

# Topic 1: How many point defects are in a material?

## Overview

The number of defects in a material is a complex problem, in part because many defects can occur at low concentrations which makes characterization or measurement approaches a challenge. Moreover, defect populations can be affected by temperature, processing conditions, other defects, and even time. However, as defects affect properties, it may be possible to connect changes in properties with defect concentrations: electrical conductivity, positron annihilation rates, material dimensions, and others that we will see in the class. On the other hand, computational approaches focus on the determination of basic thermodynamic quantities, such as the formation energy (and possibly volume and entropy) of defects, and use defect thermodynamics to predict defect concentrations.

You may not be surprised to learn that experiment and computation do not often agree on how many defects are in a material. When you think about vacancies, how do you measure what *isn't* there?

## Reading

For this first topic, you will want to read some of the seminal experimental works, and a recent paper on the computation of vacancies.

- “Measurements of Equilibrium Vacancy Concentrations in Aluminum.” R. O. Simmons and R. W. Balluffi, *Phys. Rev.* **117**, 52 (1960): doi:10.1103/PhysRev.117.52
- “Measurements of the High-Temperature Electrical Resistance of Aluminum: Resistivity of Lattice Vacancies.” R. O. Simmons and R. W. Balluffi, *Phys. Rev.* **117**, 62 (1960): doi:10.1103/PhysRev.117.62
- *Warning: a long review. Should be skimmed to get a feel for what has been done, and worth skimming the list of papers that cite it:* “Investigation of Thermal Equilibrium Vacancies in Metals by Positron Annihilation.” H. E. Schaefer, *phys. stat. sol. (a)* **102**, 47 (1987): doi:10.1002/pssa.2211020104
- “Breakdown of the Arrhenius Law in Describing Vacancy Formation Energies: The Importance of Local Anharmonicity Revealed by Ab initio Thermodynamics.” A. Glensk, B. Grabowski, T. Hickel, and J. Neugebauer, *Phys. Rev. X* **4**, 011018 (2014): doi:10.1103/PhysRevX.4.011018

## Team assignment

Someone in your group decides she wants to do some experiments for radiation resistance in Al when it's alloyed with Sb (1at.%), but she wants to know what the baseline vacancy concentration should be in her thin film sample (made via sputtering) without any irradiation. Your team will decide how to determine the vacancy concentration from room temperature up to 400°C.

1. Is there any computational or experimental values that you would trust?
2. If you need additional data, how could you get it?

## Prelecture questions

1. Intrinsic crystal A is fcc and has a vacancy content given by  $c_v = 10 \exp(-120/RT)$ , with energies in kJ/mole. Suppose that a second crystal of A contains 1 at.% of impurity element B, where the A-vacancy binding energy is 16 kJ/mole with impurities. Assuming  $\Delta S = 0$  for the complexes, what is the total vacancy concentration in the impure crystal at 1000K?
2. When trying to explain the discrepancies between vacancy concentrations measured experimentally and those estimated computationally, some authors have suggested that divacancies are important. Is this reasonable?
3. Suppose you had three samples of a pure aluminum. One sample is heavily cold-worked (high dislocation density), a second sample has a very fine grain size (typical grain size of 1 micron), and a third sample is well-annealed over a long time at 80% of the melting temperature. Assuming you could exactly measure the vacancy concentration in these three samples, are there temperatures where you would expect differences in the vacancy concentrations of these three samples? Where they would be the same? Justify your conclusions.

## Suggested background

These may help you think about the papers and questions raised; you may want to look beyond these, too.

- Course webnotes:
  - 2.1.1 Simple Vacancies and Interstitials
  - 2.2.1 Impurity Atoms and Point Defects
  - 2.2.2 Local and Global Equilibrium
  - 4.1 Point Defects in Equilibrium
  - 4.2 Point Defects in Non-Equilibrium
- Slides (on Google Drive):
  - Vacancies and Interstitials
  - Complexes

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Discussion: Sept. 10-12, 2024