Chapter S. The Structure of solids.

After having studied this chapter, the student will be able to:

1. Distinguish between a crystal structure and an amorphous structure.
2. Describe the concept of a unit cell.
3. Describe the FCC, BCC and HCP structures. Explain why FCC and HCP are both the densest packing of atoms.
4. Describe polymorphism and give an example.
5. Draw and recognize atomic coordinates in a cubic lattice
6. Draw and recognize directions in a cubic lattice
7. Draw and recognize atomic planes in a cubic lattice.
8. Draw the densest planes in FCC and BCC structures.
9. Distinguish a single crystal and polycrystalline material. Define a grain and a grain boundary.
10. Relate compositions in weight % and atomic % to the crystal structure.
11. Name and describe the point defects in a solid.
12. Describe and draw and edge and screw dislocations.
13. Describe grain boundaries and their structure.

We don’t think of materials like structural steel or solder as being crystalline because they aren’t clear, transparent, faceted, sparkling, angular, etc. Despite external appearances to the contrary, materials like metals are crystalline: their atoms are arranged in regular, periodic, three-dimensional structures called crystals. Figure S.1. for example, shows the crystalline arrangement of atoms in germanium.

Figure S.1. Transmission microscope picture showing the positions of atoms in germanium.

There are materials, especially glass and most polymers, in which the atoms of molecules are not positioned in ordered arrays; these are amorphous solids and all liquids.

Crystals are not perfect. They contain impurities, voids, misplaced atoms and other defects. It turns out, perhaps as a surprise, that the crystalline defects are responsible for many of the useful properties of materials; a perfect and perfectly pure crystal is generally useless.
The crystal structure of materials and the crystalline defects play a very large role in the properties of materials, especially in the way they deform plastically under stress. Defects are used to strengthen materials. Knowledge of the crystal structures and defects will provide us with the methods to tailor the mechanical properties of solids to their use. The knowledge of the simplest crystal structures will suffice for our purposes. Many materials, especially ceramic compounds, have very complex structures, but these are usually not manipulated to obtain specific material performance and we will not include them.

S.1. Crystal Structures

With few exceptions, the elements crystallize in one of three structures: the face centered cubic structure (FCC), the body centered cubic structure (BCC) and the hexagonal close packed structure (HCC). The important semiconductor elements silicon and germanium crystallize in the diamond structure, which is a variant of FCC.

S.1.1. Cubic Structures

Consider the structure of aluminum, for example; aluminum crystallizes in the Face Centered Cubic structure shown in figure S.2.

![Figure S.2. The Face Centered Crystal Structure. This structure extends in all directions to the end of the crystal. It is a repetition in all three directions of the unit cell, shown in blue.](image)

The structure shown, of course, extends in all directions to the border of the crystal. In this structure, we discern a **unit cell**, which is shown in blue, that repeats itself in all three directions.
Figure S.3. The unit cell of the face centered cubic (FCC) structure. It is drawn through the centers of the atoms at its edges. (a) representation of the atoms in their real size, as they touch each other. (b) representation of the centers of the atoms, showing their positions.

Figure S.3 shows the unit cell of this structure. It is a cube with atoms at its corners and in the centers of its faces, hence its name: **Face Centered Cubic (FCC)** structure. It is convenient to draw the unit cell through the centers of the atoms at its edges. Therefore the atoms at the plane centers are cut in half: the other half belongs to the neighboring cell. For the same reason, only one eighth of the corner atoms belong to the unit cell. The FCC unit cell contains 4 atoms: $6 \times 1/2 = 3$ in the faces and $8 \times 1/8 = 1$ at the corners. Besides aluminum, the metals Ni, Cu, Pd, Ag, Pt, Au, Pb, Ca and Sr possess the FCC structure.

Now let us look at the structure of iron at room temperature. It is shown in figure S.4. Its unit cell has atoms at the corners and one in the center of the cell, hence its name **Body Centered Cubic structure**.

Figure S.4. The Body Centered Cubic (BCC) structure or iron. (a) The unit cell showing the atoms in their real size and touching each other. (b) representation of the unit cell, showing the positions of the centers of the atoms, (c) a portion of the crystal showing the unit cell.

The BCC structure contains 2 atoms per unit cell, one in its center and one at its corners. Other metals possessing BCC structure are Cr, Mo, W, Ta, Na, K, etc.
The size of the unit cell is the **lattice parameter** \( a \). In cubic structures, there is only one constant because of its symmetry. Other crystal structures are less symmetrical and more than one parameter is necessary to describe them.

An abbreviated list of the crystal structures of metals and their lattice parameters is found in Table 3-2. These limited crystallographic data enable calculation of a considerable amount of information about the material provided atoms are assumed to be hard spheres.

1. **Atomic Radii.** In BCC structures, atoms of radius \( r \) touch along the cube body diagonal. Thus, as shown in Fig. S.5, \( r + 2r + r \) or \( 4r = a (3)^{1/2} \), and \( r = a(3)^{1/2} /4 \). Since \( a = 0.2866 \) nm, the calculated Fe atom radius is 0.1241 nm.

