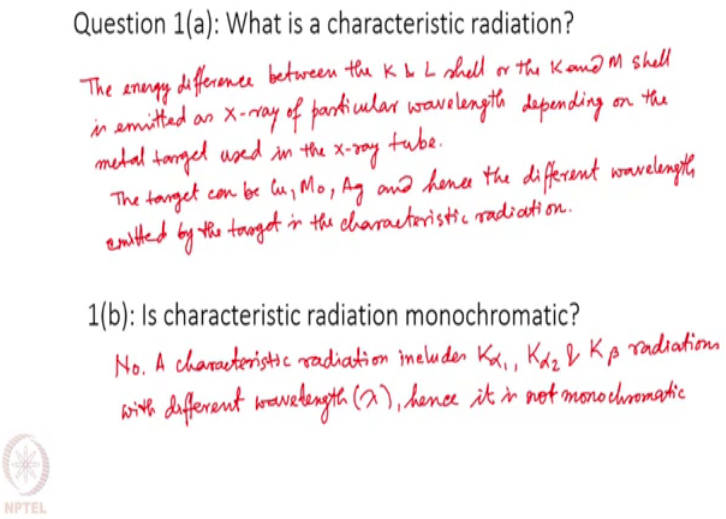
Chemical Crystallography
Prof. Angshuman Roy Choudhury
Department of Chemical Sciences
Indian Institute of Science Education and Research, Mohali

Basics, Symmetry and Equivalent Points in Crystallography
Lecture – 11
Tutorial – 1

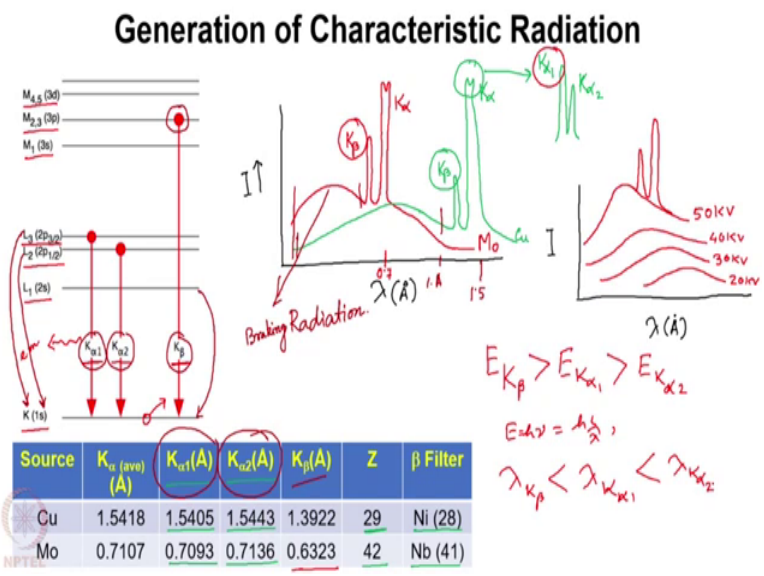
Welcome back to the course of Chemical Crystallography. In first 5 lectures, we have discussed about the origin of X-rays and about the characteristic radiations and now a little bit of instrumentation also. So, today we will try to discuss the, which question answers on these 5 lectures, the assignment was given to you.

(Refer Slide Time: 00:41)



So, let us see the questions and their answers. The first question was what is a characteristic radiation? As you know that when the highly accelerated electrons in the X-ray tube is made to fall on a particular metal target, then it removes 1 electron from the K shell of that particular metal. As a result a vacancy is created and immediately the electron from the L shell or the M shell jumps down to the K shell by emitting electromagnetic radiation and that electromagnetic radiation falls in a particular range, which is in the X-ray range

(Refer Slide Time: 01:29)



Source	K_{α} (ave) (Å)	$K_{\alpha 1}$(Å)	$K_{\alpha 2}$(Å)	K_{β}(Å)	Z	β Filter
Cu	1.5418	1.5405	1.5443	1.3922	29	Ni (28)
Mo	0.7107	0.7093	0.7136	0.6323	42	Nb (41)

