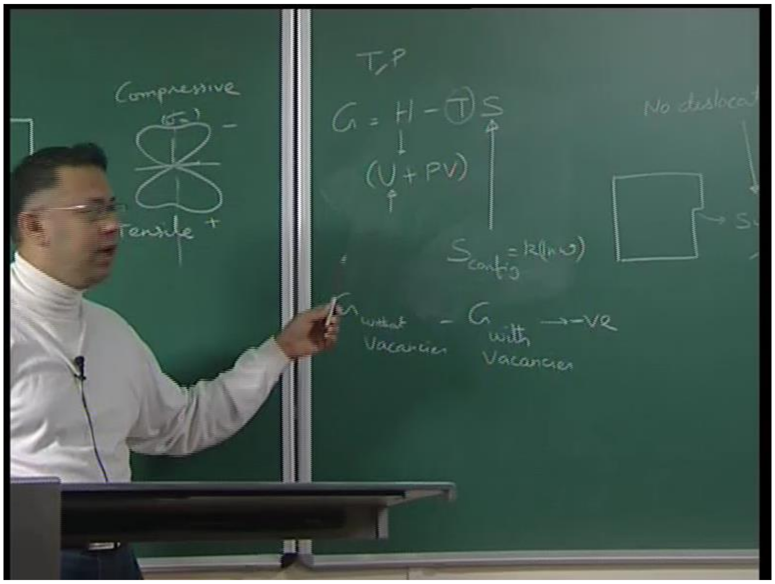

So, the stability of my system under at constant temperature and pressure, is determined by the Giff’s free energy which is given by, to build an internal energy. So, when I put a vacancy in a material, because of certain broken bonds, we can have an increase in internal energy system. But, at any finite kelvin temperature, the configurational interperial system given by S is equal to k log omega, the famous Boltzmann equation in which omega is a number of configurations possible, and k is the Boltzmann constant.

Therefore, because when I put a vacancy in a material this vacancy could actually set in one of the many lattice positions. For instance, if this is my vacancy; this vacancy could be present here, here, here, here, here, or in one of the many many possible lattice positions. And, this implies that this increases the configuration richness of the system, and that hence provides an entropy benefit. Therefore, a system with a vacancy has an higher entropy as compared to a system without a vacancy.

When you put more and more vacancies, it is going to cross the crystal more and more in terms of the internal energy, and hence enthalpy. But, there is going to be a certain number of vacancies which are going to be thermodynamically stable. In other words, if I put a certain number of vacancies, it will give me the maxo entropy benefit such that the H minus T S term, actually turns out to be negative.

And if, the state in a, I means, negative, that implies that vacancies are going to be stable. Of course, we were not talking about any number of vacancies, we are talking about a certain fixed number of vacancies which will lead to a minima and that gives you the energy function. Hence, because the fact that now in the presence of vacancy the Giffs energy can actually be reduced compared to a state where there are no vacancies. And now we are talking about certain positive kelvin temperature like we could be talking about room temperature, we could be talking about 0 kelvin, or we could be talking about 200 degree Celsius.

In such a situation, we see that there are certain equilibrium concentration of vacancies is just stable in a material, and therefore vacancy becomes a thermo dynamically stable defect. Unlike the many other defects which will be dealing with, like the example of a dislocation here, or the example of a grain boundary which are thermodynamically metastable defects. Now, what is the implication of having a defect which is stable or metastable, or as the case may be even unstable?

Of course, unstable defects are spontaneously leaves the crystal, and therefore the crystal would become free of these defects. But, a stable defect, how much ever you heat the substance or anneal the substance, would not go away. In other words, just because I have a vacancy, I cannot heat the system to get rid of the vacancies because there is an equilibrium concentration of vacancies which will always remain in a substance.

Of course, you can heat it to higher temperature; more number of vacancies becomes stable because this is the weighing term for the entropy. When, of course, I slowly cool down, then the number of vacancies if given an opportunity to leave the crystal and which will reach a new equilibrium at lower temperature, which would be a lesser number of vacancies.

On the other hand, suppose I had a system with dislocations, or a system with grain boundaries and I heat such a system, there would be a tendency for dislocations and grain boundaries to leave the crystal. And, in the process, actually reduce the Giffs energy of the crystal. So, these are important point to note that some defects less surface and thermal vibrations are unavoidable in the crystal, some defects like vacancy though inspite of being defects are actually thermodynamically stable.

The other important 0 dimensional defects which we need to consider, are actually got what you might call, the term impurity of course is a casual term, we can think of a substitutional or interstitial atoms, and that is a very important kind of defects. Though, here we are talking in terms of defects but these could intentionally be added to increase the properties. For instance, in steel we add carbon to actually increase the properties; another if you want to have a harder material that I can add carbon to it.

Similarly, I could have add substituitional impurity atoms to increase the, what you might, again the strength of a material. So, in such cases, the second atom which has been added would actually be beneficial and should be called an alloying element instead of an impurity. So, but since we are talking in terms of a perfect lattice, the presence of these additional elements actually, may actually cause distortion to the lattice. And therefore, we classify them as defects with respect to the perfect crystal which is a crystal in which there is only one species of the atoms.

The other defects which come in economic materials like the Frenkel defect and Schottky defect even briefly consider some of these as we go along. The important one dimensional defect is the dislocation and we have been briefly constrained the concept of a dislocation, and the stress field etcetera. There are other possibilities one line defects like the disclination and dispiration, which of course we will not take up during this course, in any kind of detail.

