Neutron Scattering for Condensed Matter Studies
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So far, I have described how to find out macroscopic strains in a crystallographic sample (powder sample) and how to obtain the strain values from such measurement.

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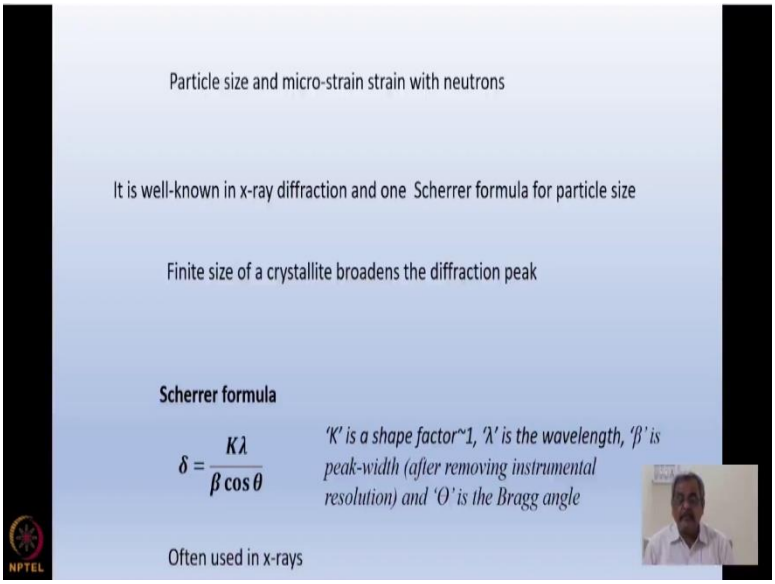

Please note that when I say powder it is not a powder in a sense that we commonly call something a powder. Here the powder means it is a solid object for all practical purposes but it has got all possible orientation of the crystallographic planes and this is the crystallographic definition of a powder sample and not the powder that we know of like a talcum powder. So, please note that when I say powder it means that there are all possible orientations (of crystallites).

So far, I have discussed macroscopic strain that means the entire crystal that is either compressed or elongated and how to study various cases of interest. I took two examples; one was welded pipes and another one was a railway track. Now, there is also microstrain in such samples.

What is the difference between microstrain and macro strain? The microstrain especially for nano crystals they vary from part to part. They cause broadening of the Bragg peak. Often, in x-ray diffraction we use Scherrer formula for particle size. The finite size of a crystallite also broadens the diffraction peak, finite size means the crystallite is small. When we say that the Bragg's diffraction peak is a delta function, actually it is not a delta function that we expect for a perfect crystal. The Bragg peak has a finite width something called a Darwin width which is in arc seconds. But for all practical purposes they are delta function and if there is a finite size of the crystal then there is a broadening of the diffraction peak, much larger than Darwin width (in arc minutes).

Hence, there are two kinds of broadenings now which are coming together: one is the particle size broadening and the other is due to the micro strain in the sample. The crystallite size we obtain using what is known as the Scherrer formula. Scherrer formula is, particle size, *'L'* is $L = \frac{K\lambda}{\beta \cos\theta}$ where K is a shape factor and is close to 1, λ is the wavelength of the beam, β is the peak width for a Bragg angle at θ.

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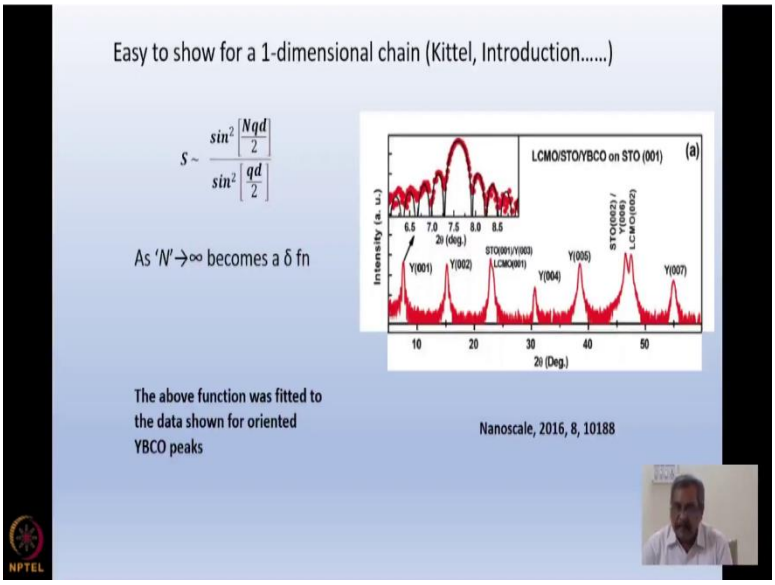

