Neutron Scattering for Condensed Matter Studies
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Week 5 Lecture 13A

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In this lecture, we will be discussing application of neutron crystallography and I will presume that almost all the samples I will be discussing are powder samples.

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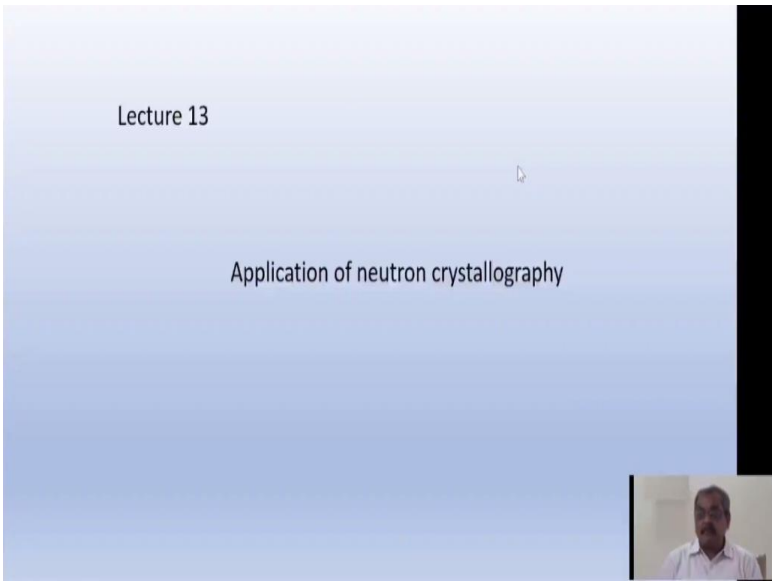

I will start with some of the practical applications of neutron crystallography and when I say crystallography, I mean crystallographic structure (determination/Identification) using neutrons and their applications. Towards the end I will come to magnetic neutron diffraction in this lecture. But before this, I will repeat a little bit of what I said in the previous lecture as it is important for us to understand various constructions and the various techniques that we use to determine the position of the Bragg peaks.

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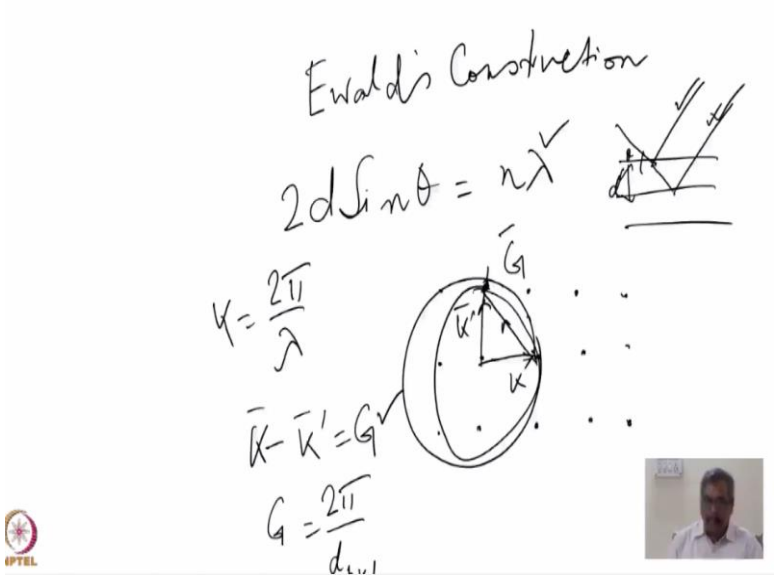

In the last lecture, I discussed something called Ewald's construction. Possibly many of you are familiar with this approach. We usually go with the formula, $2d \sin\theta = n\lambda$, Bragg law. This is the most commonly used formula and where we assume, the path difference between these two (incident and Diffracted) rays is $2d \sin\theta$, if θ is angle of incidence then the path difference should be equal to integer number of wavelengths λ for constructive interference. There is another way we can visualize diffraction which I discussed last time. If I have a reciprocal lattice here and then if I have my initial wave vector $\boldsymbol{K}$ which is of magnitude $\frac{2\pi}{\lambda}$ and a direction. When I draw it such that it ends on one of the reciprocal lattice points and then around that I draw a circle or sphere in three dimensions with that radius, whenever this sphere / circle touches one of the reciprocal lattice points, then I will have K'(scattered) vector in that direction. This is the outgoing vector due to Bragg diffraction.

