Symmetry and Structure in the Solid State
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Lecture – 31
Interference of Waves

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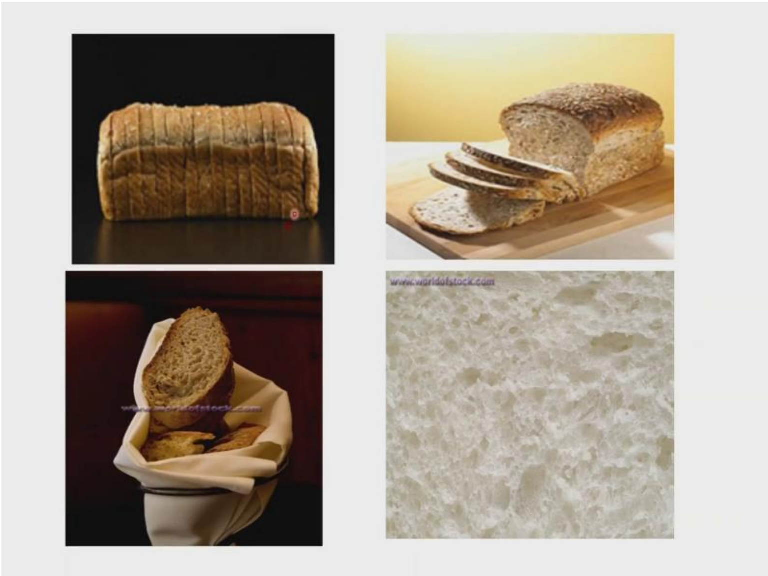

So, we come back to this slide again because this is our bread and butter in the entire course. So, we come back to this slide again. So, this is the unit cell, and we are suppose to find out the contents of the unit cell. So, how did all, how did it all began, and then how this the very beginning of understanding how to determine the structure.

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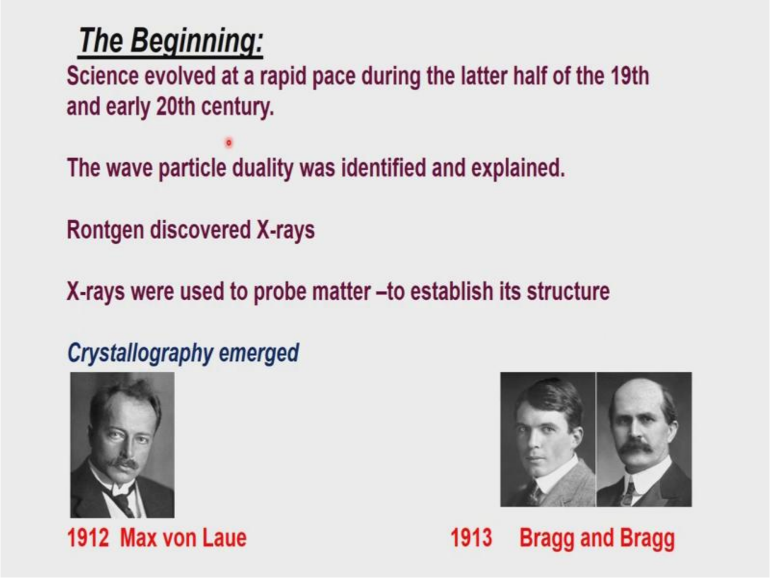

It all started in when the science, what is very interesting is science evolved at a very rapid place pace during the latter half of the 19th and early 20th century. If you look at the way in which science accumulated knowledge the accumulation surprisingly was in the last part of the 19th century and early part of the 20th century and after words it has been slogging alone.

But there was a sudden part in several issues, and one of the major once was that the waves and particles duality that was identified and explained. At the same time Rontgen discovered X-rays and then X-rays were used to probe mater and particularly crystals to establish its structure, and so crystallography emerged. Now, in 1912 Max von Laue, and in 1913 Bragg and Bragg gave the methodologies by means of which we can use X-rays to probe crystals. And therefore, establish the structure, what I mean by structure is now the positions of atoms and inside the unit cell.

