Condensed Matter Physics
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Lecture - 5
Diffraction Methods for Crystal Structures (Continued)

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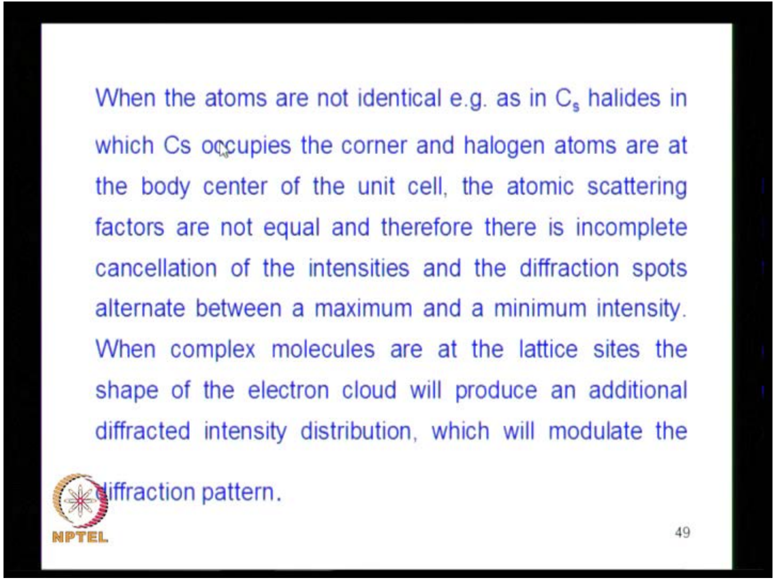

When the atoms are not identical e.g. as in C_s halides in which Cs occupies the corner and halogen atoms are at the body center of the unit cell, the atomic scattering factors are not equal and therefore there is incomplete cancellation of the intensities and the diffraction spots alternate between a maximum and a minimum intensity. When complex molecules are at the lattice sites the shape of the electron cloud will produce an additional diffracted intensity distribution, which will modulate the diffraction pattern.

In the last lectures, we saw how an x-ray diffractogram can be used to obtain information on the crystal structure of relatively simple crystalline solid.

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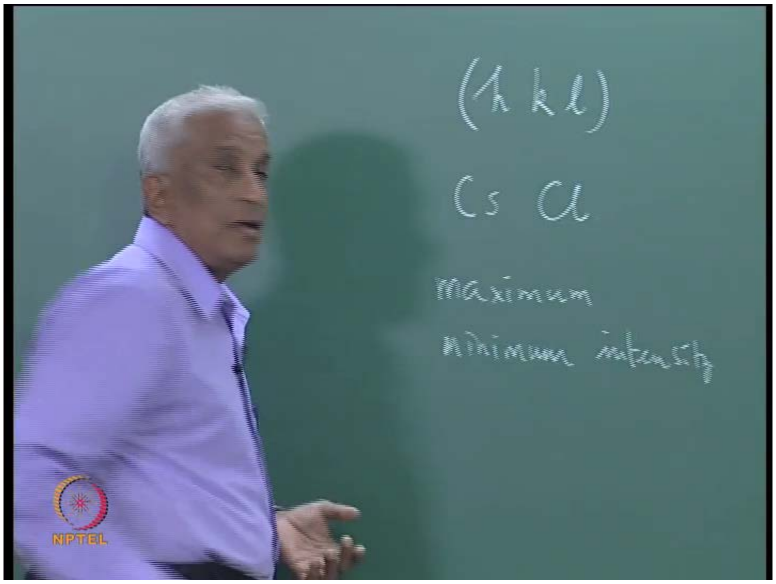

We saw also how the specific arrangement of atoms at the different sides in a crystal structure can lead to extinction rules which tell us how the particular brag reflection corresponding to a set of crystallographic planes given by the miller indices h k l will be present or absent depending on the type of crystal structures. This is because of the factors the terms in the structure factors due to the different contribution from the different atoms in the unit cell cancel each other leading to a minimum of intensity corresponding to certain combinations of h k l, the integers, which are integers. Now these extinction rules operate when they scattering produce by different atom or exactly equal and therefore lead to complete cancellation leading to a zero intensity corresponding to these combinations. When the atoms are not identical, for example, an interesting example is that of cesium chloride in which cesium atoms occupy the corner and the halogen atoms the chlorine are at the body center of the crystallographic unit cell. Now the atomic scattering factor of cesium and chlorine are not equal.

Therefore, the cancellation of the intensity is not complete and the diffraction parts then alternate between a maximum and a minimum intensity rather than maximum zero. In addition to this, when the atoms at the lattice sides are not simple atoms but instead or replaced by complex molecules, when a complex molecules occupy the crystalline lattice site. The shape of the electron cloud inside the molecule, will produce an additional diffracted intensity distribution, which will modulate the diffraction pattern.

