

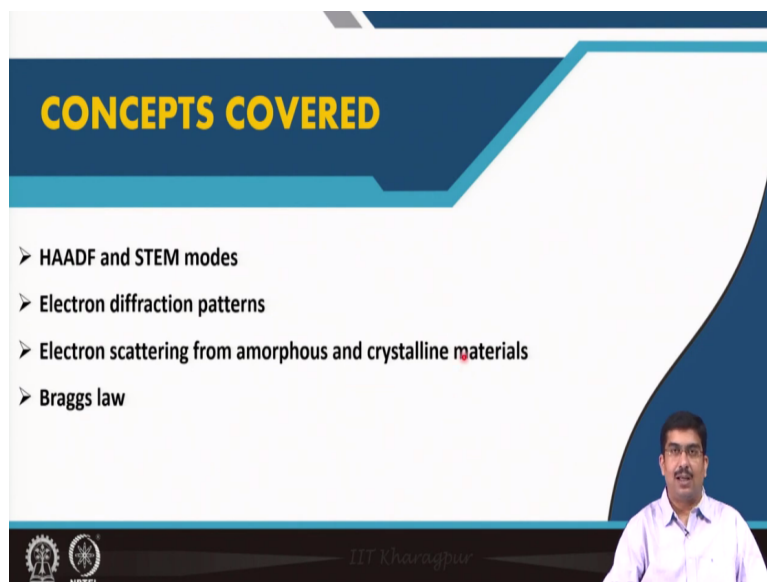
Techniques of Material Characterization
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Lecture – 19
Modes of TEM (contd.) & Electron Diffraction in TEM

Welcome to this NPTEL online certification course on techniques of material characterization. We are in week 4 and we are discussing about transmission electron microscopy. So, in the previous classes we have discussed various ways of contrast generation in TEM and then we discussed about bright field mode and last class we discussed about dark field mode and there we discussed another way of contrast generation, another source of contrast generation that is diffraction contrast.

And we just started with special type of dark field mode that is high angle annular dark field HAADF mode and we will be continuing HAADF and another important mode of doing TEM that is STEM and we will start another very important aspect of TEM that is electron diffraction.

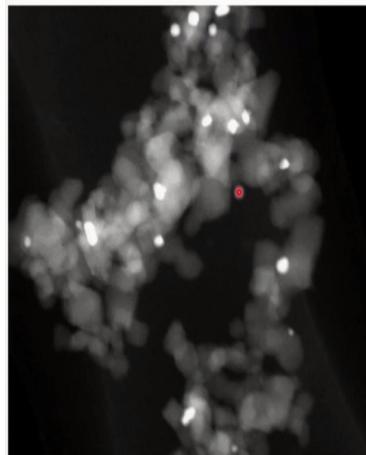
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So, the topics we have for this lecture is HAADF and STEM modes, electron diffraction patterns and electron scattering from amorphous and crystalline materials and Bragg's law.

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High angle scattering: HAADF mode



HAADF-STEM image of Au particles (bright) on TiO₂.

- The Coulomb interaction of the electrons with the positive potential of an atom core is strong.
- This can lead to scattering into high angles (designated as Rutherford scattering).
- The probability of such scattering events rises for heavier atoms, i.e. atoms with a high number of protons and consequently a high atomic number Z , offers the possibility for obtaining chemical contrast.
- Areas or particles containing high Z elements scatter stronger and thus appear bright in images recorded with electrons scattered into high angles.



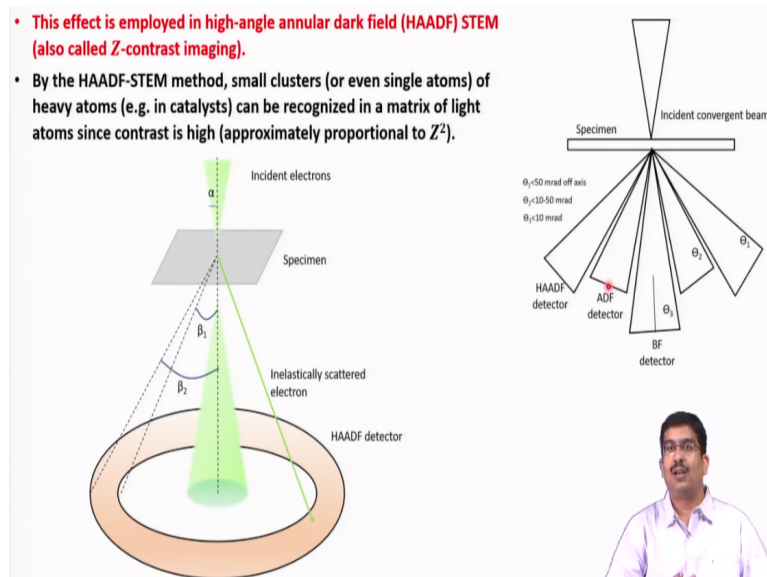
So, we will continue with the HAADF mode and HAADF mode as I said comes purely out of Coulombic interaction from the electrons with the positively charged nucleus and what happens in this case is that if the nucleus is very heavy then the Coulombic interaction will be much more that will increase the possibility of high angle scattering, the electrons will be able to scatter at a much higher angle if they are scattered by positively charged nucleus compared to the electron clouds.

