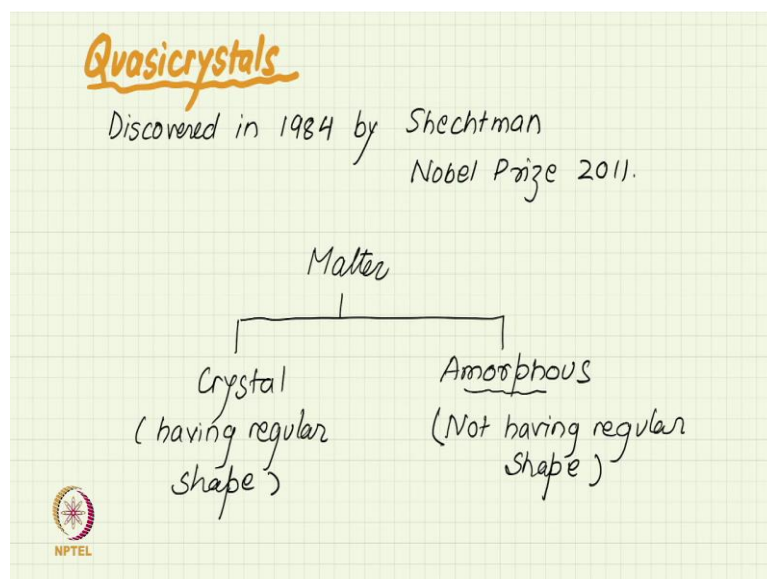
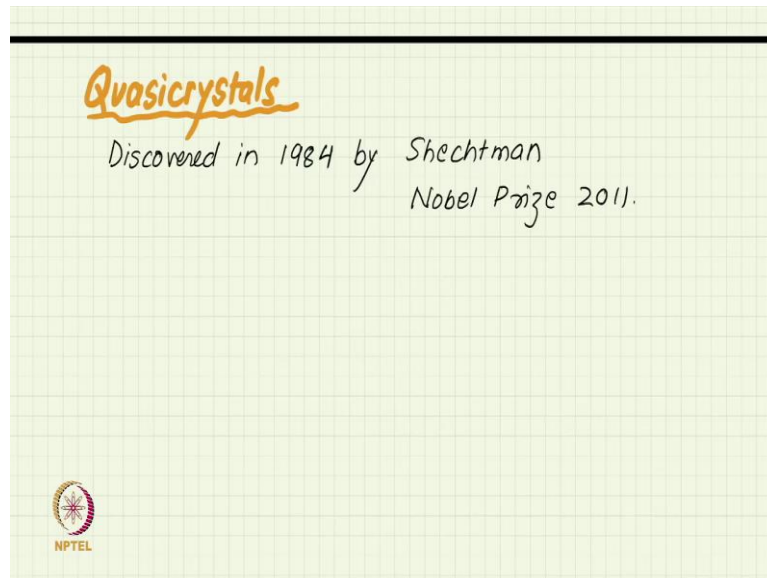


**Crystals, Symmetry and Tensors**  
**Professor Rajesh Prasad**  
**Department of Materials Science and Engineering**  
**Indian Institute of Technology, Delhi**  
**Quasicrystals**

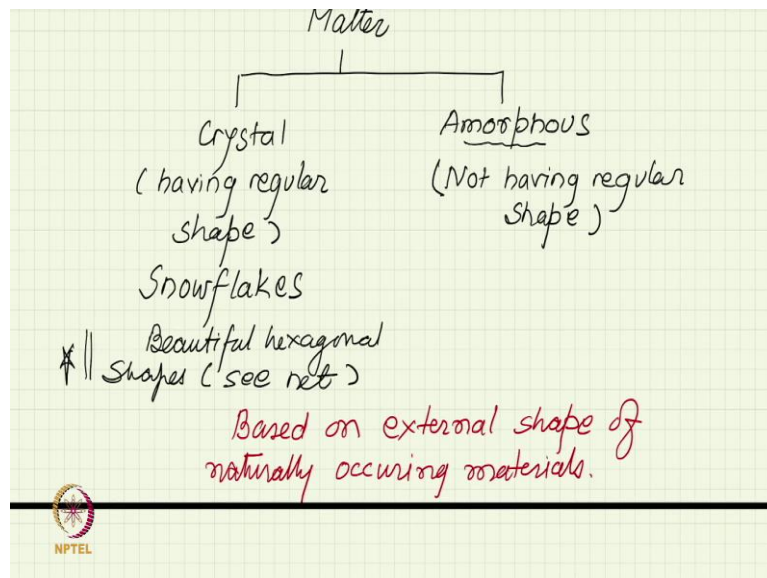
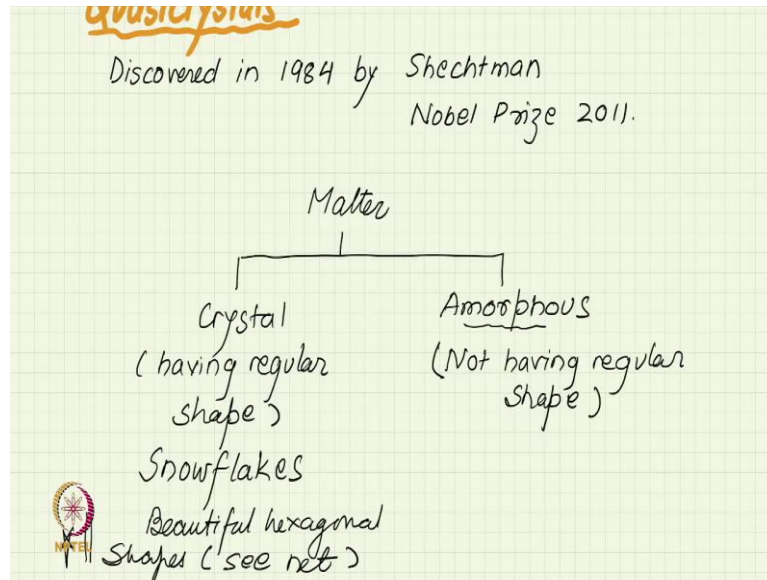
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We are talking only in terms of geometry and but how was this geometry established? How did people find that crystals are crystals or crystals are periodic? So, that has an interesting history and the history begins from the earlier classification of material into crystalline amorphous, morphing as you know changing shape, morph means shape, amorphous means not having any shape.

