Nanostructures and Nonmaterials: Characterization and Properties

Prof. Anandh Subramaniam
Prof. Kantesh Balani
Department of Materials Science & Engineering
Indian Institute of Technology, Kanpur

Lecture - 01
Introduction of Nano materials

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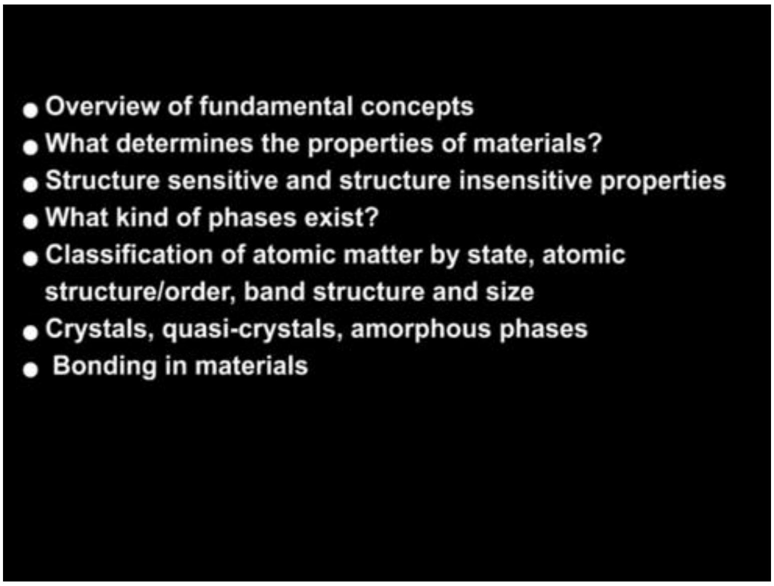

- Overview of fundamental concepts
- What determines the properties of materials?
- Structure sensitive and structure insensitive properties
- What kind of phases exist?
- Classification of atomic matter by state, atomic structure/order, band structure and size
- Crystals, quasi-crystals, amorphous phases
- Bonding in materials

Good morning, welcome to the NPTEL video lecture on nano structures and nano materials in which we will consider characterization and properties nanostructures and nano materials. My name is Anandh Subramaniam and my co instructor in the course is Professor Kantesh Balani, both of us belong to the department of materials science and engineering at IIT, Kanpur.

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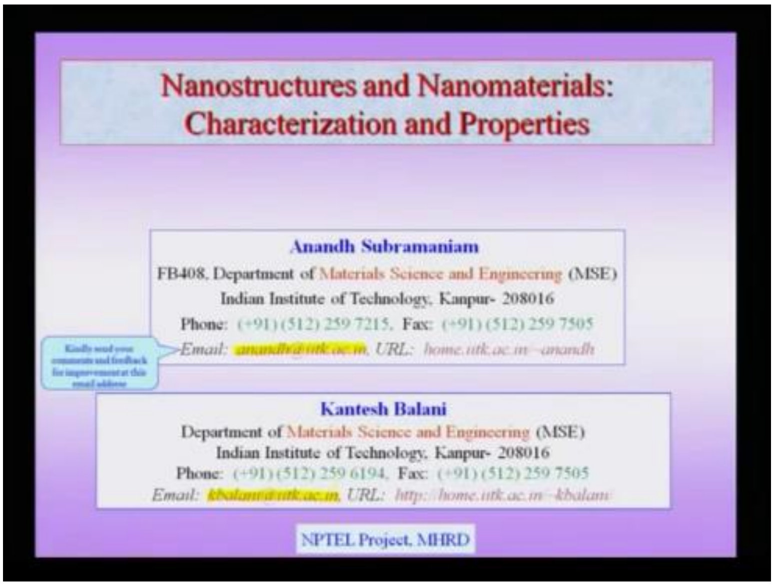

Nanostructures and Nanomaterials: Characterization and Properties

Anandh Subramaniam
FB408, Department of Materials Science and Engineering (MSE)
Indian Institute of Technology, Kanpur- 208016
Phone: (+91) (512) 259 7215, Fax: (+91) (512) 259 7505
Email: anandh@iitk.ac.in, *URL:* home.iitk.ac.in/~anandh

Kindly send your comments and feedback for improvement at this email address

Kantesh Balani
Department of Materials Science and Engineering (MSE)
Indian Institute of Technology, Kanpur- 208016
Phone: (+91) (512) 259 6194, Fax: (+91) (512) 259 7505
Email: kbalani@iitk.ac.in, *URL:* http://home.iitk.ac.in/~kbalani

NPTEL Project, MHRD

Our email addresses are anandh@itkac.in and kbalani@itkac.in, you may kindly give your feedback on any aspects of the course including any possible improvement to that lectures at these email addresses. This will help us to plan better for the future and also improve upon the contents currently being recording. As you are aware nano structures and nano materials are the age of the future a lot of interesting research is going on currently, therefore the literature has been going very fast in these areas.

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References

1. *Nanomaterials, Nanotechnologies and Design: an Introduction to Engineers and Architects*
   D. Michael Ashby, Paulo Ferreira, Daniel L. Schodek
   Butterworth-Heinemann, 2009.
2. *Handbook of Nanophase and Nanostructured Materials (in four volumes)*
   Eds: Z.L. Wang, Y. Liu, Z. Zhan
   Kluwer Academic/Plenum Publishers, 2003.
3. *Encyclopedia of Nanoscience and Nanotechnology*
   Ed.: Hari Singh Nalwa
   American Scientific Publishers, 2004.

Certain beautiful references and texts are currently available for example the encyclopedia of nanostructure nano science and nontechnology, which is edited by Doctor Hari Singh Nalva which comes in the 10 volumes. So, there is also the hand book of nano space on nanostructure materials which is edited by Van Lie Nelson. There are equally interesting and nice accessible text like the nano materials and nanotechnologies and design which is an introduction to engineers and architects.

The book by Ashvi Perera and some of these books as you can see the handbooks and, therefore they are better for consultation purpose. While, other are in the text book format like the first one by professor Ashvi nevertheless the literature in the area of nanostructures nano materials. Now, nano technology has going so fast that often a text book or a handbook written about 5 to 10 years back get soon outdated newer and newer concepts emerged. Therefore, it is very important that that students to also consult various journals and periodical publications in the area which include.

So, lot of new journal has come up in the last 10 years, so it is important for the student perspective not only to consult textbooks and handbooks. But, this is also to consult journals because area of nanostructures and nano materials, nano science and nanotechnology is going at extremely tremendously fast rate. So, with and for us simple easy accessible point of view students may consult to the first book why in no sense this book can be considered as comprehensive text on all aspects of the subject.

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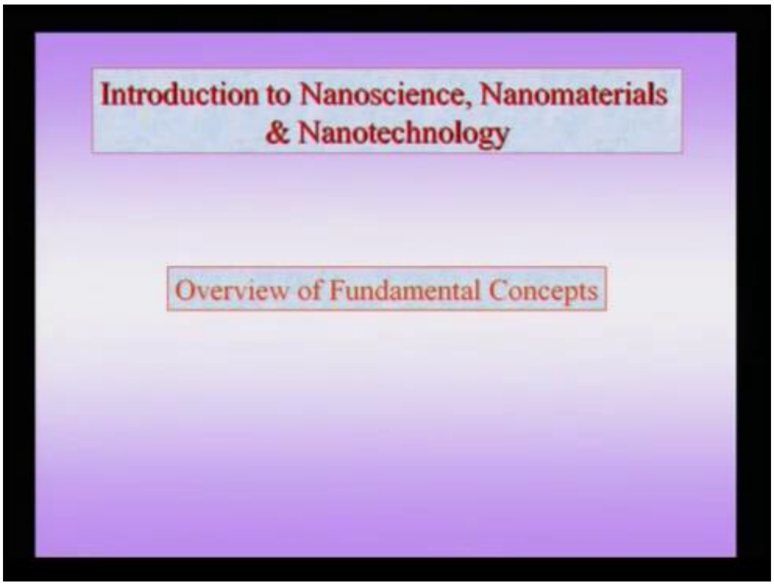

Introduction to Nanoscience, Nanomaterials & Nanotechnology

Overview of Fundamental Concepts

Let us first start with some basics, in other words let us introduce ourselves to nano science and nano materials and nanotechnology in the broadest possible way. So, this will involve an understanding of the fundamental concepts right from the outset it need be understood that nano materials or nano science. But, nanotechnology is built on a foundation which is the usual science or the physics or the chemistry or the material science which we normally study. So, it is a layer up and above which we normally study and therefore the fundamentals of these areas needs to be strong, therefore if I want to draw a schematic view this will be the foundation of basic science.

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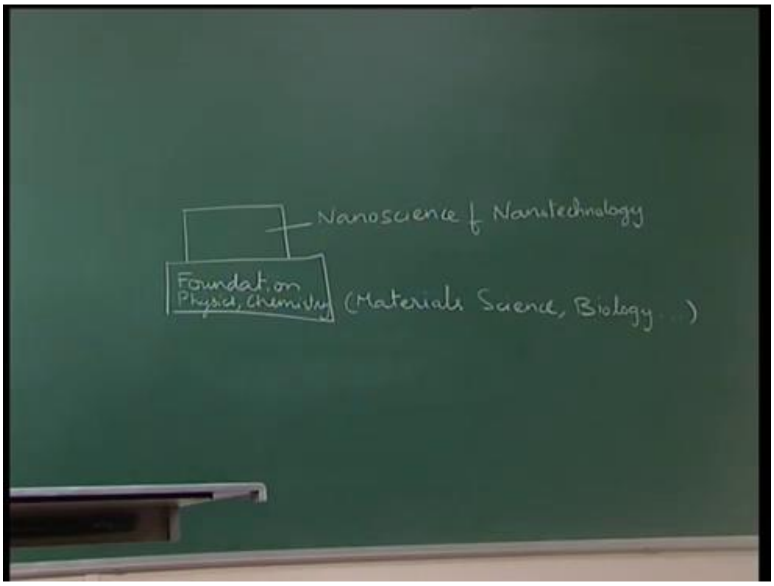

This foundation would include physics, chemistry, and material science etcetera and on this foundation resides the subject, which we can call nano science and nano technology that for a student should be aware. So, that about the fundamental subject he is devoting his carrier towards nano science is built on that subject for example suppose somebody is interested in magnetism. So, he needs to have fundamentals in magnetism strong then on that fundamentals can built up nano magnetism.