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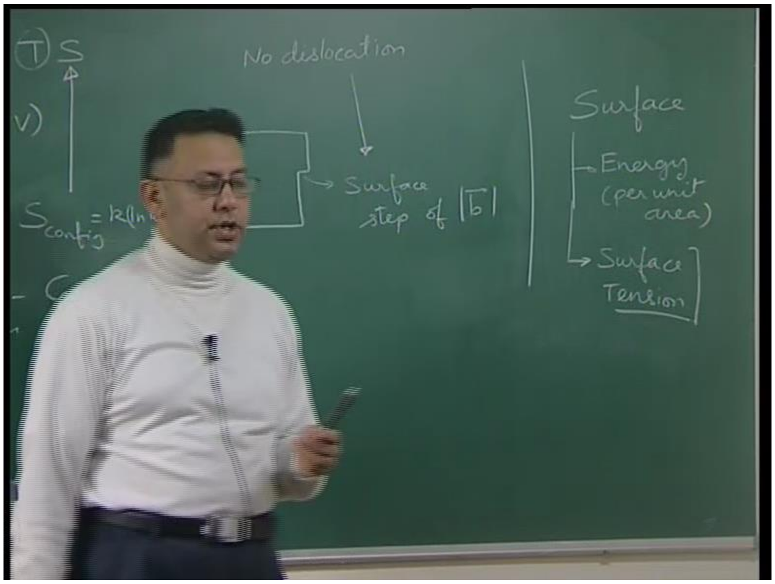

The important 2 dimensional defects are the surface which we have already talked about. And, surface represents the region of higher energy in the material and surface is also associated not only with surface energy but also with the concept of surface tension. And, this is very very important to note here, the term often associated with the surface, is sometime it is also called free surface, in reactions of any constraints.

And, there is a possibility that in certain nanomaterial the surface especially in polar materials that the surfaces actually can be under compression which is normally not found in bulk material. So, we can have a surface that associate 2 important quantities, the surface tension and the surface energy. And, we are already exposed to quite a few important aspects of surface tension, especially liquids like the capillarity effect, or insects walking on water; this is all possible because of surface tension.

And, later on, when we talk about phenomena like super hydrophicity you can see that how surface tension is at the part of those kind of phenomena which were very very important for us. We can also talk about an interface boundary which also briefly construct the sometime back, and an interface boundary is the boundary between 2 phases.

Suppose, I am taking my example which I have considered before; now, this is my interface, the one I am highlighting in red. So, this is my interface; this is my interface boundary. Now, as I pointed out when we were discussing this aspect, that the interface properties is very very important with regard to the material as a whole. In other words, if we have interfacial debonding, or any one of those phenomena, then or nucleation of cracks at the interface, then the material as a whole would actually perform poorly.

The third defect which in actually engineering our practical terms is we may even think of it as an unavoidable defect is the grain boundary. Because, unless we take extreme good care to produce the material like user, technique like a bridgemann technique or a sopransic technique, we cannot or we normally do not obtain a single crystalline material. When I take for instance, rod of copper or a rod of aluminum, or anyone of the metals we normally see in day-today-life typically, they are poly crystalline.

Of course, there are important engineering applications in single crystal, like we know, the silicone chip which goes in the formation of a computer arithmetical logic unit. Therefore, there is, there are specific examples where single crystals are specially ignored and used, one of them being with respect to computer; the other thing could be for instance single crystalline turbine blades have been used in gas turbine engines. But, these require extremely special care to make, and therefore are usually costly.

But, if I take a normal material, typically it will be poly crystalline. In other words, it will consists of single crystalline regions, and these single crystalline regions would be separated by what is known as a grain boundary; we will have a look at a example grain boundary very soon. The other kind of a 2 dimensional defect is what is called a twin boundary, and we will also talk about a twin boundary very soon.

In closed pack crystals, there is another kind of defect which comes which is called a stacking fault. And, a special kind of a stacking fault is what is called an anti phase boundary which is found in order materials. So, we can have many kinds of 2 dimensional defects. And, of course, I mean 2 dimensional, they need not be a flat 2 dimensional defect, they could be a curve; and in other words, they could have a variant curvature from place to place.

3 dimensional or volume defects for instance is can be thought of, twin, which is bounded by twin boundaries, can be thought of us a 3 dimensional or volume defect. The precipitate can be thought of us a region wherein there is a second phase sitting in a matrix. So, the second phase is actually a disruption in the order of the perfect crystal, the parent crystal or the matrix crystal, and therefore can be thought of as a defect in the parent or the perfect crystal.

And, we will take up an example sometime soon, wherein we will see that how the precipitate itself can be engineered to obtain important properties. In other words, far from being a defect in the sense of being unwanted, these precipitates actually can play a very important role in engineering the properties of a material.

The faulted region which is bounded by the stacking faults is also a region which can be thought as a 3 dimensional defect; so, I can make these connections. In other words, a precipitate is bounded by an interphase boundary, twins are bounded by twin boundaries, a faulted region is bounded by stacking faults. Voids and cracks are again typically, though how much ever you want to avoid them, the typically unavoidable in a material, and therefore atleast in a typical engineering process like casting or welding, you would notice that to some extent we would actually have some amount of these defects of voids, cracks, etcetera.

And, we shall see that these voids and cracks actually play very important role in sometimes, most of the times actually, in ways of deteriorating the properties of the crystal. But, under special circumstances like we have seen in porous materials, voids and cracks can actually be beneficial. And, not only cracks, but voids can be beneficial in giving special properties in a material like allowing to have lesser weight. So, we have considered here a broad overview of classification of defects based on dimensionality.

