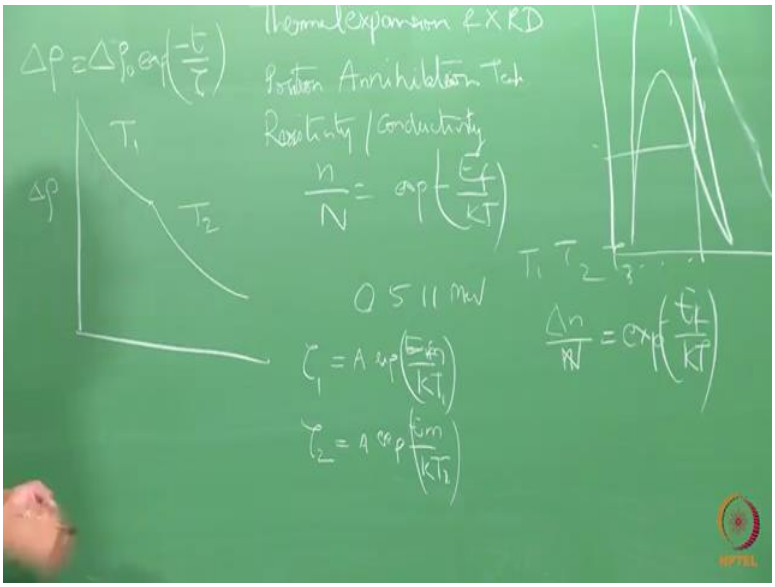
Defects in Materials
Prof. M Sundararaman
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Madras

Lecture – 10
Vacancy concentration determination-2

Welcome you all to this course on Defects in Materials. Yesterday we have covered some aspects of point defects; especially what all the different types of point defects which we have, how to find out the concentration of the point defects which are present in the sample. Then briefly mentioned about how to find out the experimental identification of the concentration of the defects and the formation energy; especially using one experiment for vacancies.

So, there are many methods which are available to find out the defect concentration. One of them is using thermal expansion and XRD combined; this is what we discussed yesterday.

(Refer Slide Time: 01:03)



Then another is positron annihilation spec technique the next.

Student: (Refer Time: 01:33).

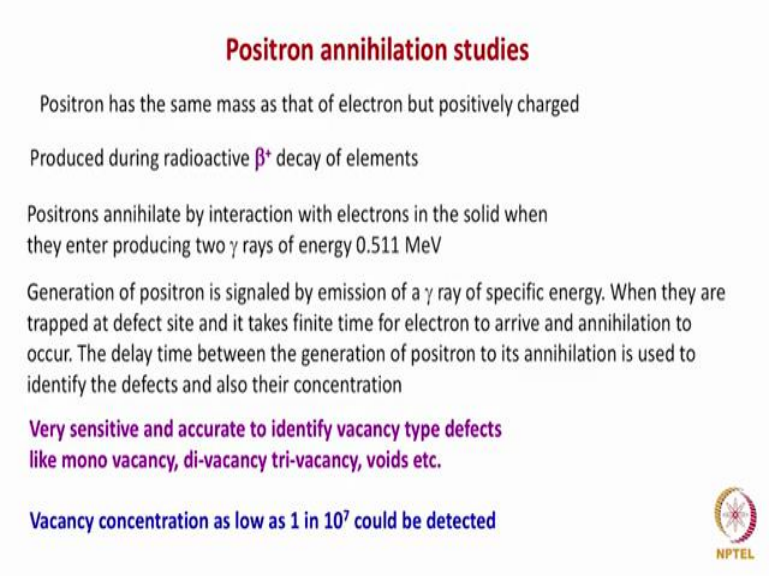
Then resistivity so conductivity ok.

Let us start with the; because since we have already mentioned I will not repeat that again about thermal expansion and x-ray diffraction. But the basic philosophy in this experiment is that whenever a material expands the thermal expansion studies we do it, it is not only that because of the lattice vibration there is an annalistic expansion in addition to it when defects are being produced in the lattice especially vacancies atoms are removed from the sample surface and they from the inside and they come to a surface. So, there is a volume increase is going to be there. So, the thermal expansion takes care of two part of it: one is the expansion of the perfect lattice plus the defects which are there also contribution due to them.

And when these defects are being present they when they do relax they give raise to some contraction or expansion of the lattice locally. So, this can be measured using x-ray diffraction. If both these information's are available using combination of a thermal expansion and x-ray diffraction we can get information about the equilibrium concentration of vacancies which are there. If we find out that get that information for different temperatures then plotting these concentration verses 1 by t we can get information about the vacancy concentration in the material.

That is because n by N equals exponential minus E f by k T. This is what essentially we use it to find out the concentration of vacancies. In another powerful technique which is there with which we can find out a concentration of vacancy is positron annihilation technique. So, you might have all studied about what all positrons; positrons are nothing but having the same masses that of electron and a charge which is positive.

(Refer Slide Time: 04:15)



And in fact this is a the first example of an antimatter which is being discovered. And how are they produced? When radioactive decay takes place of beta plus decay positrons are produced. That is in many radioactive decay electrons are emitted and the atom under goes a change to another element. Similar to that if it emits a positron then what is essential is going to happen is there the total number of proton plus neutrons remains that same, but the positive charge gets reduced by 1. Like for example, if you take sodium; sodium will transform to neon keeping the proton plus neutron number the same ok.

In this process when positrons are emitted in addition to the positrons in many cases gamma rays are also emitted to take care of this mass defect. These gamma rays are emitted simultaneously when a positron is also emitted. If we can find out this time at which it is being emitted and find out the time which is taken for this positron to enter into a sample and if it interacts with an electron and it gets annihilated then a gamma to gamma rays are emitted. But these gamma rays have got a fixed energy which is of 0.511.

So, the energy of the gamma rays which are emitted is generally 0.511 MeV energy with which 2 gamma rays will come that is this is the rest mass energy of the proton a positron on the electron when they combine together. So, this is clear? And the gamma ray which is emitted from the radioactivity that will have a very high value. For example, in the case of sodium it is about 1.27 MeV s energy of the gamma ray.