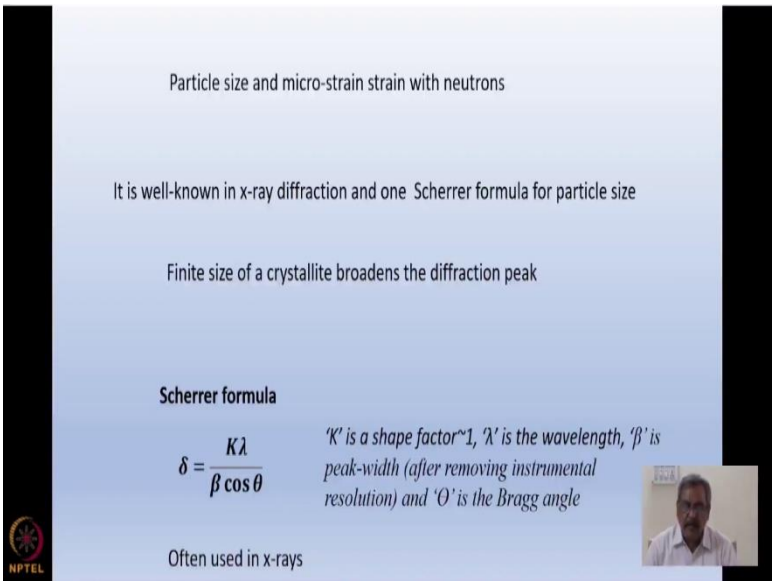

Now the I am taking you back to your master's degree days. For a one-dimensional chain of *N* lattice points, the broadening of the Bragg peak is given by $\frac{\sin^2\left[\frac{Nqd}{2}\right]}{\sin^2\left[\frac{qd}{2}\right]}$ and as N goes to infinity this expression goes to a delta function. I have shown you here that using this formula we could obtain the peak shapes for a highly oriented YBCO crystal and from there we could actually fit the *N* value. In this case the sample was a thin film.

So, for a one-dimensional chain it is easy to evaluate, but even for a three-dimensional chain the phenomenological formula of $\frac{K\lambda}{L\cos\theta}$ is used often to find out the particle size broadening. Here this particle size broadening is due to the finite size of the crystal but the fact is that the neutron has got a coherence length and the particle size should be smaller than the coherence length for this approach to be effective.

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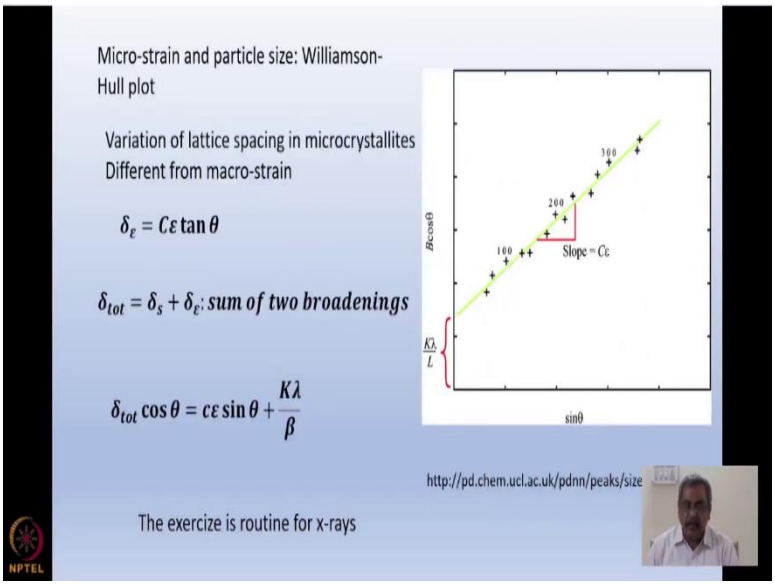

