Electron Diffraction and Imaging
Prof. Sundaraman M
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Madras

Lecture - 31
Energy dispersive Spectroscopy

Welcome you all to this course on Electron Diffraction and Imaging. In the last week we have covered some aspect of a energy dispersive analysis, but this part of this analysis especially is energy dispersive analysis is used very commonly in most of the electron microscopes to find out composition of the element. So, I thought that we will have a expanded class where we cover this part of it in detail.

Let us first start looking at how the electron beam interacts with matter. So, as the electron beam falls on the sample surface depending upon the thickness of that sample we assumed that there is sample is a thick sampled. Then the electron beam will be scattered by drastically without losing any energy as the electron beam hits that sample surface, secondary electrons could be a meter sample surface the electronics can lose energy by in plastic processes and this could lead to x-ray emission from the sampled surface though the whole electron could be completely absorbed in that sample this could give rise to specimen current.

Suppose the sample is a thin and the energy of the electron beam is very high then the electron beam can come through the sample and these electrons are called as transmitted electrons these transmitted electrons could be elastically scattered electrons which I have given. Then the other aspect is that some part of this electron could interact with the atoms and inelastic scattering could take place this inelastic scattering could be that is by electron phonon scattering or it may plasmon scattering or by ionization of the atom especially removal of electron from core levels, so that fixed amount of energy is lost by the incidental electron. These are all inelastic re scattered electron.

But when these inelastic scattering process takes place look at the consequent of it is that the ionized atom has to come back to the ground state their result in the form of x-ray emission, characteristic x-ray emission or in the form of auger electron emission.

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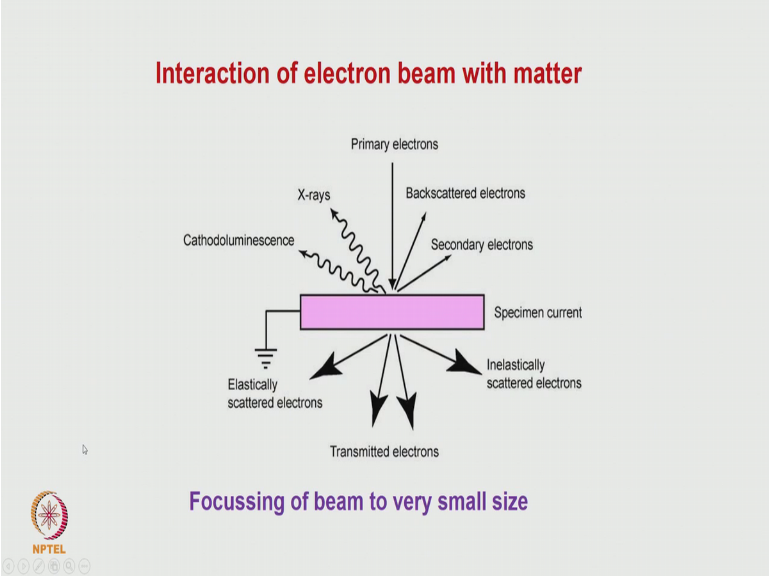

Interaction of electron beam with matter

Focussing of beam to very small size

And another important advantage with electrons is that electron beam can be focused a very small size because of which we could get using characteristic x-rays information about the composition of the sampled surface from very small areas of that sample.

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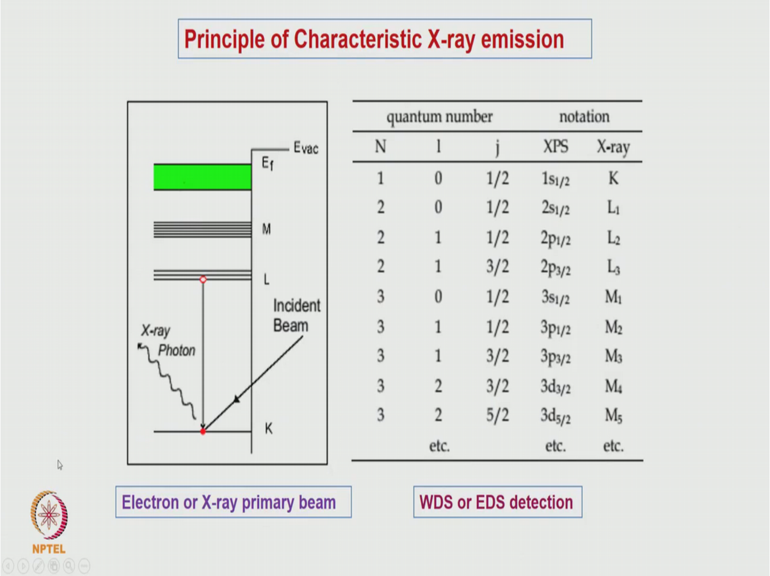

Principle of Characteristic X-ray emission

quantum number			notation	
N	l	j	XPS	X-ray
1	0	1/2	$1s_{1/2}$	K
2	0	1/2	$2s_{1/2}$	L_1
2	1	1/2	$2p_{1/2}$	L_2
2	1	3/2	$2p_{3/2}$	L_3
3	0	1/2	$3s_{1/2}$	M_1
3	1	1/2	$3p_{1/2}$	M_2
3	1	3/2	$3p_{3/2}$	M_3
3	2	3/2	$3d_{3/2}$	M_4
3	2	5/2	$3d_{5/2}$	M_5
	etc.		etc.	etc.

Electron or X-ray primary beam

WDS or EDS detection

Let us look at what is the phenomena which takes place when an incident. Electron beam falls on that sample we assume that this electron interacts with an atom knock out an electron from the K level.

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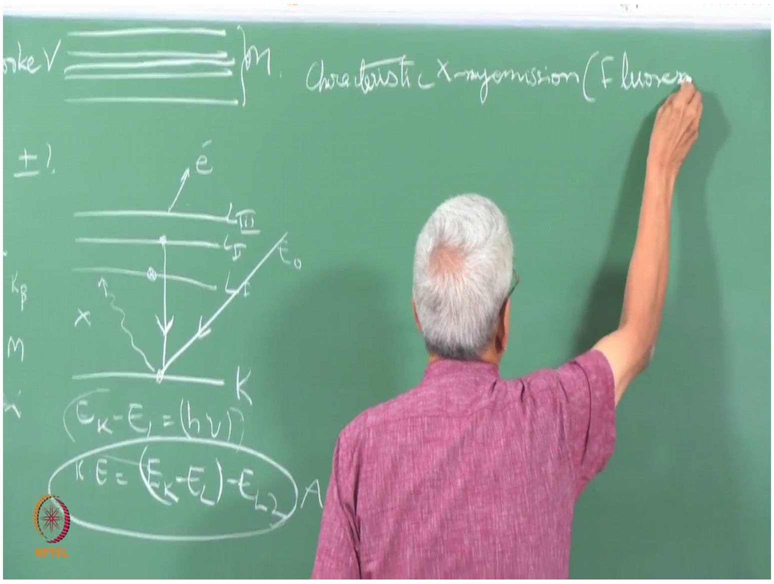

That is we have generally if we look at the line diagram we have a K level there are three L levels are there L II, L III then there will be 5 m doubles will we get. Suppose the incident electron is hitting on that sample with an energy E 0 and generally in an electron microscope the energy is of the order of 100 ke V to 300 ke V this is the energy of the incident electron beam.

We assume that it knocks out an electron from there K level. So, when then electron has been knocked out electron from this L level could come down to fill this vacancy.

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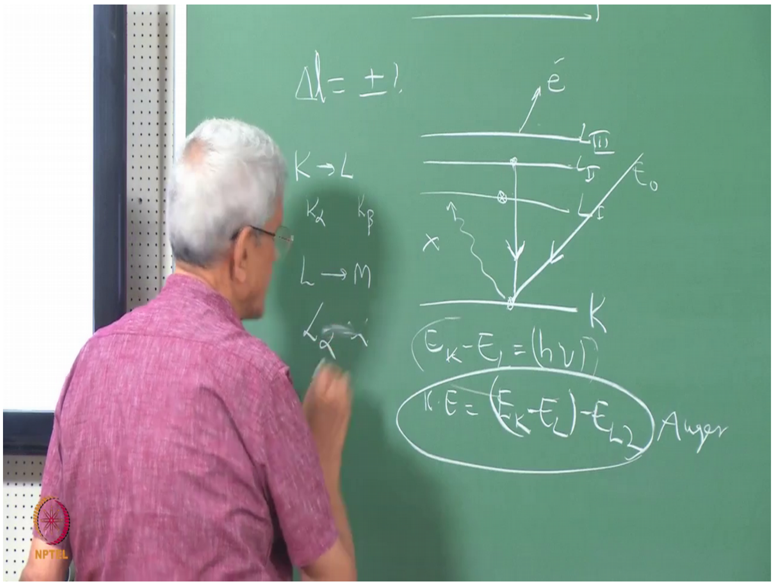

And when this comes down the difference in energy between E K minus E L this comes out in the form of x-ray which is called as the h nu. So, this since the electrons moving in different levels they are got specific combining energy associated with it the energy of the x-ray, energy of this characteristic x-ray is fixed by this transition. In this case what is essentially is going to happen is that if you measure the energy of the x-ray is which are coming out from the sample from that we can find out what is the element which is responsible for this x-ray emission.

So, essentially using this characteristic x-rays we can identify the elements which are present on that sample surface. So, we assume that that x-ray is coming out, the energy of this x-ray h nu is E K minus E L, but what is essentially important in this process is that this is not the only process which can happen when an a core ionization which has taken place the electron this energy, electron from this level has come down when this has happened the vacancy has been created in this level instead of an x-ray coming out this different in energy could be used in knock out possibly an electron from this level and this can come out. Suppose there binding energy of this electron is L 2 then the kinetic energy of the electron which comes out will be E K minus E L minus I think I will (Refer Time: 06:02) L 2.

So, this is the kind. So, kinetic energy of the auger electron depends upon the various energy levels. So, kinetic energy of auger electron this is also characteristic of the particular the element from which this emission is taking place. So, auger electron also could be used to find out the composition of the element. But what is important in this context is that once a vacancy has been created these are all the 2 processes by which the atom could come down to the ground state both has different probability or the yield for characteristic x-ray emission as well as the auger emission that some of that should be equal to 1.

We will come back to it shortly. So, essentially there are some transition rules which has to be followed when photoemission a x-ray formation takes place these rules essentially is that the delta K delta l the angular momentum this should be equal to plus minus 1 this is the rule which is followed. In this table at given that assignment of the different levels and what is the type of designation which is given for the various levels this is what is being given.