![Figure S.5. Calculation of the atomic radius in BCC structures.](image)

In FCC structures, atoms touch along the cube face diagonal (see Figure S.3) so that \( r + 2r + r \) or \( 4r = a(2)^{1/2} \), and \( r = a(2)^{1/2} /4 \). For Al where \( a = 0.4045 \) nm, \( r = 0.143 \) nm.

2. **Atomic Packing Factor.** The atomic packing factor (APF) is defined as the ratio of the volume of atoms, assumed to be spheres, to the volume of the unit cell.

   For BCC structures there are 2 atoms per cell. Therefore, \( \text{APF} = 2 \cdot 4/3\pi r^3 / a^3 \). But \( r = a(3)^{1/2} /4 \) and after substitution \( \text{APF} = (3)^{1/2}\pi / 8 \) or 0.680, a number that is independent of atomic sphere size. In the case of FCC structures, \( \text{APF} = 4 \cdot 4/3\pi r^3 / a^3 \). Since \( r = a(2)^{1/2} /4 \), evaluation of \( \text{APF} = 0.740 \). This demonstrates that of the two structures, FCC is more densely packed.

3. **The density of the material.** Since the FCC structure has 4 atoms per cubic cell of volume \( a^3 \), the number of atoms per unit volume is simply \( N = 4/a^3 \). In aluminum, with the lattice parameter \( a = 0.4045 \) nm, \( N = 4/(0.4045)^3 = 60.44 \) atoms/nm\(^3 = 6.044.10^{28} \) atoms/m\(^3 = 6.044.10^{22} \) atoms/cm\(^3 \).
From this number, we can compute the theoretical mass density (or specific mass) of the material. The atomic weight of aluminum is 26.98; this is the mass of 1 mole or $N_A = 6.023 \times 10^{23}$ atoms per gram mole. The density of aluminum is then calculated as $\rho = \frac{(6.044 \times 10^{22}/6.023 \times 10^{23}) \times 26.98}{1}$ = 2.70 g/cm$^3$. (The universal unit for density is 2.70 Mg/m$^3$ but it is seldom used in practice as it does not speak to the senses). This is a theoretical density. Materials contain defects such as vacancies and impurities and their actual density may differ from their theoretical value.

S.1.2. The Hexagonal Close Packed Structure (HCP).

Metals like Zn, Mg, Be, Ti Co and Zr crystallize in the hexagonal close packed structure shown if figure S.6. The structure consists of layers in which the atoms are arranged in a hexagonal patterns which constitutes the closest possible packing of spheres on a plane. The layers are stacked on top of each other in such a way that every atom fits into the cusp between three atoms below and above it, resulting in the closest possible packing of atoms. Figure S.6(a) shows a unit cell of the structure. This unit cell now possesses two lattice parameters, $a$ and $c$. If the atoms were perfect spheres, the ideal ratio of the two lattice parameters would be $c/a = 1.633$. The real $c/a$ ratio of most metals deviates from this value, as shown in table S.1. Hexagonal close packed crystals have the same atomic packing factor 0.74 as the FCC crystals. In fact, it can be shown that the FCC structure can be considered a slightly different stacking of close packed hexagonal planes; this will be examined later when we discuss atomic planes.

Figure S.6. The hexagonal close packed structure. (a) a unit cell; note that it has two different lattice parameters, $a$ and $c$. (b) A fraction of a crystal showing atoms touching each other.
<table>
<thead>
<tr>
<th>Metal</th>
<th>a, nm</th>
<th>c, nm</th>
<th>c/a ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>0.2979</td>
<td>0.5617</td>
<td>1.890</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.2665</td>
<td>0.4947</td>
<td>1.856</td>
</tr>
<tr>
<td>Ideal HCP</td>
<td></td>
<td></td>
<td>1.633</td>
</tr>
<tr>
<td>Beryllium</td>
<td>0.2286</td>
<td>0.3584</td>
<td>1.568</td>
</tr>
<tr>
<td>Cobalt</td>
<td>0.2507</td>
<td>0.4069</td>
<td>1.623</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.3210</td>
<td>0.5211</td>
<td>1.623</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.2951</td>
<td>0.4685</td>
<td>1.587</td>
</tr>
<tr>
<td>Zirconium</td>
<td>0.3231</td>
<td>0.5148</td>
<td>1.593</td>
</tr>
</tbody>
</table>

S.1.3. The diamond structure.