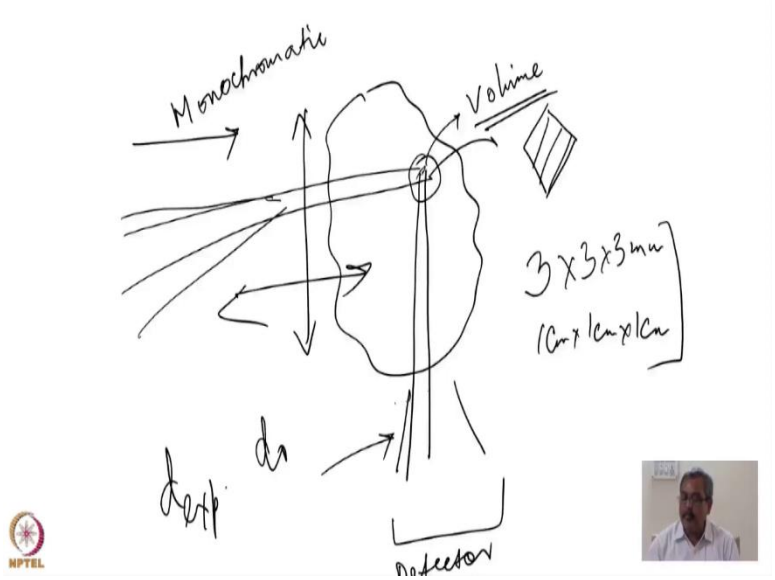

Also, there is strain related broadening, (as I mentioned). Here the strain related broadening is not a macroscopic broadening but there are defects and vacancies around a crystallographic site and also there can be stresses sometimes due to a grain boundary. Here again the Bragg peak keeps shifting because there is a micro strain operating. This means around some sites it is elongational and somewhere it is compressional and the Bragg peak gets broadened due to this microstrain.

Hence, the broadening of the peak is due to particle size and also due to micro strain. These two cause a broadening of the peak and from these two contributions we should be able to estimate the value of the particle size and also the micro strain. This is given by something known as Williamson Hull plot.

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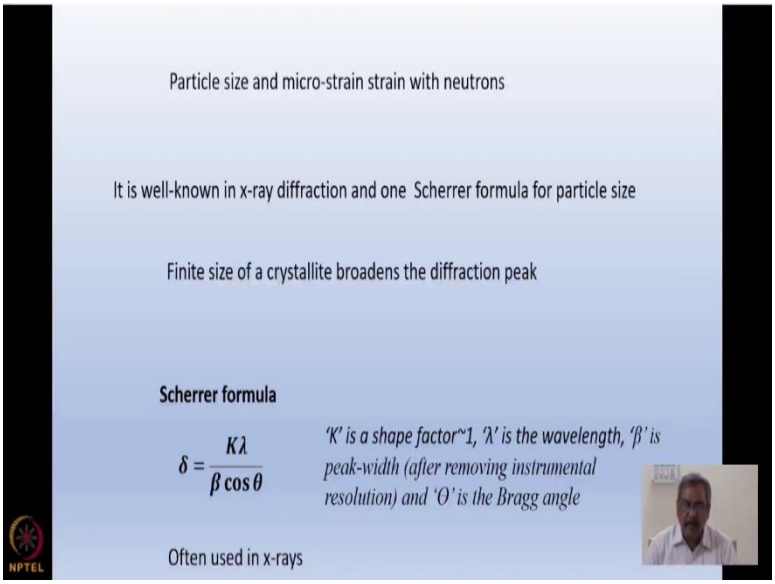

Now the variation of the lattice spacing in micro crystallites coming from micro strain is $\delta_\varepsilon = C\varepsilon \tan\theta$ where θ is the Bragg angle and there is also the broadening due to particle size which is $\delta_p = \frac{K\lambda}{L\cos\theta}$.

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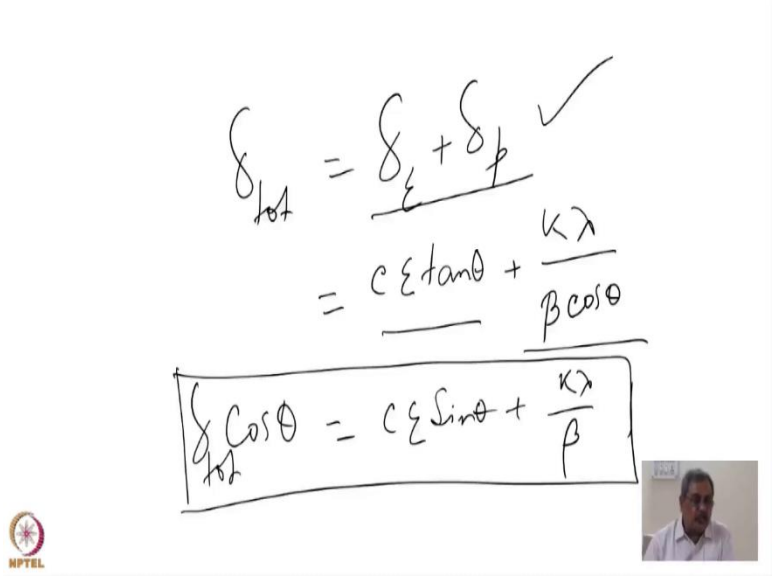

