Neutron Scattering for Condensed Matter Studies
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Week 5 Lecture 12A

Keywords: Diffraction, Structure, Dynamics, Length scales, Time scales, Time-of Flight, Frame Overlap, Choppers

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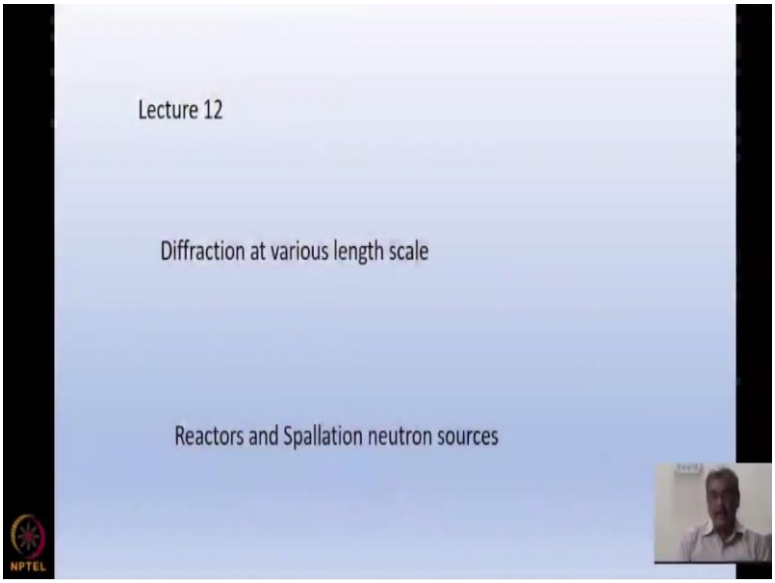

In this lecture, I will cover diffraction at various length scale. I have introduced it and in the following lectures I will discuss in details various important techniques that fall under diffraction. I will also introduce you to the fact that diffraction experiment is done in reactors and in spallation neutron sources or pulse neutron sources in two different ways. I will introduce you to both of these techniques in reasonable details.

Now, going to the fact that you can do diffraction at various length scales, what I mean is that mostly we are introduced to diffraction either using light where you talk about diffraction of the bending of beam at an edge or we talk about (x-ray) diffraction to find out crystallographic structures. Actually, diffraction is an elastic experiment where you determine structure at various length scales in various Q ranges because they are the conjugate (space *'r'* and momentum *'Q'*) of each other.

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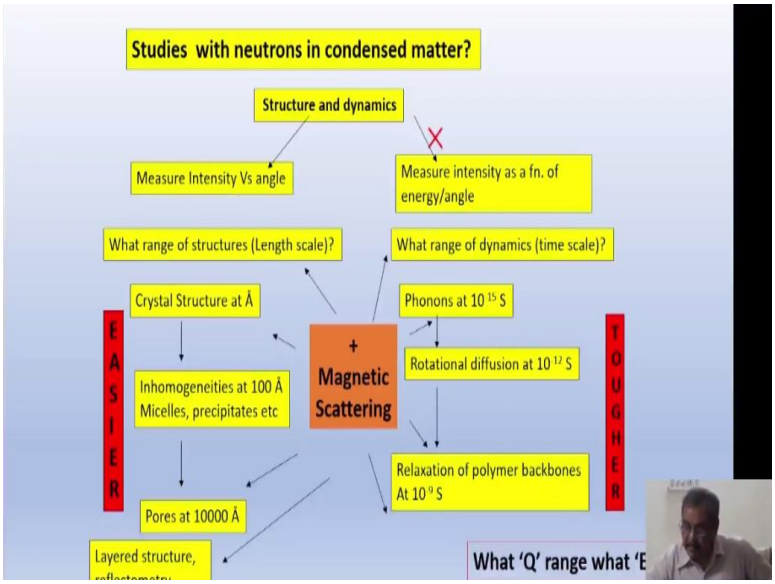

I had shown this slide to you earlier and again I am bringing to your notice that studies with neutrons in condensed matter can give us structure and dynamics (in materials). In case of structure, we measure intensity versus angle or we can translate it to intensity as a function of Q because for structure we are not bothered about energy transfer and Q is given by $\frac{4\pi \sin\theta}{\lambda}$ where *'θ'* is the angle in this slide. We measure intensity as a function of Q from where we go back to $g(R)$ which is a general correlation function in condensed matter. That means in diffraction we cover a wide range of length scales. For example, for crystal structure, we work at angstrom and sub angstrom level and for liquid and amorphous systems we can go up to fractions of an angstrom because in liquid and amorphous systems we have local (short range) structures, but no long-range order. At mesoscopic length scale, we can study inhomogeneities typically 10 to 100 Å like micelles, precipitates in metals or even pores in stones at ~ 10,000 Å. Also, under the same category of studies we have thin films where you can understand layered structures that means their thickness, interface roughness through reflectometry. Reflectometry can be done using neutrons and x-rays both. As neutrons are sensitive to magnetic moment, means all the techniques that I mentioned here has overlapping feature of magnetic scattering of neutrons.

The other half of the slide is about measurement of intensity as a function of energy and angle both. For structure I said range of structures. Likewise, in case of dynamics we check the time scale of dynamics. We can study phonons, rotational diffusions or even study slower dynamics at nanosecond time scale for relaxation of polymer backbone, using neutrons. These

experiments, per se are more difficult than the experiment where we attempt structures, because here we have to analyze the energy of the scattered beam and then the question will come at what *Q* range and in what *E* range.

Length scale is given by *Q* and energy gives us the time scale of the dynamics. If I do not use *E* measurement, then *Q* range gives us the length scale of the structure that we are trying to study.