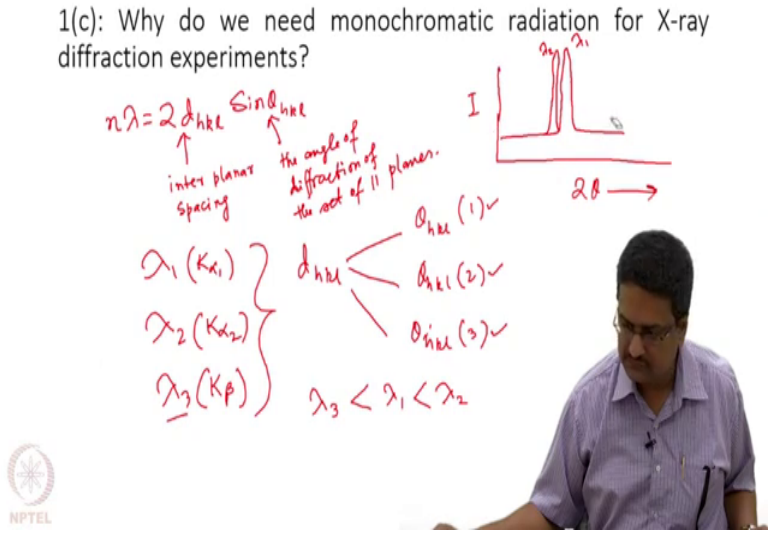
You may remember this figure, which we had discussed in one of the lectures that the, the energy difference between the K shell and L shell is the energy that is emitted when the electron jumps from that L shell to the K shell and this energy gap from the state L 2 from the state L, L 3 to 1 s or L 2 to 1 s corresponds to two characteristic radiations and these are of a given energy depending on, on what metal we are using.

So, in general when we use copper and molybdenum as different targets these radiations that we call as alpha 1, which is from, which is from L 3 2 1 s and alpha 2, which is from L 2 to 1 s are shown here. Alpha 1 and alpha 2 wavelengths are slightly different and then if the electron jumps from the M shell that is M 2 3, the 3 p orbital then the characteristic radiation is called as K beta and that K beta radiation has a slightly smaller wavelength. So, these are called the characteristic radiations. So, in short to write the answer, we should state that the energy difference between the K and L shell or the K and M shell is emitted as X-ray of particular wavelength, depending on the metal target used in the X-ray tube.

So, for our experimental purpose the target can be copper molybdenum or silver and hence, the different wavelength emitted by the target is the characteristic radiation. The next question is simple, because it says, it is a, it is characteristic radiation and monochromatic the answer is no, because the characteristic radiation that is emitted from a particular anode copper or molybdenum or silver includes different wavelengths; that

means, a characteristic radiation includes the corresponding K alpha 1, K alpha 2 and K beta radiations with different wavelength that is lambda. Hence, it is not monochromatic ok.

(Refer Slide Time: 07:19)



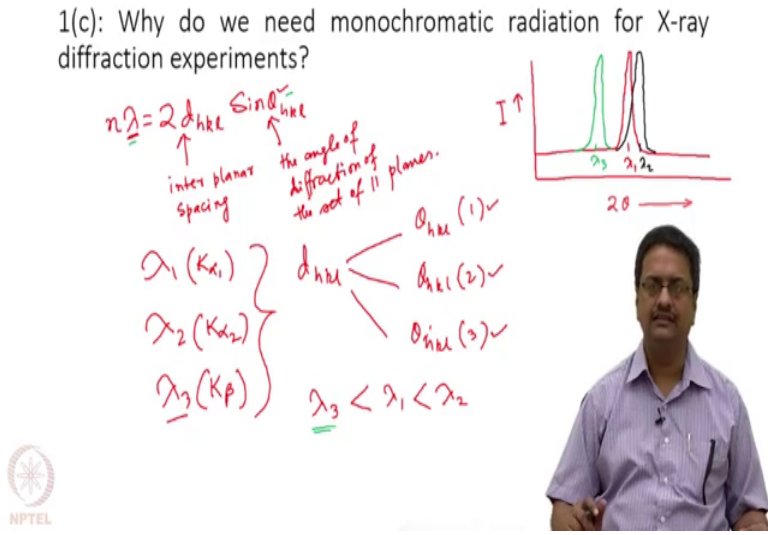
So, the next obvious question is why do we need monochromatic radiation for X-ray diffraction experiment, because in case of X-ray diffraction as we have already discussed, we use the Bragg's law, which states in lambda equal to 2 d hk l sin theta hk l, where this d is the inter planar spacing and theta h kl is the d angle of diffraction of the set of parallel planes. So, now if our source has a characteristic radiation, which is not monochromatic if we have three wavelengths suppose, lambda 1 which may be K alpha 1 lambda 2 which may be K alpha 2 and lambda 3 which may be decay beta for then for a given b hk l which is fixed for a particular crystal. We will have three different values of theta hk l.