So, the initial signal that a positron has been generated is as soon as it is generated a gamma ray is also generated, you detect that gamma ray. Then wait for the next gamma ray with that energy 0.511 MeV to be detected. The time difference between them tells the time which has taken for the positron to get annihilated within in the sample.

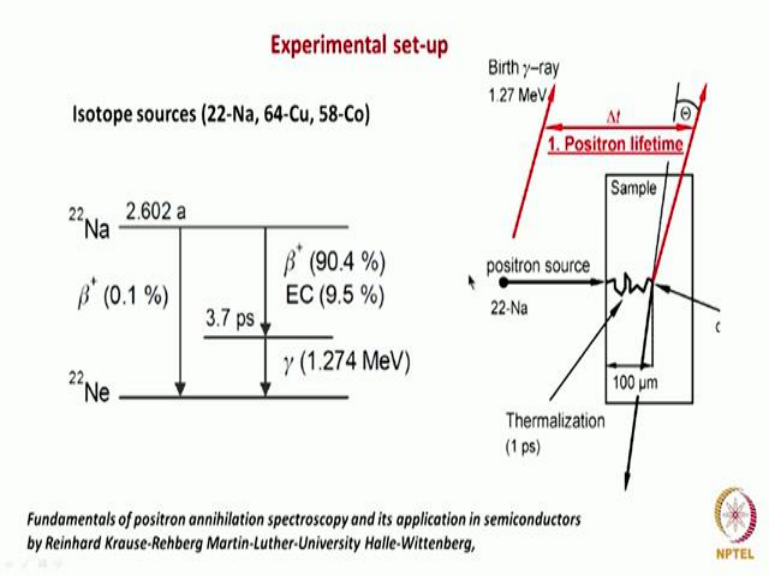
Suppose, the material contains some defects possibly the positron has to get drabbed in that defect, it has to wait for a longer period of time before an annihilation takes place with an interaction with an electron. So that time difference is what gives an indication about the nature of the defect which is present there. Generally the vacancy type of the defects one which the positron where it is stays for a longer period of time; this we will talk about it later. And this is a extremely sensitive technique, and very accurate to identify the type of defects; that is suppose the defects is going to be a mono vacancy or it is a di-vacancy or a tri-vacancy or if it is a void or many type of structural defects like dislocations.

Each of them will have a characteristic time which it takes for that defect to stay there. Identifying that time which you takes delay time which you takes for the positron to annihilate we can get information about the nature of the defect. And if you look at the peak height will always give information about the number of counts which are coming with that particular delay time we can immediately talk about what is going to be the concentration of the defects. This is the philosophy in almost all the spectroscopy techniques.

And not only that vacancy concentration as slow as 1 in 10 to the power of minus that is 1 in 10 to the power of 7 could be easily detected using positron annihilation technique. As I mentioned earlier the vacancy concentration even at melting point is of the order of 10 to the power of minus 4; 10 to the power of minus 3 to minus 4. So, three orders difference in vacancy concentration could be detected.

Let us just talk about some of the experimental techniques which are used so that one is aware of how this technique could be used to get the; and this technique gives an absolute concentration of the vacancy concentration we can detect. What all the sources of isotopes? One is sodium; that is particular isotope is important the number 22 sodium, 64 copper, and 58 cobalt this could be used. Out of each the sodium is the one which has got gamma ways with the smallest energy which is coming out of the sample surface.

(Refer Slide Time: 10:09)



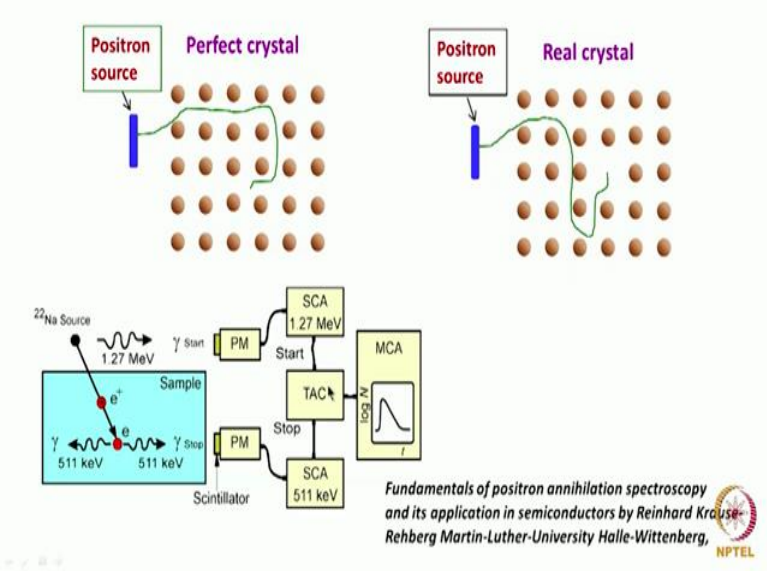
This reaction when it takes place if you look at it there are: one there is a direct transition which takes place emission of gamma positron without any gamma ray emission; that is about 0.1 percentage. And there is another one which is where we have a gamma rays also emitted. Simultaneously, this is the transition which is of interest, because we are able to simultaneously to find out that the information that are gamma rays emitted when is it is emitted, that when the positron is emitted that information is given by the simultaneous emission of the gamma ray. If you detect the gamma ray with this particular energy we know that positron also has been emitted.

Now, what is the source? This is a source which is there; you have a sample in the sample when the gamma ray enters and gamma rays got a very high energy so it travels through the sample gets thermalized normally about close to 100 micron is that depth which it travels. And then when a thermalizes and it is energy gets reduced it has to get annihilated finally. So, any material if you takeoff metallic material they contains ions which are located at different positions and also electrons which are there distributed uniformly throughout that sample; when it gets thermalized that the chance that this electron positron will interact with that electron get annihilator and gamma ray will be generated.

Suppose you assume a case where there are no defects which are present in the material then it take some specific time for the gamma ray to get annihilated, because it is being

decided by the density of the electron distribution in the sample. This is what it is going to happen.

(Refer Slide Time: 12:24)



Suppose a defect is there; the region where the defect is present like here in this case if you see it. When there is no defect irrespective of whichever be the site it moves and reaches, it does not matter whether this point or this point it is going to take almost an identical delay time which is going to be there, because the density of electron is going to be the same almost in all the regions.