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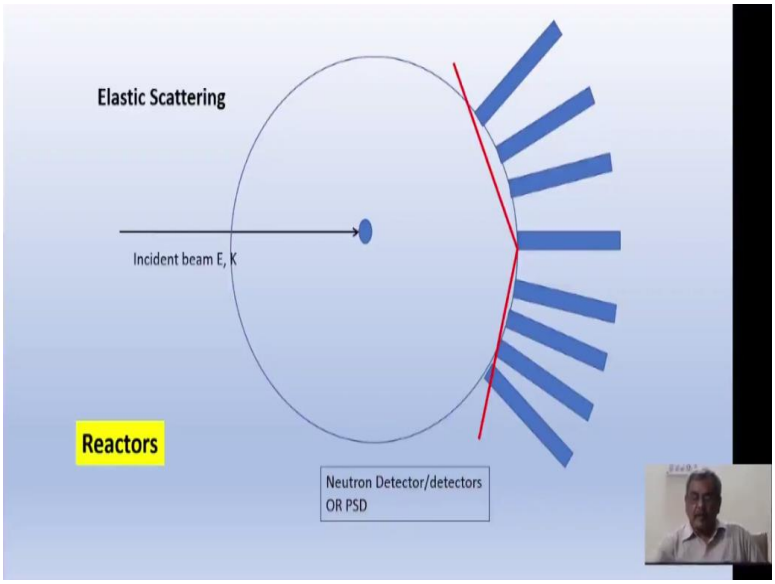

In this half of my talk, I will be in general addressing the elastic scattering. That means no energy analysis. I told earlier that in a reactor the incident beam is collimated as well as monochromatized and we defined the energy and direction where direction is given by *K* vector whose magnitude is $\frac{2\pi}{\lambda}$. The scattered beam will go on a sphere which looks like circle in two-dimensions, and then we use detectors. Detectors are (usually) inside the heavy shielding. Hence, it is difficult to cover the entire 4π (solid angle) with detectors in a reactor, using monochromatic beam.

Usually, we will be in a planar geometry where either you have the end-on detectors taking data serially angle by angle or we have got position sensitive detectors where the neutron detected at a certain position gives the direction of the neutron scattering because knowing the distance from the sample to the detector and knowing the resolution of the detector, we can tell what is the position and what is the position resolution (of neutron detected) in the experimental setup.

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This is the powder diffractometer at DHRUVA, I just show you the outside of the PSD detector bank.

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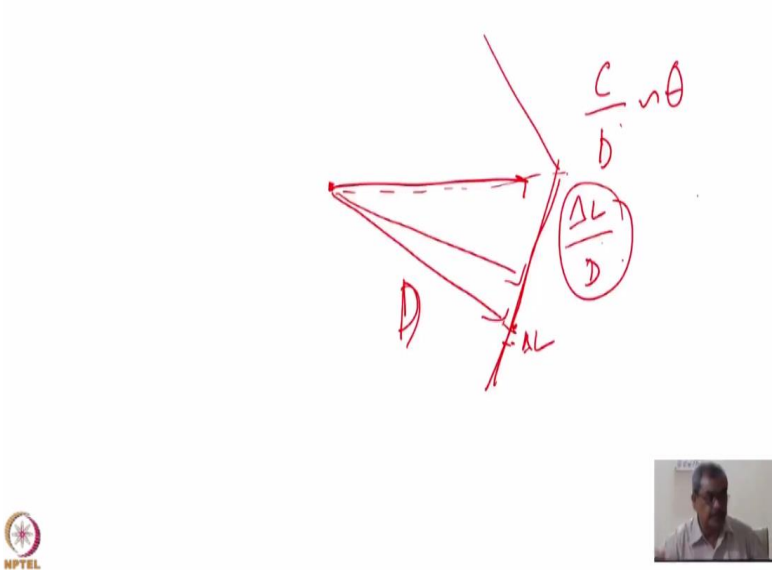

Here as I showed that there is a sample from which the neutron beam is scattered and goes in various directions and we have position sensitive detectors, the bank that I showed you. If the distance travelled by scattered neutron is *D* and the position resolution is ΔL and then the channel number divided by *D* will give an idea of the theta. ΔL/D will give you the resolution $\Delta\theta$ of the setup.

In the picture, you can see the back side of detector bank. The monochromator drum is here, at the center of which there is a monochromatizing crystal, the sample is somewhere over here and then you have this detector bank and this is the counting electronic as well as data collection software at DHRUVA.

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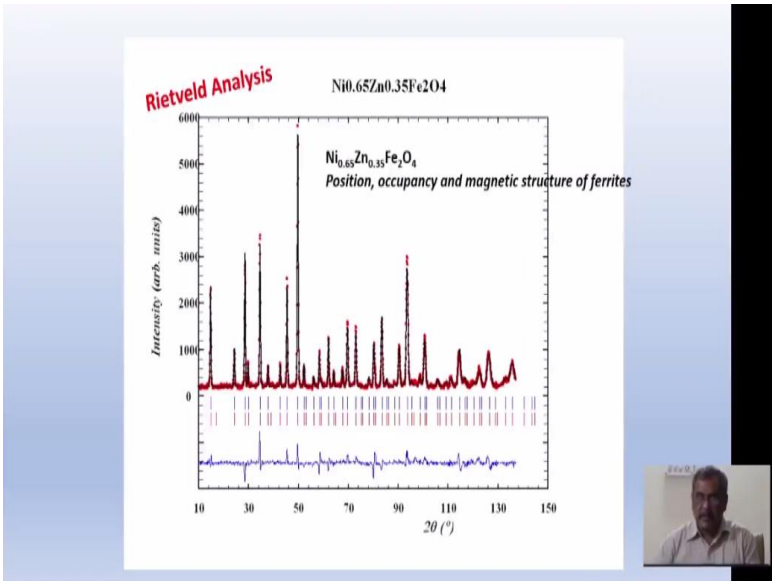

I just want to show you a typical data with Rietveld analysis. I have to introduce you to Rietveld analysis for data. Specifically, I will deal with crystallography together with magnetic crystallography because neutron is extremely important not only for finding out crystallography structure, but also to determine the magnetic structure. Actually, that is the strength of neutrons because (most) crystallographic structure can be easily detected by x-rays also.

