Techniques of Materials Characterization

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Lecture – 24
Electron Diffraction in TEM - Continued

Welcome all to this NPTEL online certification course on techniques of materials characterization. We are in week 5 and we are discussing about transmission electron microscopy. So, mostly we are discussing about electron diffraction in TEM and we have discussed so far about various concepts, how the diffraction patterns basically occur due to the regular crystal structure, regular arrangement of atoms in crystalline materials.

Then Bragg's law, we discussed order of diffraction, we discussed about reciprocal lattice, we discussed about Ewald sphere, their importance in the diffraction solving the diffraction pattern, various aspects of diffraction pattern in ideal crystal and then we are discussing about the difference between single crystal diffraction and polycrystal diffraction. How it looks like and how to read it, how to understand it.

And in the last class we discussed about very nice technique of getting a single crystal diffraction pattern out of polycrystalline material that has got selected area diffraction and then we just started discussing about how to interpret the electron diffraction patterns, how to index the electron diffraction patterns. We discussed about the camera length.

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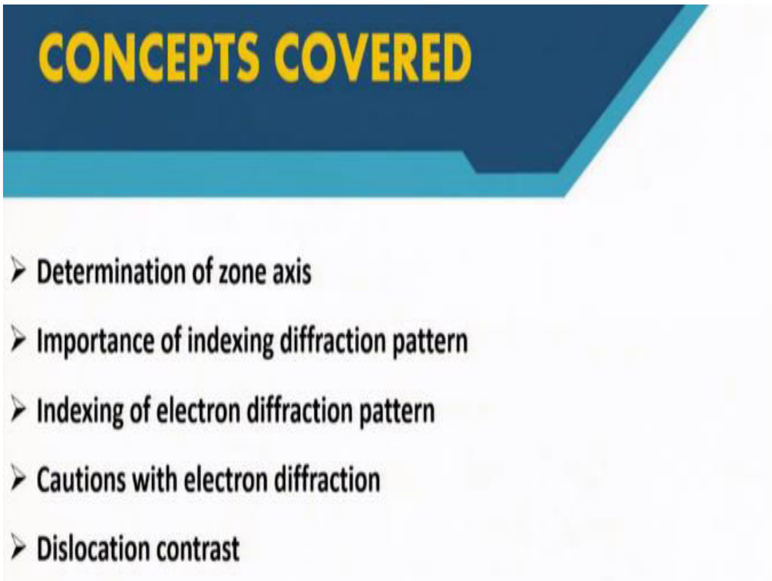

CONCEPTS COVERED

- Determination of zone axis
- Importance of indexing diffraction pattern
- Indexing of electron diffraction pattern
- Cautions with electron diffraction
- Dislocation contrast

And from there today in this lecture we will be discussing more about this interpretation of electron diffraction patterns. So, we will discuss about the determination of zone axis and the importance of indexing diffraction pattern, how the indexing of electron diffraction pattern really can be done and then certain cautions related to electron diffraction, solving the electron diffraction pattern.

And finally, we will discuss about something called dislocation contrast which is a direct outcome. So, this is an imaging method, dislocation contrast is an imaging method, but it is somehow related to diffraction.

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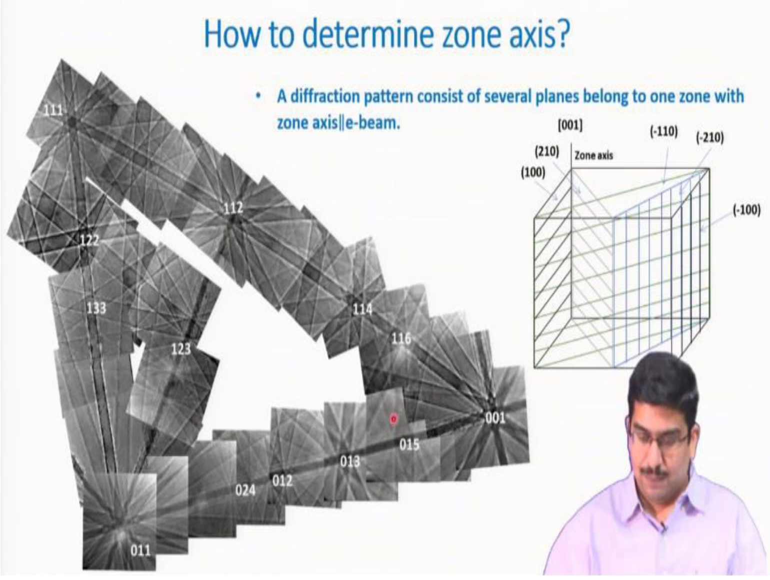

How to determine zone axis?

- A diffraction pattern consist of several planes belong to one zone with zone axis||e-beam.