But, suppose a person is interested plastic deformation then a student can learn severe plastic deformation techniques which can give rise to nano materials. Now, suppose the person is interested in chemistry then he can go ahead and device those specific chemical synthesis techniques which can produce various kinds of nano materials and nano structures.

Therefore, the fundamental subject is important like one may be interested in nano mechanics and then they a person may be interested in mechanics once the fundamentals in mechanics is strong he can go ahead and learn a subject of nano mechanics. In another words, the learning of nano materials is absolutely contingent upon learning the fundaments of various aspects of usual physics chemistry and other aspects.

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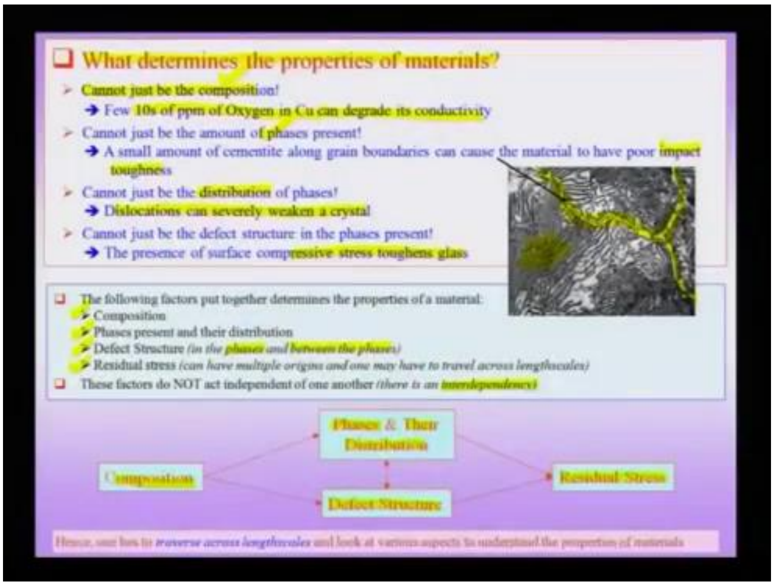

❑ What determines the properties of materials?

- Cannot just be the composition!
  - ➔ Few 10s of ppm of Oxygen in Cu can degrade its conductivity
- Cannot just be the amount of phases present!
  - ➔ A small amount of cementite along grain boundaries can cause the material to have poor impact toughness
- Cannot just be the distribution of phases!
  - ➔ Dislocations can severely weaken a crystal
- Cannot just be the defect structure in the phases present!
  - ➔ The presence of surface compressive stress toughens glass

❑ The following factors put together determines the properties of a material:
- Composition
- Phases present and their distribution
- Defect Structure *(in the phases and between the phases)*
- Residual stress *(can have multiple origins and one may have to travel across lengthscales)*

❑ These factors do NOT act independent of one another *(there is an interdependency)*

Phases & Their Distribution

Composition

Residual Stress

Defect Structure

Hence, one has to *traverse across lengthscales* and look at various aspects to understand the properties of materials

Now, one of the important reasons why we wanted to study nano science and nanotechnologies is because it gives us a beautiful new array of properties which typically not found in normal bulk materials. Now, we will see some of these properties as we go along, but it should be remembered that the origin of these properties should be absolutely clear. So, when we design our nano material we can take into account these factors and design our materials for a given set of properties which is going to be the corner stone, for the technological application for these materials.

So, let us ask ourselves this question what determines the properties of materials this is perhaps the broadest kind of question one can ask. So, the properties one could be talking could be mechanical properties like hardness yield strength fracture toughness etcetera. Now, he could also be talking about optical properties could be taking about magnetic properties electrical properties and many other possible properties including the biological properties like bio compatibility toxicity etcetera. But, we will start with a small set here and try to understand what are the factors which determine that what how these properties come about the first thing we see that.

Suppose, I put in, suppose a few tons of BBM oxygen in copper this would degrade conductivity drastically. Therefore, I need to go in for what is oxygen free hyper conductivity copper do my copper wire which is used for electrical conduction. Therefore, just knowing the composition cannot give me my properties, I need to consider for the factors for instance it is not enough that I know what are the phases present in the material to give an example. So, there is a micro graph on the right hand side there in which is this per light which is the alternating anomaly.

So, this is from carbon steel and hyper utechtoyed and you can see that along the green boundary region. Now, there is a continuous network of a second phase this phase happens to be cinematized, which is extremely built in. But, you look at the overall micro structure as you see on the micro graph you see the volume fraction of the second phase along the green boundary is small. But nevertheless the presence of this second phases is cinematized phase along which is the hard, but brittle phase of all the green boundary severely deteriorates the impact properties of the material.

Now, what we may call the impetuousness of the material, therefore just knowing the phases present is not enough for me to know the properties. So, I need to know further information about the property about the material which will tell me how their properties in the material are going to be. In other words, need to worry about the composition number 1, I need to know the phases number 2, but that is not enough. For example, if I have dislocations in a phase this can weaken a crystal severely suppose I take a single crystal and try to absolutely pure defect free a single crystal.

So, I try to measure its chasten, it is turn out to be in the order Giga Pascal, but in the presents of dislocations which are crystolgraphycally defect. So, strength of a material fall a few orders of magnitude and can severely weaken the crystal this implies that I need to know the defect in the material present apart from knowing the phases and their distribution.

But, should I stop here definitely not and the reason being that we know that the normal glass is very brittle and fractures very easily the window plain glass if any ball is thrown on the windows plain glass shatters so easily. But, we have another example of a glass that is known as the toughened glass toughened glasses consists of normal glass.

But, in which there is certain distribution of residual stresses which is especially compressive residual stress on the compressive surface of a glass this helps to toughen the glass a lot. So, that means that if I want to understand properties of a material, I need to know its composition, I need to know the phases present and their distribution. So, it is very important not only I know the phases present, but also how these phases are distributed within the material, I need to know the defect structure in the material. But, many of these terms like the defect structure and phase distribution we will consider little more detail as we go along.

This is an overview slide we want to put in a broader picture of what is the factor? One need to worry about when one is interested in knowing the properties of the material. So, when we talk about the defect structures, I am talking about the defect structure in the present like dislocations. So, in the phase and between the phases like interfacial dislocation also apart from the bulk dislocations last. But, not the least I need to know the residual stress and we shall see at the last the residual stress can have multiple origins.

So, to understand all these aspects I not only need to know for instance the phases present in the distribution, I need to know the defect structure in the distribution. Now, I also need to know my residual stress and its distribution and in doing, so I would realize these factors are not independent of one another. But, they often talk to each other, they talk to each other in across lens scales to be an example for instance. Suppose you had a coherent precipitate a coherent precipitate is not only a defect in the perfect single crystal in some scenes.

But, is also is associated with residual stress, therefore the precipitate and residual stress are intricately intermixed in the case of a coherent precipitate. Therefore, there is lot of interdependency among these factors and this inter dependency often gives rise to the properties which one observe the material. So, let us summarize this slide because it happens to be an important over view of this slid and this will tell us the tone that when have a bulk material. So, these are the nano material or a nano structures, how the properties are going to arise and how the bulk material is going to be different from the nano structure and the nano material.

Now, how can I use the very same concepts, which are present in the slide to engineer the nano structure and nano material? So, to obtain a specific set of properties, which are often very unique what is giving beauty to nano materials and nano structures? So, I need to understand the composition of the material and of course composition could be spatially varying the material. Therefore, the property could be region specific given the composition I need to understand the phases present in the material and the distribution.

So, we will also ask a question soon what do we mean by these phases what kind of phases exist and what kind of distributions can these phases could be present and how this distribution of phases is going to determine the properties. So, one example of course we have already considered that if you have as a second phase along with the green boundary, which happens to be a brittle phase. Then cracks under impact loading all can propagate all along with the green boundary and, therefore overall fracture toughness of material happens to be is very low.

But, in spite of the fact that the second phase as in the example consisted above was just present in a small volume of fraction, it is a connectivity there along the green boundary which gave it a poor impact of toughness. Additionally, we also have to consider the defect structure of the material the defect within the phases, which includes defects within the faces and of the interfaces. Now, of course the unavoidable defects of the free surface along with how the defects are distributed spatially in the material. So, if you are talking about processing technique or a low cold or high temperature how this defect structure evolves in service.

So, that means you are initial defect structure in the material of the start of the component to in service as the time progress. But, that happened that the defect structure would evolve time, so could the phases and the distribution evolve the time. Therefore, I need to also temporal evolution of these, what you means by spatially distributed phases and defects we said last.

But, not least that residual stresses play a very important role in the properties of a material this is often underestimated, in fact this residual stresses can play a very positive role. So, like this we saw in the case of toughened glass where in we introduced compressive residual stresses on the surface, which gave rise to quite bit of toughing of the glass.

But, on the other had residual stress also can also lead to warp age of the component and, therefore can be (( )) and we may want to avoid the residual stresses in many cases. So, nevertheless this presents of this residual stresses which again has to be understood spatially and temporally that means how this residual stresses distributed within the material. Therefore, how its evolving time is very important for the properties of the material, suppose we are talking about the glass compressive residual stress. Suppose, we put 10 residual stresses on the surface then the properties would have been worst then that in a material, which had compressive residual stress on the surface.

But, we will have some more look at these concepts as we go alone, therefore if one wants to understand properties of a material then he or she needs to consider various factors. So, the composition phases distribution and the defect structure and the residual stress and in doing, so I have to traverse across lens scales he needs to go from. So, as we shall see soon from the atomic lens scale to the lens scale of the entire component and this journey across lens scales has to be integrated to a form. Now, which we normally in a common usage called the property of the material, which could as we considered could be the ductility it could be the fracture toughness.