Hence, for every particular plane, we will have three peaks; one peak corresponding to theta hkl 1, peak corresponding to theta h kl 2 and one will be theta h k l 3, if we again go back to the same plot. We can see that the in terms of energy the K beta energy of K beta is greater than energy of K alpha 1 is greater than the energy of K alpha 2. As we know e is equal to h nu, which is equal to hc by lambda. So, the corresponding lambda value for K beta will be smallest then it will be the lambda for K alpha 1 and the lambda for K alpha 2. So, lambda 3 will be smaller than lambda 1 and smaller than lambda 2. So,

what will happen is suppose, if we are supposed to have a peak for a particular d value at these two theta if we assign that peak, a corresponding to the K alpha 1 radiation that is from lambda 1, then when the lambda 2 is used, which is the longest wavelength.

So, for longest wavelength d sin theta will be shorter. So, the corresponding peak for lambda 2 will appear somewhere there and a peak for corresponding to lambda 3, which is K beta radiation, which is the smallest. So, when it is, then I made a mistake here.

(Refer Slide Time: 12:53)



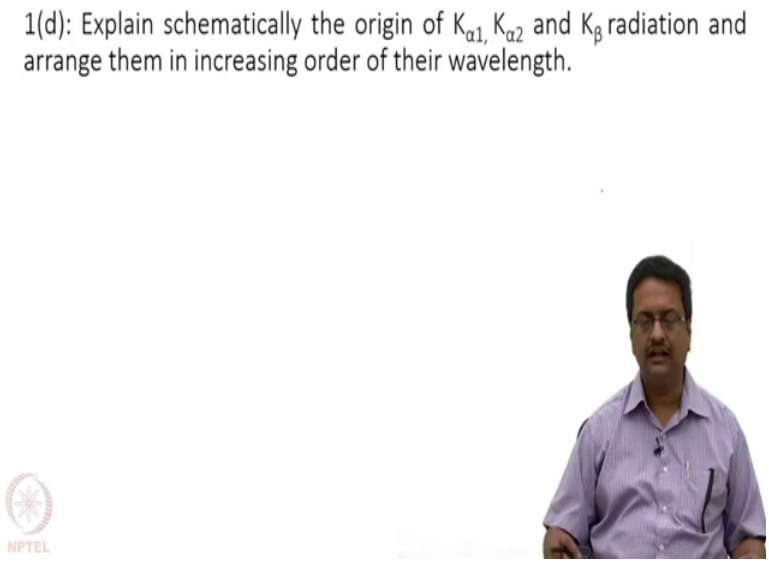
So, when this lambda 3 is smaller than lambda 1 and lambda 1 is smaller than lambda 2, if we try to understand where these peaks would appear, we plot intensity versus 2 theta and suppose, for the characteristic radiation lambda 2, which is the K alpha radiation, the peak appears at this point, which is for lambda 2; Now, which is called lambda 1 that is my K alpha 1, which we always use.

The wavelength lambda 2 is the longest highest value of lambda 2 corresponds to higher value of sin theta. So, the corresponding peak for the K alpha 2 should appear at a slightly higher wavelength like this at a lambda wavelength of lambda 2, but when we use it K beta radiation, where if you remember K beta is significantly shorter than alpha.

The corresponding peak would appear at a much smaller 2 theta value, because lambda when it is small, the 2 theta is of theta is also small. So, if the incident radiation is not monochromatic then for every reflection, we would get three distinct peaks at three

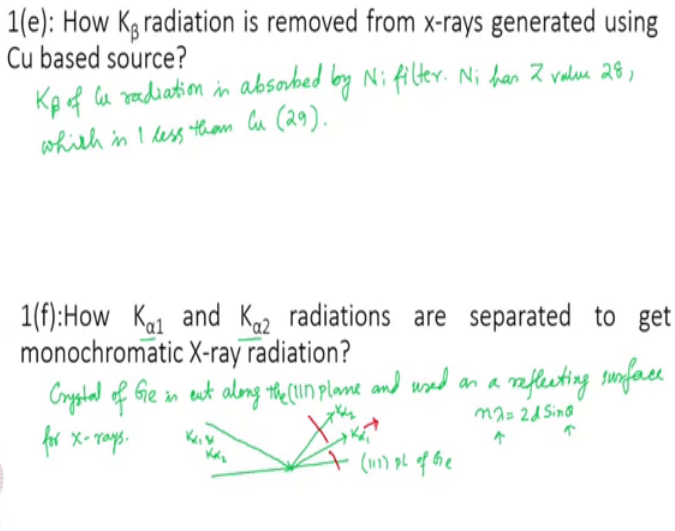
different 2 theta values and this will totally spoil our experiment in of X-ray diffraction to determine this structure. So, that is why we cannot use these characteristic radiations as it is rather, we need a monochromatic X-ray radiation.