So, we will now start to develop the methodology and then understand how this logic came into the existence because we are now having an object which is opaque like a crystal and we want to see atoms inside them. Obviously, we cannot use ordinary light. So, we use X-rays because we know X-rays are of the wavelength of 1 Å , and the size of the atom is also about 1 Å. So, there must be a way in which we can find out where the atoms are, I think that was the thought process these three gentlemen had and we will see how it went.

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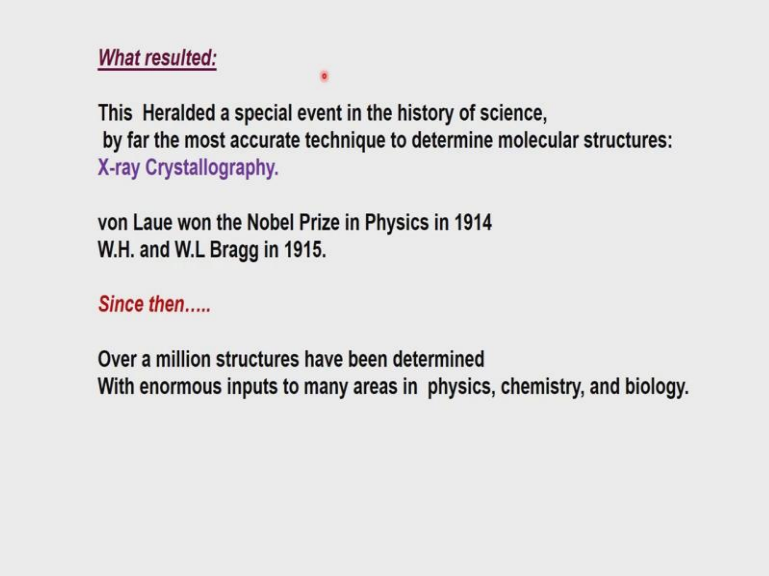

How it has now eventually resulted in. This heralded a special event in the history of science, by far the most accurate technique to determine molecular structures, the area of X-ray crystallography. Von Laue won the Noble Prize in 1914, and the Bragg's won a Noble Prize in 1915. And since then over a million structures have been determined a various sizes, shapes and content, and this has made enormous input to a many, many areas in physics, chemistry, biology, and many overlapping areas particularly of late materials science and nano sciences.

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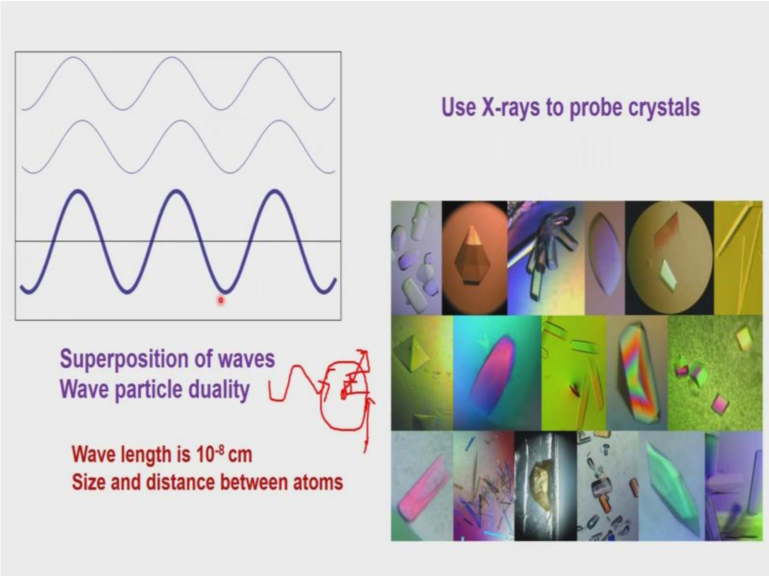

So, we therefore, have to now get an understanding of how all these can happen. Now, we said that when electromagnetic waves come in the electromagnetic waves for example X-rays are associated with a certain wave length. So, a wave is represented in this fashion, it is an oscillating electric field. And this oscillating electric field can go and fall on to the object.

