

Neutron Scattering for Condensed Matter Studies
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Week 02
Lecture 04A

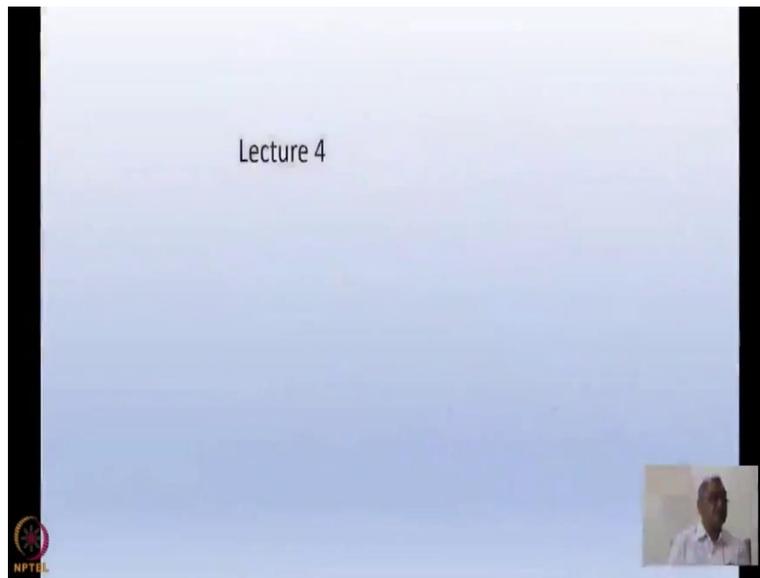
Keywords: Bragg Peaks, Debye-Waller factor, Thermal ellipsoid, Rietveld analysis

In this lecture, initially, I will give you a recap. Till the last lecture, I have derived the scattering amplitude for X-rays and neutrons. For neutrons, I used Fermi's golden rule and derived the scattering amplitude and the intensity also where square of the scattering amplitude will give us intensity.

I did the same for X-ray to compare the two scattering amplitudes and I mentioned to you in the previous lecture that the scattering amplitude remains same except we have a summation over b_j $\sum b_j e^{iQ \cdot r_j}$ when we have a potential at the site r_j and this is for a delta function potential in case of thermal neutrons. In case of X-rays, it is almost similar only instead of b_j summed over some j , I have something called f_j and then $e^{iQ \cdot r_j}$ part remains same.

So, this f_j is a form factor, I introduced for X-ray, which is the Fourier transform of the charge cloud at a point and it falls in 'Q' space, whereas, in case of neutrons I have b_j . In a plot f_j against Q it falls, but b_j remains constant. I mentioned that this is because it is a delta function in real space for a nuclear potential. Hence the Fourier transform of the delta function remains same all over Q; it is a constant value in Q. This is one advantage of neutron diffraction. But all the derivations done so far were for a lattice at 0 K. Today, I will introduce you to the temperature effect for the same diffraction. And then I will go over to bring in dynamics in our formalism that is the proposal for today. Now, I will continue with the lecture.

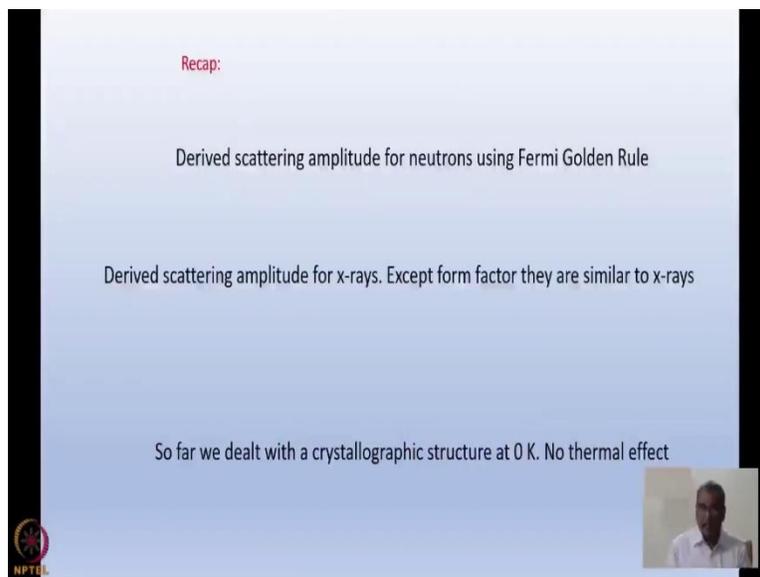
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Lecture 4

