Advanced Materials and Processes

Prof. B. S. Murty
Department of Metallurgical Engineering
Indian Institute of Technology, Kharagpur

Lecture - 12
Quasicrystals Part – I

A new class of solids called quasicrystals. So, before we go into how these quasicrystals have come up. And to understand, what these quasicrystals are. Let us have a look at, how the whole field has evolved. If you look at physical metallurgy and look at a few milestones in physical metallurgy, particularly looking at the microscopy of it and the crystal structure, and the micro structure of various materials.

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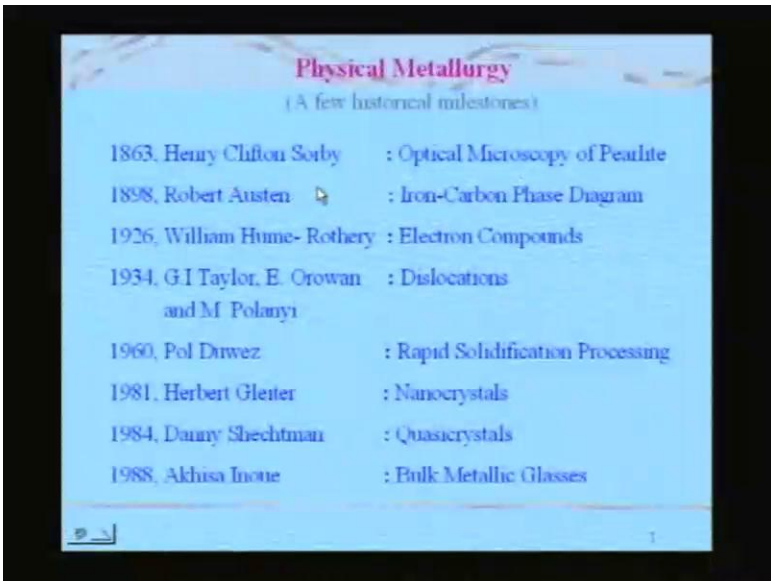

Physical Metallurgy
(A few historical milestones)

1863, Henry Clifton Sorby : Optical Microscopy of Pearlite
1898, Robert Austen : Iron-Carbon Phase Diagram
1926, William Hume- Rothery : Electron Compounds
1934, G.I Taylor, E. Orowan and M. Polanyi : Dislocations
1960, Pol Duwez : Rapid Solidification Processing
1981, Herbert Gleiter : Nanocrystals
1984, Danny Shechtman : Quasicrystals
1988, Akhisa Inoue : Bulk Metallic Glasses

It all started with, I would say around 1863, when Sorby has talked about the paralite. You all know that for a metallurgy is the most important thing is a steel. And the strength in the steel basically comes from the paralite. So, the understanding of the micro structure of paralite was very crucial those days, to understand the mechanical properties of steels. So, this was the starting point of physical metallurgy one can say.

Then, 1998 people talked about the iron carbon diagram. That was the first time, when iron carbon Austen, with his name we now called the phase Austenite. So, this is the person Robert Austen. And then we had the Hume Rothery rules, which came in 1926.

And the new type of electron compounds, which are called Hume Rothery compounds, have been discovered those days.

And then till 1954 people did not really see, dislocation though people talked about the presence of some defects, which are probably giving you the slip, but the first discovery of this dislocations or observation of this locations. In a transmission microscope, came from Taylor and Orowan. And this Orowan is a person, which whom you might have heard about the Orowan bowing, you say around a particles. When a dislocations are pushed, they bend around a particle, which is called Orowan bowing. And then one have to wait till 1960, for a metastable phases to come into picture, though we know about a few metastable phases, such as the cementite. But, processing of materials under highly non equilibrium conditions, was not known till 1960. When Pol Duwez has at Caltech developed a new technique called rapid solidification processing.

And you all know about rapid solidification processing, by now. And then it was in 81, the nano crystals have come into picture. And the Gleiter in Germany, we talked about it before. And it is at 84, Shechtman has seen a new type of a diffraction pattern. We will talk about it, a little later in greater detail. And that is what is the birth of a new class of solids called quasicrystals? So, that is 1984, Dan Shechtman will say.

And then last few classes, we have been talking about the bulk metallic glasses. That was 1988, Inoue, professor Inoue at Japan the institute of materials research, Tohoku university. He was the key person. And another gentleman in US, Bill Johnson, people call him Bill Johnson. And he is another man who has been working a lot on this.

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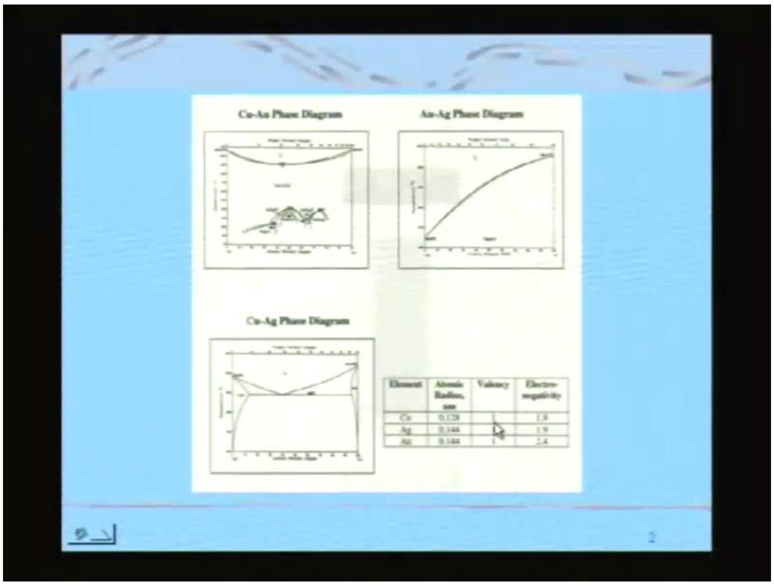

Cu-Au Phase Diagram

Au-Ag Phase Diagram

Cu-Ag Phase Diagram

Element	Atomic Radius, nm	Valency	Electro-negativity
Cu	0.128	1	1.9
Ag	0.144	1	1.9
Au	0.144	1	2.4

So, these are a kind of milestones, in this field of, I would say non equilibrium processes, and the field of a metastable materials. And if you look at how this whole thing evolved, everything started with these three very crucial phase diagrams, the copper gold, gold silver and the copper silver. I told you before that, Pol Duwez started this field with this particular three phase diagrams in mind.

He thought the copper silver gold, if you look at the atomic radii, copper is about 0.128 nano meters. Silver and gold more or less the same 0.144, that means about 1.44 Einstein's. And valiancy all of them have the same, electron negativity 1.9 for both copper and silver, whereas the gold it is about 2.4. So, if you carefully look at these three. They are all very close to each other with a small changes definitely, but when you look at the phase diagram.

The copper gold is a isomorphous phase diagram, the gold silver is again another isomorphous phase diagram, whereas the copper silver is a eutectic. The one possibility, that one can attribute this to atomic size difference. But, this atomic size difference is not too large, if you one looks at the differences, in terms percentage. Percentage is not too large. So, many people did and if you look at electron negativity, they are the same.

So, there was for quite some time, people did not understand this very well. Even now the theory of why copper silver has to give eutectic is not really clear. But, one knows, that if he can take the liquid and cool it rapidly now. One can suppress that eutectic formation and can give get the isomorphous solid solution. From one end of the copper to the other end, which is the silver. So, through out single phase field can be achieved in a copper silver.