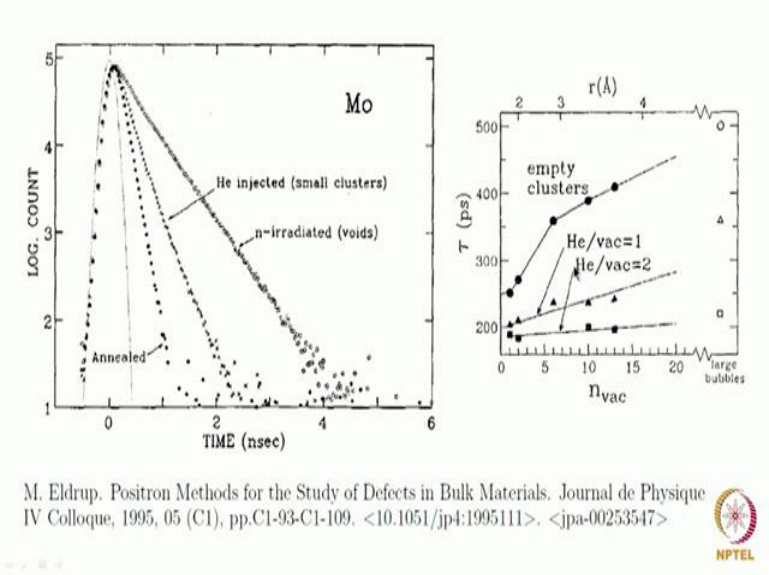
If there is a defect which is being present then you can see that what is defect; this is a region where otherwise there has been a positive ion which was there when the positive ion has been removed. Electron distribution is mostly in these regions in between and in this region the electron distribution when the defect is there some electron will try to come, but the density is going to be very small. So, if a positron comes and sits here the time which it takes to annihilate depends upon the arrival of the electron, or it is related to the density of electron which is going to be there in that region this will decide. Suppose it is a two defects which are there going to be there are more defects than the time it takes for electrons to come and interact with positron and annihilate is going to take a longer period of time; logically one can think that way.

So, this will decide. And using this delay time we can try to find out also is that how much the concentration of the defects are and also the nature of the defect both could be

identified. So, what we try to do is that try to find out then there are many other techniques this is what is called as a positron lifetime techniques. So, we are trying to find out what is the lifetime of a positron depending upon the defect your lifetime could be large or small.

Essentially the setup which consists of two detectors which will be there: one detector detects essentially the positron with which is emitted from the source with the high energy the other one; no, one detector detects the gamma ray which is emitted from the source along with a positron; the other one finds out the gamma ray which with the 0.511 MeV which is being detected. So, that time delay between these two is going to give you information about the lifetime of the positron or from that we can get information about the time nature of the defect.

(Refer Slide Time: 15:08)



M. Eldrup. Positron Methods for the Study of Defects in Bulk Materials. Journal de Physique IV Colloque, 1995, 05 (C1), pp.C1-93-C1-109. <10.1051/jp4:1995111>. <jpa-00253547>

Finally what we will be doing it is that this lifetime which is being measured will be plotted so the time which it takes versus the count. If you look here; here this is one plot this plot which corresponds to a sample which has been well annealed. This is how the positron annihilation lifetime looks like, because there would be some scatter will always be there it is not going to take place at one. Whenever positron gets trapped in a defect side the electron coming and annihilating with it. It is an average lifetime which we talked about, but there will be some distribution which will be there. So, this is an

example which I have taken from a literature, it is in malignum. In malignum a sample which has been well annealed this is how the lifetime measurement gives that plot.

When this is irradiated with injected with helium ions with some clusters some defects are also getting attached to it. Now you can see that on the right hand side the shape of this plot there is a change the slope changes. And when it is irradiated with the neutrons and where lots of voids are produced; by our techniques we can identify the voids that voids have been produced, you can see that the slope has changed.

So, the difference if you see between these two: this one that is going to get information about the difference in lifetime which is going to be there. From these plots you can get information about the type of defects which are present and their concentration. This is another plot where what is being done is there only for suppose a defect contains, number of vacancies. If it contains about 5, 10 this is what it is being shown what is going to be there lifetime how it changes with the number of defects being present. And in this particular case where there are a lot of clusters are there whether no helium ions are associated with it, then you can see that the increasing the number of vacancies in that region we can immediately notice that the lifetime increases considerably.

So, from this you can understand that this itself could be used as a technique to find out the concentration of the vacancies. Suppose you assumed that some interstitial or some other element is going to be present, then what is going to happen is that there the site when it is going to be there at an interstitial site the electron concentration is going to increase right, so it will not make much of (Refer Time: 18:04). So, the positron will get an annihilated much faster. So, that way it is extremely sensitive to vacancy type of defects present in the material. And with this method we can find out absolute concentration of vacancy in the sample.

Student: (Refer Time: 18:23) from the time (Refer Time: 18:27).

Which one?

Student: (Refer Time: 18:30) the time lap.

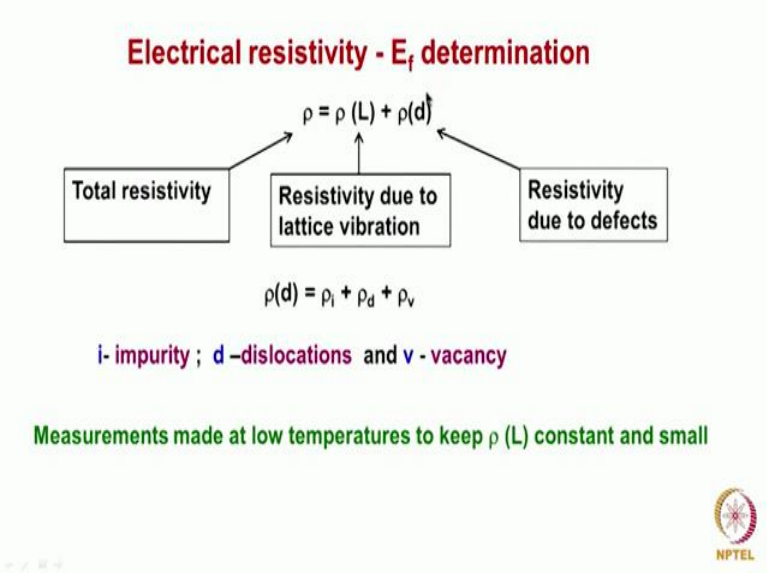
The time lapse tells you here that at for each time lapse how many counts are coming we are looking at it. Suppose the defect concentration is less then what will happen is that

this plot when you look at it either it could be one which is coming like this, if the concentration of defect is going to be there it will be coming like this correct. So far the same concentration this height if you try to look at it the counts for the same time is going to be different. That is dependent upon the vacancy the defect concentration. So, from this we can get both the information. If you look at this plot it is a log of count with a particular.