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Recap:

Derived scattering amplitude for neutrons using Fermi Golden Rule

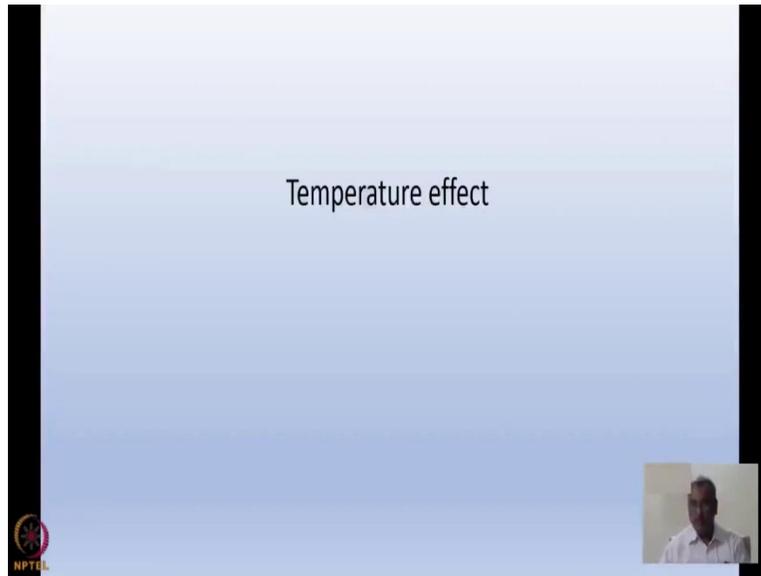
Derived scattering amplitude for x-rays. Except form factor they are similar to x-rays

So far we dealt with a crystallographic structure at 0 K. No thermal effect

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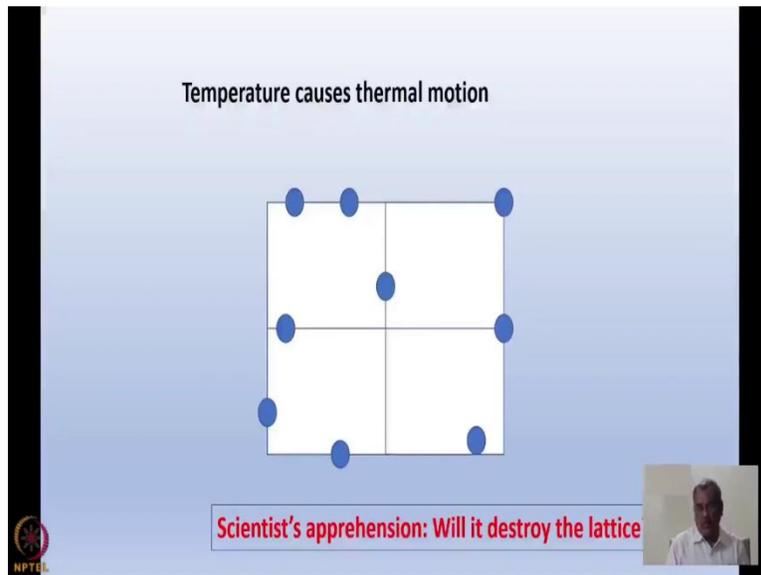


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So, what does temperature do? That is the question.

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Temperature causes thermal motion we know. Scientists were apprehensive about the fact that when we have a finite temperature then, even if we have an underlying crystal lattice, it may look somewhat like what I am showing here in this picture, because these are deviations from the mean positions. It is a square lattice, so mean positions are indicated in the grid, but at any particular temperature because of thermal motion the atoms will move.

