# Diffusion in Multicomponent Solids
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## Lecture 29
## Experimental Determination of Enthalpy of Vacancy Formation

Welcome to the 29th lecture in this open course on Diffusion in Multicomponent Solids. In this lecture, I have explained three experimental techniques which are commonly used for measurements of vacancy concentrations or the Enthalpy of Vacancy Formation. These techniques include differential dilatometry, residual resistivity and positron annihilation.

In the last class, we discussed the energetic of vacancy formation and in this lecture, we will go over some of the experimental techniques, which are used for measurement of vacancy concentration or enthalpy of vacancy formation.

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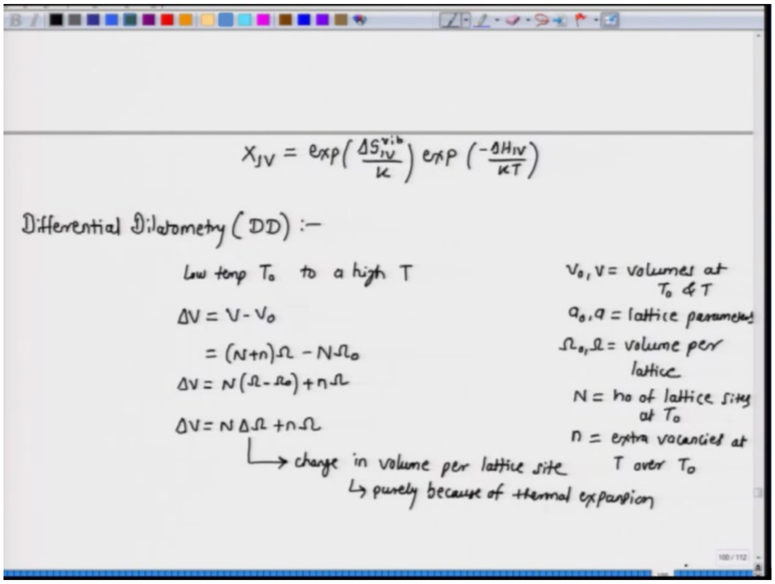

$$X_{1V} = exp\left(\frac{\Delta S_{1V}^{vib}}{k}\right) exp\left(-\frac{\Delta H_{1V}}{kT}\right)$$

Differential Dilatometry (DD) :-

Low temp $T_0$ to a high $T$

$$\Delta V = V - V_0$$
$$= (N+n)\Omega - N\Omega_0$$
$$\Delta V = N(\Omega - \Omega_0) + n\Omega$$
$$\underbrace{\Delta V = N\Delta\Omega}_{\text{change in volume per lattice site}} + n\Omega$$

↳ purely because of thermal expansion

$V_0, V$ = volumes at $T_0$ & $T$

$a_0, a$ = lattice parameters

$\Omega_0, \Omega$ = volume per lattice

$N$ = no of lattice sites at $T_0$

$n$ = extra vacancies at $T$ over $T_0$

Just a quick refresher. We got the expression for mono-vacancy concentration, $X_{1V}$ as:

$$X_{1V} = exp\left(\frac{\Delta S_{1V}{}^{vib}}{k}\right). exp\left(\frac{-\Delta H_{1V}}{kT}\right)$$

where $\Delta S_{1V}{}^{vib}$ denotes the vibrational entropy change associated with the formation of a mono-vacancy and $\Delta H_{1V}$ denotes the enthalpy of formation of a mono-vacancy. $k$ is Boltzmann constant and $T$ is the temperature in Kelvin. Now it should be noted that when we use these quantities $\Delta H_{1V}$ and ${\Delta S_{1V}}^{vib}$ in terms of per mole, then we need to replace $k$ with the gas constant $R$. Now, let us go over some of the techniques which can be used for measurement of this various parameters. $X_{1V}$ or $\Delta H_{1V}$, the first of this technique is called Differential Dilatometry or DD in short.

This technique relies upon the measurement of volume change that any metal piece undergoes upon heating. When a metal piece is heated, it experiences expansion and this expansion has mainly two contributions, the first one is purely from the thermal expansion and the second one is because of the formation of vacancies. As we have seen the vacancy concentration varies exponentially with temperature, which is clear from previous equation. As the temperature increases, vacancy concentration increases exponentially. Introduction of a vacancy, gives rise to one additional lattice site into the crystal and as the temperature increases, to maintain the equilibrium, extra vacancies are formed and the extra lattice sites are added to the crystal structure. This will give rise to the second contribution to the net volume change, which is caused upon heating. If we can measure this volume change and the individual contribution, we can relate them to vacancy concentration and that is the principle here.

Let us say a piece of a metal is heated from a lower temperature $T_o$ to a higher temperature $T$. It undergoes the change in volume equal to $\Delta V$. Let us denote the volumes at $T_o$ and $T$ by $V_o$ and $V$ respectively. The lattice parameter at $T_o$ and $T$ are denoted by $a_o\ and\ a$. Then let us consider, the volume per lattice site, which is denoted by $\Omega$. $\Omega_o$and $\Omega$ denote the volume per lattice site at the two respective temperatures. Let us suppose at $T_o$ there were $N$ number of lattice sites and as we heat it to $T$ because of the extra vacancies which have to be created to maintain the equilibrium vacancy concentration at $T$, there are $n$ vacancies which have been added. $n$ is the extra vacancies at $T$ over those at $T_o$.