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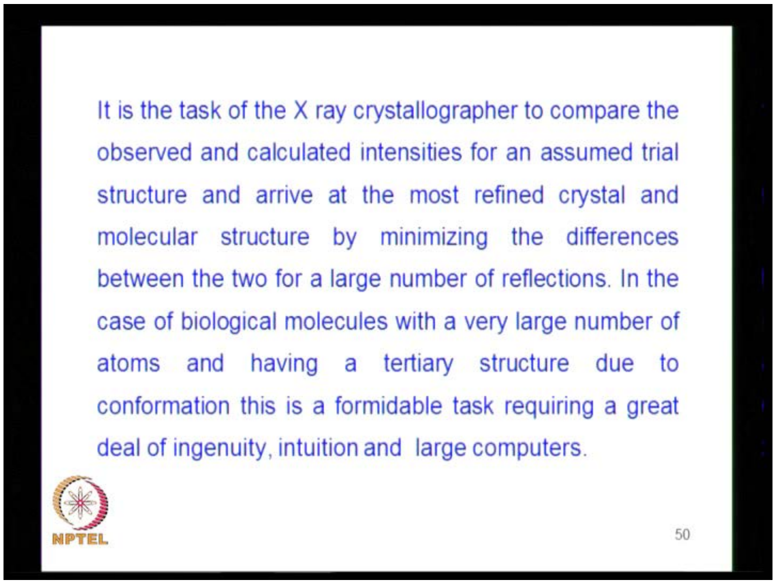

It is the task of the X ray crystallographer to compare the observed and calculated intensities for an assumed trial structure and arrive at the most refined crystal and molecular structure by minimizing the differences between the two for a large number of reflections. In the case of biological molecules with a very large number of atoms and having a tertiary structure due to conformation this is a formidable task requiring a great deal of ingenuity, intuition and large computers.

It is the task of a professional X ray crystallographer to compare the observed and calculated intensities for an assumed trail crystal structure and arrive at the best match between the observed diffraction reflection densities and the calculated ones by minimizing the differences between the two for a large number of reflections. In the case of biological molecules with a very large number of atoms and having in addition what is called a tertiary structure due to conformation this becomes interior formidable task requiring a great deal of ingenuity, intuition and also large computational facilities.

We have now seen the basic concept relating to x ray diffraction. Now the diffraction of x-rays by atoms and molecules in a crystal is relatively straightforward concept, because the incident x-rays are electromagnetic waves which are being scattered by the atoms or molecules. Now this these developments to place the beginning of the last century and therefore a big advance was made in the elucidation of crystal structures of simple crystalline solid. This marked the beginning of a great deal of insight into the nature of the the nature of the condensed matter. Simultaneously, many other important developments are taking place in different areas of science and technology in particular physics and technology.

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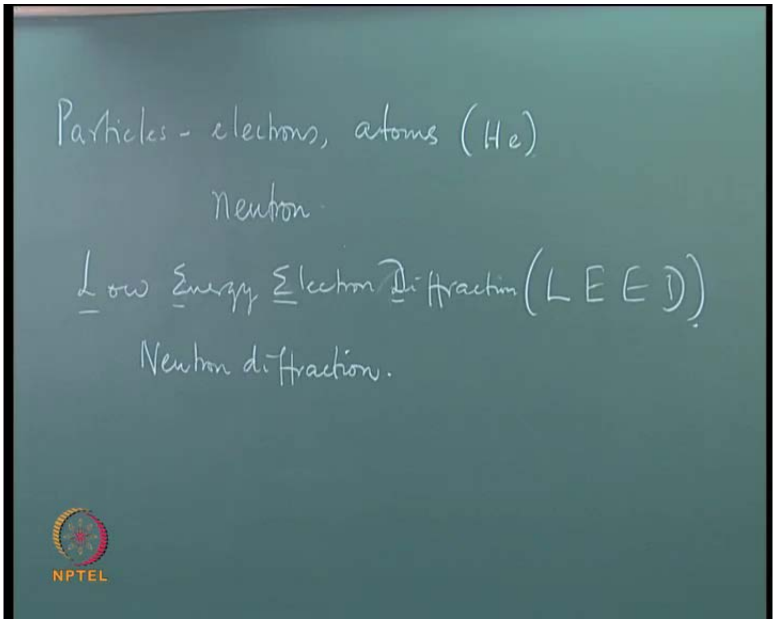

Particles - electrons, atoms (He)

neutron

Low Energy Electron Diffraction (L E E D)

Neutron diffraction.