Student: Time constant.

Time constant, that is lifetime; looking at this we can get that information about this is some defect which is in annealed sample. If some defect is being introduced into it you can we can find out that how much is the defect which is present in this sample, because the count has increased done that. That is why we get information about the.

(Refer Slide Time: 19:45)



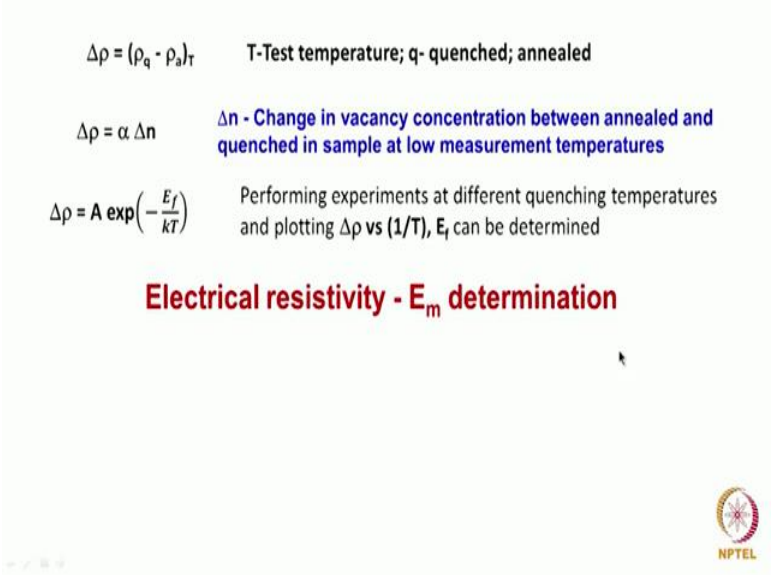
Another technique which also can be used to get information about that defect concentration is electrical resistivity or conductivity measurements. Especially in metallic sample electrical resistivity has been used to get information about point defect concentration as well as the migration energy; not the point defect concentration formation energy as well as the migration energy of defects we could get that information.

We know that resistance if you look at it, if you measure a the resistance of a material at any particular temperature is a function of 2 times 1; the lattice resistance plus the resistance the contribution to resistance which is coming from the defects which are present in the material. But the defects could be: impurities, dislocations, various types of sinks like grain boundaries all these things could be there plus vacancies could be there. So, all of them will contribute to resistivity.

If you take a sample where we assume that the concentration of impurities have been reduced to a very small value, assume highly pure material. And by some means or the other that sink concentration is kept that same. Then whatever is the defect which is contributed to resistivity change will be only due to the vacancy. That is assumption on which we go about the experiment, because some precautions have to be taken in this case to control the defect concentration in the material; that I will talk about little bit later with which we can find out the vacancy concentration.

And generally the contribution to resistivity from the lattice vibration is going to be very high. So, if you have to reduce it you do the experiment at very low temperatures. So, by lowering the temperature what are we trying to do; the contribution due to lattice vibration is reduced now the major contribution is coming only from the defects which are present in the material.

(Refer Slide Time: 22:33)



Let us take a sample which is a very well annealed sample where the concentration of we assume that the vacancies is very small. You measure the concentration that is denoted by rho q; that determines the concentration at a temperature which is a low temperature. Then that same sample if I heat it at a very high temperature and then quench it, when I quench it what is going to happen is that all the vacancies should be retained. Here we make an assumption that in reality what happens when you quench it first some of the vacancies contains to form, dislocation loops, vacancy loops, and all these sinks and they get annihilated we make the assumption that the same concentration of vacancies retained where there is a first assumption which we make it. Then the difference between the resistivity measured at a particular temperature in between a well annealed sample and the sample which has been quenched that tells the resistivity changed. That is proportional to the number of defects which are present in the material.

We carry out this experiment by taking the sample to different temperatures like T 1, T 2, T 3 like this different temperatures we take it. Allow the vacancy concentrate to equilibrate and quench it to the very low temperature and measure the resistivity. And we you know the resistivity just be measured in the well annealed sample that with the resistivity change corresponding to vacancy concentration at different temperatures. We can get that information.

That vacancy concentration we know that right from the beginning when we have derived an expression for the equilibrium concentration of vacancy is that this delta n by n equals exponential minus E f by k T correct. Or this itself will turn out to be the resistivity change is proportional to delta n. So, we get an expression connecting delta n. So, if you plot delta n versus 1 by t we can get information about the formation energy of the vacancy. Is it clear?

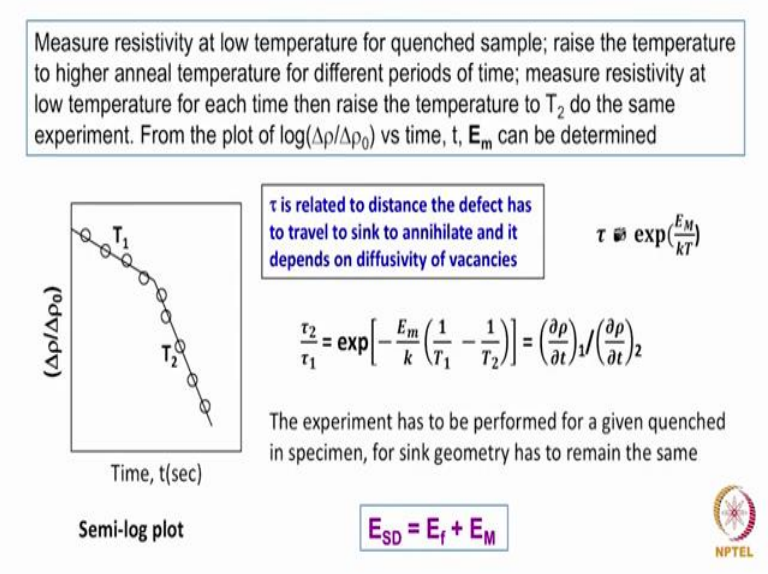
Now, the same electrical resistivity measurement could be used to find out the migration energy of the defect also. Because in this experiment what we have done is that the earlier experiment which is just no mention is that we have allowed the equilibrium concentration of vacancy to be present in the sample and we have found out what is the contribution due to that to the resistivity. And then plotting the resistivity versus 1 by t we are able to find out the only energy of formation.