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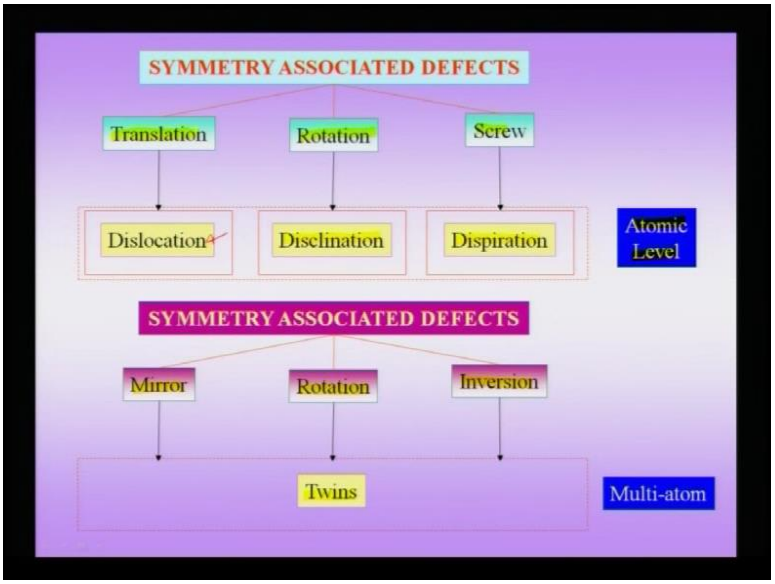

SYMMETRY ASSOCIATED DEFECTS

Translation

Rotation

Screw

Dislocation

Disclination

Dispiration

Atomic Level

SYMMETRY ASSOCIATED DEFECTS

Mirror

Rotation

Inversion

Twins

Multi-atom

So, let us now consider other kinds of classification or defects, apart from based on dimensionality. We can think of defects being associated with symmetry, like for instance, the dislocation can be thought of as been associated with the translation of symmetry of a crystal. Similarly, a disclination can be thought of as being associated with the rotational symmetry of a crystal; and, a dispiration being associated with this screw symmetry of a crystal. And, this is of course, thinking of symmetry associated defects atom atomic level.

At a certain merger level of microscopic multi atom level, we can think of as twins being associated with certain kind of symmetries like we can have mirror twins, we can have rotational twins, and also we can have inversion twins. We will see certain schematic examples in coming slides of mirror and rotation twins. In other words, suppose, I have a dislocation in a material that in some sense, is going to be also breaking my translation symmetry of the crystal. This is the reason why we call them symmetry associated defects.

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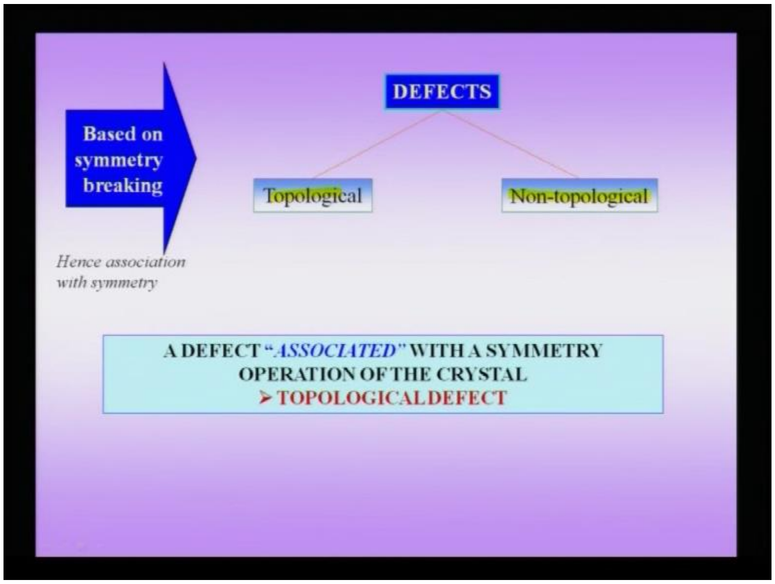

DEFECTS

Based on symmetry breaking

Topological

Non-topological

Hence association with symmetry

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

Defects based on 2 in symmetry breaking concept can be called topological defects or non topological defects. Though we are not going into details at the stage is, what is topological and topological defects, but these are genuine fields of interesting study, atleast in specific surface.

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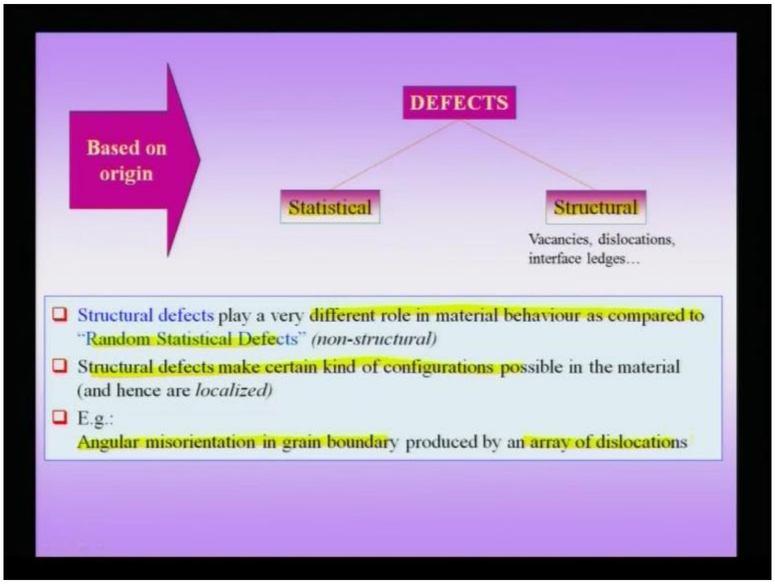

DEFECTS

Based on origin

Statistical

Structural

Vacancies, dislocations, interface ledges…

- ☐ Structural defects play a very different role in material behaviour as compared to "Random Statistical Defects" *(non-structural)*
- ☐ Structural defects make certain kind of configurations possible in the material (and hence are *localized)*
- ☐ E.g.:
  Angular misorientation in grain boundary produced by an array of dislocations

This is, we will spend a little more time over the understanding of what is called a defect classification based on origin. They can be statistical stored defects, in other words which is present in non, for non specific reason in the crystal, and what we may call a structural defects; and off course, we will, I will show you by what is one example that how a statistically stored defect is different from an structural defect.