If I have a shorter wavelength then this circle (sphere) will be larger. If I have a longer wavelength, it will be smaller. Hence, depending on wavelength the diameter of the circle with the radius $\boldsymbol{K}$ will be decided. Whenever this Ewald sphere touches one of the reciprocal lattice points, we will have a diffracted beam. That is how we wrote the selection rule that $K - K' = G$ where G is a reciprocal lattice vector whose magnitude is $\frac{2\pi}{d_{hkl}}$ for a lattice spacing of d. Please understand that the expression $K - K' = G$ and the expression $2d \sin\theta = n\lambda$ are equivalent.

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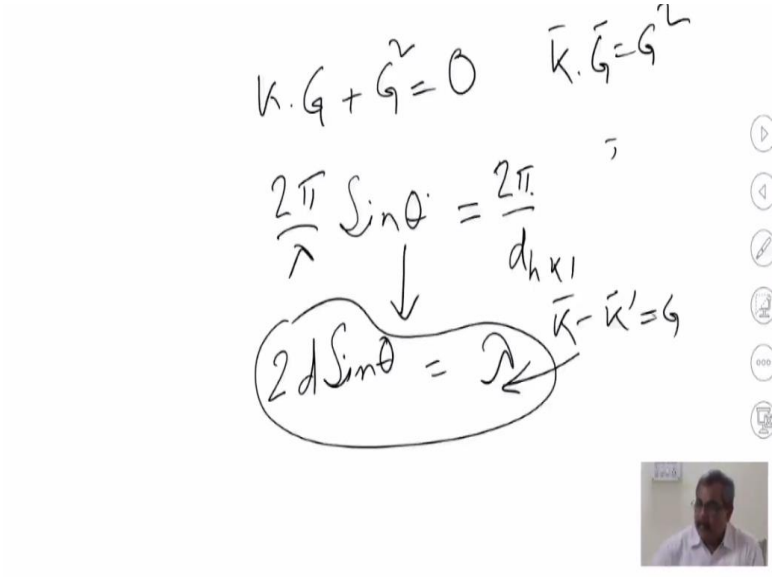

I know that I can write $2K.G = G^2$ and from this, putting $K.G = KG \sin\theta$ and the magnitudes of K and G as $\frac{2\pi}{\lambda}$ and $\frac{2\pi}{d_{hkl}}$, I will have $2d_{hkl} \sin\theta = \lambda$.

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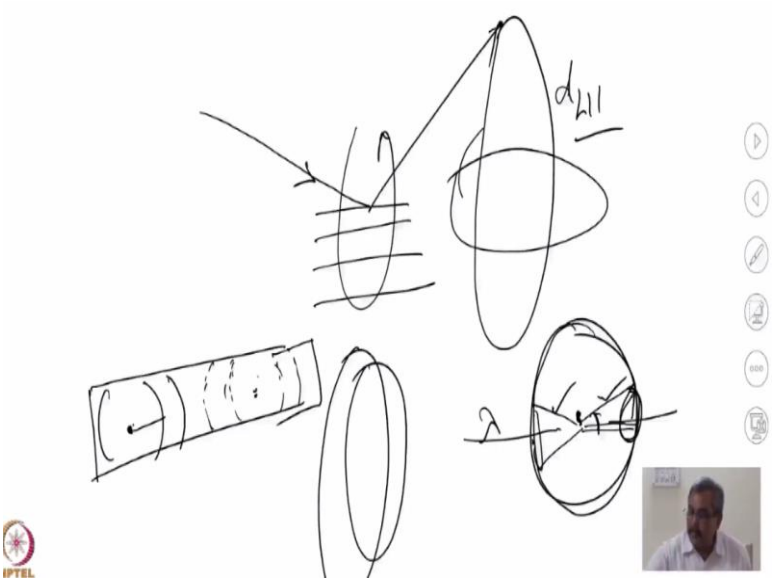

Now coming back to powder crystals. I talked about $2d \sin\theta = \lambda$ with respect to one set of crystal planes but if I rotate the crystal around the incident beam that means I have a powder crystal in which there are crystallites of all orientation then it will trace out a cone (of diffracted rays). For a powder crystal this cone is a signature of one particular d_{hkl}.