X-ray, till now, is the most important tool to find out structure of materials except for the fact that the x-rays are insensitive to low *Z* material and that is why whenever my structure has got low *Z* materials, neutron is a better choice. But more importantly if it is a magnetic structure, for example, ferromagnetic iron, nickel, cobalt or compounds like $Ni_{0.65}Zn_{0.35}Fe_2O_4$, their structures and magnetic structures are sometimes commensurate and sometimes incommensurate, and neutron is possibly the only tool to determine the structure as well as magnetic structure.

Here the data you see is angle versus intensity and the data is from DHRUVA. This is a typical data and you can see how the fit looks like and from here in case of this sample magnetic structure was determined.

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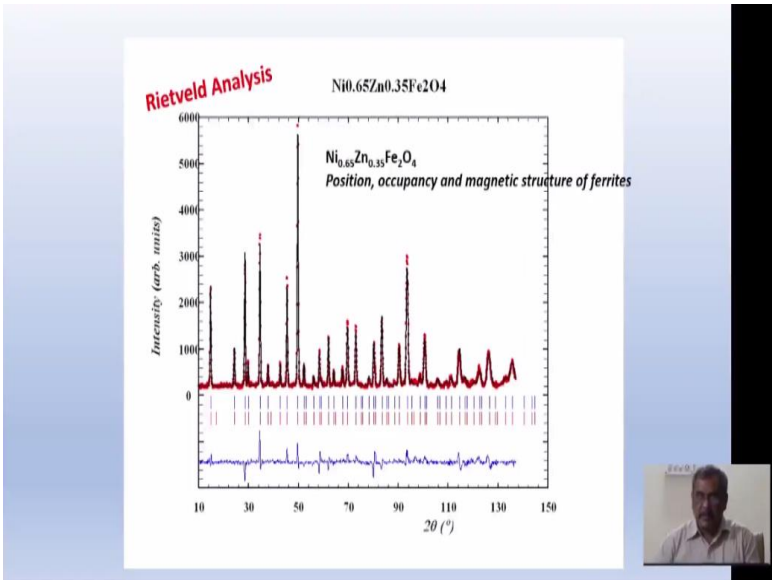

The photograph shown here is of diffractometer at ILL Grenoble which one of the most popular and possibly most used diffractometers. You can see the similarity with the previous photograph, diffractometer at DHRUVA. Here also we have a position sensitive detector bank. The beam comes on to the sample at the center of the sample table and in this case, we have much higher resolution and much better intensity. Typical structures (of instruments) are very similar in reactors where usually you have a sample surrounded by position sensitive detectors.

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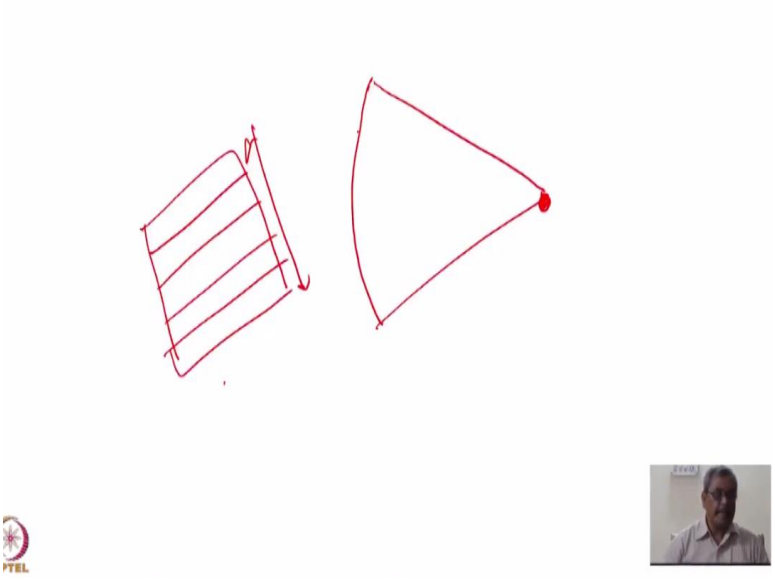

Sometimes the detector bank may (also) be vertically focused. So, you have vertically focus detectors raising the intensity detected being vertically focus and each phase has got a detector

where number of detector strips. It is bent in the vertical direction and horizontally also it gives a larger beam by bending the crystal in that direction.

So, these are the ways one can enhance intensity with a compromise between intensity and resolution in various spectrometer, but in general the powder diffractometers in most of the reactor sources look like this.

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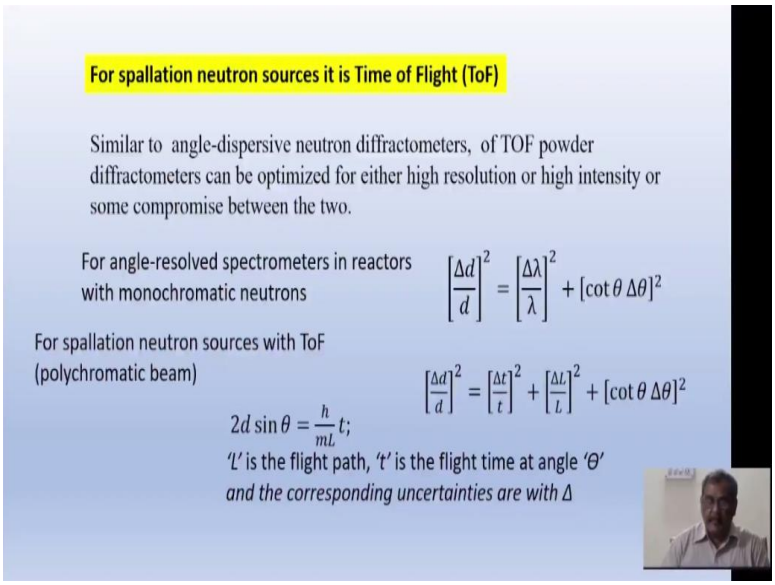