So, this was based on observing the natural material, manmade material of course, you can always shape anything into any shape you want by machining and casting or rolling you have techniques of shaping but when we say having shape and not having shape means we are looking at material as found in nature.

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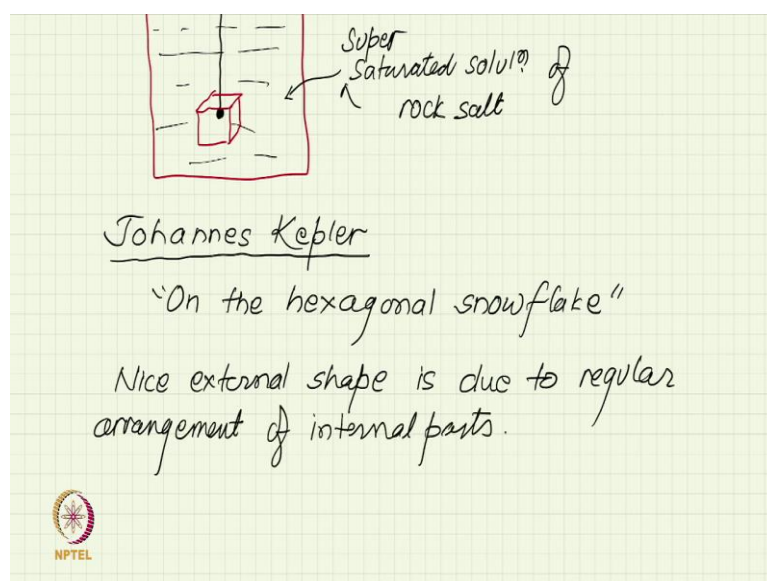
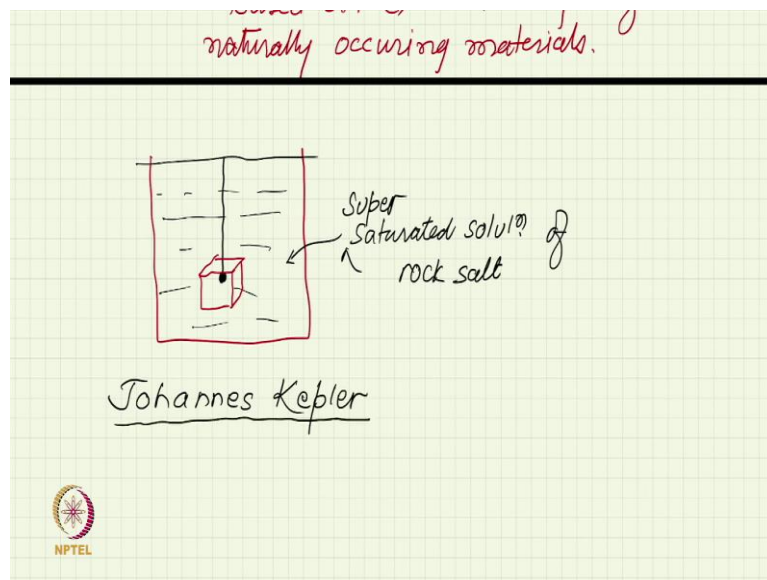


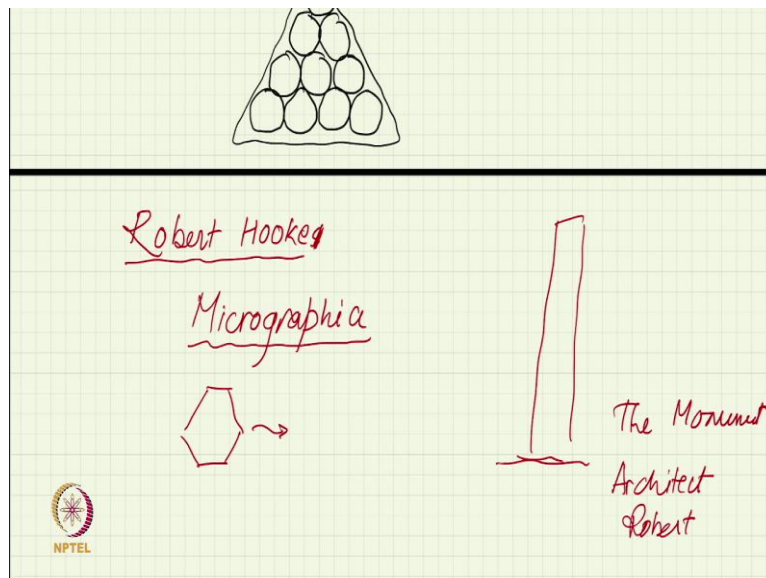
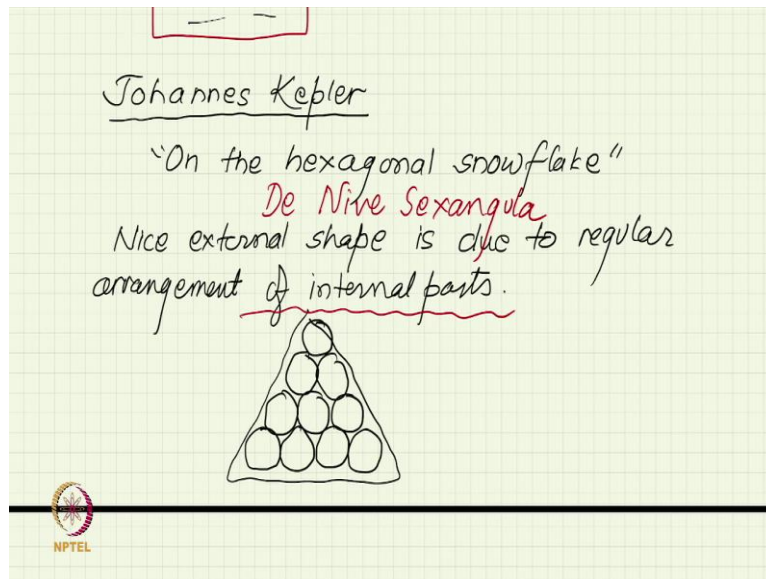
So, as found in nature for example, one of the most beautiful things which were found in nature was the snowflakes. So, thing is falling from the sky, no human being is there with his machining or designing technology and it comes in beautiful hexagonal shapes you should check images on the net, snowflake images if you see beautiful, beautiful websites are there.