After this I discussed with you the Debye-Scherrer photography in which there is a cylindrical camera with powder sample at the center. It had an entrance slit, an exit slit and then there is a

photographic plate wrapped inside the Debye-Scherrer camera. The diffracted cone is arrested on this photographic plate. When I open the strip and develop the photographic plate after powder diffraction then I get circles corresponding to various *d*-spacings on the photographic plate. The ones which are near the exit slit they are at lower *Q* values and more intense and the one which is near the entrance slit is less intense because of the form factors in x-rays going down with *Q*.

This photographic plate basically intercepts a part of this Debye-Scherrer cone, corresponding to every *d*-spacing and knowing the radius of this circle from radius of this Debye-Scherrer camera we can find out easily what is the corresponding *d*-spacing because we can easily calculate the θ for that plane for the given λ of x-ray.

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This is the same thing (in principle) we do with powder crystals using neutrons. With the powder crystals we try to get a part or a slice of the Debye-Scherrer cone and knowing the position of the detector or in case of position sensitive detector knowing the angle at which neutron hit the detector, we get the Bragg angle. We can find out the intensity and we can find out not just *d*-spacing, but we can do a Rietveld for detailed structure analysis in case of neutrons.

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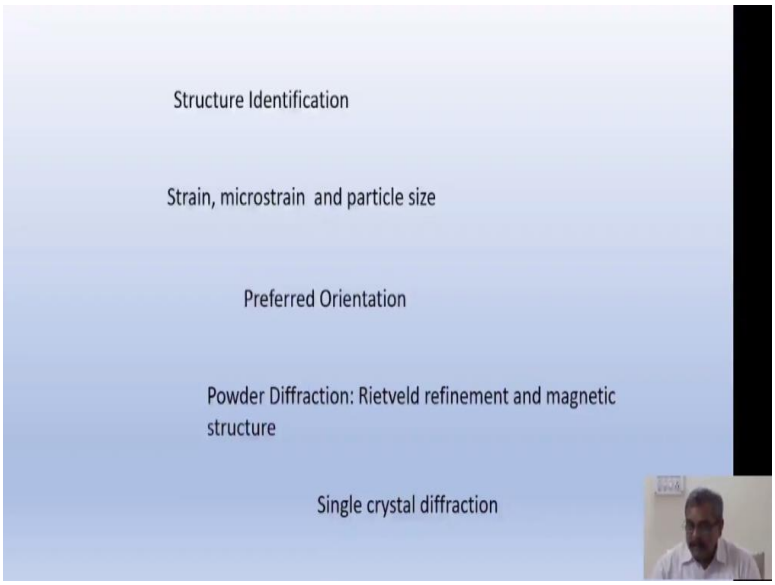

Now I will try to introduce you to various techniques that can give you structural information and also can give you strain, microstrain and particle size with neutrons. It can give preferred orientation and most importantly powder diffraction from a magnetic sample can be used to obtain the magnetic structure. Lastly, I will mention how single crystal diffraction is done. Because most of the time it is easy to make powder samples or usually, we get a powder sample instead of single crystals. But, to solve an ab initio structure in case of hydrogenous crystals, you need to grow typically sample which is few millimeters thickness and say 5-10 mm across. With this size, we can do single crystal diffraction for ab initio structure. Now with this let me get on to the studies including strain determination etc.