How will it be in a spallation neutron source? In a spallation neutron source, we have a polychromatic beam and you measure the time of flight. How do we measure time of flight?
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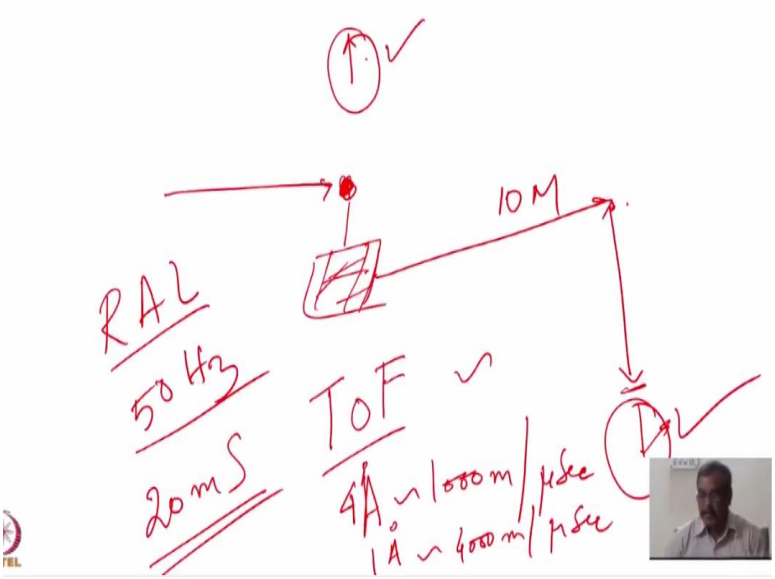

Primarily there is a proton beam which comes and hits a target which can be uranium or a high *Z* material like tantalum. When it hits a target, we start the clock. It is like starting a stop watch. The neutron goes from the target to a moderator and then it goes to the sample and gets scattered and once it comes to the detectors, I stop the clock. This way I measure the time of flight. A 4 Å neutron (typically) covers something like 1,000 m/μsec. So, you can imagine if it is a 1 Å neutron it will be covering around 4,000 m/μsec. The length scales are typically tens of meters. It can vary depending on the resolution that you demand from your system.

It is easy to measure the time of flight in this polychromatic pulse beams. If you want to do a similar experiment in a reactor then I have to chop the beam. If I chop the beam, I throw away lots of neutrons. Hence certainly I can do time of flight spectroscopy in a reactor, but at the cost of lots of neutrons. Whereas spallation neutron sources, which are pulsed neutron sources, are suitable for time-of-flight spectroscopy.

For example, the Rutherford Appleton Laboratory (RAL) has got a 50 Hz source that means 50 pulses per second and there are 20 milliseconds between the pulses. So, I can count neutrons pulse by pulse. For first pulse start the clock and when neutron is detected at detector stop it then for second pulse start the clock and when neutron detected then stop the clock and so on. That is how pulse by pulse you can do the spectroscopy.

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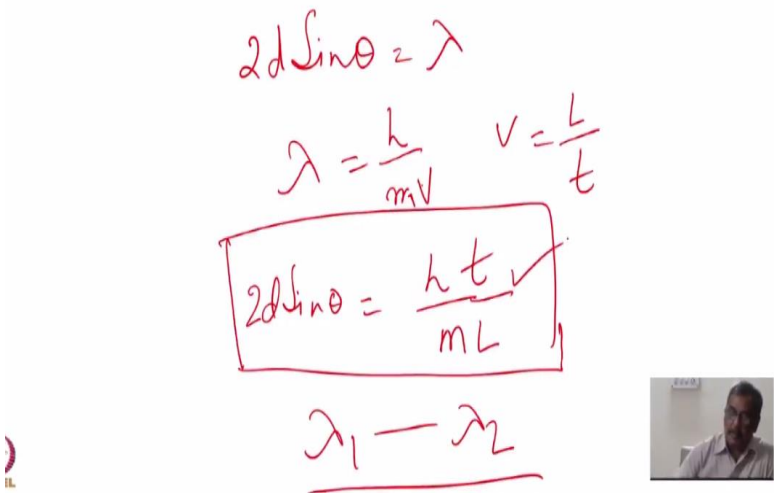

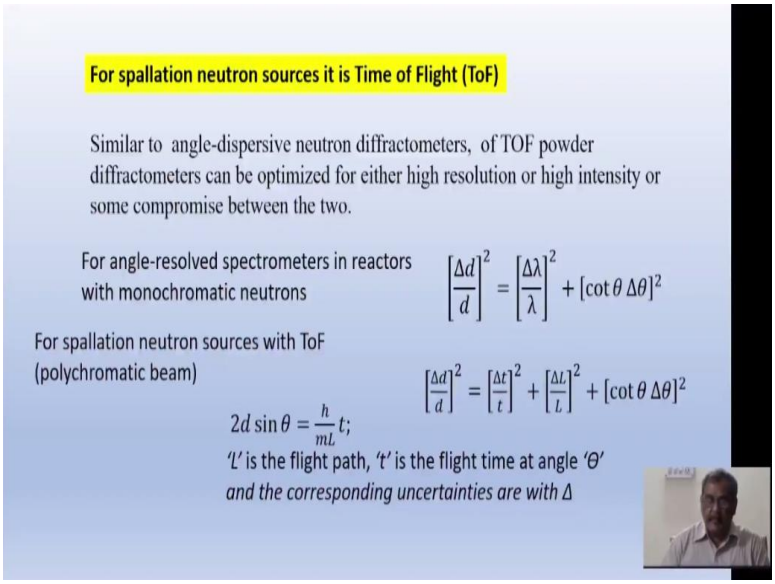

We know that Bragg law is given by, $2d\sin\theta = \lambda$ and we also know $\lambda = \frac{h}{mv}$ for any particle (de Broglie wavelength) and v for a particular wavelength of neutron is given by $\frac{L}{t}$ where t is time of flight. Using these, the Bragg's law for a pulse source for a particular time of flight in a polychromatic beam can be written as,

$$2d\sin\theta = \frac{ht}{mL}$$

In case of pulse sources, we do not try to monochromatize the source. We choose neutrons in a pulse, but of course we cannot take all the neutron. So, there is something called combination of choppers which will allow a certain range of wavelength for an application and after that we do time of flight spectroscopy using this formula.