At least when I was last checking it I found a photographer who has dedicated his life, many photographers in the past also have dedicated and there is a current photographer, I think Russian, dedicated his life to photographing and putting uploading snowflake pictures and beautiful pictures, they will capture you, capture your attention.

So, obviously they were attractive and anybody with logical thinking and all also was started to wonder how come they are having that shape? What is the reason behind this nice external shape and there were other things which were not having shape, so amorphous and crystal. So, this classification was based on external shape.

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So, when the question came that why some of and there are of course snowflakes beautiful but he as other minerals also for example rock salt, so rock salt you grow from solution but it grows as a cube, you are not shaping it as a cube.

So, that is in a standard experiment that you, you take saturated solution of salt, super saturated maybe and then on a thread you put a seed crystal because of the supersaturation salt will start depositing on this crystal on the seed but when it starts growing, you will find that the grown crystal is having nice satchet and in a cubical shape.

Again you are not there with hammer and chisel to shape it in a cube but the growth process itself is making it into a form of a cube. So, these the earlier scientists wondered, some of the greatest mind wondered and one such great mind was Johannes Kepler.

The same Kepler of Kepler's theory of planetary motion flow, he was also wondering, actually he was walking back home some time and on a snowfall and snow was falling on his coat. And some of them he looked carefully and he started wondering. And those days were when there was no DST, CSIR to fund your research and he was a researcher.

So, he has to catch some rich man, noble man who will support such kind of thinking, why snowflake is hexagonal. So, he had some Barron or some noblemen who was supporting him for his research. So, as a New Year gift to him, he wrote, so, one of one of the most beautiful New Year gift or new your card, which you can have, is what Johannes Kepler gave to his sponsor or supporter, he gave him a research paper.

So, he wrote an article on the hexagonal snowflake and he gave the theory, his thinking, that why snowflake is hexagonal, and there was the seed of modern crystallography, where he thought that these things which have nice external shape is maybe because of some regular arrangement of internal objects, internal parts. So, that was his theory.

And now, what what we draw as close packed spheres and all. So, some of the original drawing was in this paper. So, he drew some of these things like backing off his spheres. So, his spheres are having a spherical shape, they are not triangular, but as you can see in this arrangement, they are giving you a nice external triangular shape.

Now, I am writing internal parts, because that is what he also wrote something of that equivalent because he was writing in Latin, the Latin title was you will find again on the web if you search so, atoms were not there, when he was writing atoms were not discovered.

So, he can not say regular arrangement of atoms. Some sort of internal parts he thought of another great person who came and thought in the same direction was Robert Hooke, again Hooke of, Hookes law, he was also interested. Robert Hooke was again an another intellectual giant. He was interested in many things.

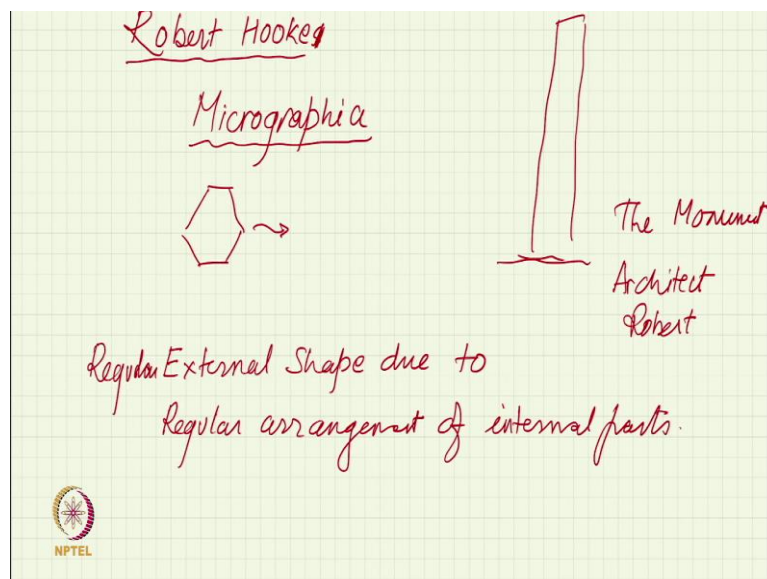
So, Hookes law is only one of his little contribution which we know by his name, but he was an architect. London has a famous, those of you who have visited or will visit London, you can go and see a monument which is called The Monument. It is a tower like our Qutub Minar and who was the architect of that monument, Robert Hooke. Why was the monument made? There was a great fire in London and fire demolished everything.

