

3

States of aggregation

- What type of bonding causes the noble gases to condense to liquids?
- What is the scale implied by the term 'nano-structure'?
- What line defects occur in crystals?

Aggregation is not solely due to the strong chemical bonds described in Chapter 2. Even noble gas atoms experience weak interatomic forces that lead to liquefaction and, except for helium, solidification at low temperatures. Although these interactions are weak in terms of bond energy, they are of vital importance, especially in living organisms. They also lead to the formation of magnetic domains (Chapter 12) and should not be despised.

3.1 Formulae and names

3.1.1 Weak chemical bonds

The strengths of chemical bonds vary widely. Table 3.1 lists the forces between atoms in a solid. The strong chemical bonds, covalent, ionic and metallic, have been described in Chapter 2. The strongest of

the weak bonds involves dipoles. Permanent dipoles are usually found on molecules containing two atoms with very different electronegativities, as described in Chapter 2. For example, a molecule of HCl has a region of positive charge, $\delta+$, associated with the hydrogen atom, and a region of negative charge, $\delta-$, associated with the chlorine atom (Figure 3.1a). The dipole moment of the molecule is 3.60×10^{-30} C m (see Chapter 11 for more information on units.) Water, an angular molecule, also has a permanent dipole moment, of 6.17×10^{-30} C m. The dipole is directed away from the oxygen atom and is augmented by the two lone pairs of electrons (Figure 3.1b). The charges making up the permanent dipole can interact with ions, and ion–dipole interaction energies, of the order of 15 kJ mol^{-1} are found. The hydration of cations, in water solution and solid hydrates, is mainly a result of ion–dipole effects.

Permanent dipoles can also interact with the charges on other dipoles in dipole–dipole interactions. These are of the order of 2 kJ mol^{-1} for fixed molecules, but the interaction is reduced to about one tenth of this value if the molecules bearing the dipoles are free to rotate.

The only elements that exist as atoms under normal conditions are the noble gases, in group 18 of the periodic table. These all have the outer electron structure ns^2np^6 and, at normal temperatures, they exist as monatomic gases. On cooling, helium (He), the lightest, turns to a liquid (with very curious properties) at 4.2 K, the lowest known

Table 3.1 Forces between atoms, ions and molecules

Type of bond	Approximate energy/kJ mol ⁻¹	Species involved
Covalent	350	Atoms with partly filled orbitals
Ionic	250	Ions only
Metal	200	Metal atoms
Ion–dipole	15	Ions and polar molecules
Dipole–dipole	2	Stationary polar molecules
Dipole–dipole	0.3	Rotating polar molecules
Dispersion	2	All atoms and molecules
Hydrogen bond	20	N, O or F plus H

boiling point of an element. Helium can only be turned into a solid by applying pressure. The other members of the family can be liquefied and solidified by cooling.

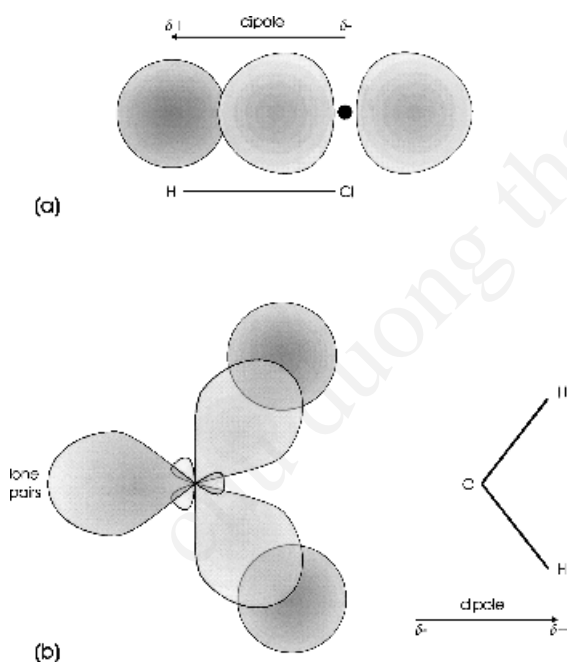


Figure 3.1 The permanent dipole in the molecule (a) HCl and (b) H₂O arises from unequally shared electrons in a covalent bond. In H₂O the lone pair of electrons also contributes to the dipole. The small charges that constitute the dipole are represented by $\delta+$ and $\delta-$. An electric dipole is represented by an arrow pointing from negative to positive

This condensation is due to weak interactions between the outer electrons on the atoms. Fleeting instantaneous fluctuations in the electron cloud surrounding these atoms create momentary dipoles, which are regions with a slight positive charge relative to regions of slight negative charge. These instantaneous charges lead to a weak attraction, which occurs between all atoms and molecules, including otherwise neutral atoms. The resultant force of attraction is called the London or dispersion force, and the interaction is called van der Waals bonding. The bond energy is approximately 2 kJ mol⁻¹. This force is responsible for the liquid states of most molecular species, such as H₂, benzene and the noble gases. The strength of the interaction increases as the size (mass and radius) of the atoms or molecules increases. Because of this, large molecules tend to exist as solids, smaller ones as liquids and light molecules as gases. This trend is exemplified by the smooth increase in boiling point of the saturated hydrocarbons, which have a series formula C_nH_{2n+2} (Figure 3.2).

These weak interactions can be represented by potential energy curves similar to those described in Chapter 2 as acting between atoms. A commonly used form of the interaction energy between a pair of atoms or molecules is the Lennard-Jones potential, $V(r)$:

$$V(r) = Ar^{-12} - Br^{-6}$$

where A and B are constants and r is the distance between the atoms or molecules. The first term on

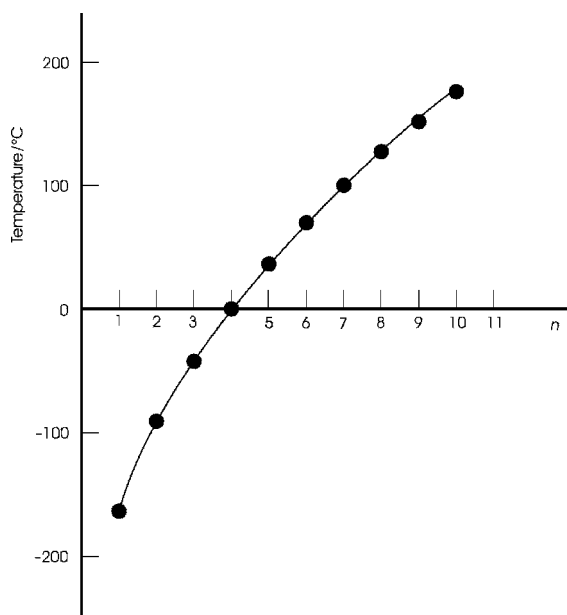


Figure 3.2 The boiling points of the saturated hydrocarbons, of formula C_nH_{2n+2} , plotted against the value of n , which is proportional to the size of the molecule

the right-hand side of this equation is a repulsive energy term and the second is an attractive energy. The potential energy, $V(r)$ passes through a minimum, V_{\min} , at a distance r_{\min} . Under normal circumstances, this would represent the bonding energy of a pair of atoms or molecules, at an equilibrium separation of r_{\min} . The Lennard-Jones potential can be written in terms of V_{\min} as:

$$V(r) = 4 V_{\min} \left[\left(\frac{r_0}{r} \right)^6 - \left(\frac{r_0}{r} \right)^{12} \right]$$

where r_0 is the value of r when $V(r)$ is zero.

Thermal energy is taken to be of the order of kT , where k is the Boltzmann constant and T is the absolute temperature. In cases where the energy of the bond, V_{\min} , is greater than kT , one can expect pairs of atoms or molecules to be stable and a liquid phase to condense. When V_{\min} is less than kT the bond would be expected to be too weak to hold the pair together and a gas is likely.

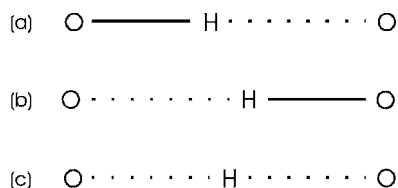


Figure 3.3 The hydrogen bond between two oxygen atoms can be thought of as a strong bond to one oxygen atom and a weak bond to the other. Two alternatives are possible (parts a and b). At high temperatures in solids the hydrogen atom is often found midway (on average) between the oxygen atoms (part c)

A hydrogen bond is a weak bond formed when a hydrogen atom lies between two highly electronegative atoms – fluorine, oxygen, chlorine or nitrogen. The bond results from the interaction of the small positive charge, $\delta+$, found in dipolar molecules containing hydrogen, with the partial charge of $\delta-$ located on the electronegative partner. It is naturally linked to the exposed lone-pair electrons on atoms such as oxygen and nitrogen. The hydrogen bond is usually drawn as a dotted bond between the electronegative atoms (Figure 3.3). This representation emphasises the fact that the hydrogen atom has an ambiguous position in the bond. At low temperatures it adopts a position nearer to one or other of the electronegative atoms, and at high temperatures it is found midway between them. The bonding to the nearer atom is then described as a normal covalent σ bond, and the bonding to the further atom is the hydrogen bond. In general the two links, $O-H$ and $H \cdots O$, for example, are not in the same straight line. The angle between them commonly deviates from 180° by 10° to 20° , and sometimes by much more.

Because these bonds are comparatively weak it follows that they not only are easily ruptured but also are formed with equal ease. Thus, hydrogen bonds form in all appropriate materials at normal temperatures. Hydrogen bonding is important in many hydrogen-containing compounds such as water (H_2O), hydrogen fluoride (HF), ammonia (NH_3) and potassium hydrogen fluoride (KHF_2). The existence of hydrogen bonds dramatically

changes many of the properties of the material. For example, HF, H₂O and NH₃ are characterised by melting points, boiling points and molar heats of vaporisation that are abnormally high in comparison with those of similar elements. The fact that water is liquid on Earth at normal temperatures is largely because of hydrogen bonding. In living organisms, hydrogen bonding is of great importance in controlling the folded (tertiary) structure of proteins. This tertiary structure largely determines the biological activity of the molecule, and mistakes in the folding can lead to serious illness. Hydrogen bonding endows solids with significant physical properties, such as ferroelectric behaviour, described in Chapter 11.

The range over which these forces are significant varies widely. Covalent bonds act over a few nanometres only. Interactions that are essentially electrostatic in nature, as in ionic bonds, operate over larger distances, and are proportional to $1/r$, where r is the interionic distance. Ion–dipole interactions decrease more rapidly, being proportional to $1/r^2$. Dipole–dipole interactions vary as $1/r^3$ for static dipoles and as $1/r^6$ for rotating dipoles. Dispersion forces also decrease as $1/r^6$.

3.1.2 Chemical names and formulae

Compounds are broadly classified as alloys, inorganic compounds or organic compounds. Alloys are metallic materials composed of varying proportions of metallic elements. Organic compounds are compounds of carbon, and make up the living world. Inorganic solids comprise everything else, such as rocks and minerals.

Molecules are groups of atoms that are linked together by chemical bonds to form recognisable units in stable structures. The formulae of molecules are written as a set of atomic symbols, with the number of atoms given a subscript to the atomic symbol. Examples are: water, H₂O; methane, CH₄; ammonia, NH₃. The molecules that are important for life, such as proteins and DNA (deoxyribonucleic acid) are extremely large. Polymers are very large molecules formed from smaller molecules, called monomers.

Although the bonds between the atoms within molecules are strong, those between molecules are usually much weaker and are of the types described above. Small molecules tend to exist as gases at room temperature, whereas larger molecules exist as liquids or form solids. The formula of a molecular solid is the same as the formula of the molecules that make up the solid.

Not all solids and liquids are molecular. Many inorganic solids and liquids are built of ions or uncharged atoms. For such solids, the formula often simply expresses the ratio of the atomic species present. For example: crystalline rock salt, NaCl, also called halite or sodium chloride, contains equal numbers of sodium and chlorine atoms, although the total number of each will depend on the size of the sample. Similarly, fool's gold, FeS₂, also called iron pyrites or iron sulphide, always contains twice as many sulphur atoms as iron atoms, although no molecules of FeS₂ exist in the crystals.

In some types of solid, the number of atoms present is not given by simple whole numbers. This is especially so for metallic alloys, where the composition range is closely dependent on temperature. For example, common brass can have a composition anywhere between Cu₆Zn₄ and Cu_{4.5}Zn_{5.5} at 800 °C. Inorganic solids are less prone to having a variable composition than are alloys, but many important examples are known. For example, iron monoxide never attains the composition FeO at atmospheric pressure but has a composition closer to Fe_{0.945}O. These types of solid are called nonstoichiometric compounds and their composition range is usually temperature dependent.

Many inorganic compounds are called by a mineral name; for example, the oxide magnesium aluminate, MgAl₂O₄, is found as the mineral spinel, and synthetic magnesium aluminate is also referred to as spinel. The mineral name is often applied to a family of compounds all with the same structure. That is, both copper aluminate, CuAl₂O₄, and nickel gallate, NiGa₂O₄, are called *spinel*s because they have the same crystal structure as MgAl₂O₄. Because of the relationship with crystal structures, use of mineral names often simplifies matters when

solids that may have an imprecise chemical formula are being discussed.