The structures we have discussed so far correspond to the densest packing possible of atoms, with a small influence of the directions of atomic bonds. The latter is responsible for the choice between FCC, BCC and HCP structure. These solids expand when they melt, that is, when the arrangement of atoms is disordered, or amorphous. In the elements of column IVA, namely carbon in its diamond form, silicon and germanium, the covalent bonds consist of sp$^3$ hybrid electron orbitals which have a strict spatial relationship with each other and impose the relative positions of the atoms to which they bond. As a consequence, the structure of these elements is not the densest possible. When these solids melt, they contract. (A familiar case of structure dictated by the direction of the bonds is ice: it contracts upon melting and water expands when it freezes. This makes ice float on water and causes the rupture of water pipes in unheated houses in winter). Figure S.7.A shows the diamond structure. Figure S.7.B shows the structure of the III-V semiconductor compound gallium arsenide. Closer examination reveals that it is in fact an FCC structure where each FCC site corresponds to a GaAs molecule.

S.1.4. The structures of compounds.

The crystal structure of compounds, which are usually ceramic and possess a mixed covalent-ionic structure, can be very complex. Their structure may be determined by the geometry of the chemical bond. This is particularly important in the compounds of carbon, silicon and germanium. Silicon nitride, Si$_3$N$_4$, for example, possesses 7 atoms per formula. Each Si atom must be surrounded by 4 N atoms in the sp$^3$ configuration we have discusses in chapter 1 and every N atom touches 3 Si atoms arranged in a plane. The result is a complex hexagonal structure.

In ionic crystals, the structure is governed by two principles: positive and negative ions must alternate for electrostatic cohesion; and the ions, which have different sizes, must touch so that the structure does not collapse. These principles
are responsible for the two structures of sodium chloride and cesium chloride, shown in figure S.8.

Figure S.8. (A) The NaCl structure (B) the CsCl structure. White atoms are Cl.

All known crystal structures can be described by the 14 Bravais lattices shown in Table S.2. and in figure S.9. These lattices represent the periodicity and the symmetry of the crystal. A lattice point does not necessary correspond to a single atom but to a whole structure that repeats itself through the crystal. For instance, the unit cell of the NaCl structure of figure S.8.A is a simple cubic cell represented at the top left of figure S.9. The reason is the following: one must move from a chlorine atom all the way to the next chlorine atom in for the crystal to repeat itself exactly. In the same vein, the CsCl unit cell of figure S.9.B is not body centered cubic, but simple cubic because the Cs and Cl sites are not equivalent.
<table>
<thead>
<tr>
<th>CRYSTAL SYSTEM</th>
<th>AXIAL LENGTHS</th>
<th>EXAMPLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>CUBIC</td>
<td>three equal axes,</td>
<td>Au, Cu, NaCl, Si, GaAs</td>
</tr>
<tr>
<td>(Simple cubic,</td>
<td>three right angles</td>
<td></td>
</tr>
<tr>
<td>Body-centered cubic,</td>
<td>a = b = c, α = β = γ = 90°</td>
<td></td>
</tr>
<tr>
<td>Face-centered cubic)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TETRAGONAL</td>
<td>Two of the three axes equal,</td>
<td>In, TiO₂</td>
</tr>
<tr>
<td>(Simple tetragonal,</td>
<td>three right angles</td>
<td></td>
</tr>
<tr>
<td>Body centered tetragonal)</td>
<td>a = b ≠ c , α = β = γ = 90°</td>
<td></td>
</tr>
<tr>
<td>ORTHORHOMBIC</td>
<td>Three unequal axes,</td>
<td>Ga, Fe₃C</td>
</tr>
<tr>
<td>(Simple orthorhombic,</td>
<td>three right angles</td>
<td></td>
</tr>
<tr>
<td>Body centered orthorhombic, Base-centered orthorhombic, Face-centered orthorhombic)</td>
<td>a ≠ b ≠ c , α = β = γ = 90°</td>
<td></td>
</tr>
<tr>
<td>RHOMBOHEDRAL</td>
<td>Three equal axes equally inclined ,</td>
<td>Hg, Bi</td>
</tr>
<tr>
<td>(Simple rhombohedral)</td>
<td>three equal angles ≠ 90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>a = b = c, α = β = γ</td>
<td></td>
</tr>
<tr>
<td>HEXAGONAL</td>
<td>Two equal axes at 120°,</td>
<td>Zn, Mg</td>
</tr>
<tr>
<td>(Simple hexagonal)</td>
<td>third axis at right angles</td>
<td></td>
</tr>
<tr>
<td></td>
<td>a = b ≠ c, α = β = γ = 120°</td>
<td></td>
</tr>
<tr>
<td>MONOCLINIC</td>
<td>Three unequal axes,</td>
<td>KClO₃</td>
</tr>
<tr>
<td>(Simple monoclinic,</td>
<td>one pair of axes not at 90°</td>
<td></td>
</tr>
<tr>
<td>Base- centered monoclinic)</td>
<td>a ≠ b ≠ c , α = γ = 90° , β ≠ 90°</td>
<td></td>
</tr>
<tr>
<td>TRICLINIC</td>
<td>Three unequal axes,</td>
<td>Al₂SiO₅</td>
</tr>
<tr>
<td></td>
<td>three unequal angles</td>
<td></td>
</tr>
<tr>
<td></td>
<td>a ≠ b ≠ c , α ≠ β ≠ γ</td>
<td></td>
</tr>
</tbody>
</table>
S.1.5. Polymorphism or allotropy.