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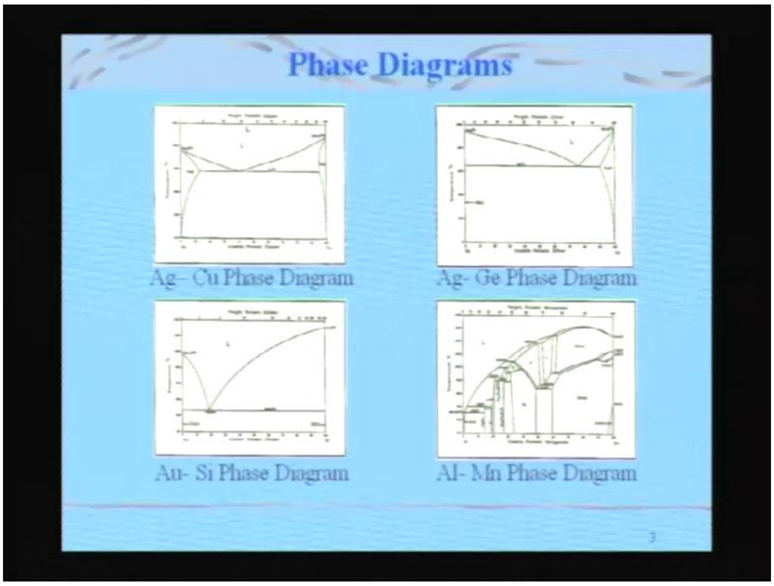

Phase Diagrams

Ag– Cu Phase Diagram

Ag- Ge Phase Diagram

Au- Si Phase Diagram

Al- Mn Phase Diagram

And the other diagrams, which Pol Duwez looked at those days, are all the eutectic phase diagrams. So, he took silver copper, this was a starting point. And then he went into silver germanium, and took again the eutectic composition. And tried to cool them rapidly, he did not get a solid solution here. But, he got a metastable crystal structure. A crystal structure, which did not exist in the phase diagram, a phase which is called gamma phase, which did not exist. And when they tried to index that, it is not this terminal solid solution. Either it is not a silver terminal solid solution, it is not a germanium terminal solid solution. So, it is a phase, which does not exist into there. So, this is what are called metastable phases, which sometimes form under fast cooling conditions, which do not exist in the phase diagrams.

So, it is possible that, they exist as clusters in the liquid, and when the liquid is cooled rapidly instead of the equilibrium phase coming out of the liquid. So, the non equilibrium phase, which can come out, because the activation barrier for that non equilibrium phase may be very small. For example, as we see in case of age hardening. We know that A l to C u does not come out. But, the G P Jones, theta double prime theta prime all these phases come out.

Similarly, you also might know that when I take a steel, quench it from high temperature from the austenite, what do I get? Martensite, when we start heating this martensite. For what is called tempering, you do not get the cementite directly. You go through another stage called epsilon carbide, which people call it F e 2.2 c. Whose crystal structure is hexagonal, which is close to that of the either the FCC structure, which is the original structure from, which the martensite is obtained.

So, as a result one can easily say that the formation of HCP, will have a lower activation barrier, than the formation of the orthorhombic the F e 3 c, which is the cementite. So, like that we know in a number of solid state, reactions such second phases, which do not exist in the phase diagram can form. And similarly, even somebody cools from the liquid to solid also, it is possible.

That some metastable phases can form. And then he took this gold silicon, this is again a eutectic. And if you compare the gold silver copper with gold silicon, you can clearly see that this is a deeper eutectic than this. Just by looking at it one can know, you look at the two pure metal melting points. And look at the eutectic temperature, compare with the two pure metal melting points in gold silicon and the eutectic.

And you can see from here, that the eutectic is much deeper than this. And when he took that particular composition which is about 20 percent silicon. And what he got was a glass. So, this was the kind of various metastable phases, that Pol Duwez has obtained in just 1 year starting from. So, extension of solid solubility, then the metastable crystal structures. And the metallic glasses.

The only thing that had to wait for a long time is, what is called the quasicrystal, which one had to wait till 1984. And unfortunately Pol Duwez did not look at it, because this is nothing but a paratactic kind of phase diagram. So, he was always looking at eutectics. And trying to look at eutectics and see, if in any eutectic can he extend a solid solubility. Because, rapid solidification one of the most important thing is extension of solid solubility.

When we talk in detail about RSP, we will discuss this. And what you can see is that, whereas in this particular case which is a basically a paratactic diagram. What we usually call it as cascade of paratactic. A number of paratactics, the classical example of such a cascade of paratactic is what system, a very common system which copper zinc. Yes, copper zinc is a cascade of paratactic you say. So, it has a number of paratactics, aluminum titanium is another. So, there are so many paratactics here.

And one basic difference between a metallic glass forming systems, and quasicrystal forming systems. Is that, you rarely get a metallic glass, in a system which shows paratactics. You need eutectics, particularly deep eutectics for a liquid to be stabilized for the glass to form. Whereas, systems with paratactics, unless you go to really very high cooling rates, you will not be able to get the glass.

So, whereas the quasicrystals are obtained in those system, where you have a number of inter metallic compounds. Mostly quasicrystals are nothing but inter metallic compounds having certain statiometrics. And that is why people call them as Hume Rothery phases. Or what are called electron compounds. Many quasicrystals stick to some e by a ratio. There are a number of quasicrystals, which have a fixed e by a ratios. We will talk about it a little later again in detail.

So, you can see that aluminum manganese, was the first system. And this was obtained at about 14 percent manganese, we will talk about it later also in detail. And so this was the aluminum manganese phase diagram, where at 14 percent manganese you have a phase called A l 6 M n. That is the phase which is called rational approximant, for quasicrystal. What is the meaning of rational approximant, that means it is crystal structure is very close to that of a quasicrystalline arrangement of atoms.

So, there are certain crystal structures, which are available in various phase diagrams. Whose structure is to some extent correlated to the quasicrystalline structure; and in all those systems, it is very easy to get quasicrystals. One such example is A l 6 M n. Another such example is in aluminum iron A l 3 f e is another phase, which is very close to that of quasicrystalline composition. So, if you take that composition, which is something like 25 percent iron and 75 percent aluminum. Such a composition can easily give a quasicrystal. There are a number of such systems, were people have obtained quasicrystals now.

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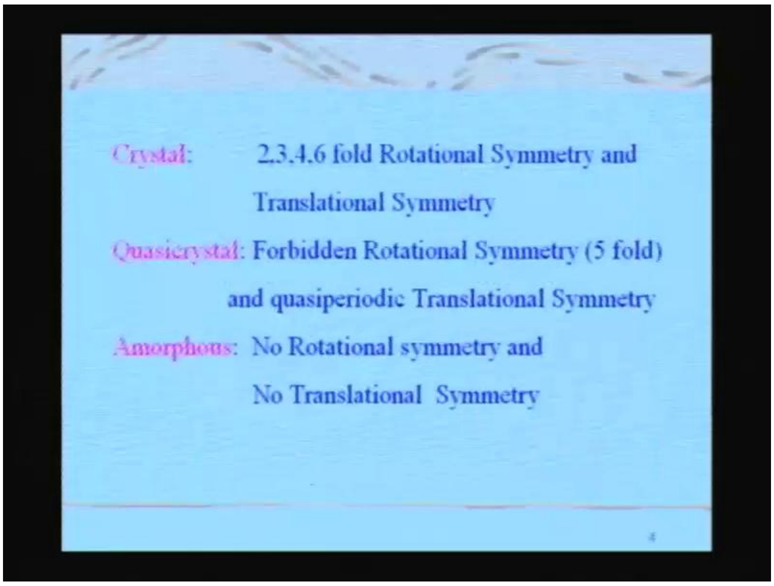

Crystal: 2,3,4,6 fold Rotational Symmetry and Translational Symmetry

Quasicrystal: Forbidden Rotational Symmetry (5 fold) and quasiperiodic Translational Symmetry

Amorphous: No Rotational symmetry and No Translational Symmetry

And how do we basically define this, where do you put this quasicrystal between the crystal and amorphous. As you can see from here, the crystal is one, which has both rotational and translational symmetry. We talked about, when we are talking about structure of materials. And what are the types of rotational symmetries, that are possible. These are what are called the crystallographically allowed symmetries. That 2, 3, 4 and 6, I will not talk about 1-fold symmetry, because 1-fold symmetry is what is called a trivial symmetry. Every structure should have a 1-fold symmetry. So, we will not talk about 1-fold symmetry. But, the 2-fold, 3-fold, 4-fold and 6-fold symmetries are called the crystallographic symmetries. And if you go to amorphous, it does not have both rotational and translational symmetry.

And when you look at quasicrystal, quasicrystal is that which has forbidden rotational symmetry, which is an example is 5-fold. It can have a 8-fold symmetry, it can have a tenfold symmetry, it can have twelve fold symmetry. Number of such symmetries, which are have been observed in a number of systems. Which do not fit with this rotational symmetry, I mean that translational symmetry.