A number of compounds, especially refractory oxides (which are stable at high temperatures), are called by older chemical names, such as calcia for calcium oxide, CaO ; magnesia for magnesium oxide, MgO ; titania for titanium dioxide, TiO_2 ; zirconia for zirconium dioxide, ZrO_2 ; silica for silicon dioxide, SiO_2 ; and alumina for aluminium oxide, Al_2O_3 . Physicists often refer to crystalline colourless aluminium oxide as sapphire, although sapphire is blue. The correct mineral name for the colourless form of aluminium oxide is corundum.

Organic compounds have an elaborate naming system, necessary because of the enormous complexity exhibited by these molecules. The rudiments are explained in Section S2.1.

3.1.3 Polymorphism and other transformations

As the temperature rises, the vibrational energy of the solid becomes similar in magnitude to the bond energy holding the atoms together, and a number of transformations take place. The temperature at which these occur varies with the pressure applied to the system, and not all changes may be possible at normal atmospheric pressure. The changes can be depicted schematically on a diagram that shows the phases present as a function of the temperature and pressure (Figure 3.4). Diagrams of this type are called phase diagrams or existence diagrams. They are discussed in more detail in Chapter 4.

In the solid, changes of crystal structure, known as polymorphism, frequently occur. For example, the asymmetrical environment of hydrogen atoms in hydrogen bonds in solids does not persist at higher temperatures, and lattice vibrations tend to cause the hydrogen atoms to occupy an 'average' position midway between the neighbouring nitrogen, oxygen or fluorine atoms, leading to a new crystal structure. Such transitions are important in a number of ferroelectric materials, (see Section 11.3).

The rise in temperature corresponds to greater and greater atomic vibration about a mean low-

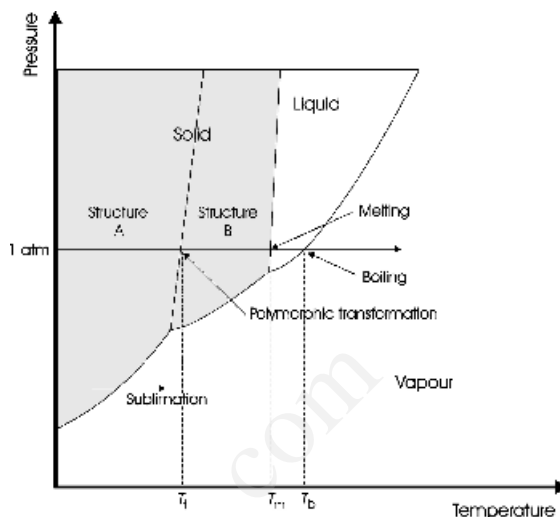


Figure 3.4 Phase diagram of a pure substance. As the temperature increases the solid can change from one structure to another (polymorphism), and transform directly to the vapour (sublimation). Normally a solid passes initially to a liquid (melting) and then to a vapour (boiling)

temperature equilibrium position of the atoms. At some point, these vibrations become so great that the atoms or molecules, although still linked together, are able to move about fairly freely. This corresponds to the liquid state.

Increased temperature will allow atoms or small groups of atoms to break away from the surface to form gaseous species. Ultimately, the whole of the liquid may be vaporised. The actual structure of the species making up the vapour will depend, largely, on the bonding in the solid. Metals often give monatomic vapours. Solids that are predominantly ionic or covalent often vaporise as small charged or neutral fragments containing small numbers of ions or atoms. Tungsten trioxide, WO_3 , for example, vaporises to yield the molecular fragments $(\text{WO}_3)_n$, where n takes values of 1, 2 and 3.

In some solids, the energy to form the liquid state is similar to the energy to form gaseous species. In this case, the solid may transform directly to the vapour without the intervention of a liquid state. This process is called sublimation. Solid iodine,

which consists of I_2 molecules linked by van der Waals bonds, transforms directly to a vapour of I_2 molecules when heated.

3.2 Macrostructures, microstructures and nanostructures

3.2.1 Structures and microstructures

The shape of an object reflects its function. The shape of a container is different from the shape of a blade, and the purposes of the two objects are readily discriminated by eye (Figure 3.5a). The

properties of an object that fit it to its functional use are based on a scale that can be called the macrostructure (Figure 3.5b). For example, a container may be glazed or porous.

Many of the measured properties of bulk materials are dominated by structures at a scale somewhere between millimetres and micrometers, called the microstructure of the material (Figure 3.5c). For example, good-quality ceramics have a microstructure that is a mixture of crystallites in glass. Much of materials processing is centred on the production of the correct microstructure in the finished product. The architecture of older silicon chips were somewhere between macrostructure and microstructure. Modern chips have architecture at a smaller

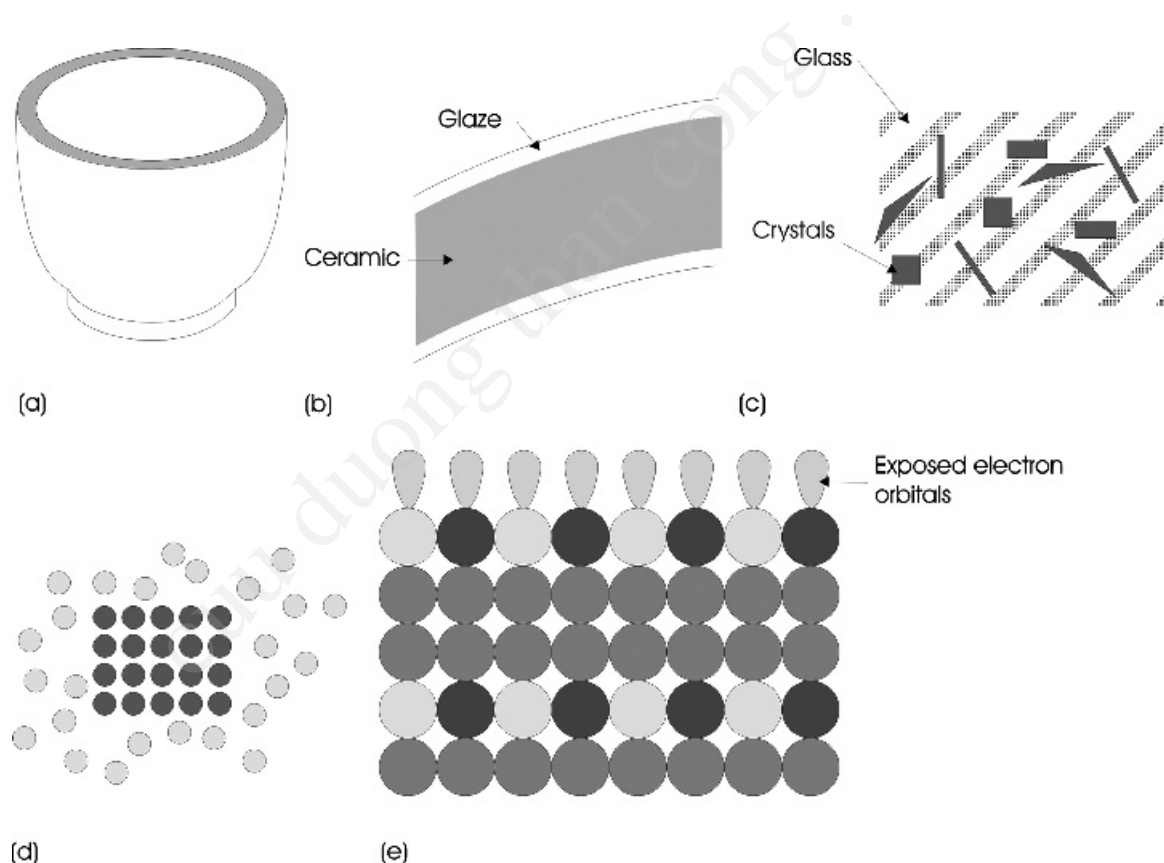


Figure 3.5 Structure and scale: (a) gross shape, a porcelain bowl; (b) the macrostructure of the bowl consists of surface glaze and ceramic body; (c) the microstructure of the ceramic consists of crystals in a glass matrix; (d) the nanostructure of the ceramic consists of atom arrays, which are ordered in the crystals and disordered in the glass; (e) the surface structure consists of exposed atoms of several types and unpaired electron orbitals

scale, somewhere between microstructure and nanostructure.

The atomic structure of the object, called the nanostructure, is at a more fundamental level again. Atomic structure lists the atoms present, their positions and whether they are ordered, as crystals, or disordered as glasses (Figure 3.5d).

The environment of an atom in the surface of a solid differs from that of the bulk (Figure 3.5e). If several atom types make up the crystal, then some surfaces will preferentially contain atoms of one species and other surfaces other species. If nothing else, the bonding of surface atoms is incomplete, meaning that electron orbitals are exposed to outside influences, leading to enhanced reactivity. Surfaces are at the heart of many chemical processes, such as heterogeneous catalysis or corrosion. They also play an important part in the operation of many electronic devices. Recently, there has been great effort put into the production of devices that are close to the atomic scale, less than about 10 nm. This area is known as nanotechnology.

Table 3.2 summarises these relationships.

3.2.2 Crystalline solids

Crystals are solids in which all of the atoms occupy well-defined locations, ordered across the whole of the material (Figure 3.6a). Considering that chemical bonds tend to operate over only a few inter-atomic distances, it is rather surprising that so much of the solid state is crystalline. Nevertheless, this is

so, and it is only with difficulty that many ordinary solids can be prepared in a noncrystalline form. Crystallography and a description of crystalline solids are to be found in Chapter 5. Single crystals are used for fundamental investigations of solid properties. Single crystals are mandatory for semiconductor devices. Single-crystal turbine blades are fabricated for superior performance. Crystals often show cleavage on certain planes, indicating that some planes of atoms are linked by weaker bonds.

Polycrystalline solids are composed of many interlocking small crystals (Figure 3.6b). Most metals and ceramics in their normal states are polycrystalline. The small crystals are often called grains, especially in metallurgy. The properties of polycrystalline materials are often dominated by the boundaries between the crystallites, called grain boundaries.

3.2.3 Noncrystalline solids

Noncrystalline solids do not have long-range order of the atoms in the structure (Figure 3.6c). There is usually some short-range order, extending over a few atom radii, but no correlation of atom positions at longer distances. There are three types of noncrystalline solid of most importance: glasses, polymers and amorphous solids.

A glass is normally defined as an inorganic substance, mostly transparent, that has passed from a high-temperature liquid state to a solid without the formation of crystals. The best-known glasses are

Table 3.2 Scales of structure

Description	Dimension (m)	Example	Analytical tool
Gross shape	≥ 1	Ceramic vessel	Visual examination
Macrostructure	10^{-2}	Surface glaze, underlying material	Magnifying glass, optical microscope
Microstructure	10^{-4}	Crystallites and noncrystalline material	Microscopy (optical, electron)
Crystal structure	10^{-9}	Crystals, glass	Diffraction (X-ray, neutron, electron)
Atomic structure	10^{-10}	Elemental compositions, atomic topography	Spectroscopy, atomic force microscopy

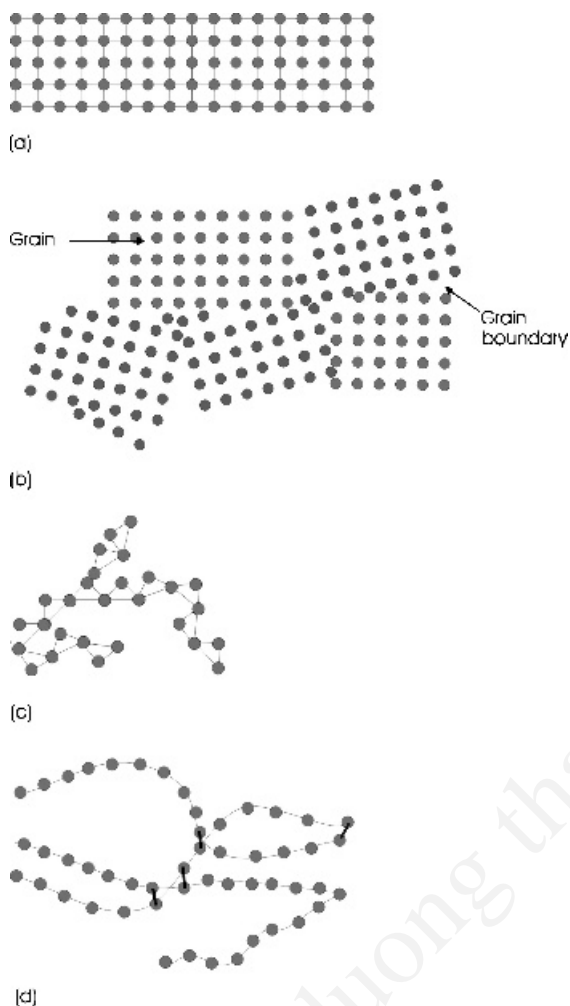


Figure 3.6 Nanostructures: (a) a single crystal, (b) a polycrystalline array, (c) a glass and (d) polymer chains linked by hydrogen bonds (shown as bars)

manufactured from silicon dioxide, SiO_2 , mixed with other oxides. They are called silicate glasses. There are a number of naturally occurring silicate glasses, including obsidian (a volcanic rock which is black because of iron oxide impurities), pumice (a glassy froth), flint and opal. These all show the typical glass properties of hardness and brittleness. However, metals and organic compounds can also solidify as a glass. For example, by boiling and cooling

crystalline sugar, an organic molecular compound, one can form glasses called ‘boiled sweets’ or toffee, depending on the other ingredients included. [If additives are used to make the melt partly crystallise during cooling, the product is fudge.] In the case of metals, a glass state is much harder to achieve. The molten material must be cooled extremely rapidly, within a time-span of the order of 10^{-6} s. This is achieved by squirting a fine jet of molten metal against a rapidly rotating copper disc that has been cooled by water or liquid nitrogen.