The term Polymorphism (or its synonym allotropy) expresses the ability of a solid to crystallize in different structures. The most important cases of polymorphism we discuss here are carbon and iron. The valence orbitals responsible for chemical bonds of carbon can be either sp³ hybrids or sp² hybrids. The sp³ hybrid bonds form diamond, which has the structure shown in figure S.7.A. It is the hardest material known.

A chemical bond formed with sp² hybrids forms graphite, which has the hexagonal structure shown in figure S.10.B. Graphite is a soft material. Its hexagonal layers glide over each other easily making graphite a solid lubricant. In 1985, scientists have been able to produce small carbon balls consisting of 60 carbon atoms with sp² bonding, named C₆₀ or Fullerenes (often also Bucky balls) after Buckminster Fuller who popularized this structure in buildings. Another variant that has been synthesized more recently is the carbon nanotube. These new polymorphs of carbon are presently the object of much research and possess interesting chemical and mechanical properties. These structures are also shown in Figure S.10.

A very important polymorphism is that of iron. At low and moderate temperature, iron has the BCC crystal structure shown in figure S4. As the material is
heated above 913 °C (1186K), its structure changes to FCC, figure S3. We shall see in
chapter X that this property of iron is at the base of the production, processing and
properties of steel.

EX. S-1  a. What is the fractional volume change in iron as it transforms from
BCC to FCC at 910°C? Assume that a(BCC) = 0.2910 nm and a(FCC) = 0.3647 nm.
b. What is the volume change if Fe atoms of fixed radius pack as hard
spheres?

ANS. The volume (V) per atom is equal to volume per unit cell / atoms per unit
cell. For BCC Fe, V (BCC) per atom = a³(BCC)/2. Similarly for FCC Fe, V(FCC)
per atom = a³(FCC)/4. Substituting, V(BCC)/atom = (0.2910)³ /2 = 0.01232 nm³;
V(FCC)/atom = (0.3647)³ /4 = 0.01213 nm³. Therefore, ∆V / V = (0.132 - 0.1232) / 0.1232 = -0.0154 or -1.54 %, a result consistent with the abrupt contraction observed
when BCC Fe transforms to FCC Fe.

If atoms packed as hard spheres, a(BCC) = 4r /3 1/2 and a(FCC) = 4r / 2 1/2.

Therefore, ∆V / V = { [4r / 2 1/2]³ / 4 - [ 4r / 3 1/2]³ /2 } / [ 4r / 3 1/2]³ /2 =
(5.657 - 6.158) / 6.158 = -0.08135 or -8.135 %.

The two values for ∆V / V differ considerably. The results for part b are
independent of lattice parameter of the involved unit cells and therefore, of the
particular metal. Obviously, atoms in real metals and iron, in particular, aren’t
hard spheres of fixed radius. Other metals like manganese and plutonium also exist
in both BCC and FCC crystal forms of different lattice parameters.


When we look at the crystal structures described in section S.1, several questions
arise. Atoms are arranged in planes in crystals; what planes are the smoothest and most
densely packed in each structure? What are the positions in the diamond lattice? In what
directions are the bonds between diamond atoms formed? It becomes clear that we need a
mathematical language to describe the positions of the atoms, important directions and
planes. For the cubic crystals, one utilizes Cartesian coordinates and the rules of
analytical geometry, which we will recall in this section. In order to make the
coordinates independent of the particular material, one uses dimensionless coordinates in
which the length of the unit cell is unity; this is shown in figure S.11.

S.2.1. Atomic Positions

Positions inside the cube are expressed by fractional numbers. Thus, the BCC
structure has atoms at positions (0,0,0), (1,0,0), (0,1,0), (0,0,1), (1,1,0), (0,1,1), (1,0,1),
(1,1,1) and (½,½,½). The positions of the atoms in the FCC structure are shown in figure
S.11.C.
Note that the directions of the x, y, and z axes are always shown as in figure S.11: the x-axis towards the reader, the y-axis to the right and the z-axis towards the top. Do not use a different system to avoid being misunderstood.

Figure S.11. The coordinates of atoms in simple cubic (SC), body centered cubic (BCC) and face centered cubic (FCC) structures.

The crystal is a three-dimensional periodic stacking of such unit cells. Therefore, the corner points are shared with neighboring unit cells. The (1,0,0) point, for instance, is also the origin (0,0,0) point of the cell in front of the one shown; the (0,1,0) point is the (0,0,0) of the unit cell to the right, as shown in Figure S.12.