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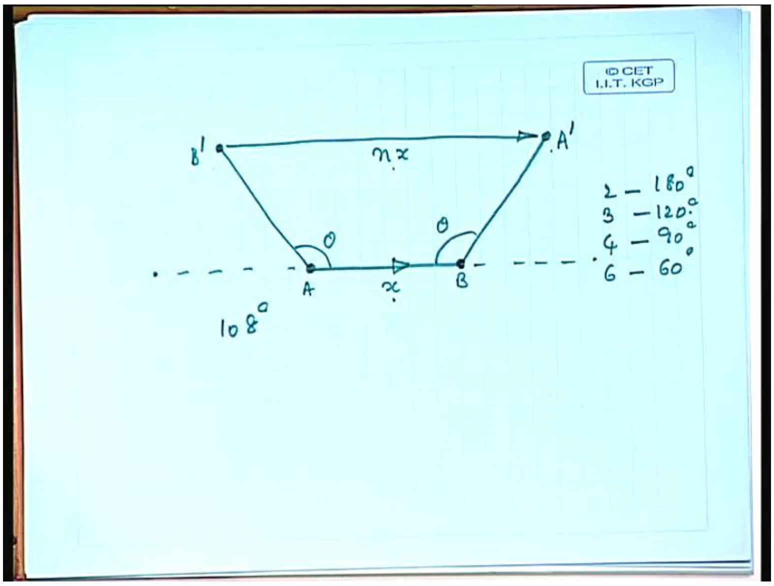

Why is that so if you look at any crystal structure with two atoms here. Let us say an atom A, another atom B here. The distance between these two, if you consider it as x, try to rotate this B with respect to the A by certain angle, certain angle theta. And similarly, rotate A with respect to B by again the same angle theta. If you now rotate and try to now look at, what is the distance between this new position, which is B dot, B dash let say.

B has been rotated and brought here, A has been rotated and brought here. This is called A dash, these are the two new atomic positions. And if you look at this direction, this direction is parallel to this atomic direction, is it not? Because these two directions are parallel, the distance between these two atomic positions. In principal if it is a crystal, it should be integral multiples of x. If this is x, this should be n into x, were n can be either 0 or 1 or 2 or 3.

If it is crystalline why because a crystal is that which has a three dimensional periodic arrangement of atoms. That is how we define, and if there is a periodic arrangement of atoms. If there is a an atomic direction like this A B direction. A dash B dash direction is parallel to A B direction. And because, this is A dash B dash is parallel to A B direction. The distance between these two atoms, should be integral multiples of this. And that is possible, only when I take a 3-fold symmetry or 2-fold symmetry or 4-fold symmetry or 6-fold symmetry. For 2-fold symmetry, the angle is 180 degrees, for 3-fold it is 120, for

4-fold it is 90 degrees, for 6-fold it is 60 degrees. If it is 2-fold symmetry, I rotate it by 180 degrees, where does this B atom will come. It will come in the same line in this direction, if it is 120 degrees you come to some point here. Similarly, if you take A it will come somewhere here. Obviously, now the new distance, if you want to call it as x dash. X dash will be equal to 3 times x 3 x.

So, similarly if I take 3-fold symmetry, then it is 120 degrees, if it is 120 degrees of rotation, then this B dash, A dash distance if you look at it, what will be, it will be 2 x. And if it is 90 degrees, then x dash will equal into x. And if it is 60 degrees x dash will be equal to 0, which is 0 into x let say n equal to 0. So, n can be 0, 1, 2 or 3 depending on what is the symmetry, but if the symmetry is 5-fold. If you rotate this B atom with respect to A atom by an angle, which is something like, how much?

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Either 72 or 108 degrees, depending on the internal angle or an external angle for a 5-fold symmetry. So, if you take a pentagon, what is the internal angle, internal angle is always 108 degrees. So, if I rotate it by 108 degrees, and you can try to calculate, what is the distance. You will see that distance will never be integral multiples of x. So, that means, a 5-fold symmetry is not compatible with the translational symmetry.

And hence, those days when the crystallography was developed for crystals, people have never considered a 5-fold symmetry to be a part of allowed rotational symmetries. That is why people call it as forbidden symmetry, it is not possible. But, you will see slowly that people have observed, such symmetries in a number of solids.

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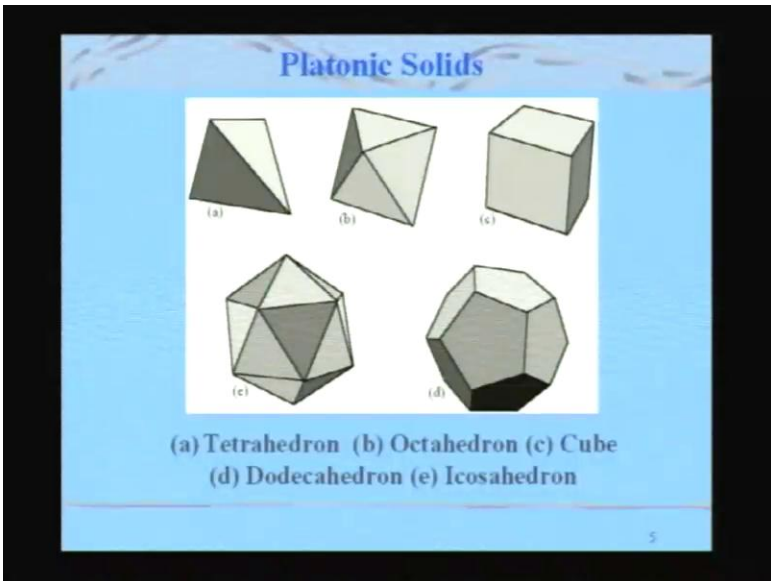

Platonic Solids

(a) Tetrahedron (b) Octahedron (c) Cube
(d) Dodecahedron (e) Icosahedron

For example, if you look at a platonic solids, which we talked about it in the first few classes. You can see two of these platonic solids, have a 5-fold symmetry. You look at the dodecahedron, you look at the icosahedron both of them have 5-fold symmetries. So, out of the five regular solids, as I told you there are no more regular solids. The maximum number of regular solids possible is only five. We have proved this, in our class.

And so out of these five 40 percent, two of them have 5-fold symmetry. But, unfortunately, the people though this was developed by Plato in even before AD started in around 500 BC. But, recently till 1984 people were unable to see any crystals, any solid materials having that kind of symmetries.

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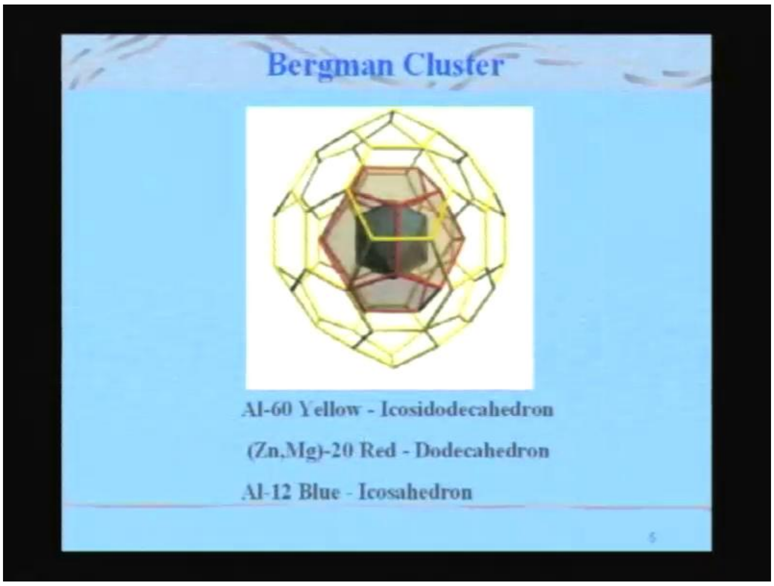

Bergman Cluster

Al-60 Yellow - Icosidodecahedron

(Zn,Mg)-20 Red - Dodecahedron

Al-12 Blue - Icosahedron

And it was only recently people have talked about it. But, when people have developed these quasicrystals. And started looking at many of the crystal structure, they started seeing yes many of this crystals have such symmetries. One such example is aluminum zinc magnesium compound. This is a compound, which has three layered kind of a structure. You have an internal layer, which is an aluminum with 12 atoms, which is nothing but an icosahedron.

