Preface

This book contains a unified approach to crystallography and the structural imperfections and defects found within crystals. The reason the authors chose for treating these two subjects together was that the study of first is necessary for a proper appreciation of the second. Understanding the idea of lattice and of the crystal classes firstly will help its relevance to the study of imperfections, defects and phase transformations in the second part of the book. Split in two parts: the “Structure of the Crystalline Solids” and the “Imperfections and Defects in Crystals”, and each broken into many chapters, this volume combines the classical and exact description of symmetry of a perfect crystal with the possible geometries of the major defects-dislocations, stacking faults, point, line, surface and volume defects, twins, and the effects of martensitic transformation in iron.

The first part of the book presents a systematic treatment of the basics of crystallography, discussing space lattice, unit cells, symmetry, point groups, crystal systems in terms of Miller indices for crystallographic points, directions and planes, and zone axis, as well. A number of important concepts such as packing factor, atomic radius, linear, planar and volume density, polymorphism, allotropes, interstitial sites in cubic and hexagonal structures, and structural features of the most representative compounds used nowadays in a myriad of applications are introduced and carefully explained. In the second part of the book the authors guide the reader in a step-by-step way through point, line, planar and volume defects, with an emphasis on their structural properties.

The book presents a large amount of the latest critically evaluated data for the properties of all elements on the periodic table of the elements, including hundreds of up-to-date crystal structure data. The structure of the book, as a whole and the individual chapters, in particular, are laid out in a way that strongly supports learning. Each chapter contains the logical presentation of concepts supported by suitable chosen examples and worked problems. Hundreds of illustrations within the text help the reader visualize crystal structures and mathematical objects, supporting important topics, but also illustrating crystalline structures found in thousands of compounds. A concise summary and plenty of review questions and problems at the end reinforce the important key points.

Containing a large number of worked example problems, exercises, and detailed descriptions of numerous crystal structures and crystalline imperfections and defects, the book was primarily intended as an undergraduate or graduate level textbook for students in both materials science and mechanical engineering meeting the topic of materials structure for the first time. It may appeal to specialists in chemistry, metallurgy, mineralogy, geology, and materials science who are interested in probing deeper into structural similarities and differences in solid-state compounds and also to educators and students who desire supplementary information about crystal structures, imperfections, and a unique comprehensive collection of the latest data for all Periodic Table elements. Non-experts and novices working on mechanical properties, mechanisms of deformation and fracture, and properties of materials, as well as industrial and academic researchers, may find this book helpful too.

This book was meant from the beginning to be a constantly evolving work on progress. Each chapter and sub-chapter of this book capitalizes on the strengths, comments, feedback and criticism that the authors expect to have from students, faculty and working professionals. As such, all readers sending any comments, suggestions, or notification of errors to the authors at support@shutterwaves.com will be greatly appreciated.

The authors,
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1. Introduction to Solids

Solid - as one of the four fundamental states of matter - has a definitive size and shape to it and is characterized by structural rigidity and resistance to changes of shape or volume. As opposed to fluids such as liquid or gas, a solid does not flow to take on the shape of its container like water, nor does it expand to fill the entire volume available to it or disappear into the air. All solids are rigid because their constituent particles have fixed positions that can only oscillate about their mean positions as opposed to the fluidity of liquids and gases in which their constituent molecules are free to move about. The state of matter usually changes as the temperature or pressure is changed. A gas that is comprised of freely and entirely disordered movable atoms or molecules has a high compressibility because of the large interatomic/intermolecular distances. As the gas cools down or it is squeezed under external pressure the kinetic energy of the constituent atoms, ions or molecules lowers and the interatomic distances decrease until a gas-liquid phase transition occurs. A liquid is characterized by almost freely movable constituent particles and relatively low compressibility because of short interatomic distances. As the temperature goes further down or if the external pressure applied to the liquid is further increased a liquid-solid phase transition occurs. Water is probably the most familiar substance that commonly exhibits in all three phases. However, many substances will exhibit the solid, liquid, and gas phases under certain conditions. For example, liquid water exists in clouds as tiny droplets condensed from water vapor in the air. In another example, we normally experience carbon dioxide ($CO_2$) as a gas, but if it were cooled down to about -78.5°C, it would convert to a solid phase. The frozen solid carbon dioxide form, known as dry ice, is used as a refrigerant and as an abrasive in dry-ice blasting. In the medical field, dry ice is used to preserve medical specimens, blood products, and drugs. It has also dermatological applications such as freezing off warts. Organs for transplants are preserved with dry ice until the recipient of the new organ is ready for surgery.

The following are the distinctive properties of the solid state:
- definite mass, volume and shape
- almost immobile constituent particles that can only oscillate about their mean positions
- very low compressibility and high rigidity
- short interatomic or intermolecular distance range
- strong interatomic, ionic or molecular forces
- long range and periodic ordering of atoms, ions or molecules.

As we may remember from our chemistry classes, the types of atomic bonding are primarily determined by the electronic configurations of the individual atoms. The arrangement of atoms in a solid depends on both external parameters such as temperature and pressure, but also on “internal” parameters such as electronic configuration of the atoms, and atomic or ionic radii, as well. These parameters determine the nature and strength of bonding between constituent atoms. Throughout next chapters of this book we will focus on solids in the crystalline state as the most prominent state of condensed matter.

2. General Properties of Solids

Melting is the process most often used to form an aggregate of atoms. When the temperature of a melt is lowered to a certain point, the liquid will undergo a phase transition to the solid state, either to a crystalline solid or an amorphous solid. The atoms, ions or molecules in a solid are tightly bound to each other, either in a
regular geometric way or irregularly. Based on the spatially arrangement, amorphous, polycrystalline and single (mono) crystals are the three general types of solids. Pure materials or mixtures whose constituents are arranged in a regular pattern throughout the entire volume of the material are called **single-crystal** materials, as pictured in Figure 1-1(a). A few examples of pure substances or mixtures that are crystalline solids at room temperature and pressure are copper, diamond, silicon (single crystal grown in a controlled environment), and sodium chloride (NaCl). In a single-crystal material there is a precise, long-range repeating order, or regular geometric periodicity, which can therefore be described as being composed of atomic, ionic or molecular building blocks that repeat across the whole volume.

Crystalline solids have a sharp melting point, but are **anisotropic** in nature. When properties of a material vary with different crystallographic orientations, the material is said to be anisotropic. Some mechanical, electrical and optical properties of crystalline solids show different values when measured along different directions in the same crystal structure. For example, in a crystalline material such copper its constituent ions are able to slip over one another or distort in relation to one another easier in some directions than others. Single crystals are produced only under carefully controlled conditions. Special applications, such as solid state components used in electronics, solar cells, and piezoelectric materials require crystalline materials. Many crystalline solids exist as fused polycrystalline masses, which are single-crystal regions called grains that are separated from one another by grain boundaries (the interface formed between grains is called a grain boundary). Usually when a molten material begins to solidify, multiple single crystals begin to grow in the liquid phase and **polycrystalline solid** forms. A grain is basically a single crystal without smooth faces because its growth was impeded by contact with another grain or a boundary surface.

At the microscopic level polycrystalline materials have a high degree of order (over many atomic or molecular dimensions), but the order is not readily apparent at the macroscopic level, as schematically pictured...
in *Figure 1-1(b)*. The atoms arranged at the grain boundaries have no crystalline structure and are said to be disordered. Electrical properties of a single-crystal material are superior to those of a polycrystalline material since grain boundaries tend to degrade them to some extent. A rapid cooling of a molten material generally results in smaller grains (a fine grain structure) while slow cooling generally results in larger grains.