So, of course if the positively charged nucleus is heavy that means it is related to the atomic number. If higher atomic number in certain regions are having elements which are of very higher atomic number so then that will make the nucleus to be much heavier than the other regions which has much lighter elements then this high angle scattering electrons, the amount of high angle scattered electrons will be much higher from those high Z or that high atomic number element region (()) (02:38) which are containing higher atomic number elements.

So, this is what will generate the contrast if we are able to capture that high angle scattered beams then this is what will form the contrast purely based on the element atomic number difference. So, we have seen some one example of this where gold particles are supported on titania support and this gold particles being very heavy will produce much higher scattering for the electrons will produce much higher number of high angle scattered beams.

And that is why those regions will appear much darker in the high angle HAADF mode because here we are capturing the high angle scattered beams only. So, this is another source of contrast generation.

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And the advantage of this HAADF mode is that in this case we are just capturing the high angle annular or high angle scattered beams. So, the number of such beams is very low. So as such the difference of high angle or difference of element the major source of contrast generation here is the atomic number difference in the material the element difference or atomic number difference is the primary source of this contrast generation.

And the number of such electrons will also be quite less. So, altogether what will happen in this case this is like dark field mode as such it is a contrast enhancement mode and this HAADF mode will even much higher will enhance the contrast will amplify the contrast difference to a much higher extent. So, we can possibly get a pure mass or pure atomic number contrast.

And can avoid the inherent mass thickness contrast in the HAADF mode because we are capturing the high angle scattered beam which are primarily forming because of atomic number higher atomic number elements. Number of electrons are less so the total intensity is less and now since the intensity of the entire beam is less the difference between regions with different atomic number which also be much higher.

So, this is why HAADF mode is a very special mode in dark field imaging and that can give you almost pure atomic number contrast that is why sometimes the HAADF mode is also called the Z contrast imaging and in this mode what happens is the contrast that you finally get, the intensity that you finally get is almost proportional to Z square so that is why. So, if you have even a little difference in the atomic number within your specimen different regions have elements with a little difference in their atomic number ultimately the contrast that generates in the HAADF mode is just multiplied just magnified by orders for magnitude by square because in this case it is in square Z square.

So, the way you do it here it is explained the way you do it you have the incident beam, you have the specimen and this is the direct beam and direct beam of course gets scattered to a little extent plus you will get a very high angle of scattering by the positively charged nucleus and if you place your detector HAADF detector this is an annular detector this is like a satellite detector that is why it is called annular dark field annular mode ADM.

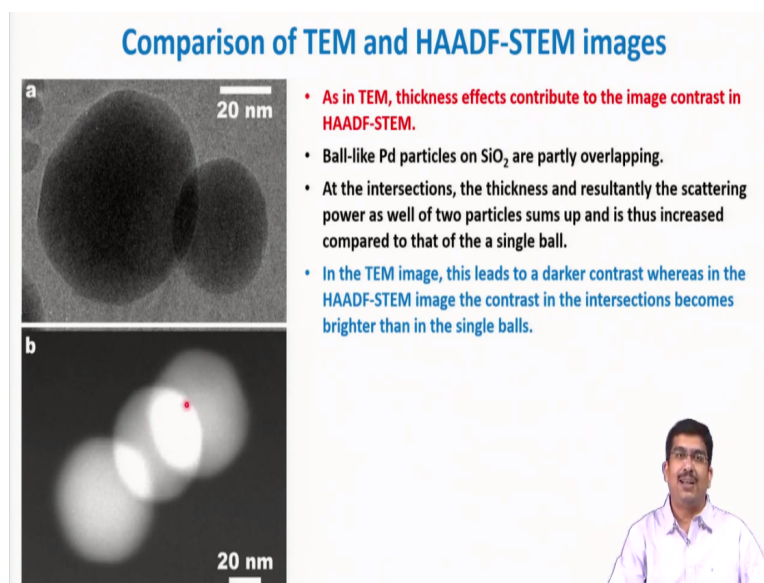
So, this annular detector if you put on the pathway of the direct beam and you do not capture any part of the direct beam here, you just capture all this high angles scattered electrons within a range because this has a finite size, the detector has a finite size so it will ultimately capture this finite range of scattered high angle scattered beam and that is how you will be able to get this HAADF images.