Because of this, it has become now possible to use not only x-rays for the diffraction studies, leading to crystal structure information, but also a variety of particles, such as electrons, other atoms such as helium for example, as well as neutron. Today we can speak of electron diffraction, in particular called low energy electron diffraction, so L E E D is known as LEED, so this is the particularly portents method of studying crystal structures using the diffraction of electrons. Similarly, neutron diffraction has become very important area which leads to additional and complementary information regarding this crystal structures.

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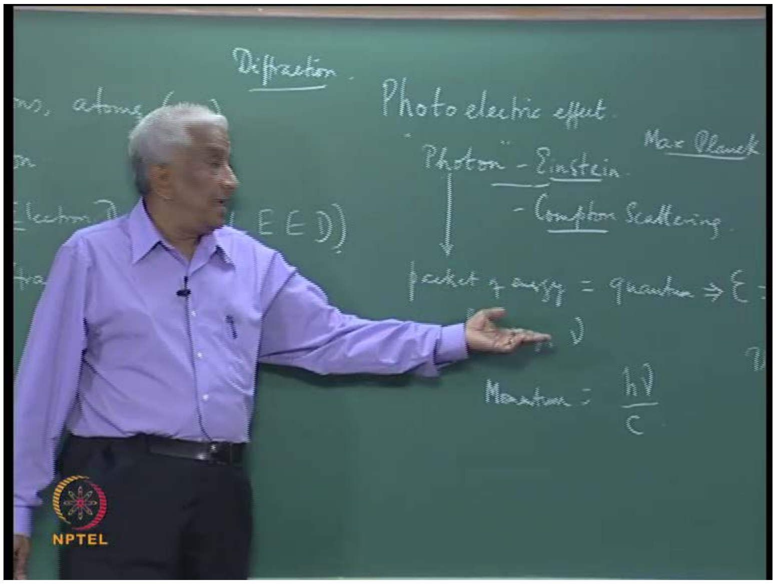

How in order to understand, how particle can particles beams can lead to diffraction, it is necessary to go back to revues of important developments regarding the nature of radiation on the one hand and particles on the other. Now it is very straightforward to understand how a wave can be diffracted, this has been understood rather well.

But at the beginning of the last century, very interesting development to place such as the discovering of the photoelectric effect in metal which means that if you said a beam of light or electromagnetic radiation, it leads to the ejection of the electrons from a metal and that's constitutes the so called photoelectric effect. I will not going to details of these, but an important development, the important of photoelectric effect stems from the fact that it will reveal a particularly striking aspect of radiation, namely the concept of photons, this is the concept which was introduced by Einstein to account for the photoelectric phenomenon.

Later Compton discover the rules regarding the Compton scattering of radiation and this could also be explained by using the photon concept. According to Planck and Einstein – Max Planck and Einstein, a photon is a packet of energy associated with electromagnetic radiation. Now this if the radiation is a pure wave monochromatic wave of frequency nu then the packet of energy corresponds to this was also called the quantum of energy this lead to the terminology quantum physics or quantum mechanics and so on. This quantum has an energy equal to h nu, where h is a constant know as the Planck's constant. This is the hypothesis which was introduced by Max Planck and later reinforced by Einstein, who named this quantum packet of energy as photon. And this concept that radiation is as not only a wave aspect but also a particle aspect as manifested by the photon was essential for the interpretation of photoelectric phenomena as well as the details of Compton scattering.

In Compton scattering it was necessary not only it invoke the concept of the energy associated with the wave, the quantum of energy but also that this quantum of energy not only has an energy e equal to h nu but also a momentum equal to h nu by C. So the photon has an energy as well as the momentum very much like a real particle – a classical particle. So the electromagnetic wave was found to have not only a wave character but also a particle character as manifested by the photon hypothesis.

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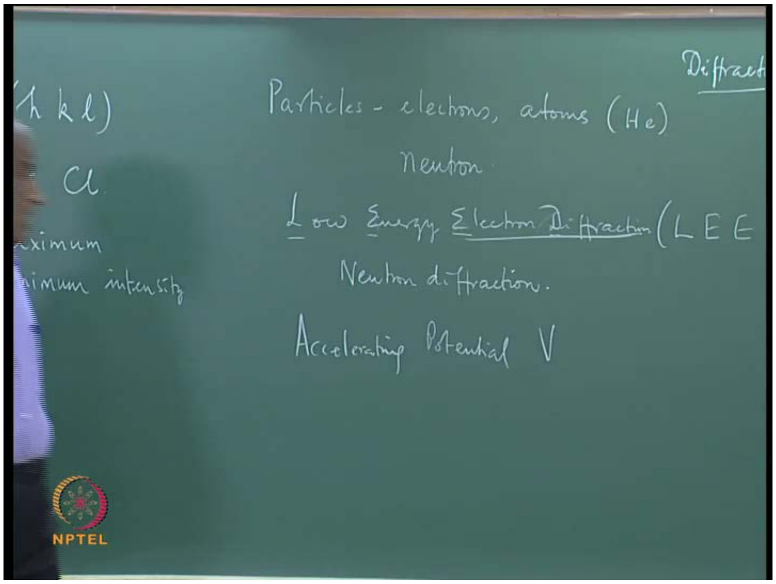