And if I look at any instant of time, it might look something like this. So, the structural experiment gives, basically, an average of such instantaneous pictures either over time and also over the entire ensemble of atoms or the whole crystal. Before the first diffraction experiment, scientists felt that there will be no regularity of the lattice can be seen. That was the apprehension. And I would like to share with you a bit of history, just a little bit. This apprehension was not by anybody, but some of the major scientists.

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The last hurdle before the experiment

The Easter vacations soon began and during that period a group of physicists traditionally met in the Alps for skiing. Here Laue discussed his idea with Sommerfeld, Wien and others

Result?

Encountering a strong disbelief in a significant outcome of any diffraction experiment based on the regularity of the internal structure of crystals.

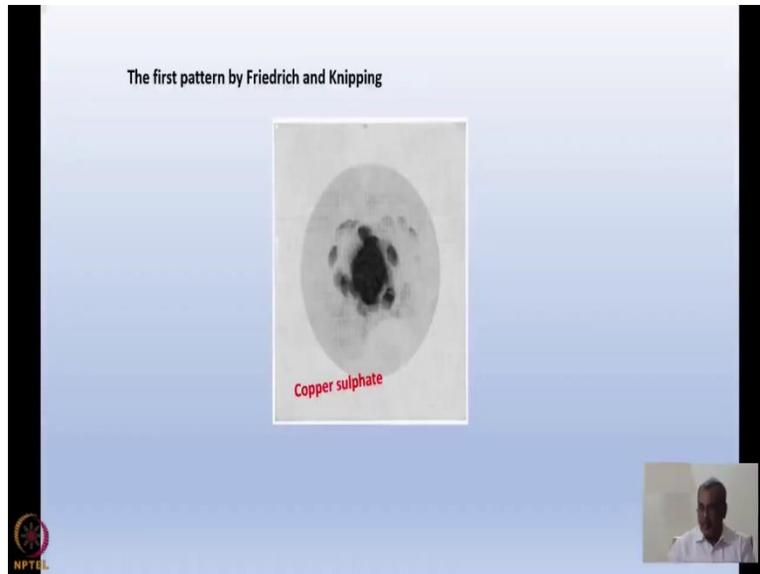
It was argued that the inevitable temperature motion of the atoms would impair the regularity of the grating to such an extent that no pronounced diffraction maxima could be expected.

NPTEL

Once Laue had the idea that materials or crystallographic material can act like a three-dimensional grating in front of X-rays, and he wanted to look at the diffraction pattern from this grating. A grating must be familiar to you, we use it in case of optical rays. He shared this proposal on a holiday, during the Easter vacation. He was in Munich University and they used to go to Alps for skiing and he discussed this problem with Sommerfeld, Wien, and other big experimentalists.

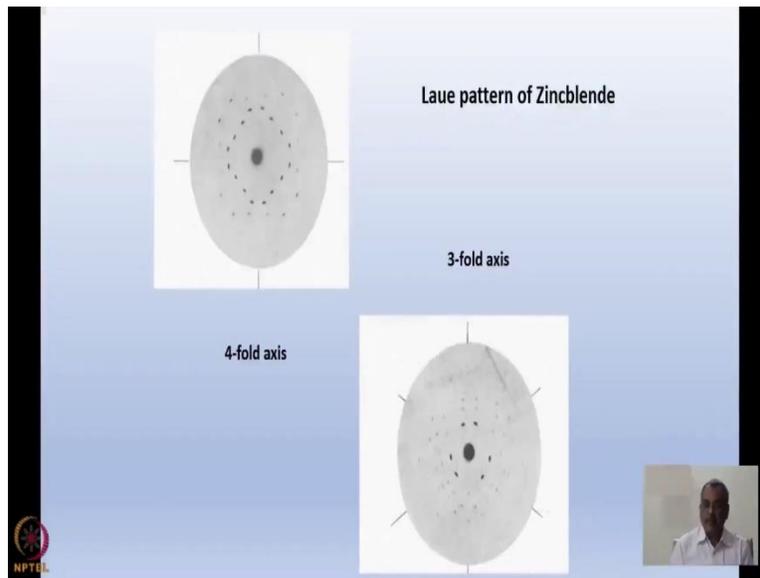
What was the result? The result was, encountering a strong disbelief in a significant outcome of any diffraction experiment based on the regularity of the internal structure of the crystals, because they said the regularity will be disturbed. It was argued that inevitable temperature motion of the atoms would impair the regularity of the grating to such an extent that no pronounced diffraction maxima could be expected. This was a view of the most established experimentalists at that day. Debye will later attack this issue and I will show you what happens.