So, the first topic how to determine zone axis? Basically by now, we have all understood that in particularly in case of electron diffraction, the electron beam comes through the zone axis. And the way zone axis is defined you know that it is basically the direction and all the diffracting planes are parallel. Because of the very small angle of electron diffraction all the planes which are parallel to this zone axis, electron beam we can imagine is coming through this zone axis.

And all the planes which are parallel to this zone axis they are basically satisfying the diffraction condition and they are forming the diffraction pattern ultimately in the electron diffraction. Now, if we do not know the zone axis from which the electron beam is coming through, we will not be able to understand the electron diffraction pattern at all because different zone axes.

If you imagine that sometime this is coming around 001, this is the zone axis, then I know for sure that in the electron diffraction pattern those spots will correspond to these kinds of planes. This will be either 210, 100, 1 bar 10, 2 bar 1 0 and so on and so forth. These are the planes which are basically satisfying the diffraction condition. So, when I try to look at the corresponding diffraction pattern, I will be looking for these planes to start with, to begin with.

But in case if we can imagine the crystal is a little bit tilted and the electron beam is instead of coming along the 001 if it is coming along some other angle let us say 1634 2 or something like that, that can have a very arbitrary axis, along that arbitrary axis the electron incident electron beam is coming meaning that is the zone axis now. So, the diffracting planes will also be correspondingly changed and it will be quite difficult.

Quite arbitrary diffracting planes and that means we will be having a very different type of diffraction pattern and that solving that will be extremely difficult. So, when we start with an unknown specimen, so now if we imagine that we have a polycrystal, if it is a single crystal we know basically more or less we know that okay fine it has grown along this direction.

So, we know exactly if we keep the single crystal in this direction in this way within the specimen holder, so more or less this is the direction or this is the zone axis we have an idea. The problem happens that when we have a polycrystalline material, and there we need to determine the zone axis a priori before we do, and we have already seen the diffraction contrast there we had discussion and now today also we will try to have a discussion about the diffraction contrast.

So, for all this purpose for even imaging, dark field imaging or even in bright field imaging and we must know the zone axis at least for diffraction pattern. So, if you want to take a selected area diffraction pattern, we must know the zone axis. But determination of zone axis is an extremely difficult task because when we put a polycrystalline specimen and we try to see the diffraction pattern we do not know, we do not have any idea.

If we are fortunate, we are possibly directly hitting any of those low index planes where the electron beam is possibly coming along 100 or 111 or 110 something like that. But if it is a completely arbitrary, then we are in a very difficult situation. We have to tilt either the beam or the specimen. So, as I said most often the beam is not tilted, beam remain stationary because that is coming around along the optic axis, it has its own advantages.

All the lenses and other things, then this entire configuration has to be changed, rather than that it is much easier to tilt this specimen. So, you can tilt the specimen and try to bring to certain known zone axis. So, you try to bring the zone axis along, try to bring the electron axis coming along certain known or certain low index planes and for that this is one of the examples that was developed by a very well-known person to me.

And during my research career this was developed by somebody else not me. But this was very useful and for at least when we are working with something like an aluminium FCC alloy, this is developed for an aluminium alloy. So, what this one is this is basically something called Kikuchi pattern, Kikuchi transmission, TEM Kikuchi patterns. And this stereographic triangle that is what it calls, so here all this Kikuchi diffraction patterns corresponding to different type of zone axis is given.

So, if you take an aluminium alloy now, unknown aluminum alloy you put it there, you take a diffraction Kikuchi and the area that you are seeing you try to take a selected area similar to selected area diffraction you bring the aperture and all but instead of diffraction pattern you take a Kikuchi pattern and you will be able to know that exactly where you are, what is the zone axis.

More importantly what you can get, let us say you are somewhere over here. You see that this is where this diffraction pattern looks something similar to this. So, you know you are somewhere over here and from this since this is for a very symmetric cubic crystal and all, you know exactly how much I have to tilt the specimen, how much tilting will take.

And in which direction along what axis I have to tilt so that I can possibly go to this 111 zone axis or I can come down possibly to 114 zone axis, 001 zone axis and so on and so forth. So, if all this angular relationship with known you can determine the zone axis finally. You can basically check it out from this known Kikuchi pattern, this stereographic triangle, you can find out exactly where you are, which is the zone axis currently or maybe some unknown axis it is fine.

But you can understand that how much tilting I have to do on my specimen and along which direction whether it is in X. Specimen tilting means it is not allowing any crystallographic direction, you have this X and Y in your specimen and the Z direction, along the Z direction the electron beam is coming. So, you need to know that exactly on X axis or Y axis how much specimen.

If it is a double tilt holder, you have too many attempts; if it is a single tilt holder there you have only one axis of rotation and this one axis of tilting and there you have to tilt it to try to bring it to some known zone axis and that tilting has a limit usually. So, if you are not able to tilt to the extent possible to bring it to any of those known zone axis, you have to possibly go to some other region in the specimen or some other specimen altogether where you can expect that amount of tilting.