How many corners are there in an icosahedron, icosahedron has how many corners? It will be 12 corners. Imagine a pentagon, another pentagon rotated with respect to each other and two vertices, one on top, one on bottom. In fact, I brought a icosahedron some time back and showed you. So, that is you look go back, you look at this, icosahedron that is e. What you have is a pentagon, one you can see one corner another corner, another corner, another corner, one behind, five corners there, another five corners here and one on top, one at the bottom. So, total you have 12 corners, at these 12 corners you will have 12 aluminum atoms, which formed by inside layer of the particular cluster, which is called Bergman cluster. Aluminum zinc magnesium cluster. And then you have a next layer, which is consisting of zinc and magnesium, with 20 such atoms, which called a dodecahedron.

Dodecahedron has 20 corners, you can look at this. This is a dodecahedron, it will have 20 corners, if you look at it. You look at any of the pentagon, so you have five corners there. And the next layer will be 10 corners surrounding this. And again at the bottom you have another pentagon. So, you have a pentagon, another pentagon at the bottom and then 10 corners coming at the centre of that. So, that is a 20 cornered dodecahedron. And then you have another, what is called icosidodecahedron with about 60atoms.

So, you can imagine how many total number of atoms are there in this, it is about 92 atoms in this cluster. And there are number of such clusters. There are also certain compounds, which have more than about 1000 atoms in the unit cell. And there are such complicated crystal structures existing. But, those days people did not really look very closely, in to these complicated structure. They said these are complicated just left it. But, then when the quasicrystals have been discovered, people started looking at them, in a closer look. And then started realizing, yes there is an icosahedral symmetry in many of these such clusters.

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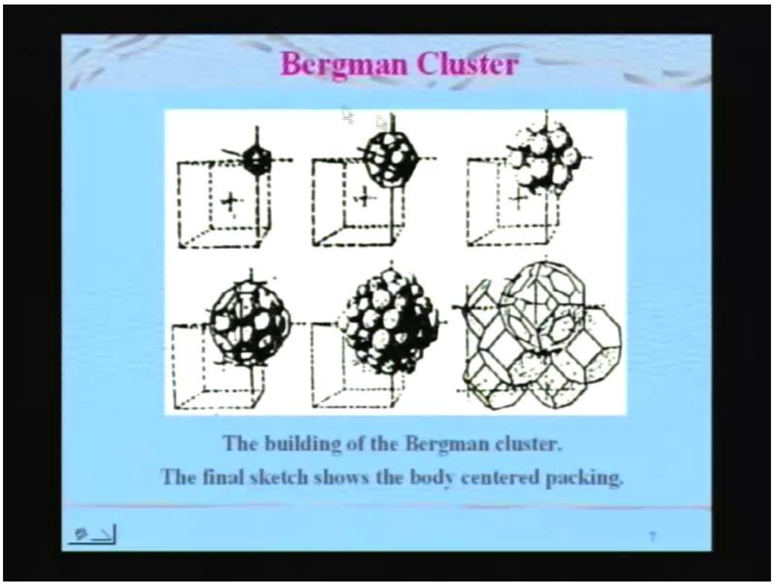

Bergman Cluster

The building of the Bergman cluster.
The final sketch shows the body centered packing.

And so this is another way of arranging Bergman clusters. You take a cubic crystal, put at one corner an icosahedron like, what you see for the aluminum in the previous Bergman cluster. And then the next layer like a zinc magnesium layer, then another next layer of aluminum. Like that, if you put it in one cluster in one corner, containing about 92 atoms. And put such 92 atoms clusters at each of the body corners.

You can imagine, you are now developing a cubic structure with this kind of clusters at each corner. And which is basically a cubic structure. But, as I told you before whenever we define a unit cell, that is why we do not talk, in terms of what are the number of atoms for unit cell. We always talk of number of Lattice point per unit cells. Because, at each Lattice point you can put 1000 atoms or 1 atom, depends on the type of material. So, in this particular material, which is aluminum zinc magnesium compound, you will have 92 atoms at each body corner. So, you can have such crystal structures. And all of them are have some icosahedron symmetry.

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Mackay Cluster

And this is another type of cluster, which has called Mackay Clusters. Again here also, you will always find an icosahedron symmetry, is slightly different from the Bergman type of clusters. But, all these have large number of atoms in them. And all of them, the common thread in among all these clusters is that they all have icosahedron symmetry.

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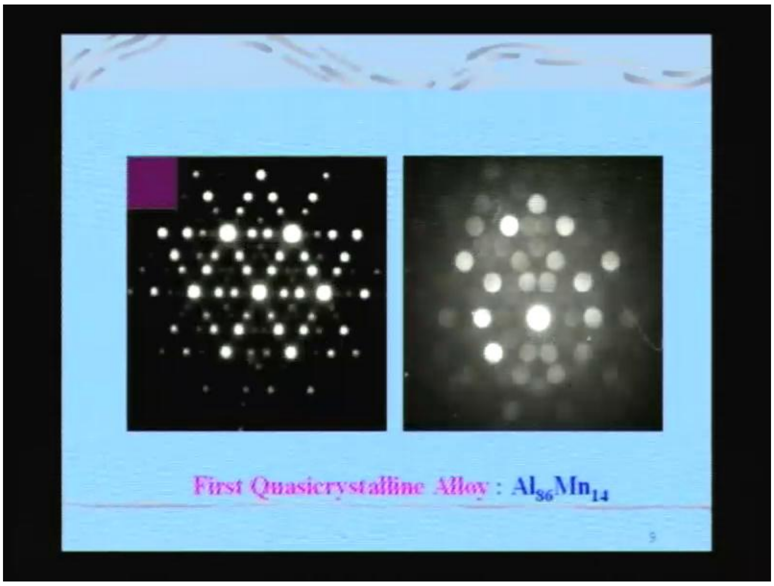

First Quasicrystalline Alloy : $Al_{86}Mn_{14}$

And when people looked at such materials in a electron microscope, this is what they saw. So, first time in 1984, when Danny Shechtman, a looked at aluminum 86 manganese fourteen alloy. What his saw was this type of a diffraction pattern. If you carefully look at this diffraction pattern, there is a central spot. What is that central spot, it is a transmitted beam in a electron diffraction. And look at the spot, which are surrounding that.

You can see, if you carefully start from one corner. And do not forget where you have started with and then count the total number of spots around that central spot. You will see, there are 10 spots. And you have another concentric circle, another 10 spot and you go to another circle, you will have another 10 spot. And like that will have, and each of them will have ten spots suggesting that, it is a 10-fold symmetry. In fact, this is another important point that should know.

That if you look at any material having a 5-fold symmetry. And look at it in a electron diffraction pattern, it does not look like a 5-fold symmetry. It will always look a 10-fold symmetry, why is this so. For example, I take cube, what is a typical symmetry of a cube, cubic crystal. It has a 4 3-folds and 3 4-folds. So, if I take an axis, which is perpendicular to the 1 1 1 plane.

That means, if I send the electron beam such that, it is going perpendicular to the 1 1 1 plane of a cubic crystal, which has been kept in the path of the electron beam. Let us say

I have put a sample in a TEM. And then oriented by sample, in such a way that the 1 1 1 plane is now perpendicular to the electron beam. Now, in the electron beam is coming through the sample, it comes across the 1 1 1 plane. And then try to see what is the symmetry of atoms around that the plane, and defected beam that you get look at the defected beams.

And what you see is, you will see a transmitted spot like that. And diffraction spots which look like this and so on. This is a first layer and there will be many order. This is called first order reflection, second order reflection will be there, third order reflection will be there. For example, Bragg’s law, we talk of lambda equal to 2 d same theta. So, there we talk about n lambda equal 2 d sine theta, which is n is the order of reflection.

So, similarly here if you take the first the first order reflection, this what you see. But, it has a 3-fold symmetry, the cube has a 3-fold symmetry. But, when you look and this what you see is, you do not see 3-fold symmetry, but a you 6-fold symmetry. And cube does not have a 6-folds symmetry why is that, the reason is simple, reason is if you look at the diffraction, the diffraction, the intensity of diffracted spot. If this is a diffracted spot, the intensity I of h k l plane is equal to what? Is equal to the square of the structure factor, yes anyone who has gone through as x-ray diffraction the all know this. So, intensity is square of the structure factor. Now, if I look at the structure factor of an h k l plane. And compare with the structure factor of h bar k bar l bar plane. Two planes which are parallel to each other.