Resolution in case of Bragg's law for a monochromatic beam with a mosaic spread is given by,

$$\left[\frac{\Delta d}{d}\right]^2 = \left[\frac{\Delta\lambda}{\lambda}\right]^2 + [\cot\theta\ \Delta\theta]^2$$

Here, first part on the R.H.S. is for wavelength resolution and the other part is the angle resolution. For polychromatic beam in case of spallation neutron source resolution is given by,

$$\left[\frac{\Delta d}{d}\right]^2 = \left[\frac{\Delta t}{t}\right]^2 + \left[\frac{\Delta L}{L}\right]^2 + [\cot\theta\ \Delta\theta]^2$$

Here, the first term is flight time resolution, 2nd is for flight path resolution and the last term is for angular resolution. All three of these can be improved if we use a detector bank far away

because if L is large then for a given ΔL for any kind of length determination $\frac{\Delta L}{L}$ will be fractionally small. Similarly, for a large T, $\frac{\Delta t}{t}$ will be small if I go farther away because longer is the length, larger t.

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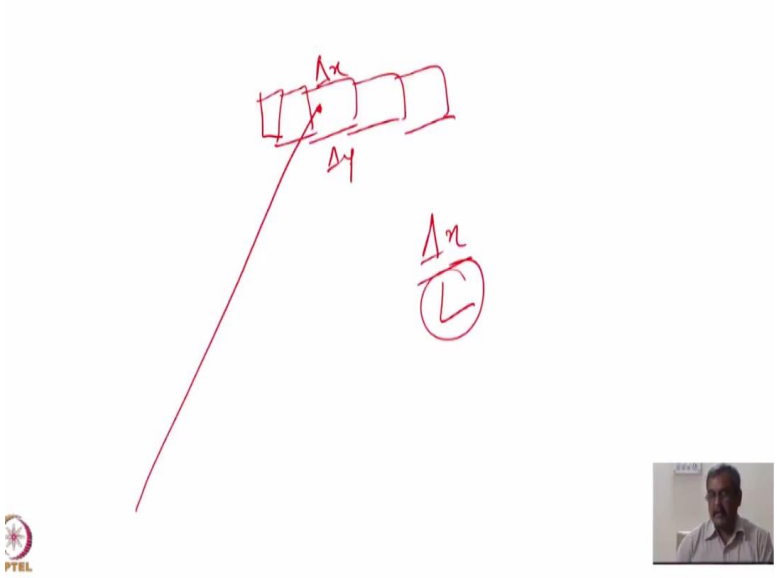

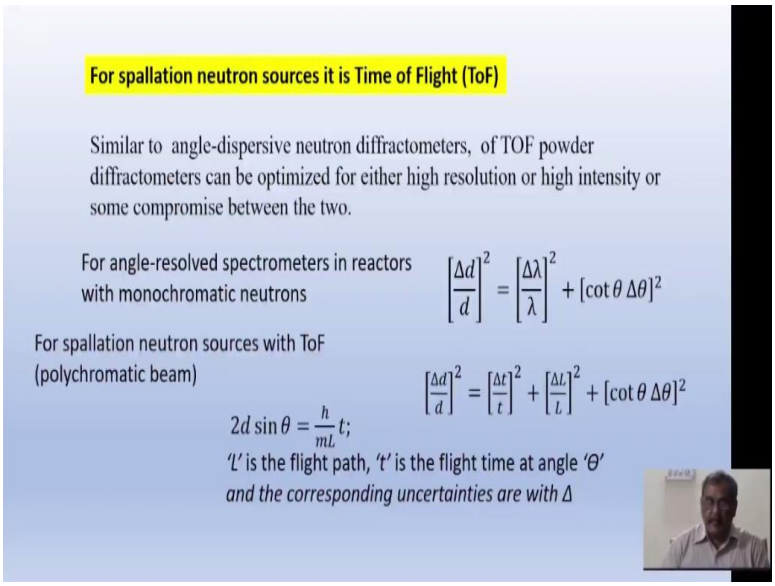

Similarly, I may use a detector bank with detectors matrix like this. One of the strips here has got some Δx, Δy spread for neutron detection then angular resolution goes as $\Delta x/L$ and larger the L, given the size of a detector, the angular resolution will be better. So, larger flight path gives larger time (resolution) and a detector bank with (smaller) matrices of detectors with better angular resolution.

In backscattering geometry $\cot\theta\,\Delta\theta$ is the best at 180° when, it is equal to 0. So, in backscattering geometry at a large distance with a long flight time we will get the best resolution, and $\Delta\theta$ can be reduced using strip detectors.

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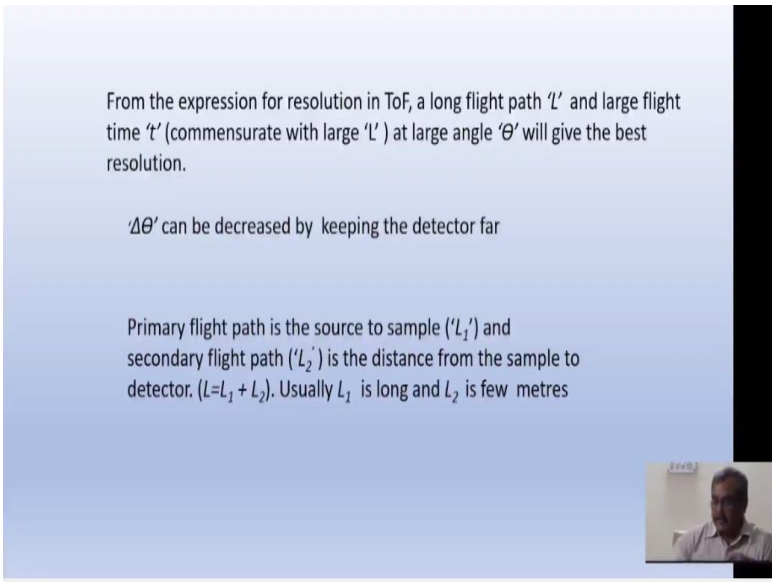

Usually in most of the experiments, the primary flight path is the source to sample, L_1 and secondary flight path is sample to the detector L_2. $L_1 + L_2$ dictates the L. Usually L_1 is kept long and L_2 is few meters except for the cases when we want to have very high resolution.