Now, we also said that depending upon where the atoms are inside the unit cell; that means, wherever there is electron density inside the unit cell, the very fact that they are electrons that are associated with the atoms, and these atoms are spherical in shape, where there is a nucleus which is positively charged and an electron which is negatively charged. So, let us write something like an atom. I hope I will be able to do that. So, let me say this is the electron density around a nucleus at the center. So, this is now positively charged, and the electron density is negatively charged.

And so what happens is when a disturbance of this kind we will come in. When we sent in a probe this is the electromagnetic radiation, and now we are thinking about X-rays which are of 1 angstrom in wavelength. They come and fall on this atom wherever this atom is sitting inside the unit cell. Imagine there is an atom in a crystal and that is sitting somewhere in therefore refer to the position x y z. If there is an atom at x y z based on our symmetry and space group determination the definition, the positions of the atoms are already available.

So, if there is an x y in case of a triclinic *P* 1 system. So, there are two atoms and so what happens is this atom now we will see the incoming X-radiation. Now, what happens is that because of the fact that we have positive and negative here, these incoming radiation which is like this we will now fall on this. And then generate a gap between the positive and the negative one. So, in other words, it creates a dipole. This therefore, develops a dipole.

So, effectively what happens is the distance between the nucleus and the electron, the electrons are perturbed. So, electrons go away, but they cannot leave the nucleus and go away. So, you develop a dipole moment. Now, electromagnetic theory says that an oscillating dipole will generates its own wave. So, what happens therefore is that from this particular atom, now another wave starts to come and that wave is shown here as a wave which is moving in.

Now, this particular wave generation depends upon where the atom is inside the unit cell. So, if the atom is somewhere from there the disturbance starts, so the disturbance with associated with this oscillating dipole will start from that point. So, if there are several hundred atoms inside the unit cell, it will start at 100 different positions. So, when such a thing happens, the waves can be the starting point of the wave can be variable.

So, in this case depending upon where that atom is or the set of atoms are these waves now will start. So, this is a let us say the first atom, the first atom wave will now start to appear depending upon where it is sitting. And then this incoming wave is still there. So, these two now undergo what is known as an interference. So, the new wave now interferes with the existing wave and what you get is a resultant wave depending upon where the positions of the atoms are with respect to the unit cell. These waves now can be constructive as you see here or destructive as you see now.

So, we can have intermediate stages as well depending upon the distribution of the electron density inside the unit cell. So, we have the unit cell; we have atoms in different parts of the unit cell. When incoming radiation comes with a certain wavelength that incoming radiation, now meets this electron density surrounding the atoms, and these now therefore the creates local dipoles. So, a large number of local dipoles get created, and each and every dipole now is capable of sending its own electromagnetic radiation because that is what electromagnetic radiation theory says an oscillating dipole generates an electromagnetic wave.

So, that electromagnetic wave therefore, is now coming from different parts of the unit cell depending upon from where it comes we can have either the wavelets adding up or the wavelets subtracting or the wavelets giving rise to some intermediate levels of waves. So, at the end of the diffraction, at the end of the experiment, when it comes outside the crystal, it could be in any of these forms it could be a highly crest to crest competition or a crest to a trough competition, depending upon that the value of the phase, the value of the intensity changes.

We are making an assumption here that whatever is the incoming radiation, the scattered radiation will also have the same frequency. This is a very important point which we must remember that in all of the X-ray diffraction and X-ray crystallographic theory, we will assume that there is no change in the frequency. So, the incoming radiation and the radiation with scatters from atoms inside the unit cell, they will have the same frequency. And this is called coherent radiation or coherent scattering. Obviously, we should be knowing that other kinds of scattering can also occur which changes the frequency, and we are going to ignore that in our discursion.