Just understand one thing that the definition of ADF detector annular dark field detector and HAADF detectors depends on basically what is the solid angle that they capture that is it. So, all of them are annular detectors only this ADF detector and HAADF detector are annular detector with the same kind of circular shape, but the main difference here is that the kind of solid angle they cover HAADF detectors covers much higher solid angle compared to ADF detectors.

So, ADF detectors also gives you contrast depending on the atomic number, but there this chances of superimposition of mass thickness contrast with the atomic number contrast is

much higher HAADF mode it is almost a pure atomic number contrast that is the importance of HAADF detector.

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Of course sometimes what happens is even in the HAADF mode the mass thickness contrast does arise. So, we have to be very cautious about that for example when you take this region this images one this is taken in a normal TEM mode in the bright field mode and this one is taken in the HAADF mode and this is for a palladium particles on silica support. So, basically HAADF mode is mostly very popular for catalyst research all of this earlier image that you see gold particles on titania.

Now you are seeing this palladium particles in silica these are all kind of all of these are catalyst for different chemical reactions and in those cases the catalyst in case of catalyst research in order to identify the true nature of this element as a function of the spatial distribution is very, very important because that somehow related to their efficiency finally in the chemical process.

So, the special distribution for those catalyst in order to know them it is very important that you normally image them in a HAADF mode and often what happens is that the atomic number difference between the support and the catalyst that is there is quite less. So, you will not be able to detect them with proper atomic number contrast you will not be able to detect them under normal bright field mode or dark field mode.

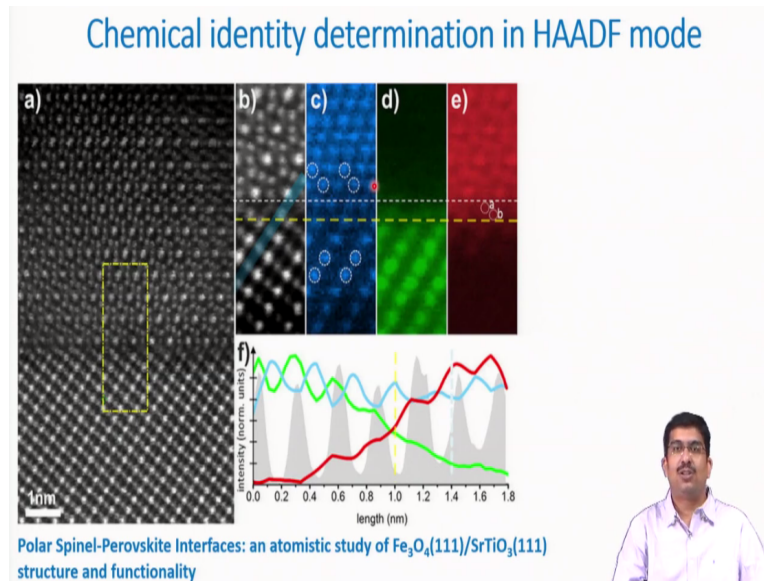
So, you tend to go to this HAADF modes for catalyst generally. So, here what happens is that you have this two palladium balls and certain regions you will see where this appears quite dark and if you look at the STEM HAADF STEM image those corresponding regions occurs at a very bright contrast. So, if you do not understand this you may wrongly interpret that this regions may contain some other element which is even higher atomic number.

But actually what is happening in this case is this palladium balls are possibly this one ball is overlapping one cluster is overlapped on another cluster. So, this regions the thickness contrast is also active so in this region that is why this regions this numbers of scattered electron high angle scattered electrons this is contributed by this palladium particle and the palladium particle which is on top.

So, that is why you are getting much higher, much brighter contrast here and that you can make you just by looking at this regions where the contrast is almost similar to this where you do not have anything else in the behind this one so those are the regions. So by looking at this you can possibly able to identify that this regions is coming out of thickness contrast not exactly a atomic number contrast.