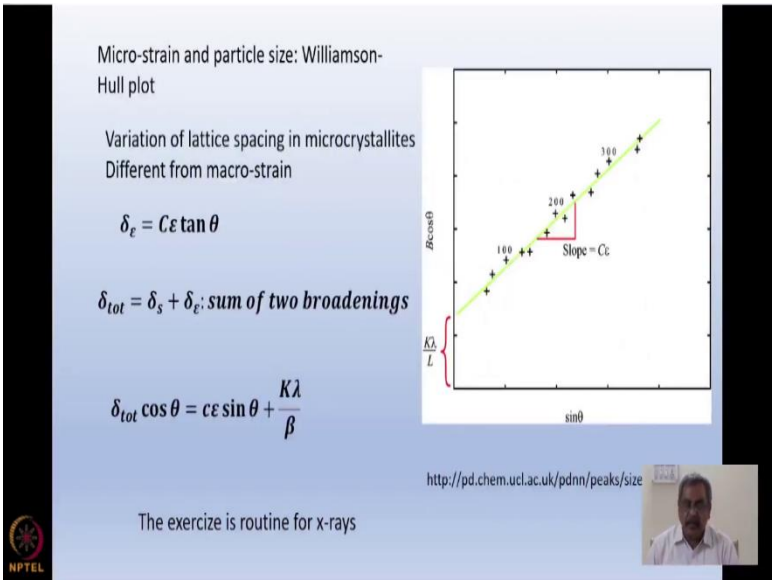

Hence, sum of two broadenings is, $\delta_{tot} = \delta_\varepsilon + \delta_p = C\varepsilon \tan\theta + \frac{K\lambda}{L\cos\theta}$. Now please note that I have written this as a summation, assuming that the broadening due to strain and the broadening due to particle size are independent of each other and I can add them. This is an assumption and if it is not true then I cannot use this formula. But, for now, I will go with the assumption that the micro strain and the particle size do not interfere and the total broadening is given by the broadening due to strain and the broadening due to particle size.

If I multiply δ_{tot} by $\cos\theta$ then it reduces to

$$\delta_{tot} \cos\theta = C\varepsilon \sin\theta + \frac{K\lambda}{L}$$

Now with this formula, which is very handy but highly macroscopic and phenomenological and often it is true for engineering samples, I can have a plot between $B\cos\theta$ (here $B = \delta_{tot}$)

and $\sin\theta$. ε can be obtained from the slope of the plot and the intercept gives $\frac{K\lambda}{L}$. Hence, from Williamson Hull plot we can obtain the micro strain ε and also the particle size. You can see here that the plot consists of points corresponding to various Bragg peaks against $\sin\theta$. So, this plot gives me strain as well as particle size in one go. But this is not microscopic and there are other more elaborate theories which I will refrain from discussing now.

Williamson Hull plot used for x-rays can also be used for neutrons.

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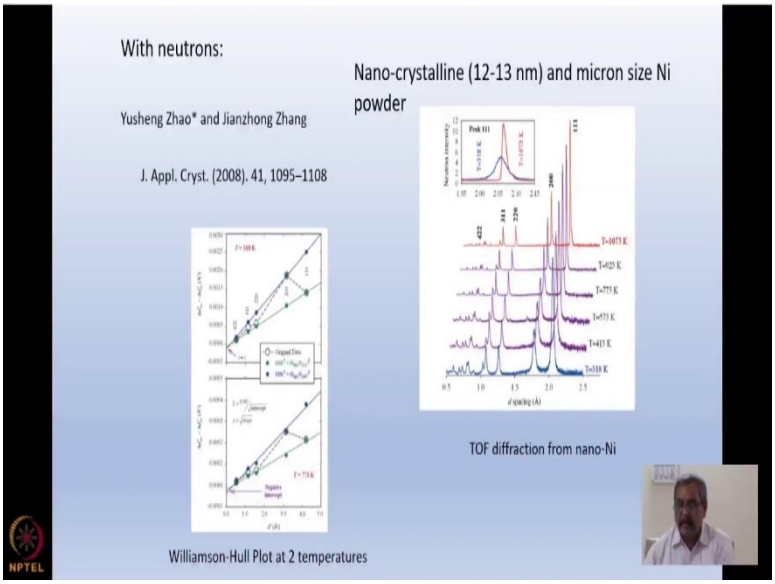