So, it could be the optical transmitters, it could be the magnetic electrical polarization it could be or polarizability or it could be the magnetic susceptibility. So, there are there are very many properties, which come about and many of these can be understood by travelling across lens scale. So, considering these factors, in the previous slide when we talked about the properties and especially when the properties, which are depend upon on micro structures. So, we were making an implicit assumption regarding the type of properties, this will become clear when I classify the properties into structure sensitive properties and structure insensitive properties.

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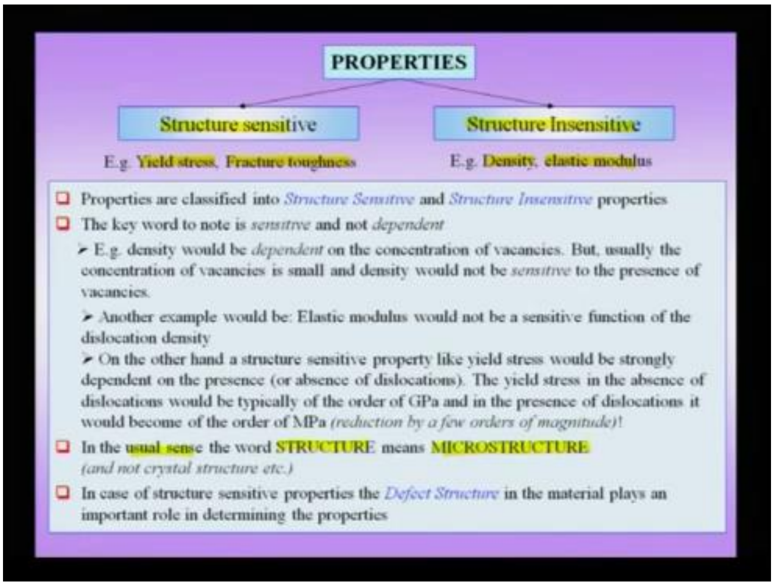

PROPERTIES

Structure sensitive

E.g. **Yield stress**, **Fracture toughness**

Structure Insensitive

E.g. **Density**, **elastic modulus**

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

We should know typically in the usual sense when we talk about structure sensitive properties it is usually meant that we are talking about micro structure sensitive properties. But, we are not usually talking about the crystal structure or any other kind of structure and, therefore we should it keep this in mind that properties can be structure sensitive and examples of such properties are ill stress fractured toughness etcetera. So, on the other hand there are properties which are structure insensitive like density elastic modulus and other kind of properties.

So, the key word in this definition is the word sensitive here we are not using the word depended, but we are using the word sensitive that means. So, that there are for instance the presence of point defects in a material would affect the density in a small way that is the density would be dependent on presence of vacancies in a crystal. But, it is, but it is not going to be the density is not going to be a sensitive function of the presence of vacancies on the other hand the yield stress of a material could be a sensitive function of the presence of the vacancies.

Therefore, we have to worry about properties from the view point, if they are structure sensitive or structure insensitive and to once again reiterate the views about the structure sensitive. So, it is usually meant we are talking about micro structure sensitive properties now this classification is very important because in the previous slide.

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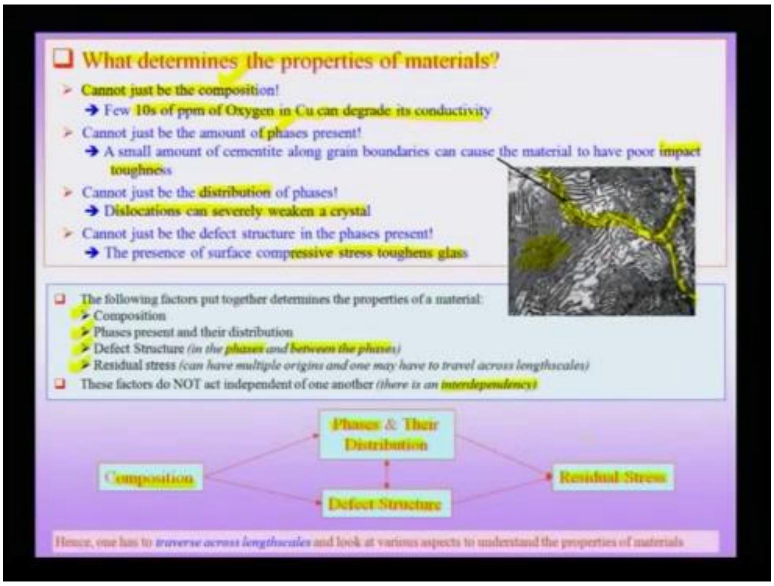

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  - ➔ Few 10s of ppm of Oxygen in Cu can degrade its conductivity
- ➢ Cannot just be the amount of phases present!
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- ➢ Cannot just be the distribution of phases!
  - ➔ Dislocations can severely weaken a crystal
- ➢ Cannot just be the defect structure in the phases present!
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❑ The following factors put together determines the properties of a material:

- ➢ Composition
- ➢ Phases present and their distribution
- ➢ Defect Structure *(in the phases and between the phases)*
- ➢ Residual stress *(can have multiple origins and one may have to travel across lengthscales)*

❑ These factors do NOT act independent of one another *(there is an interdependency)*

Phases & Their Distribution

Composition

Defect Structure

Residual Stress

Hence, one has to *traverse across lengthscales* and look at various aspects to understand the properties of materials

We had seen that the impact toughness of a material having cementite alone, the green boundaries is very poor. Now, typically this is because impact toughness is a micro structure sensitive property, now suppose I was talking about density. So, if this phase is present along the green boundary or as globe use along the material, which I can draw schematically in the board.

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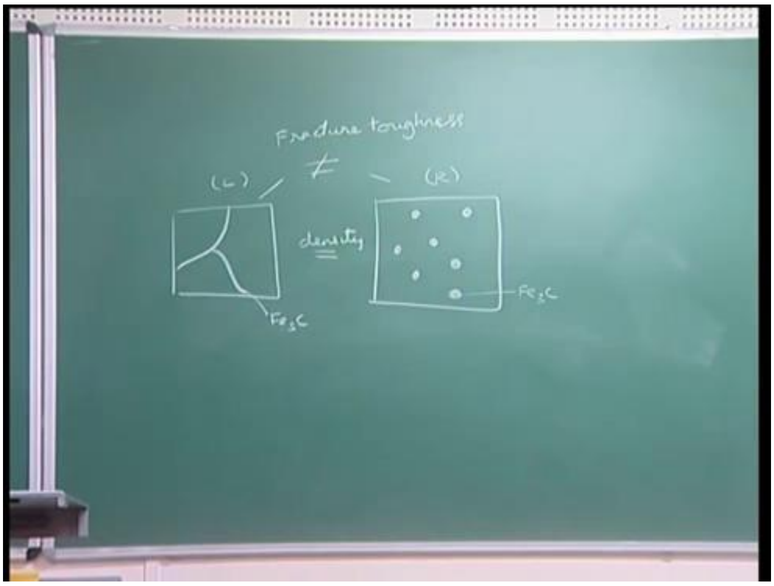

So, the case 1 is the presence of cement as continuous networks alone the green boundaries, in the second case I can think of the same cementi in the same volume fraction present as small globs in the material. So, in the figure on the left and there is a figure on the right the volume fraction of a cementite considered to be equal in both the cases. So, suppose I am talking about the structure insensitive property then I would notice the density of these two phases would be equal.

Suppose am talking about structure sensitive property a micro sensitive property like fracture toughness then they would be different for these two phases. Therefore, I need to clearly understand the distribution of phases is going to up, change my micro structure dependent properties. But, will not change micro structure independent properties and we shall see the quite few properties which are micro structure dependent.

Therefore, I need to worry about my phases in the distribution and also my defect structure an also about the residual stress. So, again if the residual stress state changes between two kinds of what we may call distributions the change in density would be negligible. But, the property like we saw impact toughness would change drastically, therefore it is very important whenever I am talking about structure sensitive property I worry about all details which cause on to form my micro structure. So, during this course of these lectures we will also evolve more functional detention of micro structure which can be used to directly correlate the tem with properties.

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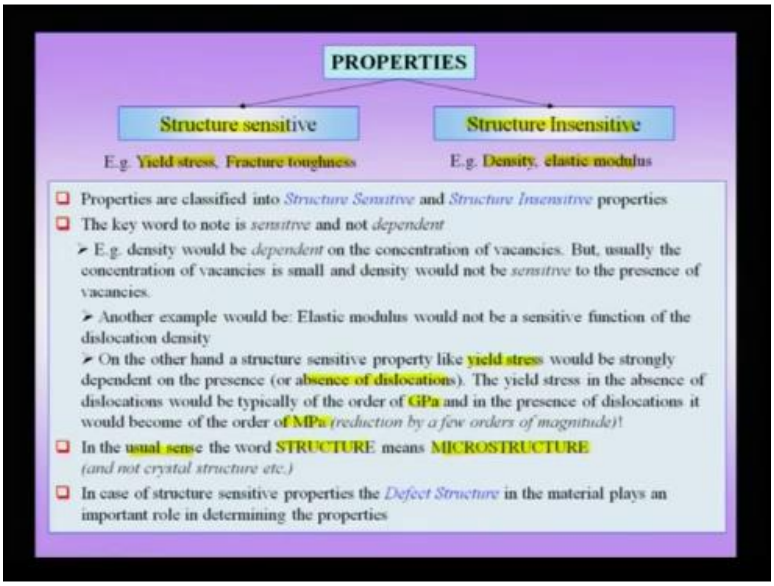

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- ☐ In the usual sense the word STRUCTURE means MICROSTRUCTURE *(and not crystal structure etc.)*
- ☐ In case of structure sensitive properties the *Defect Structure* in the material plays an important role in determining the properties

So, let me summarize this slide with giving this example, suppose am talking about the micro structure sensitive property like yield stress which in the absence of dislocations can take a very high value of the order of Giga Pascal. So, in the presence of dislocation, the crystal is severely weaken and the stress typically turns out of the order of mega Pascal it could be of hundreds of mega Pascals. But, definitely a few orders of magnitude lower that what if the crystal had no dislocations in it, therefore properties have to be understood in the context of structure sensitive and structure insensitive properties.