So, you have to be very careful while interpreting this kind of HAADF images thickness contrast still can come, but it is now the source of that thickness contrast is basically overlapping of these two particles.

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Finally another very important application of this HAADF mode is that it can be used to identify the chemical nature of certain regions in the microstructure. For example, if you look at this study where they have done spinel perovskite interfaces it is almost like you have this one spinel phase and one perovskite phase in this and this is your spinel phase, this is your perovskite phase.

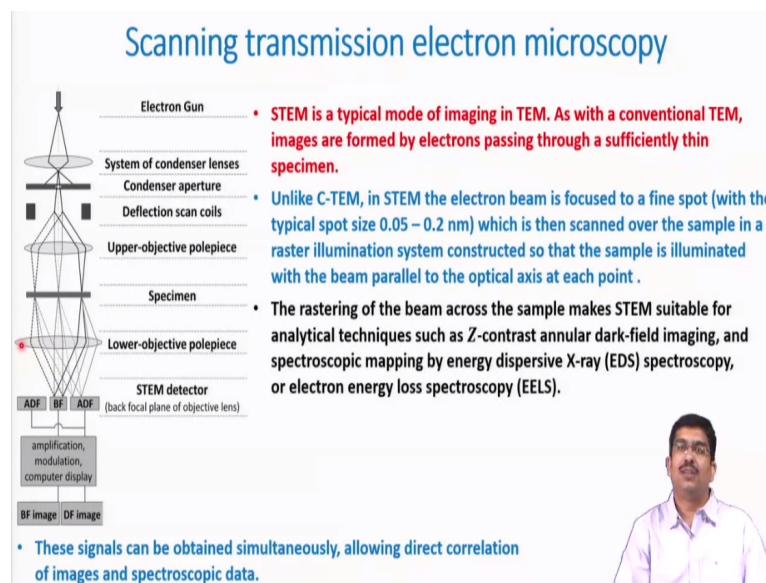
And you have this kind of number one you can go down all the way go down in the HAADF mode all the way you can go down to atomic scale atomic regions because your resolution is very, very high in HAADF mode that too if you are in HAADF STEM mode we will come to STEM mode the resolution you can nearly get a atomic kind of atomic resolution. So, these are basically representing atomic columns you can look at the scale bar these are representing the atomic columns here.

What you are doing is you are basically taking a part of this interface and trying to check the chemical identify of this different atoms and how you are doing that you are basically looking at the intensity of the beam that is coming out. The intensity of the high angle scattered beam. As I said that intensity here is generated by the high angle scattering and that is related. So, I am not going into theory, but this intensity of this beam you can relate it to the atomic number of that element.

So, if you somehow calibrate these intensities and you can relate it to the corresponding atomic number of those chemical species is present. You can exactly identify that which of these atoms are basically what is the chemical nature of that atom whether it is from iron, whether it is from strontium, whether it is from titanium and so on. So, in this way you can find out that not only this is an atomic scale image

But with this chemical information about these elements or these atoms which you are imaging so that is another added advantage of this HAADF mode. You can identify the chemical nature of those contributing elements or contributing atoms in the atomic scale.

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So, this with the HAADF mode now we are moving to the last mode to discuss in the imaging and after this we will move to electron diffraction. So, this is purely another mode scanning transmission electron microscopy STEM often you will hear that STEM mode. This is not exactly similar to dark field or bright field mode, this is not exactly similar to contrast generation, HAADF mode or so.

This is a way of doing this TEM a way of doing a regular TEM, way of operating the regular TEM. So, in some sense the STEM it is a mode and it is there in any regular TEM conventional TEM. So, in this case also this you name exactly the same setup, you need the small thin specimen. You have the condenser lens, you have objective lenses everything remains the same.

The only difference that you have here unlike a TEM is this that in a conventional TEM you are forming the direct image. So, you are using the entire beam whether it is in dark field, whether it is bright field does not matter. So, you are using the entire beam to form the image just like in optical microscope it is a direct image. So, the entire region, entire beam whatever regions this electron beam is seeing on the specimen is getting imaged.

Projected magnified of course, but it is ultimately that part of the specimen which this beam is seeing ultimately that is what forming the image. So, that is why it is called a direct image (()) (14:24) conventional TEM. In this case what is happening is that you are operating or you are making this TEM beam to raster over the specimen and forming the image pixel by pixel or a similar mechanism like scanning electron microscopy which we will discuss in scanning electron microscopy.