Suppose, we annealed the sample at a particular temperature where the vacancies are mobile then what will happen is that no more vacancies are added, but whatever the vacancies are there you are trying to allow the vacancy concentration to equilibrate by vacancies reaching different sinks and getting annihilated. That means, that now the vacancy mobility is what we are looking at it. So, if you study the mobility of vacancies then we can get information about the migration energy.

So, what we have to do is that take a sample keep it at high temperature, create some equilibrium concentration of vacancies, lower it to a temperature value measure it, you have got information about the how much is the resistivity change which is going to be there. Now the same sample raise it to a slightly higher temperature, then annihilate for different periods of time at a particular temperature, and then try to find out what is going to be there vacancy concentration in the sample. As we annealed the concentration of vacancies will gradually get reduced. Note down that is annihilate for a particular period of time bring it to the lower temperature, measure the resistivity, again take it to the high temperature, annihilate for some more time that way you get how the vacancy concentration is going to be getting reduced or the how resistivity is changing that information be collected.

If we try to plot this resistivity: rho, with respect to the initial resistivity rho 0 which corresponds to in the quench sample the plot always will be an exponential type of a plot. You know that this exponential type of plot comes because; the number of defects which are available to move to the sink is getting continuously ready. So, the rate at which the defects are getting eliminated from the sample is proportional to the number which is present. That if you try to plotted it always be an exponential plot that is what essentially we get that information. And this plot what is to; is that we call it as the relaxation time that is the time which it takes for the concentration of the defect to come to 1 by e of the original value.

(Refer Slide Time: 28:36)



So, this experiment if we carried it out at one particular temperature we get some defect concentration. How it various the resistivity? If you tried to look at this plot we start initially from here it decreases like this, now at this some of one this is done at a temperature T 1. Now if I raise the temperature or lower the temperature then a relaxation time will be different because the rate at which the atoms are going to jump. So, then I will be getting another plot corresponding to it correct.

So, if you do this experiment for different annealing time this is an isothermal experiment, because all annealing is carried out at the same one is at one particular temperature this is T 1 this is T 2. From this experiment these two plots we can find out the tau 1 and tau 2. Any of this plots if we have we can find out the slope. And this tau depends upon what is it; the migration energy the rate at which the defects are jumping and reaching the finally getting annihilated at some of the defects which are being present in the sample.

So, here then we change the temperature in this experiment if the sink concentration itself changes then what will happen is that; the rate at which the defects are getting annihilated that will change. So, that is why this experiment is performed on a sample which has been initially quenched and we do annealing at temperatures where the defect concentrations or the sink concentration does not change. So, if the sink concentration remains that same that does not; that factor corresponding to that in the resistivity

changes remains constant. So now, whatever is the change which is occurring is only due to the jump rate of the vacancy from one site to another site.

So, we can write two expressions: one corresponding to tau 1 corresponding to this part of the curve, another to this part of the curve we can find out the relaxation time. If we try to plot this, this is a sort of a plot which will happen. Versus time if you take it is a semi log plot. And the temperatures which we have taken is tau 1 and tau 2, at the point at which we have changed over from one temperature to another temperature. At this in the ratio of tau 1 to tau 2 should be equal to this sort of an expression will come. This expression one can derive it from this expression we can write it tau 1 equals this 1 by T 1 another tau 2 you take the ratio.

So, from this expression we get or from this plot when you have tau 1 versus tau 2 or this is the same as equivalent to the rate of change of the resistivity plot the slope of it we can find out the migration energy. This is how using resistivity migration energy change could be measured. Any question, is it alright?

Student: (Refer Time: 32:25).

It is not is clear, ok. Is this clear, this tau is essentially equal some constant E m by; this is clear? If I do an experiment at T 1 this will be tau 1, if I do an experiment at T 2 this will be T 2 correct. If I take the ratio of this what it will happen?

Student: (Refer Time: 33:13).

We get this expression; from a plot like this from the curvature of the plot we can find out tau 1 and tau 2 we know the temperature at which we have done it.

Student: (Refer Time: 33:31) the temperature from (Refer Time: 33:36).

Which one?

Student: (Refer Time: 33:39).

No here this is a with respect to time.

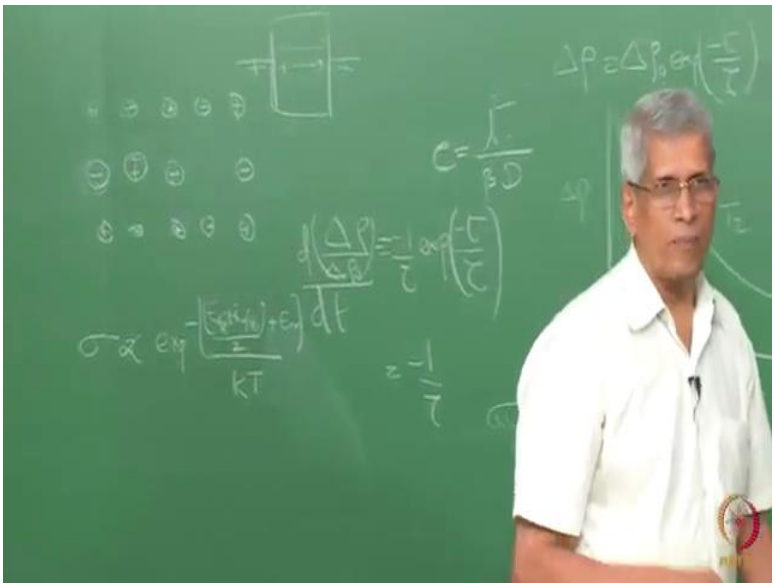
Student: So, you need to (Refer Time: 33:45).