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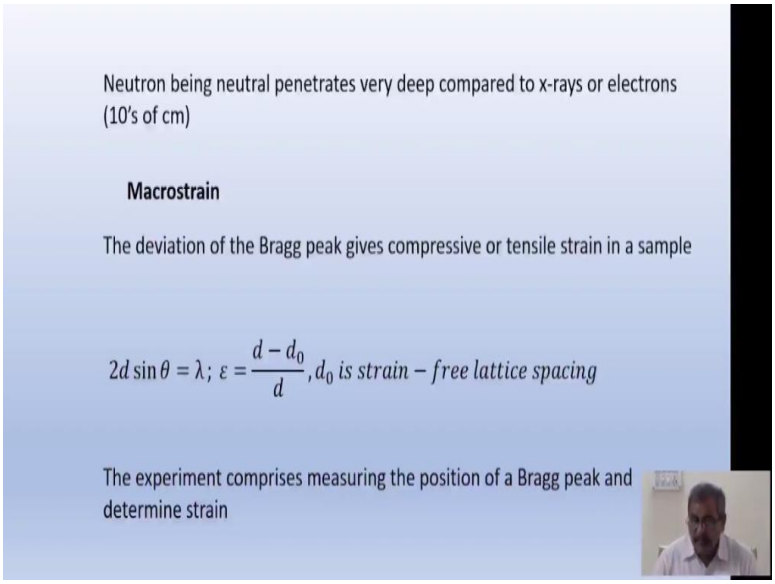

Neutrons have a very big advantage because they can penetrate very deep (in matter), if we compare the penetration depth of neutron with respect to any other radiation. For x-rays it is around tens of microns and in case of electrons it is not even 100 Å while for neutron this value goes to tens of centimeter. Hence, it is very suitable to study strain in case of industrial samples or samples of large size. This strain study in industrial samples is a very important factor when you talk about various welding joints and other kind of samples or material bodies which are under strain continuously or under repeated strain. The basic theory is very simple. If we can measure the Bragg peak from a sample then the Bragg peak can give you compressive or tensile strain in a sample simply from the Bragg relation $2d \sin\theta = \lambda$ if the Bragg peak shifts.

If it shifts to lower angle for a given wavelength of neutrons then that means d has increased other way around for lattice contraction and the macro strain for a sample under stress is given by $\varepsilon = \frac{d-d_0}{d}$ where d_0 is the lattice spacing for strain free sample.

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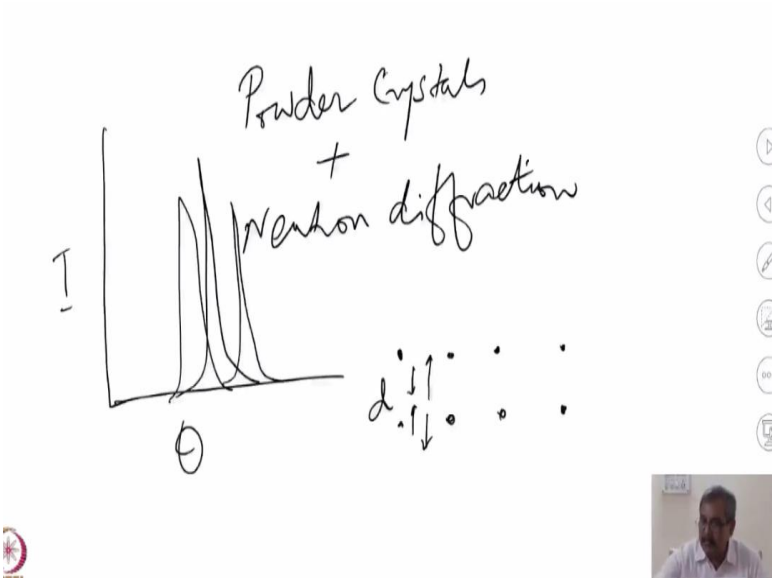