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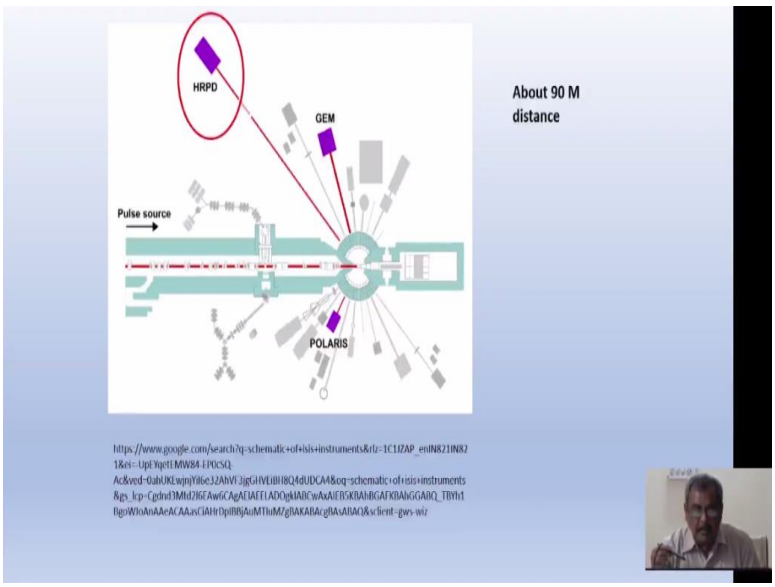

I just show you the schematic of one of the best powder diffractometers at Rutherford Appleton Laboratory. This is called high resolution powder diffractometer or HRPD, shown here in red

circle. There are detectors at shorter distances, but the high-resolution detector bank is nearly 90 m from the sample.

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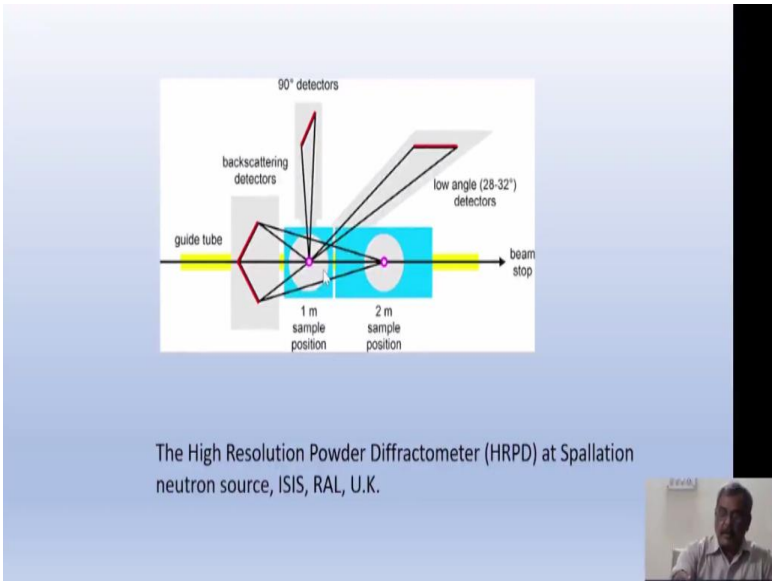

So, the neutron has to fly through 90 m path before it reaches the detectors. There are other technical difficulties which I am not discussing at the moment. You have to understand that if neutron travels through air, then it will be highly absorbed in air and then it will lose intensity. Hence, basically, it is travelling through 90 m long evacuated tubes and then they are detected at the high resolution, detector bank in HRPD. In general, this is the guide tube which brings in the thermal neutron to the sample, you have two sample positions and a low angle detector bank and of course you have the backscattering detectors in this particular experiment.

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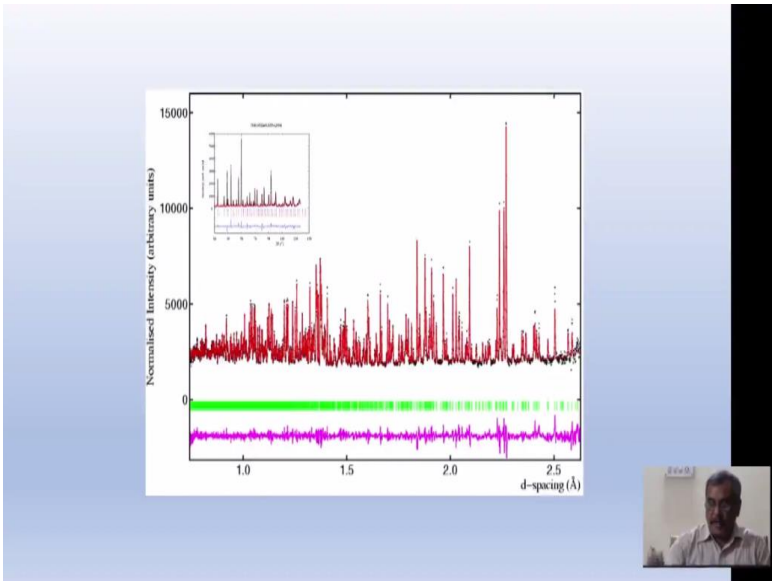

Now I show you the data from HRPD. The first thing that you can notice is that the resolution is extremely good as the peaks are extremely narrow, but the other part is that if you see this *x* axis it is in d-spacing.