$$V_o, V = Volume\ at\ T_o\ and\ T$$

$$a_o, a = lattice\ parameters$$

$$\Omega_o, \Omega = Volume\ per\ lattice$$

$$N = no. of\ lattice\ sites\ at\ T_o$$

$$n = extra\ vacancies\ at\ T\ over\ T_o$$

$\Delta V$ is simply:

$$\Delta V = V - V_o = (N+n)\Omega - N\Omega_o$$

Or

$$\Delta V = N(\Omega - \Omega_o) + n\Omega$$

Or

$$\Delta V = N\Delta\Omega + n\Omega$$

Now we have clearly got the two different parts. $\Delta\Omega$ is basically the change in volume per lattice site and as you can understand, this is purely because of thermal expansion. We are also making one assumption here and that assumption is that there is no change in volume per lattice site because of creation of extra vacancies. So, at any given temperature $T$, if a vacancy is created there is one extra lattice site which is added and that extra lattice site is assumed to have the volume $\Omega$ or the creation of a vacancy does not change the volume per lattice site. Now in practice there may be a little bit of change in volume because of creation of the vacancies.

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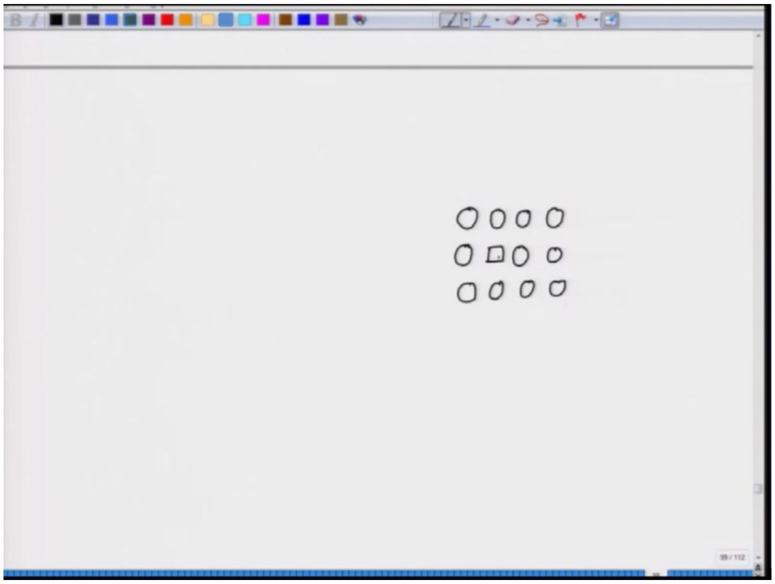

To understand this, let us consider a lattice with a vacancy and as we have seen the atoms are held at their equilibrium positions because of the balanced interactions. At equilibrium positions the interactions are balanced and the atoms stay at their equilibrium position. In fact they keep vibrating about the equilibrium positions. But when a site is vacant, locally, the interactions are not balanced and the surrounding atoms will tend to fall into this vacant site. That will give rise to some change in the volume because of creation of a vacancy. This atomic rearrangement will cause some change in volume, but that change in volume per lattice site will be negligible. So, we can neglect that.

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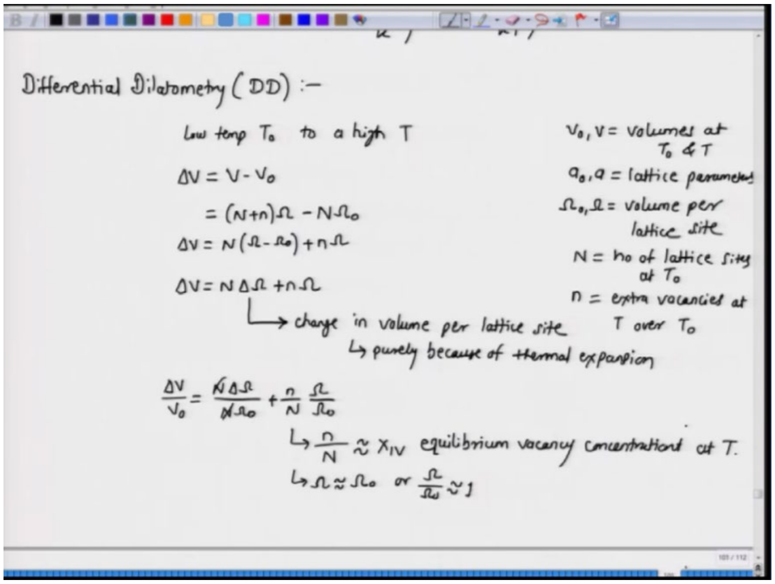

Differential Dilatometry (DD) :-

Low temp $T_o$ to a high $T$

$V_o, V$ = volumes at $T_o$ & $T$

$a_o, a$ = lattice parameters

$\Omega_o, \Omega$ = volume per lattice site

$N$ = no of lattice sites at $T_o$

$n$ = extra vacancies at $T$ over $T_o$

$\Delta V = V - V_o$

$= (N+n)\Omega - N\Omega_o$

$\Delta V = N(\Omega - \Omega_o) + n\Omega$

$\Delta V = N\Delta\Omega + n\Omega$

↳ change in volume per lattice site

↳ purely because of thermal expansion

$\frac{\Delta V}{V_o} = \frac{\cancel{N}\Delta\Omega}{\cancel{N}\Omega_o} + \frac{n}{N}\frac{\Omega}{\Omega_o}$

↳ $\frac{n}{N} \approx X_{1V}$ equilibrium vacancy concentration at $T$.