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But the fact is that it was also decided by some scientists that since X-ray machines were available at University of Munich, why not do the experiment. And I am showing you, historically, the very first X-ray diffraction that was done on copper sulfate. The first diffraction was done by two young experimentalists. You will be surprised to know that these experiments were pushed in the busy scheduled of the X-ray machine in University of Munich during off hours, but in these experimental results for first time you can see the Laue spots, or the diffraction spots on the photographic plate as expected by Laue. So, this is a pattern, today known as Laue pattern. At that time, it was not called Laue pattern where the diffraction spots could be seen.

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Very quickly, they improved the experimental setup and from the Laue pattern of zincblende (ZnS). You can clearly see it is a single crystal, the fourfold symmetry over here and the threefold symmetry over here. So, it was established that the even at a finite temperature, at that time it was whatever the room temperature in the experimental hall, Laue pattern or the diffraction patterns do appear. They do not disappear.

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P. Debye was the one to solve it: again after an animated argument at the coffee table of Cafe Lutz

I came to the conclusion that the sharpness of interference lines would not suffer but that their intensity should diminish with increasing angle of scattering, the more so the higher the temperature.

P. Debye

Temperature →

The mean position does not change.

$$I = I_0 e^{-\frac{1}{3} \langle u^2 \rangle Q^2}$$

Debye-Waller factor

In general the displacement is not spherical, but an ellipsoid, called thermal ellipsoid

The diagram illustrates the Debye-Waller factor. It shows a 3x3 grid of blue circles representing atoms in a crystal lattice. An arrow labeled 'Temperature' points to the right, indicating increasing temperature. On the right, the atoms are shown as larger blue circles, representing thermal expansion and increased displacement. Below the grid, a blue oval represents a thermal ellipsoid. A small inset video of a speaker is visible in the bottom right corner.

$$\mathbf{r}_j(t) = \mathbf{r}_j + \mathbf{u}(t)$$

The term $\mathbf{u}(t)$ comes from dynamics. Due to thermal vibration of the atoms. To be more precise: due to phonons

$$e^{-i\mathbf{G} \cdot \mathbf{r}_j(t)} = e^{-i\mathbf{G} \cdot \mathbf{r}_j} e^{-i\mathbf{G} \cdot \mathbf{u}(t)}$$

We need to do a thermal averaging of the second term




But the idea that the thermal effect will make the place or position of the atoms uncertain and kill the periodicity was still there. Debye was one to solve it, again, after an animated argument at a coffee table in a cafe called Cafe Lutz. He writes, “I came to conclusion that the sharpness of the interference lines would not suffer, but that the intensity should diminish with increasing angle of scattering, the more so the higher the temperature”- Peter Debye. What he meant is that if you see a lower temperature pattern, say 0 K, the atoms are located at the rigid lattice sites in a crystallographic structure. Now, when I raise the temperature, it is not that the atoms run away from the place rather their vibration around the mean position increases, as if the atom is expanding in size with temperature and not running away. So, from smaller size the atoms become larger. This is a dynamical effect and the atom is really not becoming larger. What we see is an average picture in time. Because of this expanded vibrational capability of the atom it acts as if it occupies larger space around the mean position. Because of this, you have something called Debye-Waller factor, which is I_0 the intensity at 0 K, times, $e^{-\frac{1}{3}\langle u^2 \rangle Q^2}$, $\langle u^2 \rangle$ is a mean squared displacement and Q will be G for Bragg diffraction. So, peak intensity does not get destroyed rather it gets diminished in intensity.