There is no one structure of glass any more than there is one crystal structure. Almost any solid can be produced in a glassy state if the melt is cooled sufficiently quickly. To some extent, glass can be thought of a product of kinetics, and the structure of a glass can depend on the rate at which the liquid is cooled. Theories of glass structure and formation must consider this (see also Section 6.3).

Glasses are described as supercooled liquids. This status of glass is revealed by the behaviour on warming. Glasses do not have a melting point. Instead, they continually soften from a state that can be confidently defined as solid to a state that can be defined as a viscous liquid.

Glasses containing several components are often found to be inhomogeneous at a scale of about 10^{-6} m. Composition variations occur that can be detected by electron microscopy. These composition variations can arise in the melt, when the various components of the system do not mix completely, rather like, but not as extreme as, oil and water. They can also arise on cooling, when some components separate by a process called *spinodal decomposition*. The degree of inhomogeneity found in the glass will depend on both of these factors.

Polymers are a class of substances that consist of very large molecules, macromolecules, built up from many multiples of small molecules, monomers. They can be synthetic (polythene, nylon) or natural (protein, rubber), and occur widely in nature as vital components of living organisms. Most polymers, both natural and synthetic, have a framework of linked carbon atoms. These are strong because the carbon atoms are linked by covalent bonds. The long molecules themselves are linked by some of the weak bonds listed in Table 3.1 and are

usually present in a disordered state (Figure 3.6d). A sheet of a solid transparent polymer such as methyl methacrylate (Plexiglas[®] or Perspex[®]) is very difficult to tell from a sheet of window glass by sight alone because the structure of these polymeric solids is noncrystalline.

Solids evaporated and then condensed onto cool surfaces usually do not crystallise and are said to be in an amorphous state. Amorphous coatings of this type are widely used in the electronics and optics industries. Such compounds will generally transform into a crystalline state if sufficient energy is supplied to allow crystallisation to occur.

Aerogels are ultra-low-density solids that have a microstructure of highly porous foam. The interconnected pores have a size of less than 100 nm and the structure can be described as of a fractal nature, with the smallest characteristic dimension being of the order of 10 nm. Aerogels have been made from many materials, but silica aerogels are the best known. These have extremely low densities, with porosities of 99.9 % available. Because of this, the physical properties of aerogels vary considerably from that of the parent material. For example, the thermal conductivity of a silica aerogel is 10^{-2} – 10^{-3} that of ordinary silica glass, the refractive index varies (depending on the porosity) from 1.002 to 1.3, compared with 1.5 for silica glass, and the speed of sound drops to 100–300 m s⁻¹ compared with 5000 m s⁻¹ in silica glass. These materials find uses ranging from thermal insulation to high-energy nuclear particle detectors.

3.2.4 Partly crystalline solids

Although most solids turn out to be crystalline, there are important groups that are partly crystalline and partly disordered. For example, glasses are not stable thermodynamically. Given enough time, a glass will crystallise. The process of glass crystallisation is called devitrification. Opal glass is a silica (SiO₂) glass prepared so that it has partly recrystallised to give a glassy matrix containing small crystallites dispersed through the bulk. These crystallites reflect light from their surfaces to create the opacity of the solid. Glass ceramics are deliberately

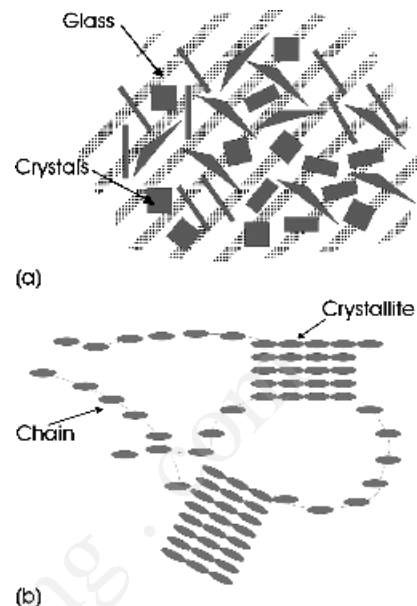


Figure 3.7 Partly crystalline solids: (a) a glass ceramic or porcelain and (b) a partly crystalline polymer

(virtually completely) recrystallised during processing to give a material with the formability of glass and the enhanced mechanical properties of a polycrystalline ceramic. Porcelain is a material consisting of a glassy matrix in which small crystals of other oxides are embedded (Figure 3.7a).

Polymers also show a natural tendency to crystallise, which is thwarted to a greater or lesser extent by the structure of the polymer molecules. Most polymers have a chain-like form. It is possible to change the average chain length created during polymerisation, and longer chains are more difficult to crystallise. The presence or absence of side-groups attached to the chain also has a considerable effect on the ease with which a polymer chain can crystallise. The partly crystalline structure of many linear polymers (Figure 3.7b) is typified by one of the simplest of polymers, polyethylene (polythene). Polyethylene molecules are 10^4 monomer units or more long and resemble thin strings. If the liquid is cooled reasonably quickly, the chains remain in an extended form. The material has a low density, a low refractive index and is very flexible. It resembles a glass. However, if the polyethylene is cooled

slowly from the melt some chains can fold up into crystalline regions 10–20 nm thick. These crystalline regions are of higher density and refractive index compared with the noncrystalline parts. Most polyethylene is a mixture of crystalline and amorphous regions, which is why it appears milky.

Many factors control the degree of crystallinity of a polymer, and these are carefully controlled in production to obtain the correct mix of crystalline and noncrystalline material.

3.2.5 Nanostructures

The nanostructure of a material is its structure at an atomic scale. Nanoparticles and nanostructures generally refer to structures that are small enough that chemical and physical properties are observably different from the normal or ‘classical’ properties of bulk solids. For example, the energy levels of isolated atoms are sharp, whereas atoms in a solid contribute to an energy band, as described in Section 2.3.2 (see Figure 2.23, page 45). At some stage, as the solid is imagined to fragment into smaller and smaller units, the energy levels must change from typically bulk-like bands to more atom-like sharp levels.

The dimension at which this transformation becomes apparent depends on the phenomenon investigated. In the case of thermal effects, the boundary occurs at approximately the value of thermal energy, kT , which is about 4×10^{-21} J. In the case of optical effects, nonclassical behaviour is

noted when the scale of the object illuminated is of the same size as a light wave, say about 5×10^{-7} m (see Section 14.11). For particles such as electrons the scale is determined by the Heisenberg uncertainty principle, at about 3×10^{-8} m (see Section 13.3).

The areas where this transition has been most apparent are microelectronics and optoelectronics. As the dimensions of microelectronic circuit elements have decreased, nanostructures are increasingly in evidence. A thin layer of a solid will have bulk properties modified towards atom-like properties in a direction normal to the layers. A thin layer of a semiconductor sandwiched between layers of a different semiconductor is called a quantum well (Figure 3.8a). In this structure, the electrons are essentially confined to the two-dimensional plane of the layers by the difference in the band structures of the two materials. They are regarded as two-dimensional from the point of view of microelectronics. Similar devices built up from several alternating layers of semiconductors are called multiple quantum well structures, or superlattices (Figure 3.8b). Structures that are small on an atomic scale in two directions are called quantum wires (Figure 3.8c). In these structures, the electrons are confined in two dimensions by the band structure of the surrounding materials and, from a microelectronics perspective, they are one-dimensional conductors. A cluster of atoms has properties rapidly approaching that of the isolated atoms. Electrons are confined to a localised region of space, and the structure is called a quantum dot (Figure 3.8d). These are

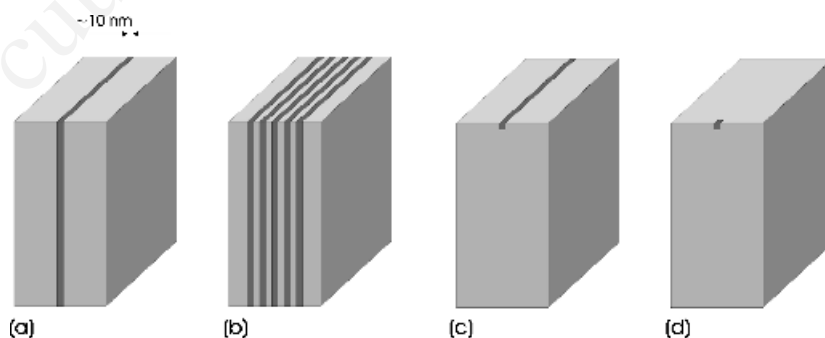


Figure 3.8 Electronic nanostructures: (a) a quantum well, (b) a series of quantum wells, to form a multiple quantum well structure or quantum superlattice, (c) a quantum wire and (d) a quantum dot

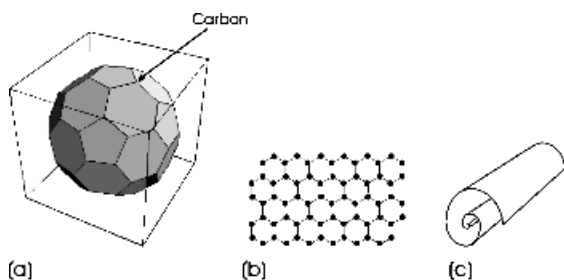


Figure 3.9 The truncated icosahedral structure of a C_{60} 'buckyball'; a carbon atom is situated at each vertex. (b) The hexagonal structure of a single sheet of carbon atoms arranged as in graphite. (c) Carbon nanotubes, which consist of similar sheets rolled up into a variety of configurations

regarded as zero-dimensional electronic structures. These structures are fabricated by using the standard techniques of the semiconductor industry. The electronic and optical consequences of these restricted nanostructures are described in more detail in Chapters 13 and 14.

Among the most commonly investigated nanoparticles are the forms of carbon called fullerenes and carbon nanotubes. Fullerenes are roughly spherical assemblies of carbon atoms linked by strong covalent bonds. The first example to be characterised, C_{60} , was called Buckminsterfullerene, as the structure (Figure 3.9a) resembled the geodesic dome structure developed by R. Buckminster Fuller. The structure of C_{60} is a truncated icosahedron, and is built of faces made up of pentagons and hexagons. A carbon atom is found at each vertex of the structure. Fullerenes have the electronic properties of quantum dots. Carbon nanotubes can be thought of as a layer of carbon atoms of the sort found in graphite (Figure 3.9b) coiled into a tube (Figure 3.9c; see also Section 5.3.7 for the structure of graphite). Carbon nanotubes behave as quantum wires. The electronic and optical properties of fullerenes and nanotubes can be modified by encapsulating other atoms, especially metal atoms, into the structure.

In the case of optoelectronics, the aim is to utilise light in an analogous role to electrons. The optical equivalents to transistors are photonic crystals. These structures interact with light in controlled and predetermined ways. Many are based on

the structure of a natural 'photonic crystal', the gemstone opal. Opals contain regular arrays of spherical silica particles with a diameter similar to the wavelength of light. This gives rise to the flashing colours in natural stones. Photonic crystals are discussed in more detail in Chapter 14.

Nanostructures exist at many levels, and as the example of opal suggests, many of these have been discovered in nature. For example, typical spider thread (there are many species of spider and many types of thread) is a polymeric material that has remarkable properties, that have been likened to the ability of a fishing net to capture a ballistic missile. These properties result from the nanostructure of the thread, which consists of interleaved crystalline and noncrystalline regions.

3.3 The development of microstructures

The development of the correct microstructure in a manufacturing process is of prime importance. It is the increasing mastery of this ability that has marked out the progression of ancient and modern civilisations. In early times, this control was achieved by trial and error. The resulting recipes were then closely guarded by tradespeople or trade guilds. The control of microstructures in modern times has come to depend on a precise knowledge of the science behind the chemical and physical changes that are taking place. This is typified by the rise of metallurgy concurrent with the development of the modern steel industry, some 100 or so years ago. Currently, the production of nanostructures and nanodevices requires considerable scientific and engineering skills.