Usually, the tilting is very less in TEM. So that tilting will bring you to some known zone axis and that is how you determine the zone axis a priori before trying to solve any electron diffraction pattern, you need to know it. And here it is shown in Kikuchi pattern, but the same thing can be done with selected area diffraction pattern as I already said that you have the reciprocal lattice and all and there you can try to get the diffraction pattern for all different kinds of orientations, zone axis and orientation.

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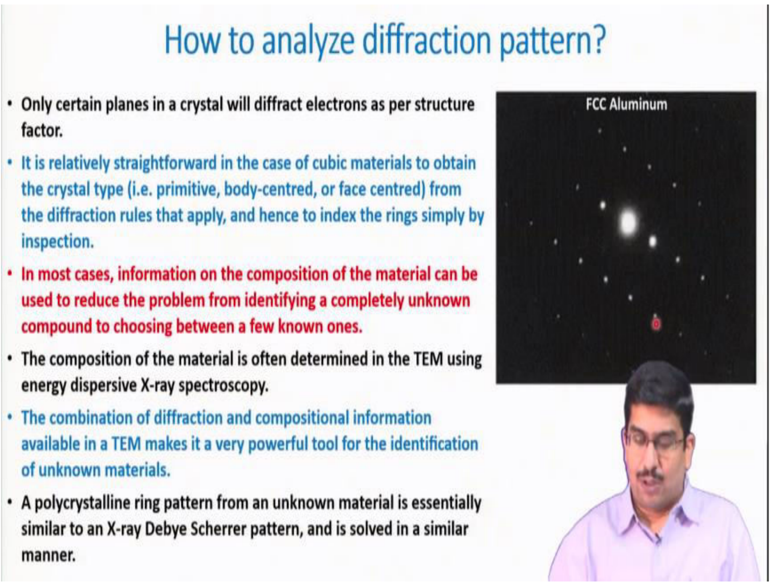

How to analyze diffraction pattern?

- Only certain planes in a crystal will diffract electrons as per structure factor.
- It is relatively straightforward in the case of cubic materials to obtain the crystal type (i.e. primitive, body-centred, or face centred) from the diffraction rules that apply, and hence to index the rings simply by inspection.
- In most cases, information on the composition of the material can be used to reduce the problem from identifying a completely unknown compound to choosing between a few known ones.
- The composition of the material is often determined in the TEM using energy dispersive X-ray spectroscopy.
- The combination of diffraction and compositional information available in a TEM makes it a very powerful tool for the identification of unknown materials.
- A polycrystalline ring pattern from an unknown material is essentially similar to an X-ray Debye Scherrer pattern, and is solved in a similar manner.

So, now how to analyze the diffraction pattern? Already I have said that if it is a cubic crystal, symmetric crystal, then corresponding to any one set of atomic planes, you will have two different spots, two spots on either side of the diffracted beam at identical distance and that distance corresponds to 1 by d. This distance between the direct beam and the diffracted beam this is 1 by d.

Now as we know from the structure factor concept, we know that only certain planes will diffract. So, from there itself we know the zone axes, let us assume that we know zone axis and we know exactly which material it is, what is the crystal structure applied before solving this diffraction pattern. If we know that that will be very helpful. So, if it is aluminium, we know it is an aluminium and that has an FCC crystal structure.

If we have this information a priori from the structure factor calculation we know exactly which are the diffracting planes and what are the forbidden reflection. So, immediately we can identify that in the diffraction pattern, the diffracted spots which are closest to the direct beam. And if we know exactly, if we know the zone axis also, then we know that this is possibly if it is coming along certain zone axis where 111 should diffract, then we know that this is possibly 111.

The closest one is 111 because that is what the first possible diffracting plane as per structure factor calculation that is what. So basically, for a cubic crystal it is quite easy if you know the zone axis. If you know the chemical identity, if you know the structure factor, if you know the zone axis, it is quite straightforward, you can able to solve. Of course, in real sense life is not always so easy, so many of the crystals.

Many of the cases you do not know anything about the crystal structure, you do not know what kind of material or and if some cases these are like you have multiphase material where the diffraction patterns, I already showed you one example when we were discussing about selected area diffraction, that many different phases may be mixed and the diffraction pattern ultimately you capture will have an overlapping or superimposition of many diffraction patterns from many different phases.

So, this is a very ideal case possibly. This this kind of a diffraction pattern is a very ideal case when you know the material, you know this zone axis, you know the structure factor, everything you know and then you get this diffraction pattern here. Of course, in TEM the good advantage is that in one single instrument, you can determine the chemical identity also.

You can go for some techniques called EDS, energy dispersive spectroscopy, you can go for even higher sophisticated techniques like EELS, electron energy loss spectroscopy, and you can try to find out the chemical identity of that specimen and even if you have a multiphase material chemical identity of different phases present in the microstructure that you are viewing.