We will have a discussing about this rastering and how it is done and so on and so forth, but in this case it is similar method what you do is that you focus this electron beam to a very fine spot unlike a conventional TEM where the spot size is much bigger than this STEM mode. Here, the spot size is very, very less almost in the atomic dimension you can see that the highest diameter that you have is nearly 0.2 nanometer which is 2 angstrom which is almost atomic separation distance and you can go to even down that.

So, for that of course you have to do not confuse this with the resolution because you still have the aberration (15:18) problem so those are restricting your resolution anyway. This is just purely the beam size. So, the beam size you make it very, very fine and then what you do is that you make that beam to raster over your specimen tool to make it fall at different, different places.

And then your image finally the image that you are forming is also you are doing it pixel by pixel. So, that is what the typical STEM mode in this case and also this beams are this fine beams is rastered in a way that finally this beam is always parallel. So, you are illuminating the specimen with this very fine spot beam electron beam as a parallel to the optical axis at each point.

So, each of this scanning point the beam is parallel you are just making it to raster on the specimen that is it. The advantage of this STEM mode is that in this case you can get number one a very good Z contrast by using annular dark field imaging you just use an ADF detector and you can get a very good Z contrast mode and at a very high resolution because of this. So, similar in a way this is quite similar to the STED mode that we discussed in case of an optical microscopy.

In the STED mode we were improving the resolution by making the beam to be very small making the optical spot there we are using fluorescent effect and the spots were much finer than the beam and that is how we were increasing the resolution. In this case also STEM mode we are increasing the resolution by making this beam very small and then covering a larger area by using the scanning mode.

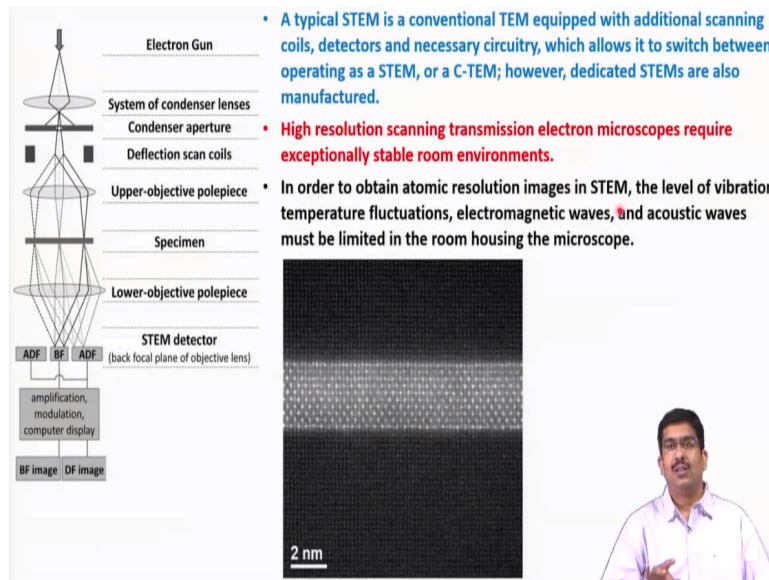
Same kind of principle almost similar type of approach and in the STEM mode and the STED mode. So, the STEM mode you can use it for Z contrast annular dark field imaging you can also use it for spectroscopic mapping because when you are making the beam fall on certain region in the specimen you will be generating some secondary signals inelastic scattering because of the inelastic scattering you generate secondary signal even in transmission electron microscope.

So like you generate disperse x-ray energy dispersive x-ray signal EDS spectroscopy you can generate or even you can get an electron energy loss spectroscopy these are the modes we are not discussing EDS we will discuss during SEM,, EELS we are not discussing basically you are keeping a detector in EELS mode what you do you keep a detector even after the fluorescent screen.

And there you capture the electrons and then you determine the chemical nature of the electrons by the amount of energy loss. So, you know the energy of the electron before they hit the specimen, we measure the energy at after they are coming out of the specimen and from the energy loss you basically identify the chemical nature of the specimen that is what you do in EELS.

And in this mode since it is in scanning way you can map the entire region. So, not only you can use it for imaging you can also use it for mapping the certain regions in your specimen with a chemical identity. So, that is the advantage of this STEM mode.

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Of course in STEM mode for doing the STEM mode what you need to have additionally in this conventional TEM within the conventional TEM what you need additional attachment is a scanning coils and we have discussed about scanning coil similar kind of scanning coils, but of course here it is a much stronger one because you are dealing with a 100, 200 kV electrons which are much more energetic.