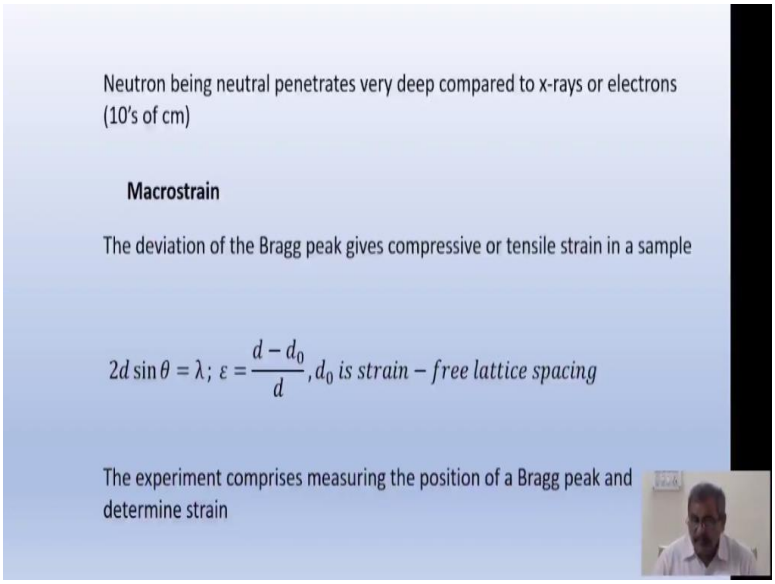

What I mean is that if I have a lattice under strain then either the *d*-spacing can shorten when it is a compressive strain or elongate (for expansion of lattice). This we can find out from the position of Bragg peak. If the lattice has elongated then we can say that *d* has increased and the (Bragg angle) theta decreases. The Bragg peak shifts to the lower value while if the lattice is compressed that means *d* has reduced and the peak will shift to higher angle. In principle the experiment is very easy to understand, but there are technical challenges which I will discuss with you. The experiment comprises in measuring the position of a Bragg peak to determine strain, but the fact remains that when I am trying to determine the strain in a sample, the sample may not be uniformly strained.

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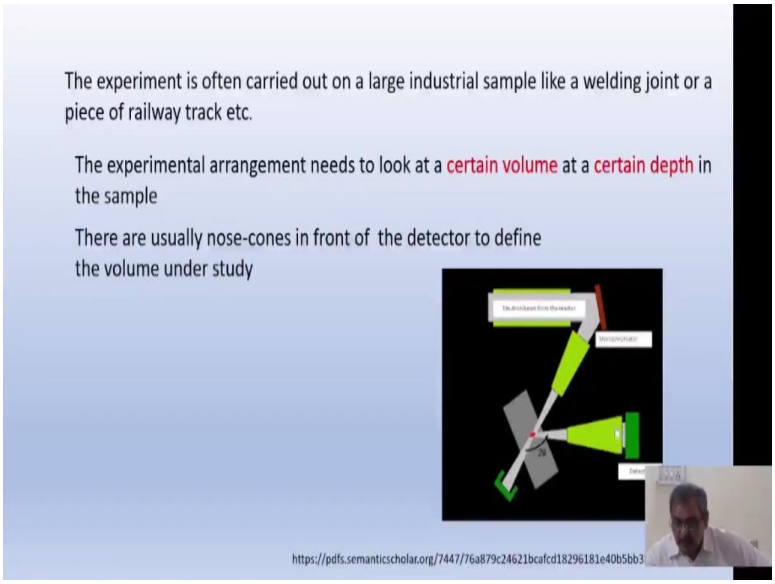

Let us consider it is a large industrial sample, for example a welding joint or a piece of a railway track. I will show you the photographs. The experimental arrangement should be such that I can select the certain volume in the sample in which I am attempting to measure the strain. This is done by using what is known as nose cones. It means we have the same arrangement as we had earlier, but detectors in end-on position. Our target is to find the strain in a (certain volume) sample. So, knowing the sample, for example, it can be stainless steel with known *d* and the λ of neutrons we can choose the angle of diffraction and we use end-on detector not a position sensitive detector to get the diffracted intensity. So, we have an incidence beam, as you can see here, and we have a large sample here and we have a detector. This is a monochromator, this is a detector, but what is unique here I can show you these two green collimators which are known as nose cones,