3.3.1 Solidification

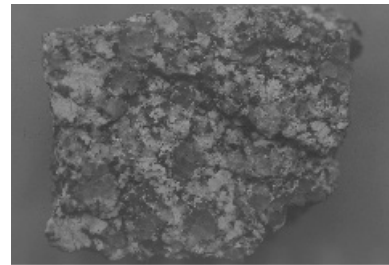
Many solids, especially metals, are produced from liquid precursors, and control of solidification is important in the development of the appropriate microstructure. Rapid solidification can lead to amorphous or poorly crystalline products. Slow cooling can lead to the formation of large crystals or single crystals. As these observations indicate,

the microstructure formed often depends on the rate of solidification.

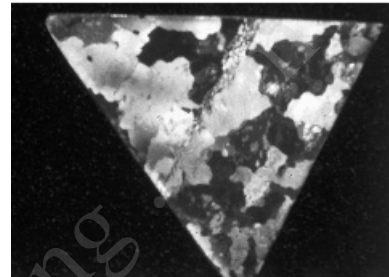
There are two important steps involved. Nucleation is the initial formation of tiny crystallites. As a liquid cools, small volumes tend to take on a structure similar to that of crystals, which will ultimately form. This occurs especially at mould edges, on dust particles and so on, which act as sites for nucleation. Nucleating agents can be added deliberately to cause this to happen. The formation of nuclei is suppressed during glass formation. If only one nucleus forms, a single crystal is produced. If many nuclei form, a polycrystalline solid results.

Crystal growth follows nucleation and contributes greatly to the development of microstructure. The resulting solid will usually contain crystals of different compounds, as in the rock granite, which is composed mainly of mica, quartz and feldspars (Figure 3.10a). Pure metals and alloys are also normally polycrystalline (Figure 3.10b). Many crystals grow from the melt with a branching shape or morphology that resembles a tree in form. These are called dendrites and the growth is called dendritic growth (Figure 3.10c). The shape of the dendritic crystal reflects the internal symmetry of the crystal structure (see Chapter 5 for more information on crystal symmetry). Cubic metals usually have ‘side arms’ perpendicular to the long growth axis, whereas in hexagonal crystals the side arms are at angles of 60° . This gives snowflakes and frost, which are dendritic ice crystals, their definitive form.

The ultimate microstructure of a solid will depend on how quickly different crystal faces develop. This controls the overall shape of the crystallites, which may be needle-like, ‘blocky’ or one of many other shapes. The shapes will also be subject to the constraint of other nearby crystals. The product will be a solid consisting of a set of interlocking grains. The size distribution of the crystallites will reflect the rate of cooling of the solid. Liquid in contact with the cold outer wall of a mould may cool quickly and give rise to many small crystals. Liquid within the centre of the sample may crystallise slowly and produce large crystals. Finally, it is important to mention that the microstructure will depend sensitively on impurities present. This aspect is discussed in Chapters 4 and 8.



(a)



(b)



(c)

Figure 3.10 Optical micrographs of polycrystalline solids. (a) Granite, composed of interlocking crystals of mica (black), quartz and feldspars (colourless); the mica crystals are approximately 2 mm in width. (b) Aluminium, consisting of interlocking grains up to 1 cm in width. (c) Rutile, TiO_2 , with a dendritic form; each ‘branch’ is a separate crystal, and the whole group forms a polycrystalline solid. The branches are perpendicular to the main crystal, revealing the underlying symmetry of the structure. The crystal is approximately 5 mm long

3.3.2 Processing

Processing refers to the treatment of a solid to alter the microstructure and external form. It is a large subject and of considerable importance in industry. Just a few processing routes are mentioned here. More information is given in the publications in the Further Reading section.

Working and heat treatment are techniques applied mainly to metals. When a metal is hammered, rolled or deformed it is referred to as working. Cold metals get harder on working as the process introduces large numbers of defects (see below) and strain energy into the sample. If the metals are heated to about half their melting point (called annealing) they can partly recrystallise and release the strain energy. This causes the metal to become softer and more ductile.

Thermoplastic polymers can easily be melted and moulded into flexible shapes. The rigidity and strength of the product can be improved by cross-linking between the polymer chains. One of the first deliberate cross-linking processes was the vulcanisation of rubber, which is used in car tyre manufacture. The process transforms sticky, soft rubber into a hard, flexible material.

The devitrification of glass to produce glass ceramics, mentioned in Section 3.2.4, is typical of processing in the glass and ceramic industries. Here, the processing aim is to overcome the brittleness typical of glasses while retaining good chemical inertness.

Sintering is widely used to make polycrystalline ceramic bodies. A powder is compressed and heated at a temperature below the melting point to produce a strong polycrystalline solid (see Section 8.4). This comes about by atomic mobility (diffusion). The presence of traces of liquid helps the process greatly. Many electrical and electronic components are produced by sintering. Some metal parts are also made via this method, and the subject area is called powder metallurgy. The main aim of processing in this general area is to produce a high-density solid with little porosity. An associated aim is to reduce dimensional changes, especially shrinkage, which preclude the use of powders to form solids with precise engineering tolerances.

Dehydration, or, more exactly, fluid phase removal, is used to form the ultraporous microstructure of aerogels. Normally, when a gel (e.g. ordinary gelatine) is dehydrated, the material shrinks and collapses. As fluid in the pores evaporates, a meniscus forms which generates large surface-tension forces. These cause the pore structure to disintegrate. The formation of aerogels is a typical processing problem: how is it possible to remove fluid while maintaining the porous microstructure? In original work, high pressures and temperatures were used to take the fluid in the material above its critical temperature (see Section 4.1.1). In this state, the fluid does not exert surface tension, and it is possible to remove it without collapse of the solid framework. A variety of related processing methods are now used for aerogel production.

3.4 Defects

Defects in crystalline solids are important because they modify important properties. For example, just a trace of chromium impurity changes colourless aluminium oxide into ruby. Metals are ductile when linear defects called dislocations are free to move. Crystals dissolve and react at increased rates at points where dislocations intersect the surface of the crystal. Thus, it is necessary to have an idea of the types of defect that form and the role that they play in the control of properties in order to understand the behaviour of solids.

3.4.1 Point defects in crystals of elements

Crystals of the solid elements, such as silicon, contain only one atom type. The simplest localised defect that we can imagine in a crystal is a 'mistake' at a single atom site. These defects are called point defects.

Two types of point defect can occur in a pure crystal: atoms can be absent from a normally occupied position, to give what are called vacancies, or an atom may be incorporated at a position not normally occupied, called an interstitial atom, and sometimes a self-interstitial atom (Figure 3.11).

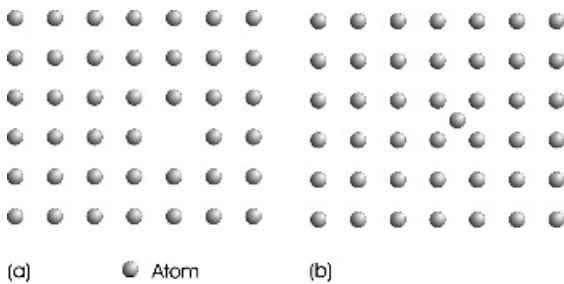


Figure 3.11 Point defects in pure crystals, such as silicon: (a) a vacancy and (b) an interstitial (shown here as a self-interstitial)

Such vacancies and interstitials, which occur in even the purest of materials, are called intrinsic defects.

For these defects to be stable, the Gibbs energy of a crystal containing defects must be less than the Gibbs energy of a crystal without defects (see also Section S3.2). The Gibbs energy varies with the number of point defects present (Figure 3.12). Initially, a population of defects lowers the Gibbs energy, but, ultimately, a large number of point defects results in an increase in Gibbs energy. The minimum in the energy curve represents the equilibrium situation that will exist at a given temperature. Thermodynamics allows the position of the

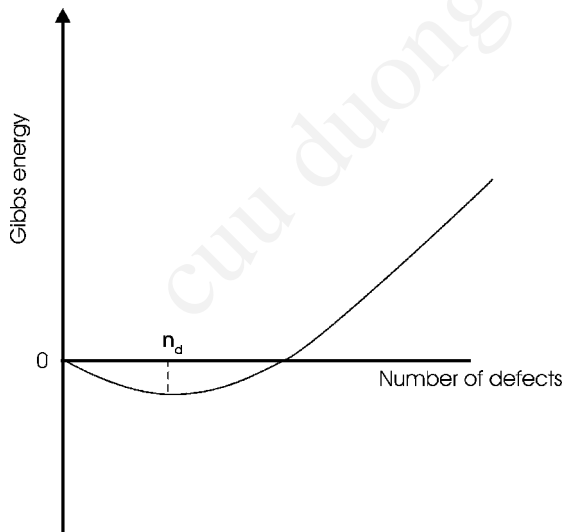


Figure 3.12 The Gibbs energy of a crystal as a function of the number of point defects present. At equilibrium, n_d defects are present in the crystal

minimum and the approximate associated number of point defects present in a crystal to be calculated. The number of defects is expressed by the formula:

$$n_d \approx N \exp\left(\frac{-\Delta H}{kT}\right) \quad (3.1)$$

where n_d is the number of defects per unit volume, N is the number of sites affected by defects per unit volume, ΔH is the enthalpy (loosely, the heat energy) needed to form a single defect, k is the Boltzmann constant and T is the temperature (in kelvin).

The fraction of atom sites which contain a defect, n_d/N , at any temperature, can be calculated if the enthalpy of defect formation, ΔH , is known.

$$\frac{n_d}{N} \approx \exp\left(\frac{-\Delta H}{RT}\right) \quad (3.2)$$

where ΔH is measured in J mol^{-1} .

To obtain the absolute number of defects in the solid, it is necessary to know the number of atoms, N , in a unit volume of the crystal. This value is often obtained from the crystal structure of the compound. The crystal structure is described in terms of the unit cell, which is a small representative volume of the crystal (see Chapter 5). We may write:

$$N = \frac{\text{number of atoms in the unit cell}}{\text{unit cell volume}}$$

For example, the unit cell of silicon is cubic, with a side of 0.5431 nm, and contains 8 atoms of silicon, which allows N to be found.

Alternatively, it is possible to obtain the same information from the density of the material, ρ . The relative molar mass of an element contains N_A atoms, where N_A is Avogadro's constant. The value of N is then given by:

$$N = \frac{\rho \times N_A}{\text{molar mass}}$$

No material is completely pure, and foreign atoms will be present. If these are undesirable or acciden-

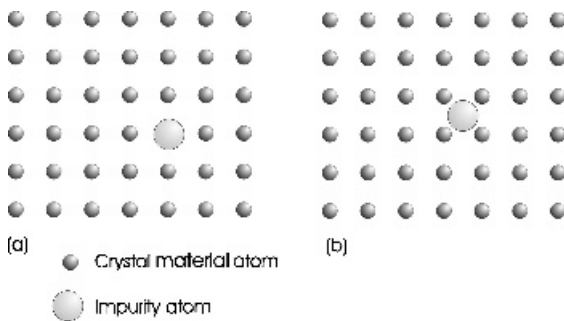


Figure 3.13 Impurity or dopant point defects in a crystal: (a) substitutional and (b) interstitial

tal, they are known as impurities, but if they have been added deliberately, to change the properties of the material on purpose, they are called dopants. Foreign atoms can rest on sites normally occupied by the parent atom type to form substitutional defects. Foreign atoms may also occupy positions not normally occupied in the crystal, to create interstitial impurities or interstitial dopants (Figure 3.13). There is no simple thermodynamic formula for the number of impurities present in a crystal.

3.4.2 Solid solutions

Some compounds, especially alloys, have quite extensive composition ranges. Close to the parent composition the structure can be thought of in terms of impurity defects in a crystal. When quite large numbers of impurity atoms enter a crystal, without changing the crystal structure, the resultant phase is referred to as a solid solution.

A substitutional solid solution is a mixture of two similar elements in which one atom substitutes on the sites of the other atoms in the structure. In the copper–nickel system, both parent phases adopt the same crystal structure. When both atom types are present, they occupy random positions in the crystal to form a substitutional solid solution (Figure 3.14a). Near to pure copper it is possible to say that the nickel atoms form substitutional impurity defects, and near to pure nickel it is possible to say that copper forms substitutional impurity defects. Substitutional alloys generally have lower thermal

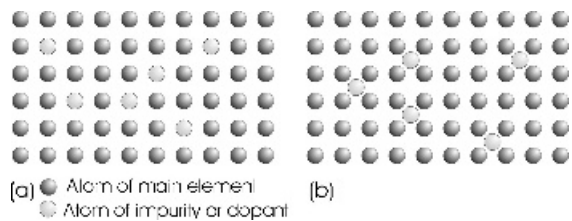


Figure 3.14 (a) A random substitutional solid solution and (b) a random interstitial solid solution

and electrical conductivity than do the pure elements, and are harder and stronger.

Interstitial solid solutions form when small atoms enter spaces between the atoms in a crystal (Figure 3.14b). The interstitial impurities must be small, with a radius less than about 60 % of the parent-structure atoms if an interstitial solid solution is to form. They are typically elements from the first row of the periodic table, such as carbon and nitrogen. Steel is the most important interstitial alloy and consists of interstitial carbon atoms in crystals of iron. Interstitial alloys are usually very hard materials, often used as hard coatings on surfaces liable to excessive wear, such as drill bits.