The structure factor of this is always nothing but negative of the other structure factor. They are same in the magnitude, but difference in the sine only. And if I look at this kind of situation. And take the square of this structure factor the intensity of the h k l plane will always be equal to intensity of h bar k bar l bar. So, if have 3-fold symmetry in a crystal. For example, if this is one spot and this is the other spot. And this is the other spot, corresponding to the 3-fold symmetry.

Then this is what I call the h k l plane some h k l plane, the h bar k bar l bar will always be here, is it not. It will have a inversion symmetry. So, h bar k bar l bar will be 180 degrees opposite to the h k l plane, if the h k l spot is here, the h bar k bar l bar will be below. And so the intensity of this h bark bar l bar will also be equal to that of the intensity of the h k l. So, because of which the moment there is a spot here. you will get another spot here with the same intensity.

Same thing is true other three spots. And because of which you looks like a 6-fold symmetry, but you will not know, whether it is a 3-fold symmetry are 6-fold symmetry. In fact, this one of the problems in finding out, if you put an unknown crystal, in to a t e m...

Student: ((Refer Time: 30:29))

No, a 6-fold symmetry is always give you 6-fold, because it is a overlapping there. So, as a result if you look at cubic crystal in t e m. Or a pin hole x ray diffraction, whether it is pin hold x-ray diffraction or t e m are basically similar. That you get, what is called the diffraction spots instead of diffraction peaks. So, if you look at the, you put a crystal inside a t e m. And then pass the electron beam, you get this kind a 6-fold diffraction pattern immediately, one thing is clear to you from this. That the crystal, that you are looking at is any of the three possible crystal structures. What are the three possible crystal structures, which can give you this kind of a diffraction pattern.

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Another is yes, there is one more possibility rhombohedron be confident. So, it is cubic hexagonal and rhombohedron, all these three have a 3-fold symmetry in them. There is no other crystal, which has 3-fold symmetry. So, from this from the elimination techniques, I can say this particular crystal I am looking at. Cannot be tetragonal, cannot be orthorhombic, and it can be either monoclinic or triclinic.

So, it has to be one of these three. And if it is one of these three, what is it, how do you find out. That is when t e m we have the facility of what is called tilting the sample. I can keep the beam, I cannot tilt the beam unfortunately, because the source for the beam is fixed. What is the source for the electron beam, it is a filament. Tungsten filament which is heated. And tungsten filament is kept at the top and that is fixed.

So, you cannot move the tungsten filament, so but what you can do it tilt your sample. When I tilt my sample, I can change the sample, the orientation of the sample from the 1 1 1 orientation to some other orientation. And if I change this orientation, if I get a 4-fold kind of symmetry. That means, a symmetry which looks like this, with a central transmitted spot. After certain rotation, the diffraction pattern changes, because some other plane will come perpendicular to electron beam.

The diffraction pattern is basically depends on, what are the planes which are perpendicular to the electron beam. And those planes gives a fraction, and that is how is get this pattern. So, the moment you get the pattern like this. From this I clearly say that, this has to be a cubic crystal rhombohedron. And hexagonal cannot have a fourfold symmetry. So, the moment I see this, I can find out that it is a cubic. So, this is how have one can find out, yes.

Student: ((Refer Time: 33:50))

Yes, we will come to that. So, this is what it is as per as the cubic is concerned. So, but and from the crystallography we know. What are the angles, what is the angle between the 1 0 0 plane and the 1 1 1 plane. This angle is known 57.3 also. And once we know this angles from a crystallography, I can till the sample by that particular angle. And then get this 4-fold symmetry. And the moment, if I do not get the 4-fold symmetry there, then it is clear.

It is not cubic, it has to be one of the other two, is it not. And so that is how one can find out. And if you one wants to confirm, that it is not really 3-fold, but it is 6-fold there is a technique for that. It is called conversion beam electron diffraction, CBED people call it. Conversion beam electron diffraction is a technique, which is a nothing but an electron diffraction technique, which used in most of the conventional electron microscopes.

Transmition electron microscopes, where really you can see the information form second layer of atoms, because when you converse the electron beam. The beam will be more intense and when it falls on the sample. Not only the information from the first layer of atoms, but from the second layer of the atoms, which are below that also you can find out. And from that one can get an idea, whether really it is a 6-fold are a 3-fold. That is how one can get information. And this is how we can find out, whether it is a really 3-fold or 6-fold. And that is how here, we can see though it looks a 10-fold, you will come in a minute, when we talk about the classification of quasicrystals.

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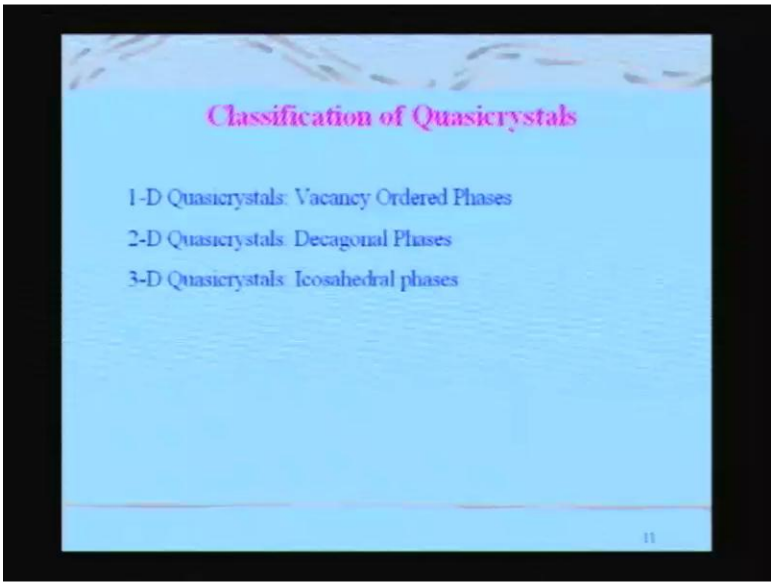

Classification of Quasicrystals

1-D Quasicrystals: Vacancy Ordered Phases

2-D Quasicrystals: Decagonal Phases

3-D Quasicrystals: Icosahedral phases

Quasicrystals have been classified in to three groups basically. One is called one dimensional quasicrystals. What are one dimensional quasicrystals, one dimensional quasicrystals means, those quasicrystals where in two dimensions, the atomic arrangement is periodic. Atoms are periodically arranged in x and y directions. Whereas, in z direction in one of the direction the atomic arrangement is not periodic.

It is a quasi periodic, it is not at the same time random. But, it is quasi periodic, we will come to the quasi periodically in a minute. So, this is what are called one dimensional quasi crystal, these are also called what are also called vacancy ordered phases. That means, in a crystal, if you can somehow make the vacancy in the crystal. And arranged in a certain ordered, you generate this kind of one dimensional quasicrystals. Because, vacancy is are always arranged in a line, like a dislocation.

So, these are what are called one dimensional quasicrystals. There also two dimensional quasicrystals, where the crystal or the sample, or the solid has periodicity in one dimensional. And quasi periodicity in two dimensions, and the 3D quasicrystals are although, where the quasi periodicity is in all the three direction, which are called icosahedral phases. The two dimensional quasicrystals are called decagonal phases, there are examples of all of them.

There certain materials which process only icosahedral kind of crystal structure. For example, aluminum manganese is one example. Aluminum copper iron crystals are such a example and there are examples for others two. ((Refer Time: 37:31)) So, let us go back to this. And have a look at this carefully. This is again a 10-fold that we are looking at. And if you closely look at some of the diffractions spots, you can see the 5-fold symmetry really there.

For example, here you look at this, the 5-fold symmetries seen there 1, 2, 3, 4, 5 atoms. They are not atoms, they are there diffractions spots, but the give some idea about atomic arrangement. And look at this, what is this kind of symmetry, what symmetry is this? It is a 3-fold symmetry or whatever it is. It is a 3-fold symmetry, because icosahedron does not have 6-fold symmetry. So, it is only 3-fold symmetry.