So, you can try to do that in one single experiment that is one of the major differences with Xray technique. If you want to do the same thing for Xray technique, you have to possibly take the specimen for another characterization technique altogether. You can go for XPS maybe to find out what are the different phases or any other technique which will give you an idea about different phases, and then you can possibly bring it back and try to get a diffraction pattern and then try to solve it.

So, this is why basically the electron microscope, I am keep on telling that electron microscope is so powerful and this is how you do that for spot pattern and similar method you can analyze the diffraction pattern for the ring patterns also that is the process is exactly same, only the typical nature of this diffraction pattern will be different if you go for spot pattern to ring pattern.

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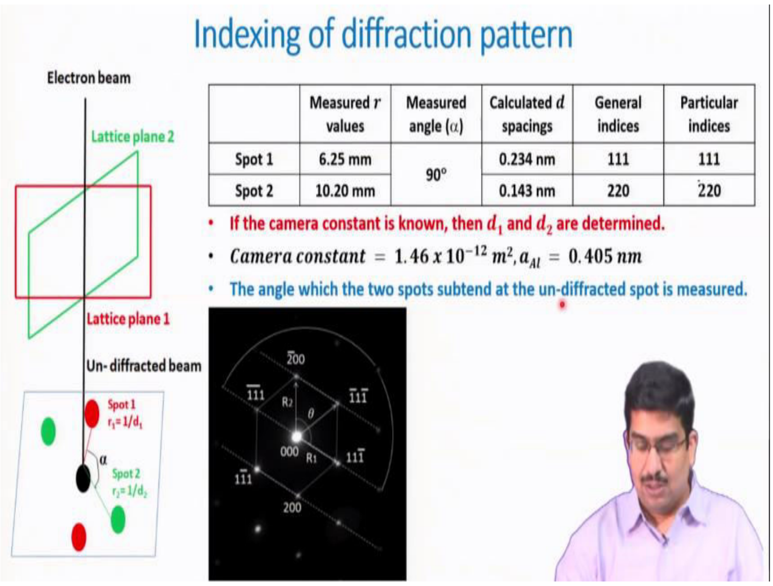

Indexing of diffraction pattern

	Measured r values	Measured angle (α)	Calculated d spacings	General indices	Particular indices
Spot 1	6.25 mm	90°	0.234 nm	111	111
Spot 2	10.20 mm		0.143 nm	220	220

- If the camera constant is known, then d_1 and d_2 are determined.
- $Camera\ constant = 1.46\ x\ 10^{-12}\ m^2, a_{Al} = 0.405\ nm$
- The angle which the two spots subtend at the un-diffracted spot is measured.

So, now let us see how you can do this indexing of the diffraction patterns. And remember again as I said I need to know or rather in this case I have all information what phase it is. That means I know the crystallographic information, I know the structure factor, I know the composition, I know the zone axis and everything. Then I can possibly follow this.

If I do not know all of these things, I have to first know the information a priori, I have to determine the zone axis, I have to determine possibly an idea about the chemical identity and then I can possibly try to index this diffraction patterns. As I said, if you know the camera constant, this is very straightforward. What you have the same electron beam coming along certain zone axis and then it is forming two set of diffraction spots at two different directions.

If you measure these distances, let us say r and r 2 that is directly corresponding to 1 by d 1 and 1 by d 2. So if you know the camera constant, you can easily measure this from this r 1 value itself, you can measure that d 1 and d 2 and then you know the chemical identity, maybe it is a little bit change, maybe it is of multiphase, but you know the chemical identity, so you know let us say it is aluminum, again so you know that this are measured r values and the measured angles.

So first you do this r value measurement and from there you know the camera constant, let us say this is the one example. This is a camera constant, so from there you can find out this d spacing of this, you can try to match it with the standard d spacing. You know the lattice parameter for aluminum, you know it is in FCC, so you can find out that this is like what is the interplanar spacing for different type of planes.

You match it and from there you can confirm that this is possibly, the first set of spots is possibly 111 and that is consistent with your structure factor calculation also because the structure factor tells you that the first set of diffraction spots should be 111. The second set of diffraction patterns spots again you can repeat the same thing and you can find out that this is coming possibly from 220 because 200 is the next one.

But in this case maybe your zone axis is something that you are getting it not from 200 but from 220. Here it is a different one, this here it is showing that it is 200, 200 type of plane, the zone axis is important. So, it is possibly along certain zone axis where you are getting 220. And what you can double check it by measuring this angle between the spot. In this case these two spots are at an angle of 90 degrees.

So, you know how to determine the angle between different planes, you can check out the angle between these two planes and you can confirm that yes they are also at 90 degree. And I already said that the symmetry and the angular relationship between various planes are also reflected in the electron diffraction pattern, from there you can double check it.