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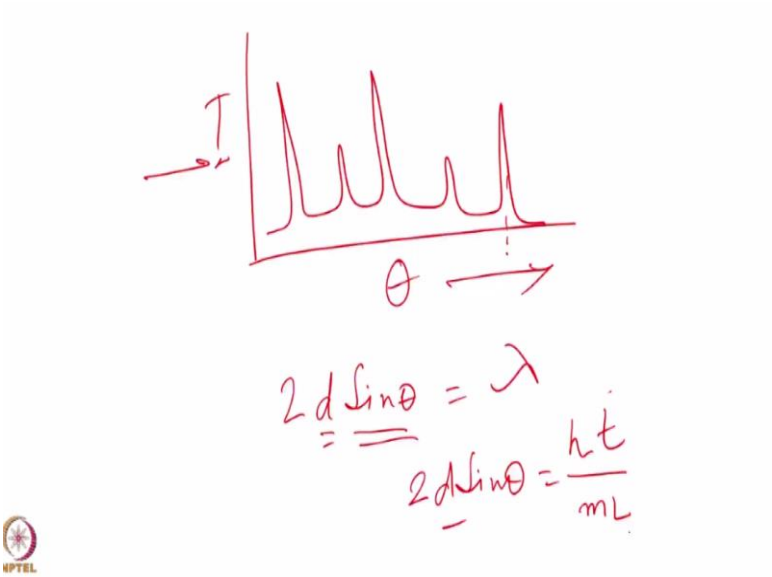

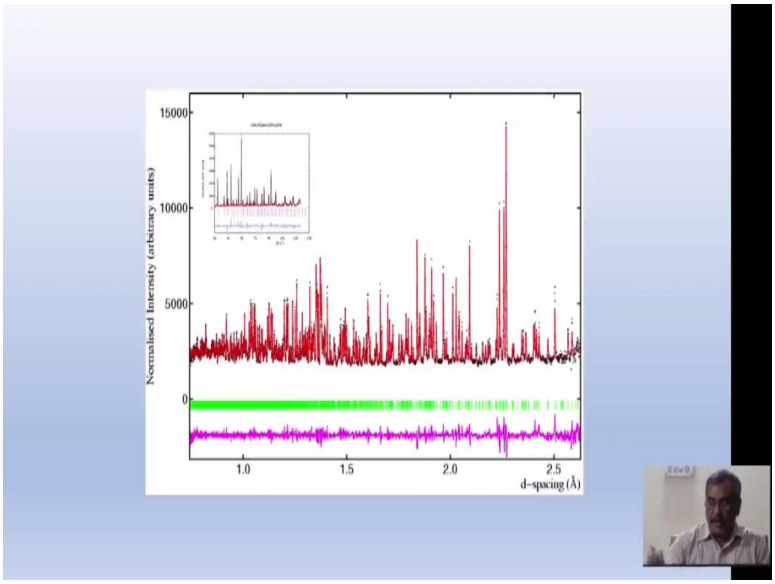

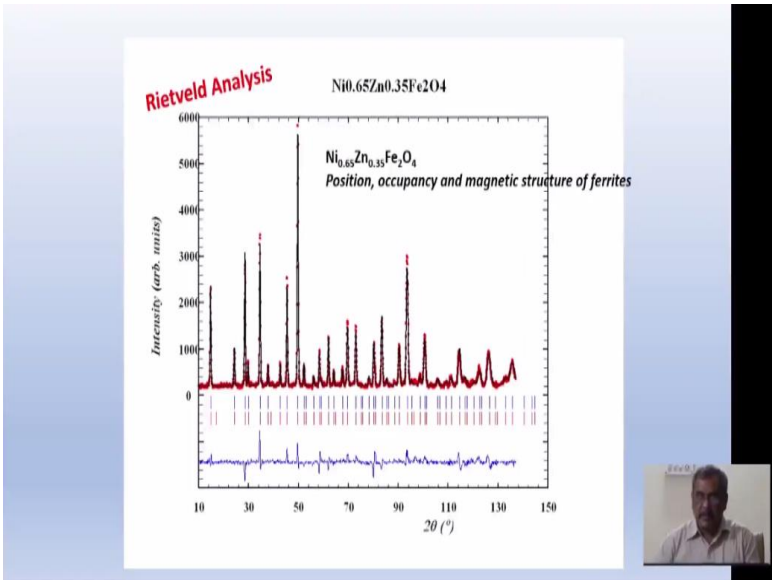

If I see the intensity as a function of angle (θ) in a monochromatic beam then using the relation, $2d \sin\theta = \lambda$, as I go to larger and larger θ then $\sin\theta$ goes up and *d*-spacing goes down. Hence, small *d*-spacing peaks comes at larger θ.

On the other hand, if I see the time-of-flight spectrum then using the formula for polychromatic beam, $2d \sin\theta = \frac{ht}{mL}$, as the *d*-spacing increases the time of flight increases for the given fixed flight path and at a given fixed angle. Here when I plot as a function of *d*-spacing or as a function of time of flight in case of spallation neutron source diffraction pattern looks like the mirror image of what we see in a diffraction pattern from a reactor source. That is why the same pattern which I showed you earlier I just want to show you here again.

This is the pattern which I showed you from DHRUVA. I have kept it as an inset to this data from HRPD. This is the time of flight or *d*-spacing axis, there you can see that these are mirror image of each other. But most importantly here you see lot of sharper peaks in case of time-of-flight spectrum at HRPD, the diffraction spectrum in a pulse source.