And in general, the displacement is not spherical, but an ellipsoid called thermal ellipsoid because in every direction, the bondings are not same, and the solid will not allow equal amplitude of vibration in all directions. Then it will rather allow an ellipsoid, and this ellipsoid will be oriented

in the crystallographic lattice I am talking about. It is called a thermal ellipsoid. Now, I will give a simple derivation of this important relation for us in diffraction.

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$$\begin{aligned}
 u_j &= \sum_j b_j e^{-i\bar{Q} \cdot \bar{r}_j} \\
 &= \sum_j f_j e^{-i\bar{Q} \cdot \bar{r}_j} \\
 \bar{r}_j(t) &= \bar{r}_j + u_j(t)
 \end{aligned}$$



If you remember scattering amplitude for x-rays is given by, $\sum_j f_j e^{-i\bar{Q} \cdot \bar{r}_j}$. For Bragg diffraction \bar{Q} becomes equal to \bar{G} and this f_j is the Fourier transform over the charge cloud volume. At any temperature t , $\bar{r}_j(t)$ will be, $\bar{r}_j + u_j(t)$, where, \bar{r}_j is position at 0 K and $u_j(t)$ is an oscillation around it at temperature t . The term $u_j(t)$ comes from dynamics, due to thermal vibration of the atoms and to be more precise it is coming from the phonon vibrations.

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$r_j(t) = r_j + u(t)$

The term $u(t)$ comes from dynamics . Due to thermal vibration of the atoms. To be more precise: due to phonons

$e^{-i\mathbf{G} \cdot \mathbf{r}_j(t)} = e^{-i\mathbf{G} \cdot \mathbf{r}_j} e^{-i\mathbf{G} \cdot \mathbf{u}(t)}$

We need to do a thermal averaging of the second term

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With this, $e^{-i\mathbf{G} \cdot \mathbf{r}_j(t)} = e^{-i\mathbf{G} \cdot \mathbf{r}_j} + e^{-i\mathbf{G} \cdot \mathbf{u}(t)}$, where $e^{-i\mathbf{G} \cdot \mathbf{u}(t)}$ is the thermal part.

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$\langle e^{-i\mathbf{G} \cdot \mathbf{r}_j} \rangle = \langle e^{-i\mathbf{G} \cdot \mathbf{r}_j} e^{-i\mathbf{G} \cdot \mathbf{u}(t)} \rangle$

$\langle e^{-i\mathbf{G} \cdot \mathbf{u}(t)} \rangle = \langle 1 - i\mathbf{G} \cdot \mathbf{u} - \frac{1}{2} \mathbf{G} \cdot \mathbf{u} \mathbf{G} \cdot \mathbf{u} + \dots \rangle$

$= 1 - \langle \mathbf{G} \cdot \mathbf{u} \rangle - \frac{1}{2} \mathbf{G} \cdot \mathbf{u} \mathbf{G} \cdot \mathbf{u}$

Now, we have to find out an average of this thing. 1st part remains fixed, we need the average of 2nd term that is, $\langle e^{-i\mathbf{G} \cdot \mathbf{u}(t)} \rangle$. We need thermal average of the 2nd term over entire ensemble. Expanding the exponential,

$$\langle e^{-iG.u(t)} \rangle = \langle 1 - iG.u - \frac{1}{2}G^2u^2 \cos^2 \theta + \dots \rangle$$

Assuming $G.u$ is small the expression can be written as, ignoring the higher order terms,

$$\langle e^{-iG.u(t)} \rangle = \langle 1 - iG.u - \frac{1}{2}G^2u^2 \cos^2 \theta \rangle$$

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$$\begin{aligned} \langle \bar{G} \cdot \bar{u} \rangle &= 0 \\ \langle G^2 u^2 \cos^2 \theta \rangle &= G^2 \langle u^2 \rangle \langle \cos^2 \theta \rangle \\ &= \frac{1}{3} G^2 \langle u^2 \rangle \end{aligned}$$

$\langle \cos^2 \theta \rangle = \frac{1}{2\pi} \int_0^{2\pi} \cos^2 \theta d\theta = \frac{1}{2} \int_0^{\pi} \cos^2 \theta d\theta = \frac{1}{2} \cdot \frac{\pi}{2} = \frac{1}{4}$