The simple unit cell thus contains only one atom at (0,0,0); the atoms at (1,0,0), (0,1,0),(1,1,0) etc. belong to neighboring cells. The BCC cells contains two atoms, at (0,0,0) and at (½,½,½). Similarly, the FCC structure has 4 atoms per unit cell, at (0,0,0), (½,½,0), (½,0,½) and (0,½,½). This periodic description is equivalent to the one given in figures S.3 and S.4, but avoids cutting atoms into halves or eighths.
S.2.2. Directions

Directions are vectors that connect any two points in a prescribed sense. Note that the directions do not depend on the length of the vector nor on its positions. In analytical geometry, the coordinates of a vector are the coordinates of its end-point minus the coordinates of its initial point. Directions are indicated by the coordinates in brackets \([\] \) and not separated by a comma. These are the Miller indices of a direction. They are always written as integers by multiplying all numbers by the largest common denominator. Thus, the direction \([301]\) in figure S.13 ends at the point \((1,0,1/3)\) and starts at \((0,0,0)\), the vector joining these points is \([1 \ 0 \ 1/3]\). Multiplying all numbers by 3 makes it 3 times longer, this is the same direction \([103]\). The main directions in cubic systems are shown in figures S.13 to S.15. Their endpoints are marked as dots. Note that the \([110]\) direction is shown twice: parallel vectors represent the same direction and have the same coordinates.
Some directions require negative coordinates. These are written with a minus sign on top of the number. Figure S.14 shows the [011] direction. Its starting point is (0,0,1) and its end point is (0,1,0). With the rule governing the coordinates of directions, we obtain \((0,1,0) - (0,0,1) = [011]\). An alternative way of obtaining the coordinates of this direction is shown in Figure S.14.B. We displace the origin to the top of the cell, as discussed with figure S.12., so that it becomes the new (0,0,0) point. In these coordinates, the end point is (0,1,-1), yielding the same direction coordinate.

Figure 14: The [011] direction. (A), [011] = (0,1,0) – (0,0,1). (B) The origin is moved.
Figure S.15. Directions with negative indices. Displacement of the origin (different for each direction) allows drawing them inside the unit cell.

When given a direction to draw, one divides all indices by the largest one to insure the vector remains inside the unit cell. Then, selecting a proper origin, one draws the vector to the end-point. Let is draw the direction

\[[412] = [1 \, \frac{1}{4} \, \frac{1}{2}]\]. Since the y-scale is negative, we move the origin to the right on the y scale; this is the starting point of the vector. Then we note the point \((1, -\frac{1}{4}, \frac{1}{2})\) and draw the vector joining these two point. This is shown in figure S.16.

Figure S.16. Drawing the direction \([412]\). The origin is moved to the right.
The edges of the cube have coordinates [100], [010], [001]. These cube edges form a family denoted by \langle 100 \rangle. In the same way, all face diagonals [110], [011] and [101] form the \langle 110 \rangle family and the space diagonals [111], [\overline{111}], [\overline{111}], [\overline{111}] form the \langle 111 \rangle family. Generally, all the permutations of [uvw] with their negatives form the \langle uvw \rangle family.

We can apply our knowledge and review the diamond structure of figure S.7. We find that carbon atoms are in all the FCC positions but that there are also carbon atoms in position \((\frac{1}{4},\frac{1}{4},\frac{1}{4})\), \((\frac{1}{4},\frac{3}{4},\frac{1}{4})\), \((\frac{1}{4},\frac{1}{4},\frac{3}{4})\) and \((\frac{3}{4},\frac{3}{4},\frac{3}{4})\). It is easy to verify, by the rule of vector coordinates, that the sp\(^3\) bonds between the carbon atoms are all in the \langle 111 \rangle family.

S.2.3. Planes

A look at figures S.2, S.4 and S.8 shows quite clearly that, in a crystal, atoms are placed on various planes. Like points and directions, crystallographic planes are identified by Miller indices.

Any three points define a plane. The following simple recipe can be used to identify a given plane in cubic crystals:
1. Express the intercepts of the plane on the three coordinate axes in number of unit cell dimensions
2. Take reciprocals of these numbers, and
3. Reduce the reciprocals to smallest integers by clearing fractions.

The resulting triad of numbers placed in parentheses without commas, \((hkl)\), is the Miller indices of the plane in question. Any time a plane passes through the origin, the above recipe will not work. In such a case it must be remembered that the origin of the coordinate axes can be arbitrarily shifted to any other lattice point. Another alternative is to translate the plane parallel to itself until intercepts are available. By either of these means it is always possible to have the involved plane slice through the unit cell. In the case of cube faces one intercept \((e.g., x is 1 and the other two intercepts extend to infinity). Therefore, 1/1 = 1, 1/\infty = 0, 1/\infty = 0, and the planar indices are \((100)\). Figure S.17 shows a number of typical planes identified with the above rule.

Other \((100)\) type planes that are equivalent have \((010), (\overline{010}), (100), (010)\) and \((001)\) indices. These 6 planes constitute the \(\{100\}\) family. Generally all permutations of \((hkl)\) with their negatives constitute the \(\{hkl\}\) family.