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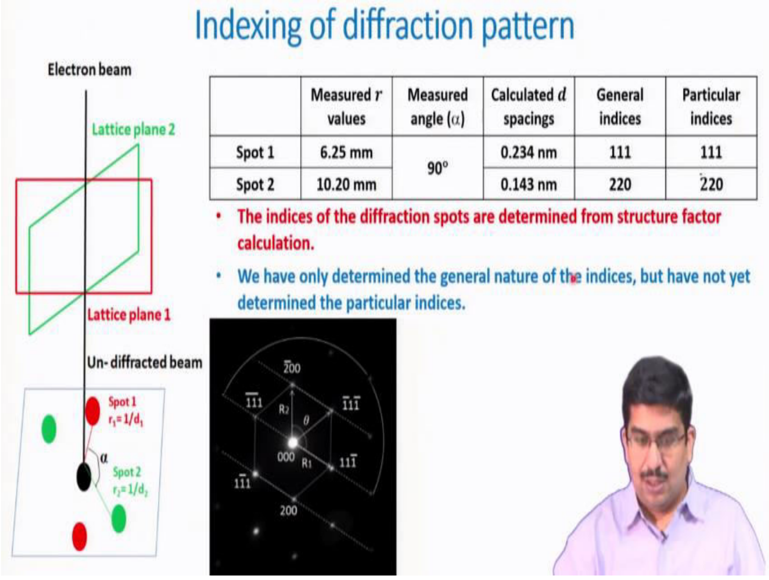

Indexing of diffraction pattern

	Measured r values	Measured angle (α)	Calculated d spacings	General indices	Particular indices
Spot 1	6.25 mm	90°	0.234 nm	111	111
Spot 2	10.20 mm		0.143 nm	220	220

- The indices of the diffraction spots are determined from structure factor calculation.
- We have only determined the general nature of the indices, but have not yet determined the particular indices.

Now, the indices from all this calculation from this exercise, the indices that you determine is not basically the exact indices, this is the general indices. These are the general nature of the indices, that means you have determined the set family of planes, you have not identified yet the exact atomic plane which is refracted, right. You have identified the family plane. So, it is that curly bracket, if it is 111. It is 111 planes with a curly bracket, not with the first bracket, not with the round bracket.

So, same thing for 220. So, this is the family of planes from this exercise measuring the r value and from there calculating with a known camera constant calculating d value and then identifying the plane through this you have measured it or you have determined the general indices or the family of planes. You have not yet identified the particular indices, Miller indices for that atomic plane.

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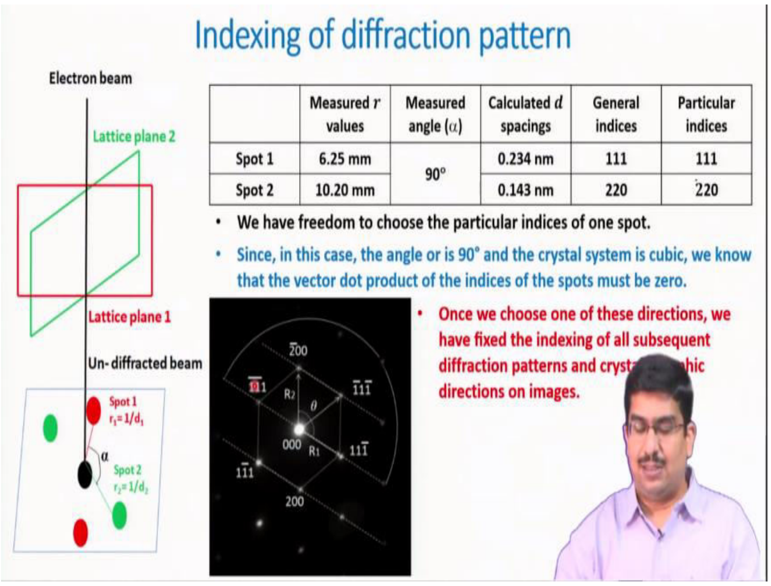

Indexing of diffraction pattern

	Measured r values	Measured angle (α)	Calculated d spacings	General indices	Particular indices
Spot 1	6.25 mm	90°	0.234 nm	111	111
Spot 2	10.20 mm		0.143 nm	220	220

- We have freedom to choose the particular indices of one spot.
- Since, in this case, the angle or is 90° and the crystal system is cubic, we know that the vector dot product of the indices of the spots must be zero.
- Once we choose one of these directions, we have fixed the indexing of all subsequent diffraction patterns and cryst[illegible]hic directions on images.

In order to do that, what we can do is that any one of these planes arbitrarily you can choose a particular index. So, let us say I have chosen 111 as a particular index, this is again not shown here, but let us say here I have chosen any of those spots as 111 in general. Then what we can do is that any plane 200 that belongs to 200 which is 90 degrees away to it I can find out the particular indices for that 200 plane, right.