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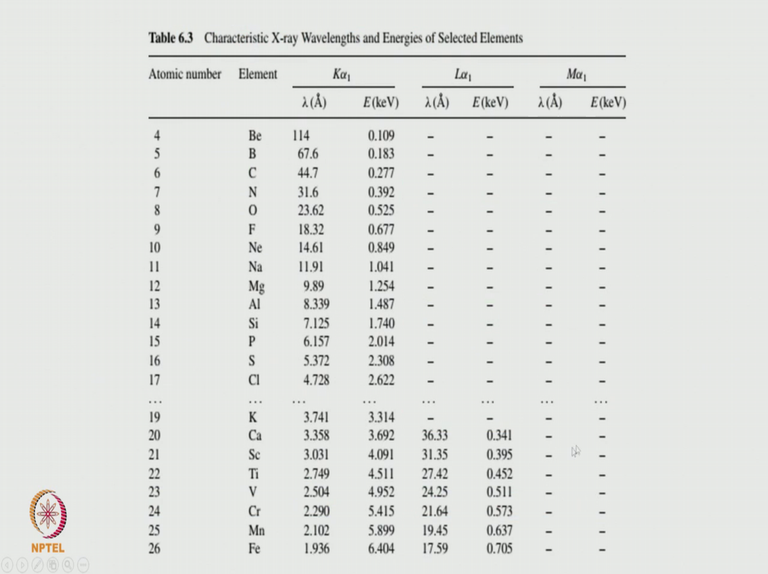

Table 6.3 Characteristic X-ray Wavelengths and Energies of Selected Elements

Atomic number	Element	$K\alpha_1$		$L\alpha_1$		$M\alpha_1$	
		λ (Å)	E (keV)	λ (Å)	E (keV)	λ (Å)	E (keV)
4	Be	114	0.109	–	–	–	–
5	B	67.6	0.183	–	–	–	–
6	C	44.7	0.277	–	–	–	–
7	N	31.6	0.392	–	–	–	–
8	O	23.62	0.525	–	–	–	–
9	F	18.32	0.677	–	–	–	–
10	Ne	14.61	0.849	–	–	–	–
11	Na	11.91	1.041	–	–	–	–
12	Mg	9.89	1.254	–	–	–	–
13	Al	8.339	1.487	–	–	–	–
14	Si	7.125	1.740	–	–	–	–
15	P	6.157	2.014	–	–	–	–
16	S	5.372	2.308	–	–	–	–
17	Cl	4.728	2.622	–	–	–	–
…	…	…	…	…	…	…	…
19	K	3.741	3.314	–	–	–	–
20	Ca	3.358	3.692	36.33	0.341	–	–
21	Sc	3.031	4.091	31.35	0.395	–	–
22	Ti	2.749	4.511	27.42	0.452	–	–
23	V	2.504	4.952	24.25	0.511	–	–
24	Cr	2.290	5.415	21.64	0.573	–	–
25	Mn	2.102	5.899	19.45	0.637	–	–
26	Fe	1.936	6.404	17.59	0.705	–	–

In the next slide this is with respect to copper I had given the energy level values.

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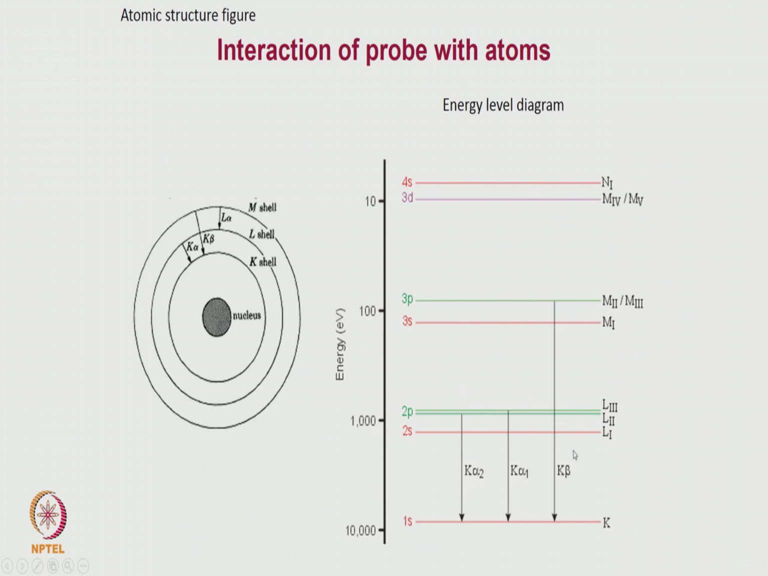

Atomic structure figure

Interaction of probe with atoms

Energy level diagram

And in this particular table what is essentially is being given is the energy of the various K alpha radiation or L alpha radiation or m alpha radiation for different elements. So, essentially if you look at it if the transition is from vacancy is created in K level and an electron from L level comes down and we call it as the K alpha if it is from m level that can also happened K alpha 1 alpha to similarly K beta peaks we will come. Similarly the vacancy is created in L level and the electron from higher level m level comes L to m then this we call it as an L alpha, type of a transition these are all the designations which are used for the various transition.

But what is essentially important here is that suppose we take the case of a calcium here the energy of the K alpha x-ray is essentially 3.69 ke V, but if you look at the energy of the L alpha x-ray it is 3.41.

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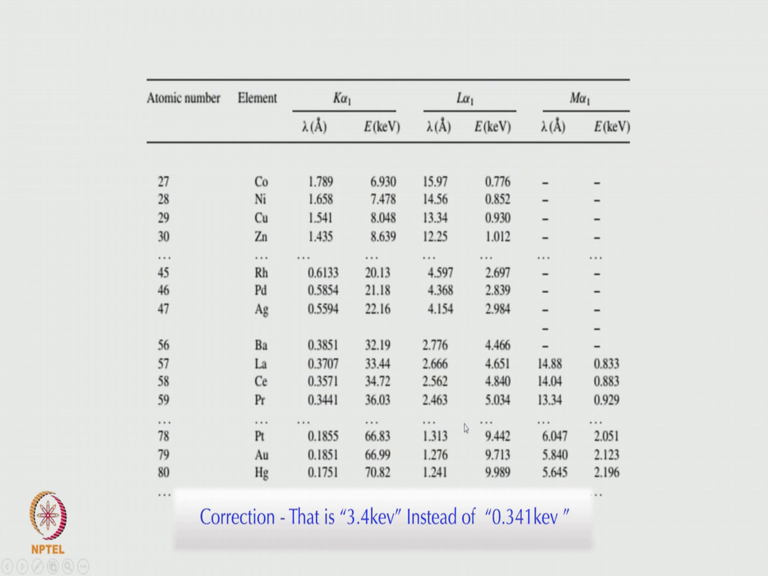

Atomic number	Element	$K\alpha_1$		$L\alpha_1$		$M\alpha_1$	
		λ(Å)	E(keV)	λ(Å)	E(keV)	λ(Å)	E(keV)
27	Co	1.789	6.930	15.97	0.776	–	–
28	Ni	1.658	7.478	14.56	0.852	–	–
29	Cu	1.541	8.048	13.34	0.930	–	–
30	Zn	1.435	8.639	12.25	1.012	–	–
…	…	…	…	…	…	…	…
45	Rh	0.6133	20.13	4.597	2.697	–	–
46	Pd	0.5854	21.18	4.368	2.839	–	–
47	Ag	0.5594	22.16	4.154	2.984	–	–
						–	–
56	Ba	0.3851	32.19	2.776	4.466	–	–
57	La	0.3707	33.44	2.666	4.651	14.88	0.833
58	Ce	0.3571	34.72	2.562	4.840	14.04	0.883
59	Pr	0.3441	36.03	2.463	5.034	13.34	0.929
…	…	…	…	…	…	…	…
78	Pt	0.1855	66.83	1.313	9.442	6.047	2.051
79	Au	0.1851	66.99	1.276	9.713	5.840	2.123
80	Hg	0.1751	70.82	1.241	9.989	5.645	2.196
…							…

Correction - That is "3.4kev" Instead of "0.341kev "

Similarly if you look for copper 8.048 is the energy of the K alpha x-ray whereas, the L alpha x-ray is essentially 0.93. So, compare to K alpha the L alpha has got very small energy only even for elements like gold are mercury if you look at it they are the energy of the K alpha is of the order of 60 to70 ke V and the L alpha has got energy close to 10 ke V.

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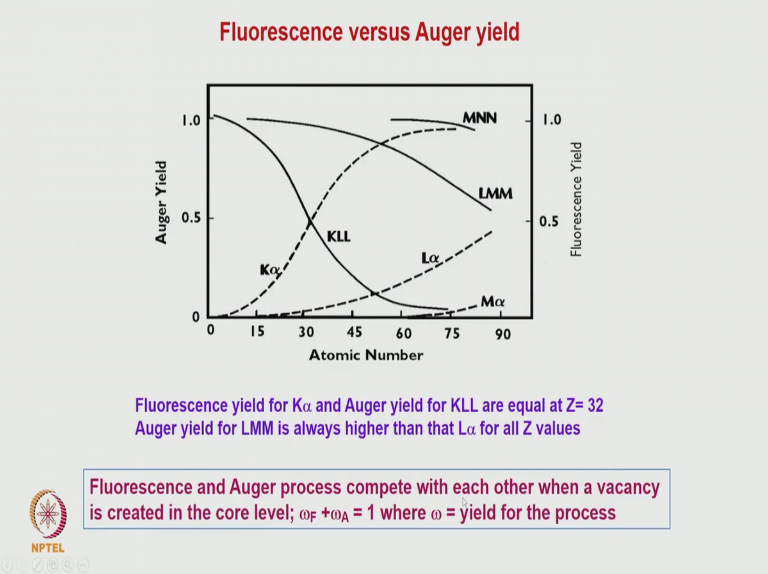

Fluorescence versus Auger yield

Fluorescence yield for Kα and Auger yield for KLL are equal at Z= 32
Auger yield for LMM is always higher than that Lα for all Z values

Fluorescence and Auger process compete with each other when a vacancy is created in the core level; $\omega_F + \omega_A = 1$ where ω = yield for the process

As I mention there will 2 processes by which the atom can come to the ground state - one process essentially is x-ray characteristic x-ray emission, characteristic x-ray emission this is also called us generally use those fluorescence the other is auger emission and these are all the 2 process by which an the atom has to come to ground state. That means, that the probability of both the process to take place if you take the some of the probability of both the processes w for x-ray plus w for auger this should be equal to 1.

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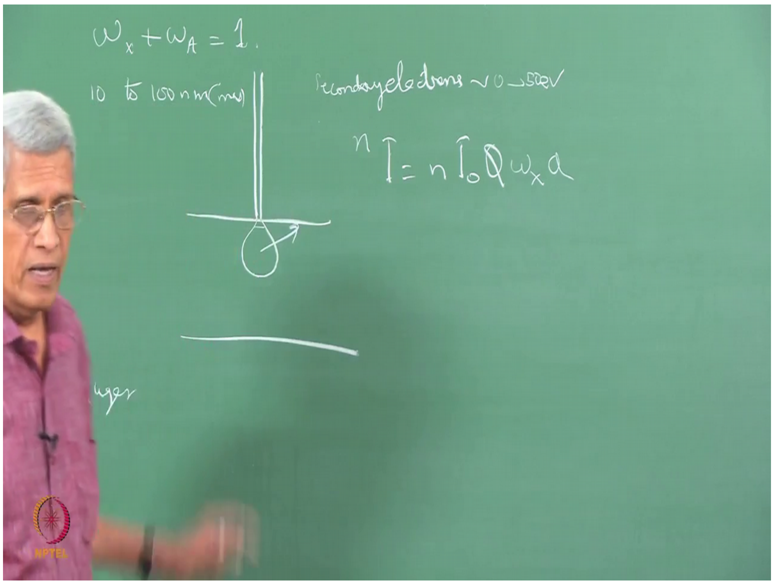

The question arises why I am talking about all this things because when we wonder to find out quantitative information about the elements which are present on the surface this information about the L and all this things are very much important.

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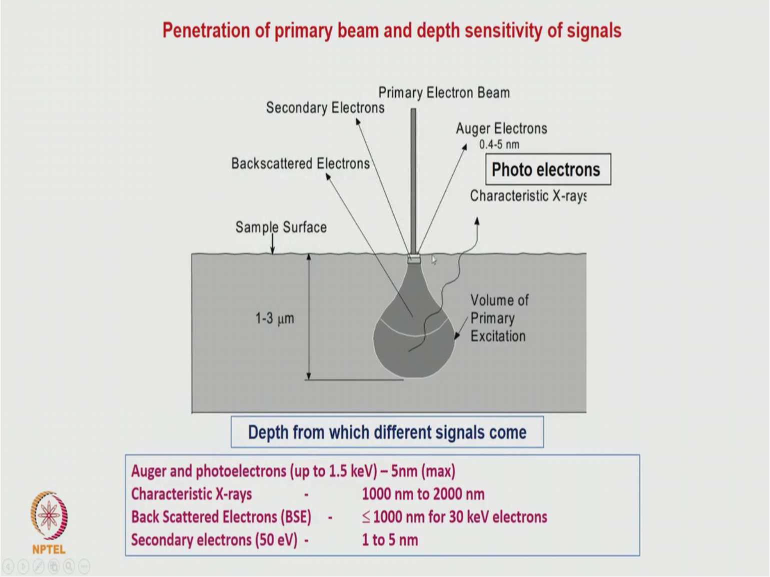

Penetration of primary beam and depth sensitivity of signals

Depth from which different signals come

Auger and photoelectrons (up to 1.5 keV) – 5nm (max)
Characteristic X-rays - 1000 nm to 2000 nm
Back Scattered Electrons (BSE) - ≤ 1000 nm for 30 keV electrons
Secondary electrons (50 eV) - 1 to 5 nm

Before we go further let us look at when the electron beam enters on to the on the sample what are the types of processes by which the electronic can lose energy suppose that sample is quite thick verifying beam of electron we have put on that sample surface. The secondary electrons are emitted from very small region of the sampled very close to the surface generally it is almost right from the surface the secondary electrons are emitted and generally the energy of the secondary electrons is of the order of 0 to 50 electron volt maximum energy.