In the slide, I have shown the example of Williamson Hull plot used for nano crystalline and micron size nickel powder using neutrons. Nano crystalline means the micron size powder also have nano crystallites of typically 120-130 Å size. Here time of light diffraction data has been used in a spallation source That means t this is just a mirror image of the kind of diffraction data that you will get using neutron at monochromatic sources

Increase in *d* spacing means time of flight is increasing and the small angle peaks come from large *d* spacing. In the inset I have shown that when you anneal the sample, there is a broad peak which is shifting to larger theta which means that the lattice is relaxing to a lower value of *'d'* and the peak is also becoming narrower that means annealing at 1000 °C the particles are growing in size.

With respect to the diffraction data obtained, Williamson Hull plot should be square summation but in principle they are the same and you can see that the particle size and the microstrain both can be obtained from the Williamson Hull plot using neutrons.

This completes the part that I want to discuss with you about macro strain, micro strain and particle size. Two techniques which I discussed here are more of interest for industrial problems and many times these are used to find out strain in welding joints or even samples which have been stressed for a long time like the railway track I showed.

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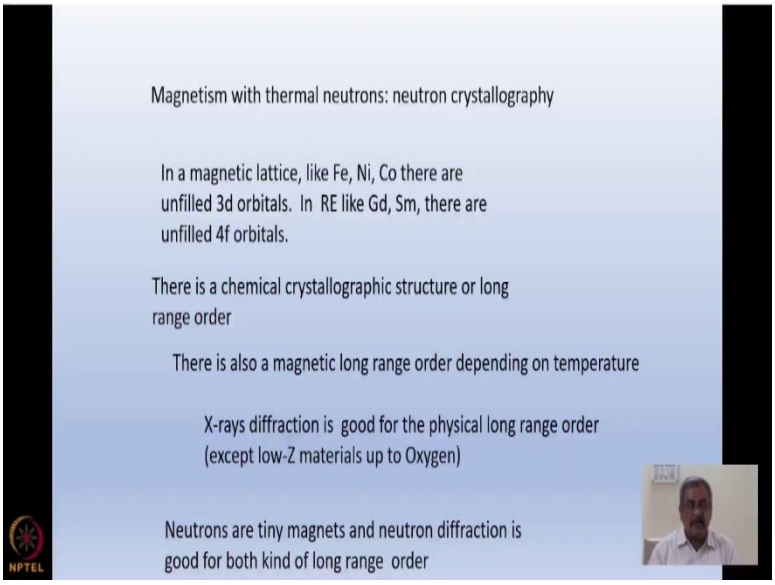

Next part of my talk is the most interesting for the people who are interested in magnetism, because I will be discussing the neutron diffraction from magnetic lattice with elements like Fe, Ni, Co which are 3*d* elements or rare earths like Gd, Sm etc. which have unfilled 4*f* orbitals.

These unfilled shells give rise to magnetism in materials and we can consider this atomic magnetism as a spin sitting at a lattice site. Now there is a chemical structure that means long range order in a crystallographic lattice and along with that there is also magnetic long-range order depending on the temperature of study.

X-ray diffraction is good for the physical long-range order of a crystallographic structure. X-ray is an extremely powerful tool and in synchrotron you can have x-ray beams which are extremely narrow and of micron size and in intensity possibly at least 10^8 orders stronger than highest intensity possible in a neutron source. So, x-ray diffraction is very good for finding out long range physical order or crystallography structure in samples except low *Z* materials because x-rays cannot see atoms up to oxygen (due to low scattering cross-section). Hence, samples with atoms of hydrogen to oxygen are not studied by x-rays and again for that you have to come back to neutrons. Neutrons are also tiny magnets, hence almost all the time when we do neutron diffraction, we are doing it with an intention of finding out chemical as well as magnetic long-range order.

In my next lecture I will introduce you to some extent with the elementary magnetic interactions in solid state causing long range order and then how we can decipher them using neutron diffraction.