In order to draw the \((hkl)\) plane, take the inverse, \(1/h\) and place it on the x-scale, place \(1/k\) on the y scale and \(1/l\) on the z-scale. These three points define the plane which can be drawn by joining them. If one of the indices is zero, the plane is parallel to the corresponding axis (it joins it at \(\infty\)). For every negative Miller index, move the origin to the other extremity of the corresponding cell axis as discussed with figure S.12.
The (100) plane

The (111) plane

The (101) plane

The (110) plane, origin moved to the right.

The (1 2 2) plane. The origin is shifted on all thee axes.

The (133) plane intersects the y and Z axes at 1/3.

Figure S.17. Some representative planes in cubic crystals.
S.2.3.1. Dense planes and directions.

The planes with densest atomic packing are of interest in the plastic deformation of metals, they are the planes along which brittle materials cleave; they are also the chemically most stable planes; The densest directions, along which neighboring atoms touch each other are also of interest in plastic deformation. Figures S.2 and S.4 show crystals bounded by their \{100\} faces. In FCC crystals, Figure S.2. shows that the atoms touch each other along the \(<110>\) family of directions. In the BCC structure, we have seen in figure S.5 that atoms touch each other along the space diagonals or \(<111>\) family of directions.

The \{111\} planes are the densest planes in the FCC structure. This is easily verified by drawing a (111) plane and placing the atoms on the FCC positions. The same figure will show, as well as S.2 and S.3. that the densest directions are \(<110>\). An FCC structure that is truncated by a (111) plane in figure S.18, shows the dense packing of the latter. In fact, one can show that the FCC structure is a stacking of densely packed (111) planes, just as the hexagonal close packed structure. Thus both structures have the same atomic packing factor \(\text{APF} = 0.74\).

![Figure S.18. FCC structure cut to reveal the (111) plane.](image)

In the BCC structure, the densest planes are \{110\} and the densest directions, in which atoms touch, are the \(<111>\) family. This is illustrated in figure S.19.
Figure S.19. The (110) plane of the BCC structure. (a) inside the unit cell, (b) plane drawing. The dense directions A-C-E and D-C-B are space diagonals of the <111> family.


Most solid objects that we know are polycrystalline solids consisting of numerous small single crystals or grains of random orientation. In these grains, errors abound in the perfect placement of atoms and the stacking of planes. Such effects tend to be magnified at the interfaces where grains fit together. At the outset a distinction should be made between such crystallographic defects, and gross manufacturing defects and flaws like cracks and porosity. Here our concern is with lattice defects having atomic size dimensions. What are the implications of such defects? What properties are influenced by them? These questions will be addressed in various ways in subsequent chapters with the benefit of additional concepts and knowledge of material properties. It will be found, and may be surprising at first, that defects are responsible for many desirable properties: defects are tools that are used to strengthen materials and they are essential in the creation of semiconductor devices. They deserve to be examined more closely.

S.3.1. Point Defects.

A good way to appreciate point defects is through Fig. S.20. All of the defects involve one or, at most, two atoms.

S.3.1.1. Vacancies

These defects exist in all classes of crystalline materials and are represented by a missing atom from a lattice site (Fig.S.20a).

The presence of a vacancy can cause a local relaxation or redistribution of atoms and electrons surrounding it. This accounts for their importance in phenomena involving atomic motion or diffusion in solids. Lattice atoms or impurity atoms that are completely surrounded by nearest neighbor lattice atoms are not mobile. But if there is an adjacent vacancy then the two can exchange places and atomic motion is possible. This subject is addressed again in Sect.xxxx when mass transport in solids is discussed.
S.3.1.2. Impurities.

These are foreign atoms in the material. Some impurities are undesirable and must sometimes be removed by purification. Silicon, used to produce integrated circuits, for instance, can tolerate less than one impurity per 10 million Si atoms. Other foreign atoms are introduced for their beneficial effects. Examples are the doping of semiconductors to make them n- or p-type conductors. Impurities are also introduced to increase the electrical resistance and the mechanical strength of metals. Impurities are substitutional when they occupy a regular crystal site otherwise occupied by a host atom; they are interstitial when they fit in the interstices between the host atoms. Host atoms can also be displaced and occupy interstitial sites as shown in Figure S20a.

Figure S.20. Point defects in solids

S.3.1.3. Point Defects in Ionic Compounds
In alkali halides and metal oxides where positive and negative ions populate lattice sites, point defect structures are more complex. Maintenance of charge neutrality is the reason. To visualize the issues involved let us consider Fig. S.20b depicting an electrically neutral lattice composed of monovalent (positive) cations and (negative) anions. Creation of a cation vacancy means the absence of a single positive charge or an effective negative lattice charge. This defect can not exist by itself because the lattice is no longer electrically neutral. Therefore, a negative ion vacancy is created at the same time and the associated pair (positive ion vacancy + negative ion vacancy) is known as a Schottky defect. Another defect shown in Fig. S.20c consists of a cation that hops into an interstitial site. The resulting cation vacancy-interstitial atom is known as a Frenkel defect.