At the microscopic level **amorphous solids** have order only within a few atomic or molecular dimensions, in which atoms, ions or molecules are positioned in an irregular manner with no long-range order, as shown in *Figure 1-1(c)*. For example, common glass is usually made from crystalline silicon dioxide (SiO₂), also known as silica or quartz sand. When the quartz sand is melted and the liquid is cooled rapidly enough to avoid crystallization, an amorphous solid called “glass” is formed. Amorphous solids do not show a sharp phase change from solid to liquid at a definite melting point. The physical properties of amorphous solids are identical in all directions along any axis so the material is said to be **isotropic**. Example of amorphous materials at room temperature and pressure are glasses, many ceramics, and synthetic fibers. Pure materials such as phosphorus (P) or sulfur (S) exist also in amorphous form. Amorphous materials soften over a range of temperature and can be molded and blown into various shapes; just remember how artists create such beautiful shapes of molded and blown glass! Amorphous materials also have the tendency to flow, though very slowly. For example, if you were about to check the thickness uniformity of glass panels fixed to windows or doors of old buildings you will always find them as being slightly thicker at the bottom than at the top. This happens because the glass constituents flow down very slowly over time and makes the bottom portion of the panel slightly thicker. Amorphous solids are isotropic in nature, which means, the value of any physical property would be the same along any direction. It is because there is no long range order of the constituent particles and the arrangement is irregular along all directions.

The specific crystalline structure a solid material adopts depends on the material involved and how it was formed. Usually solids that are formed by slow cooling will tend to be crystalline, while solids which are frozen rapidly are more likely to present an amorphous state. For example, monocrystalline silicon that is used in semiconductor industry is obtained by slowly cooling down molten polycrystalline silicon in a process called crystal growth. Real single crystals are not perfect; they always have imperfections such as impurities, extra or misplaced atoms, missing atoms (voids) and other defects. While many properties of crystalline systems depend upon the periodic lattice arrangement, other properties (i.e. ductility, malleability, strengthening, and conductivity just to name a few) can be improved by adding defects or dopants to the crystal. On the other hand, unintentionally induced defects can also have a profound impact on the properties of materials. Like liquids, solids are condensed phases whose basic properties are determined by the nature of the interactions holding their constituent particles together. Based on these fundamental interactions, we can broadly classify solids as ionic, metallic, covalent or van der Waals. For example, a crystal of cesium chloride (CsCl) is an ionic solid because cesium anions and chlorine cations are held together by strong ionic bonds. In metallic solids, the positive ions are held together by a high density of shared and delocalized electrons. Copper, silver, gold and aluminum are common examples of metals. In diamond (an allotrope of carbon), silicon, germanium and α-tin (gray tin, or non-metallic tin) the atoms share electrons and form strong covalent bonds. Some solids, particularly molecular halogens, diatomic molecules of nonmetals, all noble gases at very low temperature, and most organic compounds, are held together by van der Waals forces. Our primary emphasis put on each chapter of this book will be on single crystalline solids whose atoms are bonded strongly enough to form a rigid structure with a unique arrangement of atoms, ions, or molecules that result in a regular and periodic geometric pattern.

### 3. Space Lattice, Conventional and Primitive Unit Cells

A space lattice – called also a **Bravais lattice** - is a three-dimensional array of regularly spaced points coinciding with the atom, ion or molecules positions in a crystalline structure. A space lattice is illustrated as points in space, representing the atoms, or ions or molecules of the crystalline solid, which can be connected with geometrical lines to form repeating shapes. Conversely, the collection of the lattice points that describe the crystalline solid defines a **crystal lattice**. The concept of crystal lattice is illustrated in *Figure 1-2* using an
infinite two-dimensional (2-D) array of lattice points and also in Figure 1-4 using a three-dimensional (3-D) array of lattice points. Each lattice point in Figure 1-2 can be translated a distance \( a_0 \) in one direction and a distance \( b_0 \) in a second noncollinear direction to generate the two dimensional lattice. If we add a third no collinear direction then we will generate a three-dimensional lattice, such pictured in Figure 1-4.

A **unit cell** is the smallest structural unit or building block that possesses the highest symmetry present in the lattice that can describe completely the crystal structure. A unit cell is not a unique building block (entity), which is pictured in Figure 1-2, where various possible unit cells are illustrated for a two-dimensional space lattice. The unit cell B can be translated in directions \( a_1 \) and \( b_1 \), the unit cell C can be translated in directions \( a_2 \) and \( b_2 \), the unit cell D can be translated in directions \( a_3 \) and \( b_3 \) and the unit cell E can be translated can be translated in directions \( a_4 \) and \( b_4 \), thus the entire two-dimensional space lattice can be generated by using appropriate translations of either of these unit cells. Repetition of the unit cell generates the entire crystal. As sketched in Figure 1-3, a unit cell is seen as an ‘imaginary’ parallel sided region of a crystalline structure from which the entire crystal can be constructed by purely translational displacements. The content of the unit cell must represent the chemical composition of that crystalline material. These repeating patterns, which generate symmetries in a crystalline material, allow us to easily identify specific properties of solids.

A **primitive unit cell** is the smallest unit cell that can be translated through all vectors to completely recreate the entire Bravais lattice without overlapping or leaving voids. A primitive unit cell contains just one Bravais lattice point. The primitive unit cell is smaller or equal in size to the unit cell. In many cases, it is more convenient to use a (conventional) unit cell that is not a primitive unit cell. For example, a unit cell may be chosen to have orthogonal sides, while the sides of the primitive unit cell of the same lattice system may not be orthogonal. Figure 1-4 illustrates a 3-D array of atoms in a periodic lattice that can be represented as a sum of primitive unit cells. In a single unit cell – as the one pictured in Figure 1-5, a set of axes \( x, y, \) and \( z \), describes the edges of this unit cell. The lengths of the edges are defined by distances, known as lattice parameters (or lattice constants) as follows:

- \( a \) on the \( x \)-axis
- \( b \) on the \( y \)-axis
- \( c \) on the \( z \)-axis
Every equivalent lattice point in the three-dimensional crystal lattice can be found using the vector

$$\mathbf{r} = m\mathbf{a} + n\mathbf{b} + o\mathbf{c}$$

where \(m\), \(n\), and \(o\) are integers whose values depend on the lattice site and the magnitude of the vectors \(\mathbf{a}\), \(\mathbf{b}\), and \(\mathbf{c}\) are called the lattice constants of the unit cell. Very often it is more convenient to deal with a conventional (non-primitive) unit cell, which has additional lattice sites inside its volume or on its surface, is larger, and it exhibits the symmetry of the lattice more clearly, as we will see it later in this book.

4. Crystal Systems and Bravais Lattices

In crystallography the concept of symmetry describes the periodic repetition of structural features. There are two general types of symmetry operations used; translational symmetry and point symmetry. Earlier we discussed that if a specified motif - the unit cell - is translated linearly and repeated many times at fixed intervals throughout space then it will produce a space lattice. Thus the concept of lattice is directly related to the translational symmetry operation. In 1848 the French physicist **Auguste Bravais** (1811-1863) discovered that there are 14 unique lattices in the three-dimensional crystalline systems grouped in 7 crystal lattice systems. These lattice systems are cubic, tetragonal, hexagonal, orthorhombic, monoclinic, rhombohedral, and triclinic. The Bravais crystal lattices are classified in Table 1-1 and schematically pictured in Figure 1-7.