Then auger electrons are emitted from the sampled surface this auger electron generally comes from a depth of a about 0.4 to 0.5 nanometers, then the backscattered electrons comes from a sufficiently small that is this backscattered are the elastically scattered electrons which are coming from a larger depth of that sample. And then characteristic x-rays are coming from much larger depth 1 to 3 micron and if we take because when the primary electron beam has entered finally, it has to lose all its energy the energy it loses depending upon what is the range which it has and the range is quite large it is of this order 3 to 4 microns in this case.

So, what we can make out is that as the electron beam falls on that sample surface signals secondary electrons are generated from a depth which is very small auger electrons are also generated from depth which is very small, backscattered electron comes from a depth which is large, and if you look at the size of the region from which the signal is coming even though this is the beam size it is coming from a large region so; that means, that the spatial resolution becomes poor. And the depth resolution is also quite large and x-rays come from deep within that sample.

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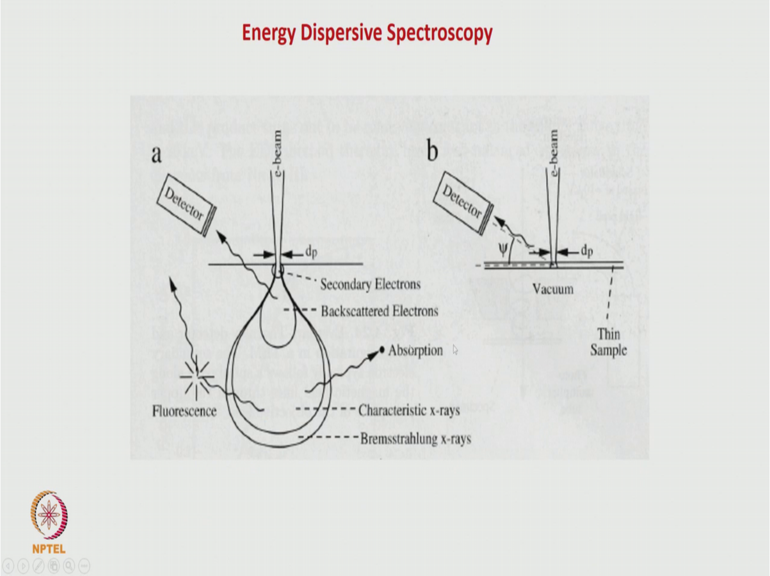

Energy Dispersive Spectroscopy

So, this is about 1 to 3 micron, this same thing is what is being shown here, but when this x-rays are being produced what is essentially important is that that x-rays has to finally, reached the detector without losing any energy then only we can accurately determine what is the element which is responsible for this x-ray emission. If that x-ray looses the energy continuously we will not be able getting a peak and we will not be able to identify what is the element which is responsible for this x-ray emission this is generally goes into the background. So, there is a depth from which the x-ray comes out and not only that as that x-rays comes out of that sample surface part of this x-ray is being undergoes absorption so; that means, that suppose this contains about something like 1000 atoms maybe around 100 atoms half the x-ray is (Refer Time: 14:15) 100 atoms of glass there energy. So, the number of the counts which corresponding to a specific value of energy gets reduced; that means, that the composition analysis it introduces an error.

So, we have to account for all these factors to find out what is the exact composition of that sample surface. Similarly fluorescence is the process in which has the x-ray comes out of the sample surface in addition to the absorption, if it contains an another element this x-ray can knock out an electron from the core level in that and can give raise to that other element the second element which is being second element which is present to give rise to characteristic x-ray, in that process part of this original x-ray which has been generated from this volume where the electron beam falls. There is a, it getting reduced this will also lead to error or we have to compensate for all these things to find out the actual concentration of that sample.

But this is a case which is being shown where suppose the sample becomes extremely thin like in the case of a TEM this is the case which we see in the case of a bulk sample in the case of an SEM are electron probe micro analyzer. In the case of a TEM the sample thickness is generally of the order of may be 10 to 100 nanometers maximum. So, because of this the absorption and fluorescence is going to be very small. We will talk about it a little bit later.

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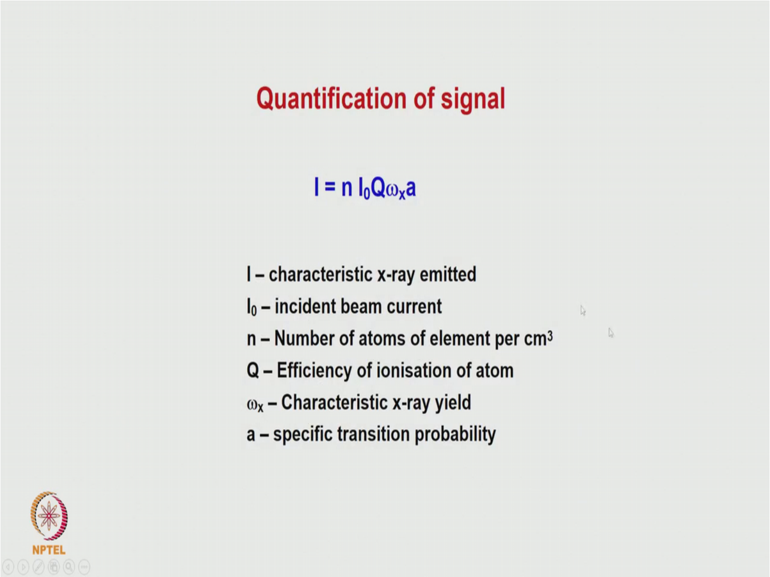

Quantification of signal

$$I = n\, I_0 Q \omega_x a$$

I – characteristic x-ray emitted

I_0 – incident beam current

n – Number of atoms of element per cm^3

Q – Efficiency of ionisation of atom

ω_x – Characteristic x-ray yield

a – specific transition probability

Suppose you wanted to quantify the signal which is coming what are factors which we have to take it into account that is as we have seen the beam is the x-ray suppose we assume that x-ray is being generated from this volume of that sample. What is the total number of electron atoms of a particular species which is going to be present in that region per unit volume that is what n tells. And I 0 is the current density are the number of electrons which are following are the rate at which the electrons are entering into that sample. These are all the various ways in which this I 0 could be represented.

As this electron passes through it not all electrons are going to give rise to inelastic scattering only a small fraction give raise in elastic scattering which results in ion core ionization of that atom Q is the factor which defines the efficiency of this ionization of that atom. Then as I mentioned when a core ionization has taken place then what is essentially going to happen is that all these core ionization does not result in characteristic x-ray emission only a part of it. So, that is what is given by this factor omega x which is called as the characteristic x-ray yield and then another process which has to take is also a is called the specific transition probability. Because we know that the electronic can come down to a ground state either from this level L 2 or L 3 both the levels it can come each has got different specific probability that is why we know that between alpha 1 and alpha 2 if we see that one is a ten percentage of that other. So, that factor also should be taken into account when we try to quantify and find out what is going to be there, intensity of the photons which are coming out of that area.

So, these are all the factors which we have to take it into account. This is as for as the generation of that x-ray is concerned.

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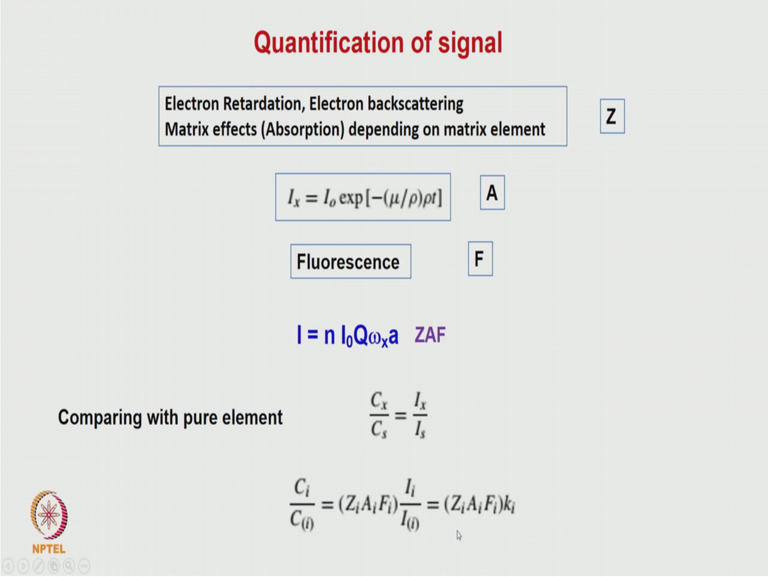

Quantification of signal

Electron Retardation, Electron backscattering
Matrix effects (Absorption) depending on matrix element

Z

$I_x = I_o \exp[-(\mu/\rho)\rho t]$

A

Fluorescence

F

$I = n\, I_0 Q \omega_x a$ ZAF

Comparing with pure element $\frac{C_x}{C_s} = \frac{I_x}{I_s}$

$$\frac{C_i}{C_{(i)}} = (Z_i A_i F_i)\frac{I_i}{I_{(i)}} = (Z_i A_i F_i)k_i$$

Student: Sir.

Then the other aspects which is a going to we have to take into account is when this x-ray is going to come out from this region. So, what we have written this formula essentially I equals n into I 0 into Q into omega x into a, this is the formula which we had. This tells us how the amount of x-ray which is generated within this volume, is all this x-ray going to comes to a detector or not that is a next question. This x-rays has it comes out, this x-ray could be scattered by various processes and it can lose energy. One is by the electron retardation it can give part of that energy the electron will be elastically scattered a little bit. So, the x-ray loses energy there are various effects. So, this is what is called as an a Z, we just take that must this is a contribution from there.

Then the next term is that as that x-ray passes through the sample we know that there is a because of various process absorption florescence there is going to be a reduction and that is the term which we call it an a and then fluorescence is that another one which is responsible for it suppose like if you take ion and then if you take chromium then what is going to have been the chromium fluorescence can take place. So, the ion signal, signal could come down a factor which we have to take into account this is what essentially.

So, if you take all these factors into consideration then what is going to be the signal which is going to reach the detector is going to be this multiplied by this factors. So, this is what the signal which is going to come, but to get quantitatively what is going to be that signal theoretically if you try to look at it we should know Q omega x and all this factors which we required these not very easy to get this information we can do some experiment and experimentally we can determine this which we will discuss shortly. Suppose you compare this one way in which we can get this information is suppose some concentration of the element is present in this region, I can use a few word standard we know that the 100 percentage x-ray emission whatever is the information if the concentration has to be 100 percentage, if I compare between these 2 that is what essentially which is being returned the concentration this is n is that equivalent to concentration.

C x by the standard sample if I take it this ratio of that piece should be equal to the ratio of the concentration elements which are going to be there provided this terms are also going to be there correct you multiply it by the is ZAF correction also will come. The generally in an energy dispersive spectroscopy which we consider in an electron microscope since the sample is thin absorption could be neglected similarly fluorescence affect is also going to be small.