Which one?

Student: You need to (Refer Time: 33:49).

No here, that is why we assume that if we take two different samples the tau depends upon what are factors.

(Refer Slide Time: 34:12)



The tau depends upon a factor which is essentially; what is factors tau depends on? Tau depends upon when the length which it is has two travel the defect to reach the sink and a constant beta and the diffusivity. Diffusivity is at a particular temperature rate is being fixed.

So, essentially irrespective of what the concentration the rate at which it is going to jump if they sink distribution is fixed then l is going to be fixed only the diffusivity determines how the tau is getting affected.

Student: From the tau.

Yeah.

Student: (Refer Time: 35:04) non-linear function of (Refer Time: 35:06).

Yes, because this is an exponential function.

Student: But, when we take (Refer Time: 35:11).

Yeah.

Student: Because we are getting ratio (Refer Time: 35:13).

Yeah.

Student: So, so far that (Refer Time: 35:18).

See, if you take a derivative of this expression what will happen?

Student: (Refer Time: 35:27).

Delta 0 is a constant we take it by d b d t.

Student: Minus 1 by tau into (Refer Time: 35:36).

Minus 1 by tau into exponential of minus t by tau, correct; so this factor essentially is a this itself we can plot it; no, from the tau whatever be the value which you take it this will be what it will turn out to be; if you take a log of this one.

Student: (Refer Time: 36:05).

Then you will have; so you understand that this quite simple.

Student: (Refer Time: 36:11).

Where it will be cutting it you get this tau.

Student: (Refer Time: 36:19).

It is clear?

Student: Yeah.

This way you can immediately find out what the tau is. Let us say that, so this way it is very neat experiment with which we can find out the migration energy.

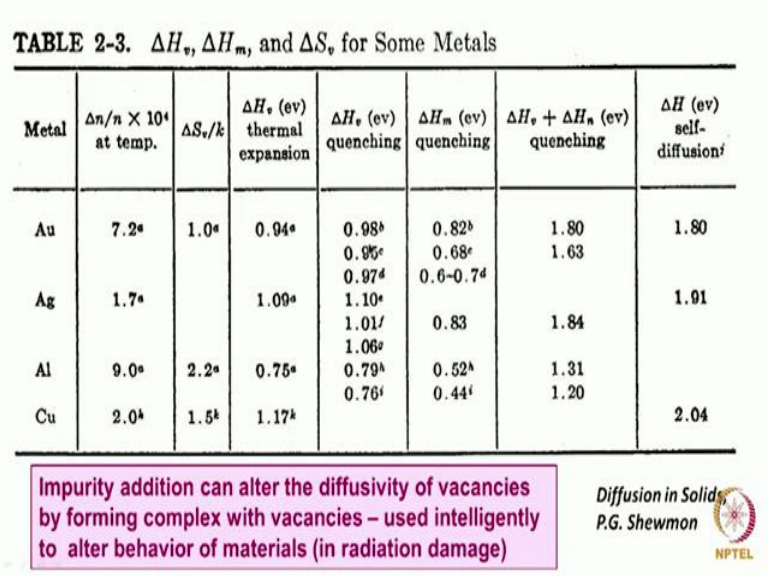
So, using resistivity two types of experiment on the same sample; we can find out the formation energy as well as migration energy of the defect. And this total energy is the energy which we using most of the diffusion experiments to tell that this is what the activation energy correct for diffusion. The values of migration and formation energy

which has been calculated for different types of defects are given here; is taken from the literature. And you can make out that here that v 1 and v 2 what it corresponds to is one: v 1 corresponds to mono vacancy, v 2 corresponds to a di-vacancy, what are the activation energies.

With using this information one can find out what is going to be the self diffusion of vacancies in the material that requires both the energy, not what is energy which is required for a vacancy to be formed, what is required the energy which is required for the vacancies to move. Then only we will get information about the self diffusion as the energy which is required for self diffusion vacancies to take place. That is what the information which is provided in this table.

This information is very much necessary when diffusion has to take place, because diffusion is essentially assisted by vacancies.

(Refer Slide Time: 38:12)



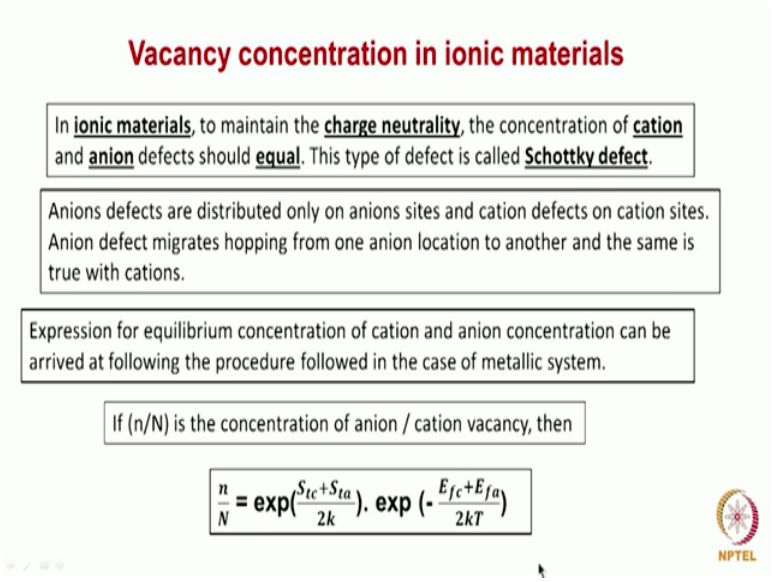
This is the same information which is being provided in this viewgraph also, but what is essentially important is that in many cases when we consider a defect which is mobile. In a pure metal it is very easy because it is adjacent atoms are going to be all the same identical type of an atom. Quite often in an alloy or a material which contains some impurities it can so happened that in a region that is if you consider a defect which is being present this atom could be an another type of an atom. If it is a different type of an atom assume that it has got a larger size then if it remains very close to a vacancy it is

able to accommodate part of the stream. Then if it has to move the whole complex has to move not the vacancy alone.