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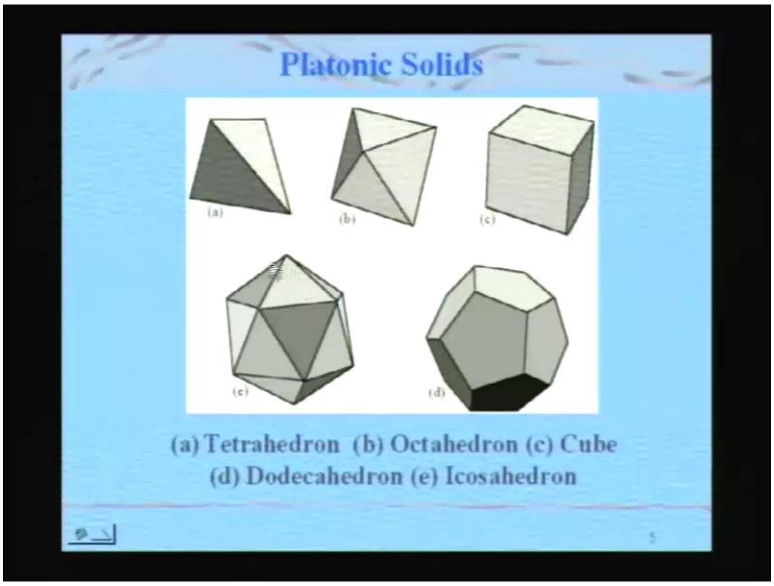

Platonic Solids

(a) Tetrahedron (b) Octahedron (c) Cube
(d) Dodecahedron (e) Icosahedron

How do you know whether icosahedron 3-fold symmetry, you can see here. There all equilateral triangles. So, it has a 3-fold symmetry. So, that is why we call it as m 5 3 or 5 3 m kind of crystal symmetry for a quasi crystal. And if you look at ((Refer Time: 38:36)) this carefully, what you see in any direction you look at any one direction. One interesting thing that you see, is that the spots are not equally spaced.

You see look at probably here also. Let us say look at this direction, in this 10-fold symmetry. Look at any one direction in one line, you can see this distance and this distance and this distance look at. There are not equally spaced, and that is a characteristic of a quasi crystal. In a crystal any direction you look at it. All the spots will be equally spaced, because there is periodicity inside the crystal.

Here there is no periodicity, it is a quasi periodicity. And what is this quasi periodicity will come to it in a minute.

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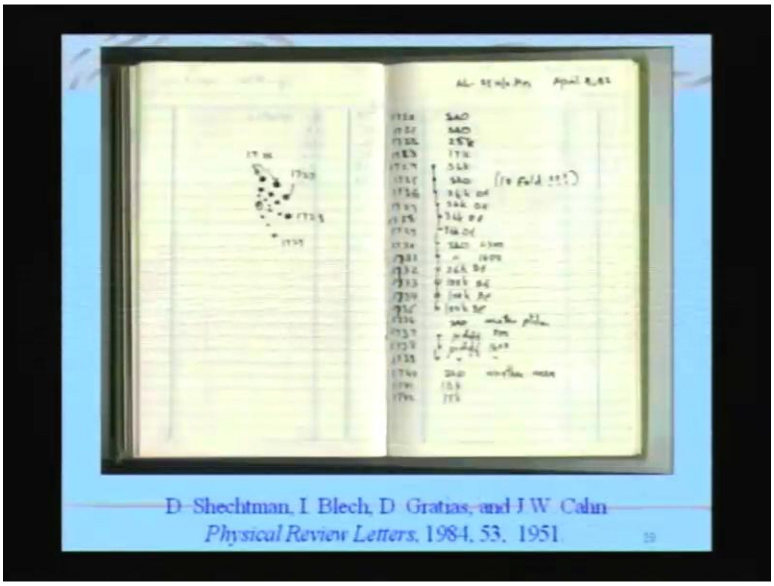

D Shechtman, I Blech, D Gratias, and J W Cahn
Physical Review Letters, 1984, 53, 1951

So, this kind of diffraction patterns is possible. And in 1982, Shechtman for the first time has observed that kind of a 10-fold. And this the log book of the Shechtman, which he has written a written that a day which April, 8th 1982. Where he has observed the 10-fold and puts question mark, because that was the first time somebody observing a 10-fold in a t e m. He was quite exited and then draw that particular diffraction pattern here. Part of the diffraction pattern, and try to take from each part what is called dark field.

And try to look at that sample more carefully. And found that it look same, you from which ever spot is choose. And since then but he took almost 2 years to publish this. 1983 in physical review later he published it. So, he took 2 years really confirm, whether this is really 10-fold. And then repeated in this experiment, number of made a new alloy of the same composition.

And had a look at that and then finally, he has confirm that, yes it is not an artifact in a t e m. It is not the t e m is miss behaving it, but its sample which is behaving that way.

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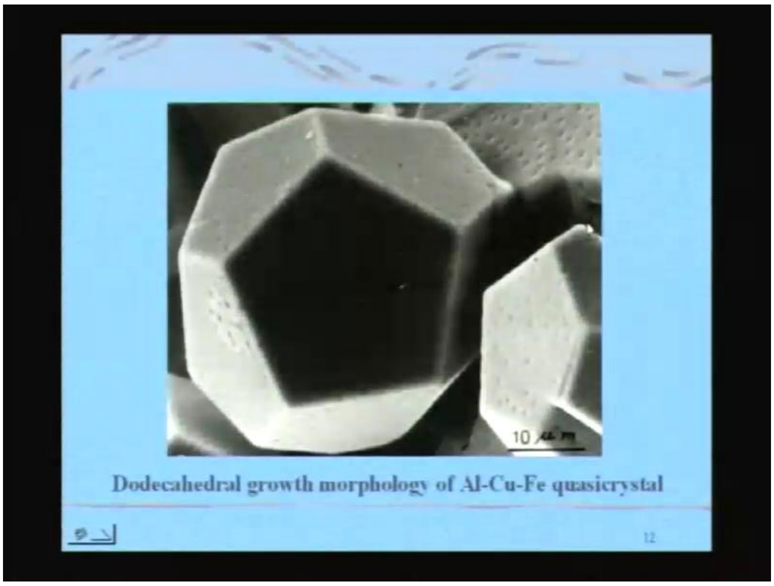

Dodecahedral growth morphology of Al-Cu-Fe quasicrystal

12

And then you can see this kind of images. This is nothing but a grain an aluminum copper iron quasicrystal in grain, which shows a clear. And what kind of solid is this?

Student: ((Refer Time: 40:54))

It is a dodecahedron yes, so this is not a model. It is a grain in a material, it a same picture of a sample in an aluminum copper iron. So, this clearly tells you that, the internal symmetry of a material is many times reflected from the outside geometry of material. That is why when people try to look at sodium chloride crystals. That is when peoples started talking about the crystal structure. In fact, those these people have that a external shape, is same as that of the crystal structure.

So, that is why morphology, polymorphism, when the word came morphology nothing but the shape. So, polymorphism is nothing but the crystal structure. So, the morphology and crystal structure, people used to use it very synonymously those days. Because, they know that in many cases this kind of thing happens. But, not in all cases, you take aluminum, all aluminum graces do not show you this kind of thing. Though it has a FCC structure, it is because of the constraints during growth.

When aluminum grains are growing, the other grains are there around it, which constraint from their growth. But, if an aluminum individual grain is allowed to grow in a environment, which is not constraint by anything else. It would definitely take this kind of a shape. And that is what is called, I mean not this exact shape, but whatever is the shape for the FCC crystal. This is what is called gibes shape of a any crystal. If you have ever heard, every nucleus has certain shape. For simplicity whenever we do calculations, which assume a spherical particle, spherical nucleus. But, no nucleus is really spherical, each nucleus has a particular shape, which has been deiced by the actual crystal structure of the material.