Both of these solid solutions can become ordered, and this frequently occurs in alloys if they are heated for lengths of time at moderate temperatures. In this case, the crystal adopts a new structure that is no longer regarded as containing impurity defects (see Chapter 5).

3.4.3 Schottky defects

The situation in ionic compounds is slightly more complex than in metals because the ionic charges must remain balanced when point defects are introduced into the crystal. Take the compound sodium chloride, which contains equal numbers of sodium (Na^+) and chlorine (Cl^-) ions and has the chemical formula NaCl . To separate out the effects of the anions from that of the cations it is convenient to refer to the anion sublattice for the Cl^- array and to the cation sublattice for the Na^+ array.

Vacancies on the cation sublattice will change the composition of the compound. As the constituents

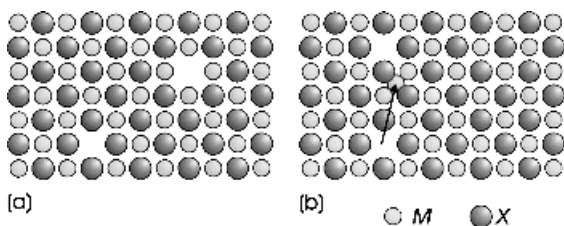


Figure 3.15 Point defects in an ionic crystal of formula MX : (a) Schottky defects and (b) Frenkel defects

are charged, this will also alter the charge balance in the crystal. If x vacancies occur, the formula of the crystal will now be $Na_{1-x}Cl$ and the overall material will have an excess negative charge of x^- , because the number of chloride ions is greater than the number of sodium ions by this amount. The formula could be written $[Na_{1-x}Cl]^{x-}$. If x vacancies are found on the anion sublattice, the material will take on an overall positive charge, because the number of sodium ions now outnumbers the chlorine ions, and the formula becomes $[NaCl_{1-x}]^{x+}$. Now, crystals of sodium chloride do not normally show an overall negative or positive charge or have a formula different from $NaCl$. This means that equal numbers of vacancies must occur on both sublattices.

The defects arising from balanced populations of cation and anion vacancies in any crystal (not just $NaCl$) are known as Schottky defects (Figure 3.15a). Any ionic crystal of formula MX must contain equal numbers of cation vacancies and anion vacancies. In such a crystal, one Schottky defect consists of one cation vacancy plus one anion vacancy. (These vacancies need not be near to each other in the crystal.) The number of Schottky defects in a crystal of formula MX is equal to one half of the total number of vacancies. In crystals of more complex formulae, charge balance is also preserved. The ratio of two anion vacancies to one cation vacancy will hold in all compounds of formula MX_2 , such as titanium dioxide, TiO_2 . Schottky defects in this material will introduce twice as many anion vacancies as cation vacancies into the structure. In crystals with a formula M_2X_3 , a Schottky defect will consist of two vacancies on the cation sublattice and three vacancies on the anion sublattice. In Al_2O_3 ,

for example, two Al^{3+} vacancies will be balanced by three O^{2-} vacancies.

Under equilibrium conditions, the Gibbs energy of a crystal, G , is lower if it contains a small population of Schottky defects, similar to the situation shown in Figure 3.12. This means that Schottky defects will always be present in crystals at temperatures above 0 K, and hence Schottky defects are intrinsic defects. The approximate number of Schottky defects, n_s , in crystal with a formula MX , at equilibrium, is given by:

$$n_s \approx N \exp\left(\frac{-\Delta H_s}{2kT}\right) \quad (3.3)$$

where N is the number of M atoms per unit volume (equal to the number of nonmetal atoms per unit volume) affected by Schottky defects, ΔH_s is the enthalpy (loosely, the heat energy) required to form one defect, k is the Boltzmann constant and T is the temperature (in kelvin). Sometimes, Equation (3.3) is written in the form:

$$n_s \approx N \exp\left(\frac{-\Delta H_s}{2RT}\right) \quad (3.4)$$

In this case, ΔH_s is in $J mol^{-1}$ and represents the enthalpy required to form 1 mole of Schottky defects, and R is the gas constant ($J K^{-1} mol^{-1}$). The fraction of vacant sites in a crystal as a result of Schottky disorder is given by:

$$\frac{n_s}{N} \approx \exp\left(\frac{-\Delta H_s}{2RT}\right) \quad (3.5)$$

where ΔH_s is measured in $J mol^{-1}$. (Remember that this formula applies only to materials with a composition MX .) The formation enthalpies of Schottky defects in some alkali halides are given in Table 3.3.

The fraction of vacant sites at any temperature can be calculated if the enthalpy of defect formation, ΔH_s , is known. To obtain the absolute number of defects in the solid, it is necessary to know the number of atoms, N , of the appropriate type in a unit volume of the crystal. As with elements, this

Table 3.3 The formation enthalpy of Schottky defects, ΔH_S , in some alkali halide compounds of formula MX

Compound	$\Delta H_S/\text{J}$
LiF	3.74×10^{-19}
LiCl	3.39×10^{-19}
LiBr	2.88×10^{-19}
LiI	1.70×10^{-19}
NaF	3.87×10^{-19}
NaCl	3.75×10^{-19}
NaBr	2.75×10^{-19}
NaI	2.34×10^{-19}
KF	4.35×10^{-19}
KCl	4.06×10^{-19}
KBr	3.73×10^{-19}
KI	2.54×10^{-19}

Note: all compounds listed have the *halite* structure

value is often obtained from the unit cell (see Chapter 5):

$$N = \frac{\text{number of appropriate atoms in unit cell}}{\text{unit cell volume}}$$

Alternatively, it is possible to obtain the same information from the density of the material, ρ . The relative molar mass of a compound contains N_A atoms of each type, where N_A is the Avogadro constant. The atomic density of each atom type present in the crystal is given by:

$$N = \frac{\rho \times N_A}{\text{molar mass of compound}}$$

3.4.4 Frenkel defects

It is possible to imagine a defect in ionic crystals similar to the interstitial defects described above. Such defects are known as Frenkel defects. In this case, an ion from one sublattice moves to a normally empty place in the crystal, leaving a vacancy behind. One Frenkel defect consists of an interstitial ion plus a vacancy (Figure 3.15b). Because the total number of ions present does not change, there is no

need for charge balance to be considered. For example, a Frenkel defect on the anion sublattice in calcium fluoride, fluorite, CaF_2 , consists of one F^- ion displaced to an interstitial site. It is not necessary to displace two ions to form the Frenkel defect.

Frenkel defects occur in silver bromide, AgBr . In this compound some of the silver ions (Ag^+) move from the normal positions to sit at usually empty places to generate interstitial silver ions and leave behind vacancies on some of the usually occupied silver sites. The bromide ions (Br^-) are not involved in the defects. (Frenkel defects in AgBr make possible black and white and colour photography on photographic film.)

The presence of a small number of Frenkel defects reduces the Gibbs energy of a crystal and so Frenkel defects are intrinsic defects. The formula for the equilibrium concentration of Frenkel defects in a crystal is similar to that for Schottky defects. There is one small difference compared with the Schottky defect equations: the number of interstitial positions that are available to a displaced ion, N^* , need not be the same as the number of normally occupied positions, N , from which the ion moves. The number of Frenkel defects, n_F , present in a crystal of formula MX at equilibrium is given by:

$$n_F \approx (NN^*)^{1/2} \exp\left(\frac{-\Delta H_F}{2kT}\right) \quad (3.6)$$

where ΔH_F is the enthalpy of formation of a single Frenkel defect, k is the Boltzmann constant and T is the absolute temperature (in kelvin). This is also often expressed in molar quantities:

$$n_F \approx (NN^*)^{1/2} \exp\left(\frac{-\Delta H_F}{2RT}\right) \quad (3.7)$$

where the values for ΔH_F are in units of J mol^{-1} , and R is the gas constant. The formation enthalpies of Frenkel defects in some compounds of formulae MX and MX_2 are given in Table 3.4.

The fraction of interstitials, $n_F/(NN^*)^{1/2}$, at any temperature, can be calculated if the enthalpy of defect formation, ΔH_F is known. To obtain the

Table 3.4 The formation enthalpy of Frenkel defects, ΔH_F , in some compounds of formula MX and MX_2

Compound ^a	$\Delta H_F/\text{J}$	Compound ^b	$\Delta H_F/\text{J}$
AgCl	2.32×10^{-19}	CaF ₂	4.34×10^{-19}
AgBr	1.81×10^{-19}	SrF ₂	2.78×10^{-19}
β -AgI	0.96×10^{-19}	BaF ₂	3.06×10^{-19}

^aFrenkel defects on the cation sublattice of *halite* structure compounds.

^bFrenkel defects on the anion sublattice of *fluorite* structure compounds.

absolute number of defects in the solid, it is necessary to know the number of ions affected by Frenkel disorder, N , and the number of sites that can accept an interstitial, N^* , in a unit volume of the crystal. These values can be assessed by a consideration of the crystal structure of the compound. The two numbers N and N^* are not usually identical, but in cases where they are, the formulae in Equations (3.6) and (3.7) become identical to those for Schottky defects, Equations (3.3) and (3.4).

3.4.5 Nonstoichiometric compounds

Although molecules have a fixed formula and composition, many nonmolecular solids are found to exist over a range of compositions. This variation is considered normal in alloys but unusual in nonmetallic compounds such as oxides. However, not all such solids have a definite and fixed formula, especially at high temperatures. Nonmetallic materials with a composition range are called nonstoichiometric compounds. Two ways in which this composition variation can occur are described below.

Zirconia, ZrO_2 , is an important oxide as it remains inert and stable at temperatures of up to 2500°C and finds uses in many high-temperature applications. Unfortunately, pure zirconia fractures when cycled repeatedly from high to low temperatures because the crystal structure changes at approximately 1100°C . This shortcoming is overcome by reacting zirconia with calcia, CaO . The material that is formed exists over a wide composition range. This nonstoichiometric phase, which has

a cubic unit cell, is called calcia-stabilised zirconia. Although it is not stable to room temperature, transformations to other structures are very slow at lower temperatures. For practical purposes calcia stabilised zirconia can be cycled from high to low temperatures without problem. This significant modification in the properties of zirconia is brought about by the introduction of defects into the crystal.

As with Schottky defects, it is important that charge balance is maintained during the reaction of ZrO_2 and CaO . Cubic calcia-stabilised zirconia crystallises with the *fluorite* (CaF_2) structure. In the present case, the parent material is ZrO_2 . The stabilised phase has Ca^{2+} cations in some of the positions that are normally filled by Zr^{4+} cations, that is, cation substitution has occurred (Figure 3.16). As the Ca^{2+} ions have a lower charge than the Zr^{4+} ions, the crystal will show an overall negative charge if we write the formula as $\text{Ca}_x^{2+}\text{Zr}_{1-x}^{4+}\text{O}_2$. The crystal compensates for the extra negative charge by leaving some of the anion sites unoccupied. For exact neutrality, the number of vacancies on the anion sublattice needs to be identical to the number of calcium ions in the structure. Thus, each Ca^{2+} added to the ZrO_2 produces an oxygen vacancy at the same time. The formula of the crystal is $\text{Ca}_x^{2+}\text{Zr}_{1-x}^{4+}\text{O}_{2-x}$.

Calcia-stabilised zirconia provides a good example of the consequences of incorporating an ion with

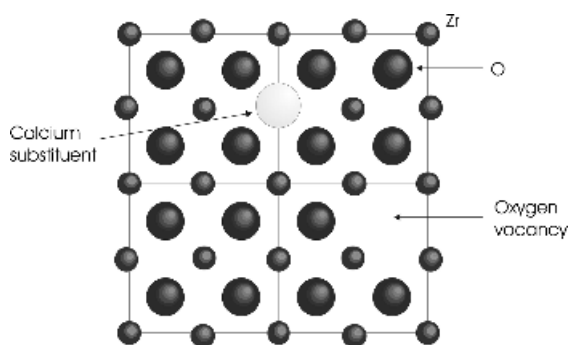


Figure 3.16 The structure of calcia stabilised zirconia. The crystal contains a number of Ca^{2+} ions substituted for Zr^{4+} ions. Each Ca^{2+} ion is accompanied by an O^{2-} vacancy to maintain charge neutrality. The unit cell is outlined

a lower valence into a crystal structure. When a material is 'doped' with substitutional impurity cations of lower charge, anion vacancies are a common method of achieving charge balance. This has a significant effect on the properties of the solid, as the diffusion coefficient of oxygen ions is greatly increased, to the extent that the material is widely used as a solid electrolyte in electrochemical cells and sensors (see Section 9.3.7).

In cases where a cation of higher valence is substituted for the native cation in a crystal, charge balance will also be disturbed. This can occur, for example, if Mg^{2+} impurities are present in a crystal of NaCl. The Mg^{2+} cations will occupy Na^+ sites forming substitutional impurity defects. In order to maintain charge balance, each Mg^{2+} impurity must be balanced by a vacancy on the cation sublattice. As a rule, in a crystal that contains substitutional impurity cations of a higher charge, cation vacancies tend to form in the sublattice of the lower charged ions.