This is one thing which is going to. In fact this in property has been used in many cases especially in radiation damage situation to control the vacancy concentration in the material. That means, suppose you have generated some vacancy this vacancies agglomerate together to form voids; that means a vacancy should move. If you introduce some impurity into the material so that the vacancy forms a complex with it now the rate at which the vacancies going to move is getting reduced drastically as a function of time if you look at it the concentration of the agglomeration of vacancies to voids could be reduced considerably.

Especially in materials which has to be used for a structural materials in nuclear applications. That is especially in stainless steels, some titanium is being added because the titanium form some complexes with vacancy. So that it can reduce this vacancy mobility.

(Refer Slide Time: 40:38)



Though so far what we talked about is vacancy concentration in essentially metals. Suppose we consider vacancy concentration ionic materials: the material. The resistivity in ionic material or the conductivity in ionic material does not depend upon the electron concentration all depends upon the charge carriers which have the ions which has to move. And that is what is going to control the concentration. And another important fact

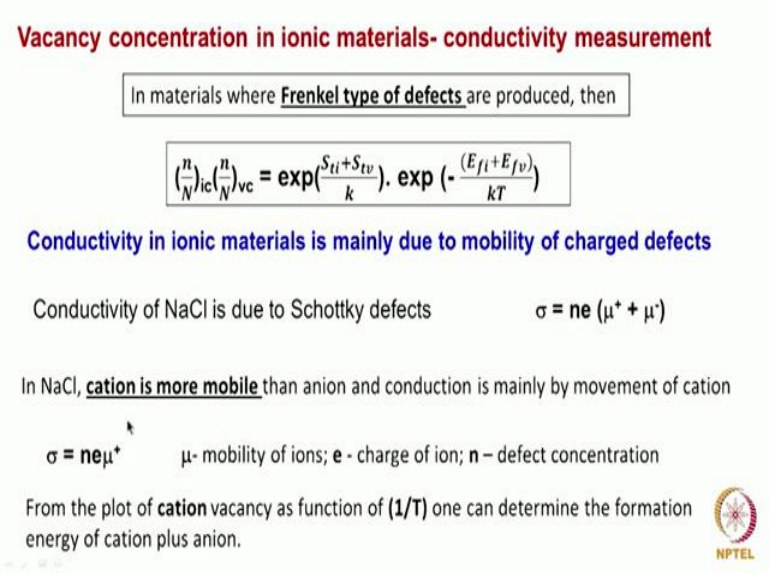
which has to consider in ionic material is that we have to maintain the charge neutrality always. When you have to maintain the charge neutrality if a cation vacancy is going to be there some value then the anion vacancy also has to be of the same value. This is what we called as a Schottky defect correct.

Then when they have to migrate? A cation vacancy will move from one cation site to another cation site and that is how they migrate. Similarly anion also will move from one anion site to another anion site. So, essentially this we can consider it a something like two types of sub lattices are there: one lattice is made up of all anions another lattice is made up of cations. So, from one anion site to at another anion site if you have to move it has to go across the sites in between there are some cations will be there through which it has to push through, but it will always go to a site which is from one anion to an another anion only. The same is true for cations as well.

The expression for equilibrium concentration of cations and anions: this derivation is similar to what we have derived for a vacancy concentration metallic system. Only thing which I have to consider it is that the total number of lattice sites if it is a n in for cations another n is going to be for anions that is if it is. So, totally 2 n will be the total number of sites and that defect concentration also if it is n in anion sites n in cation sites so that will be the total two n will be the anion in the cation site. Then if try to find out the ratio of in any particular site anion concentration, then it is given by this expression; this expression derivation is very similar that is you write an expression for the this anions alone I will put it and similarly an another expression for cations we can write it and the product of this is going to give you the concentration of the defects correct.

With that one can derive at this expression.

(Refer Slide Time: 43:49)

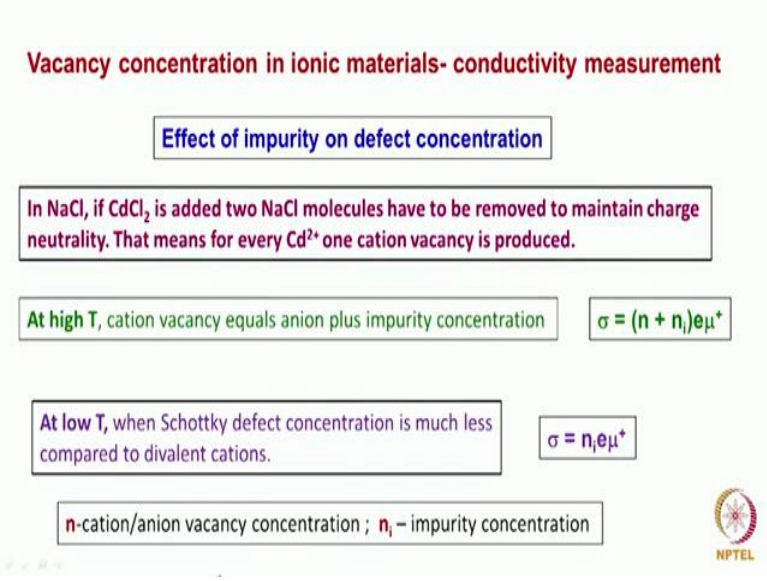


Similarly, we mentioned earlier that we can have a Frenkel type of a defect where one vacancy is created, and of an anion and the anion sits at an interstitial position, there also the concentration can be written when expression similar to that. So, essentially if you look at the conductivity; is this clear? Now if you look at the conductivity, if you apply a voltage positive and the negative voltage if you connect it all the negative ions will move towards this side correct positive ions will move towards this side correct then net current is the sum of both. But when an electron we consider they move very fast, whereas here it is an ion which has a larger size so it is movement is rather slow. So, the rate at which the current flows, because current is nothing but the rate of change of cha flow of charge d q by d t. So, that depends upon the mobility with which these ions are drifting from one end to the other end.

So, if you look at that for example if you take sodium chloride in an ionic material; both the sodium ion also will remove chlorine ion also will remove. So, the conductivity is nothing but sigma equals n into e that is both the charge movement. But normally what has been seen in many of this material; the size of the anion is going to be very large, cation size is small. So, cation moves much faster compared to that of the anion. Mobility is high, because of that essentially the conductivity is controlled by cation vacancy mobility.