![Figure 1-4. A space lattice in a crystalline solid looks like as an infinite three-dimensional array of atoms that are arranged in an ordered network where each atom has identical surroundings (the reduced-sphere unit cell is highlighted in pink-dashed line above).](image)

![Figure 1-5. A generalized primitive unit cell of a space lattice showing the lattice constants \((a, b, c)\) along with corresponding angles between them \((\alpha, \beta, \gamma)\). The entire infinite lattice is specified by the primitive vectors \((\mathbf{a}, \mathbf{b}, \mathbf{c})\).](image)

![Figure 1-6. A crystal in a shape of a trapezohedron is composed of 24 trapezium-shaped faces, 48 edges and 26 solid angles. Its faces are symmetrical, quadrilateral figures. All faces intersect two of the crystallographic axes at equal lengths and intersect the third crystallographic axis at a smaller distance. The minerals of the garnet group, and two silicate minerals, analcime (hydrated sodium aluminum silicate) and leucite (potassium alumina silicate), are the only common minerals that form the trapezohedrons.](image)
Crystalline systems are cubic, tetragonal, hexagonal, orthorhombic, monoclinic, trigonal, and triclinic. Five of the crystalline systems are essentially the same as five of the lattice systems, but the hexagonal and trigonal lattice systems differ from the hexagonal and rhombohedral lattice systems.

**Figure 1-7.** The fourteen Bravais conventional unit cells grouped in seven different crystal lattice systems.
A crystal family is determined by the smallest set of space groups belonging to the same lattice. In three dimensions there are six crystal families; five of them are the same as crystal systems and lattice systems, except that the hexagonal and trigonal crystal systems are combined into one hexagonal family. As mentioned in Table 1-1 in three dimensions (3-D) there are 14 different Bravais crystal lattices which belong to 7 crystal systems and 6 crystal families. The spherical “dots” (or small spheres) in Figure 1-7 indicate lattice points. In all the cases the conventional unit cell is represented by a parallelepiped whose sides are \( \mathbf{a}, \mathbf{b}, \mathbf{c} \) with angles \( \alpha, \beta, \gamma \). The relationship between the magnitude of the vectors \( \mathbf{a}, \mathbf{b}, \mathbf{c} \) (referred as lattice parameters \( a, b, c \)) and the angles \( \alpha, \beta, \gamma \) determines the crystal lattice system. All lattice points that are located at the corners or on the faces of the unit cell are shared by other identical conventional unit cells.

As shown in Figure 1-7 there are four basic types of unit cells: (1) simple, (2) body-centered, (3) face-centered, and (4) base-centered. A simple lattice has sites only at the corners, a body-centered lattice has one additional point at the center of the unit cell, a face-centered lattice has six additional points, one on each side (or face), and the base-centered lattice has one additional point at the center of the base of the unit cell. In all simple lattices the unit cells are primitive unit cells while in all the non-simple lattices the unit cells are non-primitive. The volume of a primitive unit cell is equal to the volume of the conventional unit cell divided by the number of sites (spheres or dots representing atoms, ions or molecules). The most symmetrical crystal system is cubic; all unit cell edges are equal and all angles between the edges are equal to 90°. The least symmetrical crystal system is triclinic; all unit cell edges are unequal and all angles between the edges are not equal to each other and also not equal to 90°. In the cubic system there are three types of unit cells: simple or primitive cubic (SC), body-centered cubic (BCC), and face-centered cubic (FCC). The difference between these unit cells is in the number of lattice points per unit cell. In the tetragonal system there are only two unit cells: simple and body-centered. In the orthorhombic system all four types of unit cells are represented while the monoclinic system has simple and base-centered unit cells. The hexagonal, rhombohedral, and triclinic lattice systems have only one simple type of unit cell.

When describing and illustrating crystalline structures it is useful to consider the atoms or ions as being solid (hard) spheres with well-defined radii. In this atomic hard sphere model the spheres representing nearest-neighbor atoms touch one another and the shortest distance between two like atoms is one diameter, as used in physics and chemistry books while defining the atomic radius (see also references [59] and [60]).

Table 1-2 features some structural properties of the elements on the Periodic Table of the Elements, including the type of lattice systems, lattice parameters, and atomic radii of the elements in their solid state. As noticed, about 80 % of the elements (especially metals and metalloids) crystallize in either the cubic or hexagonal crystalline systems. Other important data (as illustrated below) such as atomic weight, melting points, density in solid state at room temperature or near melting point, electron configuration, and electronegativity (Pauling negativity number) are data compiled for almost every single element in our periodic table, as illustrated in Figure 1-8.
<table>
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<th>Symbol</th>
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<th>First ionization energy, ([kJ/mol])</th>
<th>Melting point, [K]</th>
<th>Density near r.t. or m.p. ([grams/cm^3])</th>
<th>Type of lattice or crystal system at standard temperature and pressure ((STP)) or at ((SP)) or at melting point</th>
<th>Ionic radius ***, ([pm])</th>
<th>Covalent radius **, ([pm])</th>
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<td>S</td>
<td>16</td>
<td>S</td>
<td>3.15</td>
<td>102</td>
<td>102</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
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<td>17</td>
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<td>3.0</td>
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<td>133</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
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<td>72(2+</td>
<td>72(2+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>20</td>
<td>Ca</td>
<td>3.0</td>
<td>176</td>
<td>176</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Note:** \(a, \beta, \gamma = 90^\circ\) for cubic lattices, \(a = \beta = \gamma = 120^\circ\) for hexagonal lattices, \(a = \beta = \gamma = 90^\circ\) for trigonal lattices.

**TABLE 1-2. Physical, chemical and crystallographic data of the elements on the Periodic Table**
Figure 1-8. Periodic Table of the Elements containing up to 16 physical and chemical data for each of the 118 elements.
5. Most Common Crystal Structures among Natural Elements

More than 90% of naturally occurring and artificially prepared solid materials are crystalline. A large variety of minerals such as salts (i.e. $\text{NaCl}$, $\text{KCl}$), pyrite, zircon, quartz, calcite, tourmaline, orthoclase, aragonite, gypsum, albite (several of them are listed in Table 1-3), as well as metals, carbon allotropes (diamond and graphite), silicon and germanium, all have crystalline structures. Looking at the Table 1-2 we may notice that about 90% of metallic elements crystallize predominantly in one of the three Bravais lattices: body-centered cubic (BCC), face-centered cubic (FCC), and hexagonal (HEX) structures. Therefore, these three important types of crystal lattice structures – out of the 14 different types of Bravais crystal lattices - will be addressed in a broader detail throughout this book. Throughout this volume we will also use cubic-close packed (ccp) and hexagonal closest-packed (hcp) names as alternate names for the face centered cubic (FCC) and hexagonal (HEX) unit cells when describing closest packed structures in which the constituent atoms, ions or molecules have been packed in the most efficient (least volume) way possible.