↳ $\Omega \approx \Omega_o$ or $\frac{\Omega}{\Omega_o} \approx 1$

Now if we divide both the side of this equation by the original volume $V_o$:

$$\frac{\Delta V}{V_o} = \frac{N\Delta\Omega}{N\Omega_o} + \frac{n\Omega}{N\Omega_o}$$

We can approximately take $\frac{n}{N} = X_{1V}$ that is the equilibrium concentration of vacancies at temperature $T$. This is because the temperature $T_o$ is usually selected at a very low value and the temperature $T$ is at a very high value. Because of which the vacancy concentration at $T$ is much higher than that at $T_o$. So, the change in vacancy concentration is approximately equal to the new vacancy concentration established at temperature $T$ and we can approximately take this equal to $X_{1V}$:

$$\frac{n}{N} \sim X_{1V}$$

Also the change in volume per lattice site is also not significant. So:

$$\Omega \sim \Omega_o \quad or \quad \frac{\Omega}{\Omega_o} \sim 1$$

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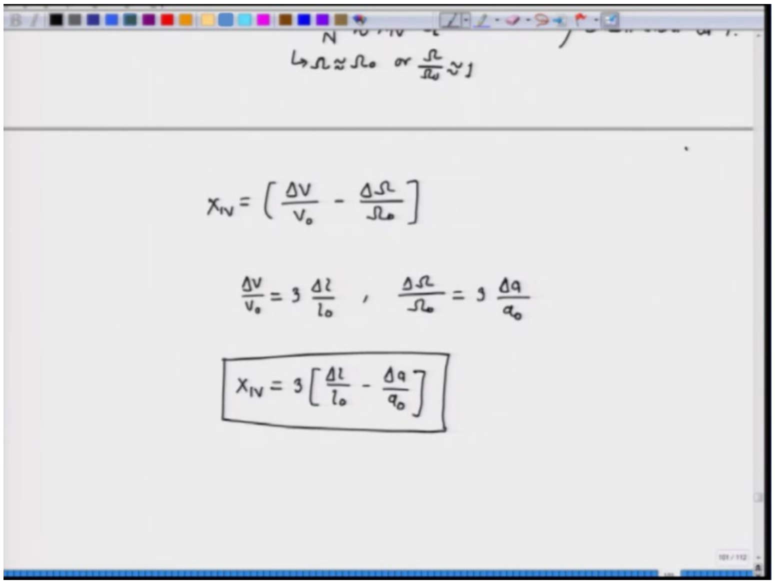

$\hookrightarrow \Omega \approx \Omega_o$ or $\frac{\Omega}{\Omega_o} \simeq 1$

$$X_{1V} = \left(\frac{\Delta V}{V_o} - \frac{\Delta \Omega}{\Omega_o}\right]$$

$$\frac{\Delta V}{V_o} = 3\frac{\Delta l}{l_o} \quad , \quad \frac{\Delta \Omega}{\Omega_o} = 3\frac{\Delta a}{a_o}$$

$$\boxed{X_{1V} = 3\left[\frac{\Delta l}{l_o} - \frac{\Delta a}{a_o}\right]}$$

If we rearrange we get:

$$X_{1V} = \left[\frac{\Delta V}{V_o} - \frac{\Delta \Omega}{\Omega_o}\right]$$

Now the linear dimensions are easiest to measure. We can relate this $\frac{\Delta V}{V_o}$ or $\frac{\Delta \Omega}{\Omega_o}$ to the linear dimensions and typically the relative change in volume is equal to approximately three times the relative change in linear dimensions. When we talk about the piece of metal:

$$\frac{\Delta V}{V_o} = \frac{3\Delta l}{l_o}$$

where $\Delta l$ is the change in length because of heating from $T_o$ to $T$ and $l_o$ is the original length of the metal piece at $T_o$. What can be said about $\frac{\Delta \Omega}{\Omega_o}$ ? $\Omega$ refers to the volume per lattice site and when it comes to the lattice, we can take the linear dimension as the lattice parameter. So,:

$$\frac{\Delta \Omega}{\Omega_o} = 3\frac{\Delta a}{a_o}$$

Where $\Delta a$ is the change in lattice parameter, because of the heating from $T_o$ to T, and $a_o$ is the lattice parameter of the metal piece at $T_o$.

We can write this as:

$$X_{1V} = 3\left[\frac{\Delta l}{l_o} - \frac{\Delta a}{a_o}\right]$$

This gives us an idea about how we can go about measuring vacancy concentrations by measuring the linear dimensions. If you can measure $\frac{\Delta l}{l_o}$ for the overall metal piece and $\frac{\Delta a}{a_o}$ which are the changes in lattice parameter then we can measure the vacancy concentration at a given temperature $T$. How do we go about this, obviously we need to make measurements of lattice parameters. So, we need to use X-ray diffractometer and typically there are dedicated X-ray diffractometer which are equipped with measurement of small changes in linear dimensions of the metal piece. At the same time the change in lattice parameter is tracked and they are related to the vacancy concentration.

Of course we also need the XRD to be equipped with high temperature measurements so that we can do the measurements at different temperatures. This is an equilibrium measurement technique which means that at every temperature before the measurement, we equilibrate the sample so that the equilibrium vacancy concentration at that temperature is established. To make sure that we are measuring the equilibrium vacancy concentrations, typically the measurements are done during heating as well as during cooling. Every time before the measurement at the given temperature the sample is equilibrated so that the equilibrium vacancy concentration is established. Though it looks very simple, in fact the measurements are very critical. We need very high accuracy and precision. Because the values of $X_{1V}$, the equilibrium vacancy concentrations are typically very small.