S.3.2 DISLOCATIONS

Dislocations are defects that extend along a line of atoms in a crystalline matrix. They exist in all classes of solids but are most easily visualized in cubic lattices. There are two fundamental types of dislocations- the edge and screw. An edge dislocation can be imagined to arise by cutting half way into a perfect crystal lattice, spreading the cut apart and then inserting an extra half plane of atoms. The resulting edge dislocation defect, denoted by a perpendicular symbol ⊥, is the line of atoms at the bottom of the inserted plane. It is shown in Fig. S.21a together with one of its chief attributes- the Burgers vector. If a closed loop clockwise traverse is made about a perfect lattice, then the end point coincides with the starting point. A similar traverse around a region containing the core of an edge dislocation will not close, and the vector connecting the end point to the initial point is known as the Burgers vector \( \mathbf{b} \). Its magnitude is one lattice spacing.
at very high resolution.

Figure S.22 Transmission electron micrograph of an edgy dislocation in germanium.

The second type of dislocation can be imagined to arise by first making a cut halfway into the lattice. Then one half is sheared up, the other down until a total relative displacement of one atomic spacing occurs. The resulting screw dislocation is shown in Fig.S.21b together with the Burgers vector that defines it. Making a clockwise circuit about the axis of the dislocation is like going down a spiral staircase. The closure error or Burgers vector is parallel to the screw axis. In this case $\mathbf{b}$ is parallel to the dislocation line.

It frequently happens that a single continuous dislocation line acquires mixed edge and screw character merely by turning a 90° angle corner in the crystal. A plan view of such a mixed dislocation structure is depicted in Fig.S.23.
Figure S.23 Curved dislocation with mixed edge and screw components that emerge at mutually perpendicular surfaces.

S.3.3 GRAIN BOUNDARIES

Virtually all of the materials considered till now have been single crystals. In them the ordered atomic stacking extends over the whole material. All sorts of precious and semi-precious gems found in nature are essentially single crystals. Single crystals are grown for commercial electronic (silicon, quartz), magnetic (garnets), optical (ruby) and even metal turbine blade applications. They can weigh 50 kg and be 30 cm in diameter.

Almost all materials used in engineering, however, are polycrystalline. They consist of a large number of small crystals, or grains, that differ from each other by their crystalline orientation. This is illustrated in figure S24 for the case of brass.

Figure S.24. The grains structure of $\alpha$ brass.
The grains are usually a few micrometers in size, but their size can vary from several millimeters down to a small fraction of a micrometer. In some materials, different grains can also composed of different substances. **Grain boundaries** are the interfaces between the grains.

The simplest model of a grain boundary involves tilting two adjacent single crystal grains relative to each other by a small angle \( \phi \), as illustrated in Fig.S.25a. When the crystals are welded together at the interface (Fig.S.25b), the grain boundary consist of isolated edge dislocations stacked vertically a distance \( L \) apart, where \( L \) is essentially \( b/\phi \).

Since grain boundaries are relatively open structurally, atoms attached to the boundary tend to be more energetic than those within the bulk. Therefore, grain boundaries are the preferred location for chemical reactions (e.g., etching, corrosion) as well as the solid state mass transport effects discussed in Chapter zzz (e.g., diffusion, atomic segregation, phase transformation, precipitation etc.). Furthermore, grain boundaries help resist the processes of deformation under stress. But they are weaker than the bulk and when the material breaks, the fracture often propagates along a grain boundary.

![Figure S.23. Small angle grain boundary. When the difference in orientation between two grains is a small angle, the grain boundary takes the form of an array of dislocations.](image-url)
Summary.

1) Most solid materials are crystalline: their atoms or molecules are arranged in symmetrical structures that are periodic over extended space. Most materials applied in structural applications are polycrystalline; they are composed of a large number of small crystals called grains; many functional materials are single crystals. Glasses and most polymers are amorphous, like liquids: their atoms or molecules assume random positions.

2) Most elements crystallize in the Face Centered Cubic (FCC), the Body Centered Cubic (BCC) or the Hexagonal Close Packed (HCP) structure. Compound materials, especially ceramics, present complex crystal structures.

3) Polymorphism is the ability of a material to crystallize in different structures. It is also called allotropy.

4) The unit cell of a structure is the volume that repeats itself in three dimensions throughout the crystal. Atoms in the corners, edges, and faces of a unit cell are shared with the neighboring cells. The length of the edges of the unit cells is the lattice parameter. Cubic crystals have only one lattice parameter $a$ by reason of symmetry; hexagonal crystals have two lattice parameters, $a$ and $c$, more complex structures have three lattice parameters.

5) Positions of atoms, directions and planes in cubic crystals are described in
Cartesian coordinates where the length of the cell is unity. The coordinates of directions and planes are the Miller indices. Directions are written in whole integers in brackets [ ]. Planes are designated in whole numbers in parantheses ( ). All directions and planes with the same character (e.g. edges of the cube or face diagonals, faces of the cube) have Miller indices that are permutations of the same coordinates, including their negatives (e.g. [100], [010], [001] for edges) and form a family of directions e.g. <100> or a family of planes e.g. {111}.