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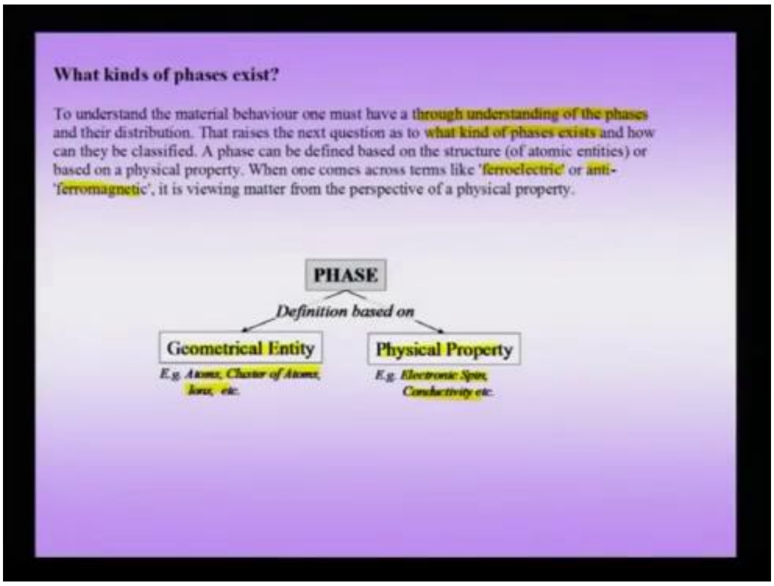

What kinds of phases exist?

To understand the material behaviour one must have a through understanding of the phases and their distribution. That raises the next question as to what kind of phases exists and how can they be classified. A phase can be defined based on the structure (of atomic entities) or based on a physical property. When one comes across terms like 'ferroelectric' or anti-'ferromagnetic', it is viewing matter from the perspective of a physical property.

PHASE

Definition based on

Geometrical Entity

E.g. Atoms, Cluster of Atoms, Ions, etc.

Physical Property

E.g. Electronic Spin, Conductivity etc.

So, in the use when we were trying to understand the properties on of the word we are introduced is the phases we need to understand what is meant by a phase. Further, of course what is meant by, understand by what is meant by the distribution of phases, so to understand the material behavior one must have a thorough understanding of the phases and the distribution? So, we raise the question what kind of phase exists and how they can be classified for an easier understanding of the diverse kinds of phases which present in themselves.

So, a phase can be defined based on a geometrical entity or a physical property and this is a very important classification because when I am talking about crystal made up on atoms or cluster of atoms and ions etcetera. So, I am typically considering the definition of a phase based on a geometrical entity like for instance a copper crystal which is a crystalline phase has copper ions sitting at the lattice point.

Suppose I am talking about the sodium chloride crystal then the sodium and chlorine ions sitting in one of the atom position, the other in a position neighboring to a lattice point. But, we have a definition of a phase which is purely based on a physical property for example we could be talking about the electrons spin or equivalently a magnetization in vector.

So, we could be talking about the conductivity of a material and many other properties which are considerable. Therefore, in this context often we can talk about the material being Ferro electric and anti Ferro magnetic, we can talk about the conducting material and insulating material, an insulating phase as we want to call it. Therefore, this perspective for a Ferro electric material or a anti Ferro material of conducting phase is from point of view of a physical property. So, not from the point of view of a geometrical entity and often we may come across this situation, there when am trying to generate a crystal and as we know a crystal can be defined as…

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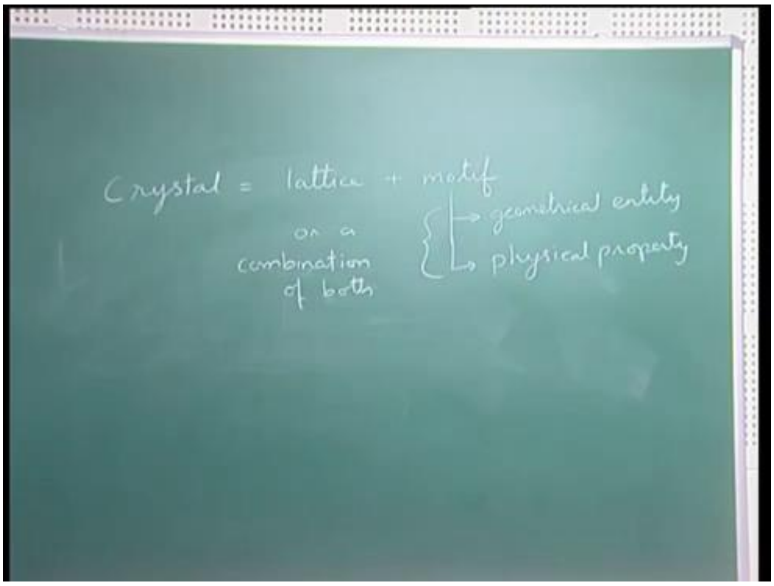

In other words, suppose I am trying to generate a crystalline phase in which I have a lattice and I decorate this lattice with a motive this lattice can be a geometrical entity like we considered as atoms cluster of atoms ions etcetera. Now, it can be a physical property and in the case of a physical property as we saw we could have magnetization vector as a physical property. But, there are cases I need to consider both of them and the combined geometrical entity along with the physical property goes into decorate a lattice point in the formation of a crystal, so let us take an example of this.

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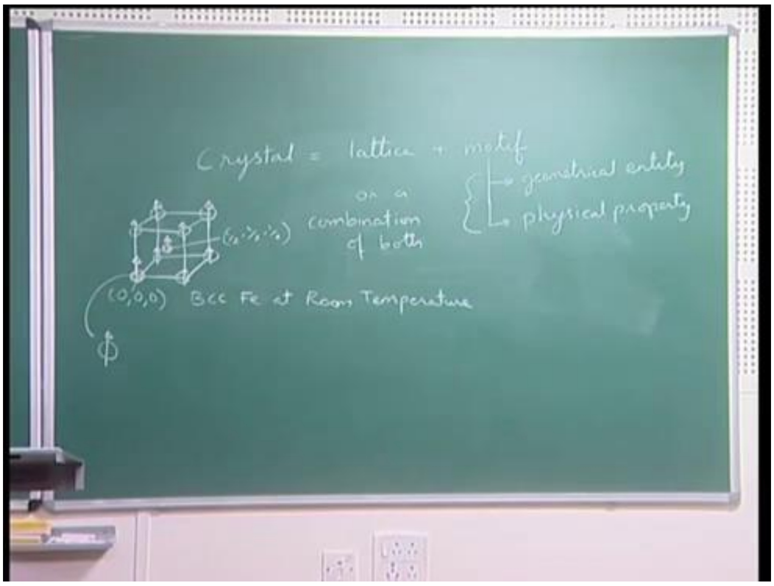

Suppose, I am talking about let me consider BCC ion is the bcc lattice has been decorated with an iron ion and this structure I am considering at room temperature. So, that means that is below mercury temperature and this implies the iron would be Ferro magnetize temperature. Now, that implies that each lattice point not only I have an atom like this, but I can associate with each one of this atoms with a magnetization vector. So, this magnetization what makes iron Ferro magnet that means that I can consider all my atomic lattice point being decorated by an iron ion.

So, which also has in it magnetization are arise from the electros pin and also from the orbital motion of the electron. Though the orbital motion is often quenched, the crystalline form of iron, therefore if I see that I have now described this crystal in terms of the geometrical entity, which happens to be the iron ion. But, also with it, I have to describe in terms of physical property which is known my magnetization vector which is the starting point, wherein we defined a phase based on the geometrical entity or a physical property.

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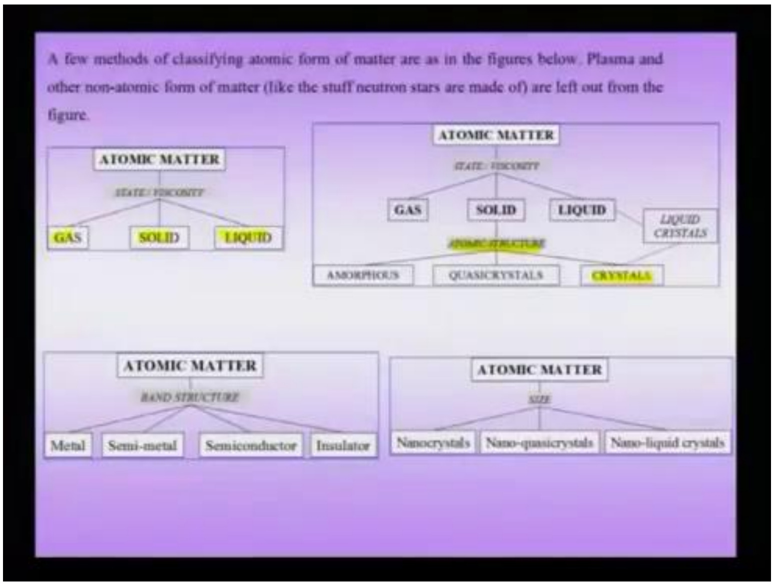

A few methods of classifying atomic form of matter are as in the figures below. Plasma and other non-atomic form of matter (like the stuff neutron stars are made of) are left out from the figure.

So, few of those methods of classifying phases is shown in the slide which is being presented to you. So, the important thing we note here is of course we are considering the atomic form of mater in all this classification matter can exists in non atomic form like plasmas and other free fundamental particles. But, we are ignoring those kind of states of matter, therefore we are simplifying the understanding here to atomic form of matter. Now, from school days we know that atomic form of mater based on state or viscosity can be classified into the gasual state the solid state and the liquid state.