In fact, X-ray diffraction experiments ignore this change in the frequency, the change in the frequency leads to different kinds of effects. One of them for example is the so called Compton effect. There is a change in momentum and so on in this particular situation where we discuss X-ray diffraction we consider only coherent radiation.

Now, the coherent radiation will be ensuring whether we will have these waves coming in and out depending upon different kinds of positions of the atoms. And therefore, in principle, we will get now these waves coming out of the system. So, when these waves come out of the system, we should have a measure. So, we will keep a detector at the position across this scattering experiment region, and find out what is this intensity or what is the or what is the intensity of these wave, what is the strength of these waves.

So, any wave in this in general is characterized by two quantities; one is the amplitude of the wave they extent to which it goes up and down that is the amplitude of the wave with respect to 0. So, in this case, as you see depending upon where the atoms are, the amplitude is going from the highest value to the lowest value, so that is the amplitude.

Now, the amplitude variation depends upon how the wave up there is interacting with the wave down here and therefore, these depends upon where the origin of the second wave is. If the second wave is starting exactly at this point, you see the maximum let me trace it, when it is starting exactly at this point you get the maximum value here; and when it is starting exactly here, you get the minimum value so that is referred to as the phase of the wave.

So, there are two things which qualify a wave, one is the amplitude of the wave, the other is the phrase associated with the wave. It is so happens that this amplitude which is coming out can be detected on a detector, and the detector measures the intensity. Intensity is proportional to the square of the amplitude. So, therefore from measuring the intensity by taking the square route we get the amplitude modulus of the wave.

However, the phase that is associated with the wave cannot be determined experimentally. And this is the so called phase problem in crystallography. So, we will come to the detail of it later, but what is happening here is that these waves therefore, can constructively and destructively interfere.

And I have shown a picture here a various kinds of crystals that can be artificially grown or can naturally occur and so on. The logic here is essentially that we use X-rays to probe, because X-rays are of the wavelength of 1 Å , which is essentially the size and distance between atoms in inside the crystal. And therefore, that is very useful to see where the atoms are in principle.

So, we measure therefore the intensity of the scattered wave which is coming out in some sense. How do we do these experiments, because you see there is a unit cell the atoms are distributed all over the unit cell of course with obeying the symmetry rules which we have formulated depending upon the space group, we will have so many number of equivalent points. So, the atoms and molecules will follow the alignment and the assignment given to them in terms of the equivalent points.

And therefore, they are not in random positions they are in well defined positions with respect to the symmetry which we have defined that is the advantage of studying a single crystal. In a single crystal the arrangement of the atoms and molecules follow the rules of the symmetry which we have fixed.

For example, the in a case of a space group like P 1 for every x y z we and nothing else. These nothing else is very important because we therefore, know where to relate these atoms which we find out from these experiment to the space group conditions, and therefore, generate the content of the unit cell. So, X-ray diffraction their X-ray scattering is the one which is recommended. Use the word diffraction too early I will define that little later stage.

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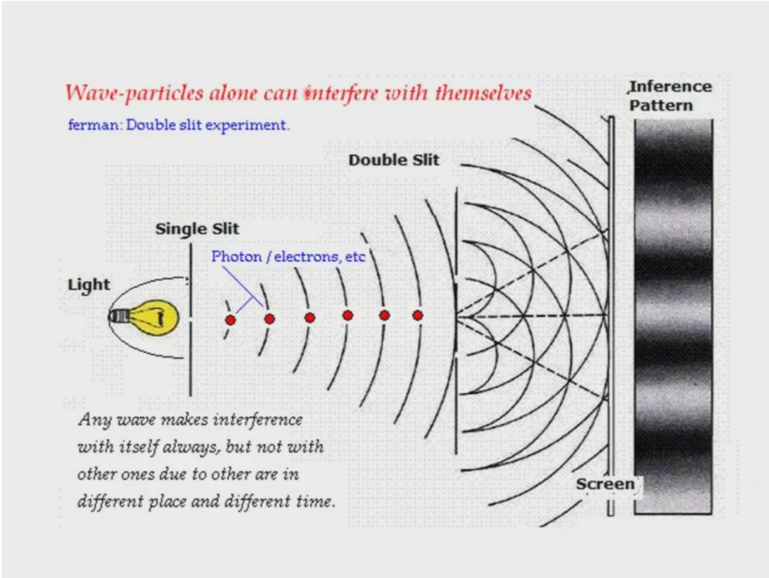