So, in order to deviate them, in order to make them scan that scanning coil has to be much more powerful than an SEM scanning coil. So, that is the difference otherwise those scanning coils are exactly having the same kind of purpose, same kind of construction as compared to the scanning coils we have discussed. So, similar kind of construction for both SEM and STEM mode.

And normally this STEM mode is always kept in conjugation with the conventional TEM so you can either have the bright field mode, dark field mode direct imaging and then you switch to the STEM mode where your scanning coils comes into play and you can raster this

one, but in recent times because of the advantage of this very high resolution the dedicated STEM systems are also getting available.

And most often this dedicated STEM systems has much more aberration corrected lenses, you can go for HAADF, you can go for HAADF STEM mode and you can get something like this kind of an image which is taken in a HAADF STEM mode, the image that I showed you in the first introductory lecture this is an HAADF, STEM image and here you can see that this images are almost having atomic resolution plus the chemical identity.

So, from this you can know that what is the chemical identity because it is taken in a HAADF mode and since it is taken in a STEM mode you can almost get and resolution close to the atomic separation of this. One problem with the STEM mode is that this high resolutions STEM mode is of course very exceptionally stable room temperature because this is very sensitive to vibration.

So, if you want to do STEM you have to make sure your entire room is completely vibration free and that level of vibration free is very, very difficult to achieve then it can also get affected by temperature fluctuation, it can get affected by electromagnetic waves because then what happens is basically the beam rastering is a big problem and any small little even if you clap in front of the electron microscope then the beam just gets disturbed.

And then you will be losing this scanning rastering and there will be some problem. So, even normally the stem very high resolution work when you do those microscopes are completely separated even the operators do not sit in front of them it is remotely operated generally such high resolution STEM systems. So, electromagnetic waves is another problem because we are dealing with electromagnetic lenses, electrons are charged particles.

So, electromagnetic shielding is a very big issue in case of this high resolution STEM and then acoustic waves also must be the sound waves also can interfere with this working of this STEM microscope so that also need to be stopped. So, altogether making the room ready for STEM images is really a difficult one and can cost almost quite comparable amount of that

machine itself. So that is real big challenge to make the rooms ready for housing such microscopes.

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So, with this we stop our discussion about imaging in transmission electron microscope and now what we will be discussing is electron diffraction phenomena in electron. So, many of the concepts here what we discuss is equally applicable to x-ray diffraction. So, we will not repeat those concepts and we will be wherever those concepts comes we will try to focus on the general nature of it.

I will try to discuss even with a x-ray with the perspective or x-ray diffraction there, but we will be sort of restricting mostly to the electron diffractions with our this discussions.

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Electron diffraction pattern

- An electron beam which has passed through a thin specimen contains two components: elastically scattered electrons and inelastically scattered electrons.
- **Electron diffraction pattern: Spatial distribution of the scattered electrons.**
- **It helps to deduce information about the arrangement of the atoms in the specimen.**
- To explain diffraction, regarding the electron as a particle is not sufficient and its wave properties must be taken into account.

Now electron diffraction pattern. So, first of all what is electron diffraction pattern. So, whenever electrons we have already understood whenever electrons passes through the specimen there are two different thin electron transparent specimen. There are two different kinds of interaction happens elastic interactions and inelastic interaction and for all matter electron diffraction has everything to do with elastic interaction or elastic scattering.

Inelastically scattered electrons are not useful for the diffraction purpose. The primary reason for that is this the diffraction or the entire diffraction phenomena needs of it depends on the interference of electrons where you need to know basically the wavelength of those incoming electrons and the phase of these electrons. So, any change if inelastic scattering is happening then this λ .

This wavelength of electron, phase of the electrons will completely change and will not be in coordination. So, the interference will be completely quite random if there is inelastic scattering involved only inelastic scattering the energy does not change only it is a direction of this electron change. So, wavelength does not change phase can change, but wave length does not change.

And diffraction is all about the wavelength of the incoming electrons (24:15) we will come to it when that then it would be making more sense, but just remember that diffraction is purely and about elastic interaction or elastic scattering. So, electron diffraction patterns is basically

you can give a definition that it is showing the special distribution of the scattered electrons and scattered electron beams only part of the scattered electrons which are scattered at a typical angle with a special type of relationship with the incident beam.