(Refer Slide Time: 15:09)



The next question is already explained in the lecture explains theoretically the origin of K alpha 1 K alpha 2 and K beta radiation and arrange them in increasing order of their wavelength. So, we have already done that in the previous problem. So, what we need is to show this particular diagram, which is now being flashed in the screen. We should draw this diagram, explain the origin of different radiations alpha 1, alpha 2 and beta and then arrange them in terms of their wavelength as I have done for the previous problem.

(Refer Slide Time: 15:51)



Now, the question is how do we remove the K beta radiation? So, the next question is how to, how K beta radiation is removed from x-rays generated using copper based sources? It is good that we have a periodic table and we have lot of information about these elements available in the literature. So, what we observe that for a particular characteristic radiation of any source, there is an element with Z equal to minus 1 that is just the previous element in the periodic table, which absorbs the corresponding K beta radiation of a particular metal.

What happens is, if you use copper as a source then the K beta of copper radiation is absorbed by nickel filter. Nickel has the Z value just 1 less than copper 28, which is 1 less than copper, which is 29. So, if you use a nickel, filter nickel, a plate of a nickel, of a given thickness in front of the X-ray source then it will eliminate all the beta radiation and we will get, only became alpha radiation. Remember, alpha is also it is not a single wavelength, it is two wavelengths; alpha 1 and alpha 2. So, that is the origin of the next question, how K alpha 1 and K alpha 2 radiations are separated to get monochromatic X-ray radiation?

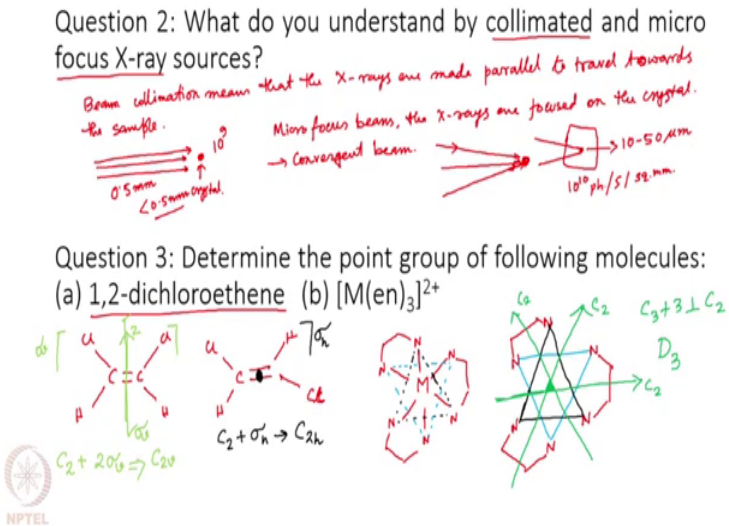
This separation is difficult and it also involves a loss of intensity of both alpha 1 and alpha 2 and it is done by using a monochromator, which is actually a crystal of germanium. So, what is done is a crystal of germanium is used. It is crystal of germanium is cut along the 1 1 1 plane, which you may not understand right now. You

add the moment you take it as miller indices of that particular plane I, which I will explain which plane we are talking about this plot along the 1 1 1 plane and used as a reflecting surface for X-rays.

So, if we have a particular surface the 1 1 1 plane of germanium exposed to the x-rays and if I have a radiation, which contains both K alpha 1 and K alpha 2. When it gets diffracted, the two radiations get diffracted at two different angles, because we know n lambda is equal to 2 d sin theta, higher the wavelength, higher will be the theta value. So, this in, this direction the K alpha 1 will be diffracted, while K alpha 2 will be diffracted in a different direction.

Of course, this reflection from 1 plane will reduce the intensity of both alpha 1 and alpha 2, but it will then separate guide the two beams in two different directions. So, now, by placing a shattered somewhere here, one can eliminate the possibility of K alpha 2 coming out of the instrument and one can only take the K alpha 1 out and then use this radiation for the X-ray diffraction experiments.

(Refer Slide Time: 21:15)



Now, the next question is what do we understand by the collimated beam and micro focus X-ray sources a beam collimation means that the X-rays are made parallel to travel towards the sample, which means the X-rays generated from the source is made to travel parallel like this, towards the sample, which is placed somewhere here.

But then when we say micro focus in case of micro focus, the x-rays are focused on the crystal that is it becomes a convergent beam. So, what happens in that case is all the beams are converged in such a way that it falls and converges on the crystal. So, in that case even if we have a large crystal, the beam can be converged and made to focus at a very small region of the crystal, which could be even 10 to 50 microns in size.