Let us go to the next slide, how is the all this happening, it is all of this is happening because of the following. It is a very simple experiment which can be done with light, in fact this experiment as an analogy which I will draw with respect to crystals in a little while from now. Suppose, we have a light source, and then it has a certain wavelength. The wavelength of the light can be taken as about 5500 Å . Suppose, you take sodium light you know the wavelength of the sodium light.

Now, let us say it passes through a single slit in a screen. So, we block it up everywhere, except that you allow it to go out of a slit. Then from this slit now we will act as though it is a source of radiation, the slit will act as a source of radiation. And the scattering the waves will now emanate from that particular slit point in a spherical fashion. So, the distribution is spherical. So, there is a spherical wave front which comes out of this slit.

So, this slit is now an object and that object generates spherical waves. So, if the in the place of a slit, there is an there is an atom let us say. The atom now acts as a source because we saw that the dipole develops. So, the atom, atom acts as a source of electromagnetic radiation, and it sends out spherical wave front, but at sufficiently very large distances this becomes more or less a straight line.

So, the it is like you know take a stone, and then go to a pond, and throws the stone into the pond. The central part where stone falls into the way into this pond, you will have circle of waves emanating. And these waves become bigger and bigger, and bigger. And if you see at a distance of about 50 feet or so, it will be weaker also, at that the same time you will see more or less it is spreading entire length of the pond effectively it becomes a plane wave.

So, we make an approximation that whenever we do this kind of an analysis where we send an X-rays beam on to the unit cell or a crystal which is consisting of unit cells, the scattering a vectors, the scattering waves will be emanated from each and every atom. And each and every atom will generate a spherical wave front, and these spherical wave fronts move further, and as they go to very large distances they make plane waves.

And therefore, these can be treated as plane waves, mathematically it essentially means that the mathematical equation that can be fitted is exponential i k dot r,[exp (ik.r)] where k is called a wave vector, r is a position vector. We will give more details of that as we go along, but at this moment what is happening is that, if you have a single slit, you get spherical wave fronts coming out and at sufficiently large distances you get a plane wave.

Suppose, at a certain distance instead of very going to very large distances, suppose this little distance later I the so each of these now represent the wave which is coming out of this particular hole which is that of a slit though I will put more than one slit. Then I put more than one slit let us say I put two slits, each and every slit as you see shown here will generate its own set of spherical wave fronts. So, there is a spherical wave front which starts from here, and another spherical wave front which starts from here because these two now are the resources.

So, there are two position sources on this particular screen, and therefore, two spherical waves will start. Now, when two spherical waves will start at this point and they start going up in their position. You see that a similar thing to what is happening here will occur. So, we have this wave which is coming from one source, this is the wave from the other source, and therefore, these two will constructively or destructively interfere depending upon the overlaps of the wave fronts at these positions as I shown here.

So, whenever we have an overlap, we get a bright line; and whenever we do not have any overlaps we get dark lines. And this is the process of interference. So, if you now extended to three dimensions, and imagine that there is a three-dimensional screen with different slits put into that, then we will get this lines converting themselves to spots.

And therefore, we will get bright and dark spots. If you now look at this diagram a little more carefully and say that I do not put these two slits here, I will put one slit up there and one slit up there, then the two slits now will generate wave fronts, but these wave fronts are now different from what is shown here in the diagram because they start from different positions.