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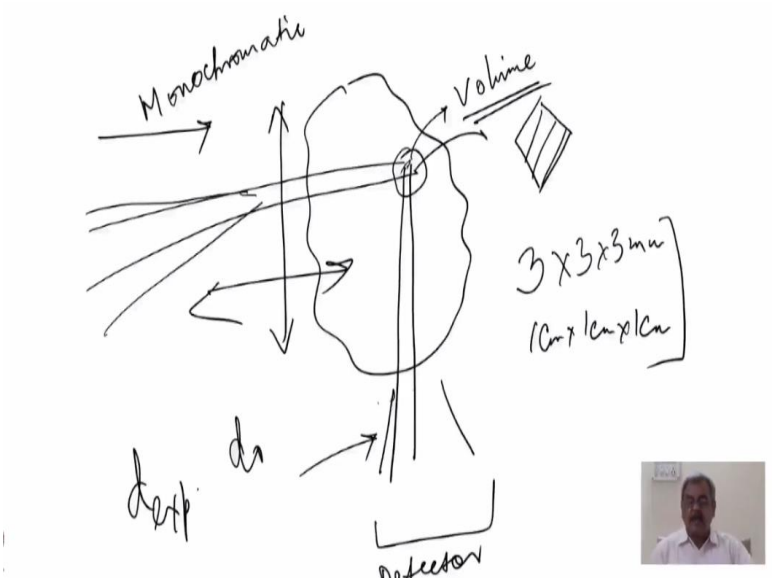

Why this nose cones are required?

Because I have a large industrial sample, but I want to determine the strain in certain small volumes. If I make a tight cone like this, of course it will also reduce the resolution to some extent, then the beam is focused and then if I have another nose cone on the detector side then the outgoing beam also has to pass through this nose cone. In the drawing I have scaled up everything to make it clear. This nose cones dictate what is the volume from which the diffraction is taking place. This volume can be as small as $3 \times 3 \times 3$ mm^3 or maybe $1 \times 1 \times 1$ cm^3 depending on how tight you make the nose cone.

Now, let us consider that the incoming monochromatic beam and the Bragg reflected beam, for a certain wavelength in a certain direction, going to a detector. By properly positioning the sample in front of the beam you can choose the volume that we are planning to study. That means now this industrial sample needs to be moved up and down, left and right and if you look at the three dimensions then there may also be rotations. With this we can figure out which volume of the sample is getting irradiated for certain setting of the sample and then we can see the diffracted beam, get the d experimentally and can compare it with d_0 (the strain free state lattice spacing). Now this is a question that how do you decide what is the d_0 value without the strain. That is done, if we know that a part of the sample is strain free, by getting diffraction data from there. For example, if you are trying to detect the strain around a welding joint, getting data from reasonably away from the joint. Now we know that where the welding joint is and I might go farther away from the welding joint and measure the d-spacing and consider

that as d_0 and then compare it with the d-spacing that we obtain from the sample volume around the welding joint.

With this, I can figure out what is the strain in a given volume and I can keep on sliding, rotating, translating my sample in the beam path so that I can find out, for example for a welding joint, across the welding joint what are the strains and make a map of the strain values in a welded joint. This is a very desirable technique, sought after, nowadays. But the fact is that often the samples can be to the tune of tonnes in weight. That means they are very heavy samples. So, we should have the translation stages, rotational stages which can handle such heavy loads.

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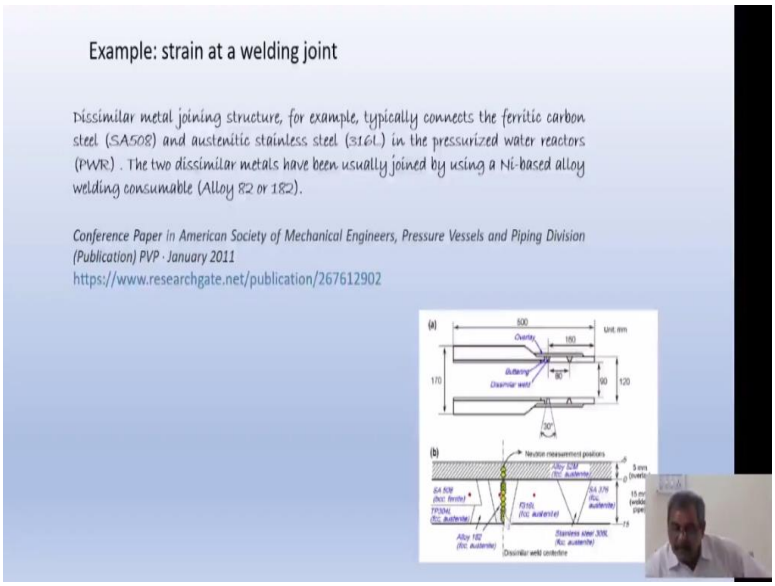