So, then Robert Hooke along with Christopher, were charged with rebuilding of London after that devastating fire, so he was one of the chief town planner and architect of London, after the devastation and as a memory to remember that fire he also made, constructed this tower. So, that is called The Monument.

He, he was also interested in looking at Sun and he was developing a telescope, by which you can look at the sun, so that he called Helioscopes, a telescope through which you can look at the sun. All material scientists should do your salutation to Robert Hooke not for the Hookes law but for microscopy, he is the original microscopist, he wrote the first book on microscopy called Micrographia.

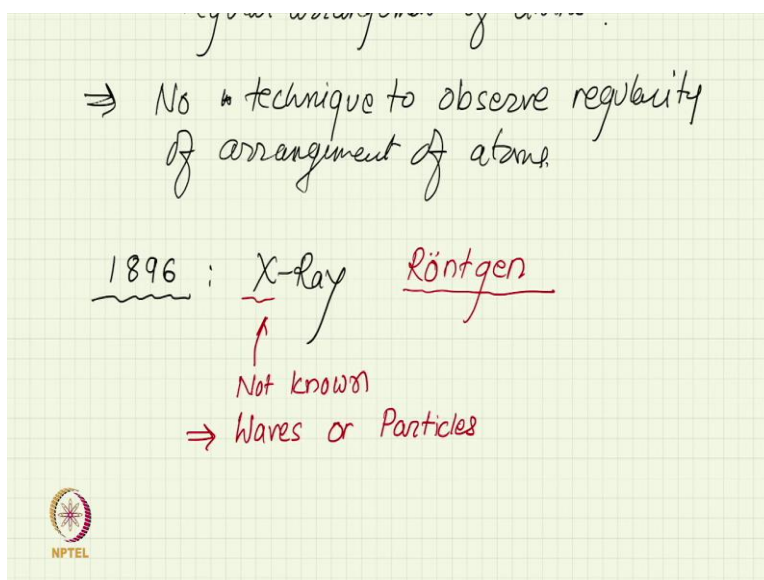
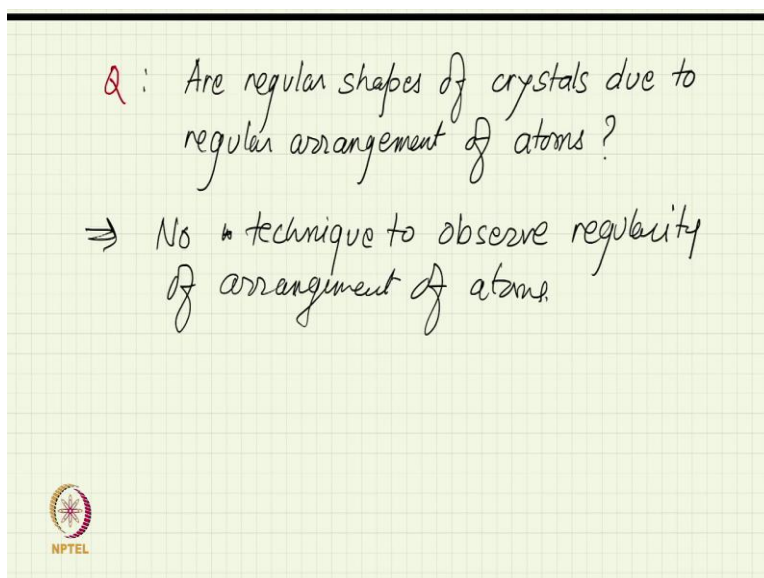
All hundreds of years ago 1700's I think micro graphia, in micro graphia he also studied some of the crystals and he found nice external shapes of those crystal again he gave a theory similar to Robert Hooke came after Kepler. Again he gave the same theory that the external shapes are because of some internal arrangement.

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But it was left because first of all it was not known what is that internal thing which is being arranged and how to find that none of these things were there, so his postulate also was regular.

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Then came atom, when an atoms came atoms were discovered, then these postulates had some more concrete bases, that regular arrangement of internal parts means regular arrangement of atoms. So, then the question came, so, the question was formulated in terms of atoms that are regular shapes of crystals due to regular arrangement of atoms but there was no way, no technique to look at regular arrangements. So, the question remained a question.

Regularity of arrangement of atoms then in 1896 another breakthrough after several years, maybe these were in 1780s or something was happening. And then, of course, atoms came in the beginning of 20th century 1900 or so, and just before the beginning of 20th century, in 1896 a new phenomenon was discovered and that was X-ray by Rontgen. Probably home laden, I am not sure.

Why were X-ray's called X-ray existential unknown what was not knowing whether they are waves or particles, that was the question, it was discovered, it was found that it is blackening the photographic that was the accidental discovery. That is another interesting history, which you should read. Now, all the things that are available on net, you should go and find out.

So, he was doing an experiment, he was putting photographic film under black paper, as you know, photographic film will get exposed in light. So, black paper is used to protect it, he was doing the experiments in darkroom, he was using what, what is called the cathode ray tubes, where the electrons were just like our x ray tubes, which we used for now our X ray diffraction equipment.

So, those equipments had not come, X-ray was not discovered, but he had a metal target on which high energy electrons were heading. And he had photographic films in his lab. And he found that the photographic films despite being in the dark room, despite being covered in black paper, are getting exposed, what is exposing it.