The importance of this classification is that by statically stored or a random statistical defect has a different role in material behavior as compared to what you might call a structural defect. A single defect can also go from being a statistically stored defect to a structural defect. And, in fact, we have already considered one such example, but we will return to that example once again in the, from a view point of classifying defects as statistically stored or structural.

Structural defects typically make certain configurations possible in a crystalline material, and therefore they are localized to a certain region in the material. For instance, the angular misorientation at a grain boundary can be produced by an array of dislocations. So, this is a very important concept that the dislocations which are present along, for instance, a low angle grain boundary and we will see actually a beautiful arrays of picture in the coming slide.

Such a dislocation which is making possible the misorientation, typically a low angle misorientation possible between 2 regions of a, or 2 crystals is what you might can be thought of as a structural array of dislocations. Now, let us consider one example which will may amplify, exemplify things a little more.

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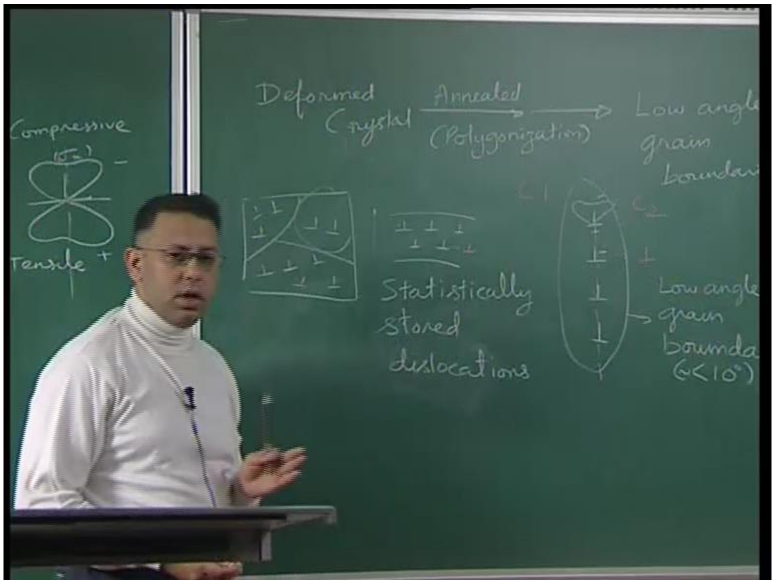

Now, we are seeing the process wherein we have taken a deformed crystal, and they are annealed. And, the process which occur durings this annealing is called polygonization which like to the formation of. In a deformed crystal actually, if I now consider a poly crystalline material, and I am just going to draw some screw schematics here. There are going to be lot of dislocations.

And off course, and though I am using a symbol for an edge dislocation, a single edge dislocation in the crystal could actually have a mixed character, it could be partially screw, it could be partially edge, and therefore it could have a general character; so, I am just drawing a some schematic of showing these dislocations. And, if I am looking at a single crystal, single grain boundaries, the single grain actually could bend because of the presence of these dislocations.

Now, during the annealing process these dislocations can come together to actually form an array one below the other. And, we have already seen that the reason for formation of these arrays is because of lowering of energy. Now, this is my compressive region of the dislocation, and this is my tensile region. And, the tensile region of this dislocation partially allows the compressive region of the dislocation below it. And therefore, they would rather tend to align in this format, rather than the randomly position in the crystal.

This kind of a distribution of dislocations I would call as an. And, in the formation of process, in the formation process, where you actually end of forming what is this called a low angle grain boundary. And, we will see a picture of this in a, coming soon. And, as you can see, this low angle grain boundary actually consists of an array of dislocations. This specific low angle grain boundary being considered here is what is called a low angle twin boundary.

And, suppose, I were to construct a low angle twist boundary, such a low angle twist boundary would actually consist of an array of screwed dislocations. But, what we are seen here is that this statistically stored dislocations in the process of this annealing, actually go on to form what is called a structural dislocation. Now, this structural dislocation, and off course I do not always have to start with statistically stored dislocation to form a structural dislocation; this is not a necessity. I just take an beautiful example where such a transformation actually takes place.

Now, in this structural dislocation, or this low angle grain boundary, the structural dislocation has been localized to the grain boundaries. So, it is now; and it is providing a structural feature here. In other words, it is accommodating the tilt between the 2 regions of the crystal which I can call, crystal 1 and crystal 2. So, the miss orientation between these 2 regions which is now I just pointed out, this small missorientation of something like that can be of 50 degrees has been accommodated by this array of dislocations.

Now, suppose, if I try to plastically deform this specimen, we saw the this specimen. It is clear that these dislocations are free to move because they play no structural role in the material. On the other hand, if a dislocation, this dislocation needs this boundary then the missorientation angle is going to change. And therefore, it is energetically not feasible and are not that easy to drive a dislocation away from this boundary.

Also, this is already in the low energy configuration. And, when the this dislocation leaves the energy system is going to be higher, therefore more work has to be done to drive this dislocation away from this boundary as compared to a dislocation moving from here to a neighbouring position like this. Therefore, you can clearly see that a structural dislocation though in terms of its characteristics, this is also edge dislocation, it is also an edge dislocation. This form a localized structural dislocation, and its response to an external stress is going to be different as compared to a statistically stored dislocation.