Diffract

(h k l)

a

ximum

imum intensity

Particles - electrons, atoms (He)

neutron

Low Energy Electron Diffraction (L E E

Neutron diffraction.

Accelerating Potential V

In the year nineteen naught five, a person called Louis De Broglie, he proposed a very interesting hypothesis known as the particle wave aspect, wave character of a particle of particles. He said it main argument was that since nature love symmetry, so if wave can have a wave as well as the particle aspect then a particle must also exhibits not only particle light characteristic but also wave light characteristic, so he said associated with the particle, we can also ascribe a wave character. And the wavelength of such a wave associated with the particle, let us say it is De

Broglie wavelength was shown by him to the h by p, where h is the same Planck's constant and p is the linear momentum.

A direct verification of the De Broglie hypothesis was found in the case of electron diffraction. So if the electrons which are particle associated with the definite linear momentum can exhibit wave like characteristic, there will be a De Broglie wavelength associated with a given electron of linear momentum p and the De Broglie wave length is given by just h by p where h is the Planck's constant. So that means that electrons the wave associated with electrons can also be diffracted very much like x-rays, so that is the concept of electron diffraction. So you can generate particles electrons of definite linear momentum by accelerating the electrons to by the certain electrical potential and that associated with that linear momentum, you will have a wavelength – the De Broglie wavelength. And that will determine the features of electron diffraction by solids.

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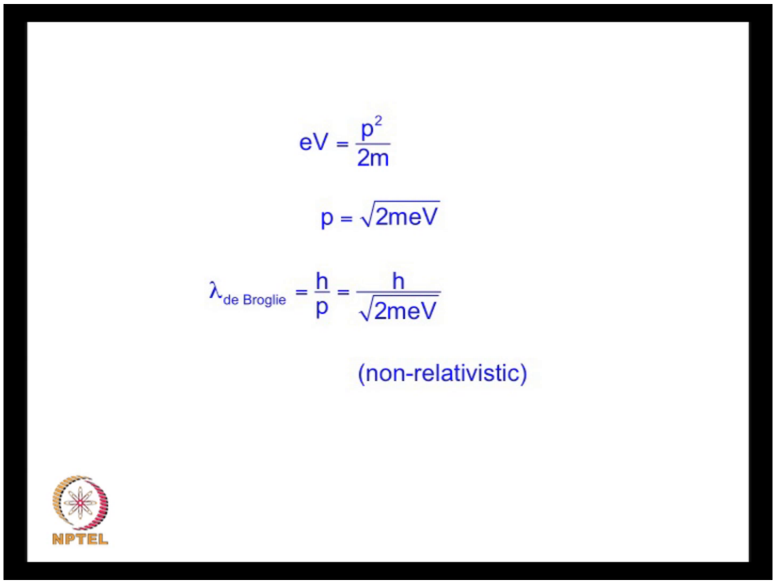

$$eV = \frac{p^2}{2m}$$

$$p = \sqrt{2meV}$$

$$\lambda_{\text{de Broglie}} = \frac{h}{p} = \frac{h}{\sqrt{2meV}}$$

(non-relativistic)

Now we can go a little further and ask if an accelerating potential, accelerating the electron beam is V, V whole then the energy content is, so this comes about by simply equating the energy gained by the electrons in the accelerating potential to the associated wavelength. And that's gives you a way to relate the De Broglie wavelength to the accelerating potential. So if we know a given accelerating potential, we know what will be the wavelength associated with the electrons wave which are which can then be diffracted by a solid, very much like x-rays are. So this is the basic principle of the low energy electron diffraction. Now the only thing is unlike x-rays, which can penetrate very deeply to a great extends of crystalline solid, the electron cannot penetrate inside a crystalline solid, so the electron diffraction is usually confined to atoms and molecules which are within a few atomic distances from the surface of the crystalline solid. So usually this is a technique which is employed to find out about the structures of atoms and molecules which are closed to the structures of the crystalline solids.