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>Examples of natural crystals</th>
<th>Crystal System</th>
<th>Examples of natural crystals</th>
</tr>
</thead>
<tbody>
<tr>
<td>2. Hexagonal</td>
<td>Apatite, Beryl, Zincite, $\beta$-Quartz</td>
<td>6. Triclinic</td>
<td>Plagioclase, Albite, Axinite, Kyanite,</td>
</tr>
<tr>
<td>3. Orthorhombic</td>
<td>Topaz, Sulfur, Baryte, Olivine, Aragonite, Andalusite, Chalcolite</td>
<td>7. Trigonal (includes hexagonal &amp; rhombohedral lattice systems)</td>
<td>$\alpha$-Quartz, Calcite, Corundum, Tourmaline, Dolomite, Magnesite, Rhodohrosite, Hematite, Siderite, Cinnabar</td>
</tr>
<tr>
<td>4. Tetragonal</td>
<td>Zircon, Rutile, Scheelite, Chalcopyrite, Vesuvianite</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The study of crystalline structures is important not only for a better understanding of some physical properties of materials but also provides the necessary knowledge to learn how to differentiate two minerals made out of the same constituent atoms. For example, let us take in consideration two commonly used minerals; diamond and graphite. Both diamond and graphite are made out of the same element; carbon (it is said that diamond and graphite are the allotropes of carbon). Diamond is a very hard, transparent, non-conductive and colorless material, being used in cutting materials and tools as well as in jewelry (a very expensive gemstone too), while graphite is a soft, electrically conductive and dark colored material found in pencils and motor carbon brushes. Additionally, there are other two allotropic forms of carbon, fullerenes and carbon nanotubes, which exhibit strong covalent bonding similar to that in the sheets of graphite structure. The reason diamond and graphite are so different from each other is because the carbon atoms are bound and stacked together differently into two different crystalline structures. Diamond is comprised of carbon atoms bounded and stacked tightly together in a tridimensional network (each carbon atom is bonded by strong covalent forces to other four carbon atoms), making it a very strong material (the hardest natural material), while graphite is composed of carbon atoms that are arranged in rings bonded by strong covalent forces in planar layers (sheets) loosely bonded and stacked together in parallel sheets (each carbon atom is covalently bonded to three surrounding carbon atoms in the same layer), making it a soft material. This example shows us how important is to know what atoms are in that mineral and how those atoms are stacked together within the crystal. In another example, it is known that crystal planes with atoms (ions) that are closely packed slide easier by each other compared to those planes with lower packing densities. Gold, which has an FCC (ccp) crystal structure, exhibits more ductility (they deform plastically more readily under load conditions before breaking) than iron, which crystallizes in a BCC structure. Metals such as chromium, iron, molybdenum and tungsten that crystallize in a BCC structure, although cubic, are not closely packed, but they form strong structures. Platinum, copper, silver and gold, which crystallize in an FCC structure, are ductile materials because of the cubic close packing property. Hexagonal closely packed (hcp) metals such as titanium, cobalt,
7. Crystallographic Points, Directions and Planes

Special directions and planes within crystal structures play an important role in explaining properties such as plastic deformation, electrical or thermal conductivity, spatial expansion, hardening etc. For example, graphite has high values for thermal and electrical conductivity along the layer planes (a-direction) and low values perpendicular to these planes (c-direction). In graphite (an allotrope of carbon) the carbon atoms are arranged in rings (similar to a honeycomb lattice) bonded by strong covalent forces; each carbon atom is covalently bonded to three of its neighboring atoms in the same layer (Figure 1-24).

The fourth valence electron of each atom is present between different layers and is free to move about. These free electrons make graphite a good conductor of electricity. In the planar direction, which is parallel to the carbon rings (a-direction), the crystal is very strong (the internuclear distance is just 142.1 pm). The layer planes formed by these carbon rings are then bonded together by much weaker van der Waals’s forces, so the crystal is very weak along the direction perpendicular to the layer planes (along c-direction, as illustrated in Figure 1-24). Thermal expansion of graphite is low in the parallel plane layers and high in the perpendicular direction. Different layers can slide one over the other; this makes graphite a soft solid and a good solid lubricant.

Figure 1-24. Crystalline structure of graphite

Figure 1-25. Some representative planes in an FCC crystal system using the ball and stick model.
A “family” of planes contains all planes that are crystallographically equivalent. For other crystalline structures (i.e. rhombohedral, monoclinic) the face planes are not all symmetrically related. For example, the (111), (111), (111), (111), (111), (111), (111), and (111) planes all belong to the {111} family in cubic crystals. Also, in the cubic crystalline system only, planes having the same indices, regardless of order and sign, are equivalent. In general, all permutations of \((hkl)\) with their negatives constitute the \(\{hkl\}\) family. Families of planes are very important in interpretation of X-ray diffraction patterns, shapes of monocristalline materials, and the movement of dislocations (slips) in materials.
Therefore, the atoms occupy 68.02% of the volume of the unit cell. Lithium, sodium, potassium, rubidium, cesium, chromium, iron are few examples of elements with BCC crystal structures.

The volume density for a metal with a body-centered cubic crystalline structure can be obtained using the following formula:

\[
\rho = \frac{n \cdot m_a}{V_{uc}} = \frac{2 \cdot A}{a^3 \cdot N_A} = \frac{3 \sqrt{3} A}{32 R^3 N_A} \rightarrow \rho_{bcc} = \frac{3 \sqrt{3} A}{32 R^3 N_A}
\]

where cube’s edge \( a \) is related to the radius of the atom by \( \sqrt{3}a = 4R \).

### 9.3 Packing Factor, Atomic Radius, and Volume Density for FCC Crystals

In a face-centered cubic unit cell, the atoms lying along the face diagonal are in contact with each other. Thus the diagonal of each face must have a length of \( 4R \), where \( R \) is the radius of an atom, as illustrated in Figure 1-49. From Pythagoras, the length of the face diagonal is \( \sqrt{2}a \), where \( a \) is the lattice parameter. Therefore, the length of the face diagonal of the FCC structure can be related to the radius of the atom by \( \sqrt{2}a = 4R \). Hence,

\[
R = \frac{\sqrt{2}}{4} a
\]

The number of atoms contained in the cube is four: half atom from each of the six faces and one-eighth of an atom of each of the eight corner atoms, which counts for a total of four atoms per unit cell. The volume of one atom is \( \frac{4\pi R^3}{3} \) and the volume of the unit cell is \( a^3 \). After substituting the volume of the atoms and the volume of the unit cell in the packing factor for the FCC, then we have:
9. Packing Factor, Atomic Radius and Volume Density

The atoms occupy 74.05% of the volume of the FCC unit cell. In metals, the packing factor of 0.74 in the FCC crystal structures is the most efficient packing possible. Calcium, aluminum, copper, silver, gold, and lead are elements with FCC crystal structures at room temperature. The volume density for a metal (or any compound) with an FCC crystalline structure can be obtained using the following formula:

\[
\rho = \frac{n \cdot m_a}{V_{uc}} = \frac{4 \cdot A}{a^3 \cdot N_A} = \frac{\sqrt{2}A}{8R^3N_A} \rightarrow \rho_{FCC} = \frac{\sqrt{2}A}{8R^3N_A}
\]

where cube’s edge \( a \) is related to the radius of the atom by \( \sqrt{2}a = 4R \).

9.4 Packing Factor, Atomic Radius, and Volume Density for HEX Crystals

Earlier in Chapter 6 we demonstrated that the difference between the FCC and hcp is related to the stacking sequence; the hcp layers cycle among the two equivalent shifted positions with an alternating ABAB... arrangement (see Figure 1-50), where the atoms of the third plane are in exactly the same position as the atoms in the first plane, whereas the FCC layers cycle between three shifted positions. Consequently, the face-centered cubic and ideal hexagonal close-packed structures both have a packing factor of 0.74, consist of closely packed planes of atoms, and have twelve close neighbors (coordination number CN12). To determine the ideal c/a ratio for an hcp structure and then to demonstrate that the packing factor of a hcp structure is 0.74 let us firstly consider the tetrahedron labeled as ABCD, which is reconstructed on the right side of Figure 1-50. The atom at point D is midway between the top and the bottom faces of the hcp unit cell. Thus \( \overline{OD} = c/2 \), where point O represents the centroid of the equilateral triangle ABC through which the segment \( \overline{OD} \) is perpendicular on the top face of the hcp unit. Atoms at A, B, C, and D, all touch one another, so the distance
Thereupon the percentage volume change upon cooling, when tin transforms from $\beta$-Sn to $\alpha$-Sn is:

$$
\% \Delta V = \left( \frac{V_{\alpha-Sn} - V_{\beta-Sn}}{V_{\beta-Sn}} \right) \cdot 100 = \frac{34.157 \times 10^{-30} \text{ m}^3 - 27.054 \times 10^{-30} \text{ m}^3}{27.054 \times 10^{-30} \text{ m}^3} \cdot 100 = 26.3 \%
$$

As noticed, tin expands about 26.3 % during the allotropic phase transformation at 13.2 °C (56 °F or 286.35 K). This allotropic transformation, termed tin pest, could have serious repercussions when considering a solder joint lifetime in electronic components. As we know tin represents a major component in almost all soldering materials used in electronics. During their lifetime, electronic components are exposed to a wide range of environmental and temperature variation (e.g. -50 °C to 120 °C) that could diminish the reliability of the solder joint. A temperature change within the range -50 °C to 120 °C, for example, causes strain within the solder joints coming from the difference in thermal expansion coefficients between each component that constitutes the joint but also from the phase transformation.