I have chosen some examples from the literature. This is a work done to understand the joint of ferritic carbon steel and austenitic stainless steel through a welding. You can see that here in this figure a welding joint is made between these two pipes and this is a part of a reactor. It is important to know because often such welding joints go through thermal cycling. Hence, determination of how good is the welding joint and what is the sort of strain distribution around the welding joint is necessary. This is more of an engineering problem then a basic science problem. Neutron does excellent job of mapping the strain, for example, here you see these are the sample volumes as I explained to you just now which have been (selectively) irradiated by the nose cone and small (irradiated) volume here gave the strain in this location.

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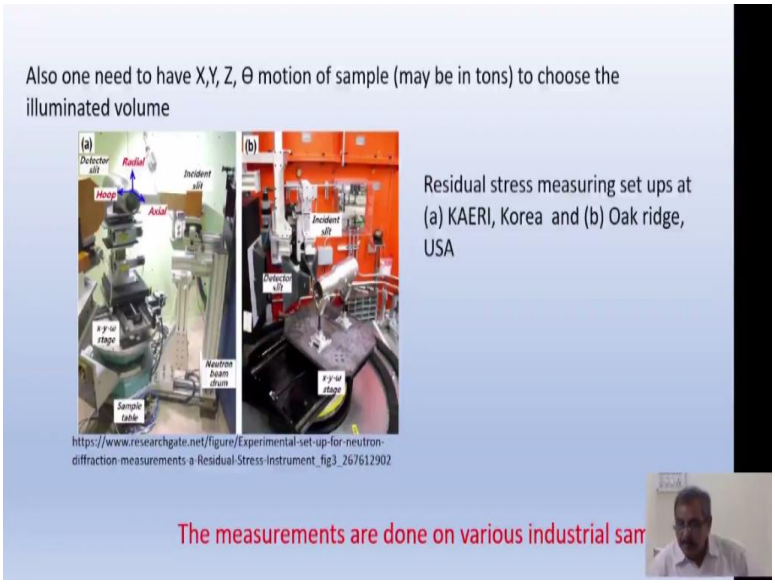

In this photograph of a setup you can see that this is the (X,Y,Ω) stage. This experiment was done at two locations for the same welding joints. You can see the sample here with the welded pipe joints and you can see the incident slit and the detector slits. For steel the diffraction angles are typically close to 90°. We can move the sample and get various volumes (irradiated) as I explained.

You can see for this welded joint we can do scanning along the body of the welded joint and also, we can do a radial direction scanning, that means across the thickness of the tube. So, all these studies can be done and strain mapped and then decision can be taken about the quality.

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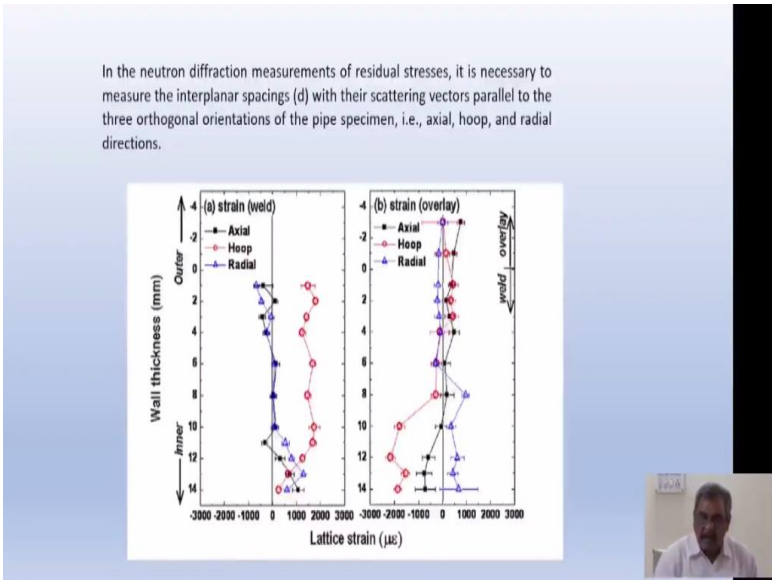

Here I show the plot in axial direction, means along the axis of the cylindrical tubes radial means as you go out in a cylindrical geometry and hoop is along the surface of the sample. They have tried to plot the strain overlaying the axial hoop and radials together over here across the welding joint and they have mentioned the lattice strain in some unit over here. This is a practical example which has been done using a nickel-based alloy welding material (for the sample pipes).