So, for other kind of structural these are the statistically stored defects like a vacancy. For instance, suppose when I am talking about vacancies, again I can have structurally stored vacancy, or I can have, I mean, statistically stored vacancies or structural vacancies. As I pointed out, the vacancies are typically unavoidable in a material because we are always at positive kelvin temperature, and therefore, there is a equilibrium concentration of vacancies. But, there is a possibility that vacancies arise because of other reasons as well.

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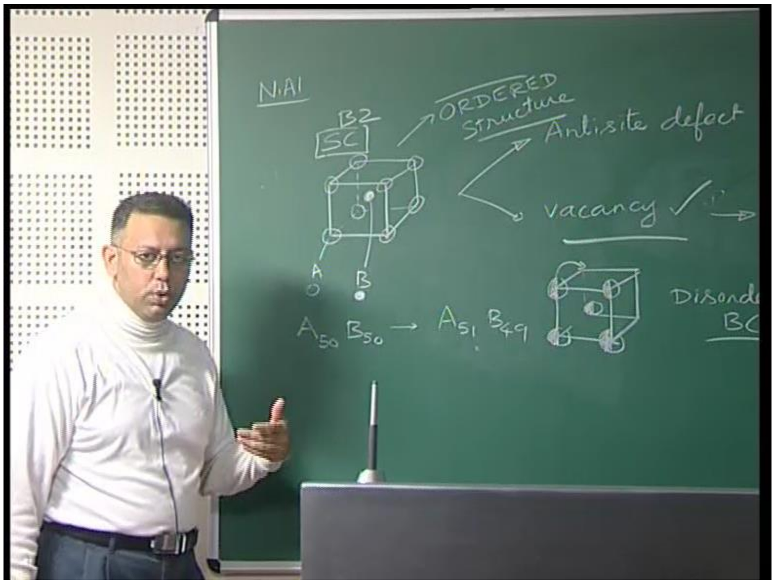

I am going to consider one such example. Let me consider a, B 2 phase, which is a symbol cubic phase having a composition, A 50, B 50. Now, it is possible that some of these A, B kind of phases, one example could be, NAI phase, for instance, they have certain tolerates at non stiochiometry. For instance, when I want to make not a, A 50, B 50 phase, but there could be a possibility that this is not actually, A, B, is not a line compound. And, it can actually tolerate a little amount of deviation from stachiometry.

And, let me now assume that this can become, A 51, B 49. In other words, this is now an A rich composition with respect to the perfect stiochiometry of A 50, B 50. Now, when I am trying to make this A rich composition there are 2 possibilities which represent myself - one is I can actually put a anti site defect, or I can put a vacancy. In other words, suppose I start putting, A atoms in the B sub lattice, then I can get actually a A rich composition.

As you might be aware that this kind of a structure is called an ordered structure, and this ordered structure is sometimes also referred to as a super lattice. And, this super lattice can be thought of as 2 inter penetrating simple cubic sub lattices. One simple cubic sub lattice having its origin at 0 0 0, another sub lattice having its origin at half, half, half. And therefore, this simple cubic super lattice can be thought of having 2 sub lattices - one completely occupied by A, another completely occupied by B.

Now, if I start putting A atoms in B sub lattice, then I can make this composition, A rich. Another possibility of making an A rich composition is by actually putting vacancies in the B sub lattice. So, off course, the system, depending on the system specificity, and in which direction are we actually considering the off stoichiometry, I may try to make an A rich composition or B rich composition, it, certain systems will actually show a preference for vacancies in one of the sub lattices.

Now, this vacancy which I have introduced purely because of off stoichiometry with respect to a ordered compound. So, this vacancy is very different from the thermal vacancies which arose because of thermodynamic reasons. So, this vacancy is there because of off stoichiometry. And now, if this vacancy has been put in the B sub lattice, and I am talking about vacancy diffusion or atomic diffusion as a specific, what you might call, mechanism of the property which is under my consideration, then, in a completely, off course, disordered system, A and B sub lattice is being equivalent.

And, some of these would be vacant giving rise to, for the reason of thermal vacancies. And, it jump from, and off course, I can schematically represent disordered unit cell as follows; and, so forth. All the lattice points are being occupied, and this disordered structure is a B C C, has a B C C lattice at its heart. Now, off course, all the lattice points are occupied by 50 percent probability of occupation of the B atom, and 50 percent occupation probability with the A atom. And, some of these are vacant sides, then any of the A or B atoms could jump to its neighboring side without any problem.

Because, now, this is an ordered structure, the, if an A atom jumps to the B side because it is vacant, and this vacancies being a structural vacancy, the energetic feasibility; it is not energetically feasible to do so. That implies, that the diffusion arising from the structural vacancies is going to be different from that arising from the thermal vacancies. The thermal vacancies can be reside in any one of the lattice points; on the other hand, this structural vacancies is localized to one of the sub lattices, it is not randomly positioned anywhere in any of the sub lattices.

And, the very fact, now these vacancy is a structural vacancy makes it, makes its role in diffusion different from that of a thermal vacancy in diffusion. So, it is clear from atleast couple of these examples that when I classify these defects into either structure or statistical, it gives me a handle on the properties, and gives me the ability to recognize the role of the defect in determining the specific property under consideration.