(c) The atomic packing factor is calculated as the ratio of the volume occupied by the atoms in the unit cell and the volume of the unit cell, as follows

$$
\text{Atomic Packing Factor} = \frac{\text{total volume occupied by atoms in the unit cell}}{\text{volume of the unit cell}}
$$

For an atomic radius of 151 pm for Sn in $\beta$ form the atomic packing factor is:

$$
APF = \frac{V_{\beta-Sn} \cdot 4}{V_{\alpha-Sn} \cdot 4} = \frac{4\pi (151 \times 10^{-12} \text{ m})^3}{108.216 \times 10^{-30} \text{ m}^3} = 0.5353 = 53.53 \%
$$

Note: Chemists still believe that the downfall of unstoppable Napoleon’s army marching toward Russia in December 1812 was army uniforms themselves. All of the army’s clothing had tin buttons. As explained above when exposed to a bitter cold, as French army encountered in Russia that time, tin disintegrates into a fine powder because of allotropic phase transformation. Could the disintegration of tin buttons lead to the downfall of one of the greatest armies throughout history? Many historians do not believe in this theory of Napoleon’s defeat, but this explanation demonstrates the extent to which everyday materials and their properties could affect and change the course of history.

### 11. Interstitial Sites in Cubic and Hexagonal Structures

In all crystal structures there are small empty spaces (called also holes, gaps, sites, interstices) between regular host atoms (or ions) into which smaller – usually different – interstitial atoms (or ions) may be placed. These locations are called interstitial sites. An atom (or ion), when placed into an interstitial site, touches two or more regular atoms (or ions) in the lattice. This interstitial atom (or ion) has a coordination number equal to the number of the atoms (ions) it touches. For cubic and hexagonal crystalline structure, the interstitial sites are categorized in three types: cubic, tetrahedral and octahedral sites (see Figure 1-57, where the octahedral and tetrahedral interstitial sites in hexagonal and cubic unit cells are illustrated).

The cubic interstitial site, with a coordination number of eight, occurs in the simple cubic crystalline structure. An atom or ion in the cubic site touches eight other atoms or ions located at the corners of the cube. An octahedral interstitial site for an (interstitial) atom is the space in the interstices between six host atoms that form an octahedron, in which four octahedral sites are positioned in a plane and the other two interstitial sites are positioned in symmetrical positions, just above and below. An atom or ion in the octahedral site touches six other atoms or ions.

The octahedral interstitial sites, with a coordination number of six, exist in FCC, HEX and BCC crystal structures as illustrated in Figure 1-57. A tetrahedral interstitial site is the space in the interstices between four host atoms that form a tetrahedron. An atom or ion in the tetrahedral interstitial site touches four other atoms or ions. In a tetrahedral site the interstitial site is in the center of a tetrahedron, in which three atoms, touching each other, are in plane, and the fourth atom sits in the symmetrical position on top.
The tetrahedral interstitial sites, with a coordination number of four, exist in all crystals with FCC, HEX and BCC structures, as shown in Figure 1-57. Studying interstitial sites for the most prominent simple crystals is important because we can derive more crystalline structures of compounds with two or more elements by partially or completely filling the interstitial sites with atoms or ions of a foreign (extrinsic) type, e.g. carbon C in iron Fe, gallium Ga in arsenic As or oxygen O in silicon Si. This analysis is especially useful for learning and understanding crystalline structures of compounds with dissimilar atoms or ions sizes where “small” atoms or ions (often cations) fit into the interstices between “large” atoms or ions (often anions) and plays an important role in determining solubility of impurities and phase stability of alloys. As we will see later there are a number of possible interstices to choose – depending on which atom, or ion, would fit best. So let us determine the number and size of interstitial sites in some basic crystalline structures.

### Number and Sizes of Interstitial Sites in SC, BCC, FCC and HCP Crystalline Structures

The size of an interstitial atom is defined as the diameter of the maximum hard sphere which can be accommodated in the interstitial site without distorting the lattice by pushing the surrounding host atoms apart. In all calculations below we will provide the ratio between the radius of the interstitial atom and the radius of the host atom. Later on we will see that a certain range for the radius of the interstitial atom to the radius of the host atom radius will define what type of coordination the interstitial atom might have.

#### 11.1 Interstitial Sites in SC Crystal

There is only one interstitial site in a cubic simple crystal structure, located at the center of the cube, which has the coordinates \( \left( \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right) \). The radius of the largest sphere that can be placed in the cube’s interstitial site without pushing the regular atoms apart can be simply obtained by analyzing a plane within the cube that contains the interstitial atom and the host atom in a touching condition.
However, for FCC unit cell the cube’s edge length (lattice parameter) $a$ is related to $R$ as $a = 4R/\sqrt{2}$; therefore, solving for $r$ from the above equation gives

$$2r = a - 2R = \frac{4R}{\sqrt{2}} - 2R \rightarrow r = \frac{2R}{\sqrt{2}} - R \rightarrow r = \left(\frac{2}{\sqrt{2}} - 1\right)R \rightarrow \frac{r}{R} = (\sqrt{2} - 1) = 0.414$$

So if the interstitial atom or ion has a radius $r$ that is larger than 0.414 $R$, then the interstitial atom (or ion) will push the surrounding atoms slightly apart and will have a coordination number of six. Thus for a host atom of radius $R$, the size of an octahedral interstitial site for FCC structures is approximately $0.414/0.291 = 1.42$ times than that for BCC structures.

### 11.5 Tetrahedral Interstitial Sites in FCC Crystals

The tetrahedral interstitial sites in FCC unit cells are located at $1/4$ along the space diagonal away from the corners of the cube (as pictured in Figure 1-62 (a)-to-(e)). There are eight tetrahedral interstitial sites, twice as many as host atoms or octahedral interstitial sites in an FCC structure. The centers of all eight tetrahedral interstitial sites are located at the center of each small cube that may result from hypothetically dividing the unit cell into eight small cubes, having the coordinates $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and all crystallographically equivalent sites.

In the drawings illustrated in Figures 6-62(d) and (e) are shown the atoms lying on cube’s diagonal plane (110) of the FCC unit cell; the tetrahedral interstitial site is located $1/4$ along the space diagonal away from the right upper corner of the cube (as pictured in Figure 1-62(e)). In a touching condition the sum of the radius of the interstitial atom that will just fit into the tetrahedral interstitial site ($r$) and the radius of the host atom ($R$) must equal $1/4$ of the diagonal length ($\sqrt{3}a$); that is

$$r + R = \frac{\sqrt{3}a}{4}$$

**Figure 1-62.** The 2-D and 3-D arrangement of host atoms and tetrahedral interstitial sites in an FCC unit showing the relationships between geometrical parameters used to calculate the radius of the tetrahedral interstitial atom. (a) tetrahedral interstitial sites with their coordination polyhedra in a reduced-sphere unit cell representation; (b) tetrahedral interstitial atoms in an isolated hard-sphere unit cell representation; (c) locating cube’s diagonal plane (110) in the unit cell; (d) cube’s diagonal view (cutaway diagram), showing the host atoms and tetrahedral interstitial atoms laying on the diagonal (110) plane; (e) 2-D representation of cube’s diagonal plane (110), showing the geometrical relations between the radius $R$ of a host atom, radius $r$ of a tetrahedral interstitial atom, and lattice parameter $a$.