$\frac{1}{3} \langle u^2 \rangle G^2$

$$\begin{aligned} e^{-iG \cdot \bar{u}} &= e^{-\frac{1}{6} \langle u^2 \rangle G^2} \\ I &= I_0 e^{-\frac{1}{3} G^2 \langle u^2 \rangle} \end{aligned}$$

$$\begin{aligned}
 \langle e^{-i\vec{G} \cdot \vec{r}} \rangle &= \langle e^{-iG \cdot u(t)} \rangle \\
 \langle e^{-i\vec{G} \cdot \vec{u}(t)} \rangle &= \left\langle 1 - iG \cdot u - \frac{1}{2} G^2 u^2 \cos^2 \theta + \dots \right\rangle \\
 &= 1 - \langle iG \cdot u \rangle - \frac{1}{2} G^2 \langle u^2 \cos^2 \theta \rangle
 \end{aligned}$$

$$\langle e^{-iG \cdot u(t)} \rangle = 1 - \langle iG \cdot u \rangle - \langle G^2 u^2 \cos^2 \theta \rangle$$

Now, the second term $\langle iG \cdot u \rangle$ is linear, where u the displacement can be in any direction, for a sphere it can be in any direction equally, hence this dynamical average $\langle iG \cdot u \rangle = 0$. The 3rd term, $\frac{1}{2} \langle G^2 u^2 \cos^2 \theta \rangle = \frac{1}{2} G^2 \langle u^2 \rangle \langle \cos^2 \theta \rangle$. The average of $\cos^2 \theta$ for a sphere or a spherical distribution is $1/3$. Hence, $\langle G^2 u^2 \cos^2 \theta \rangle = \frac{1}{3} G^2 \langle u^2 \rangle$. Putting these results in the above expanded expression,

$$\langle e^{-iG \cdot u(t)} \rangle = 1 - \frac{1}{6} G^2 \langle u^2 \rangle$$

Under the assumption that other higher order terms are much smaller. We can write,

$$\langle e^{-iG \cdot u(t)} \rangle = e^{-\frac{1}{6} G^2 \langle u^2 \rangle}$$

Now, the form factor has the term $e^{-\frac{1}{6} G^2 \langle u^2 \rangle}$ and the intensity (I) of that is, $I = I_0 e^{-\frac{1}{3} G^2 \langle u^2 \rangle}$, where I_0 the intensity at 0 K gets diminished by this exponential factor. As we raise the temperature u square increases, the value of the exponential term decreases and I decreases. Also, if you go to higher and higher Q values that means as you go to higher angles of diffraction, then the G value increases again I decreases.

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$$\langle e^{-iG \cdot u} \rangle = 1 - i \langle G \cdot u \rangle - \frac{1}{2} \langle (G \cdot u)^2 \rangle + \dots$$

$$\langle (G \cdot u)^2 \rangle = G^2 \langle u^2 \rangle \langle \cos^2 \theta \rangle = \frac{1}{3} G^2 \langle u^2 \rangle$$

$$= 1 - \frac{1}{6} G^2 \langle u^2 \rangle = e^{-\frac{1}{6} G^2 \langle u^2 \rangle}$$

