

Learning Objectives

After studying this chapter you should be able to do the following:

1. Describe both vacancy and self-interstitial crystalline defects.
2. Calculate the equilibrium number of vacancies in a material at some specified temperature, given the relevant constants.
3. Name the two types of solid solutions, and provide a brief written definition and/or schematic sketch of each.
4. Given the masses and atomic weights of two or more elements in a metal alloy, calculate the weight percent and atom percent for each element.
5. For each of edge, screw, and mixed dislocations:
 - (a) describe and make a drawing of the dislocation.
 - (b) note the location of the dislocation line, and
 - (c) indicate the direction along which the dislocation line extends.
6. Describe the atomic structure within the vicinity of (a) a grain boundary, and (b) a twin boundary.

4.1 INTRODUCTION

imperfection

Thus far it has been tacitly assumed that perfect order exists throughout crystalline materials on an atomic scale. However, such an idealized solid does not exist; all contain large numbers of various defects or **imperfections**. As a matter of fact, many of the properties of materials are profoundly sensitive to deviations from crystalline perfection; the influence is not always adverse, and often specific characteristics are deliberately fashioned by the introduction of controlled amounts or numbers of particular defects, as detailed in succeeding chapters.

point defect

By “crystalline defect” is meant a lattice irregularity having one or more of its dimensions on the order of an atomic diameter. Classification of crystalline imperfections is frequently made according to geometry or dimensionality of the defect. Several different imperfections are discussed in this chapter, including **point defects** (those associated with one or two atomic positions), linear (or one-dimensional) defects, as well as interfacial defects, or boundaries, which are two-dimensional. Impurities in solids are also discussed, since impurity atoms may exist as point defects. Finally, techniques for the microscopic examination of defects and the structure of materials are briefly described.

Point Defects

4.2 VACANCIES AND SELF-INTERSTITIALS

vacancy

The simplest of the point defects is a **vacancy**, or vacant lattice site, one normally occupied from which an atom is missing (Figure 4.1). All crystalline solids contain vacancies and, in fact, it is not possible to create such a material that is free of these defects. The necessity of the existence of vacancies is explained using principles of thermodynamics; in essence, the presence of vacancies increases the entropy (i.e., the randomness) of the crystal.

The equilibrium number of vacancies N_v for a given quantity of material depends on and increases with temperature according to

Temperature-
dependence of the
equilibrium number
of vacancies

$$N_v = N \exp\left(-\frac{Q_v}{kT}\right) \quad (4.1)$$

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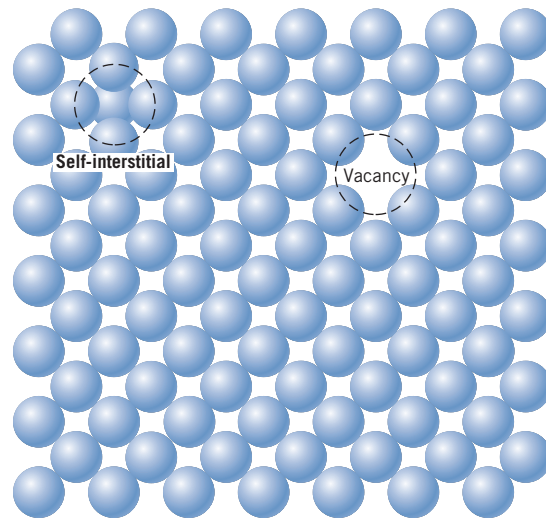


Figure 4.1 Two-dimensional representations of a vacancy and a self-interstitial. (Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 77. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

Boltzmann's constant

In this expression, N is the total number of atomic sites, Q_v is the energy required for the formation of a vacancy, T is the absolute temperature¹ in kelvins, and k is the gas or **Boltzmann's constant**. The value of k is 1.38×10^{-23} J/atom-K, or 8.62×10^{-5} eV/atom-K, depending on the units of Q_v .² Thus, the number of vacancies increases exponentially with temperature; that is, as T in Equation 4.1 increases, so also does the expression $\exp -(Q_v/kT)$. For most metals, the fraction of vacancies N_v/N just below the melting temperature is on the order of 10^{-4} ; that is, one lattice site out of 10,000 will be empty. As ensuing discussions indicate, a number of other material parameters have an exponential dependence on temperature similar to that of Equation 4.1.