So, the difference is in case of collimated beam, we have to use a crystal which is smaller than the collimated size. So, if the collimated is of 0.5 millimeter in diameter, we should use crystals, which are less than 0.5 mm, but here the beam is very small, but one can use a larger crystal and the focus is on the crystal. So, that we get a very-very large intensity on the source. So, if the intensity on the crystal for a collimated source is about 10 to the power 9 photons per second per square millimeter. It can be increased to 10 to the power 10 photons per second per square millimeter. So, a 10 times increasing the flux can be achieved by doing micro focus getting a micro focus, the next question, which was given is based on your previous knowledge of a point groups and symmetry elements.

So, what we need to see here; we need to draw these molecules and try to find out the symmetries that are present in that. So, this is one two dichloroethene as you know, this has two different isomers, this is the cis form and this is the transform, this is form if you look at it carefully, if you should be able to identify that there is a twofold axis the molecular plane is a mirror plane that is present there.

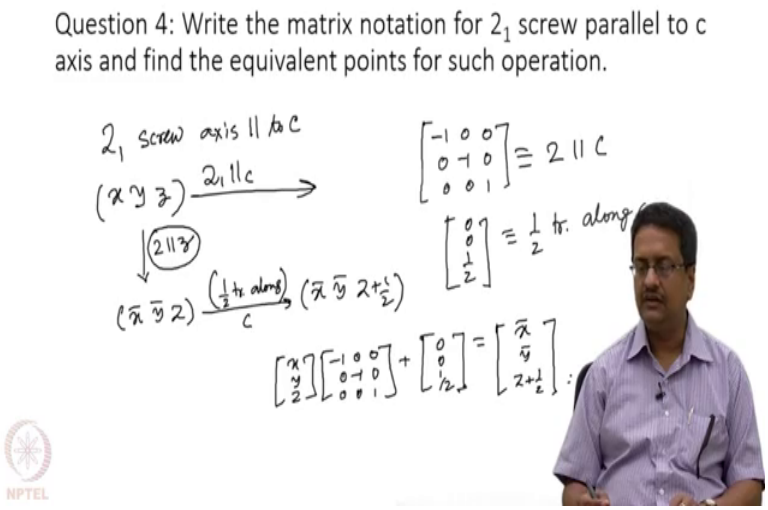
So, that molecular plane is a sigma v, because it is containing the axis of this particular. So, it contains the twofold axis and the sigma v and then there is another mirror plane, which is perpendicular to the plane of projection, but again contains the twofold axis. So, that is also another sigma v. So, this particular molecule has a C 2 plus it has 2 sigma v s. So, immediately the point group becomes C 2 v.

Now, if you look at the other molecule, which I have drawn here, that is the trans, then the trans molecule has a twofold perpendicular to the plane of projection and it does not have 2 sigma vs. So, this is not a C 2 v, but what it has is a sigma h plane, which is the plane of projection. So, C 2 and a sigma h makes it C 2 h point group. The second one is a metal ethylene diamine complex. So, if we write the metal complex in it is octahedral geometry, it should be written like this.

So, now if we try to look at this particular molecule using two sets of planes, one containing these three atoms, which I am joining with black ink and another containing another three atoms, which I am joining with the blue ink. So, if I redraw that and then write the atoms and join them, what we can see is, if we consider a threefold axis passing through the center of these two overlapping triangles, there is a C 2.

The C 3 axis passing through that overlap center of the overlapping triangles and then we have three perpendicular two folds going like that 1 2, these are all C 2s. So, it has a C 3 plus three perpendicular, C 2s and no other symmetry present. So, this becomes a D 3 point group.

(Refer Slide Time: 30:38)



So, the last question of this tutorial was write the matrix notation for 2 1 screw parallel to c axis and find the equivalent points for such operations. So, when I am saying that it is at 2 1 screw axis parallel to c; that means, if I have xyz, I apply 2 1 parallel to c. It is equivalent to doing it twofold parallel to z, which means it becomes x bar z and then a mirror perpendicular to z makes it no and then this half translation along c, we will make it x bar y bar z plus half.

So, we need a matrix for two parallel to z and a matrix for half translation along C. So, the matrix for two parallel to z is minus 1 0 0 0 minus 1 0 0 0 1 is equivalent to two parallel to c and translation is 0 0 half, which is half translation along c to the point xyz,

we apply minus 1 0 0 0 minus 1 0 0 0 1 and then we add the translation component 0 0 half, then it makes it as x bar y bar z plus half.

So, this is how one can do this transformation of coordinates using different symmetry elements like screw axis and glide planes using matrix.