So, we from our knowledge of phase temperature pressure temperature diagram, we know that there are coexistences lines. Now, coexistence points where a gasoline solid could co exist where as solid and liquid could co exist, but all these three states of maters could also co exists at certain triple points. But, this is simple an well understood concept that we can have based on state of viscosity three forms of matter which is gas solid and liquid.

But, more interesting way of looking at these forms of mater is from an atomic structure perspective which is shown in the diagram in the right hand side. So, that is we can have classification of atomic form of mater based on the atomic structure means where are these atoms position in the material.

Now, as I pointed out when I am talking about the atomic structure I could also include in this picture the structure based on the other physical properties like I could overlay.

But, as I told you like magnetization associated with this atoms on top of this picture, so to let us start with consider the atomic structure of the mater. So, most common atomic form of mater which we usually consider which we have defined in the previous slide is the crystalline form of matter crystal.

So, a crystal as we have seen so on in a coming slide is defined based on two important certain that it is order and it is periodic it is order not only positional. But, it is orientational order whenever we have considering various orientation and it is periodic in the case we construct here clearly see the magnetization vectors are ordered orientation.

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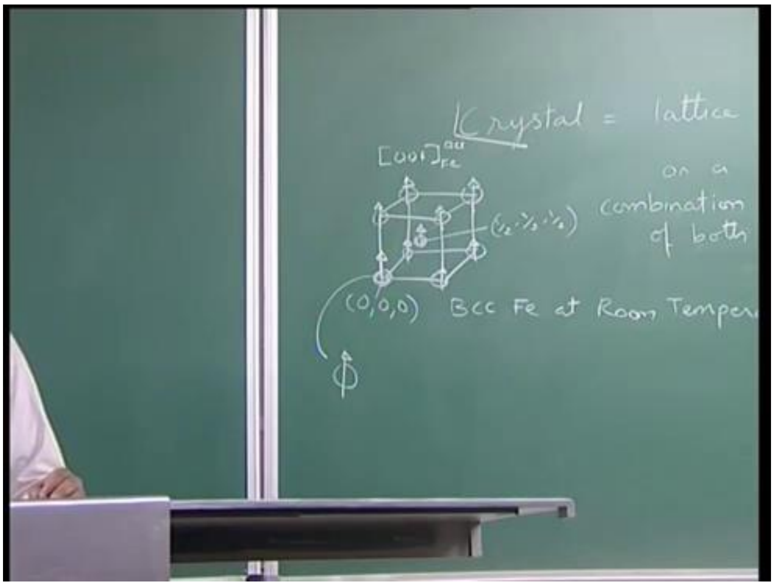

So, that means they are all pointing in this direction in this case we can think of it as b 0 0 1 directional in BCC, therefore the order we are talking about here the orientational and positional. So, the crystal being considered as in the stricter scene orientational order and positional order often real crystals as we shall see lot of criteria which are imposed on ideal mathematical crystals are relaxed. Therefore, we may have crystals of various degrees of relaxed definition, which we shall consider.

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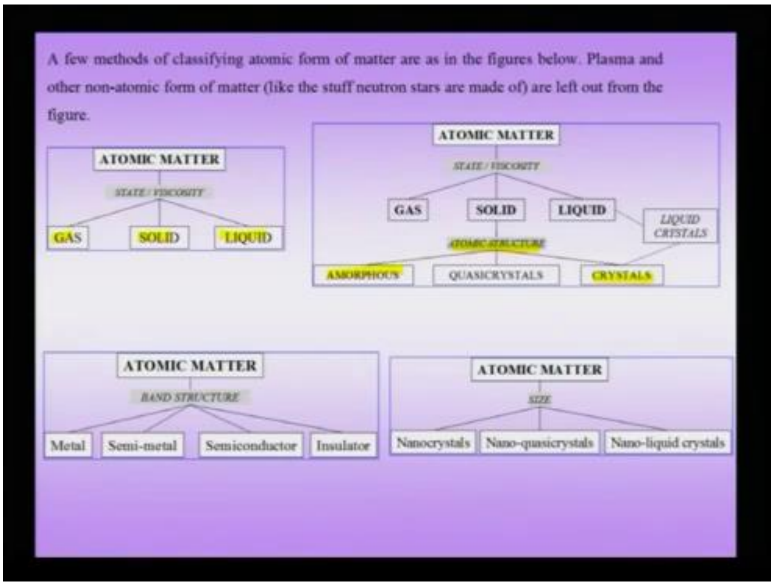

A few methods of classifying atomic form of matter are as in the figures below. Plasma and other non-atomic form of matter (like the stuff neutron stars are made of) are left out from the figure.

So, there are other forms of matter in the other extreme to crystals what are called amorphous or glassy materials or glasses in which case there neither there is positional order nor there is orientational order. Therefore, it can be thought of as material at best having short range order, but definitely not long range order of course when I am define. So, when I am defining a crystal if based on a combination of both geometric entity and a physical property, it so might happen one of the two is ordered and the other is disordered for instance, suppose if I take the same ion about the curing temperature.

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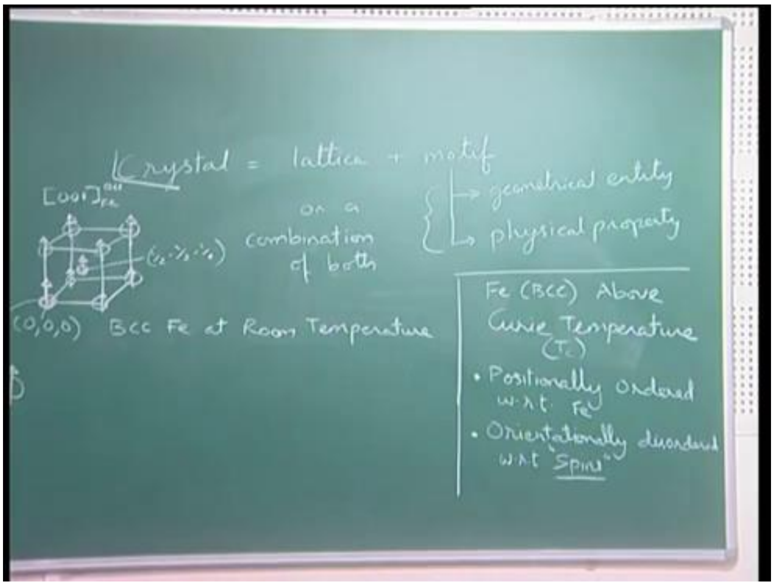

So, suppose am talking about the ion crystal above the curing temperature in spite of the atoms is vibrating above the lateral position we considered them to be positional ordered. But, you can clearly see that the magnetization directions which were all alone the same direction have been lost and crystal will go from a Ferro magnetic state to a para magnetic state. Now, in which case we will find that with respect to the physical property now it has become disordered, therefore when I am defining a crystal, I have to define either based it on the physical property or the geometrical entity or both.

So, when I am talking about the disordering or the amorphousness it can come from either the physical property or the geometrical entity. Therefore, we have a material, which is completely crystalline like in the case of BCC ion above the mercury temperature with respect to the atomic position.

But, it is definitely disordered with respect to the physical property and especially in this spin orientation further to this important matter like crystalline amorphous materials. So, there is a third class of materials though not that well studied or that well applied in terms of engineering applications they are the quasi crystals.

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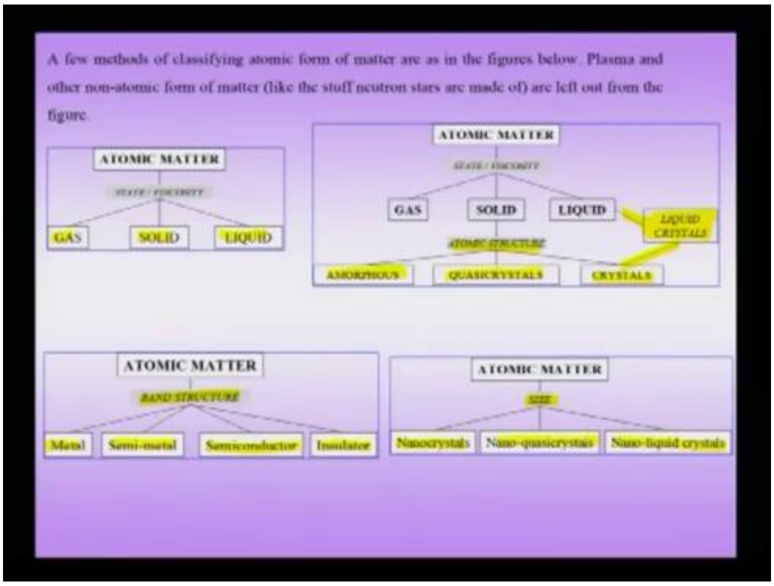

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They are in the international tables of crystallography classified under higher dimensional crystals, in other words sometimes they are considered as part of crystal themselves. But, here we have given them separate positions because they represent definitely a third state of matter and in some sense I have to understand the picture of its structure. So, as consisting of crystalline cosaic crystalline amorphous phases added to that there are other classifications of important class of materials which are between liquids and crystals which we have shown here which is liquid crystalline materials.

So, as all of you know that many other displays and calculator etcetera are made from liquid crystals, they are the LCD displays or what you call. So, as you can see later on during the course any one of these entities we are talking about the crystallites or the amorphous regions in matrix etcetera could turn nano crystalline.

So, that means that I need to know my basics regarding these atomic orderings of mater and then I go to the next level which is my understanding some of these lenses scales could become nano. So, another way of classifying atomic form of mater is using the band structure based on the band structure a material can be a metal it can be an insulator or it can exists in one of the intermediate states like what is known as semi metals or a semi conductor.

Now, when we talking about the band structure it should be clear, now way of classification should not clash with any other way of classification of mater for instance a material could be amorphous and still could be metallic. So, in other words we call it as metallic glasses, now they have produced materials which are bulk metallic glasses. In other words, which have a large cross section of area or large volume of materials which is fully amorphous, but it is metallic a material could be an insulator. But, also could be amorphous for example we know our silicate glass it is typically a very good insulator, but it is amorphous.