For FCC structures the cube’s edge length (lattice parameter) $a$ is related to to $R$ as $a = 4R/\sqrt{2}$; therefore, solving for $r$ from the above equation gives
Zinc anions occupy the diagonally opposite tetrahedral interstitial sites to minimize cation-cation electrostatic repulsion. Zinc blende has a bulk density of 4.09 g/cm³ and its edge length (lattice parameter) is 5.421 Å, where the radius of the Zn²⁺ cation is \( r_{\text{Zn}^{2+}} = 74 \text{ pm} \) and the radius of the S²⁻ anion is \( r_{\text{S}^{2-}} = 184 \text{ pm} \). The ratio of cation to anion radius is about \( \frac{r_{\text{Zn}^{2+}}}{r_{\text{S}^{2-}}} = 0.402 \), and according to Pauling’s rule mentioned in Table 1-7, Zn²⁺ cations should have a coordination number of 4. Indeed, both zinc and sulfur ions have tetrahedral coordination. Consistent with a 1:1 stoichiometry, there are four sulfide anions to match the four zinc cations found completely within the unit cell. The atomic packing factor for zinc blende is about 70%. A range of III-V compounds (i.e. elements from Groups 13 and 15 of the periodic table) have the zinc blende structure and some of them, for example GaAs, are important semiconductors used in electronics (the structure of GaAs is identical with the ZnS structure). The lattice parameters of some crystal compounds with zinc sulfide (sphalerite) structure are presented in Table 1-13.

### Table 1-13. Crystal compounds with zinc sulfide (sphalerite) structure

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice Parameter (Å)</th>
<th>Lattice Parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>AIAs</strong></td>
<td>5.6605</td>
<td>5.832</td>
</tr>
<tr>
<td><strong>AlP</strong></td>
<td>5.451</td>
<td>6.077</td>
</tr>
<tr>
<td><strong>AlSb</strong></td>
<td>6.1355</td>
<td>6.481</td>
</tr>
<tr>
<td><strong>GaAs</strong></td>
<td>5.6534</td>
<td>6.0583</td>
</tr>
<tr>
<td><strong>GaP</strong></td>
<td>5.4505</td>
<td>5.869</td>
</tr>
<tr>
<td><strong>GaSb</strong></td>
<td>6.0959</td>
<td>6.478</td>
</tr>
</tbody>
</table>

**14.7 Wurtzite, ZnS**

While the zinc blende (sphalerite) structure is derived from the cubic close-packed structure by placing atoms of a different type at the lattice points at every other tetrahedrally coordinated interstitial sites, the same compound of zinc sulfide, ZnS with a related structure can be obtained by filling alternately layers of tetrahedrally coordinated interstitial sites in the hcp structure, as illustrated in Figure 1-74. This is the \( \beta \)-ZnS or wurtzite structure as it is usually called. Wurtzite has a calculated density of 4.09 g/cm³ and its lattice parameters \( a = 3.823 \text{ Å} \) and \( c = 6.261 \text{ Å} \), where \( \frac{c}{a} = 1.638 \) is quite close to the ideal, which is equal to 1.633 for the hexagonal close-packing. The closest distance between a host cation (S²⁻) and a tetrahedral interstitial site filled with a cation (Zn²⁺) in the hcp structure is \( 3c/8 \approx 1.225R \) (according to the data presented in Table 1-7), where \( R \) is the ionic radius of S²⁻. Each ion in ZnS is tetrahedrally coordinated with four ions of the opposite type. Compounds such as AgI, CdS, CdSe and GaN also crystallize in wurtzite structure.
1. Types of Imperfections and Defects

Crystalline solids have a very regular atomic arrangement. That is, these ideal crystals are solid materials in which the atomic order extends uninterrupted over the entirety of the specimen in all directions with atoms positioned in an orderly and repeated pattern. In reality all crystalline substances that are said to be pure are essentially solid solutions with very low impurity content, since absolute purity is virtually unachievable; real crystals always have certain defects or imperfections, and therefore, the arrangement of atoms in a crystal differs from that of ideal ones. The vast majority of crystalline solids are polycrystalline, being composed of many small crystals or grains having different crystallographic orientations. Even the grain boundary – the interface separating two adjacent grains – constitutes a defect since there is some atomic mismatch in between the grains. Natural crystals contain defects due to the uncontrolled conditions under which they were formed. When the crystallization process occurs at fast to moderate rate usually crystal contains defects often in abundance. Single crystals are formed when the process of crystallization occurs at extremely slow rate; and even these crystals are not free of defects. For example, a chemically pure and structurally perfect diamond would be perfectly transparent with no hue, or color. In reality no gem-sized diamonds are absolutely perfect. For example, the presence of structural defects in the crystal lattice affects the color and can make these crystals valuable as gems. A certain concentration of nitrogen atoms as the main impurity in the diamond crystal will give the gem stone an intense yellow or occasionally brown tint while scattered boron atoms within crystal matrix will make the diamond glow light blue when exposed to light. Artificial crystal prepared in laboratory will also contain defects and imperfections, although considerable control of the growth process may affect their type, concentration and overall distribution.

Basically the defects are deviations or irregularities in the arrangement of constituent particles of the crystal. While the term “defect” carries with it the connotation of undesirable qualities, defects are responsible for many of the important properties of materials used today in our daily life. Material science and engineering involves studying the structure of a myriad of materials from metals, ceramic, polymers to semiconductors, nanomaterials, and biomaterials, including but not limited to their intrinsic or extrinsic defects, and relating them to their properties. A defect free ideal semiconductor, for example a silicon or germanium crystal, would be of little use in electronics; if the silicon crystal is impurified with small concentrations of impurities such as boron, aluminum, phosphorus or arsenic then its conductivity increases by several orders of magnitude compared to that of a high purity crystal, thus the new semiconductor will have the desired property needed for today’s modern electronics. There are many properties of greatest technical importance such as ductility, mechanical strength, conductivity, hysteresis, dielectric strength, crystal growth, and many others that are greatly affected by relatively minor changes in the crystal structure caused by defects and imperfections. Someone may think that we should call crystal imperfections those lattice deviations and irregularities that are intentionally introduced into materials to improve in a desirable way some of its properties and name crystal defects those undesirable deviations or irregularities from perfect crystalline structure of a material that can
Point Defects

Point defects are basically the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance. Point defects occur due to imperfect packing of atoms during crystallization or they can take place due to vibrations of atoms at high temperatures. Point defects are always present in crystals. A point defect - seen as an imperfection occurring at an isolated lattice point - will always induce strain in its immediate vicinity. Usually point defects are classified in two categories; **intrinsic defects**, which exist in pure materials, and **extrinsic defects**, which are caused by impurity atoms or solute atoms in host matrix. Basically there are three major types of point defect: vacancies, interstitials and impurities. The point defects are primarily formed by

(a) Thermal fluctuations during crystallization.
(b) Quenching (rapid cooling used in material hardening) from higher temperatures.
(c) Irradiation with particles and ions of high energy (e.g. linear accelerator, cyclotron, nuclear reactor)
(d) Severe deformation through hammering or rolling.

2.1 Intrinsic Defects

Vacancy defects and interstitial defects are the two types of intrinsic defects. One of the intrinsic defects is formed when an atom is missing from a particular (Bravais) lattice site, creating a **vacancy**, which causes a decrease in density of the substance and change the electrical properties of the material. Figure 2-1 shows a (100) plane in a BCC crystal containing a vacancy.