self-interstitial

A **self-interstitial** is an atom from the crystal that is crowded into an interstitial site, a small void space that under ordinary circumstances is not occupied. This kind of defect is also represented in Figure 4.1. In metals, a self-interstitial introduces relatively large distortions in the surrounding lattice because the atom is substantially larger than the interstitial position in which it is situated. Consequently, the formation of this defect is not highly probable, and it exists in very small concentrations, which are significantly lower than for vacancies.

EXAMPLE PROBLEM 4.1**Number of Vacancies Computation at a Specified Temperature**

Calculate the equilibrium number of vacancies per cubic meter for copper at 1000°C. The energy for vacancy formation is 0.9 eV/atom; the atomic weight and density (at 1000°C) for copper are 63.5 g/mol and 8.4 g/cm³, respectively.

¹ Absolute temperature in kelvins (K) is equal to °C + 273.

² Boltzmann's constant per mole of atoms becomes the gas constant R ; in such a case $R = 8.31$ J/mol-K.

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Number of atoms
per unit volume for
a metal

Solution

This problem may be solved by using Equation 4.1; it is first necessary, however, to determine the value of N , the number of atomic sites per cubic meter for copper, from its atomic weight A_{Cu} , its density ρ , and Avogadro's number N_A , according to

$$\begin{aligned} N &= \frac{N_A \rho}{A_{\text{Cu}}} \quad (4.2) \\ &= \frac{(6.023 \times 10^{23} \text{ atoms/mol})(8.4 \text{ g/cm}^3)(10^6 \text{ cm}^3/\text{m}^3)}{63.5 \text{ g/mol}} \\ &= 8.0 \times 10^{28} \text{ atoms/m}^3 \end{aligned}$$

Thus, the number of vacancies at 1000°C (1273 K) is equal to

$$\begin{aligned} N_v &= N \exp\left(-\frac{Q_v}{kT}\right) \\ &= (8.0 \times 10^{28} \text{ atoms/m}^3) \exp\left[-\frac{(0.9 \text{ eV})}{(8.62 \times 10^{-5} \text{ eV/K})(1273 \text{ K})}\right] \\ &= 2.2 \times 10^{25} \text{ vacancies/m}^3 \end{aligned}$$

4.3 IMPURITIES IN SOLIDS

alloy

A pure metal consisting of only one type of atom just isn't possible; impurity or foreign atoms will always be present, and some will exist as crystalline point defects. In fact, even with relatively sophisticated techniques, it is difficult to refine metals to a purity in excess of 99.9999%. At this level, on the order of 10^{22} to 10^{23} impurity atoms will be present in one cubic meter of material. Most familiar metals are not highly pure; rather, they are **alloys**, in which impurity atoms have been added intentionally to impart specific characteristics to the material. Ordinarily, alloying is used in metals to improve mechanical strength and corrosion resistance. For example, sterling silver is a 92.5% silver–7.5% copper alloy. In normal ambient environments, pure silver is highly corrosion resistant, but also very soft. Alloying with copper significantly enhances the mechanical strength without depreciating the corrosion resistance appreciably.

solid solution

The addition of impurity atoms to a metal will result in the formation of a **solid solution** and/or a new *second phase*, depending on the kinds of impurity, their concentrations, and the temperature of the alloy. The present discussion is concerned with the notion of a solid solution; treatment of the formation of a new phase is deferred to Chapter 9.

solute, solvent

Several terms relating to impurities and solid solutions deserve mention. With regard to alloys, **solute** and **solvent** are terms that are commonly employed. “Solvent” represents the element or compound that is present in the greatest amount; on occasion, solvent atoms are also called *host atoms*. “Solute” is used to denote an element or compound present in a minor concentration.

Solid Solutions

A solid solution forms when, as the solute atoms are added to the host material, the crystal structure is maintained, and no new structures are formed. Perhaps it is