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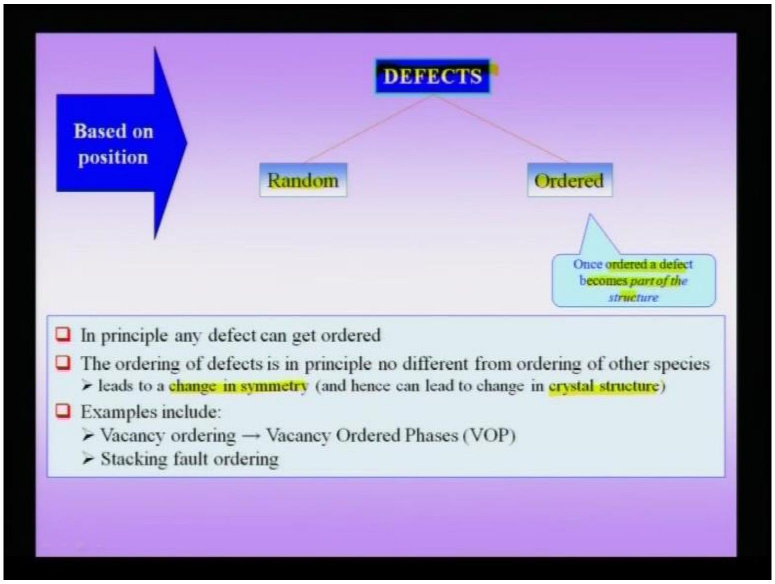

Based on position

DEFECTS

Random

Ordered

Once ordered a defect becomes *part of the structure*

- ❑ In principle any defect can get ordered
- ❑ The ordering of defects is in principle no different from ordering of other species
  - ➢ leads to a change in symmetry (and hence can lead to change in crystal structure)
- ❑ Examples include:
  - ➢ Vacancy ordering → Vacancy Ordered Phases (VOP)
  - ➢ Stacking fault ordering

Now, another important classification which we are implicitly already taken up in the example here, or atleast set the tone for understanding those kind of defects in the example we considered, is based on the position - a defect can be random or it can be ordered. And, the important difference between the 2 is that, an ordered defect, once it is been ordered, becomes part of the structure; and, this becoming part of the structure can actually lead to a change in symmetry and hence lead to a change in the crystal structure.

In principle any of the defects we have considered can actually get ordered. But, some of the important defects which tools in ordering we need to consider are the vacancies and the stacking fault. For an example, off course, we will consider just ordering of the vacancies for now, but other defects can also get ordered. And, when they get ordered, obviously their overall collective behavior is going to change.

In some sense, we already noted that this dislocations along the grain boundary in some sense is ordered because now the average spacing of all these dislocations is fixed by the misorientation angle between the 2 crystals. In some sense, they are ordered defects. But here, we are still talking about a 3 dimensional crystal and a defect actually at the interface. If suppose, in the case, example of vacancies and stacking faults in the defects within the crystal these have a, in some sense, have a more profound influence on the very definition of the crystal itself.

So, let us perhaps consider this, but this is an important consideration as far as the symmetry of the crystal goes. Now, let me consider as a schematic the, A, B, kind of a structure. We are already noted, because now I am considering off stoichiometry, the vacancies in the B sub lattice are localized to the B sub lattice. So, in some sense, they have been localized to the sub lattice. So, they are ordered atleast within the sub lattice. But, to go from there to perfectly ordered vacancy which we call as a vacancy ordered phases, it has to be positionally ordered even within the sub lattice.

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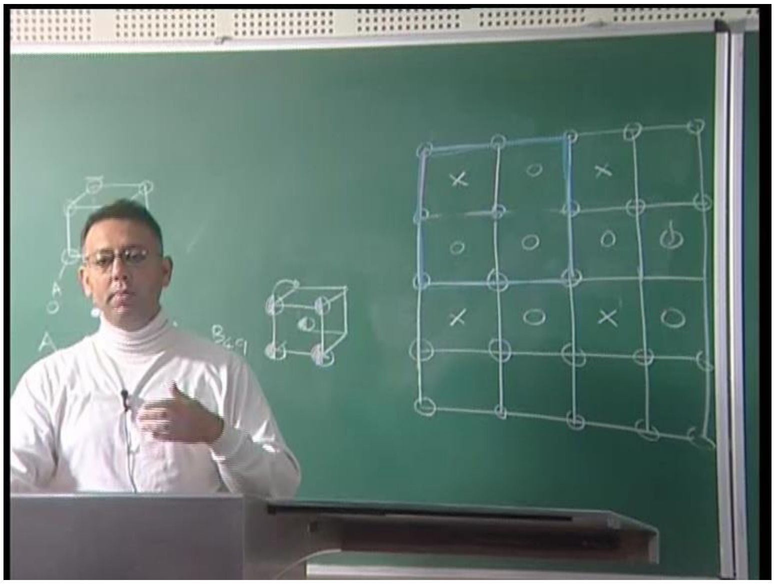

So, let us think of how we can do that. Suppose, for simplicity let me consider 3 unit cells of a square and a lattice. Now, assuming that the vacancy can be present anywhere; in other words, any one of the atoms can be seen randomly; then, such a structure we can think of as consisting of random vacancies. But, instead of being present random anywhere, let me for simplicity think of this structure having vacancy here.

And, off course, correspondingly, if I am talking about next ended crystal, and let me extend this crystal, would have a vacancy here, would have a vacancy here, and would have a vacancy here. And, off course, all the other points I can fill with atoms. Now, this is what we call vacancy ordered phase to see that my original unit in the crystal would have been a unit cell like this, a small unit cell.

Now, when the vacancies get ordered you can see that no more unit cell has expanded, and this whole big is my unit cell; sorry, this is not my unit cell, let me correctly draw the unit cell. The unit cell would be; this is my unit cell. So, therefore, the lattice parameter on the symmetry at the fundamental level has been altered because of the ordering of vacancies. And, that is why these ordered structure, ordered defects have a different role to play in the crystal as compared to a random defect. In other words, an ordered defect can actually become part of the structure, and therefore it can alter the very definition of the crystal.