In that case this expression will reduce to: one which is nothing but sigma equals only because this term will be absent only this n e mu plus. Suppose we measure a sample; measure it is conductivity, as a function of the cation is a time and plot the conductivity versus 1 by t then we can get information about the formation energy correct, this is what we can get information. But since here the cation moves rather slowly not only about the formation energy it essentially gives the diffusion of the ion itself; that information which it comes.

(Refer Slide Time: 47:27)



That is essentially it will be not formation plus the mobility, because the rate at which it is moves is not like that of an electron. So, the mobility information also comes into the picture. This will become clear when we go along. If you look at that impurity concentration, because no material is pure material some impurity will be present the impurity in most of this ionic material could be. Another ion which has been added which has got a different balanced stage.

Let us consider an example: cadmium chloride is added to sodium chloride or it could be a calcium chloride. Then, what is going to happen is that the site which if the sodium ion is replaced and the cation site and it is occupied by a cadmium two plus. That means, to maintain the charge balance one sodium ion has been removed from another site. Assume that in this a divalent ion is there. So, maybe in an adjacent site the vacancy is created so that the charge neutrality is being maintained. Then what is going to happen?

Student: Sir.

Yeah.

Student: Property of the defective (Refer Time: 49:20) the vacancy would be closer to this (Refer Time: 49:26).

Vacancy will be closer to a defect if it is very far away then what is going to happen is that space charge effect is going to come into the picture. So, generally they assume to be closer to it. Generally they preferred to be closer to the site, but this is also depending upon the temperature. So, that is what we will come talk about it later.

So, essentially what is going to happen is that, if a defect is being present in the sample some impurity concentration is there. At a high temperature if you take that sample; at high temperature the concentration of the impurity which is added is very small. So, the most of the concentration of the defect is essentially due to a Schottky defects. So, if you look at the conductivity; the conductivity will have two parts which will come, because the Schottky defect when we talk about it it means that the concentration of the anion vacancy and the concentration of the cations vacancies are the same.

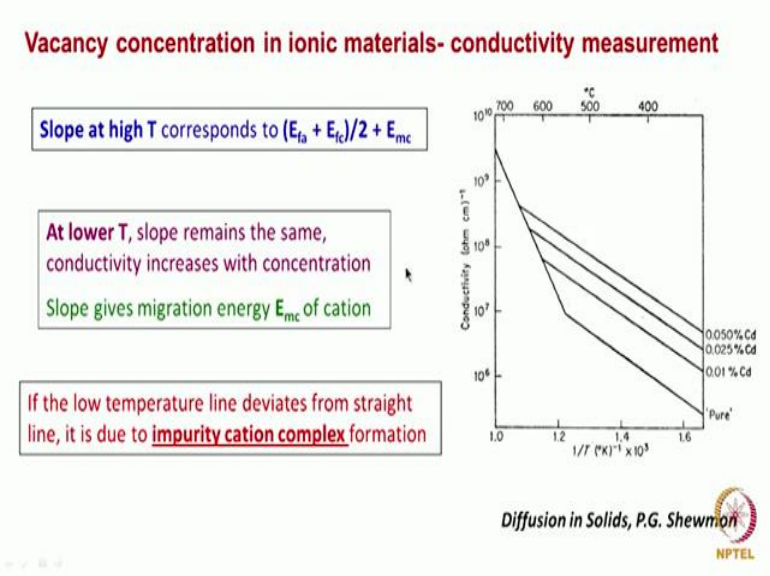
By the addition of the impurity into the system we have generated depending upon if n i is the concentration of the impurity which we have added, corresponding to that that much number of cation vacancies also introduced; so the cation vacancies always now more than that of the anion vacancy in the material.

So, the contribution to conductivity is going to come from two terms: one due to the cation we can see which is generated by the defects the generated by the impurity, and another is due to defect which is created in the lattice. So, the conductivity will be turn out to be the sort of an expression. Suppose we look at the conductivity at very low temperature then what will happen?

Student: (Refer Time: 51:42).

At low temperatures the Schottky defects are going to be very small, then the impurity concentration is the only one which is going to decide how much is going to be the cation vacancy in the material correct. And mobility depends upon the (Refer Time: 52:09).

(Refer Slide Time: 52:10)



If we do a plot; conductivity versus 1 by t then this is the nature of the plot which we normally get it. Here this one part corresponds to high temperature where the concentration of the defects is essentially coming from Schottky defects. And in that if you look at the slope of this plot this corresponds to the formation energy of the cation and the anion, and also because since this ions moved with different mobility the mobility of the ion also comes into the picture. If you look at the lower temperatures; there the concentration of the defect is decided by the concentration of the impurity which we have added correct. At different temperatures the mobility will change that is why we get different conductivity.

Now, if you look at the slope here, the slope at this curve corresponds to only the migration energy. That is what we are plotted here is essentially 1 by t versus rho conductivity. So, if you try to plotted this especially gives is essentially proportional to; correct. So, this term is going to correspond to from the slope we will be able to get; this is the way the conductivity is going to change correct. Essentially what we are finding out the defect concentration at various temperatures, and at lower temperatures the defect concentration is fixed. So, only the mobility decides how the conductivity is going to vary.

So that gives information only about the migration, because the concentration of the defects when it is constant this part will not come into the picture. So, using this sort of a

plot we can get information about both the migration energy as well as the formation energy all these information we can get it.

Quite often what happens is that this will is not a straight line especially the lower part. Why it is not a straight line? As you pointed out earlier that is this defect could form a complex with the defect that impurities that is the divalent impurity and the vacancy forms a complex which assume to close by and they would try to prefer to move together. If that happens those complexes will change the behavior of the plot and it will be curved. That is what in reality in many situations, generally, especially to very low temperatures. At high temperatures what can happen is that the defect can still be mobile this effect will not be seen, but low temperatures this is very prominent.

Now, what will do is that we will break here, and then talk about how impurity concentrates. So, what we have considered so far; a vacancy concentration in metallic material as well as in ionic material how to determine we have discussed, using various techniques: one is thermal expansion and x-ray diffraction; another is resistivity technique and another using positron annihilation technique.

We will stop here now.