

## 4. Experimental Techniques for Studying Point Defects

### 4.1 Point Defects in Equilibrium

#### Differential Thermal Expansion Method

- How can we measure *directly* the type and concentration of point defects and, if we do it as function of temperature, extract the *formation energies* and *formation entropies*?
- Simple question - but there is essentially only one *direct* method: Measure the change of the lattice constant  $a$ , i.e.  $\Delta a$ , and the change in the specimen dimension,  $\Delta l$ , (one dimension is sufficient) simultaneously as a function of temperature.
  - What you have then is the differential thermal expansion method also called the  $\Delta l/l - \Delta a/a$  method.
  - This method was invented by **Simmons** and **Balluffi** around **1960**.
- The basic idea is that  $\Delta l/l - \Delta a/a$  (with  $l$  = length of the specimen =  $l(T, \text{defects})$ ) contains the regular thermal expansion *and* the dimensional change from point defects, especially vacancies.
- This is so because for every vacancy in the crystal an atom must be added at the surface; the total volume of the vacancies must be compensated by an approximately equal additional volume and therefore an additional  $\Delta l$ .
  - If we subtract the regular thermal expansion, which is simply given by the change in lattice parameter, whatever is left can *only* be caused by point defects. The difference then gives directly the vacancy concentration.
  - For a cubic crystal with negligible relaxation of the atoms into the vacancy (so the *total* volume of the vacancy provides added volume of the crystal), we have

$$3 \left( \frac{\Delta l}{l} - \frac{\Delta a}{a} \right) = c_v - c_i$$

- With  $c_v$  = vacancy concentration,  $c_i$  = interstitial concentration.
  - We have to take the *difference of the concentration* because interstitial atoms (coming from a vacancy) do *not* add volume.
- This is quite ingenious and straightforward, but not so easy to measure in practice.
- The measurements of both parameters have to be very precise (in the  $10^{-5}$  range); you also may have to consider the double vacancies.
  - But successful measurements have been made for most simple crystals including all important metals, and it is this method that supplied the formation energies and entropies for most important materials.
- The link shows a [successful measurement](#) of  $\Delta l/l - \Delta a/a$  for **Ag + 4% Sb**.
- Some values mostly obtained with that method are shown in the following table (after **Seeger**):

Element	$c_v$ at $T_m$	$H_F$ [eV]	$S_F$ [k]
Cu	$2 \times 10^{-4}$	1,04	0,3
Ag	$1,7 \times 10^{-4}$	0,99	0,5
Au	$7,2 \times 10^{-4}$	0,92	0,9
Al	$9 \times 10^{-4}$	0,65	0,8
Pb	$1,7 \times 10^{-4}$	0,5	0,7
Na	$7 \times 10^{-4}$		
Li	$4 \times 10^{-4}$		
Cd	$6,2 \times 10^{-4}$		
Kr	$3 \times 10^{-3}$		

### Positron Annihilation

A somewhat exotic, but still rather direct method is measuring the time constant for positron **annihilation** as a function of temperature to obtain information about vacancies in thermal equilibrium.

- What you do is to shoot [positrons](#) into your sample and measure how long it takes for them to disappear by annihilation with an electron in a burst of  $\gamma$  - rays. The time from entering the sample to the end of the positron is its (mean) life time  $\tau$ .
- It is rather short (about  $10^{-10}$  seconds), but long enough to be measured, *and it varies with the concentration of vacancies* in the sample. Since electrons are needed for annihilation and a certain overlap of the wave functions has to occur, the life time  $\tau$  is directly related to the average electron concentration available for annihilation.
- A nice feature of these technique is that the positron is usually generated by some radioactive decay event, and then announces its birth by some specific radiation emitted simultaneously. Its death is also marked by specific  $\gamma$  rays, so all you have to do is to measure the time between two special bursts of radiation.

Vacancies are areas with low electron densities. Moreover, they are kind of attractive to a positron because they form a potential well for a positron - once it falls in there, it will be trapped for some time.

- Since an average life time of  $10^{-10}$  s is large enough for the positron, even after it has been thermalized, to cover rather large distances on an atomic scale, some positrons will be trapped inside vacancies and their percentage will depend on the vacancy concentration.
- Inside a vacancy the electron density is smaller than in the lattice, the trapped positrons will enjoy a somewhat longer life span. The average life time of all positrons will thus go up with an increasing number of vacancies, i.e. with increasing temperature.