So, on the other hand a material could be a crystal and could be a metal for example copper is crystalline and as we will see that it is actually not single crystalline. So, typically a copper conductor wire consists of many crystals in many orientations which we call a poly crystalline material and, therefore copper wire is poly crystalline. But, it is metallic we can also consider many ceramics like silicon nitrite etcetera which are also poly crystalline, but not good conductors therefore one way of class. So, classification should not clash with another way of classification like for instance mercury is liquid at room temperature.

But, mercury is a metal, that means is a good conductor of electricity, and essentially what we are taking about there from the band structure perspective I am classifying mercury to a metal. But, from a liquid from the flow property viscosity property, I classify it to be a liquid, therefore when I am making a classification, we should be clear that what is the basis of the classification. So, we should be able assign materials into each one of these boxes based on the classification, we are considering good examples of semiconductor is silicon germanium.

So, solid solutions of silicon and germanium etcetera semi metals are those in which there is a band gap, but the band gap is across the case space. But, in other words if you are considering the integration of cross case space then you do not have a band gap, but these is a band gap. Suppose you are considering a k value, another way classification of mater which is very important from this course perspective is what is called classification based on size. So, each one of these entities we have talked about actually end up in the nano size, for example we will consider these lectures as you can see is a revision and sought of consideration of the basics.

Now, once again and some of these things would define would have been defined in previous fundamental lectures before for you. Therefore, based on size we have nano crystals we have nano liquid crystals if you want we can have nano quasi crystals we can even have regions which are amorphous. But, have a very small special extern which we can cal call for instance an amorphous if you like we could have for instance an insulting matrix in which we could embed a metallic particle.

In other words, here based on size itself it is all nano additionally it is also nano in perspective of being a metal which is conducting or band structure there are regions which are regions that are nano. Therefore, I can take each one of these entities in the diagram and make it nano, for instance I can have a nano droplet which is residing on a substrate in a gaseous environment and, so let me draw a schematic of that.

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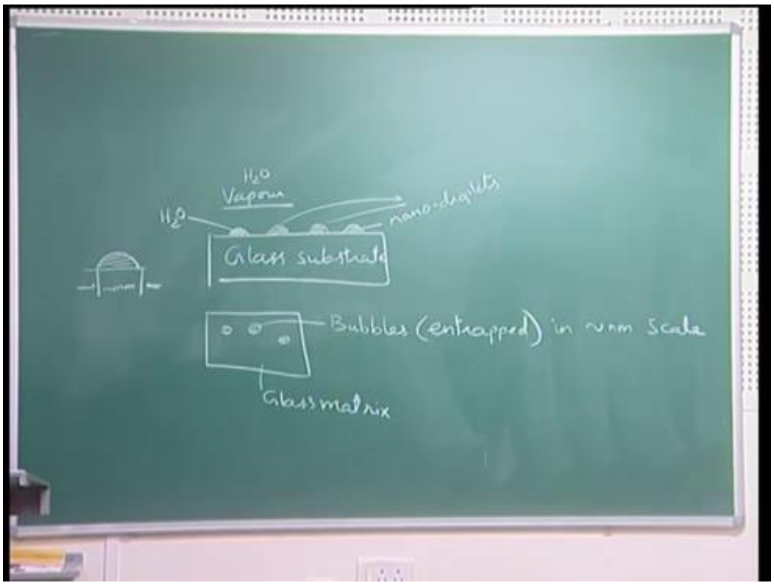

So, here I have considered a glass substrate on which nano droplets water condensed from the vapor phase and assuming that there is equilibrium existing. Then I can visualize that there is water here and water as droplets and size of the droplet size is that is nano in this and I am saying it nano. So, typically using it in more general sense of definition, which means that the size is of the order nano meter, therefore I can think of these droplets.

So, if I take an individual droplet think of this dimension to be in the nano meter regime may be a few 10s of nano meters of a few 100s of nano meter. Therefore, I can take each one of these entities in the picture and can visualize it that they are in the nano scale I have, I can invert this problem. So, I can a glass substrate in which there are vapor space in nano scale I can put small bubbles of water vapor. So, I am visualizing here certain gas bubble or vapor bubbles which are entrapped in a glass matrix which are the nano scale, therefore let me summarize this slide for you.

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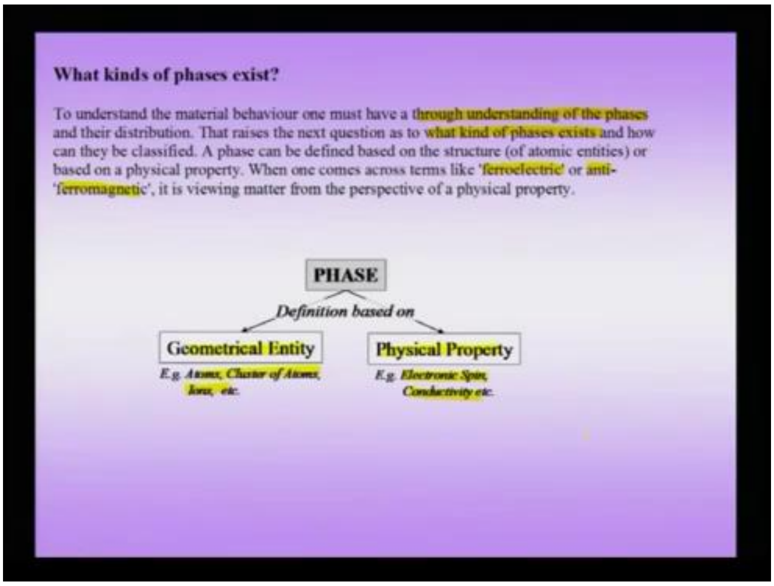

What kinds of phases exist?

To understand the material behaviour one must have a through understanding of the phases and their distribution. That raises the next question as to what kind of phases exists and how can they be classified. A phase can be defined based on the structure (of atomic entities) or based on a physical property. When one comes across terms like 'ferroelectric' or anti-'ferromagnetic', it is viewing matter from the perspective of a physical property.

PHASE

Definition based on

Geometrical Entity

E.g. Atoms, Cluster of Atoms, Ions, etc.

Physical Property

E.g. Electronic Spin, Conductivity etc.

So, in the previous slide we saw that phase here we are restricting to those phases ourselves which is made up of atomic specious and when I mean atomic specious I am taking about atoms, ions and molecules, cluster of atom etcetera. So, these atomic specious can form, based I can define a space based on geometrical entity or a physical entity.

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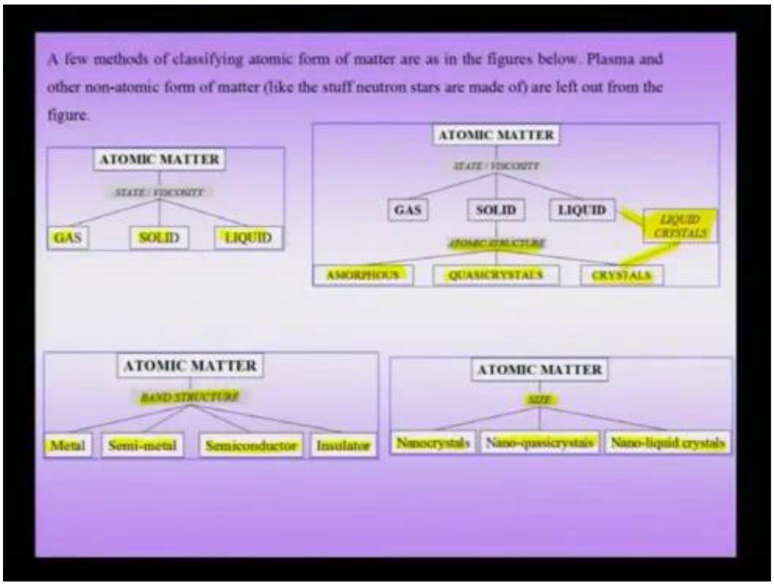

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ATOMIC MATTER
STATE / VISCOSITY
GAS | SOLID | LIQUID

ATOMIC MATTER
STATE / VISCOSITY
GAS | SOLID | LIQUID
LIQUID CRYSTALS
ATOMIC STRUCTURE
AMORPHOUS | QUASICRYSTALS | CRYSTALS

ATOMIC MATTER
BAND STRUCTURE
Metal | Semi-metal | Semiconductor | Insulator

ATOMIC MATTER
SIZE
Nanocrystals | Nano-quasicrystals | Nano-liquid crystals

Now, atomic mater can be classified in various ways and all these classifications are important especially when we are talking about. Finally addressing the questions of import questions like what is nano in a nanostructure of what is nano in a nano material or what is so important about nano. So, based on state or viscosity we have the gas solid liquid picture based on atomic structure we can have amorphous crystalline or quasi crystalline states of mater.

So, there intermediate state between the important stages like crystalline in the liquid state which we can thought of as liquid crystalline state. We also seen based on the band structure we can have metals semi metals semi conductors and insulators. So, as we know that in case of metals the valence band overlaps with the conduction band that means, that means that infinite amount of energy which is supplied can small amount of energy being supplied.

So, it can actually take or promote an electrons to a high energy level and because there is no band gap in the case of insulator. Now, there is a band gap between the conduction bands and usually the value of this band gap is very small, then you call it a semi conductor in a semi conductor. So, even room temperatures have found that many electrons have been promoted from the valance band to the conduction band.

Therefore, a semi conductor room temperature would show some conductivity the importance difference between these semiconductor and metal be the metal conductivity degrades the temperature. While a semi conductor conductivity increases with temperature bases on size which is pertinent to this course we can think of some of the, we can think we are speaking in terms of some figures above. So, we can have nano crystals, nano quasi crystals, nano liquid crystals and as we have seen here we can have nano vapor phases etcetera, very good question, mister Anil Kumar has a very important question.