Now this is possible today only because of advances in ultra high vacuum technology which means that you have to have a clean surface, which is not contaminated, so advances in ultra high vacuum technology and also the preparation of clean surfaces, this is necessary for the observation of electron diffraction. So the electrons accelerated by the low voltages will have De Broglie wavelength which would be comparable to crystal lattice spacing. So they can be diffracted by the atoms in the crystal lattice, so similar arguments also apply to the case of neutrons. So we have also the possibility of diffracting neutrons.

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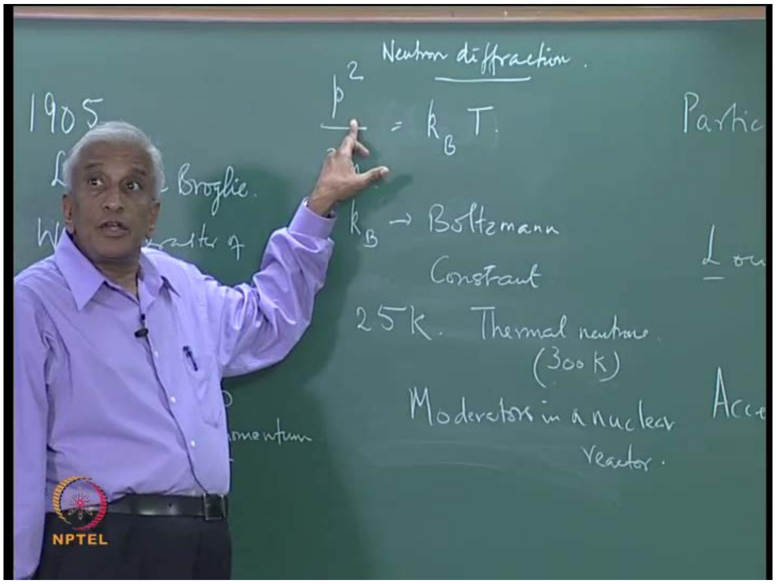

So this leads to a kinetic energy p square by two m for the neutrons corresponding which are at a temperature T, here k B is the Boltzmann constant k B is the Boltzmann constant. Usually the neutrons which are usually produced in nuclear reactor are much faster, so you have to slow them down to room temperature which is three hundred k or to much lower temperature. So you will do this by using what are known as moderators in a nuclear reactor, which are used to slow down the neutrons to sufficiently low temperature, so that the associated wavelength - De Broglie wavelength which are related to the linear momentum can be suitable for the observation of neutron diffraction in solids and liquids. So this is the basic principle behind neutron diffraction.

Now in the case of electrons, you can readily focus them by so called magnetic lenses, so as to produce an image as in a microscope. Now neutrons which are not readily available in large numbers in nature, but we have to use a nuclear reactor in order to do this. So these were the reasons why developments in electrons diffraction and neutron diffraction have to await major development in nuclear reactors and so on. Now the neutron unlike electron do not interact with the charge distribution of atoms and molecules in crystalline solid instead they interact with the nucleate of atoms in a solids. So they are these interactions are nuclear forces.

So in the case of x-ray diffraction for example, the interaction is with the charge cloud and therefore the x-ray diffraction is used in the case of elements having a high atomic number, because the atomic number tells you how many electrons are there associated with a given atoms. So it is preferable in order to have sufficiently large amount of x-ray diffracted intensity is necessity to have elements of high atomic number. So x-ray diffraction is a method which is not very useful given the structural information from a solid containing elements are relatively low atomic number, for example hydrogen is required.

Whereas, neutrons are very suitable in this case, because neutrons interact with the nuclear, nuclei of an atom, and therefore, the atomic number is not relevant. So neutrons can be used when you want to obtain information for example about the position of hydrogen atoms. In addition, neutrons also posses a magnetic movement that means that this scattering a neutrons is not only taking place by the nuclei but also by the spin magnetic movement of the atoms in the solid. So this renders neutrons diffraction to be an ideal tool for the study of magnetically ordered structures. So we will take this up when we discuss magnetic ordering in solids for the movement, we will simply mention this.

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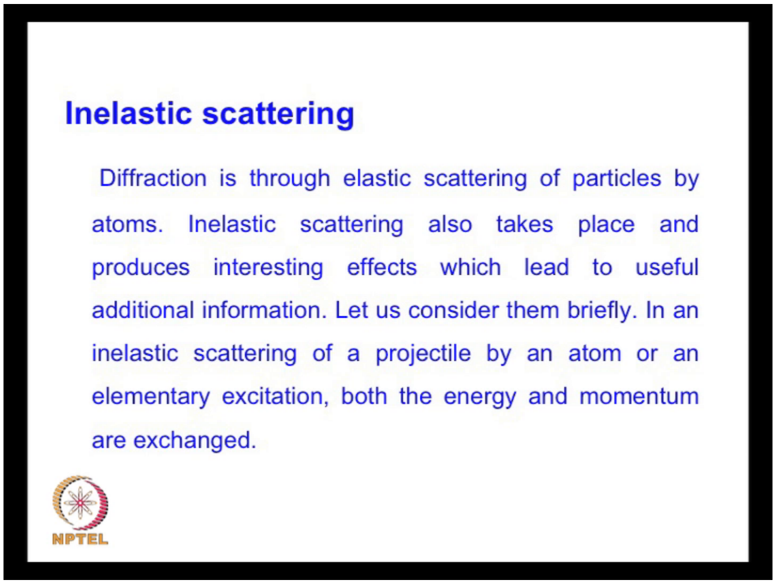