Those electrons spatial distribution of those scattered electron which are having a special relationship with the incident beam. So, if you capture that then that is what is the diffraction electron diffraction pattern. So, we already discussed about this when you have a diffraction grating you have the direct beam which is the 0th order beam and then you have all other first order, second order, third order diffraction beam.

And if you capture this diffraction beams here then you will be able to get something called this electron diffraction pattern. This is a electron diffraction pattern from a single crystal of sodium chloride the way you capture this basically you have this objective lens and you are putting your imaging plane on this back focal plane of those objective lenses then you will be getting the electron diffraction pattern.

Now, if you keep this imaging plane here what you will be getting is the image. Here, this beams are getting diffracted beam and direct beams these are getting focused on this back focal plane whereas here they are mixed. So, this will form this mixed beams are getting focused here. So, this is the imaging plane and this is the diffraction plane. So, normally in an electron microscope this lenses are electromagnetic lenses.

And the imaging plane is fixed the fluorescent screen is fixed what you do is that you just change this focal length of the objective lens or projector lenses and all you change basically the focal length and from there you switch between the diffraction mode or you capture either the diffraction pattern or you capture this imaging it is just a matter of putting some switches or clicking some options in the software.

And you will be basically changing this focal length of the objective lens and projector lenses and all other lenses to system and you will be either seeing this diffraction you will be either seeing that back focal length of the objective lens or you will be seeing this imaging plane

here. So, that is how you can capture the diffraction electron diffraction pattern and they will basically look like this how to interpret them we will be discussing here.

And one thing you must remember is that for electron diffraction what the electrons need to be considered as wave there is no particle nature it is not of any importance in the discussion of electron diffraction. So, it will be the wave nature of the electrons will always be considered here.

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Scattering of electrons

- Solely incoherent scattering of the incident, nearly coherent electrons takes part if the scattering centers are arranged in an irregular way, especially in amorphous compounds.
- Although the scattering happens predominantly in forward direction, the scattered waves have arbitrary phases in respect of each other.
- An enhancement of the wave intensity because of constructive interference in certain directions can not happen.

Crystalline **Poly-crystalline** **Amorphous**

The slide features three diagrams of atomic arrangements: a regular grid for crystalline, a cluster of smaller regular grids for poly-crystalline, and a disordered cluster for amorphous. A small inset image of a man in a white shirt is visible in the bottom right corner of the slide area.

Now scattering of electrons of course how it happens if we imagine three different type of materials. We have the crystalline material, we have the polycrystalline material which is just a variation of crystalline material and we have the amorphous material. So, the main difference between them is that in case of a crystalline material all these atoms are arranged in a particular way.

Polycrystalline material is just as I said basically the same thing, but different regions are arranged in a different manner just that, but the arrangement is still there, amorphous material this arrangement is very, very random that is the basic difference between a crystalline, polycrystalline, amorphous material. So, we will just concentrate on crystalline amorphous material here.

So, what happens is that let us say an electron beam hits this crystalline material versus an electron beam hits this amorphous material here and those electrons which are hitting here they are nearly coherent electrons or they are perfectly in phase all of the electrons have the same wavelength, all of the electrons are having perfectly in phase and they are just hitting this atoms now.

And atoms are working now as a scattering center. So, if we concentrate on this amorphous material if we just think about this amorphous material. Here, the scattering centers are arranged in a completely random manner. So, this atoms the distance between the atoms is very random it is varying over a range, their arrangement, their environment everything is very different.

So, what happens is that once the scattering happens elastic scattering happens from them then the scattered waves that is coming out of it or the amount of scattering the direction of scattering all of these things is very, very random is case of this amorphous material. So, in electrons maybe hitting when they come and incident on this amorphous material they are nearly in phase, they are all coherent, they are in phase.

