

Imperfections in Solids

Point Defects

Vacancies and Self-interstitial

The simplest of the point defects is a **vacancy**, or vacant lattice site, one normally occupied from which an atom is missing (Figure below). 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:

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

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 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

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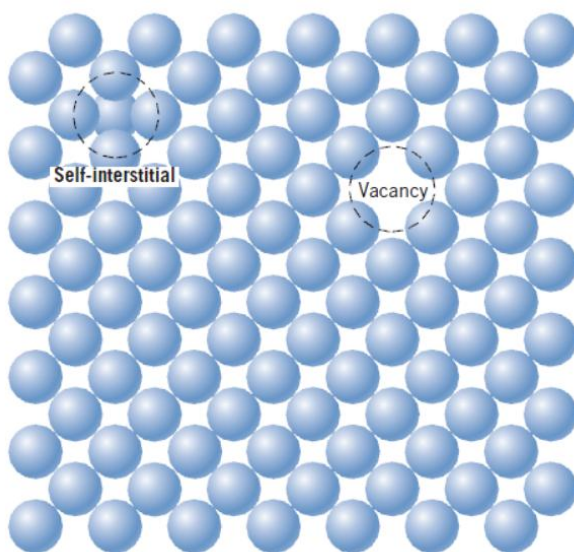


Figure Two-dimensional representations of a vacancy and a self-interstitial.

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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.

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 10²³ 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.

Alloying is used in metals to improve mechanical strength and corrosion resistance.

For example, sterling silver is a 92.5% silver % copper alloy.

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.

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 useful to draw an analogy with a liquid solution. If two liquids, soluble in each other (such as water and alcohol) are combined, a liquid solution is produced as the molecules intermix, and its composition is homogeneous throughout. A solid solution is also compositionally homogeneous; the impurity atoms are randomly and uniformly dispersed within the solid.

Impurity point defects are found in solid solutions, of which there are two types:

substitutional and **interstitial**. For the substitutional type, solute or impurity atoms replace or substitute for the host atoms (Figure below).

There are several features of the solute and solvent atoms that determine the degree to which the former dissolves in the latter, as follows:

1. *Atomic size factor.* Appreciable quantities of a solute may be accommodated in this type of solid solution only when the difference in atomic radii between the two atom types is less than about $\pm 15\%$. Otherwise the solute atoms will create substantial lattice distortions and a new phase will form.
2. *Crystal structure.* For appreciable solid solubility the crystal structures for metals of both atom types must be the same.
3. *Electronegativity.* The more electropositive one element and the more electronegative the other, the greater is the likelihood that they will form an intermetallic compound instead of a substitutional solid solution.
4. *Valences.* Other factors being equal, a metal will have more of a tendency to dissolve another metal of higher valency than one of a lower valency.

An example of a substitutional solid solution is found for copper and nickel. These two elements are completely soluble in one another at all proportions. With regard to the aforementioned rules that govern degree of solubility, the atomic radii for copper and nickel are 0.128 and 0.125 nm, respectively, both have the FCC crystal structure, and their electronegativities are 1.9 and 1.8; finally, the most common valences are for copper +1 (although it sometimes can be +2) and +2 for nickel.

For interstitial solid solutions, impurity atoms fill the voids or interstices among the host atoms (see Figure below). For metallic materials that have relatively high atomic packing factors, these interstitial positions are relatively small. Consequently,

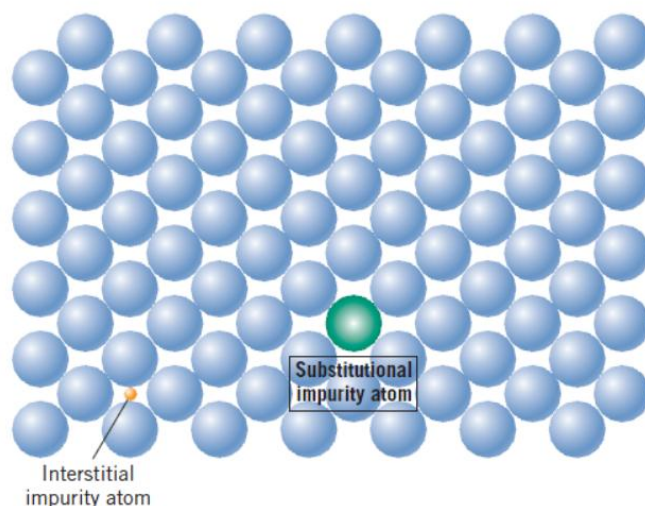


Figure Two-dimensional schematic representations of substitutional and interstitial impurity atoms.