It is also possible to vary the composition of a solid by introducing extra atoms into spaces within the crystal. This process is called interpolation. The likelihood of finding that a nonstoichiometric composition range is due to the presence of interpolated atoms in a crystal will depend on the openness of the structure and the size of the impurity. One of the most important groups of materials in this category, the interstitial alloys, has been described in Section 3.4.2 and is considered further in Section 6.1.5.

Another group of materials that use interpolation are layered structures, in which atoms are taken in between weakly held layers. The resulting compounds, often called insertion compounds, or intercalation compounds, are finding increasing use in batteries (see Section 9.3.6). These are typified by disulphides such as TiS_2 and NbS_2 . The structure of TiS_2 is of the CdI_2 (cadmium iodide) type (Figure 3.17). It is made up of weakly bound layers of composition TiS_2 . Small atoms such as lithium (Li) can enter the structure between these layers to form nonstoichiometric phases with a general formula Li_xTiS_2 . Because the bonding between the layers is weak this process is easily reversible, so the compound can act as a convenient reservoir of Li atoms in lithium batteries. For reasons of efficiency,

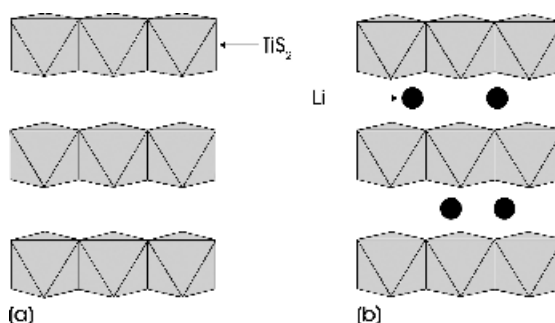


Figure 3.17 (a) The structure of TiS_2 , composed of layers of TiS_6 octahedra, linked by weak bonds. (b) Insertion of Li (or other) atoms between the layers

TiS_2 has now been superseded by other compounds in modern batteries.

Another group of insertion compounds of importance are derived from graphite. The layers of carbon atoms in graphite are only weakly linked by van der Waals bonding. Atoms and molecules are able to enter the structure between the layers, into the so-called van der Waals gap. As with Li_xTiS_2 , lithium inserted into graphite, Li_xC , is used as a battery material (see Section 9.3.6). The material that forms when fluorine is incorporated, CF_x , is used as a solid lubricant (see Section 10.3.1). The strongly electronegative fluorine atoms bond covalently to the carbon atoms, which forces the layers further apart, with the result that CF_x is a better solid lubricant than is pure graphite.

3.4.6 Edge dislocations

It has long been known that the theoretical strength of a metal crystal is far greater than the strength normally observed. Moreover, metals can be deformed easily and retain the new shape, a process called plastic deformation, whereas ceramic solids fracture under the same conditions. The typical mechanical properties of metals are due to the presence of linear defects called dislocations.

Although there are many different types of dislocations, they can all be thought of as combinations of two fundamental types. Edge dislocations consist

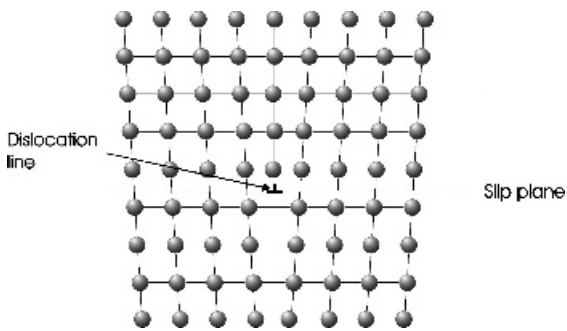


Figure 3.18 An edge dislocation, consisting of an extra half plane of atoms inserted in a crystal. The dislocation line is perpendicular to the plane of the figure, and is marked by \perp . The slip plane is the crystal plane of preferred movement of the dislocation

of an extra half-plane of atoms inserted into the crystal (Figure 3.18). These dislocations are instrumental in allowing metals to undergo plastic deformation. The dislocation line is marked by \perp . It runs normal to the plane of the drawing. The slip plane, lying perpendicular to the dislocation line, is the plane along which the dislocation moves. If a shear force is applied to the crystal the dislocation glides (moves), to reduce the shear, resulting in a permanent deformation, recognised as the step in the crystal profile (Figure 3.19; see also Section 10.1.9). In essence, only one line of bonds is broken each time the dislocation is displaced by one atomic spacing, and the stress required is relatively small. If the same deformation were to be produced in a

perfect crystal, large numbers of bonds would have to be broken simultaneously, requiring much greater stress. The presence of edge dislocations successfully explains the deformation properties of metals. Similarly, if dislocation movement is impeded or impossible, the material becomes hard and brittle. This is so in ceramics, in which dislocation movement is impeded, at least in part, by the charges on the ions.

The disruption to the crystal introduced by a dislocation is characterised by the Burgers vector. The Burgers vector of a dislocation is determined by drawing a circuit in the crystal, from atom to atom, in a region of crystal away from the defect (Figure 3.20). This is called a Burgers circuit. The Burgers circuit starts and ends on the same atom in a perfect crystal (Figure 3.20a), but will not do so if the circuit contains a dislocation (Figure 3.20b). The vector describing this failure, running from the start atom to the end atom, is the Burgers vector, \mathbf{b} , of the dislocation. The Burgers vector of an edge dislocation is perpendicular to the dislocation line.

A perfect dislocation has a Burgers vector equal to an atom-to-atom vector in the crystal. As the energy of a dislocation is proportional to b^2 , the most common dislocations in metals have small Burgers vectors.

3.4.7 Screw dislocations

Screw dislocations, the second important category of dislocation, looks rather like a spiral staircase.

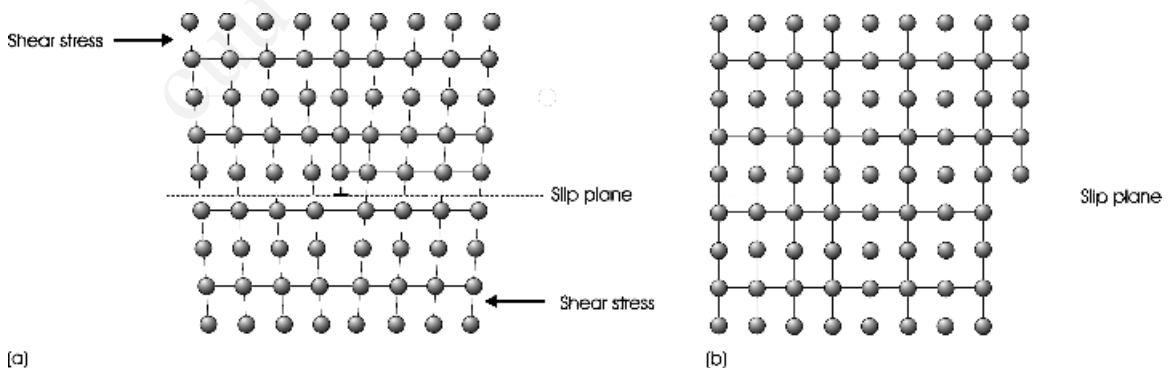


Figure 3.19 Application of a shear stress to a crystal containing an edge dislocation (part a) can cause the dislocation to move out of the crystal to leave a surface step (part b)

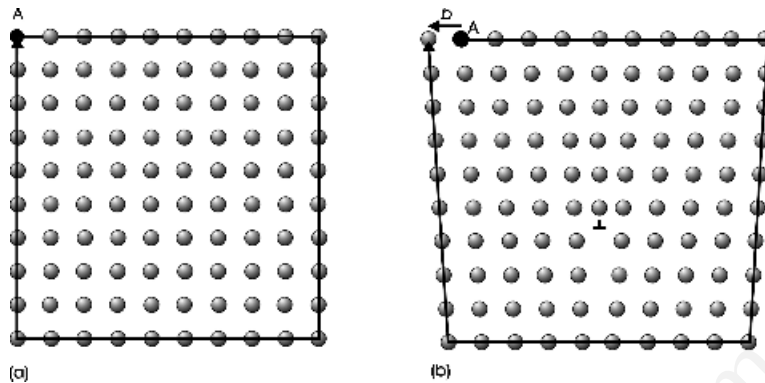


Figure 3.20 (a) A Burgers circuit in a perfect crystal (heavy line) will be closed; (b) the same circuit in a crystal containing a dislocation will remain open. The vector required to close the circuit, b , is the Burgers vector

The dislocation can be formed (conceptually) by cutting halfway through a crystal and sliding the regions on each side of the cut parallel to the cut, to create spiralling atom planes (Figure 3.21). The dislocation line is the central axis of the 'staircase'. The Burgers vector of a screw dislocation is parallel to the dislocation line. Screw dislocations play an important part in crystal growth.

3.4.8 Partial and mixed dislocations

Dislocations can be imaged and their Burgers vectors determined by using transmission electron microscopy. This technique has shown that many dislocations have a Burgers vector that is less than the repeat distance of the structure. These are called partial dislocations.

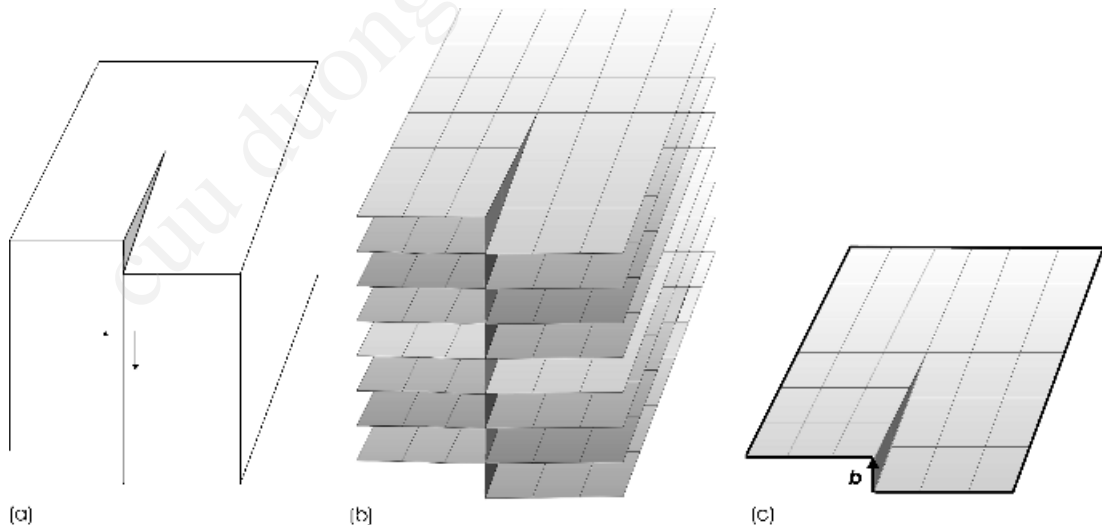


Figure 3.21 (a) A screw dislocation can be formed by cutting a crystal and displacing the halves. (b) The planes around a screw dislocation spiral around the dislocation line like a spiral staircase. (c) In a screw dislocation the Burgers vector, b , is parallel to the dislocation line

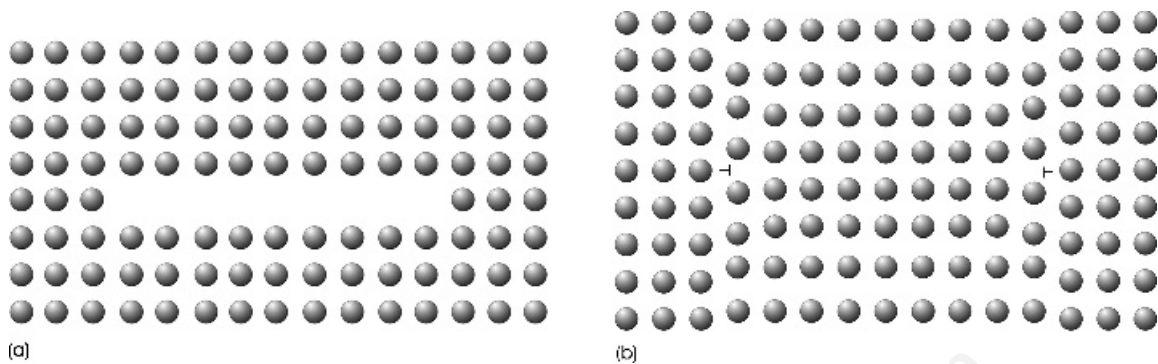


Figure 3.22 (a) Aggregation of vacancies on a plane in a crystal. (b) Formation of an edge dislocation loop by collapse of the crystal in the vacancy region

A dislocation line separates a region of crystal that has moved relative to an adjoining part. This disruption means that the dislocation must either end on the surface of a crystal or else form a closed loop. Dislocation loops have been found to occur frequently in crystals. One way in which a dislocation loop can form is by the aggregation of vacancies on a plane in a metal crystal (Figure 3.22). Vacancy populations are relatively large at high temperatures and, if a metal is held at a temperature near to its melting point, these defects can migrate from site to site (see Section 7.4). If sufficient vacancies aggregate, a dislocation loop can form. The dislocation that delineates the loop is an edge dislocation. As dislocation loops grow, they can change character, so that at one part of the loop the Burgers vector is parallel to the dislocation line and at another part it is parallel to it. That is, the character of the dislocation changes from pure edge to pure screw. Elsewhere on the loop, the dislocation has an intermediate character and is called a mixed dislocation.