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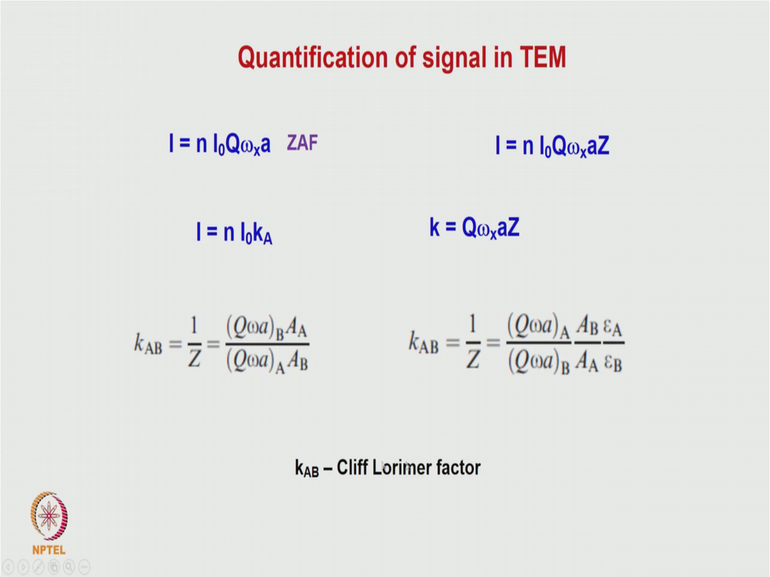

Quantification of signal in TEM

$I = n\, I_0 Q \omega_x a \quad ZAF$

$I = n\, I_0 Q \omega_x a Z$

$I = n\, I_0 k_A$

$k = Q \omega_x a Z$

$$k_{AB} = \frac{1}{Z} = \frac{(Q\omega a)_B A_A}{(Q\omega a)_A A_B}$$

$$k_{AB} = \frac{1}{Z} = \frac{(Q\omega a)_A}{(Q\omega a)_B} \frac{A_B}{A_A} \frac{\varepsilon_A}{\varepsilon_B}$$

k_{AB} – Cliff Lorimer factor

If we take that into consideration this term is ZAF will go and only that is Z will come into the picture this is what is going to be the expression which gives what is going to be the intensity of the signal which is going to reach the detector.

So, here we can write n I 0 these terms Q all these terms put together we can write it as a factor k A for that specific element or a K we can call it; that means, that this K is a factor which has to be determined. So, this K contains the probability of x-ray translation, the x-ray probability of x-ray yield the transition probability for the specific peak which we are looking for then the a Z which corresponds to the atomic number of the element how it reduces the signal strength and then Q is the probability for ionization core ionization of that sample all these factors.

So, this is using a standard if you do it this terms will going to be that saying as apart from the number. So, that way using a standard we can comparing it we can get the concentration very accurately that is one way. That means, that for suppose a sample contains ten elements we know the all the elements in the periodic table we should have a pure elemental standard for all of them and we have to maintain the identical current to measure this intensity which is going to be a quite a TDS one. So, most of the time because of this what we do is that we use a standard less technique which is essentially nothing, but the relative concentration relative concentration what we do is that suppose n elements are present.

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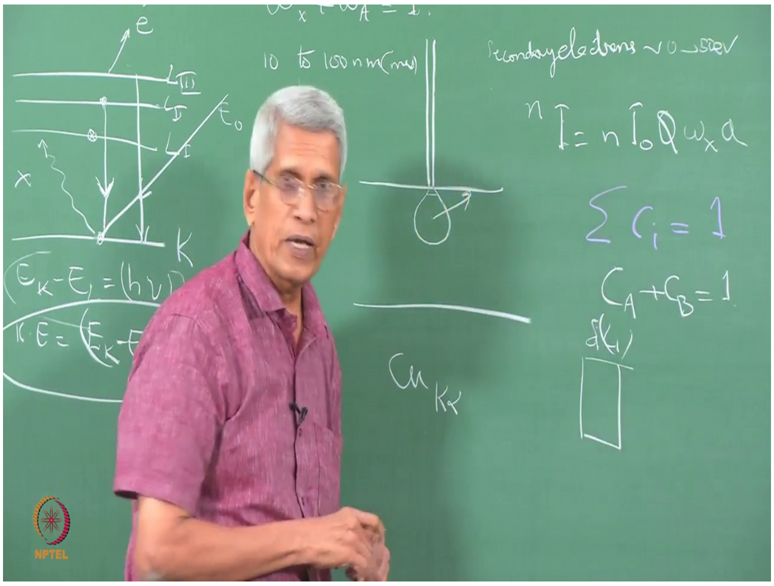

The concentration of all the elements there C i should be equal to 1, this is the philosophy which we a follow. In such a case let us assume a case where there are only two elements are there then what will happen the concentration elements A and B, C A plus C B should be equal to 1.

We are going to get a signal from C A we can write an expression like this similarly we can write an another expression for C B, if you take the ratio of it then this is the sort of a term which we will come where this term corresponding k corresponding to element A, one corresponding to element B. So, this ratio k A B this is called as a elemental sensitivity factor, this factor is not a constant it can vary from the geometry of that system from two different microscopes depending upon the detectors you can have two different values these are not that same. The simplest way in which one can do it is theoretically whatever the values which has been calculated one can do it, but that does not give the correct values it is better to find out the elemental sensitivity factors.

This factor k A B is called as the Cliff-Lorimer factors where we are not using any standards. And in this case this, in this particular case what we have assumed is that we are not taken the detector efficiency into account generally what is an detector efficiency is also added epsilon A and epsilon B for the two elements. So, then there is completes this expression and this tells this is what the k A B which is going to be.

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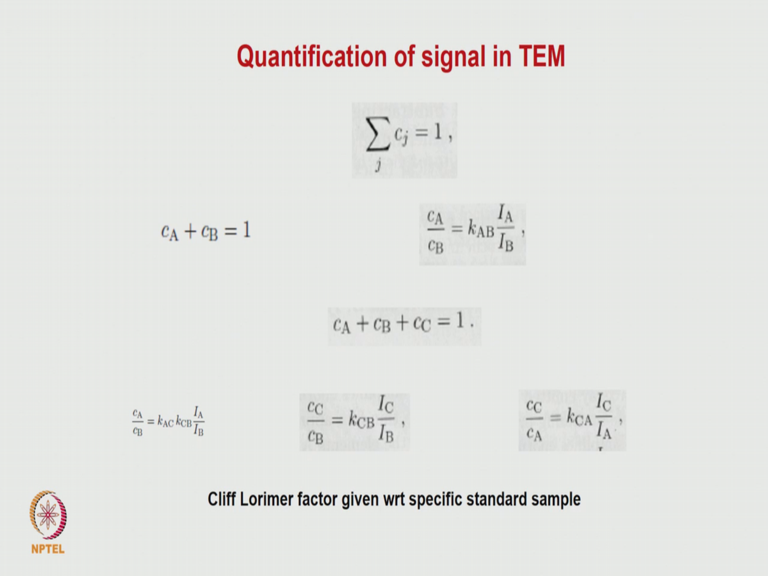

Quantification of signal in TEM

$$\sum_j c_j = 1 ,$$

$$c_A + c_B = 1$$

$$\frac{c_A}{c_B} = k_{AB} \frac{I_A}{I_B} ,$$

$$c_A + c_B + c_C = 1 .$$

$$\frac{c_A}{c_B} = k_{AC} k_{CB} \frac{I_A}{I_B}$$

$$\frac{c_C}{c_B} = k_{CB} \frac{I_C}{I_B} ,$$

$$\frac{c_C}{c_A} = k_{CA} \frac{I_C}{I_A} ,$$

Cliff Lorimer factor given wrt specific standard sample

I have already mentioned for a 2 elements suppose 3 elements are going to be there, generally what happens most of the time we use essentially is a nickel based super alloys or stainless steel or aluminum alloys where one concentration of one element matrix element is very high others are small.

So, we can take that as a standard and with respect to that we can find out the ratios. So, what is in fact, what is essentially is being done is that this experimentally one can determine k A B with an equipment for various elements what the value for the same identical conditions you have got it with respect to a particular element which we take then and we can take the ratio for each one of them and try to find out what the value of k A B is going to be.

This is what essentially these tables are available which are there library which are there in the software which is being used by most of the commercial softwares which are available. So, essentially this factor suppose there elements are there C A by C B, C B by C C then we can have C A by C. So, this sort of factors which are there from the tables which are available here if you look at it with respect to concentration of the element C we have taken this ratio and calculated what the Cliff-Lorimer factors is going to be; that means, that the ratio of the concentration is not the same as the ratio of the intensities there is a factor which comes into the picture.

So, in experimental condition what is normally being done is that suppose you have a sample you assume that it is a single phase that is where one can do this experiment easily then find out the composition very accurately using either weight chemical technique are electron microprobe. So, that we know what is the concentration of the element and then that same sample thin down in the TEM you look at it find out what is going to be the ratio of the intensity of the peaks which are going to come and from this expression we can find out what the value of k A B will be. That is essentially how we can find out this Cliff-Lorimer factors accurately.

So, we have, so far we have talked about how to get the relative concentration as well as the absolute concentration how we can determine, what all the terms which are involved that briefly we have discussed are not gone into the more details of it that you can look into the standard books which are available which gives it in great detail.

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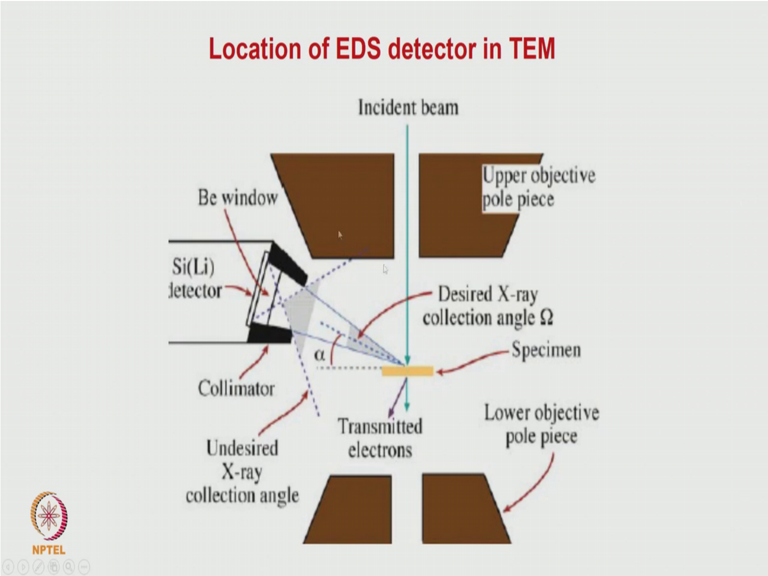

Location of EDS detector in TEM

In an electron microscope let us come back to a microscope and see hoe exact physically where is the detect where exactly is the detector is place in a microscope this is the pole piece there some gap normally the gap is surround the 2 or 3 millimeters the pole piece gap which is going to be very small in the sample is there at the middle. And close to the as close to the pole piece the detector is being in certain and the detector is inserted in such a way that the maximum solid angle which submits to collect that is then that that is what is going to decide the efficiency of collection of that x-ray because the x-ray is emitted from the sample in all the direction.

If you look at the x-ray which is emitted in this direction the absorption is going to be maximum, if you consider the x-ray which is going to be emitted in this direction absorption is minimum. So, up to some certain angled the absorption is very small which can be neglected. So, that angle is in the case of a microscope it is about 30 degrees. So, that is what essentially is being done that for that essentially the detector should be kept at an angle so that it submits an angle this alpha which is as an 30 degrees. This is how and one has to be extremely careful because finally, the chemical analysis essentially is something which we have added as a one which gives more information, but the basic job of microscope is to give the best image resolution so that one cannot compromise.

So, one has to introduce the detector in such a way that it does not affect the performance of the pole pieces because no way the pole piece should be effected that put some limitation on what is the sort of analysis which could be performed using EDS in a microscope.