Inelastic scattering

Diffraction is through elastic scattering of particles by atoms. Inelastic scattering also takes place and produces interesting effects which lead to useful additional information. Let us consider them briefly. In an inelastic scattering of a projectile by an atom or an elementary excitation, both the energy and momentum are exchanged.

There is another important aspect of scattering.

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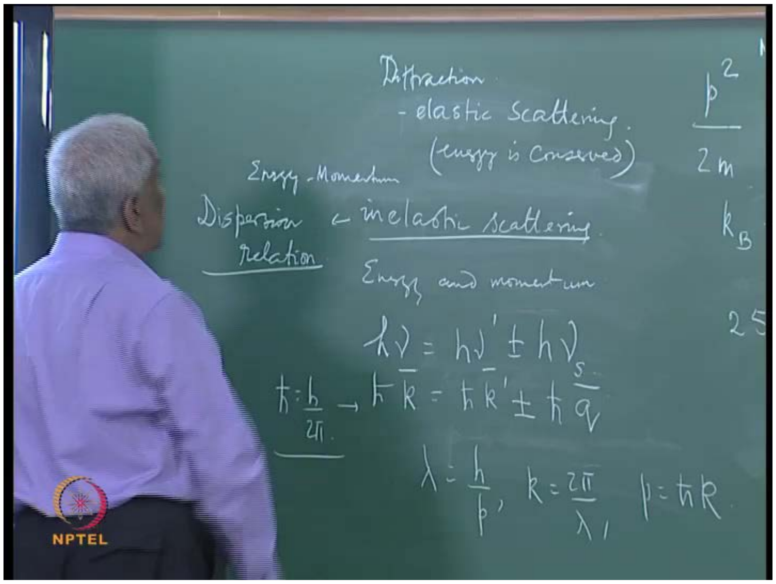

Diffraction

- elastic Scattering.

(energy is Conserved)

Energy - Momentum

Dispersion relation ← inelastic scattering

Energy and momentum

$\hbar \underline{\nu} = h\underline{\nu}' \pm h\nu_s$

$\hbar = \frac{h}{2\pi} \rightarrow \hbar \bar{k} = \hbar \bar{k}' \pm \hbar \bar{q}$

$\lambda = \frac{h}{p}, \quad k = \frac{2\pi}{\lambda}, \quad p = \hbar k$

$\frac{p^2}{2m}$

k_B

25

So far we discussed diffraction by waves and particles in solids. In addition to diffraction, which is an elastic scattering process, we can also have which means that energy is conserved. We can also have inelastic scattering. An inelastic scattering event in one in which the energy is not conserved, but energy is transferred by the incident beam to the scattered, scattering centered. So now there is change of energy and momentum transfer takes place in such an inelastic scattering event.

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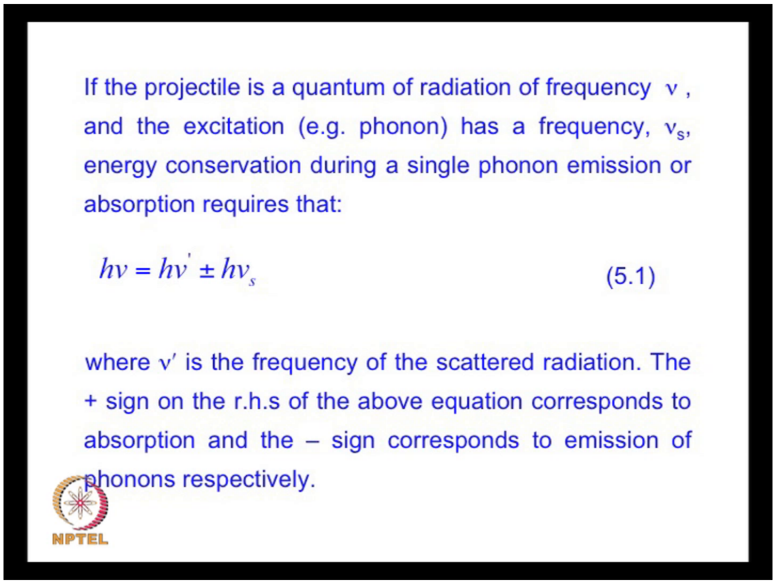

If the projectile is a quantum of radiation of frequency ν, and the excitation (e.g. phonon) has a frequency, ν_s, energy conservation during a single phonon emission or absorption requires that:

$$h\nu = h\nu' \pm h\nu_s \qquad (5.1)$$

where ν' is the frequency of the scattered radiation. The + sign on the r.h.s of the above equation corresponds to absorption and the – sign corresponds to emission of phonons respectively.