3.4.9 Multiplication of dislocations

Dislocations are introduced into solids when they crystallise. In addition, dislocations form in materials subjected to stress. There are a number of mechanisms by which new dislocations can form, but most require an existing dislocation to become

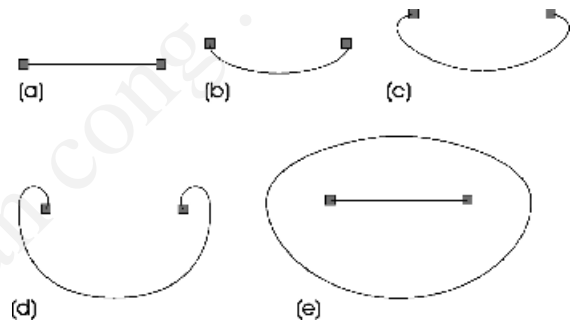


Figure 3.23 A dislocation pinned at each end (part a) can respond to stress by bowing out (parts b–d) to form a dislocation loop and reform the pinned dislocation (part e)

trapped, or pinned, in the crystal, so that glide can no longer occur. One of these involves a length of dislocation pinned at each end (Figure 3.23a). This is called a Frank–Read source. When stress is applied to this defect, the pinned dislocation cannot glide to relieve the stress, but it can bulge out from the pinning centres to achieve the same result (Figure 3.23b). Further stress increases the degree of bulging (Figures 3.23c and 3.23d), until both sides of the bulge can unite to form a dislocation loop and a new dislocation between the pinning centres (Figure 3.23e). A Frank–Read source can continually emit dislocation loops during stress, thus significantly multiplying the dislocation density in a crystal.

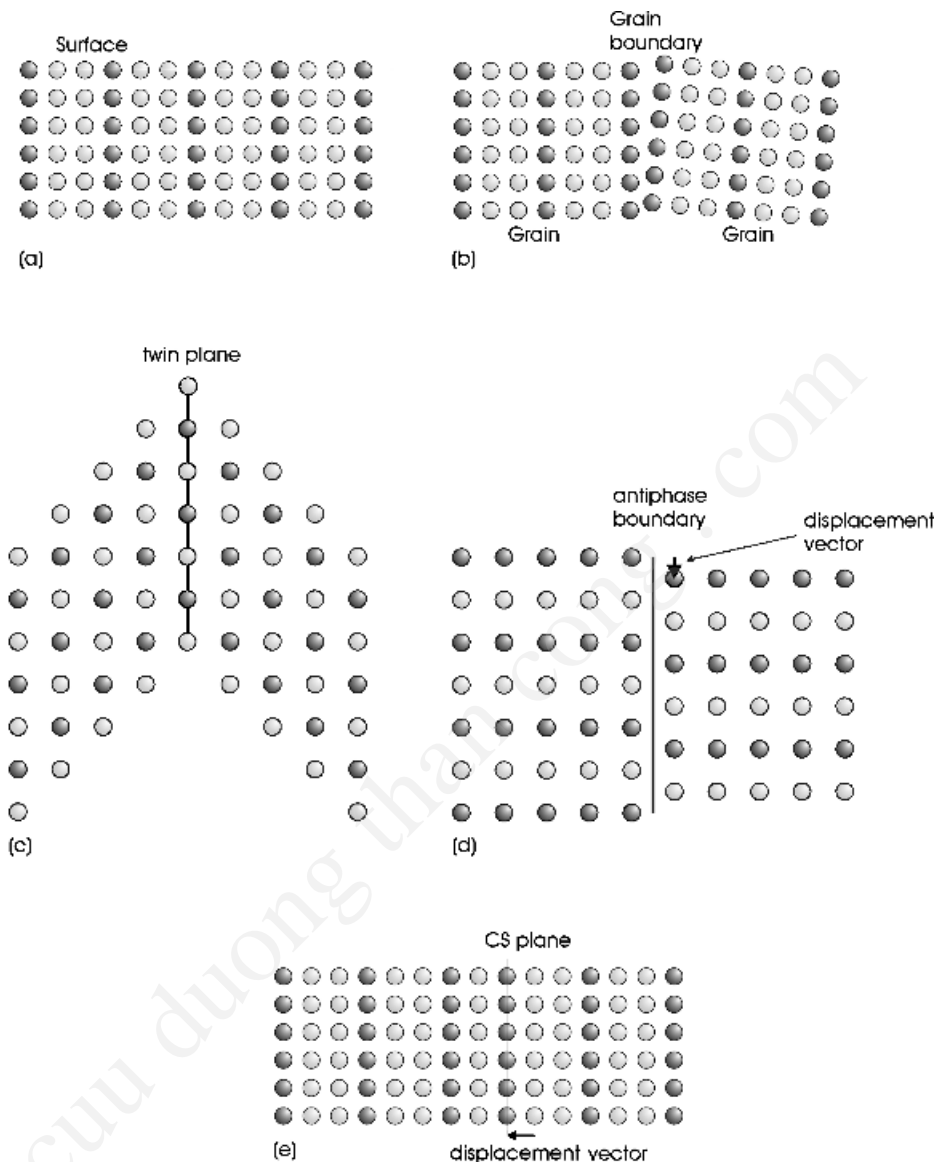


Figure 3.24 Surfaces and boundaries in a crystal: (a) the external surface; (b) grain boundaries; (c) a twin plane; (d) an antiphase boundary and (e) a crystallographic shear plane

3.4.10 Planar defects

Planar defects are two-dimensional surface defects. In many cases, the most important planar defects in a solid are the external surfaces (Figure 3.24a). These may dominate chemical reactivity, and solids designed as catalysts, or, for example, for use in gas

filters, must have large surface areas in order to function. Rates of reaction during corrosion are frequently determined by the amount of surface exposed to the corrosive agent.

Grain boundaries are boundaries between crystallites in a polycrystalline array (Figure 3.24b). The energy of these boundaries, much of which is

surface energy, depends on the planes of the boundaries. Annealing (i.e. heating for extended periods at temperatures high enough to allow for extensive atom diffusion) will cause rearrangement to occur, leading to lower-energy configurations. In these cases there is often a relationship between the crystallography of the material and the boundary planes. Grain boundaries are invariably weaker than the crystal matrix, and the mechanical strength of many solids is a result of the presence of grain boundaries and does not reflect the intrinsic strength of the crystallites making up the solid. In metals, grain boundaries prevent dislocation motion and reduce the ductility. Grain boundaries also increase the electrical resistance of a polycrystalline solid compared with that of a single crystal and introduce scattering and opacity into otherwise transparent solids.

Twin boundaries are boundaries in a crystal in which the crystal matrix on one side of the boundary mirrors the crystal matrix on the other (Figure 3.24c). The mirror plane, or twin plane, may not be identical to the plane along which the two mirror-related parts of the crystal join, which is called the composition plane. Twin boundaries affect mechanical, optical and electronic properties of materials in a similar way to grain boundaries.

Antiphase boundaries (APBs) are boundaries within a crystal across which one part of the crystal has been displaced with respect to the other side (Figure 3.24d). The vector describing the displacement of the two parts of the crystal is parallel to the boundary plane. When the displacement vector of the boundary is at an angle to the interface so that there is a collapse of the crystal, the boundary is called a crystallographic shear (CS) plane. In these latter boundaries, one or more planes of atoms are removed with respect to the parent structure, as shown in Figure 3.24(e), and the composition of the crystal changes. Regular arrays of crystallographic shear planes in a crystal lead to a series of new compounds, called a homologous series. For example, removal of oxygen from titanium dioxide (rutile), TiO_2 , causes arrays of CS planes to form. When these are ordered, members of the homologous series $\text{Ti}_n\text{O}_{2n-1}$, Ti_9O_{17} and $\text{Ti}_{10}\text{O}_{19}$, for

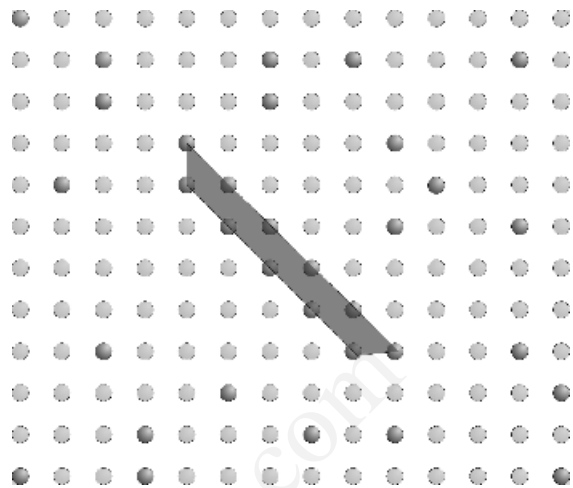


Figure 3.25 A precipitate formed by clustering of atoms in a crystal

instance, are produced. The value of n in a homologous series formula is a function of the spacing of the crystallographic shear planes. Large values of n correspond to wide spacing.

3.4.11 Volume defects: precipitates

Volume defects are regions of an impurity phase in the matrix of a material. Precipitates in a solid represent most volume defects (Figure 3.25). Precipitates form in a variety of circumstances. Solid solutions are often not stable at low temperatures, and decreasing the temperature of a solid solution slowly will frequently lead to the formation of precipitates of a new crystal structure within the matrix of the solid solution. Glasses are inherently unstable, and a glass may slowly recrystallise. In this case, precipitates of crystalline material will appear. Precipitates have important effects on the mechanical, electronic and optical properties of solids. Precipitation hardening is an important process used to strengthen metal alloys. In this technique, precipitates are induced to form in the alloy matrix by carefully controlled heat treatment. These precipitates interfere with dislocation movement and have the effect of significantly hardening the alloy.

Answers to introductory questions

What type of bonding causes the noble gases to condense to liquids?

The noble gases, in group 18 of the periodic table, have the outer electron structure ns^2np^6 . This stable electron configuration does not lend itself to strong bonding and, at normal temperatures, the noble gases exist as monatomic gases. The condensation of these gases into liquids is a result of weak interactions between the outer electrons on the atoms. Fleeting instantaneous fluctuations in the electron cloud surrounding these atoms create momentary dipoles. These instantaneous charges lead to a weak attraction, which occurs between all atoms and molecules, including the noble gases. The resultant force of attraction is called the London or dispersion force and the interaction is called van der Waals bonding. The bond energy is approximately 2 kJ mol^{-1} . The strength of the interaction increases as the size of the atoms increases, so that the boiling points of the noble gases form a series: He, -268.9°C ; Ne, -246.1°C ; Ar, -185.9°C ; Kr, -153.2°C ; Xe, -108.1°C ; Rn, -61.7°C .

What is the scale implied by the term 'nanostructure'?

The nanostructure of a material is its structure at an atomic scale. Nanoparticles and nanostructures generally refer to structures that are small enough that chemical and physical properties are observably different from the normal or 'classical' properties of bulk solids. The dimension at which this transformation becomes apparent depends on the phenomenon investigated. In the case of thermal effects, the boundary occurs at approximately the value of thermal energy, kT , which is about $4 \times 10^{-21} \text{ J}$. In the case of optical effects, nonclassical behaviour is noted when the scale of the object illuminated is of the same size as a light wave, say about $5 \times 10^{-7} \text{ m}$. For particles such as electrons, the scale is determined by the Heisenberg uncertainty principle, at about $3 \times 10^{-8} \text{ m}$.

Nanostructures exist at many levels and many of these have been discovered in nature.

What line defects occur in crystals?

The line defects that occur in crystals are called dislocations. There are many different types of dislocations but they all can be thought of as combinations of two fundamental types: edge and screw dislocations. Edge dislocations consist of an extra half-plane of atoms inserted into the crystal. The dislocation line is the termination of this half-plane. The Burgers vector of an edge dislocation lies perpendicular to the dislocation line. These dislocations are instrumental in allowing metals to undergo plastic deformation. Screw dislocations are analogous to a spiral staircase. The dislocation can be formed in principle by cutting halfway through a crystal and sliding the regions on each side of the cut parallel to the cut, to create spiralling atom planes. The dislocation line is the central axis of the 'staircase'. The Burgers vector of a screw dislocation is parallel to the dislocation line. Screw dislocations play an important part in crystal growth.

Dislocations that have a Burgers vector that is less than the repeat distance of the structure are called partial dislocations. Dislocations that have a Burgers vector that is neither parallel nor perpendicular to the dislocation line are called mixed dislocations. Dislocation loops are closed, and occur within the bulk of a crystal. One way in which a dislocation loop can form is by the aggregation of vacancies on a plane in a metal crystal. As dislocation loops grow, they can change character, so that at one part of the loop the Burgers vector is parallel to the dislocation line and at another part it is perpendicular to it. That is, the character of the dislocation changes from pure edge to pure screw. Elsewhere on the loop, the dislocation has an intermediate character.