Let us say it starts at this position, then this fellow which is shown as a spherical wave front will now be positioned there. And when it is positioned there and this fellows now moved away to this position, that means, the d value the distance between the two slits is increased to higher values. Then what happens is that the number of overlaps that will occur between the two waves will now be opposite, it will now have more parts as you as you increase the distance between these two, we will have more spots or less spots what will you have.

So, I will increase the distance. So, here you had this direction in which you got a line in this case, but you will get a spot in three dimensions you get a spot in three dimension. And whenever there is a intersections occurring you will get light and dark lines here. Now, if we increase the distance between these two what will happen to the distance between those two. You think about it, you think about it. And so what happens is that the d value the distance between the atoms is now increased, in this case let us say this is an atom position, this is an atom position, and light source is now falling over right away on these two are waves which are generated and overlap occurs.

So, what happens to these lines, do they come closer or they move forward is something which you think, I am not going to tell you and that will make you understand the process of interference much more clearly. So, if I can go and give you a hint, the hint is in this diagram. Suppose, in this diagram, instead of this wave coming up here the wave is move to some other position.

So, then what will happen, the intensities will it reduce or increase is a different story, but whether the interference which is occurring between these two will it be same or will it be different, obviously, you know it was going to be different. Suppose, I put these two holes closer to each other then what will happen? If you put the holes closer to each other, these will now spread further.

So, the distance between these lines will become larger, if the holes are closer to each other. If the holes are farther away from each other, these will become closer to each other. So, imagine a ultimate situation, in the ultimate situation I will bring these two these two holes closer and closer and closer and I come to a single position, then what will happen it will go back to this position.

So, if there is a single atom, it will go back to the scattering coming from the single atom. Whereas, when we have a collection of atoms, the collection of atoms when they are very, very close to each other, this distance will go further away, and when they are farther from each other this will come closer. So, there is a inversion associated with this or what we call as reciprocity that is associated with that.

We can see these from a very old experiment we have all done in our school it is a typical high school experiment where we were given a convex lens, and we were ask to find the wavelength of sorry the focal length of this lens. The focal length of the lens we all knew the formula 1 over f equals 1 over u plus 1 over v ($1/f = 1/u + 1/v$). So, where u and v are the distances of the object to the screen, and the object to the sorry the distance of the object to the let us go to that picture.

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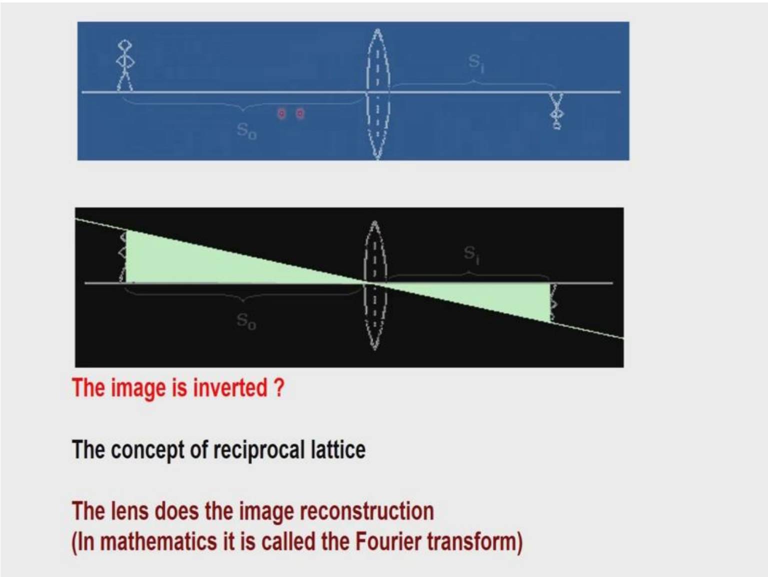

The distance of the object to the lens is u and distance of the lens to the object is v. So, here is a situation where there is an object in this case I have shown a picture. Now, in this picture, now goes to the convex lens. So, lights is scattered from different points on this, and all the lights scattered from different points will generally emanate at sufficiently large distances. It imitates a plane wave which is appeared. So, all these are now plane waves which intersect at this point, and this lens now does the job of what is known as a image reconstruction.