So the conditions which have to be satisfied are that not only the energy has to be conserved if nu is the frequency of the incident beam and nu prime is that as the scattered radiation and nu s is the frequency of a quantum if the projectile, which corresponds to the quantum of radiation of frequency nu s. Then the condition is that h nu equal to h nu prime plus or minus h nu s. The plus corresponds to the absorption and minus corresponds to emission of the quantum of so you can have absorption or emission for example of an excitation such as a phonon as we will see later.

So this is the relation that has to be satisfied in order that energy is conserved. In addition, we also need to have momentum conservation, which means that we must have h cross k where h cross is h by two pi; h cross k equal to h cross k prime plus minus h cross q. This is the momentum conservation equation. See we saw that the De Broglie wavelength is h b y p, so k is just two pi by lambda, therefore the momentum p become simply h cross k that is the basis of ((Refer Time: 26:28)) in the momentum conservation in the in terms of the wave vector h k, k prime and q.

So, both these conditions have to be satisfied in the case of a inelastic scattering event, which means that if we study the distribution in energy and momentum of these scattered particle as the function of the scattering angle then it is possible to extract information about the energy momentum relationship in a solid, for a given scattering angle. So this is usually a very important information, so by studying the inelastic scattering, we can obtain information about the energy momentum relationship, which is also know as the dispersion relation. So this is a dynamical information, because it gives you relation between the energy and the momentum, we will discuss this also in later lectures.

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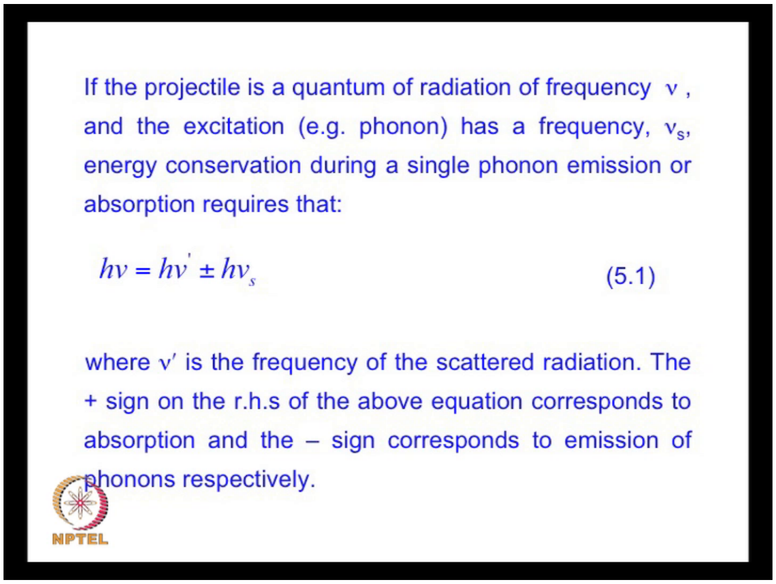

If the projectile is a quantum of radiation of frequency ν , and the excitation (e.g. phonon) has a frequency, ν_s, energy conservation during a single phonon emission or absorption requires that:

$$hv = hv' \pm hv_s \qquad (5.1)$$

where ν' is the frequency of the scattered radiation. The + sign on the r.h.s of the above equation corresponds to absorption and the – sign corresponds to emission of phonons respectively.

Just for completeness, we will give some information about how the electron diffraction experiment is the lead is carried out. So you have a cathode which serves as the gun for the electrons, so the electron beam is incident on a sample and then you have a fluorescent screen and then you can observe the electron beam which are accelerated by a potential on the by looking at a angular distribution on a fluorescent screen. So that is the experimental arrangement for electron – low energy electron diffraction.