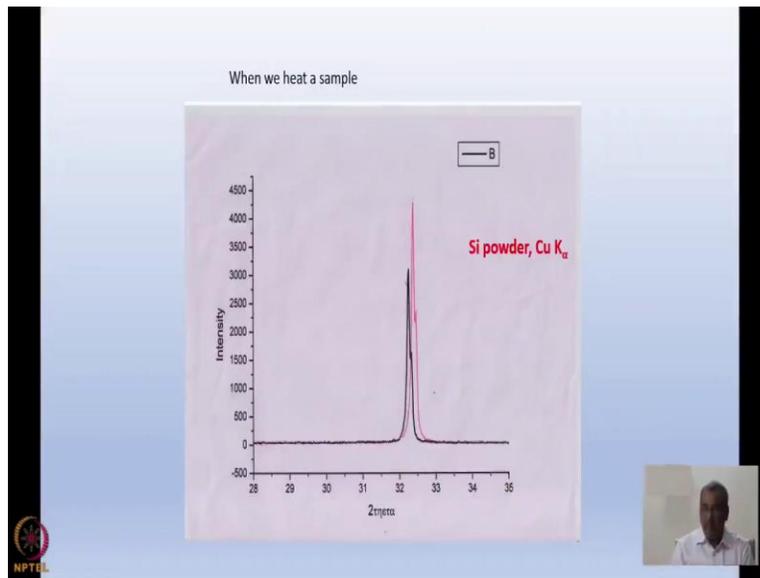
$I = I_0 e^{-\frac{1}{6} G^2 \langle u^2 \rangle}$
Back-door entry for dynamics!




So, this is most important effect that when you raise the temperature, we do not lose the Bragg peaks. But because of the vibration of the atoms around the mean position, their apparent size increases, this factor u square is the apparent size that increases for the X-rays or even for neutrons.

Then the intensity falls with the $e^{-\frac{1}{6} G^2 \langle u^2 \rangle}$ factor. This is a backdoor entry for dynamics. Basically, I am trying to evaluate the intensity or the structure factor for a lattice and the finite temperature brings in dynamics and also this factor.

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$$2d \sin \theta = \lambda$$



Just to give you a taste of it, I had done the experiment with silicone powder using copper K-alpha radiation. So, I am just showing you the diffraction data for silicone powder, which I took at room temperature and also at 200 °C. The red one is the data taken at room temperature and the black one is the same peak at 200 degrees centigrade., You notice that the intensity has reduced and that is caused by the thermal vibration.

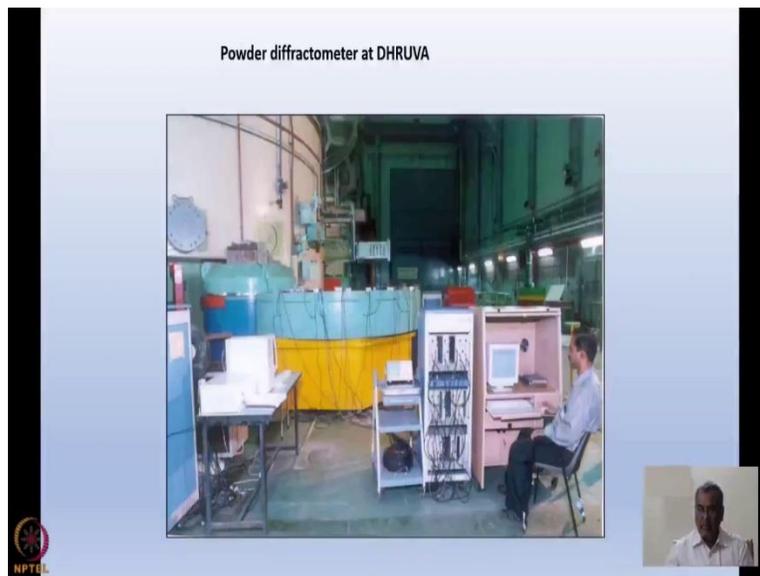
This is basically the Debye-Waller factor for this specific peak that I was measuring. But you must have also noticed I am sure, that the peak position has shifted. We have not talked about peaks

shifting in our derivation so far. This is for the simple reason that when I heated the silicone powder not only that thermal vibration causes the reduction intensity, but also the lattice expanded.

$2d \sin\theta = \lambda$ is the Bragg's Law, and according to this law if the lattice expands that for the same wavelength, the angle (theta) has to decrease to maintain the equality in Bragg's Law and this shifting is a signature of that. So, you have the Debye-Waller factor reducing the intensity of the lattice. And the expansion of the lattice causes shifting of the peak.