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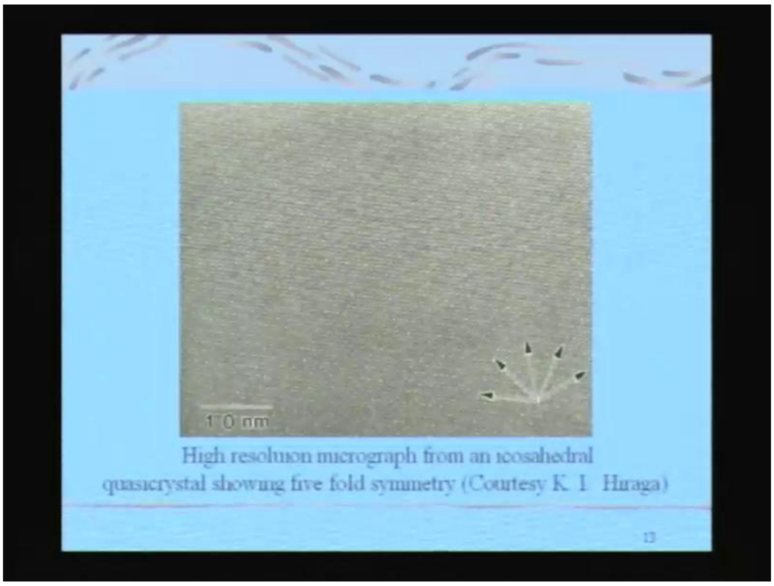

High resolution micrograph from an icosahedral quasicrystal showing five fold symmetry (Courtesy K. I. Hiraga)

This is the high resolution image from a quasicrystal. You can see these directions, which are marked here, which clearly show you the atomic planes. Each dot, white dot that you are seeing is nothing but an atom. And the five directions indicating the 5-folds symmetry in that.

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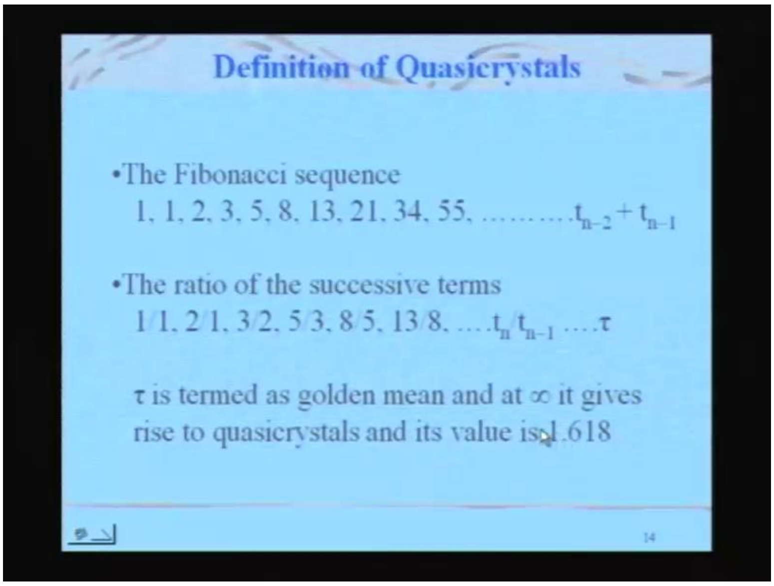

Definition of Quasicrystals

- The Fibonacci sequence
  1, 1, 2, 3, 5, 8, 13, 21, 34, 55, ...$t_{n-2}+t_{n-1}$
- The ratio of the successive terms
  1/1, 2/1, 3/2, 5/3, 8/5, 13/8, ...t_n/t_{n-1} ....τ

  τ is termed as golden mean and at ∞ it gives rise to quasicrystals and its value is 1.618

And if you look at the basis of quasicrystallography, what is quasi periodicity, quasi periodicity is basically can be explain, by what is called this Fibonacci sequence. What is the Fibonacci sequence, Fibonacci sequence is nothing but you start with one, number 1 let us say. And in principal you start with 0, always keep adding the consecutive 2 numbers.

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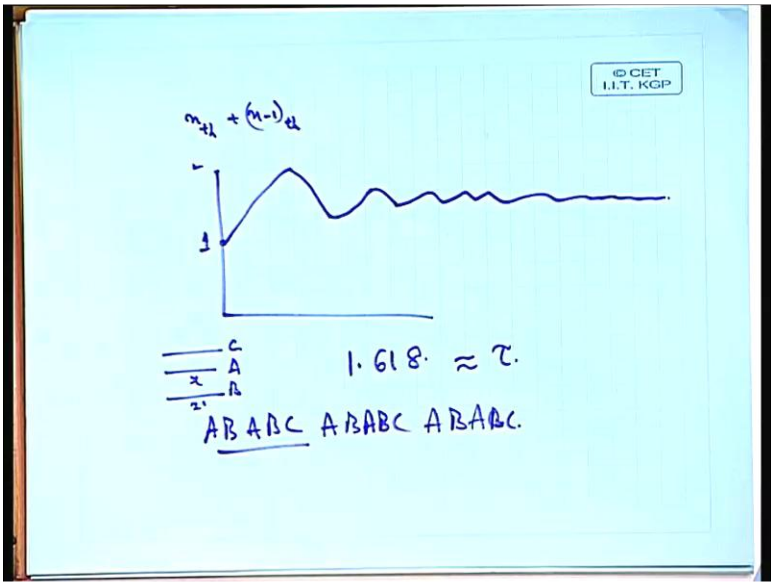

That means, add n th number plus n minus 1 th number. If you keep on adding generate another number. And so you get a sequence, it is like a geometric sequence, x shifting that you are adding the two consecutive number. So, 1 plus 1, if you look at it 1 plus 0, if there is 0, there it would be 1, 1 plus 1 is 2, 2 plus 1 is 3, 3 plus 2 is 5, 5 plus 3 is 8, 8 plus 5 is 13. So, this is kind of sequence that you can generate, and if you look at the ratio of successive terms.

The first two terms are 1 by 1, then you have 2 by 1, then 3 by 2, 5 by 3, 8 by 5, 13 by 8 like that. If you keep on taking the ratio of the n plus 1 terms by n th term, this ratio keeps on fluctuating. And finally, becomes... For example, first if you look at ratio, first it is 1, then it goes to 2. That means, goes to 2, then it is become 3 by 2 that means, it comes to 1.5, then it goes to 5 by 3, 5 by 3 is how much?

Student: ((Refer Time: 45:17))

1.66, so it goes up again. Then, it is 8 by 5 is 1.6, it is comes down, and keeps on fluctuating like this. And finally, it becomes constant. And what is that constant value, that is what is called golden mean, which equivalent to 1.618, which is called tow. And that is what is called the periodicity of a quasi crystal. So, the periodicity in a quasi crystal is given by this golden mean. That means, there is always atoms arranged in a fashion. In such way, that they repeat after some time instead of in a normal crystal.

You have a distance, let say Lattice parameter which we call. And this Lattice parameter is repeats. Here you may have a arrangement, such as A B, A B C. And then that A B, A B C repeats. And again A B, A B C. If you define A as one distance x, B as another distance x dash and C as some other distance. So, you can see the atomic arrangement will be such that, they will be repetition. For example, if you look at the pervious diffraction pattern here, I said the distances are not equal.

((Refer Time: 46:58)) This distance is different from this distance. And this distance is different from this distance. But, if you carefully take this distance, multiply this distance by golden mean, you will get this distance. The distance between the transmitted spot and the second spot, will be equivalent to the distance between the transmitted spot and the first spot.

Similarly, the distance between the transmitted spot. And the second spot multiplied by the golden mean, will be equivalent to the distance between transmitted spot. And the third spot and so on, so forth. So, there is a some kind of periodicity not exactly equal.

But, there is a relation between the distances. And that relation is nothing but a quasi periodicity and that is what we call a quasi periodicity. And this different from completely randomness, it is not completely random.

But, at the same time is not completely periodic. So, its somewhere in between and that is why we call them as quasi periodic. This is observed from the crystal strictures. A number of such crystals have got this kind of an arrangement. And how you get it, you will see if you take this kind of a thing.