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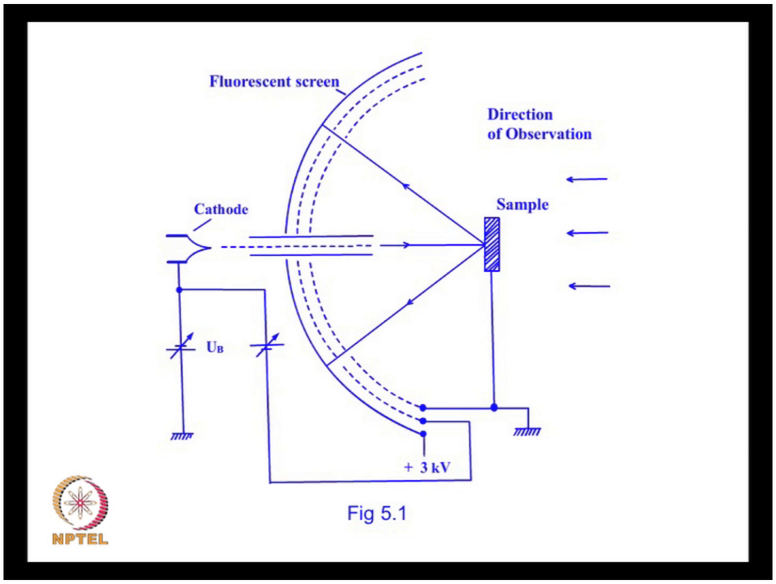

Fig 5.1

The corresponding experimental arrangement for the neutron diffraction is shown here. In this figure, where you have a reactor and you have monochromator which will produce a collimated beam of single energy neutrons, the moderators everything is in the nuclear reactor which will slow down the neutron beam. And then you have a neutron detector, which will measure the distribution of the neutrons at different angles, scattered at different angles. So these are the details of the neutron diffraction experiment.

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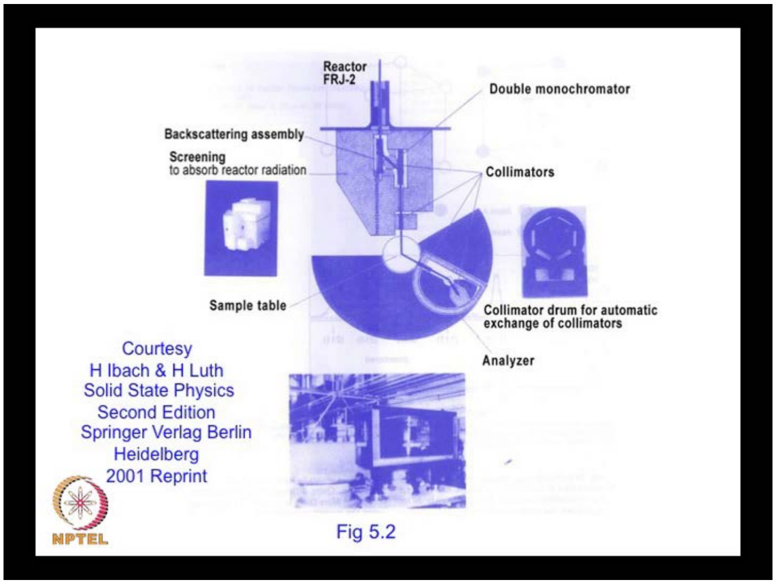

Courtesy
H Ibach & H Luth
Solid State Physics
Second Edition
Springer Verlag Berlin
Heidelberg
2001 Reprint

Fig 5.2

Now particularly interesting case here is that of ion and cobalt, now the metal alloy of ion and cobalt has a body centered cubic lattice. In which the ion and cobalt atoms are distributed completely randomly at any given lattice position in this body-centered lattice, that is what is known as disordered solid in which there is no ordering of ion and cobalt atoms in specific lattice sides, they are free to occupy any position in the crystal lattice. Now as you go down in temperature, you can arrive at an ordered arrangement in which the ion and cobalt atoms freeze preferentially at either the vertices of the cube at the lattice side or at the body-centered. So you have atom a and atom b in this case ion and cobalt.

Now ion and cobalt do not have comparable equal scattering factors for neutrons. Therefore, when you go arrive from the disordered to the ordered face, you will find that because of this selective occupation, there is a cancellation of intensity as we discussed in the connection with the extinction rule. So you will find that reflection corresponding to the reflection such as one zero zero and then one one one and then two one zero, these are all reflections in which h plus k plus l is odd. And these are the reflection which are extinguish in the case of a bcc structure as we discussed already. And since the scattering intensities are not completely equal for the ion and cobalt, there will be incomplete translation.

So you will have a you will have additional you will see that in the disordered structure, these reflections are not present; while in the ordered structure these reflection start appearing that is because of the preferential occupation at the body side, body centered side – body centered. So that corresponds to the order, disordered transition. So neutron diffraction can be used to study the process of ordered, disordered transition in metals in as in this case. We will leave the details of magnetic scattering and magnetic ordering using different neutron diffraction later lecture.