Theoretical Density and Vacancy Populations

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By using the crystal geometry of metallic and ionic solids, along with basic information about the composition, we can determine the a theoretical density for the material. While this number will often simply be close, the difference between the predicted and measured densities can garner additional information about the material. In particular, it can tell us about the number of vacancies present in the material (a function of both the temperature and the processing of the material itself) which in turn impact properties.

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1 Crystal Systems

Before one can talk about density, the geometry must first be established. Some definitions must also be laid out. A unit cell is a repeating unit that fills space, like a tile in a repeating mosaic. An atom or molecule can be split between two, or even eight, different unit cells, but in reality it is in one piece. The cell parameter, denoted a, is the length of the edge of a unit cell, and is often expressed in terms of the radius of the atoms in the cell. Each of these are easily visualized.

SC: Simple cubic would be a cube with one atom (or molecule, if that is our basis) on each of the eight corners. As each atom is shared between eight other neighboring cells, each only contributes an eighth, so only one total atom is actually in the cell. The cell parameter would simply be twice the atom radius, as they would be touching along the face edges. Each atom is coordinated by 6 other atoms.

BCC: Body centered cubic is similar to BCC, but with one additional atom at the center of the cube. This causes the number of total atoms in the cell to be 2, and the cell parameter to be $\frac{4}{\sqrt{3}}R$ as it is close packed along the body diagonal. Each atom is coordinated by 8 other atoms.

FCC: Face centered cubic is similar to BCC, but at the center of each of the faces is an additional atom, split between two cells. There are a total of 4 atoms or basis in a FCC unit cell. The cell parameter can be expressed as $2\sqrt{2}R$, by geometry, as the atoms are close-packed (edge to edge) along the face diagonal. Each atom is coordinated by 12 other atoms.

HCP: Hexagonal close packing is unlike the cubic unit cells in the way it is visualized. It is a hexagonal prism, with an atom at each of the 12 corners, and three in a triangle inside the prism, for a total of 6 atoms per cell. The cell parameter can only be expressed in terms of two seperate parameters, one for the edge length, and another for the prism height. Each atom is coordinated by 12 other atoms. Like FCC, HCP is also close packed, the difference in fact is simply in the layering order.

2 Density Equation

The equation for density is fairly straightforward, essentially being "How much stuff" divided by "How much volume", by the following equation, where W is the molecular weight of the atoms or molecules of the basis, n is how many lie inside the unit cell (see above), N_A is Avagadro's number ($6.023 * 10^{23}$), and V is the volume of the cell, being the cell parameter cubed.

$$\rho = \frac{Wn}{N_A V} = \frac{Wn}{N_A a^3} \tag{1}$$

2.1 Example

If copper has an FCC crystal structure, an atomic radius of 0.128nm, and an atomic weight of 63.55 grams per mole. What is the theoretical density?

First we need to find the cell parameter. As it is FCC, we use $a = 2\sqrt{2}R$ to find a to be .362nm.

Also, FCC has 4 atoms per cell, so $n = 4$.

$$\rho = \frac{63.55 * 4}{6.023 * 10^{23} * (0.362nm)^3} \tag{2}$$

However, densities are often given in terms of grams per cubic centimeter, so we convert the cell parameter appropriately.

$$\rho = \frac{63.55 * 4}{6.023 * 10^{23} * (3.62 * 10^{-8})^3} = 8.89g/cm^3 \tag{3}$$

This is very close to the accepted density of 8.94 grams per cubic centimeter.

3   Vacancies and Vacancy Density

Due to entropy and the need to find the lowest energy state, solids will generally have some equilibrium number of vacancies. That is, empty places on the crystal lattice, where atoms would theoretically be. This causes experimental densities to be slightly off from predicted densities. This population of vacancies varies predictably with temperature by the following relation, where N_D is the number of defects, N is the number of sites, E is the activation energy to create one vacancy, k is the boltzman constant, and T is temperature:

$$\frac{N_D}{N} = e^{\frac{-E}{kT}} \tag{4}$$

3.1   Example

What is the equilibrium vacancy ratio for copper at 1000 C? $E = 0.9$eV per atom, and $k = 8.62 * 10^{-5}$eV per atom kelvin, $\rho_{Cu} = 8.4$ grams per cubic cm. How many vacancies exist in one cubic meter of copper at the same temperature?

We dive right in and substitute in the known values.

$$\frac{N_D}{N} = e^{\frac{-0.9}{8.62*10^{-5}*1273}} = 2.74 * 10^{-4} \tag{5}$$

To find the actual number of vacancies, we need to find the number of sites that exist in one cubic meter of copper.

$$N = \rho_{Cu} \frac{N_A}{MW_{CU}} * 1m^3 = 8 * 10^{28} \tag{6}$$

$$N_D = 2.74 * 10^{-4} * 8 * 10^{28} = 2.19 * 10^{25} \tag{7}$$