So, when he did careful experiments, then he found that the source of that blackening is coming from his tube. So, something is coming from the tube and hitting the photographic plate and is able to penetrate through the black paper. So, there is something some ray, but it was not known, he could not establish. So, the name X was given to it.

So, what was not known, whether it is arrays, whether it is waves or particles, that was pre quantum days. So, this question was important. Now, of course, wave particle, duality, its photon or its wave. You may this question is not important, but those days this question was important that whether it is waves or particles because things were either waves or particles.




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Q: Are regular shapes of crystals due to regular arrangement of atoms?

⇒ No technique to observe regularity of arrangement of atoms.

1896 : X-ray     Röntgen

↑  
Not known  
⇒ Waves or Particles




regular arrangement of atoms?

⇒ No technique to observe regularity of arrangement of atoms.

1896 : X-ray     Röntgen

↑  
Not known  
⇒ Waves or Particles

Q2



So, then came an interesting character called Von Lave he put he had an interesting insight suddenly, two different questions. Question one are regular shapes of crystals due to regular arrangement of atoms, question two, are X rays waves or particles totally unrelated questions, but in his mind, these two questions came together and he had a postulate he thought optical diffraction was known. So, waves diffract through grating, what is grating?


Grating is periodic spacing of lines periodic scatterers. So, light which is waves through the diffraction grating one dimensional periodicity because lines are only translated in one direction they get diffracted, he had this bright idea that if X rays is a waves and if crystals are periodic arrangement of atoms, so that is also periodic scatterers.

But maybe in three dimensions just like the diffraction grating is periodicity in one dimension, the crystal if it was not known that crystals are periodic, but if crystals are periodic and it was not known that X rays are waves but if X rays are waves, then these waves can be diffracted by crystal in the same way light waves are diffracted by grating.

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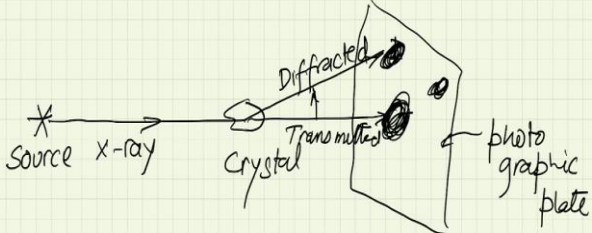
von Lave

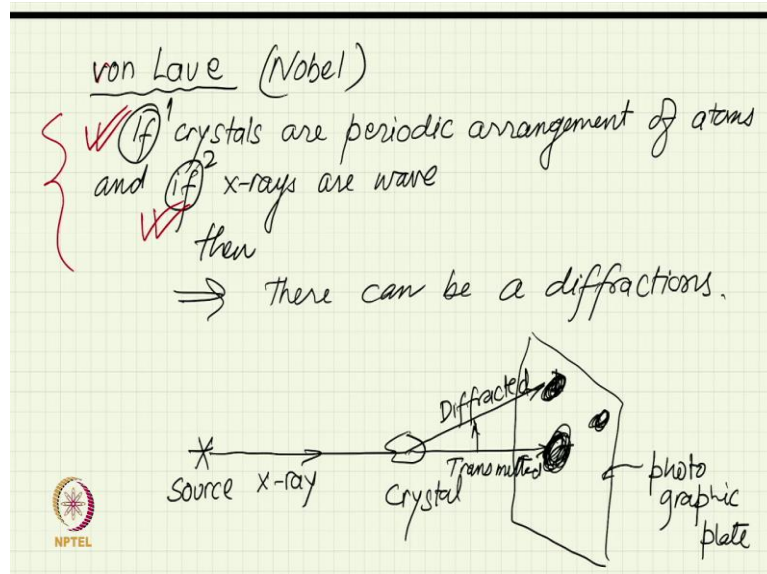
(if)<sup>1</sup> crystals are periodic arrangement of atoms  
and (if)<sup>2</sup> x-rays are wave  
then  
⇒ there can be a diffractions.



von Lave (Nobel)

{ ✓ (if)<sup>1</sup> crystals are periodic arrangement of atoms  
and (if)<sup>2</sup> x-rays are wave  
✓ then  
⇒ there can be a diffractions.





So, if crystals are periodic double if 1 and then f 2, then so, he set up or his collaborators he was a theoretician, so, he had experimentalist to help him, so, that then they set up the first X ray diffraction experiment in the world where a crystal was obtained X-ray source was obtained X-ray source was hit and a photographic plate was kept a technique which is still called Lave technique of X-ray diffraction.

What is the diffraction? If you sign some wave on something, you expect the wave to travel through that something. So, that will be a straight through beam a transmitted beam if everything is not absorbed, you should get a transmitted beam maybe weaker than the original because some is absorbed, but you should expect a transmitted beam. However, if that is all you get, then there is no diffraction.