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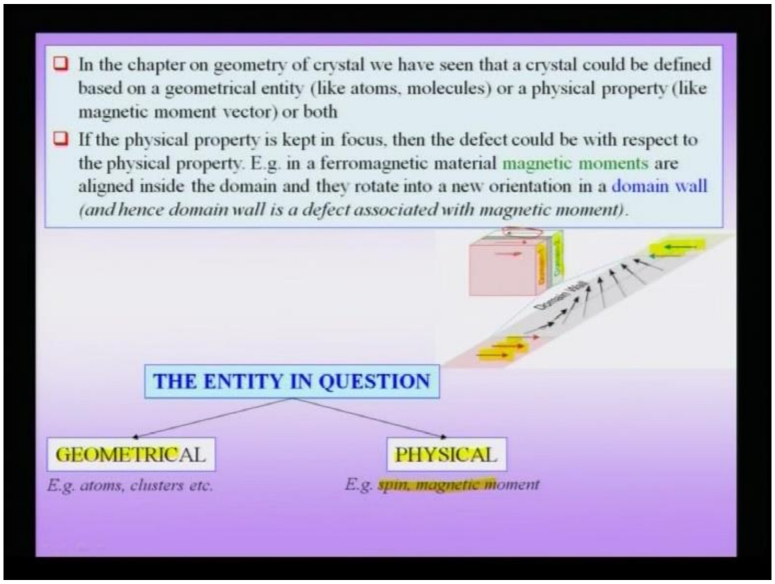

- ☐ In the chapter on geometry of crystal we have seen that a crystal could be defined based on a geometrical entity (like atoms, molecules) or a physical property (like magnetic moment vector) or both
- ☐ If the physical property is kept in focus, then the defect could be with respect to the physical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

THE ENTITY IN QUESTION

GEOMETRICAL

E.g. atoms, clusters etc.

PHYSICAL

E.g. spin, magnetic moment

Last but not the least, let us consider how a defect can be classified based on a geometrical entity or a physical property. Now, when I am talking about, for example, a domain wall in a ferromagnetic material, then the domain wall is not defined with respect to the crystal structure.

It is defined with respect to the magnetization of the spin vector in the magnetic domain. Since, I am talking about a ferromagnetic material in domain 1, all the spins are going to be aligned in the same direction.

Similarly, in domain 2, all the spins are going to be aligned in the same direction, and this direction has been shown schematically as an arrow mark in this direction; in this for domain 1, and for domain 2 it has been shown as a vector in the other direction. Now, a domain wall represents a defect in the domain structure, exactly analogous to a grain boundary in a crystal structure.

But, here we have to use the definition based on a physical property like as we have done here, the magnetic moment of a spin vector, rather than using a structural definition like an atom or an ion or a molecule. Therefore, when I am talking about defect classification based on a physical property, we come across other kind of defects which are normally not with, merely when I am talking about the atomic of the geometrical entity. And, the example I have considered here is what is called a magnetic domain wall.

And, as you can see here, in the magnetic domain wall, the magnetization vector actually rotates out of plane and goes into a new orientation when you reach the domain which is adjacent to domain 1, which is has been labeled as domain 2. This kind of a wall, off course is called an block wall. And, in thin films the other kind of walls possible like, the neel wall, etcetera, wherein actually the rotation of, in the neel wall the rotation of magnetization spins occurs in plane rather out of plane as shown in this figure.

But, nevertheless, the domain wall represents a region of higher energy; it represents a region of disturbance with respect to the perfect ordering which is present in the, either in the domain 1 or domain 2, and therefore can be considered as a defect in the domain structure. So, when I am trying to understand the physical property based definition, then additional kind of defects can arise in a material like, a magnetic domain wall.

Or, off course, when I am talking about ferro electric material, then there will be domain walls in ferro electric materials where the dipoles on either side would be oriented differently, and therefore the ferro electric domain wall would represent again a region of high energy. And, this hence becomes an important basis for definition of defects in materials which is, which takes us to additional kind of defects which are present.

Suppose I have a polycrystalline material which is also ferro magnetic, then I would notice that the grain boundary is automatically also a domain wall boundary. But, domain wall, domain boundary is themselves often have been found to be continuous across grain boundary. So, this is an additional observation. One important thing is that, within a single grain which is based on single crystal structure, the single crystal could be divided into multiple domains. And, the reason for doing so is actually a lowering of energy of the material which is otherwise in a single crystal would be leading to high magneto static energy.

So, domain wall, inspite of having high energy and tolerate it in materials, in order to overall reduce the energy of the system which involves magneto static energy which throws out external magnetic fields. So, before we close this session, let us consider some of what you might call gallery of some of the defects, some of which you may be already talked about; some of which perhaps we have briefly mentioned but not gone into any kind of detail, and some new ones.

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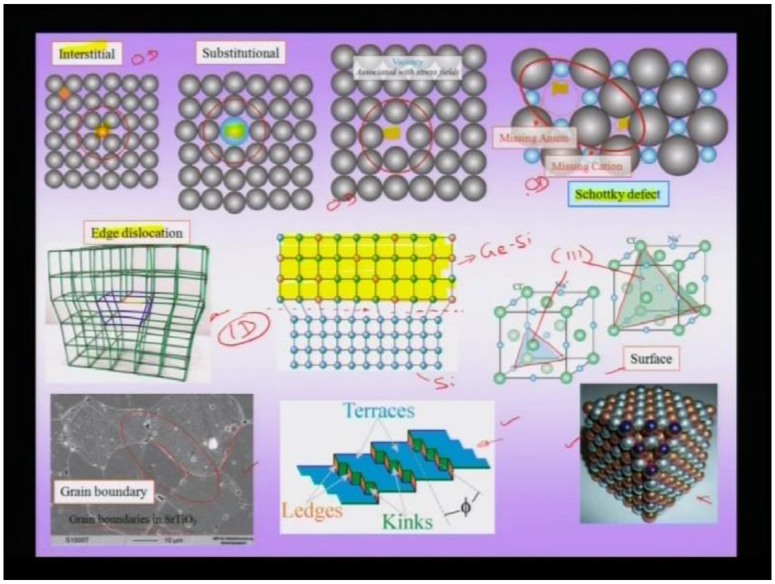

So, let us start with point defects like the interstitial which has been shown here, and a vacancy which were talked about lot of detail right here. And, this is 2 kinds of point defects are shown here - one is the interstitial which is present in the interstitial void of a material. Or, if one of the atoms has been replaced in the lattice by a atom which is been colored blue here then this would be called as a substitutional defect or substitutional alloying element.