So, this image reconstruction takes place and you get the image of this object. And then you say that the focal length of this lens is 1 over *f* equals 1 over u plus 1 over *v*. And we get the value of *f*. This was a high school experiment which we performed. In this case there is a lot of lesson to learn, one is that light fell on these object and scattered in all possible directions. And these all possible directions were caught in different by the presence of a convex lens, and this convex lens had a good job of doing the image reconstruction.

So, it did the image reconstruction and got as an image. So, what is happening is that these object went through this focus as I see here, and therefore, this is the focus of the lens and you get the object image. And therefore, you see the image of the object gets formed in an inverted fashion to the existing object, and this is brings us to the, what is known as the concept of reciprocal lattice. We will talk about the reciprocal lattice in more detail as we go to the discussion of what happens with X-rays.

We can right now ask a question what happens with X-rays. Suppose, this, this particular person we have shown here has broken his hand. Imagine a situation where he has broken his hand and so we now sent in X-rays on him on his hand ok. So, now, X-rays come and fall here. The wavelength of X-rays is now 10^{-8} Å or in that region angstrom region. And instead of light which was about 5000 Å this convex lens was able to do the image reconstruction.

If X-rays are used and we want to do the image reconstruction, there are two things we will have to do, one is it depends upon the value of the refractive index of the material. So, if the material refractive index in this case of glass, glass refractive index we know the value of the refractive index. So, the refractive index is the one which we will do this job of reconstruction, and so we get an image of the object.

Suppose, we are sending in an X-rays beam here then again it will be scattering in all directions, but in order to find it to focus and bring it to a focal length (Refer Time: 25:14), we will have to make the lens slightly bigger than the size of the earth. So, it will be a very huge lens if at all you make it from glass, and it will be slightly bigger than the size of the earth, so it is almost impossible to make it.

And the image will be form somewhere far away in space, you will get an image you will get the broken and indicated in this inverted image, but then you have to go somewhere in space, use ISRO's newest launches, and then go there in space and see whether you can get an image. So, effectively this experiment is impossible to perform.

Imagine a situation where you have kept a crystal here. So, each and every point in the crystal now becomes a scattering point depending upon the positions of the atoms inside the unit cell, sorry, it is the atoms which do the scattering; it is not the crystal which does the scattering. It is the atoms which do the scattering, it is the electron density associated with the atom which will do the scattering.

So, therefore, this scattered electromagnetic waves will come in all possible directions. So, we have to therefore find some ways and means by which we can do the image reconstruction. One of the advantage disadvantages we will further have if we really do this instead of bringing in an a convex lens, we do mathematically, we do what is known as a Fourier transform.

If we do a Fourier transform, then it is in principle possible to construct the image of the object. However, if you want to do that operation, we should know the phase angle of each and every wave which is emanating. Unfortunately, the way in which we are doing the experiment, we are actually stopping the out coming radiation and measuring its intensity. The intensity has given us the amplitude of the wave to determine the phase then we should know where the atoms are and that is our job anyway.

So, since in a unit cell we our job is to find where the atoms are. And if you want to know the phase information, we should know where the atoms are, these becomes an unsolved problem. And so we therefore, have to worry about how to determine the phases.

This is a very big issue which will be taken up later on when we actually discuss the determination of the structures. At this moment there is no convex lens that is why we are having this course; otherwise if we had a convex lens of a suitable kind we could have got the image of the object, and therefore, seeing these atoms inside the crystal that experiment unfortunately cannot be done now.

So, instead what we do therefore is to do it mathematically, but we do it mathematically we use the Fourier transforms, what to do the Fourier transforms we need desperately need the phase information. The phase information is not available, because we know do not know where the atoms are. Here we know where the hand is, where the where these and so on in these object, but in the case of a unit cell and the crystals inside containing electron densities, we do not, so that is why we have a problem. And this particular problem we will discuss in the future classes.