The atoms surrounding a vacancy tend to be closer together, thereby creating a state of tension in the surrounding lattice which ultimately distorts the lattice planes. If a neighboring atom moves to occupy the
2. Point Defects

vacant site, the vacancy moves in the opposite direction to the site which used to be occupied by the moving atom. One way of producing vacancies is through thermal generation. When the temperature increases, thermal vibration of the atoms increases; therefore, there is an increased probability that individual atoms will jump out of their lattice positions of lower energy into interstitial sites of higher energy.

At higher temperatures, vacancies can move from one site to another more frequently and their most pronounced effect is to govern the migration of impurity atoms in crystals (e.g. concentration of these vacancies influences the rate of diffusion of impurities though the crystal in solid state diffusion or powder sintering technological processes). The creation of a vacancy from a region of perfect lattice involves breaking the bonds between the atom to be moved and its neighbors and recouping about half of these in its surface position (as illustrated in Figure 2-1). In a simplistic way we may consider that the energy of vacancy formation is roughly equal to the enthalpy of vaporization (known also as latent heat of vaporization, which is the enthalpy change required to transform a given quantity of substance from a liquid to a gas at a certain temperature) because the common process of vaporization requires breaking of bonds of surface atoms to form free gas atoms.

![Figure 2-1. Creation of a vacancy on a (100) plane in a BCC crystal by moving an interior atom to the surface of the solid. A vacancy is an empty lattice site.](image)

The vacancy concentration in pure elements is very low at low temperatures, but increases exponentially as temperature increases. At thermodynamic equilibrium, the formation and removal rates are equal: \( V + A_{\text{surf}} = \text{Null} \), where “Null” denotes the perfect crystal, \( V \) is a single vacancy, and \( A_{\text{surf}} \) is an atom on the surface of the solid (adatom). The fraction of lattice sites that are vacant (vacancy concentration) at a given absolute temperature \( T \) is approximately given by the following equation:

\[
\mathcal{n} = N_0 e^{-E_v/k_BT}
\]

where \( n \) is the number of vacant sites per unit volume, \( N_0 \) is the number of (Bravais) lattice sites per unit volume, \( E_v \) is the called the enthalpy of formation of a single vacancy and represents the enthalpy change required for vacancy formation (or simply, it is the energy required to move an atom from the interior of a crystal to its surface), \( T \) is the absolute temperature (in Kelvin degrees), and \( k_B \) is Boltzmann’s constant. For example, in a silicon crystal in order to form a vacancy by removing an atom from its regular lattice site, we have to break four covalent bonds simultaneously in its diamond structure. The formation energy of such vacancy in intrinsic silicon is about 3.17 eV, while the formation energy in \( p \)-type silicon is 3.01 eV and 3.14 eV in \( n \)-type silicon. In other example, the vacation formation energy in a single crystal of FCC copper with
adjacent grains differ in chemical composition and/or in lattice parameters, the interface between them is called phase boundary. Interfaces within crystals appear inside a crystal and are of two types: stacking faults which are defects in the sequence of planes of atom positions in the crystal and antiphase boundaries, which are defects in the sequence of atom distributions over the crystalline planes.

### 4.1 Free Surface

The free surface of a crystal is one of the basic two-dimensional defects of a crystal. Free surfaces are created when a bulk crystal is split or when micro-cracks and cracks form on existent surfaces. The new generated surface is the place where molecules from a liquid or gas phase come into contact with the host atoms. All atoms at the surface of a crystal will have a lower coordination than those in the bulk because of missing outer bonds (the atoms in the free surface are bonded on only one side). For example all atoms in a (111) surface of an FCC crystal have a coordination number of 12−3=9. The configuration and the spacing of the atoms in the first few planes at the interface adjust to accommodate the asymmetry of bonding that is responsible for the bonding interactions across the interface and by chemical changes in the interfacial plane. As we know the simplest surfaces are the close-packed planes forming smooth (100) and (111) surfaces, but real surfaces exhibit features like steps, kinks, or vacancies as illustrated in Figure 2-18. In reality we shall call such surfaces atomically rough.

![Figure 2-18](image.png)

**Figure 2-18.** Ball model representation of a real (atomically rough) crystal surface with steps, kinks, adatoms, and vacancies in a closely-packed crystalline material. Adsorbed molecules, substitutional and interstitial atoms are also illustrated.

All surface defects play an important role for the overall surface properties. For example, during crystal growth a pair of screw-dislocations of opposite sign of the Burgers-vector promotes growth at the step sites of the surfaces. By investigating a crystal with a scanning tunneling microscope (STM) we may see the surface exhibiting atomic terraces separated by either straight or kinked atomic steps. Line defects on surfaces are steps, boundaries between different domains of adsorbate structures, and dislocations. The dangling bonds at the interface solid-liquid or vapor provide favorable sites for the adsorption of atoms (impurities) that do not fit well into the bulk crystal. An adatom is an atom adsorbed on a surface so that it will migrate over the surface (mobile atom adsorbed on a surface). Line and point defects and their motion as they migrate across the surface have become visible in the last a few decades thanks to the Surface Tunneling Microscope (STM) technology. Figure 2-18 shows a model of a close-packed (111) surface containing natural steps with kinks in
it. It also shows an adatom-vacancy pair, $A-V$, on the close-packed surface, created by an atom jumping from its normal position in the close-packed plane onto the surface. If a kink atom moves away from its position in a step, it generally leaves another kink atom. A surface vacancy $V$ may be created when a vacancy in the bulk diffuses to the surface and in the presence of mobile adatoms will easily be filled. If vacancies diffuse to an atomically rough surface, and emerge on a step, they will create kinks or step vacancies. In a similar way interstitial atoms will emerge as adatoms on close-packed surfaces or be incorporated on steps in atomically rough surfaces. The crystalline lattice of surface layers is distorted and it corresponds to a high concentration of dislocations accumulating on the surface. As a consequence, the solid body surface has excessive energy compared with deeper layers in the crystal and its energy is proportional to the surface area.

The surface energy for a crystallographic plane will depend on its packing density in crystal (i.e. see the planar density in Part 1, Chapter 7). The higher the packing density, the greater the number of nearest-neighbor atoms, and the more atomic bonds in that plane that are satisfied, and, consequently, the lower the surface energy. From the solutions to Example Problems #8 and #9, planar densities for FCC (100) and (111) planes are $2/\sqrt{\pi}a^2$ and $4/3\sqrt{\pi}a^2$, respectively, where $a$ is the unit cell edge length (lattice parameter). The atomic radius of an atom in a face-centered cubic structure is related to the lattice parameter $a$ as $R = \sqrt{2}a/4$. Substituting in the above expressions the planar densities for FCC (100) and (111) planes are $1/4R^2 = 0.25/R^2$ and $1/2\sqrt{3}R^2 = 0.29/R^2$, respectively. Therefore, the planar density for (111) plane is greater than the planar density for (100) plane and, consequently the (111) plane will have the lower surface energy.