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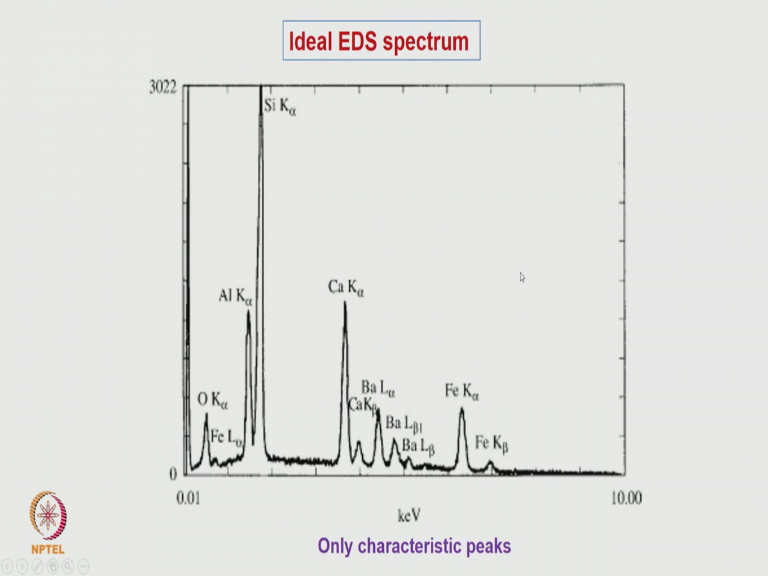
Ideal EDS spectrum

Only characteristic peaks

If you look at the type of a spectrum an ideal spectrum if you look at it because we have a detector the signal is coming and it we have trying to analyze that signal, from whatever we have discussed so far essentially the characteristic peaks of all the elements which are present in the sampled surface from that volume should reach the detector and it should give rise to some peaks that is what we should observed the ideal case.

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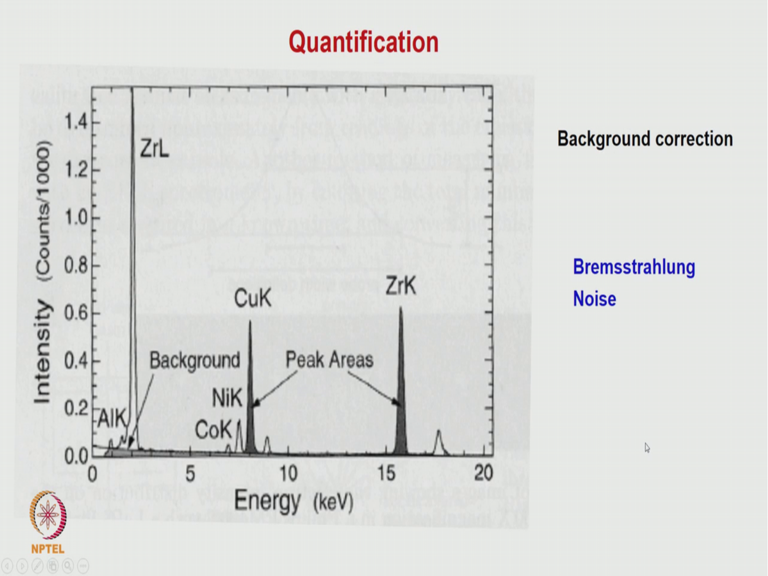

Quantification

Background correction

Bremsstrahlung

Noise

What is it is happening? Here you can see that that is not the case which happens in real cases and generally the signals which are being generated if you look at the line width of these x-rays they are going to be from 1 to 10 electron volt. But what is the normal resolution which we talk about in an SEM that is EDS attached to an SEM or a TEM we can get it is about something like 120 to 130 electron volt; that means, that resolution is quite poor. We will talk about a little bit later what is the reason for such a poor resolution we get it in an EDS technique.

Then there are many other peaks also which come which are called as Fourier speaks all these things we have talk on for. So, when we wonder to do a quantification the first and foremost thing is that even in an ideal condition the background could come the background could come from Bremsstrahlung and the noise. So, the signal to noise ratio we have to correct for it. So, the Bremsstrahlung has to be eliminated from the spectrum which we have obtained and then from that peak to noise ratio also we have to get that information then only we know how many counts which are coming from exactly from the sampled that is from the elements which are present on the sample and not due to Bremsstrahlung or not due to a background correct at that position.

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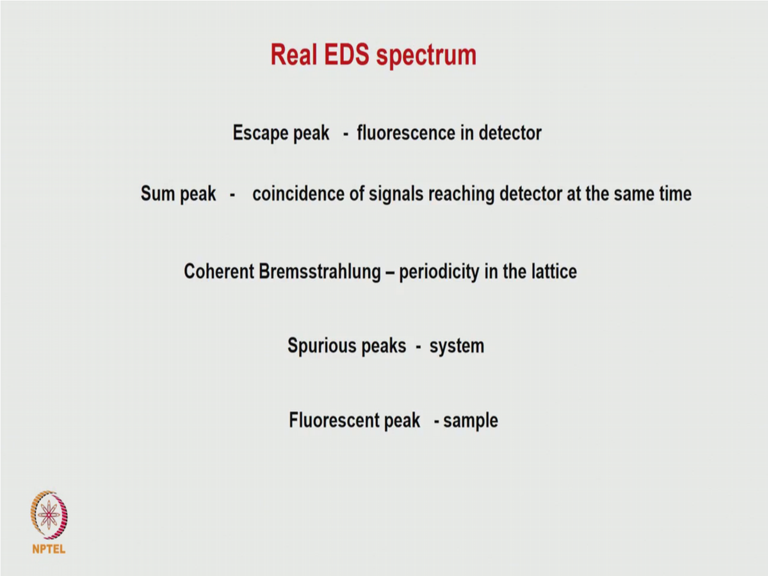

Real EDS spectrum

Escape peak - fluorescence in detector

Sum peak - coincidence of signals reaching detector at the same time

Coherent Bremsstrahlung – periodicity in the lattice

Spurious peaks - system

Fluorescent peak - sample

So, in a real EDS spectrum if you look at it that is where one has be extremely careful because most of the softwares which are available they give some calculation and analysis, but one should be take sufficient care to see to it that all the spurious information which is there is eliminated before one does quantification for which what are the things which can come. One an escape peak escape peak is what it is called us its due to appearance in a fluorescence in the detector. There is as the x-ray beam with a particular learning suppose we assume that x-ray from a copper K alpha x-ray is entering in to a detector the detector is nothing, but a silly detector which is normally used as it enters into it initially it is a there is called as a region or the dead layer where no information is being collected.

In this layer has the x-ray enters it can cause a fluorescence here. So, if it cause a fluorescence here; that means, that it ionizes that silicon K alpha so some part of the x-ray comes out with losing some specific energy; that means, that the reduction in energy of the copper K alpha as occur and a copper K alpha energy minus this energy corresponds to its around 1.74 KV at that position you get an another peak. So, that is a spurious peak. We will say that silicon is present, but the sample may not contain silicon. So, this is one thing which can happen.

Then another what is can happen is the some peak we assume that every x-ray signal which is generated is by a process that is this process we assume that as an each electron beam enters the current is such that the sample is. So, thin that when it undergoes only one process scattering process which undergoes and x-ray of a particular energy is generated and that is the only x-ray which is being detected, when the next general and comes it generates characteristic x-ray from some other element that come separately it is being detected.

So, each is done sequentially that is what is being done suppose a counter (Refer Time: 35:59) what can happen if that x-rays are generated simultaneously from two regions both of them reach the detector, both of them the signal processing will not be able to identify them as two separate once. So, essentially how does that detector detects it has the x-ray passes through this thin region it produces the electron volt pears and that requires in the case of silicon about something like three point data electron volt then if you know the energy we can how many electron volt pears will be produce. If simultaneously they produce the total charge which we collected that is what we counted as corresponding to specific energy of the electrons. So, if two electron x-rays from the same milli man reach simultaneously to x-rays then that will be counted as a peak with the double the energy that will give rise to another peak it is a spurious peak ok.

Then what is called as a coherent Bremsstrahlung that is especially on a crystalline material when the bema is along the specific along the shown axis and arranged then the beam enters Bremsstrahlung is radiation which is being produced because of the coherency of the beam this can give rise to some peaks which are appearing at different energies on the overall background that is one process you can take place.

Another is a spurious speak what is the spurious peak that is as the electron beam enters into the sample.

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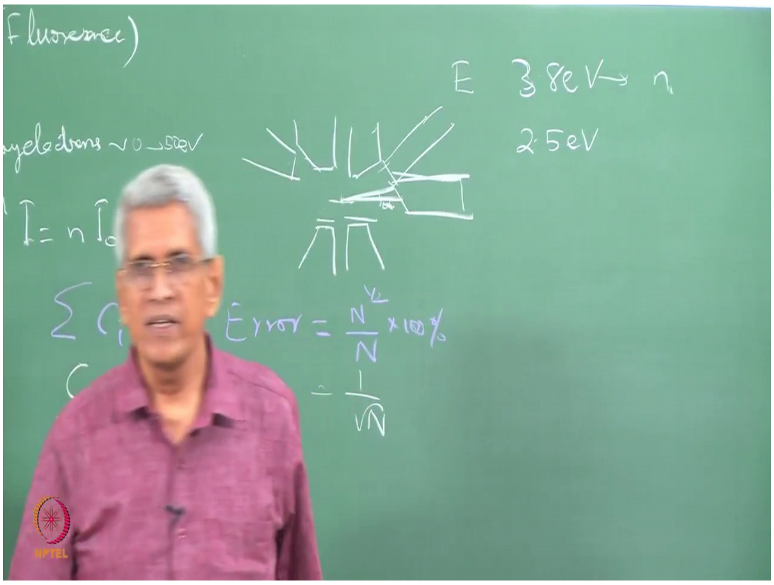

That is we have that this is the lower pole piece upper pole piece and this is the lower pole piece then this is where the sample is there we have the detector which is kept here the electron beam is falling on to a sample and coming out further, but in that process that may be a aperture here or the pole piece copper winding is there.

Everywhere this electron beam can heat and the x-rays can be produced all this x-ray is a could reach this detector they are also characteristic x-rays. So, this will give rise to a peaks corresponding to them because finally, when we look at the spectrum we look at the spectrum tried to find out what all peaks which are come. So, this requires some typical alignment to C t if the spurious peaks do not comes, but we have to be careful about it to identify that the peaks which we have got it in that sample or what we feel the peaks whether they are spurious peaks or whether the peaks corresponding to actually the one which has come from the area in which the electron beam has fallen that one has to be careful about.

Then the florescence peaks which can come all these are the factors what is the effect of the fluorescence peak - the fluorescence peak will also increase the intensity of one peak and reduce the intensity that is suppose this florescence peak matches with an another element. So, intensity of that element peak will go and the intensity of the original elements from which the x-ray has been produced that will come down.

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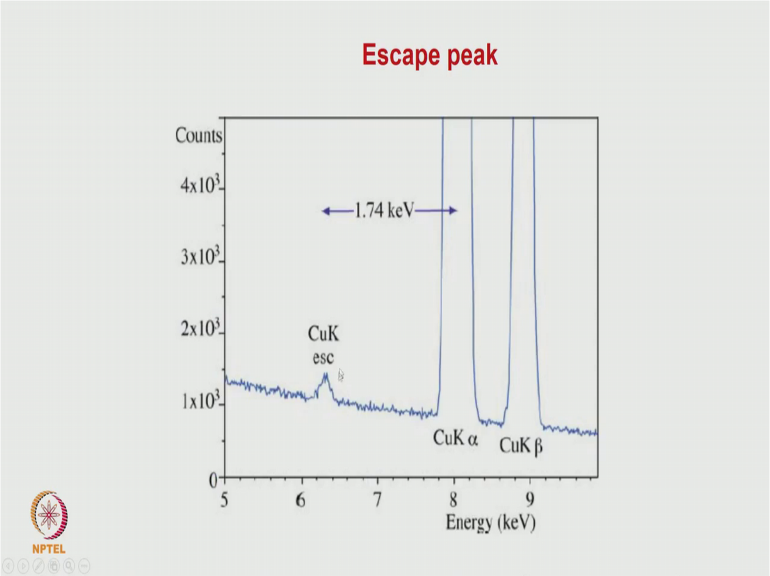
Escape peak

So, this is just showing some examples of peak where copper K alpha and its around 8 KV and you can see that around 6.2 you have a another peak comes escape peak this is an escape peak. Some peak is here it is a magnesium peak in the sample and say is the especially when the counter rate is very high that is where you get all this, then because for this purpose we have to reduce the counter rate considerably.