From this relationship that the angle is 90 degree and the crystal system is cubic that the vector dot product of the indices for these two spots 111 and the one that belongs to 200, 220 family of planes that must be 0 and from there I can find out exactly which 220 plane is diffracting. If this is 111, then the spot which is 90 degrees to this one must be 220, so the same.

And if I know this is 111, so you can see it here; if we have one set of planes 1 bar 1 1, the other side of the plane is immediately you can identify that has to be bar 1 1 bar 1. So, similarly if you have let us say this one is 111, the other side of it you know that this has to be bar 1 bar 1 bar 1. So, if something is 220 the other spot will be 2 bar 2 bar 0 something like that. So, this exercise you can continue.

You know the angular relationship between various planes, you can go on continue this and that way you can index all the planes, the particular indices, not the general indices. So, generally indices you can determine for all sets of planes. So, you can determine it for 111, you can determine it for 220 and from the angular relationship other spots also you can determine.

So, the same way you can repeat it and you can determine other, you can first determine the other set of planes general indices from the d value, you can double check it from the angular relationship and from that angular relationship you can find out the particular indices for that family of planes as well. For entire thing, one arbitrarily you have to choose just one of these particular indices for one of the set of planes.

Rest of them you can find out from the angular relationship that is how you can index possibly the entire diffraction pattern. Again, as I said this is very much under identical conditions and most often it is full of problems. So, I am just indicating a couple of practical problems other than all the problems that I told you multi-phase material, super imposition of diffraction patterns and then identifying the zone axis, identifying the chemical identity; all of these things are valid.

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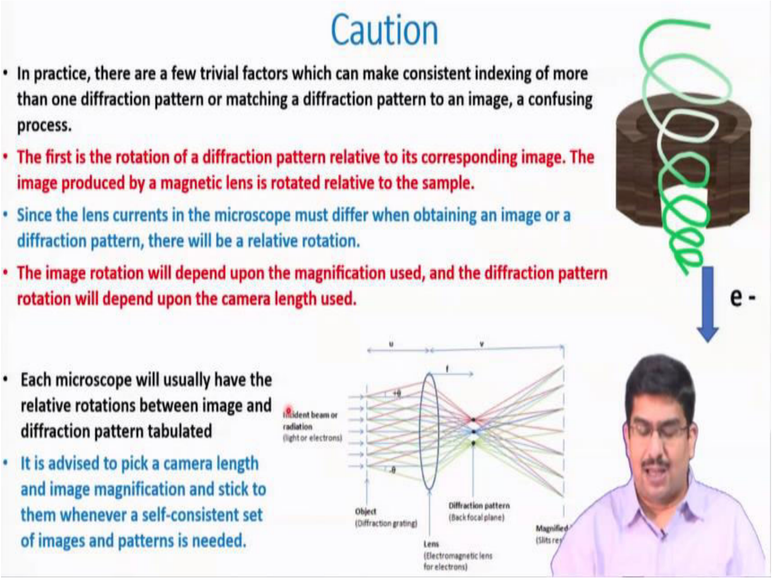

Caution

- In practice, there are a few trivial factors which can make consistent indexing of more than one diffraction pattern or matching a diffraction pattern to an image, a confusing process.
- The first is the rotation of a diffraction pattern relative to its corresponding image. The image produced by a magnetic lens is rotated relative to the sample.
- Since the lens currents in the microscope must differ when obtaining an image or a diffraction pattern, there will be a relative rotation.
- The image rotation will depend upon the magnification used, and the diffraction pattern rotation will depend upon the camera length used.

- Each microscope will usually have the relative rotations between image and diffraction pattern tabulated
- It is advised to pick a camera length and image magnification and stick to them whenever a self-consistent set of images and patterns is needed.

Plus there are a couple of issues which one has to keep in mind, these are practical problems and this is related to the microscope itself. Other problems most of them as I said most of the other problems are related to the specimen, multi-phase materials, zone axis determination and structure factor all of these are related to the specimen. Now, in the microscope also there are a couple of issues which can interfere in the indexing of these patterns, electron diffraction pattern.

So, first of all we know that rotation of this electron beam, so this helical movement of the electron beams through the specimen, the spiral pattern. In the spiral pattern the radius getting tighter and tighter. So, finally it follows a helical path the electron beam and there also when we discussed about this, we discussed about one thing that very rarely this helical movement here this electron beam undergoes an integral number of rotation.

So, that means the image often gets rotated and this needs to be rectified. So, this same problem will happen for the diffraction pattern and in diffraction pattern, it is again one more level of difficulty is that what you do in case of diffraction, when you do the diffraction pattern, when you capture the diffraction pattern basically you are doing capturing this back focal plane.