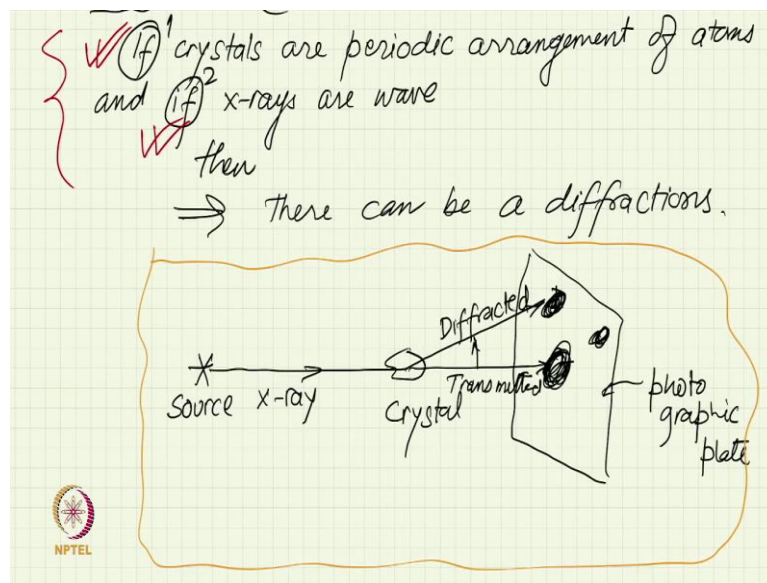
Diffraction means that there is some interaction between the material and the wave to generate beams in direction other than the incident beam other than the transmitted beam. So, if there is been in a direction other than the transmitted beam, that is a diffracted beam. And they set up this expert they were not knowing whether you will find the diffracted beam or not. When they set up the experiment, they did find that there was a large patch in the transmitted region.

But there were patches away from the transmitted region showing that the crystal is diffracting. So, it was a very happy experiment, very lucky experiment for which he got Nobel Prize. Lucky in the sense that diffraction happened so, diffraction happened. So, both the questions were answered in positive because both conditions were required for diffraction

to happen. If diffraction did not happen, then he would not be able to answer any of this question because maybe X-rays wave but crystal is not periodic.

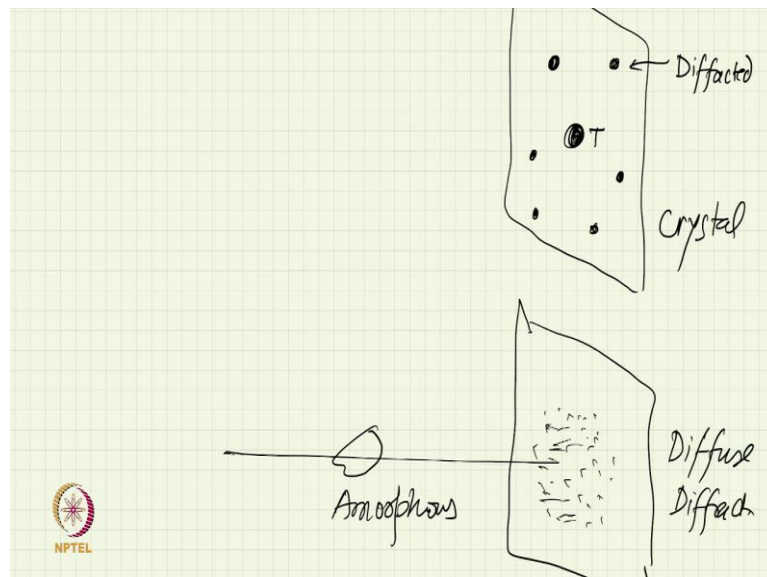
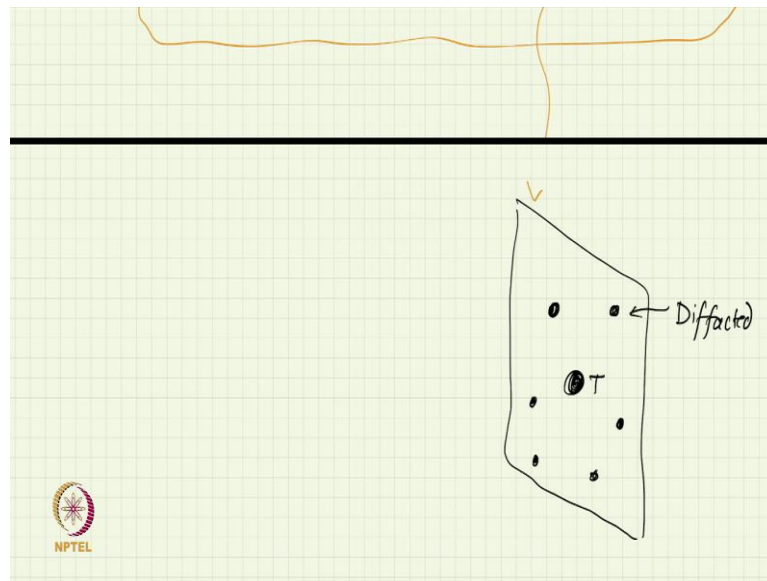
That is why you did not get the diffraction or maybe X-ray is not wave and crystal is periodic. That is why you are not getting diffraction. So, since the he got the positive result, both questions got answered and established that crystals are periodic arrangement of atoms. So, that was the historical experiment. In fact, this is considered to be one of the greatest experiments of all time in science, if you would Google you will find it listed somewhere in one of the greatest experiments of all time.

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And this also providing this also this experiment also provided not only answer to the question that crystals are periodic arrangement of atoms, but also in the experimentalist hand it provided a tool called X-ray diffraction by which to investigate and study those crystal structures. So, the crystal periodicity can now be fine found by X ray diffraction.

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Now, the way I have drawn here the diffraction pattern is a discrete diffraction pattern there is a transmitted beam then there are diffracted beam so this since this is how crystallography began an idea set in people's mind and it is not that amorphous matter do not diffract, amorphous matter also diffract.

If you put an amorphous thing, glassy thing that is also diffract only their diffraction will not be sharp spots, they will scatter also beam, but it will be a heavy, heavy scattering in all place instead of sharp diffraction peaks as in the crystal. So, this idea form that if you see sharp diffraction pattern, it is crystal, if you see a diffuse diffraction pattern it is amorphous.