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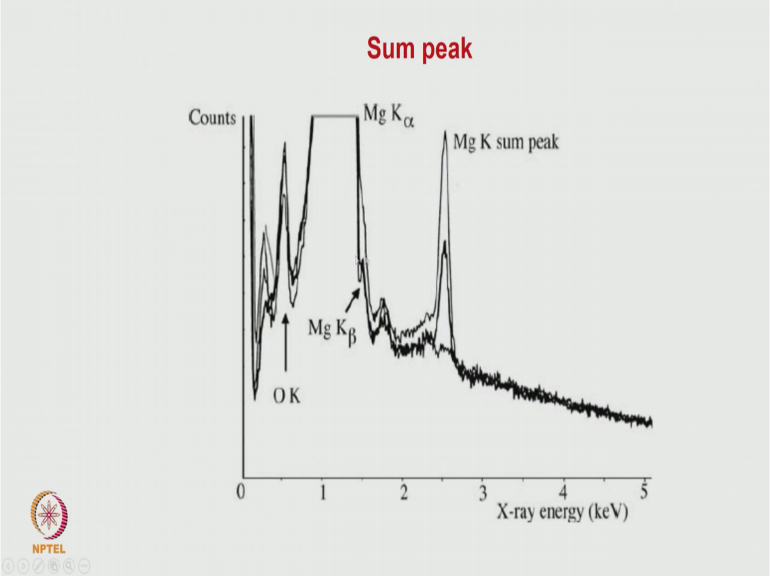
Sum peak

Now we can see that that is a peak which has come corresponding magnesium some peak comes this may correspond to some other element. So, we will think that is another element is present in that sample which may not be the case. So, one should understand the all these things and make correction for it before we try to do quantification we have to choose what all the elements which has to be considered, what all the peaks which have to be considered and we have to assign them that this corresponds to a particular element in the process we have to eliminate all this spurious effects.

This is like here you can see that the copper L alpha and this is the copper K alpha peak in between this is an escape peak there are some lots of peaks which are coming it has to these are all the coherent Bremsstrahlung peak.

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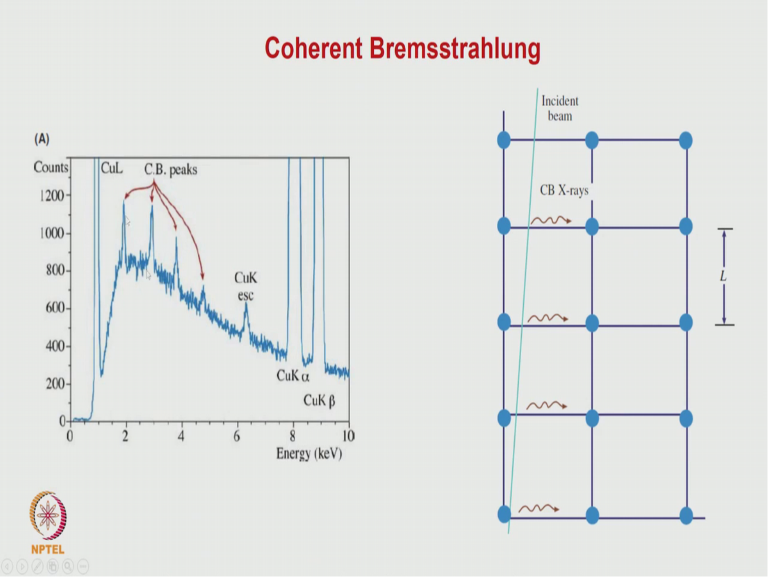

Coherent Bremsstrahlung

This comes from as the incident beam falls onto the sample correspond close to this is that is one of the reasons why we always say that one should be far away from dynamical condition when we wanted to do EDS analysis to get then only you can get two composition. Close to small in as small in index shown axis patent we will get a lot of not only spurious peaks, we do not get the correct information about that composition of the elements present in the sample surface also, this I will come to you shortly.

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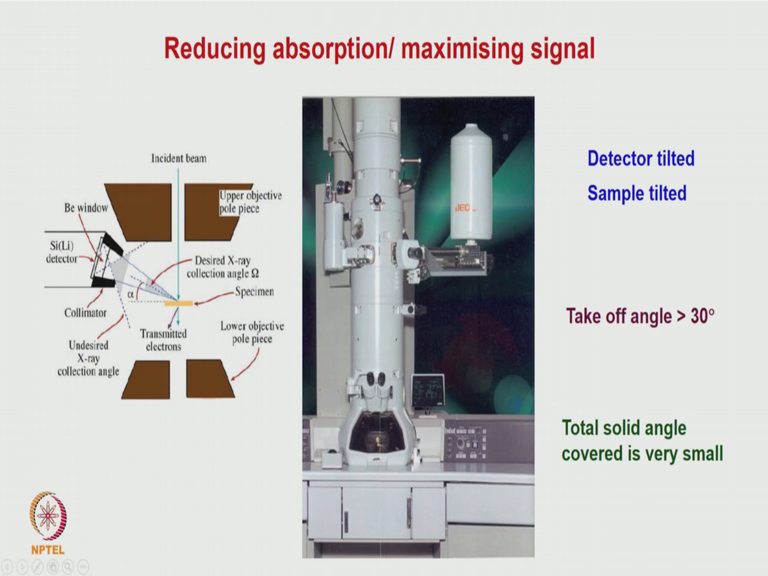

Reducing absorption/ maximising signal

Detector tilted

Sample tilted

Take off angle > 30°

Total solid angle covered is very small

Where do this spurious peaks come? As I mentioned that the electrons when passes through the sample this is where the specimen generated continuum x-ray is there.

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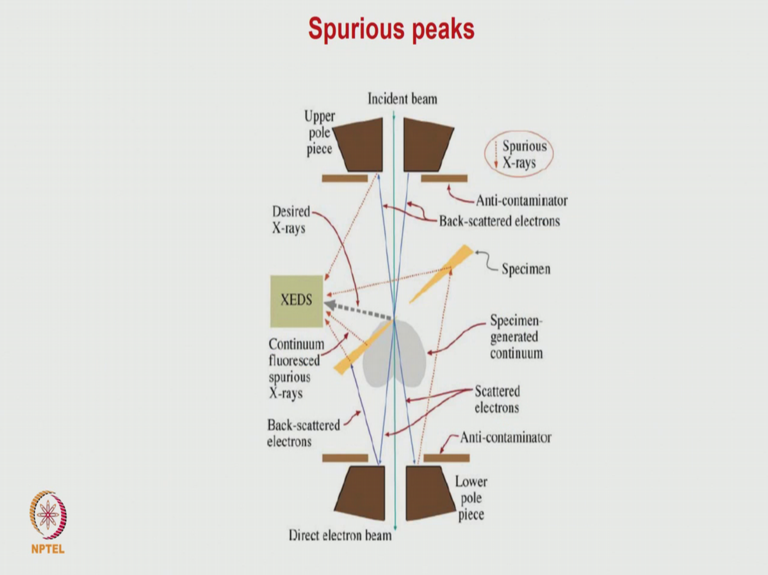

Spurious peaks

Then these electrons because it is being focus to a point on that sample surface then it diverges then it may be heating so many places, from here also x-ray will be produced this x-ray when it is produced it passes through it, it will be heating the thicker region of the sampled it can produce fluorescence. There are so many ways in which this information it will produce most of the microscope if you look at it the whole days which we use our copper which is going to be there. So, even the sample may not contain copper, but we will get a lot of signal corresponding to copper the only way this can be reduced is to use beryllium holder, so that low is Z elements essentially the x-ray process of x-ray is generation efficiency is very small. And that is why if you wonder to do EDS analysis the chemical composition analysis of a sample one should not look at the sample in the normal holder one should put the sample in a beryllium holder.

And then another important aspect is that generally if you put to improve the contrast we introduce an objective aperture, the objective aperture is either platinum or aluminium that also we will just sufficient x-rays and diamonds the detector. So, it is better to do the chemical analysis when we do the aperture should be removed, so that we can reduce the background noise as well as the spurious signals could be reduced considerably. These precautions have to be taken.

Then I mentioned that if you have to maximize that signal or to reduce that absorption that should maximize the signal also that is the detector should be kept at an angle which is greater than 30 degrees, this could be achieved in two ways - one is that like in this particular case it looks like that the detector is perpendicular to the beam direction. But what is being done here is that if you look at it at the end of it this rod where the detector is kept it is inclined like this because of this since is the detector is kept like this inclined like this the angle which its satisfies this angle these essentially 30 degree we can maintained or the other option is that you can keep the detector coming like this. So, then also this same angle could be done. These are all the 2 approaches which are used practically to increase the take off angle.

And in spite of all these things the area of the detector is either 10 millimeter squared or 50 millimeter squared that is what it is going to be or that the millimeter square and of the x-ray which is going to come over the solid angle only a small fraction at a position which we are trying to collect it. So, one has to take as much precaution is possible so that all the x-rays maximum signal reaches the detector.

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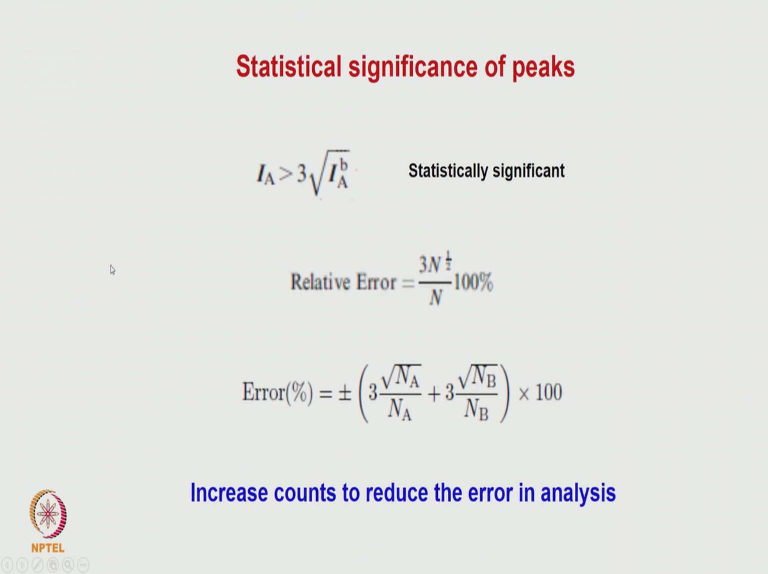

Statistical significance of peaks

$I_A > 3\sqrt{I_A^b}$ Statistically significant

$$\text{Relative Error} = \frac{3N^{\frac{1}{2}}}{N} 100\%$$

$$\text{Error}(\%) = \pm\left(3\frac{\sqrt{N_A}}{N_A} + 3\frac{\sqrt{N_B}}{N_B}\right) \times 100$$

Increase counts to reduce the error in analysis

This is the statistical counting process. So, statistics plays a part. So far what we talked about it is identifying the signal that is characteristic peaks which are present in the spectrum which we are obtained. How do when do we decide that some peak which appears is not a noise, but it corresponds to a single. For that the strategic one what is the background peak and if the peak high the intensity is 3 times more than that of square root of this peak height then we can say that the peak is statistically significant because with 99 percentage confidence we can tell that that is a peak which is going to be there.