That means you are changing the magnification, you are changing the focal length and when you do this imaging it is here and your image plane is always here. So, when you try to capture the back focal plane you basically change the focal length of this objective lenses or for that matter all other objective lenses, projector lens and final projector lenses and as imaging lenses, all lenses you change to this adjustment and this change in focal length usually you do by changing the current, lens current.

That means the magnifications of these lenses are different for imaging condition and for capturing the electron diffraction pattern. So, this magnification is a different, correspondingly the lens currents are also different. So, that means what happens is that the image rotation is also different when you are capturing the image versus when you are capturing the diffraction pattern.

Then this rotation of this electron, this helical rotation, this helical path for the electron will also differ when you capture this image versus when you capture the diffraction pattern. That means, now you can get into a big trouble because this image rotation depends upon the magnification used that is for the image and for the diffraction pattern this will depend upon the camera length that you are using.

So, now, if you do not know about this that at this magnification what is the image rotation, how much is the image rotation or at this image camera length what is the diffraction pattern rotation; if you do not know this interrelation you will not be able to probe the right area and this may be a big problem when you go for something like selected area diffraction, we will see that.

So, that is why usually microscopies what they do again they have a tabular form, they have a calibration already done and that will tell you that for this camera length and this magnification this is the relation between or this is the relative rotation between the diffraction pattern and your image. These days everything is software controlled and that thing is already written in the software.

Usually, software knows that at this magnification at this camera length, basically what is the image rotation and what is the diffraction pattern rotation and where how much correction I have to make and why this correction is needed, now I am coming to that.

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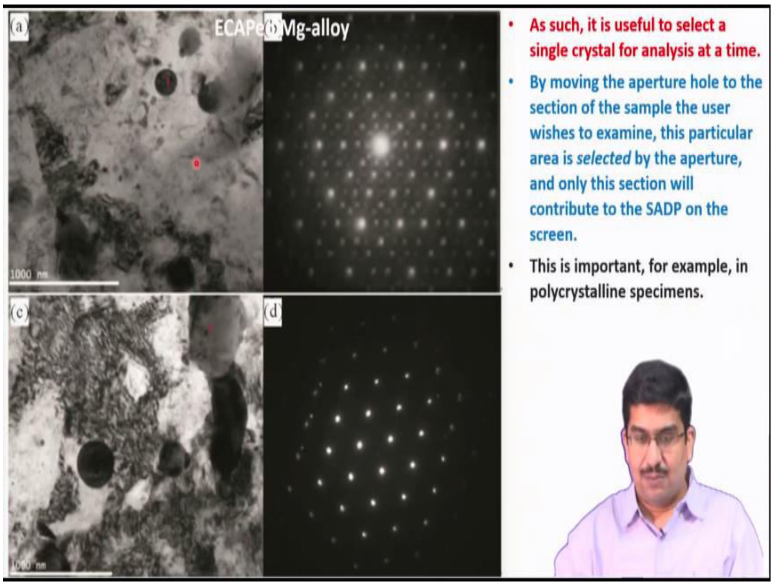

- As such, it is useful to select a single crystal for analysis at a time.
- By moving the aperture hole to the section of the sample the user wishes to examine, this particular area is *selected* by the aperture, and only this section will contribute to the SADP on the screen.
- This is important, for example, in polycrystalline specimens.

Let us say you have this, as I said this is an area and you have this another phase where you are interested to capture a diffraction pattern, selected area diffraction pattern. Now this is the image that possibly you are seeing but with a certain type of rotation which is corrected. Then you click it here you wanted the machine to put that selected area diffraction pattern in such a way that only that much of beam coming out from this phase is captured.

But because of this electron rotation and that physically possibly your electron beam is somewhere else because the image is rotated, you do not know exactly how much rotation is there. So, even if you want to choose this area, if you do not know this image rotation, you may be capturing some other area. You are seeing it, on the screen you are seeing it that is fine but physically some other area may have been selected because the original image is rotated here.

So, that is why the machine or the software should know that exactly how much image rotation is already happened so that it knows when I try to capture a diffraction pattern from this area then this should be the image rotation. This is the area physically in the specimen, this is the area which I need to select and that then again selected area diffraction aperture will only choose beams coming out from there and there also there is an image rotation is involved.

So, this interrelation is very important. This is one of the major issues when you are trying to capture a selected area diffraction pattern, this is a practical issue.