Pictured schematically in Figure 2-19, micro-cracks are defects that occur due to creation of new surfaces. When one of the conditions such as mechanical loading, temperature cycle, geometry of the micro-crack, chemical composition, etc. is favorable for these micro-cracks to grow and merge with other micro-cracks then a crack is formed. For example, hot tears are cracks due to heavy shrinkage strains set up in the solid casting just after solidification. An existing crack starts propagating when one of the conditions mentioned above, such as mechanical loading, temperature cycle, chemical composition, or geometry of the crack is favorable for it to grow. Once a crack reaches a critical size, the cross-sectional area of the intact part of the material is reduced to the extent that the applied stress (usually a cyclic loading) exceeds the ultimate strength of the material leading to fracture. Fracture is the final separation of a single body into pieces and always occurs as a result of an overloading condition. For engineering materials there are only two possible modes of fracture, ductile and brittle. The main difference between brittle and ductile fracture is usually attributed to the amount of plastic deformation that the material undergoes before fracture occurs. Ductile materials show large amounts of plastic deformation while brittle materials show little or no plastic deformation before fracture.
4.2 Interfaces between Crystals

Majority of crystalline solids in nature are polycrystalline. They are composed of a large number of crystallites or grains of the primary constituent, and may also contain several distinct constituents (phases) of different chemical composition and crystal lattice. Grains can range in size from nanometers to millimeters across (mostly between 1 \( \mu \)m to 1 mm). A grain boundary is a general planar defect within a polycrystalline solid and represents the interface separating neighboring grains of different crystalline orientation.

Large- and small-angle grain boundaries along with phase boundaries, a local dislocation and different crystallographic planes in a microstructure are shown in Figure 2-20. Grain boundaries act as barriers to dislocation movement because adjacent grains have different lattice orientation, thus limiting the length and motion of dislocations.

![Figure 2-20. A 2-D schematic illustration of a polycrystalline structure showing grain boundaries and two-phase interfaces. The interfaces between adjacent grains constitute grain boundary.](image)

Generally, the strength of a material increases as the size of its crystallites (grains) decreases. As a polycrystalline material solidifies, grains with irregular shapes, sizes and crystallographic orientation form. The size and number of grains within a microstructure is controlled by the rate of solidification from the liquid phase. A rapid cooling rate produces smaller grains whereas slow cooling results in larger grains. Interfaces between grains and free surfaces of grains are reactive and atomic impurities tend to segregate in those regions. Grain boundaries also tend to decrease the electrical and thermal conductivity of a crystalline material.

The second type of interface between two adjacent grains that differ in chemical composition and/or in lattice parameters is called phase boundary (also illustrated in Figure 2-20), which is also treated as a surface defect in crystallography.
(2) The parent matrix should be continuous while the hard, dispersed phase particles should be discontinuous. Any crack in the discontinuous and brittle precipitate will stop propagating at the precipitate-matrix interface.

(3) The dispersed second phase particles should be relatively small and numerous, increasing the probability that they will interfere with moving dislocations since the area of the interface between the host matrix and second-phase precipitate increases.

(4) Second phase particles should possess an approximate rounded shape, rather than elongated, needlelike or sharp edged, because a rounded shape is less likely prone to initiate a crack.

(5) Larger amounts of precipitates are expected to increase the strength of alloy.

Precipitations of smaller second-phase particles that were formed as a result of precipitation from a supersaturated solid solution are in general coherent with the parent lattice. Such precipitations interact with moving dislocations by means of coherent strengthening (usually when precipitations have sizes of a few nanometers) or semi-coherent strengthening (when precipitations have sizes ranging from dozens to hundreds of nanometers, as illustrated in Figure 2-33). The second type, precipitations of larger second-phase particles that were formed during grain crystallization usually have incoherent interphase boundary, hence dislocations cannot cross them.

![Figure 2-33](image)

Figure 2-33. Graphical representation of dispersed phase particles throughout a parent lattice that are used in strengthening alloys by interfering with moving dislocations. In above example, the phase precipitate, which is magnified to the right, is semi-coherent with the parent lattice and has smaller parameters than the parent structure, which causes deformation in the lattice and the resulting stress field will interact with moving dislocations.

In general, an ageing process will lead to the precipitation of the second-phase particles. On one hand this process limits the effect of solid solution strengthening, but on the other hand results in precipitation strengthening the alloy. Prolonged ageing, however, results in wider inter-particle spacing, which in turn causes dislocation looping around the second-phase particles. In turn, the alloy starts weakening, which simultaneously becomes more ductile. In annealed steels for example the pearlite colonies in the ferrite matrix act as the second-phase particles where they are much finer (submicron dimension) than the size of the grains of the ferrite matrix. Technologically, dispersion strengthening of metals and alloys is usually accomplished by incorporating chemically stable submicron size particles of a nonmetallic phase that impede moving dislocations at higher temperatures. For example nonmetallic particles such as \( \text{CaO}, \text{MgO}, \text{Al}_2\text{O}_3, \text{SiO}_2, \text{MgO} \),
SUMMARY

A solid is a substance or material that has a definitive size and shape to it and is characterized by structural rigidity and resistance to changes of shape or volume. The solid state is one of the four fundamental states of matter. A solid does not flow to take on the shape of its container like water, nor does it expand to fill the entire volume available to it or disappear into the air. All solids are rigid because their constituent particles have fixed positions that can only oscillate about their mean positions as opposed to the fluidity of liquids and gases in which their constituent molecules are free to move about. The atoms, ions or molecules in a solid are tightly bound to each other, either in a regular geometric way or irregularly.

**Single-crystals** are pure materials or mixtures whose constituents are arranged in a regular pattern throughout the entire volume.

Anisotropy is the quality of exhibiting properties with different values when measured along (crystallographic) axes in different directions. Anisotropy is most easily observed in single crystals of solid elements and compounds, in which atoms, ions, or molecules are arranged in regular lattices.

Isotropy is the quality of exhibiting the same properties when measured along (crystallographic) axes in different directions. Isotropy is most easily observed in amorphous solid, liquids, and especially in gases.

**Polycrystalline solid** comprises of single-crystal regions called grains that are separated from one another by grain boundaries. Polycrystalline materials are composed of a large number of crystallites or grains of the primary constituent, and may also contain several distinct constituents (phases) of different chemical composition and crystal lattice.

**Amorphous** solids have order only within a few atomic or molecular dimensions, in which atoms, ions or molecules are positioned in an irregular manner with no long-range order.

A space lattice – called also a Bravais lattice - is a three-dimensional array of regularly spaced points coinciding with the atom, ion or molecules positions in a crystalline structure. A space lattice is illustrated as points in space, representing the atoms, or ions or molecules of the crystalline solid, which can be connected with geometrical lines to form repeating shapes.

A collection of the lattice points that describe the crystalline solid defines a crystal lattice.

A unit cell is the smallest structural unit or building block that possesses the highest symmetry present in the lattice that can describe the crystal structure.

A primitive unit cell is the smallest unit cell that can be translated through all vectors to completely recreate the entire Bravais lattice without overlapping or leaving voids. A primitive unit cell contains just one Bravais lattice point. The primitive unit cell is smaller or equal in size to the unit cell.

The conventional **body-centered cubic** (BCC) unit cell is an arrangement of atoms in which the unit cell consists of eight atoms at the corners of a cube and one atom at the body center of the cube.

The conventional **face-centered cubic** (FCC) unit cell is formed by placing an atom at each corner of a cube and one atom at the center of each of the six faces of the cube.

The conventional **hexagonal close-packed** (HCP) unit cell consists of three layers of atoms. The top and bottom layers contain six atoms at the corners of a hexagon and one atom at the center of each hexagon. The middle layer contains three atoms nestled between the atoms of the top and bottom layers, hence, the name close-packed.

**Point coordinates**: the location of each point within the unit cell is specified in terms of its coordinates as fractional multiples of the unit cell edge lengths (i.e., in terms of unite cell parameters a, b, and c). In other words, the distance is measured in terms of the number of lattice parameters we must move in each direction of the x, y, and z axes of coordinates to get from the origin to the point in question. So the coordinates of any point are written as three distances in terms of the fraction along each axis, with commas separating the numbers in round brackets.

A crystallographic direction is defined as the vector that connects any two points in a crystal.