So, when you are talking about nano is it purely a lens scale problem, is it issue related to properties as we shall see soon very specifically address this very question using with a lot of slides. So, that it is both often in loosest sense we would define something to be nano structure or nano material. So, based on some lens scale in the problem as we have seen often in the problem everything, which is the material is nano. It is particularly well defined part of the system which is in the nano scale we call it nano meter, typically you call it as tens or best 100 of nano meters.

But, that does not make it interesting for us to study this materials it is not going to give me benefit if going to this scale of say 100 of nano meters. So, it would give me some special properties, therefore we will see that unless there is some benefit of properties it is not worth taking trouble to go down to the nano dimensions. But, because we shall see towards the end of the introductory chapter, there are lot of disadvantages nano materials also there are lot of challenges which are open to us. Therefore, we need to address the efforts towards the benefit issue before we go to nano scale, therefore in the truer sense as you I think you have implicitly pointed out.

So, it is the properties which is going to tell you it is nano or not and we will also see cases examples, wherein there is nothing in the material in nano scale. But, materials property behaves in the nano way and we will take up those examples also, wherein this specific question which you have asked here could be clearly exemplifies. So, that would be very important for us because when there is a benefit in properties and as we shall see very soon that not only there are often benefits in properties. But, there are absolutely new properties are arising when you go to the nano scale which has no counter parts the bulk.

So, I can mention some names for you, since we have the phenomena of super para magnetism or we have the phenomena of giant magneto resistance system. So, these have no bulk analogs that mean I cannot typically realize super para magnetism in an iron particle which will be in the order of millimeter size. So, in need to get down to the nano dimension before I even see this phenomena known as super para magnetism or if I am talking about giant magneto resistance.

Then the scale problem has to be reduced before it becomes viable for me or it becomes the phenomena of super para magnetism. Therefore, when I am talking about nano materials or nano science even though I am talking in the size what we call usual usage sense, I am always keeping properties at the heart of it. Typically, I would keep one property in focus, but some time you have synergetic multiple properties improving when you go down to the nano scale.

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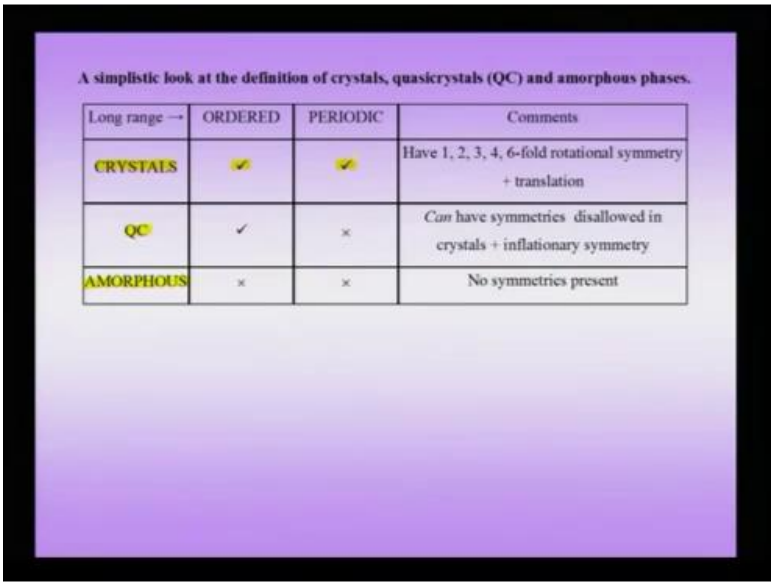

A simplistic look at the definition of crystals, quasicrystals (QC) and amorphous phases.

Long range →	ORDERED	PERIODIC	Comments
CRYSTALS	✓	✓	Have 1, 2, 3, 4, 6-fold rotational symmetry + translation
QC	✓	×	*Can* have symmetries disallowed in crystals + inflationary symmetry
AMORPHOUS	×	×	No symmetries present

We have talked about three terms in the previous slide, it is worthwhile to mention that what is the basis for definition of these three terms and we should not confuse a one term with the other three terms. So, we had considered based on the atomic order crystalline quasi crystalline and amorphous and in this context, we have clearly said when we, when we defining these terms we would worry about atomic entities.

So, what we call it geometrical entities and also the physical properties or could even talking about both of them put together and crystals are based on lattice. So, of course more formal and rigorous definition of a crystal this is an asymmetric unit plus a space group. So, in conjunction with what is known as why Q C of positions which is assigned in these atomic entities on to the space group positions, but we will use a simpler understanding. Here, in this course, simplified definition where in we are talking about a crystal to be a lattice plus to a motive because it is more accessible to a general student a crystal is ordered and periodic.

So, we are already mentioned the order we are talking about orientation and positional and, but the heart of the definition of a crystal lies in a symmetry. So, as I pointed out can be captured terms which is known as the space group, but for now, since we are sticking on the lattice and motive definition we have to note that a crystal is typically has rotational symmetry or inverse of symmetry. Now, mirror symmetry addition to translation if a crystal has only translational symmetry, it has no other symmetry like no rotational symmetry.

So, no inversion symmetry of mirror symmetry then you can think of higher order like schools symmetry or glide reflection symmetry. Then such a crystal having only translation symmetry is called try clinical crystal, but typically symmetry has higher symmetry, then water try clinical symmetry would have like for instance a cubic crystal can be given symmetry.

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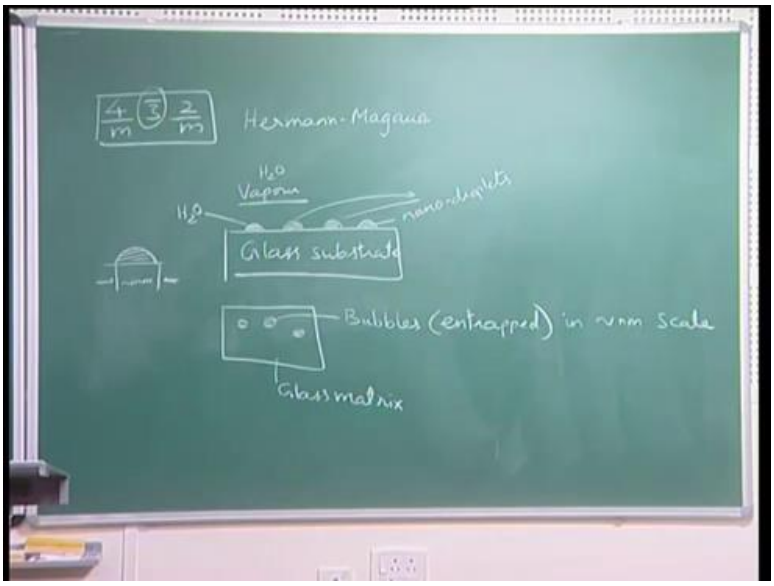

So, of course this is not only the symmetry, cubic crystal can have in other words what we call as the hollow hydal class of cubic and cubic lattice would have this kind of symmetry. So, whenever you see a three in the second place and this is what I m writing as the Hermann Magana symbol, Hermann Magana symbol is a representation of point groups. Then I clearly see that they are higher symmetry that they have of translation and whenever this happens to a crystal the kind of rotational symmetry that allowed in a crystal are one obviously 2, 3 and 6.

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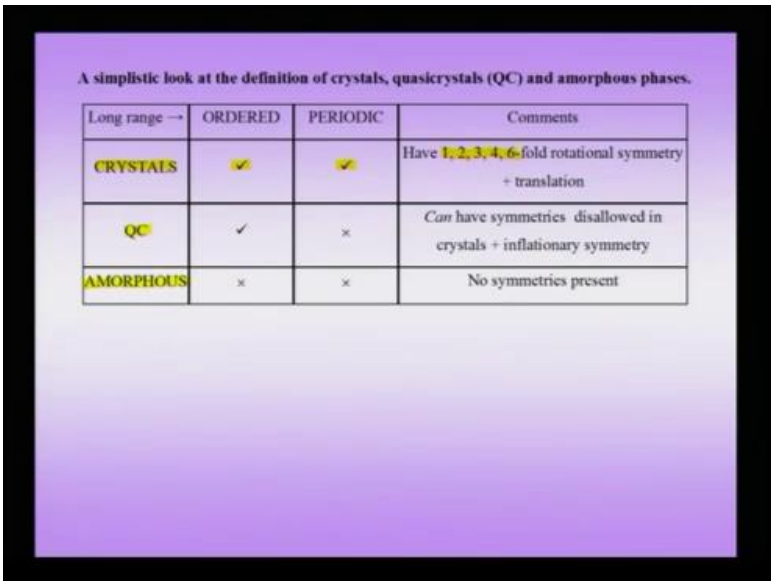

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Now, the symmetry rotational symmetry is allowed in a crystal, of course these symmetries can be normal rotational symmetries or that what we call root of inversion symmetry which are given a bar symbol having 1, 2, 3, 4, and 6.

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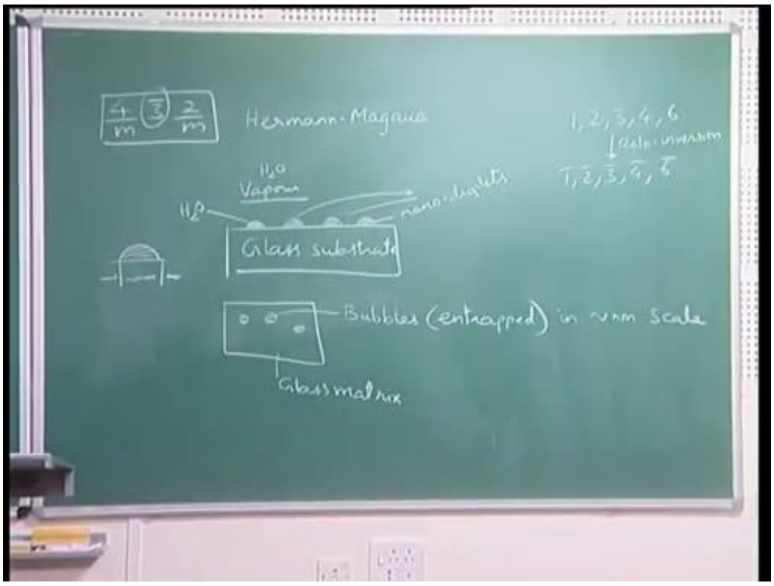

So, I could also have 1 bar, 2 bar, 3 bar, 4 bar and 6 bar symmetry, nevertheless the presence or absences of these symmetries is not going to destroy a crystal, but the absence of translation symmetry is definitely going to destroy crystal.