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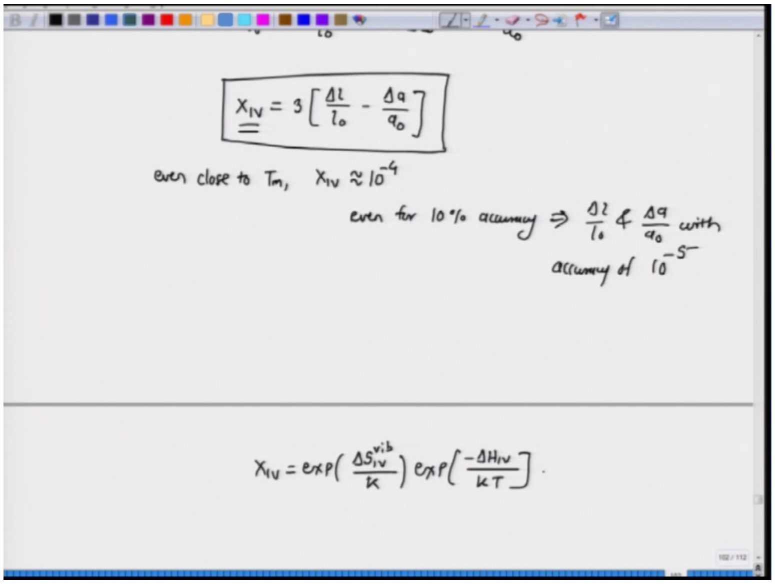
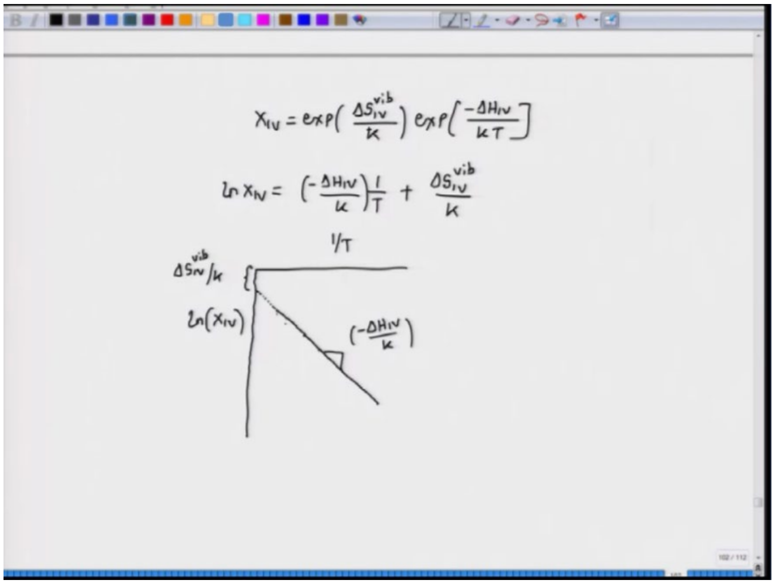


$$\boxed{\underline{\underline{X_{1V}}} = 3\left[\frac{\Delta l}{l_o} - \frac{\Delta a}{a_o}\right]}$$

even close to $T_m$, $X_{1V} \approx 10^{-4}$

even for 10% accuracy $\Rightarrow \frac{\Delta l}{l_o}$ & $\frac{\Delta a}{a_o}$ with accuracy of $10^{-5}$

$$X_{1V} = \exp\left(\frac{\Delta S_{1V}^{vib}}{k}\right) \exp\left[\frac{-\Delta H_{1V}}{kT}\right].$$



$$X_{1V} = exp\left(\frac{\Delta S_{1V}^{vib}}{k}\right) exp\left[\frac{-\Delta H_{1V}}{kT}\right]$$

$$\ln X_{1V} = \left(\frac{-\Delta H_{1V}}{k}\right)\frac{1}{T} + \frac{\Delta S_{1V}^{vib}}{k}$$

Even close to melting temperature, $X_{1V}$ is typically:

$$X_{1V} \sim 10^{-4}$$

Which means if we expect about 10 % accuracy, we need to measure $\frac{\Delta l}{l_o}$ and $\frac{\Delta a}{a_o}$ with accuracy of $10^{-5}$. That is when we have a very high vacancy concentration of about $10^{-4}$. So, the measurements have to be done with very high accuracy.

Now one advantage of this method is that it gives the absolute concentration of vacancies, $X_{1V}$ and since $X_{1V}$ is:

$$X_{1V} = exp\left(\frac{\Delta S_{1V}{}^{vib}}{k}\right).exp\left(\frac{-\Delta H_{1V}}{kT}\right)$$

if we do the measurements, at different temperatures, it also helps in evaluating $\Delta H_{1V}$ as well as $\Delta S_{1V}{}^{vib}$. If we take log on both sides:

$$\ln X_{1V} = \left(\frac{-\Delta H_{1V}}{kT}\right)\frac{1}{T} + \frac{\Delta S_{1V}{}^{vib}}{k}$$

If we plot the log of vacancy concentration as a function of reciprocal of temperature we should be able to plot the data with a straight line. The slope of it will yield the value of $\Delta H_{1V}$. The slope would be equal $\left(\frac{-\Delta H_{1V}}{kT}\right)$ and the intercept will give the value of $\Delta S_{1V}{}^{vib}$.