That if you look at the spectrum which commercial software give all this information how this peaks are chosen, but one should also be aware that this is the way in which it is being done. Then another is if we are chosen like this what is going to be error corresponding to each peak, suppose we count some n number of counts if with one sigma confidence level if you wonder to count then the error is going to be N to the power of half by N it is a percentage this is how we can rough sense this. If it is 3 sigma three times it is going to be there. So, that gives the relative error and we know that this will finally, we will turn out to be 1 by root N correct; that means, that higher the counts we the more the counts which we collect the error is going to be less and less.

So, in all this analysis what is essentially important is that we should collect as much signal as possible. So, if two elements are going to be there then we can find out what is going to be the total error and what is this error going to decide, this is going to tell is that what is the confidence with which we can talk about the concentration of the elements. This is going to tell you that in which a significant digit you have to stop suppose somebody gives a combustion up to second decimal place that is 25.56 is the concentration then one has to be very careful about it is that it is really possible or not. As per if you look at that then one should know what is the total counts which have to be collected to go to that accuracy whether that experiment has been performed to that level or not. These are all very important.

There are various types of detectors which could be used these are called silly detectors, intrinsic germanium detector, then silicon drift detectors, then calorimeters wave length dispersive detectors.

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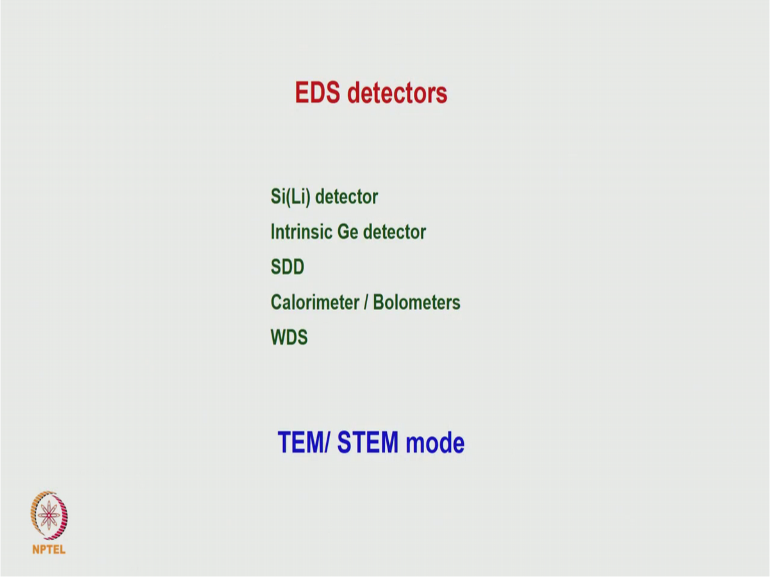

EDS detectors

Si(Li) detector
Intrinsic Ge detector
SDD
Calorimeter / Bolometers
WDS

TEM/ STEM mode

Let us take the case of the EDS detectors which are used which are silly intrinsic germanium detectors are silicon drift detectors. In all these things the process by which the x-ray with characteristic x-ray we detect it is as the x-ray pass of through the sample we assume that its being completely stopped, then it loses energy by creating some electron hold pears and in the case of silicon the energy is about something like 3.8 electron volt is to quite in the case of germanium it is 2.5 electron volt which is required.

That means, that further same energy of the x-ray the number of electron hold pears which will be generated is more in germanium. So, the sensitivity is high for germanium. So, if you one can afford to use that that is good though it is expensive and this process is also a statistical process there is various other process by which it can lose energy. So, suppose the number of whole phase which is for a particular energy E it produces for one x-ray it may be producing a number n 1 electron hold pears the further same characteristic x-ray the second signal which comes it may not be producing n 1 it may be producing n 2.

So; that means, that for the same energy of the incident x-ray there is a difference in the energy of the difference in the number of electron hold pairs which are being produced and that means, that the charge which is collected is not the same for all the characteristic x-rays from a particular element reaching the detector. This will grow is to a broadening this broadening is the one which gives rise to that 123 electron volt direction, but if we use another technique like WDS wave length dispersive analysis there we can find out the x-ray energy very accurately because they are we are not using the energy we are using the dispersion of the wavelength associated with the characteristic x-rays there we can solve them or the other way in which these called bolometer microcalorimeter.

In the microcalorimeter all the energy which comes you can find out that energy which is sub that will be the same there also the solution this is what is that energy resolution which is going to be very good. And another is that if you wonder to find out composition of large are for sample in a TEM mode if you try to scan the image resolution will go down is better if you do in a scanning transmission mode where we can scan on different area of that sample and from each area we can collect the spectrum we can do, we can do a quantitative analysis which is possible. This is all because of the computing power which was not possible the earlier.

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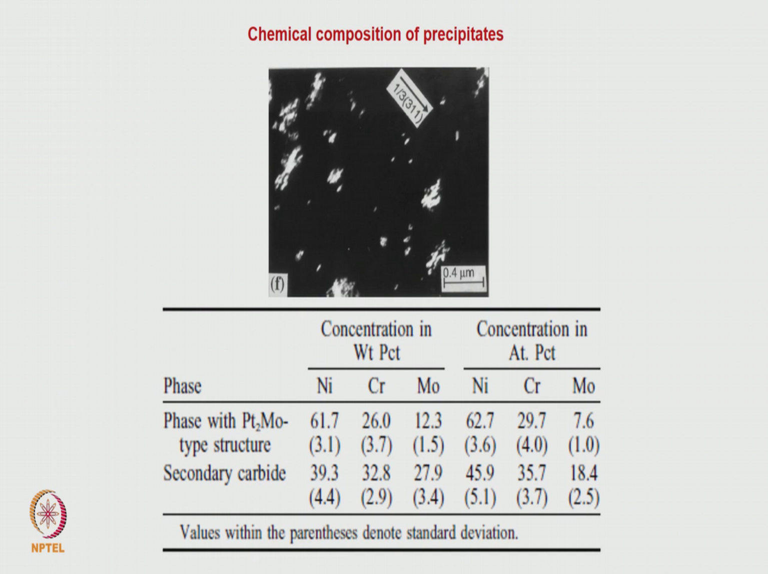

Chemical composition of precipitates

Phase	Concentration in Wt Pct			Concentration in At. Pct		
	Ni	Cr	Mo	Ni	Cr	Mo
Phase with Pt_2Mo-type structure	61.7 (3.1)	26.0 (3.7)	12.3 (1.5)	62.7 (3.6)	29.7 (4.0)	7.6 (1.0)
Secondary carbide	39.3 (4.4)	32.8 (2.9)	27.9 (3.4)	45.9 (5.1)	35.7 (3.7)	18.4 (2.5)

Values within the parentheses denote standard deviation.

This is an example we are using a stationary beam in a transmission electron micro scope the composition which has been determined from there precipitates which are of the order of, which are very small size about point one micron size and we could accurately determine the composition. Here we have used as I mentioned earlier there is a composition has been determined from (Refer Time: 52:09) other sources independently and in a single phase that is how this analysis has been performed.

Another is normally you see that the earlier people used to give x-ray mapping how the distribution of the various elements are have done they are what is being done is that correspond, you put a window choose a window corresponding to a specific element when an x signal comes corresponding to that it is being marked at that specific position as a dot which is coming a bright dot, but whether the dot is coming from a bremsstrahlung or a background we do not know. The present the information we have all the information is collected from each pixel each region now one can do remove all the background can everything and try to find out, the quantitatively what is going to be the signal which is coming and then we can get it.

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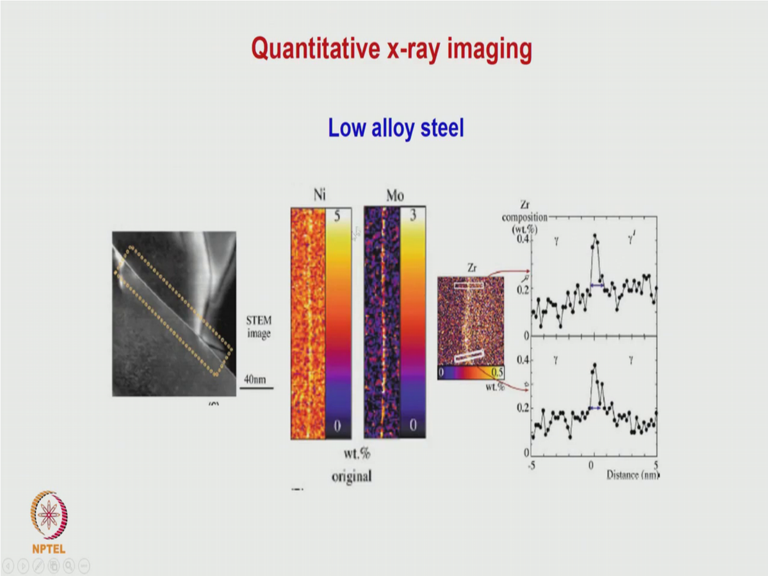

Quantitative x-ray imaging

Low alloy steel

These plots are corresponding to such. So, that we can find this is in a low alloy steel how nickel and the molybdenum zirconium are segregated along the grain boundaries this sort of information on can get it that is possible in present the micron because one the earlier the counting was statistics as using an analogue type of a system now they are all being done in a digital form. That is what it has made all the improvements.

Then let us talk about a resolution what are the types of resolutions which we look for.

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Resolution

Spatial resolution
Depth resolution
Energy resolution

We have already discussed I am just trying to point out. One since we use an electron beam a spatial resolution which is important as I have shown the earlier like in these case even though the beam spatial resolution of the beam is very small as for as x-ray is concerned this is what the spatial resolution is in the case of SEM or in EPMA. Whereas, in the case of TEM since we use the sample to be very small the x-ray is coming from a very small region, spread is very small, so the spatial resolution is very good.

Another important factor is that suppose we wanted to improve a open the spatial resolution what we have to do it the beam has to be made finer and finer; that means, that the aberration has to be corrected. If you can correct the spherical aberration then we can make the beam as fine as possible. So, in aberration corrected microscopes spherical aberration could be corrected and another is when we use field emission gun then we can increase the intensity in the very small region the current density could be electron current density could be increase considerably with these we could do analysis from extremely small regions of the sample. Then the energy resolution essentially is determined by the detector that we have no control over it. So, we have to accept that if you wonder the better energy resolution we have to go for they mentioned that barometer. The problem of a barometer essentially is that it has to be from micro Kelvin that is the only problem, temperature. Whereas like HDD detectors and all even with a peltier cooling one can after them you do not require a liquid nitrogen cooling of the detectors.

Here I am just showing an example of how in an EPMA this is the beam size and this is the volume.

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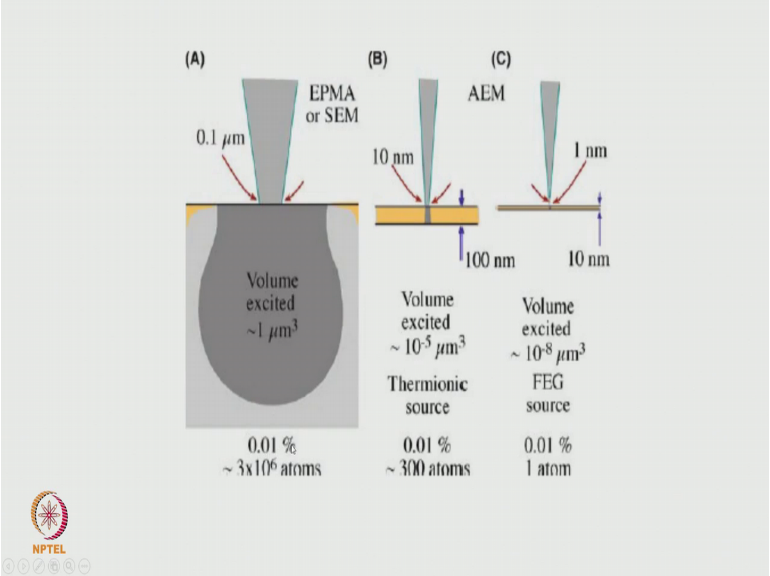

If you wanted about 0.01 percentage concentration which we wanted to detect then the number of atoms which are going to be there in this case is 3 into 10 to the power of 6 atoms in this volume. Suppose in an conventional atomic conventional analytical electron microscope 10 nanometer bema size if you choose it 100 nanometer the volume excited is 10 to the power of minus 5. If you use thermionic source for this 300 atoms are going to be analyzed for this concentration if you use 1 nanometer beam size and 10 nanometer sample size with FEGS that this one. Essentially almost like only one atom may be present in this region to give this concentration to get the signal from this it is not trivial right.