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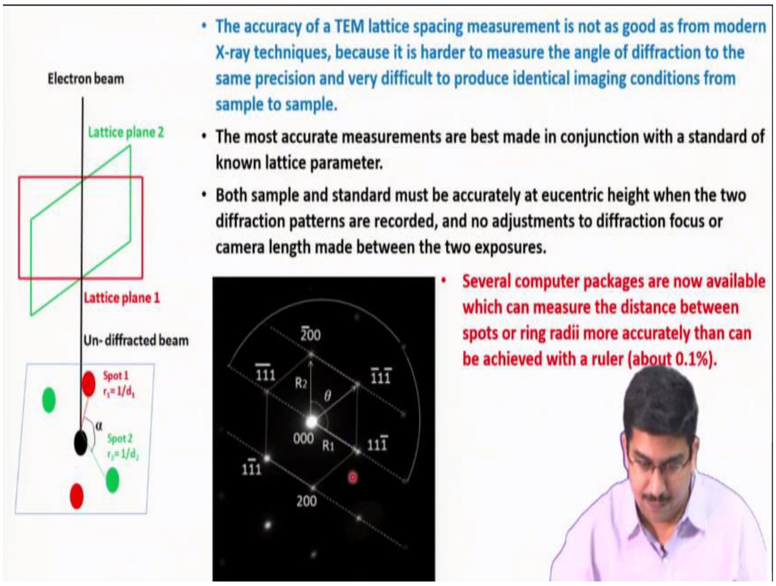

- The accuracy of a TEM lattice spacing measurement is not as good as from modern X-ray techniques, because it is harder to measure the angle of diffraction to the same precision and very difficult to produce identical imaging conditions from sample to sample.
- The most accurate measurements are best made in conjunction with a standard of known lattice parameter.
- Both sample and standard must be accurately at eucentric height when the two diffraction patterns are recorded, and no adjustments to diffraction focus or camera length made between the two exposures.
- Several computer packages are now available which can measure the distance between spots or ring radii more accurately than can be achieved with a ruler (about 0.1%).

Another word of caution is that the accuracy of TEM lattice spacing measurement this is not as good as any X-ray technique. There are two reasons, two parts of it, we will come to that. But here the most accurate method of calculating the lattice parameter for any unknown specimen or for even a known specimen, sometimes you want to know the changing lattice parameter.

Let us say because of some alloying, because of some changes in the composition you want to know exactly how much change is there in the lattice parameter interplanar spacing then the electron diffraction pattern is not a good method as compared to the X-ray diffraction technique. First of all, this is because the electron diffraction pattern, the entire indexing of the diffraction pattern, the entire determination of this lattice spacing this interplanar spacing and so on is an entirely an image-based technique.

So, in image-based technique what you are measuring here is basically the distance from this direct beam to this diffracted beam, the r value, you are measuring the r value and it is entirely done using an image and here again you have the operator's discretion comes into play. So, somebody can measure a different distance and somebody else can measure another different distance.

And also this is related to here the measurement of this angle that there is every possibility that there are certain error involved into it. Obviously, these days you have better computer packages which can measure this distance artificially. I mean using the image analysis tools, this can be measured even in a better way than in case of a manual measurement.

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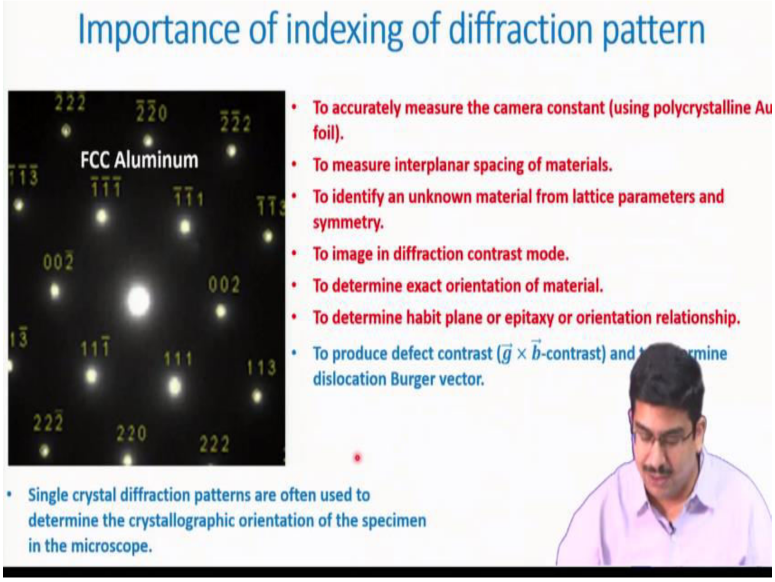

Importance of indexing of diffraction pattern

- To accurately measure the camera constant (using polycrystalline Au foil).
- To measure interplanar spacing of materials.
- To identify an unknown material from lattice parameters and symmetry.
- To image in diffraction contrast mode.
- To determine exact orientation of material.
- To determine habit plane or epitaxy or orientation relationship.
- To produce defect contrast ($\vec{g} \times \vec{b}$-contrast) and mine dislocation Burger vector.

- Single crystal diffraction patterns are often used to determine the crystallographic orientation of the specimen in the microscope.

So with this, we will stop it here and we will continue with this importance of diffraction pattern measurement, identifying the diffraction patterns and one of the very important examples of or a very important implication of measurement of electron diffraction pattern in form of something called dislocation contrast. So, we will discuss that in the next class. Till now, bye.