Now the intercept is at $\frac{1}{T} = 0$ which is not possible. So, we have to just do the extrapolation of the data that we have obtained to the $\frac{1}{T} = 0$ axis, to get to $\Delta S_{1V}{}^{vib}$, that is the vibrational entropy change due to formation of a mono-vacancy. There is one point to be noted here, when we do this measurement, we are talking about mono-vacancies. But it should be noted that these measurements do not separate the mono-vacancies or di-vacancies or other higher clusters of vacancies. It just measures the vacancy concentration. But typically we can take it as mono-vacancies. Because the di-vacancy concentration will be much lesser as we have seen in last class. Even near to melting temperature for platinum, the di-vacancy concentration was about three orders of magnitude lower than the mono-vacancy concentration. So, the error involved in mono-vacancy concentration is much lower even if you assume that the entire vacancy concentration belongs to the mono-vacancies. Now, let us look into some results from the literature.

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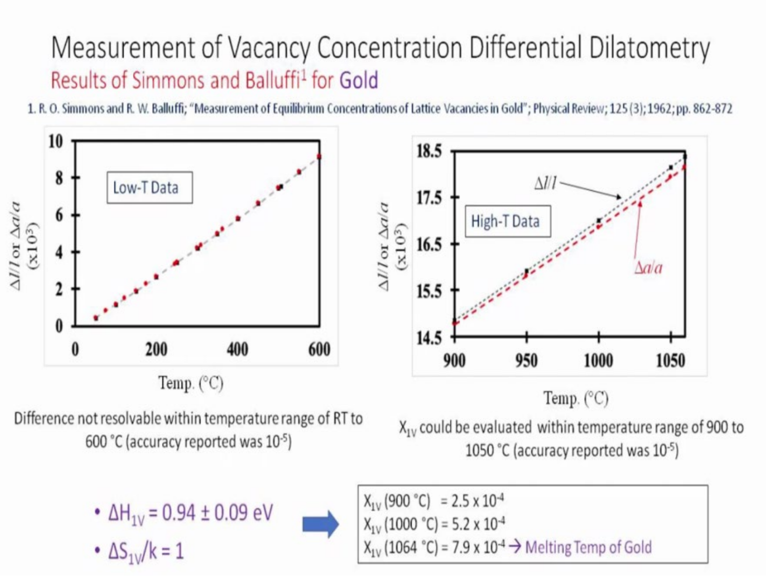

Measurement of Vacancy Concentration Differential Dilatometry

Results of Simmons and Balluffi[1] for Gold

1. R. O. Simmons and R. W. Balluffi; "Measurement of Equilibrium Concentrations of Lattice Vacancies in Gold"; Physical Review; 125 (3); 1962; pp. 862-872

Difference not resolvable within temperature range of RT to 600 °C (accuracy reported was $10^{-5}$)

$X_{1V}$ could be evaluated within temperature range of 900 to 1050 °C (accuracy reported was $10^{-5}$)

- $\Delta H_{1V} = 0.94 \pm 0.09$ eV
- $\Delta S_{1V}/k = 1$

$X_{1V}$ (900 °C) = $2.5 \times 10^{-4}$
$X_{1V}$ (1000 °C) = $5.2 \times 10^{-4}$
$X_{1V}$ (1064 °C) = $7.9 \times 10^{-4}$ → Melting Temp of Gold

Here I am showing the results from the classic work reported by Simmons and Balluffi on the measurement of equilibrium vacancy concentration in gold using the differential dilatometry technique. This plot is a plot of $\frac{\Delta l}{l_o}$ or $\frac{\Delta a}{a_o}$ versus temperature and this is in the smaller range of temperature, from room temperature to 600 °C. Now they have reported the measurement accuracy of about $10^{-5}$ in the measurements of $\frac{\Delta l}{l_o}$ or $\frac{\Delta a}{a_o}$ and in this temperature range up to

600°C, the changes in vacancy concentration is not significant. So, the changes in this $\frac{\Delta l}{l_o}$ or $\frac{\Delta a}{a_o}$ were not in the detectable limit and you can see all these measurements overlap in this temperature range. But at higher temperature range, 900 to 1050 °C you can see that the difference between $\frac{\Delta l}{l_o}$ and $\frac{\Delta a}{a_o}$ is detectable. $\frac{\Delta l}{l_o}$ is of course higher than $\frac{\Delta a}{a_o}$ and the difference is increasing with increasing temperature.

They then plotted in this temperature range 900 to 1050 °C, $X_{1V}$ versus $\frac{1}{T}$ and they could get the enthalpy of vacancy formation and vibrational entropy of vacancy formation and the values they obtained were:

$$\Delta H_{1V} = 0.94 \pm 0.09\ eV$$

$$\frac{\Delta S_{1V}{}^{vib}}{k} = 1$$

where $k$ is the Boltzmann constant. With these parameters if we estimate the vacancy concentration at 900 °C, it is:

$$X_{1V}(900\ °\mathrm{C}) = 2.5 \times 10^{-4}$$

$$X_{1V}(1000\ °\mathrm{C}) = 5.2 \times 10^{-4}$$

$$X_{1V}(1064\ °\mathrm{C}) = 7.9 \times 10^{-4} \qquad Melting\ point\ of\ Gold$$

So, this was about the differential dilatometry.