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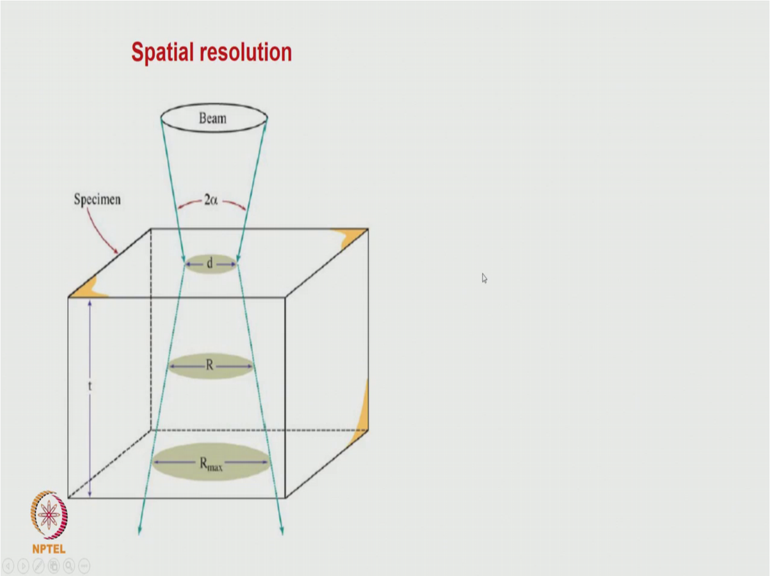

Spatial resolution

So, essentially as I mentioned to get more spatial resolution as the beam spreads if the sample is thin the spread of beam will be reduced considerably. So, that the beam size is the same as a spatial resolution. Then the depth resolution is very important in the case of SEM as well as EPMA what is the depth from each the signal is coming that depends upon the primary beam energy as well as the escape death of the x-ray which is being produced from what thickness, essentially like in ACM its essentially about 1 or 2 microns; that means, that we do not get through surface composition of that sample.

And another thing also is that since we do not know what is the thickness of the second phase particle its always there is a doubt that whether that entire signal is generated from the full volume of the precipitate or not. Whereas in the case of TEM this out can be cleared because we know that we are able to observe the image of the precipitate we know that how much is the thickness precipitate contributes to how much is the thickness that is supposed this is a sample a precipitate I assume to be a rectangular once going to be here.

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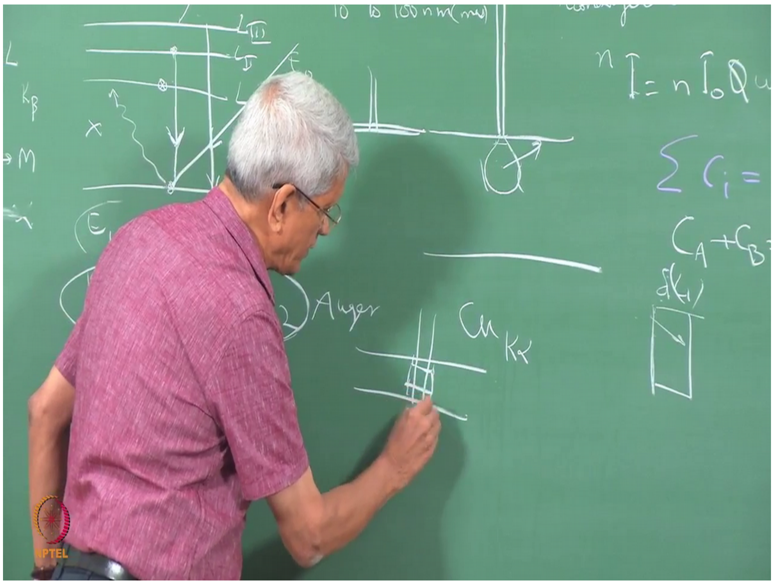

When the electron beam passes through it we know how much is the volume x-ray is generated from that precipitate how much from this. So, we can account for all these things which is not possible. There is suppose this region does not contain precipitate from this region we can find out a composition then we can apply a correction so that we can find out what is (Refer Time: 28:12).

These are all things which one has to depending upon the type of information which we look for, one has to think about it and device experiments same and get the correct information. Then this determines also the peak to background as well as the peak signals that is going to determine what is the minimum detectable fraction whereas, in the case of many of the weight techniques or emission a optical emission atomic emission spectroscopy and all where we can detect to a much accuracy PPM levels we can do it, but that is not possible in this. Here may be at this if you can do 1 atom percentage to 0.2 an atom that itself is contained as great, but for that we have to take a lot of precaution.

And another is for high is a Z elements is where we can use this to find out the composition with some confidence because low is Z elements below 1 alloy ke V absorption is going to be quiet high. We may be able to obtain a peak corresponding to a particular element, but to find out the composition accurately is going to be it is not a trivial task that requires a lot of extra care which has to be taken.

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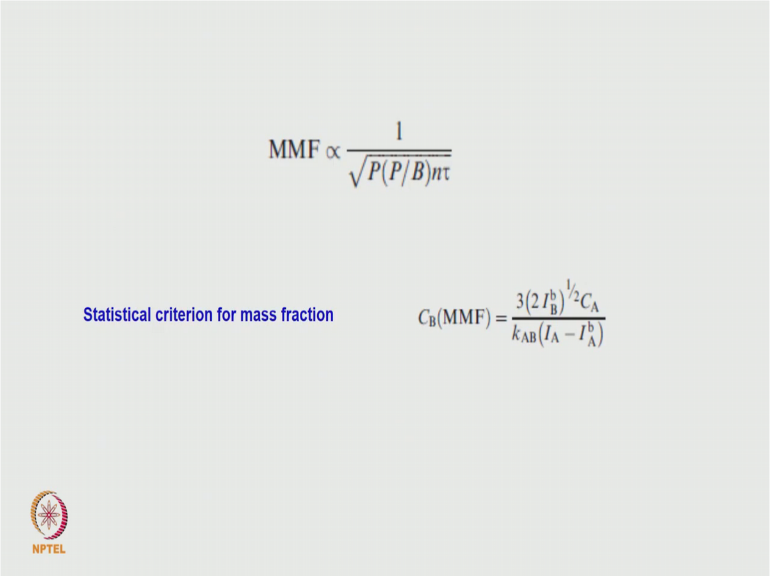

$$\mathrm{MMF} \propto \frac{1}{\sqrt{P(P/B)n\tau}}$$

Statistical criterion for mass fraction

$$C_B(\mathrm{MMF}) = \frac{3\left(2I_B^b\right)^{1/2} C_A}{k_{AB}\left(I_A - I_A^b\right)}$$

Another is very important is what is called as an Alchemi this is essentially if you make that beam into a very fame focus to beam and channel through. That is like in the present the microscope with FEG and aberration corrected microscope you can have a beam of the order to 0.1 nanometer we can make that beam pass through particular shown axis.

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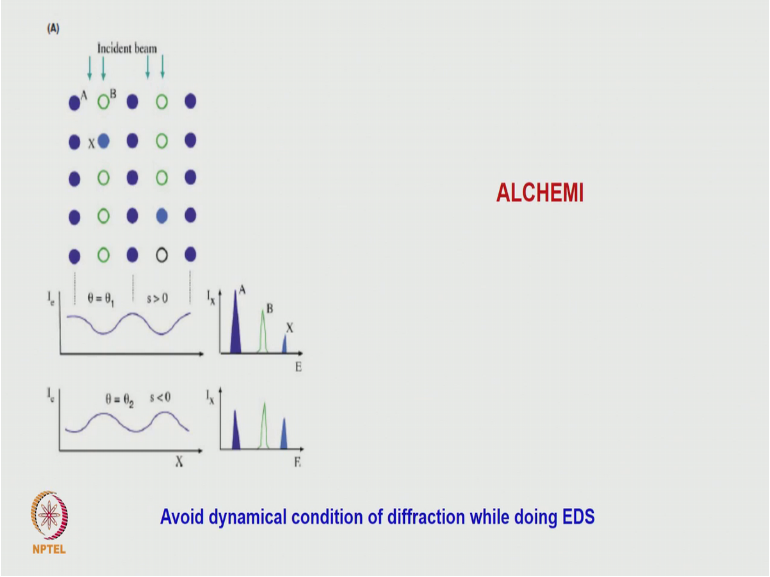

ALCHEMI

Avoid dynamical condition of diffraction while doing EDS

Then depending upon which direction it passes through we can make it see some particular element or some element may not be contribution be, there is the what is being shown here with theta equals theta 1 it say C is greater than 0. You can see that the corresponding to A B, correspond A element B element and that x the peaks corresponding to them the intensity of the peaks come and when s is less than 0 here you can see that that peak height has changed in an another direction. Using this information we could identify which position the atom is occupying in the lattice this is called the atom slight equation by chemical analysis.

Another thing also which is very important is that when the electron beam is passing through the sample depending upon which block will be excited, either the electron concentration could become very high on the atom surface or it could be high in between the atom surface depending upon that if electrons are going to be we distributed suppose these are all the atoms which are there, suppose this is the way the electron distribution is going to be there one of the block wavers; that means, that seems the intensity of the electron is maximum here possibility of interacting with the atom is very high in this particular case. So, the signal strength will be there.

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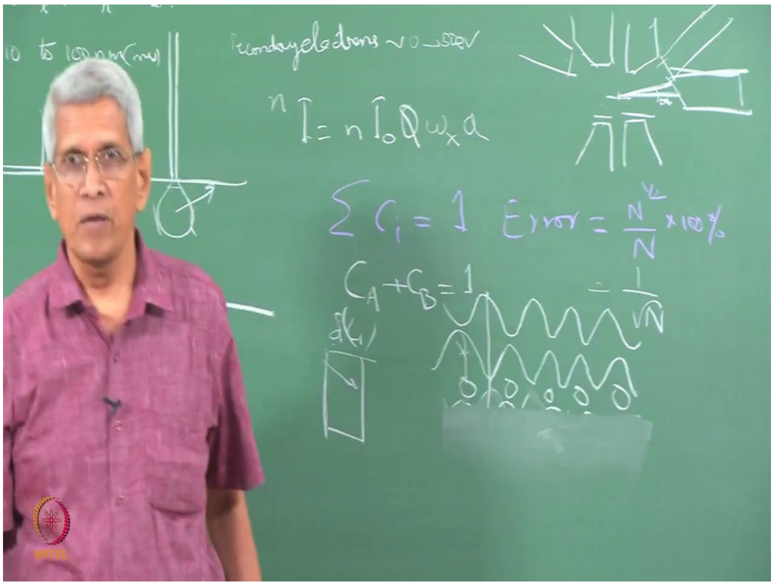

Suppose it is the other way round. So, this is an one 80 degree pay shift here the concentration of electron here going to be constant more between that region; that means, that the interaction of electron with the atom is going to be less. So, the x-ray characteristic x-ray generation probability reduces this is what it is going to happen when we are close to Bragg condition. There is one of the reason why I mentioned that if you choose one should be far away from Bragg condition to find out the true composition of the sampled surface. That is essentially avoid dynamical condition of diffraction while doing EDS. I will stop here now.

Thank you.