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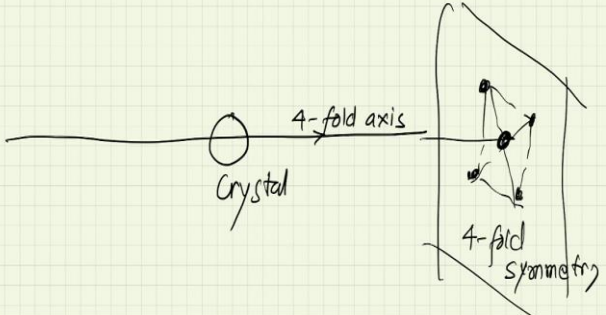
Sharp diffraction  $\Rightarrow$  Crystal =  
Diffuse "  $\Rightarrow$  Amorphous

Crystal  $\Rightarrow$  Diffraction Pattern  $\Rightarrow$  Crystal Symmetry




Diffuse "  $\Rightarrow$  Amorphous

Crystal  $\Rightarrow$  Diffraction Pattern  $\Rightarrow$  Crystal Symmetry



The diagram illustrates the relationship between a crystal and its diffraction pattern. On the left, a circle represents the 'Crystal'. A horizontal line with an arrow pointing to the right is labeled '4-fold axis'. This line passes through a rectangular box on the right that represents the '4-fold symmetry' of the diffraction pattern. Inside this box, four points are arranged in a square, with arrows indicating the 90-degree rotational symmetry between them.




1984 Shechtman Electron diffraction  
in TEM

Al-Mn

Sharp diffraction → Crystal

↓

10-fold                      10-fold ?




Crystal → Sharp Diffraction

Quasicrystal → Sharp Diffraction

Amorphous → Diffuse "

Not Periodic Quasiperiodic Order



And we have also seen that crystal is having symmetry. So, the diffraction pattern of crystal shows that symmetry. So, for example in Lave's experiment in Lave's experiment, if you have a crystal and suppose the beam is traveling along the 4 fold axis of the crystal then the pattern which you will get will also have the fourfold axis. So, you will have a straight through beam and other beams will organize let us say in a squarish fashion having 90 degree rotational symmetry about that.

So, the whole pattern will also have the 4 fold axis. So, people were happy crystals give a sharp diffraction pattern and from the symmetry of the sharp diffraction pattern you can find the symmetry of the crystal. This is where the problem began that in 1984, when shechtman did his experiment and he was not doing X-ray diffraction, but electron diffraction in transmission electron microscopy, microscope TEM.

What he found he was working with aluminium magnesium alloy and he was looking at the diffraction pattern what he found that he is getting sharp diffraction pattern which is indicating that it is crystal but the symmetry of the sharp diffraction pattern was 10 fold and in Shechtman time, this crystallographic restriction theorem which I taught you was well established that no crystal can have 10 fold symmetry and only crystals can give you sharp diffraction.

Now we just stuck with a diffraction pattern which is sharp indicating crystal that there is also having 10 spots regularly arranged 10 fold symmetry. So, in his notebook just he wrote 10 fold question mark and he started wondering about it, often see, now that the PhD scholars, you should be very very careful in if your results are not matching with theory.

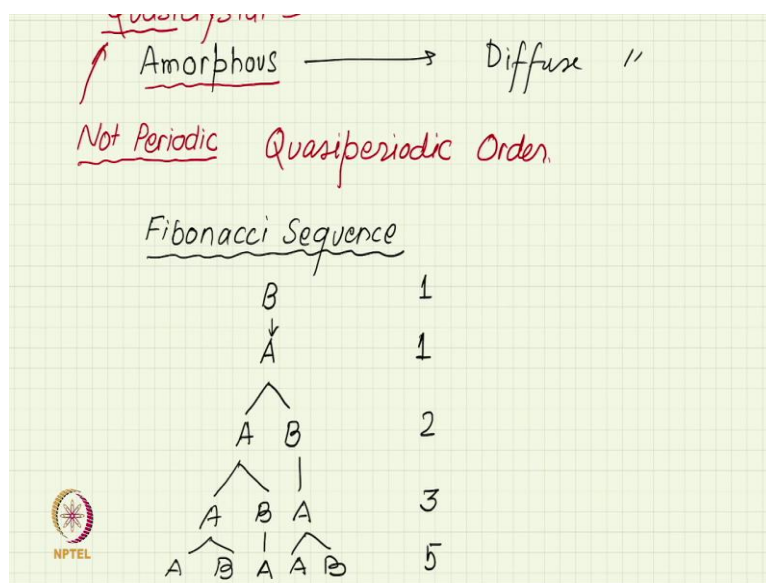
So, this is an example of a result not matching with theory, he could have easily thrown this in a bin kuch gadbad hua bhai ye to log hasenge, my bolunga mujhe 10 fold crystal mil gaya, everybody will say you have a look at your experiment repeat it or do something. So, he repeated the experiment it was repeatable he was getting the 10 fold symmetry.

So, the issue was, so, finally what got established that this logic that only crystal can give you sharp diffraction had to be revised. That and a new class of material was found. So, Crystal gives you sharp diffraction pattern Amorphous with a diffused diffraction but now between crystal and amorphous came Quasi crystal which also can give you sharp diffraction pattern and why quasi because they are not periodic.

Does not, not periodic means random no, amorphous is random no order, but you can have order which is not periodic and what was found that these quasi crystals have quasi periodic order.