Further reading

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Problems and exercises

Quick quiz

- 1 Hydrogen bonding is found in:
 - (a) Solid and liquid hydrogen
 - (b) Hydrocarbons
 - (c) Compounds containing oxygen and hydrogen
- 2 Van der Waals bonds are a result of:
 - (a) Dispersion forces
 - (b) Ion–dipole forces
 - (c) Dipole–dipole forces
- 3 Nonstoichiometric compounds have:
 - (a) A mineral composition
 - (b) A variable composition
 - (c) A metallic composition
- 4 A refractory oxide is:
 - (a) An oxide that is difficult to prepare
 - (b) An oxide that is rare
 - (c) An oxide that is resistant to high temperatures
- 5 Alumina is another name for:
 - (a) Silicon oxide
 - (b) Aluminium oxide
 - (c) Zirconium oxide
- 6 Sublimation is characteristic of compounds containing:
 - (a) Ionic bonds
 - (b) Metallic bonds
 - (c) Van der Waals bonds
- 7 The microstructure of a solid is at a scale of:
 - (a) $1-10^{-3}$ m
 - (b) $10^{-3}-10^{-6}$ m
 - (c) $10^{-7}-10^{-9}$ m
- 8 A polycrystalline sample is:
 - (a) A polymer
 - (b) A powder
 - (c) Composed of small crystals
- 9 A glass is:
 - (a) A noncrystalline inorganic solid
 - (b) A crystalline inorganic solid
 - (c) A solid containing silica
- 10 Sintering is a process that involves:
 - (a) Cross-linking polymer chains
 - (b) Heating powdered ceramics or metals until the particles unite
 - (c) Cold working a solid to make it harder
- 11 An important step in the fabrication of opal glass and glass ceramics is:
 - (a) Devitrification
 - (b) Sintering
 - (c) Quenching
- 12 In a quantum well, electrons are confined in:
 - (a) Three dimensions
 - (b) Two dimensions
 - (c) One dimension
- 13 Fullerenes are:
 - (a) Large carbon molecules with a roughly spherical form
 - (b) Large carbon molecules with a roughly tubular form

- (c) Large carbon molecules with a chain-like form
- 14 Intrinsic point defects are:
 (a) Always present in a solid
 (b) A result of impurities in a solid
 (c) Grains in a solid
- 15 The number of different intrinsic point defects possible in a single crystal of a pure element is:
 (a) One
 (b) Two
 (c) Three
- 16 The number of intrinsic point defects expected to predominate in a crystal is:
 (a) One
 (b) Two
 (c) Three
- 17 A Schottky defect in a crystal of potassium bromide, KBr, consists of:
 (a) A potassium vacancy and a bromide interstitial
 (b) A potassium vacancy and a bromide vacancy
 (c) A potassium interstitial and a potassium vacancy
- 18 A Frenkel defect in a crystal of silver bromide, AgBr, consists of:
 (a) A silver vacancy and a bromide interstitial
 (b) A silver vacancy and a bromide vacancy
 (c) A silver interstitial and a silver vacancy
- 19 Calcia-stabilised zirconia contains:
 (a) Interstitial defects
 (b) Substitutional defects
 (c) Interpolation defects
- 20 The Burgers vector and dislocation line are normal to each other in:
 (a) A screw dislocation
 (b) A partial dislocation
 (c) An edge dislocation
- 21 The Burgers vector and dislocation line are parallel to each other in:
 (a) A screw dislocation
 (b) A partial dislocation
 (c) An edge dislocation
- 22 A dislocation loop has:
 (a) No Burgers vector
 (b) A Burgers vector always normal to the loop
 (c) A Burgers vector that changes along the periphery of the loop
- 23 Dislocations are:
 (a) Planar defects
 (b) Line defects
 (c) Point defects
- 24 Dislocation movement occurs by:
 (a) Motion in the slip plane
 (b) Motion perpendicular to the slip plane
 (c) Motion of the slip plane
- 25 A twin boundary in a solid is an example of:
 (a) A line defect
 (b) A planar defect
 (c) A volume defect
- 26 A precipitate is a:
 (a) Point defect
 (b) Planar defect
 (c) Volume defect

Calculations and questions

- 3.1 The potential energy between a pair of atoms or molecules is given approximately by a Lennard-Jones potential, which has the form

$$V(r) = Ar^{-12} - Br^{-6}$$

where $V(r)$ is the potential energy, A and B are constants, and r is the separation of the atoms or molecules. The term Ar^{-12}

represents the weak attractive London force, and the term $B r^{-6}$ represents a repulsive term arising from the interaction of the core electrons. For a pair of argon atoms, $A = -1.78 \times 10^{-134} \text{ J m}^{12}$ and $B = -1.08 \times 10^{-77} \text{ J m}^6$.

Plot the attractive and repulsive potential energies. [Note: not shown in answers at the end of this book.] Estimate the minimum potential energy of the pair, which can be considered the bonding energy of a molecule of argon, and the interatomic separation of this molecule.

- 3.2 By equating the thermal energy (kT , where k is the Boltzmann constant and T is the temperature, in kelvin), with the bonding energy, estimate the temperature at which argon atoms are likely to start to form pairs, and so form a liquid, by using the data in Question 3.1. Compare this with the boiling point of argon (see Question 3.22).
- 3.3 If the atoms in liquid argon are surrounded by 12 nearest neighbours on average, estimate the energy of evaporation of the liquid.
- 3.4 The Lennard-Jones constants for neon (Ne), are $A = -4.39 \times 10^{-136} \text{ J m}^{12}$, and $B = -9.30 \times 10^{-79} \text{ J m}^6$. Calculate the bonding energy and equilibrium separation of a pair of neon atoms.
- 3.5 The Lennard-Jones constants for helium (He), are $A = -4.91 \times 10^{-137} \text{ J m}^{12}$, and $B = -4.16 \times 10^{-80} \text{ J m}^6$, and for xenon (Xe), are $A = -2.54 \times 10^{-133} \text{ J m}^{12}$, and $B = -5.66 \times 10^{-77} \text{ J m}^6$. Using these values and those in Questions 3.1 and 3.4, estimate the Lennard-Jones constants for krypton (Kr).
- 3.6 Derive the relationship

$$V(r) = 4V_{\min} \left[\left(\frac{r_0}{r} \right)^6 - \left(\frac{r_0}{r} \right)^{12} \right]$$

from

$$V(r) = Ar^{-12} + Br^{-6}.$$

[Note: derivation is not provided in answers at the end by this book.]

- 3.7 The enthalpy of formation of vacancies in pure nickel is $\Delta H = 97.3 \text{ kJ mol}^{-1}$. What is the fraction of sites vacant at 1100°C ?
- 3.8 The enthalpy of formation of vacancies in pure copper is $\Delta H = 86.9 \text{ kJ mol}^{-1}$. What is the fraction of sites vacant at 1084°C ?
- 3.9 The enthalpy of formation of vacancies in pure gold is $\Delta H = 123.5 \text{ kJ mol}^{-1}$. The density of gold is 19281 kg m^{-3} . What number of atom positions is vacant at 1000°C ?
- 3.10 The enthalpy of formation of vacancies in pure aluminium is $\Delta H = 72.4 \text{ kJ mol}^{-1}$. The density of aluminium is 2698 kg m^{-3} . What number of atom positions is vacant at 600°C ?
- 3.11 Calculate how the fraction of Schottky defects in a crystal of KCl varies with temperature if the value of ΔH_S is 244 kJ mol^{-1} . [Note: the answers at the end of this book gives values for $T = 500 \text{ K}$; $T = 1000 \text{ K}$.]
- 3.12 Calculate the number of Schottky defects in a crystal of KCl at 800 K . The unit cell of this material is cubic with a cell edge of 0.629 nm . Each unit cell contains 4 K^+ and 4 Cl^- ions.
- 3.13 The enthalpy of formation of a Frenkel defect in silver bromide, AgBr, is $1.81 \times 10^{-19} \text{ J}$. Estimate the fraction of interstitial silver atoms owing to Frenkel defect formation in a crystal of AgBr at 300 K .
- 3.14 Silver bromide, AgBr, has a cubic unit cell with an edge of 0.576 nm . There are four silver atoms in the unit cell; assume that there are four interstitial positions available for silver atoms. Calculate the absolute number of interstitial defects present per cubic metre at 300 K .
- 3.15 Calculate the enthalpy of formation of Frenkel defects in sodium bromide, NaBr, using the data on the number of defects, n_F , present given in Table 3.5.

Table 3.5 Number of Frenkel defects, n_F , as a function of temperature, T

T/K	n_F/m^{-3}
200	1.428×10^2
300	7.257×10^{10}
400	1.636×10^{15}
500	6.693×10^{17}
600	3.687×10^{19}
700	6.468×10^{20}
800	5.538×10^{21}
900	2.943×10^{22}

- 3.16 The energy of formation of Schottky defects in a crystal of calcium oxide, CaO, is given as 9.77×10^{-19} J. Calculate the number of Schottky defects, n_s , present in CaO at 1000 °C and 2000 °C. How many vacancies are present at these temperatures? CaO has a density of 3300 kg m^{-3} .
- 3.17 Calculate the number of Schottky defects in a crystal of magnesium oxide, MgO, at 1500 °C. The enthalpy of formation of Schottky defects in MgO is 96.5 kJ mol^{-1} , and the density of MgO is 3580 kg m^{-3} .
- 3.18 Calculate the number of Frenkel defects present in a crystal of silver chloride, AgCl, at 300 K, given that the material has a cubic unit cell of edge 0.555 nm that contains four silver atoms. Assume that the interstitial atoms occupy any of eight tetrahedral sites in the unit cell. The enthalpy of formation of a Frenkel defect in AgCl is 2.69×10^{-19} J.
- 3.19 Calculate the number of vacancies in a crystal of nickel oxide, NiO, at 1000 °C, given that the enthalpy of formation of Schottky defects is 160 kJ mol^{-1} , and the density is 6670 kg m^{-3} .
- 3.20 The fraction of Schottky defects in nickel oxide, NiO, at 1000 °C is 1.25×10^{-4} . The cubic unit cell contains four nickel atoms and has a cell edge of 0.417 nm. Calculate the number of nickel vacancies present.
- 3.21 The number of Schottky defects in lithium fluoride, LiF, which has a cubic unit cell

containing four lithium and four fluorine atoms, with a cell edge of 0.4026 nm, is $1.12 \times 10^{22} \text{ m}^{-3}$ at 600 °C. Calculate the activation energy for the formation of these defects.

- 3.22 The melting points and boiling points of the noble gases are given in Table 3.6. Explain

Table 3.6 Melting points (Mpts) and boiling points (Bpts) of the noble gases

Element	Mpt/°C	Bpt/°C
Helium	N.A.	-268.9
Neon	-248.6	-246.1
Argon	-189.4	-185.9
Krypton	-117.4	-153.2
Xenon	-111.8	-108.0
Radon	-71	-61.7

N.A. Not applicable.

- these trends and why the melting and boiling points are so close. [Note: answer is not provided at the end of this book.]
- 3.23 A total of 9 mol% of Y_2O_3 is mixed with 91 mol% ZrO_2 and heated until a uniform product with high oxygen ion conductivity is obtained. The resulting crystal is a stabilised zirconia with the formula $\text{Y}_x\text{Zr}_y\text{O}_z$. Determine x , y and z , explaining your answer.
- 3.24 CaO forms a solid solution with Bi_2O_3 to give a material with a high anionic conductivity. If 10 mol% CaO is reacted with 90 mol% Bi_2O_3 , what is the formula of the final solid and what are the numbers and types of vacancies created?
- 3.25 What defects will form in the crystals made by adding small amounts of compound A to compound B:
- $\text{A} = \text{LiBr}$, $\text{B} = \text{CaBr}_2$?
 - $\text{A} = \text{CaBr}_2$, $\text{B} = \text{LiBr}$?
 - $\text{A} = \text{MgO}$, $\text{B} = \text{Fe}_2\text{O}_3$?
 - $\text{A} = \text{MgO}$, $\text{B} = \text{NiO}$?
- 3.26 What defects will form in the crystals made by adding small amounts of compound A to

compound B:

(a) A = CdCl₂, B = NaCl?

(b) A = NaCl, B = CdCl₂?

(c) A = Sc₂O₃, B = ZrO₂?

(d) A = ZrO₂, B = HfO₂?

- 3.27 Show that the number of metal atom sites in a crystal of composition MX is given by

$$N = \frac{\rho \times N_A}{\text{relative molar mass of } MX},$$

where ρ is the density of MX , and N_A is the Avogadro constant. Sodium chloride, NaCl, has a density of 2165 kg m⁻³. The unit cell, which is cubic, with a cell of edge 0.563 nm, contains four Na and four Cl atoms. Calculate the number of atoms of sodium per cubic metre by using (a) the unit cell dimensions and (b) by using the density and molar mass. [Note: derivation is not provided in answers at the end of this book.]