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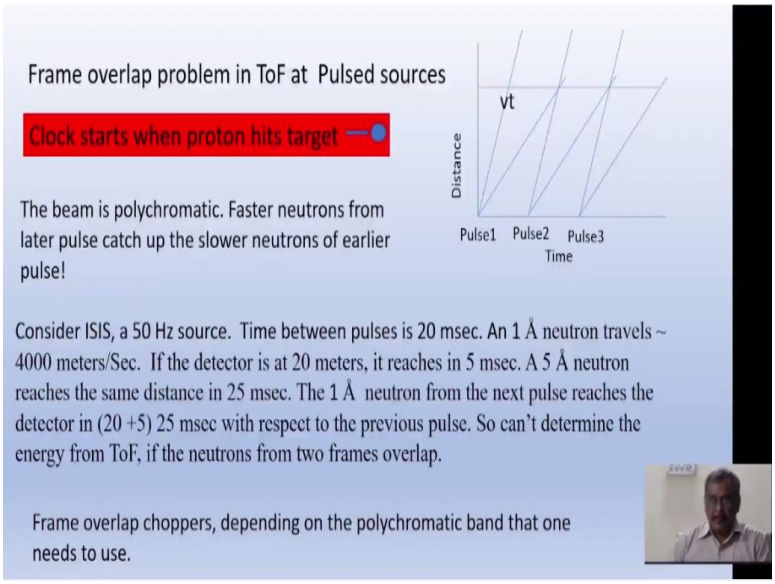

But there is a very serious issue which is known as frame overlap problem in time-of-flight spectroscopy at pulsed sources. I had started the clock when the proton has hit the target say at $t = 0$.

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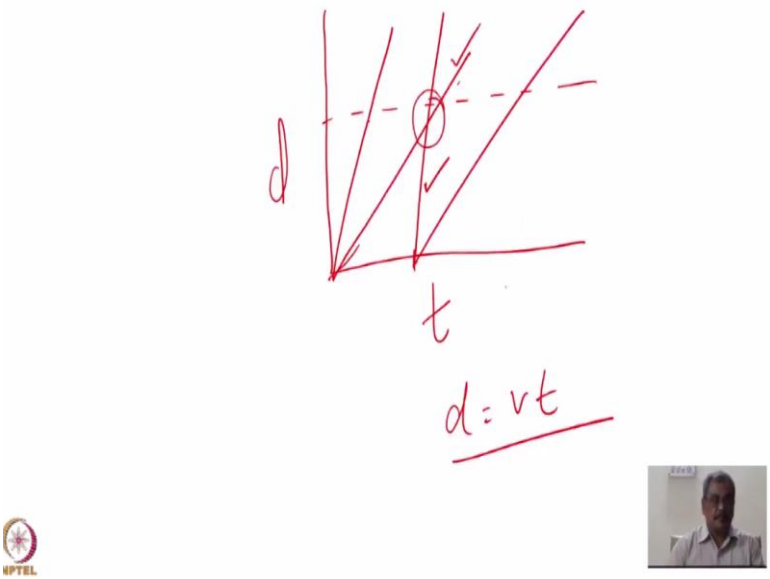

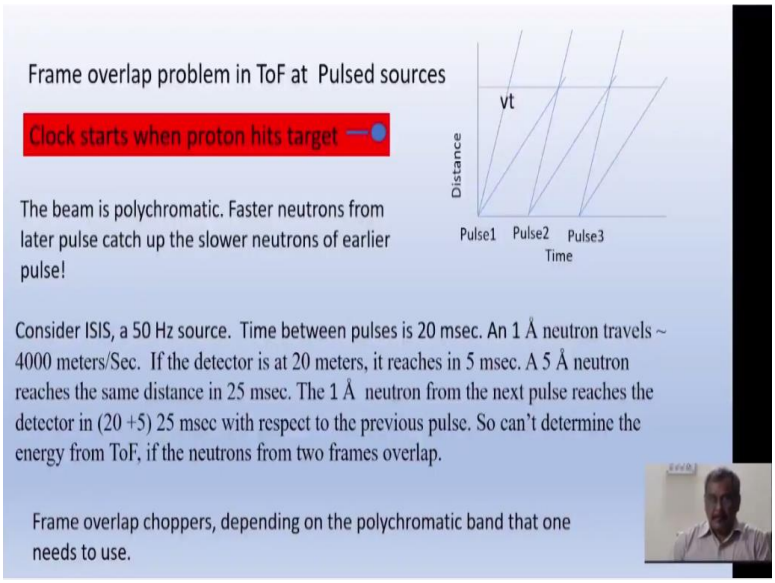

After that, with all uncertainties regarding moderation (of neutron) and transport of the neutron beam, I have a neutron beam of spectrum with fast and slow neutrons. This axis is time and the other axis is distance. We know distance is given by velocity × time. For smaller velocity it goes slower and reaches the same distance at a much later time.

This is the band of neutrons which have been allowed to pass through my choppers. This is the band which I will be using for diffraction and I need to measure time of flight. Let us consider the next pulse. Again, I have the same band and it goes like this, but now imagine this one (previous pulse) and this one (later pulse). The slower neutron of the previous pulse is taken over by the faster neutron of the next pulse. This is like you might have witnessed sometimes in a race. Some competitors are lagging by one full lap. And because they are going in circles you do not know whether he is first or he is the last because you see the other competitors moving with him. This is known as frame overlap. This is the fact that the slower neutrons of the previous pulse are caught up by the faster neutron of the next pulse.

This is what I try to show you pulse 1, pulse 2, pulse 3 through the chopper. The same range of wavelength passes. But when I go to very long distances there is a good chance that the pulses will be overlapping when the beam is polychromatic in case of pulse neutron sources. For an example, again consider ISIS which is a 50 hertz source. The time between the pulses is 20 msec. Now a 1 Å neutron is travelling at 4,000 m/sec. If the detectors are at 20 m, it reaches the detectors at in 5 msec that we can see. A 5 Å neutron is 5 times slower. So, it reaches the same detector in 25 msec. Then the 1 Å neutron from the takes 20 + 5 = 25 msec because it takes 5 msec to reach and we started 20 msec later.

So, the 5 Å neutron of the previous pulse has been caught up by the 1 Å neutron of the next pulse and we cannot determine the time of flight if I allow this frame overlap. That is why we not only use polychromatic beams, but we also need to use frame overlap choppers that restrict the wavelength band depending on how far you want to put the detectors and in turn, that depends on what is the resolution that you are demanding in this experiment.