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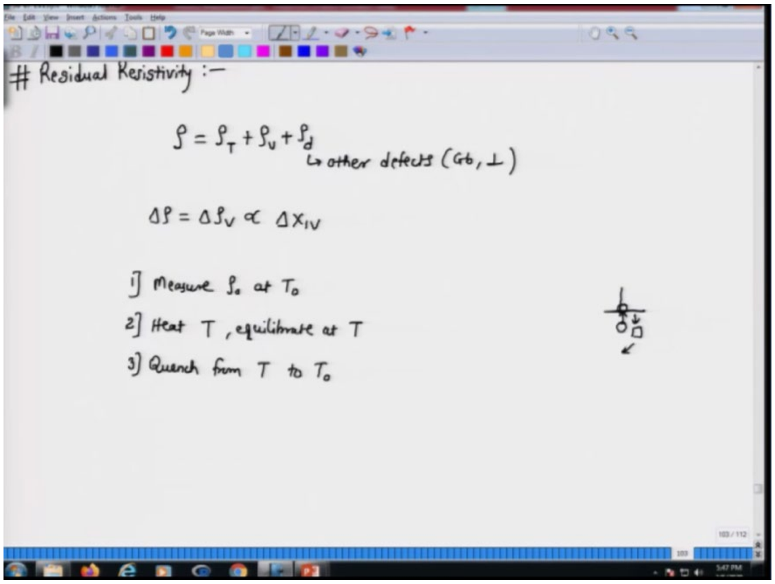

# Residual Resistivity :—

$$\rho = \rho_T + \rho_v + \rho_d$$

$\hookrightarrow$ other defects (Gb, $\perp$)

$$\Delta\rho = \Delta\rho_V \propto \Delta X_{1V}$$

1] Measure $\rho_o$ at $T_o$

2] Heat $T$, equilibrate at $T$

3] Quench from $T$ to $T_o$

The next technique that we are going to talk about is the residual resistivity measurement. As the name suggest, this technique relies upon measuring the resistivity of a sample and relating it to the vacancy concentration. The resistivity of a metal basically has different contributions. One is of course from the phonons or thermal vibrations of atoms and other one is from the defects which are present in the crystal lattice of the metal. The first contribution is $\rho_T$ and the other sue to defects include vacancies, grain boundaries, dislocations, impurity atoms and other defects.

Since we are interested in vacancy measurement, let us separate the vacancy contribution and the contribution due to other defects. Let us call the contribution from the vacancy to be $\rho_V$ and $\rho_d$ to be the contribution due to other defects, including grain boundary, dislocations, etc. Now if we can measure the resistivity of the same piece of metal in two different conditions, such that the $\rho_T$ and $\rho_d$ is constant in the two conditions but only $\rho_V$ changes, then all the change in the resistivity is only because of the change in vacancy concentration. So, we basically want to make:

$$\Delta\rho = \Delta\rho_V \propto \Delta X_{1V}$$

So, how do we go about this, we have to first take a piece of metal and equilibrate it at a lower temperature and measure its resistivity. The first step is, measure $\rho_o$ at $T_o$ , then heat the metal piece to a high temperature $T$, equilibrate at $T$ so that the equilibrium vacancy concentration at temperature $T$ is achieved and then quench, from $T$ to $T_o$.

Now if the grain boundary and dislocation density is not affected, then essentially, we get back the sample at temperature $T_o$ with quenched in vacancies from higher temperature $T$. Whenever we are heating or cooling, as the temperature changes, system tries to achieve the equilibrium vacancy concentration and this is done by diffusion of vacancies to sources or sinks. If the vacancies have to be created there are sources like grain boundaries, dislocation and surfaces. For example if there is a dislocation and if a vacancy has to be created, an atom from the crystal will jump into the dislocation and the vacancy from the dislocation will make a reverse jump and will be introduced into the crystal. This is the way a vacancy is created. Similarly, grain boundary or surfaces can act as sources of vacancies when we heat the sample to a higher temperature. Now when the equilibration starts at higher temperature, you can understand the vacancy concentration near the defects would be very large. But the equilibrium wants that the vacancy concentration should be uniformly distributed throughout the bulk of the crystal. The vacancies then have to diffuse from there to the other parts of the lattice and the equilibration will take some time. Similarly, when the temperature is reduced, the extra vacancies or the vacancies which are in excess of the equilibrium concentration at that temperature have to be gotten rid of and that occurs by diffusion of these vacancies towards the defects. Now the same defects would now act as sinks. That means that the creation or annihilation of vacancies requires time because it is driven by diffusion. By quenching from higher temperature $T$, we are not giving enough time to vacancies for annihilation and the excess vacancy concentration will be retained at the lower temperature.

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And the fourth step here is to measure $\rho$ again at $T_o$. But the difference between step one and step four is that in step one the resistivity was that of well annealed sample. Step four, the resistivity is of quenched sample. Now if the density of dislocations and the grain boundary area remains constant, the only contribution to the change in resistivity is going to be from the change in vacancy concentration. This is because we are doing the measurements at the same temperature, $\rho_T$ is also same and then we can write this.

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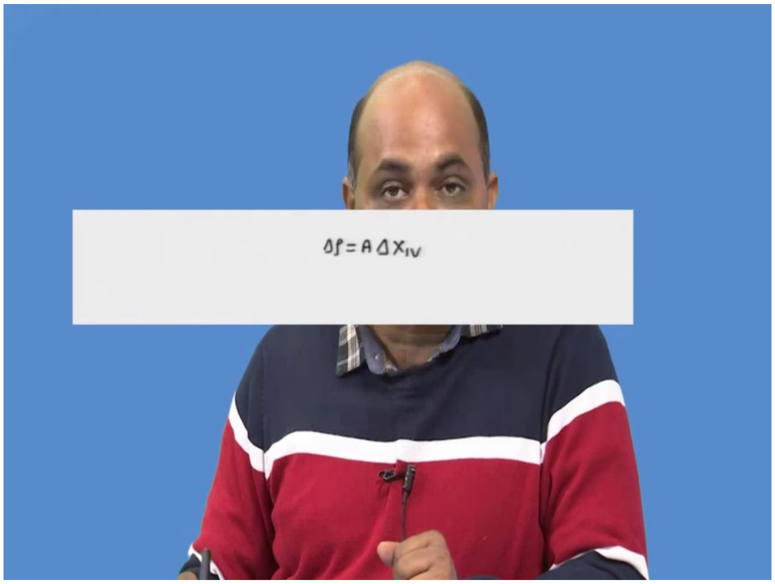