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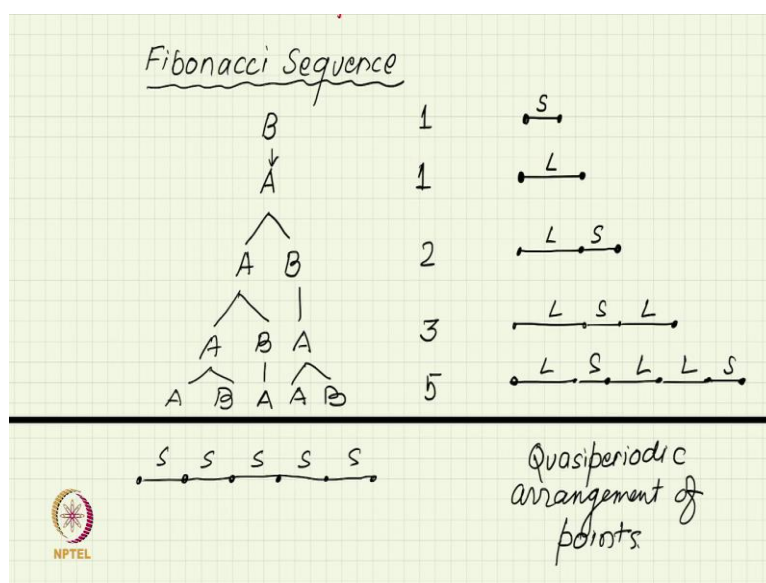


Let me just give you a one dimensional example of quasi periodic order which is very well known in this quasi crystal literature, 3d is more challenging. So, let us start with what is called a Fibonacci sequence. Fibonacci studied rabbit, he said that when he made a model that let us say that there is a baby rabbit in a month time it will become adult and then adult will give rise to a baby.

Then in the next month, again the adult will give rise to a baby and baby will become adult. So, you carry on a goes to AB, if you do not like rabbit or adult or baby, you must already be getting confused and that how a single adult can give a baby or things like that. So, you just can think of a transformation that B transformed to A and A transforms to A and B, a pair.

So, B becomes A in each generation B becomes A and A becomes A,B if you see the number of rabbits or number of these elements, that is what in number theory is known as Fibonacci number. So, you have 1 1 2 3 5. So, every number is sum of the two previous numbers.

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Now, how does it relate to the quasi periodicity in quasi periodicity you can Think of that you have by B you think of a small segment and by A you think of a large segment so, you have two length scales, a periodic arrangement of points has one length scale AA. So, let us say S S S S S. So, this is a periodic set of points all points separated by S, but now, I start making my points separated according to the Fibonacci sequence.

So, wherever I get A I put a long and wherever I get B, I put short, so long, short, long short, long, long, short, long, long, short think of repeating this process I have repeated only 5 times repeating this process for longer and longer iterations, more and more iterations, you will get a sequence of long and short segments is it periodic? It is not periodic you have already seen long short long long short.

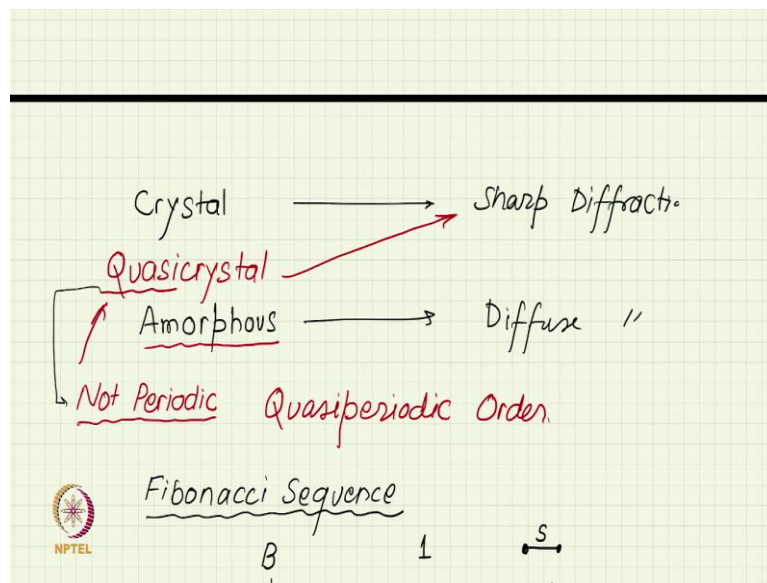
If you had LS LS LS that will also periodic or if you had LLS LLS LLS that is also periodic, but in this process, you will never in this Fibonacci process, you are never assured to have periodicity. You do not have periodicity, but is it random you are getting it by a very systematic mathematical process. So, even in nth iteration, you know that this is what you will get.

Whereas, if I start throwing L and S really randomly by tossing the coin, that head means L and tail means S, then I will get a random sequence of L and S. So, that will be a one dimensional amorphous sequence of points. If L and S are thrown randomly. If L and S are

thrown in a Fibonacci sequence, then it is neither random nor periodic and this is what gives you the so called Quasiperiodic.

So, quasicrystal is a 3 dimensional generalization of this thing. So, instead of a single unit cell, there also they have 2 unit cells and 2 unit cells pack together. And, but their packing is not totally periodic. But it is still they have some, but it is not totally random also, that you do not have any kind of unit cells, you do have 2 unit cells, which are arranged in some particular quasi periodic fashion.

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So, since they are not restricted now, by translational symmetry, so our crystallographic restriction theorem that derived from periodicity, so these quasi crystals are free from the restriction imposed by periodicity. That is why they can have symmetries which are not allowed for crystals.

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arrangement of  
points

Quasicrystals → Not Periodic but Quasiperiodic  
→ Crystallographic Restrictions  
not applicable  
→ Can have noncrystallo-  
graphic symmetry  
→ 5-fold axis.

Al-Mn QC : Icosahedron



In fact, what segments we saw in the diffraction pattern as 10 fold axis was really a 5 fold axis and aluminium manganese quasicrystal was shown to have icosahedron symmetry.