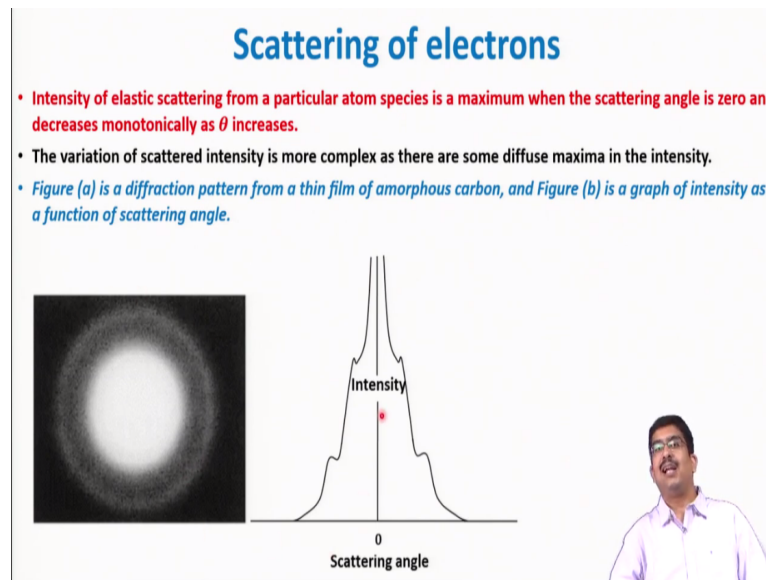
But after they are scattered from here they maybe in phase, they may be out of phase also most obvious is that they are all out of phase, but in the forward direction of course some part as we already understood that some part of the incident electron will pass through without having any kind of interaction that will form the direct beam. So, along those directions of course what we can have is that most of the scattering will happen environmentally in that direction low angle scattering we will have.

But still the scattered beams can have arbitrary phases either with respect to each other or even with respect to the incident electron that is the transmitted electron direct. So, they may be having quite arbitrary phases. Now, if we consider certain particular directions with respect to the incident direct beam any particular direction those electrons the electron scattered along those particular directions because the scattering centers are now completely random orientations.

These electrons will have some different type of phases. So, they will not have all those electrons will not be having same phase along any of the directions. I cannot have all the electrons if I choose let us say 30 degree with respect to the incident beam at the scattering direction 30 degree with respect to the electron beam. I cannot ensure that all the electrons which is scattered at this 30 degree are in phase because the scattering centers itself are arranged very randomly.

So, the constructive interference along certain particular directions is not possible it is very less along that.

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What it will happen what then in such situations what we can expect is that in from a random arrangement for an amorphous material the scattering angle, the maximum intensity if I take the intensity of the scattered beam, if I take the intensity of the entire beam. So, at scattering angle zero that means the direct beam the transmitted beam direct beam there the intensity will be the maximum.

And rest of the positions the intensity should decrease with the scattering angle as the scattering angle increases we already see that the low angle scattering probability is highest and higher angle scattering probability is slowly it is getting lower and lower. So, the intensity also correspondingly will decrease. So, at scattering angle zero that is the direct beam the intensity should be the highest.

And the rest of the places the scattering intensity should be with as a function of the scattering angle the intensity will go down monotonically. So, intensity of the scattered beam should decrease monotonically with the scattering angle, but the point is this is not what we see even from an amorphous material. If we take this intensity if we just take a diffraction pattern or the intensity of the scattered beam.

As I said diffraction is nothing, but the special distribution of the scattered beam. So, if we take this scattered beams and if we take them on a plane and just take the intensity if we just taking the intensity means over a line we are integrating this entire diffraction pattern over a line we are taking this, we are getting this intensity. What we will see that even from a very amorphous material like this one is taken from amorphous carbon.

The intensity is of course highest at the zero scattering angle at zero theta, the scattering angle intensity is highest that is the direct beam and then intensity of course decreases with intensity scattering angle, but we still have at certain particular scattering angles we have diffuse maxima. So, those regions the intensity is suddenly higher than the corresponding the regions next to them.

So, it is not really a monotonic decrease in intensity with scattering angle. There are diffused maxima present at certain particular scattering angles and those are the scattering angles where diffraction is happening that means there is some kind of a constructive interference happening even for an amorphous material and this itself says that even in the amorphous material.

Our basic assumption here that this amorphous material is completely random is not true. At certain length scale even the amorphous materials are having some regular arrangement of this scattering centers and this is why it is finally showing even in the diffraction pattern it is finally showing some diffuse maxima and basically this diffused maxima if you look at here this diffused maxima is coming out of this circle.

So, rest of the portion if it is a continuously decreasing with scattering angle. So, I will have the most intense direct beam and slowly, slowly, slowly, slowly the intensity should go down, but here I am seeing that even after the direct beam I am getting another circle, another region which is quite intense compared to the next region next to it this side it is black and this side also there is a black region suddenly I get some amount of intensity here.

So, this diffuse maxima proves that some relationship exists between this scattering angle and the incident electrons. So, some directions there is a chances of constructive interference happen even with amorphous material. We will stop it here and in the next classes we will be discussing about the scattering from crystalline material and then we will move to Braggs law and so on. Thank you and good bye.