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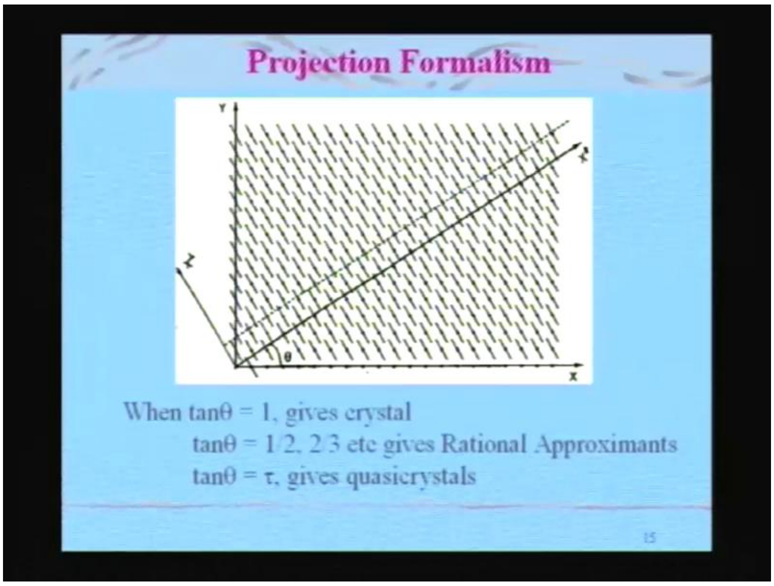

Projection Formalism

When $\tan\theta = 1$, gives crystal

$\tan\theta = 1/2, 2/3$ etc gives Rational Approximants

$\tan\theta = \tau$, gives quasicrystals

What you see is that, you can also generate this kind of quasi periodic arrangement. If you take a two dimensional crystal and project it to one dimension. What you see here, is a two dimensional crystal. For example, these lines that you have, imagine them as atomic positions in a two dimension. So, you have a periodic arrangement of these lines in this direction, and also in this directions.

One can also do it three dimension, but it is more difficult, so we are showing it in two dimension. So, if you take a two dimensional arrangement of atoms. And draw a line at a certain angle and draw another line, which is parallel to the first line, that you have drawn. That means, 0 x dash for that you draw another parallel line, which is dotted line there, and chose all those points, which fall into this domain.

If you call that as a window, whatever atom, atomic positions or Lattice points, which are following in to a domain, you chose them. And then project them on to this x. If you chose for example, within this domain, ((Refer Time: 49:27)) this falls, this falls, this falls, this one falls, this one, this one and this one, this one. They are so many fall in to that. All of them project them on to a one line which is this line, which is horizontal line x direction, if you project and now look at the distances between this projected spots.

Student: ((Refer Time: 49:49))

That is just to have a choice, if you do not have a window, there will be innumerous number of atomic positions, which have to be projected. Instead projected innumerous number, we define a certain number of atoms, which can be projected. Because, if you project a large number of them. then you will have to many atoms, to many points projected on to it. All of them get clustered, so it becomes very difficult.

So, as a result we chose some window. This window can be of a any choice. That is not important, what is important this angle. Now, if this angle is having a certain finite value, if the tan theta is 1. Then the projection, that means when is tan theta 1, if theta is 45. So, if the theta is 45, then you chose all those spots, which fall in to this window. Or all those spots intersect, this particular line. And project them, what you see is the distances between projected spots will be equally spaced.

And that is nothing but a crystal, that is what is a periodic arrangement? So, you can call it as one dimensional crystal. A two dimensional crystal has been projected in to one dimensional crystal now. Instead of this tan theta being 1, if this tan theta has certain finite value, such as 1 by 2, 2 by 3 like that. Then, you get what are called rational approximants. I said certain crystal structures, which have some similarity quasi crystal, these are what are called rational approximants.

So, the distances between the projected spots will be such that, they will not be periodic. But, at the same time they will not be a quasi periodic also, and if this tan theta is tow 1.618, that is when you get a quasi crystal. So, that is why now a days, people imagine a quasi crystal is nothing but a crystal in a higher dimension. And he has been projected in to a lower dimension to give you a quasi crystal.

Like this, if you can see a two dimensional crystal can be projected in to a single dimension, as a quasi crystal in arrangement of spots. By choosing appropriate angle, which is nothing but the tow, tan tow a tan theta being equal to tow. Instead of that, if I take a four dimension, if at all four dimensional solids that is existing. And project in to a two dimensional plane.

What I get is a two dimensional quasi crystal, if I choose the angle appropriately. And one can extend it in to a six dimension. There are 1000's of people in this field, who are doing what is called quasi crystallography which is simply nothing but mathematics. Where projection mathematics we call it. So, where people take a crystals, imagine what would have been, if it in six dimension. And if each of these two dimensions, project it you get one dimensional quasi crystal.

And if you take a six dimensional cube, if there is a six dimensional cube. And if that is projected, what you end of is in a three dimensional icosahedron quasi crystal. This is just mathematics. But just to understand what is the relation between quasi crystal in to a crystal, because we know crystals, but we do not really know quasi crystal, how to understand quasicrystals, in terms of crystals.

And if you want to look at, what are the for example, if you look at this icosahedron. How many axis are required to define icosahedra quasi crystal. For example, if a solid have a quasi crystal in structure. A normal cubic structure, when I am talking of various planes I talk of h k l three indices. If I go to a hexagonal I go in to four indices, if I talk in to terms of quasi crystal, I have to have six indices system. Five indices for each of this pentagonal corners, one for the C axis.

But, in principal one can convert the six indices in to three indices. Like the way we convert the four indices, in hexagonal in to three indices system. So, one can convert these things. And that is how people talk, in terms of the quasi crystallography.

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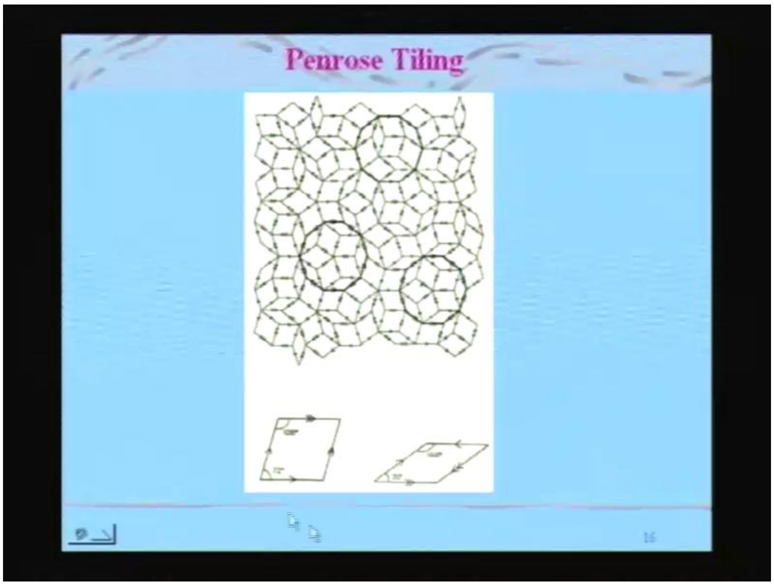

Penrose Tiling

And one can get take this kind of a tiles. And tell them together with various rules. And get 5-fold symmetries, these are what are called Penrose tiling. A number of people are working on such tilings, which are mathematics.

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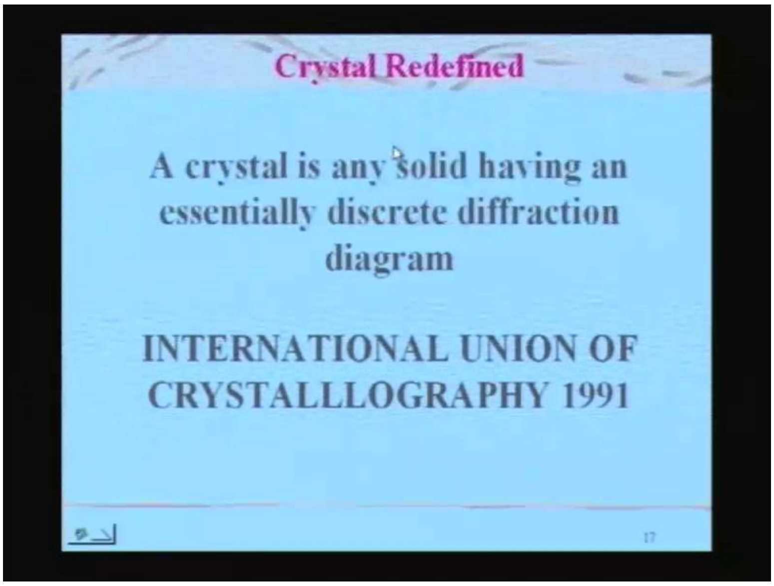

Crystal Redefined

A crystal is any solid having an essentially discrete diffraction diagram

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And now finally, we can come to the definition of a crystal, which has been modified in 1991; where they say any crystal having an essentially discrete diffraction pattern, is a crystal. Just to you include a quasi crystal, because all quasicrystals give you a discrete diffraction pattern. And that is how we define a crystal. With this we stop and continue in the next class.

Thank you.