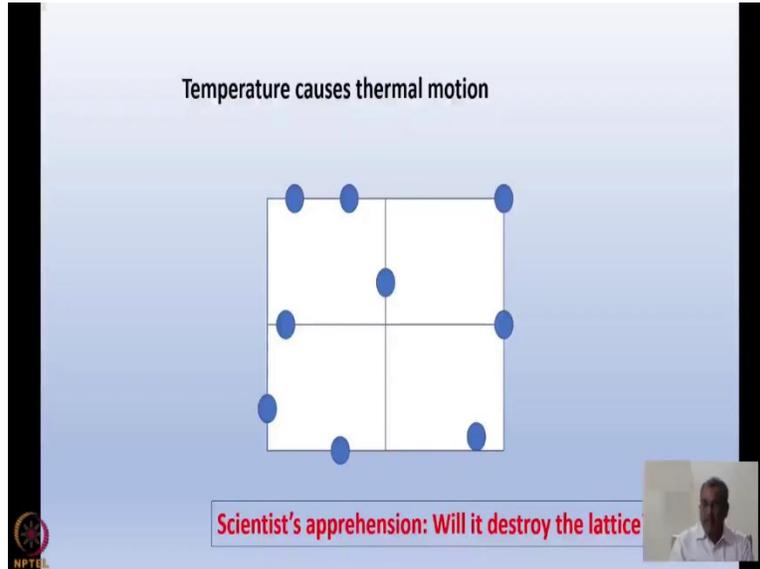
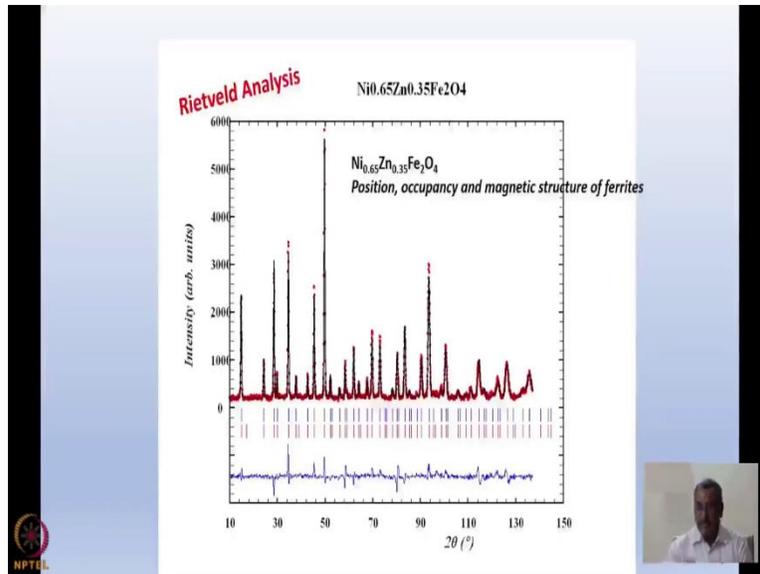
You might have also noticed that there is a small hump here that is related to instrumental resolution. Actually, copper has two alpha lines, $K_{\alpha 1}$, $K_{\alpha 2}$ and also K_{β} , and the observed splitting is due to these two K_{α} lines. This is an experimental result, which really demonstrates that their Debye-Waller factor takes care of the thermal effect. Actually, in diffraction experiments, this is also one parameter, which is fitted to find out the extent of atomic vibration.

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The instrument shown in figure is a powder diffractometer using position sensitive detectors. I am throwing terms at you and which I will explain later. The data taken looks somewhat like this.

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This is how the peak positions come in a neutron diffraction experiment. They are fitted using a specific package known as Rietveld package, extremely popular today among all the people who want to fit their neutron or x-ray diffraction data. And typically, this is how it looks at a finite temperature. But how long this trend will continue? I must say that the scientist at the beginning, were not absolutely wrong because when you keep heating your sample, once the sample starts melting, then the lattice is destroyed.

And once the lattice is destroyed, the picture that I showed earlier, which was the apprehension of the scientists, that indeed happen. When the lattice structures start melting, you have the atoms moving from the mean positions, it goes to a liquid state and you do lose the Bragg peaks. But till

the lattice is intact it is the vibration which caused by the thermal motion and you do not lose the Bragg intensity, but you have a reduction in intensity. With that I end this module.