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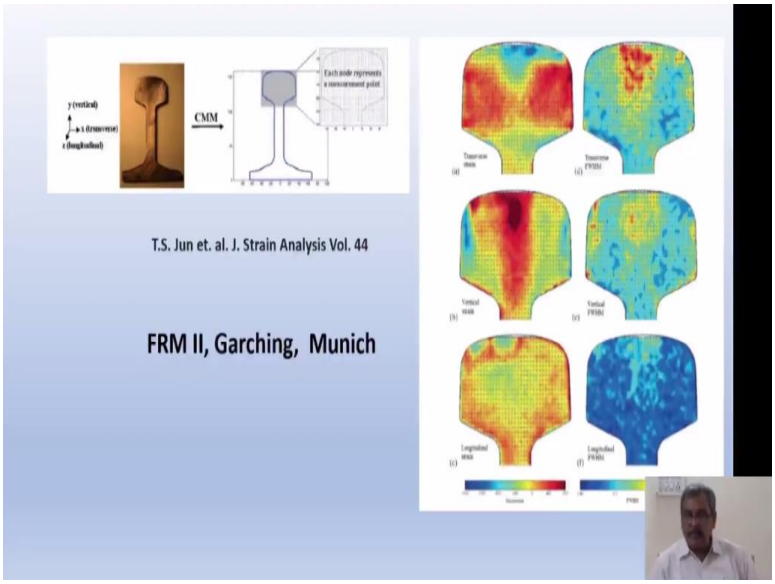

This experiment was done at FRM II Garching. This is a piece of a railway line which had seen a lot of passage of trains over it used and the strain mapping was done using neutron diffraction.

You can see the map. The red is the more stressed part. You can see (strain map) on this section of the railway line. They did mapping of the various parts of this railways line.

This map was obtained from the strain measurement using as I showed you earlier the diffraction technique with tight nose cones for the incoming and the outgoing beam. This is macroscopic strain on large samples. I mean at least the strain part are larger than microns and you can see that the volumes can be 10 cm^3 to 100 cm^3 for such studies, depending on the opening in the nose cones for such experiments.

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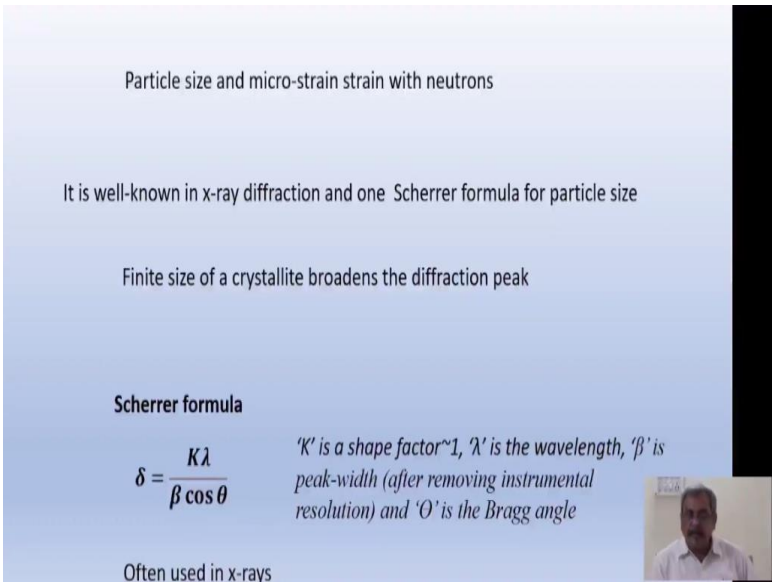

There is another way of doing particle size and microstrain measurement using neutron. This technique is well known with respect to x-rays and in the next part of the lecture I will attempt to explain to you how the same thing is done using neutrons.