So:

$$\Delta\rho = A\Delta X_{1V}$$

Where $A$ is a constant. So, how do we keep the grain boundary and dislocations constant. That is why it is important to start with a well annealed sample. The sample has to be first equilibrated at a high temperature so that the grain growth takes place and the grain boundaries are well stabilized. There should not be any further grain growth or elimination of smaller grains during the subsequent high temperature heating. Preferably a large grain sample is used so that there would not be much significant in the grain boundary area. Similarly, the dislocations density will be minimized after annealing. But during quenching dislocation may be introduced. So, we have to take care that the dislocations are not introduced during quenching. We can try to avoid the introductions of new dislocation by first quenching it to a lower temperature. Let us say to a 100 °C and then from there to the lower temperature $T_o$. Now this lower temperature $T_o$ is typically sub-zero temperature, -70 , -80 °C. Because at that temperature, the contribution from thermal vibrations is going to be very low.

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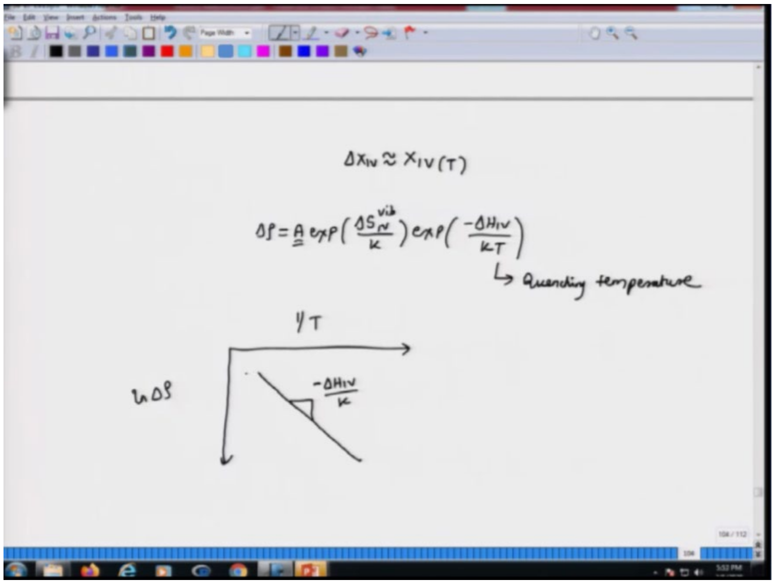

$$\Delta X_{1V} \approx X_{1V(T)}$$

$$\Delta\rho = \underline{\underline{A}}\exp\left(\frac{\Delta S_{1V}^{vib}}{k}\right)\exp\left(\frac{-\Delta H_{1V}}{kT}\right)$$

↳ Quenching temperature

So, the change in $\Delta\rho_v$ is going to be prominent. Now this $\Delta X_{1V}$ can be approximately taken as equal to $X_{1V}$ at the quenching temperature $T$ as the difference between $T$ and $T_o$ is going to be very large. And we can write:

$$\Delta X_{1V} \sim X_{1V(T)}$$

$$\Delta\rho = Aexp\left(\frac{\Delta S_{1V}{}^{vib}}{k}\right).exp\left(\frac{-\Delta H_{1V}}{kT}\right)$$

and remember this $T$ here is the quenching temperature. Now with this technique we can measure $\Delta\rho$ from different quenching temperatures and plot the logarithm of $\Delta\rho$ versus $\frac{1}{T}$, again we will get a straight line, whose slope gives us the value of $\Delta H_{1V}$. But, with this technique we do not get the absolute concentration of vacancies because there is this constant $A$, which we do not know. Since A is not known, from the intercept we cannot actually determine $\Delta S_{1V}{}^{vib}$. So, this is a simple technique, it does not give the absolute vacancy concentration. But we can get $\Delta H_{1V}$ based upon residual resistivity measurement. Let us look into some of the literature data.

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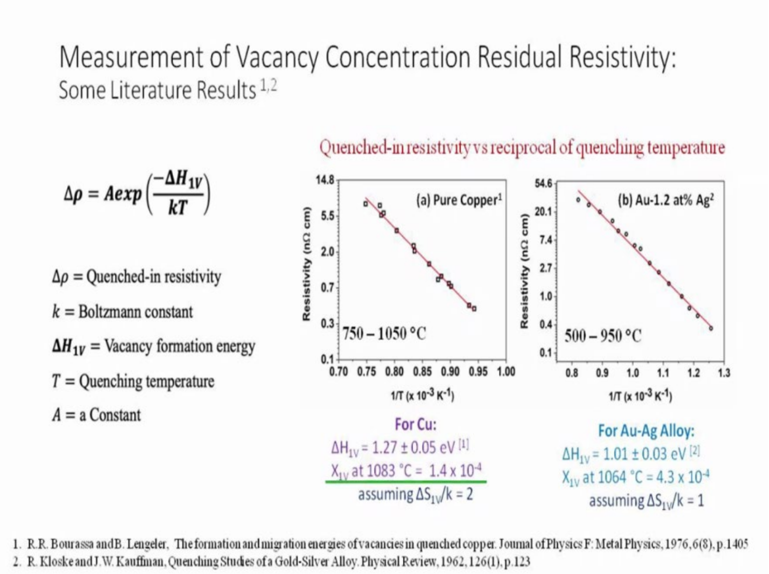