This can be easily quantified in a good approximation as follows.

- Lets assume that on the average we have  $n_0$  (thermalized) positrons in the lattice, split into  $n_1$  "free" positrons, and  $n_2$  positrons trapped in vacancies; i.e.

$$n_0 = n_1 + n_2$$

- The free positrons will either decay with a fixed rate  $\lambda$  given by  $\lambda_1 = 1/\tau_1$ , (with  $\tau_1 =$  (average) lifetime), or are trapped with a probability  $\nu$  by vacancies being present in a concentration  $c_V$ .
- The trapped positrons then decays with a rate  $\lambda_2$  which will be somewhat smaller then  $\lambda_1$  because it lives a little longer; its average lifetime is now  $\tau_2$ .
- The change in the partial concentration then becomes

$$\frac{dn_1}{dt} = -(\lambda_1 + \nu \cdot c_V) \cdot n_1$$

$$\frac{dn_2}{dt} = -\lambda_2 \cdot n_2 + \nu \cdot c_V \cdot n_1$$

This system of coupled differential equation is easily solved (we will do that as an [exercise](#)), the starting conditions are

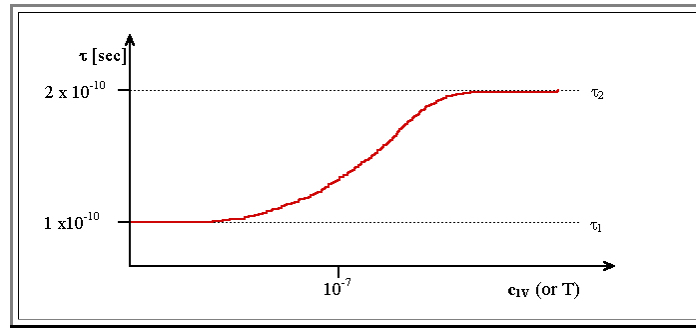
$$n_1(t=0) = n_0$$

$$n_2(t=0) = 0$$

- The average lifetime  $\tau$ , which is the weighted average of the decay paths and what the experiment provides, will be

$$\tau = \tau_1 \cdot \left( \frac{1 + \tau_2 \cdot \nu \cdot c_V}{1 + \tau_1 \cdot \nu \cdot c_V} \right)$$

The probability  $\nu$  for a positron to get trapped by a vacancy can be estimated with relative ease, the following principal "S" - curve is expected. By now, it comes as no surprise that no effect was found for Si.



The advantage of positron annihilation experiments is its relatively high sensitivity for low vacancy concentrations ( $10^{-6}$  -  $10^{-7}$  is a good value), the obvious disadvantage that a quantitative evaluation of the data needs the trapping probability, or cross section for positron capture.

Some examples of real measurements and further information are given in the links:

[Life time of positrons in Ag](#)

[Life time of positrons in Si and Ge.](#)

Paper (in German): [Untersuchung von Kristalldefekten mit Hilfe der Positronenannihilation](#)

A [large table containing values for Hf](#) as determined by positron annihilation (and compared to values obtained otherwise) can be found in the link

### Exercise 4.1-1

Derive the Formula for  $\tau$

## More Direct Methods for Measuring Point Defect Properties

There isn't much. Some occasionally used methods are

- Measurements of the *resistivity*. Very suitable to ionic crystals if the mechanism of conduction is ionic transport via point defects. But you never know for sure if you are measuring intrinsic equilibrium because "[doping](#)" by impurities may have occurred.
- *Specific heat* as a function of  $T$ . While there should be some dependence on the concentration of point defects, it is experimentally very difficult to handle with the required accuracy.
- Measuring *electronic noise*. This is a relatively new method which relies on very sophisticated noise measurements. It is more suited for measuring diffusion properties, but might be used for equilibrium conditions, too. The illustration in the link shows a [noise measurement](#) obtained upon annealing frozen-in point defects.

However, the view presented above (and in the chapters before) is not totally unchallenged. There are serious scientists out there who claim that things are quite different, especially with respect to equilibrium concentrations of vacancies in refractory metals, because the formation entropy is much higher than assumed.

- The method of choice to look at this is *calorimetry* at high temperature, i.e. the measurement of the specific heat. A champion of this viewpoint is Y. [Kraftmakher](#), who just published a book to this point.