6) The unit cell of the FCC structure contains 4 atoms; one at the corners and three in the centers of the faces. Its atomic packing factor is the largest possible with spheres. Its densest planes are {111} and its densest directions are <110>.

7) The unit cell of the BCC structure contains 2 atoms, one at the corners and one in the center of the cube. Its atomic packing factor is lower than that of FCC. Its densest planes are {110} and its densest directions <111>.

8) The HCP structure is a stacking of close packed, hexagonal, planes of atoms. Its atomic packing factor is the same as for FCC, the largest possible with spheres.

9) A crystallographic direction is a vector, independent of the latter’s length. [120] = [240] = [½ 1 0]. It is written with the set of smallest integers. It extends from the origin to the atom with the same coordinates, (from the origin to the point (1/2,1,0) in our example. For directions with negative indices, it is convenient to shift the origin to the other edge of the corresponding axis.

10) A plane is defined by the three points at which it intersects the coordinate axes. One notes the point of intersection (one or a fraction); its inverse is the Miller index. To draw the (hkl) plane, one writes the inverse 1/h and draws it on the x axis, one draws 1/k on the y and 1/l on the z axis and joins the three points to draw the plane. When h = 0, 1/h = \infty and the plane is parallel to the x axis.

11) Crystal defects are departures from the periodic array of atoms. They are responsible for many useful properties of materials.

12) Point defects are vacancies, interstitials and impurities. The latter can be substitutional or interstitial.

13) Dislocations are line defects. The edge dislocation is the edge of an additional plane of atoms. The screw dislocation is a line along which the crystal is sheared by one unit cell.

14) Grain boundaries are the interfaces between grains.

Questions and Problems.

S-1. Compute the radius of nickel, gold, chromium and tungsten atoms.

S.2. Compute the atomic densities of nickel, gold, chromium and tungsten.

S.3. Compute the specific mass (mass density) of nickel, gold, chromium and tungsten.

S-4. a. Rhodium has a lattice parameter of 0.3805 nm and the atomic radius is 0.134
nm. Does this metal have a BCC or FCC structure?

b. Niobium has a lattice parameter of 0.3307 nm and the atomic radius is 0.147 nm. Does this metal have a BCC or FCC structure?

S.5. Draw the (111), (110) and (100) planes of copper and place the atoms on each so that they touch.

If one was to build these planes with solid spheres, and one was to put a similar sphere onto them, on which plane could one move the sphere with least resistance? In what direction would it move with least resistance?

S.6. Draw the (111), (110) and (100) planes of chromium and place the atoms on each so that they touch.

If one were to build these planes with solid spheres, and one were to put a similar sphere onto them. On which plane could one move the sphere with least resistance? In what direction would it move with least resistance?

S.7. Based on atomic weights and structural information show that gold and tungsten essentially have the same density. Calculate the density of each.

S.8. Demonstrate that the densities of FCC and ideal HCP structures are identical if sites are populated by atoms of the same size and weight.

S.9. Cobalt exists in an FCC form with \( a = 0.3544 \) nm. What is the theoretical density of the FCC form of Co? What is the theoretical density of HCP Co?

S.10. What are the Miller indices of planes 1, 2 and 3 in Fig.S.25?

S.12. Draw the (110), (110) (011), (1 11) and (221), (2 1 1) planes in a BCC structure and draw the centers of the atoms that sit on them.
S.13. Draw all the directions of the $<111>$ family and give the Millers indices of each.

S.13 Draw the (100) and the (200) planes of the BCC and FCC structures and draw the centers of the atoms that sit on them.

S.11. What are the Miller indices of directions 1, 2 and 3 in Fig.S.26?

![Figure S.26](image)

S.14 A vacancy moves from the surface of a crystal towards the interior: what do the atoms of the crystal do when this happens? Discuss how vacancies increase the diffusion rate in solids.

S.15. Look at the structure of an edge dislocation and justify that “pipe diffusion”, which is the diffusion of atoms along a dislocation core, is much faster than in the bulk.

S.16. Look at a drawing of an edge dislocation and discuss the elastic deformation of the crystal around the dislocation. Can you see that two dislocations repel each other? State why.

S.17. Observe a grain boundary and justify why diffusion along a grain boundary is much faster than through the grains.

S.18. Explain why surface diffusion is faster than grain boundary-, pipe- or bulk diffusion.

S.19. The surface energy is caused by the unsatisfied bonds of surface atoms that lack the neighbors they would have inside the crystal. Study figure S.24 and give reasons why 1. the grain boundaries have a surface energy (i.e. a grain boundary energy) and 2. why the grain boundary energy is smaller than the surface energy.

S.20. Grain growth. When a solid is heated enough so that atoms can move (diffuse), grain boundaries move in such a way that larger grains become larger and smaller grains
shrink until they disappear. Study figure S.24 and give reasons why 1) grain boundaries can move and 2) the larger grain (middle of the picture) will grow and the smaller grains (corners of the picture) will shrink and disappear.