We can have a pair of defects like, we can have a missing an ion in conjunction of the missing cat ion, in a ionic substance; and off course, a pair of them go missing because then the overall charge neutrality is maintained. Therefore, such a combination is called a schottky defect which is in combination of a missing an ion and a missing cat ion, typically which are positioned close to each other.

We already seen the example of an edge dislocation, and we also such an edge dislocation can actually present at an interface between 2 materials. And, in this example, this, there is material A on this side which actually is a solid solution. For example, this could be a solid solution between germanium and silicon. And, this could be a silicon, for instance. And, this dislocation which is present between the 2 materials can be thought of as an interfacial miss led dislocation.

And, in some sense, an interfacial miss led dislocation belongs to the class of structural defects and not to a random defect because now it is localized to this interface between Ge. Si, and Si; there is an interfacial miss dislocation is a structural dislocation unlike the random dislocation which is the one which is shown in the left hand diagram. We can tick of surfaces in ordered structures like for, this is now the 1 1 1 surface in an ordered structure. And, of course, this is a nice ball model, and this is super lattice structure.

And, suppose I am talking about ionic material, I can notice that if I make the same 1 1 1 surface, it can either consist of purely of sodium atoms as this surfaces, or it can consist purely of chlorine ions, sodium ions or chlorine ions, and therefore these surfaces in polar materials can, in ionic materials can be polar. So, these 2 are polar surfaces cuts along other surfaces like for instance this is now the 1 1 1 surface which is been shown here, suppose, I make a 1 0 0 kind of a cut in such a material then I would notice that that surface would be 1 polar. So, surfaces can be polar or non polar even in a single ionic material.

Then, we have also seen the example of a grain boundary; and one such example is in the case of the grain boundary shotshoot titanate which is a ceramic. And, you can see that some grain boundaries are randomly curved, some of them can be reasonably straight as well. We would also said that there are defects in materials which are unavoidable, and one of them was the surface. And now, this figure here shows not only a surface but certain other defects within the surface which we call ledges and kinks, and we will come to it perhaps later during the series of lectures.

Therefore we have the surface here; these are examples of the surfaces here, here, which are 2 dimensional defects. A grain boundary which is again a 2 dimensional defect; an edge dislocation which can be a random statistically stored edge dislocation or a structural edge dislocation localized when interface, both these are 1 dimensional defects; then, off course, we have point defects here which is 0 dimensional on the top. So, you collapse of many kind of defects which are shown here.

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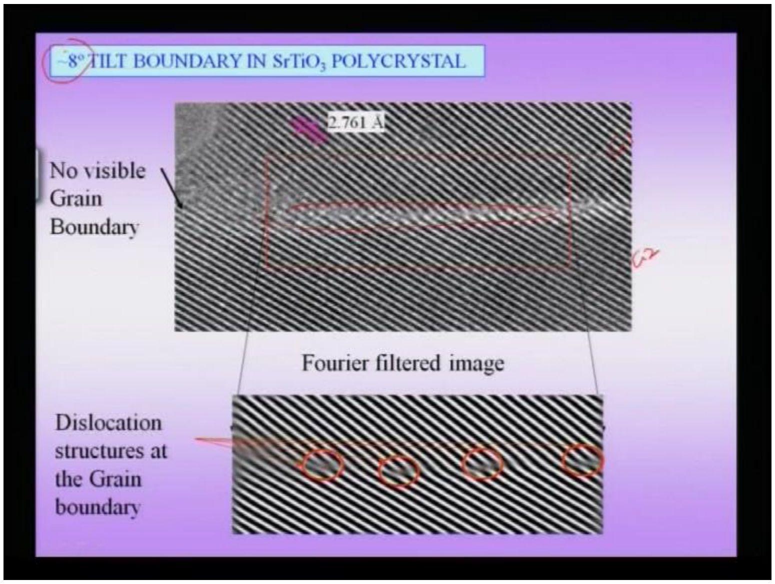

~8° TILT BOUNDARY IN $SrTiO_3$ POLYCRYSTAL

No visible Grain Boundary

Fourier filtered image

Dislocation structures at the Grain boundary

But, what we have to remember is that many of these defects are what are going to play an very important role in the properties of the material. And, to show on a, one of the examples which have been talking about quite a bit today, is the case of the low angle grain boundary. So, this is an actual transmission electron micrograph in a stonoshm titanic poly crystal in which this region is a low angle grain boundary. So, this is my grain 1, and this is my grain 2. And between that, the low angle grain boundary, and when I have a Fourier filtering image, actually you can see the dislocation cores nicely in such a low angle grain boundary.

In other words, I can clearly see an array of dislocation sitting along the grain boundary which is now as a small miss orientation of about 8 degrees; it is an 8 degree tilt boundary, and therefore it is leading to a small miss orientation which I pointed out is a characteristic of the low angle grain boundary. And clearly, therefore this dislocation I am describing here is leading to the miss orientation, and therefore is a structural dislocation.