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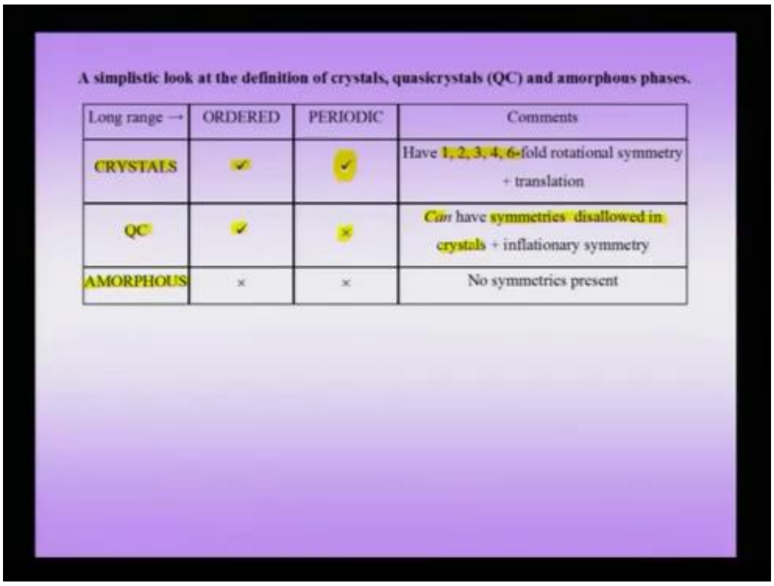

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This translation symmetry otherwise been called periodicity for crystal and typically crystals are periodical in all the 3 dimensions. But, we can also think of crystals which are crystals in lower dimensions like a graphing line sheet, we can think of a crystal in 2 dimensions. Therefore, crystals are those, which at least have translational symmetry, but typically have higher symmetry which includes rotational symmetry like 2 fold, 3 fold, 4 fold and the 6 fold.

So, on the other hand, there are other states of matter like quasi crystalline state which are not periodic, but which are ordered the kind of order for quasi crystal displays would require little more thought, little more description. Now, for that kind of an order, but this kind of an order we are talking about typically the kind of order we would see in a pentro styling.

Now, we may call it as a structural log of a Fibonacci sequence, but important point regarding quasi crystal is that quasi crystal can have that symmetry which are allowed in crystals of course. So, they may have allowed crystallographic like the 4 fold or the 6 fold, but in addition to these symmetry they may have symmetries which are disallowed in the crystallographic world.

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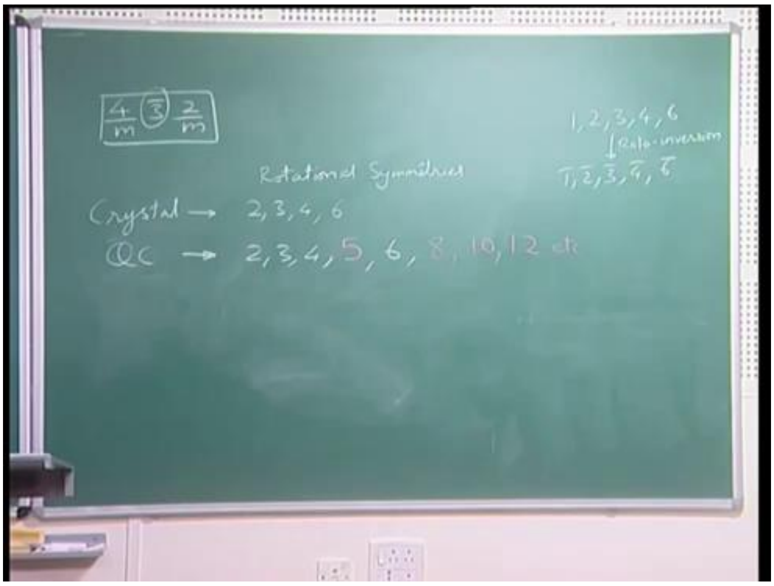

So, for instance, for quasi crystals, quasi crystals which are not allowed in the crystallographic world like 5 fold, 8 fold and 10 fold or 12 fold. But, more importantly a crystal has translational symmetry while a quasi crystal has something known as an inflationary symmetry.

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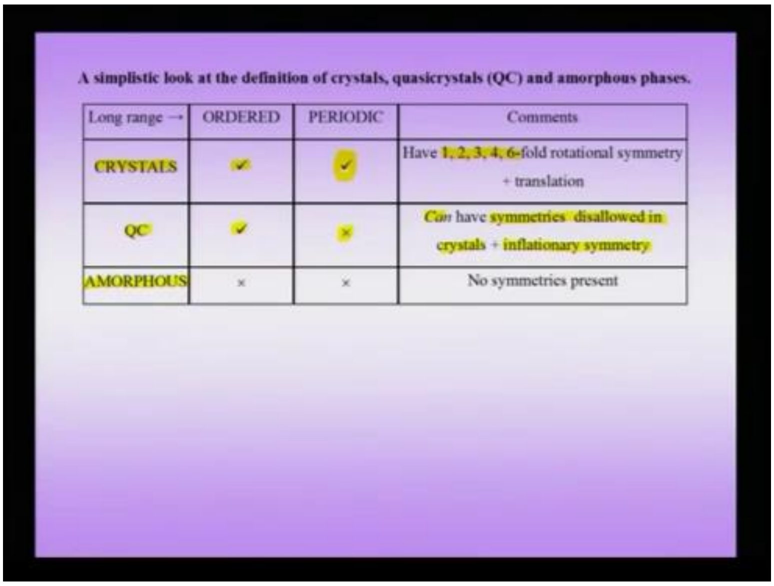

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Though we are not considering in that symmetry in details, but it is an important point to note readers have to look up some of the literature. So, in the area of quasi crystals to understand how a quasi crystal is different from a crystal, but from the perspective on nano world we need to know that we could have a material. So, for instance polymer matrix in which I could disperse nano quasi crystals and this could give me certain important benefits in terms of the properties.

For example, this very experiment I am talking about dispersing quasi crystals and polymers not necessarily of always nano sized. But, if you do this then such a material would have polymer would have aberration to resistance and added to that, instead that you put a hard material like silicon carbide crystal into a polymer matrix, it will also have high resistance.

But, the counter face will be very high, but suppose I put quasi crystals were as the counter face would be small, therefore there are areas in which quasi crystal can be applied interestingly. So, the other interesting spectrum we saw was amorphous phases, wherein there is no symmetry is present. So, that means it is neither periodic nor is it ordered that implies that one end of the spectrum I have crystals which are ordered and periodic.

Now, the other end of the spectrum I have amorphous phases and often this amorphous structures are called glasses though there are subtle pint. But, which are technically called or used to differentiate the amorphous structure from a glassy structure for now we will not consider it from an atomic structure perspective we will treat them equivalently. Therefore, an amorphous structure or a glassy structure is neither ordered nor periodic, this atomic order automatically would translate into the kind of properties of each one of these phases would show off.

So, for instance we know that a crystal can have defects like dislocations and, therefore they are plastically deformable. You can easily form them at room temperature, at various shapes and an amorphous phase, on the other hand it cannot be plastically deformed, would typically fracture. Now, you know the glass silicon glass at room temperature is very brittle if you heat it up to high temperature it can flow like a fluid, it will have a low viscosity.

Then it can be blown and it can be made various shapes like including glass bottle, therefore this atomic structure automatically translates into the properties. So, whenever I am using any of these crystalline or quasi crystalline or amorphous phases, I would worry about their atomic structure.

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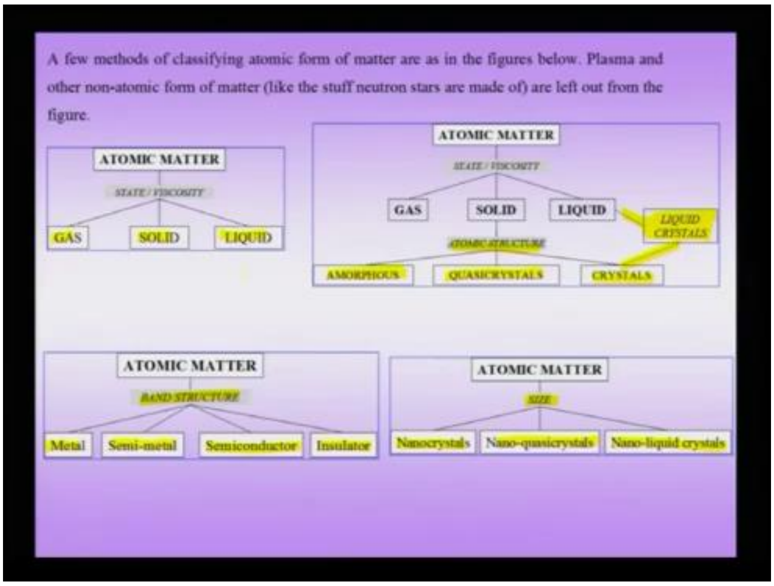

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AMORPHOUS
QUASICRYSTALS
CRYSTALS

ATOMIC MATTER
BAND STRUCTURE
Metal
Semi-metal
Semiconductor
Insulator

ATOMIC MATTER
SIZE
Nanocrystals
Nano-quasicrystals
Nano-liquid crystals

So, I would worry about their band structure, and I would also worry about the size before I engineer a material which then we could use in an engineering application.