Measurement of Vacancy Concentration Residual Resistivity:

Some Literature Results[1,2]

$$\Delta\rho = Aexp\left(\frac{-\Delta H_{1V}}{kT}\right)$$

$\Delta\rho$ = Quenched-in resistivity

$k$ = Boltzmann constant

$\Delta H_{1V}$ = Vacancy formation energy

$T$ = Quenching temperature

$A$ = a Constant

**For Cu:**

$\Delta H_{1V} = 1.27 \pm 0.05$ eV [1]

$X_{1V}$ at 1083 °C = $1.4 \times 10^{-4}$

assuming $\Delta S_{1V}/k = 2$

**For Au-Ag Alloy:**

$\Delta H_{1V} = 1.01 \pm 0.03$ eV [2]

$X_{1V}$ at 1064 °C = $4.3 \times 10^{-4}$

assuming $\Delta S_{1V}/k = 1$

1. R.R. Bourassa and B. Lengeler, The formation and migration energies of vacancies in quenched copper. Journal of Physics F: Metal Physics, 1976, 6(8), p.1405
2. R. Kloske and J.W. Kauffman, Quenching Studies of a Gold-Silver Alloy. Physical Review, 1962, 126(1), p.123

I have shown the results from couple of papers here. The first one is from Bourassa and Lengeler, who measured the vacancy concentration by residual resistivity measurement in pure copper and they used the quenching temperature in the range of 750 to 1050 ℃. You can see a nice straight line fitting is obtained and they measured $\Delta H_{1V}$ to be:

$$\Delta H_{1V} = 1.27 \pm 0.05\ eV$$

for copper. With this if we determine $X_{1V}$ at the melting temperature of copper it comes out to be around:

$$X_{1V} \; at \; 1083\,^{\circ}\mathrm{C} = 1.4 \times 10^{-4} \; site \; fraction \quad assuming \quad \frac{\Delta S_{1V}}{k} = 2$$

Again, $\Delta {S_{1V}}^{vib}$ cannot be measured by this technique, this is just what I have taken from other data. Another example is from the work of Kloske and Kauffman. They measured the residual resistivity in the temperature range of 500 to 950 °C. This was the quenching temperature in the gold alloy containing 1.2 atomic percent silver and they obtained in this alloy $\Delta H_{1V}$ to be:

$$\Delta H_{1V} = 1.01 \pm 0.03 \; eV$$

$$X_{1V} \; at \; 1064\,^{\circ}\mathrm{C} = 4.3 \times 10^{-4} \; site \; fraction \quad assuming \quad \frac{\Delta S_{1V}}{k} = 1$$

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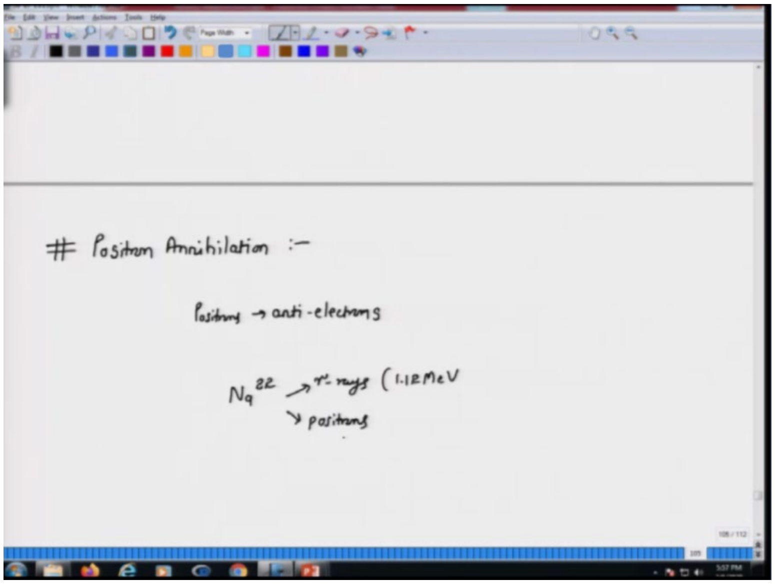

# Positron Annihilation :-

Positrons → anti-electrons

$$Na^{22} \rightarrow \gamma\text{-rays} \; (1.12 \, MeV$$
$$\searrow positrons$$

This was the second technique for vacancy measurement. The third one that I will talk briefly here is based upon positron annihilation. Some of the radioactive isotopes emit positrons while they are decaying. These positrons are nothing but the anti-particles. They have the same mass as electrons and they also have the same magnitude of charge as that of an electron. But the charge has the opposite sign of electron, these are positively charged particle.

In a sense they are anti-electron and when the positrons combine with electrons, they emit two gamma rays. What essentially is done in this technique is the piece of metal is kept close to a radioactive isotope. The most commonly used radioactive isotope is Sodium 22. This emits gamma rays of energy about 1.12 MeV and positrons.

The positrons will go into the piece of metal and there they will combine with the free electrons of the metal and emit gamma rays of the energy about 511 Kilo-electron volts. Now when these positrons go into a vacant site of the metal piece, there is an absence of core electron in the vacancies and it will take time for the positron to combine with the electron. So, we say that the positrons are trapped in the vacant sites and more the number of vacancies, more positrons will be trapped and then the average lifetime of the positrons will increase with the vacancy concentration. This is the principle which is used in measuring the vacancy concentration from the lifetime measurement of positrons. This was the third technique, we will stop here today, thank you.