Guided Learning Unit 1: Simple ideas of Crystallography

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Introduction and synopsis

Though they lacked the means to prove it, the ancient Greeks suspected that solids were made of discrete atoms packed in a regular, orderly lattice to give crystals. Today, with the 21st century techniques of X-ray and electron diffraction and lattice-resolution microscopy available to us, we know that all solids are indeed made of atoms and that most (but not all) are crystalline. The common engineering metals and ceramics are made of many small crystals, or grains, stuck together at grain boundaries to make polycrystals. Many properties of crystalline materials e their strength, stiffness, toughness, conductivity, and so forth e are strongly influenced by their atomic packing.

Crystallography is a geometric language for describing the three-dimensional arrangement of atoms or molecules in crystals. Simple crystalline and non-crystalline structures were introduced in Chapter 4. Here we go a little deeper, exploring a wider range of structures, interstitial space (important in understanding alloying and the heat treatment of steel), and ways of describing planes and directions in crystals (crucial in the production of single-crystal turbine blades, beverage cans, and microchips).

Exercises are provided in Parts 1e5, so do these as you go along; solutions are provided at the end.

PART 1: Crystal structures

Three-dimensional crystal lattices may be characterised by the repeating geometry of the atomic arrangements they contain, particularly exploiting their high degree of symmetry. Most atomic bonding gives a well-characterised equilibrium spacing between neighbouring atoms, so for the purposes of understanding crystal packing, the atoms may be treated as hard spheres in contact. Spheres can be packed to fill space in various different ways e in fact there are 14 distinguishable three-dimensional lattices. If you are a crystallographer or mineral scientist, you need to know about all of them. But engineering materials, for the most part, are based on three simple structures, and we concentrate on these.

Each lattice is characterised by a unit containing a small number of atoms, which repeats itself in 3D e the unit cell.

DEF. The unit cell of a crystal structure is the unit of the structure, chosen so that it packs to fill space, and which, translated and stacked regularly, builds up the entire structure. The primitive unit cell is the smallest such cell.

Figure GL1.1 shows the most important unit cells. The first lattice is the *triclinic* unit cell, which is the most general e the edge lengths (or *lattice constants*) a, b, and c are all different, and no angle is 90^{0}. The other 13 space (or *Bravais*[1]) lattices are all special cases of this one e for example, for all the cubic unit cells, a ¼ b ¼ c and a ¼ b ¼ g ¼ 90^{0}.

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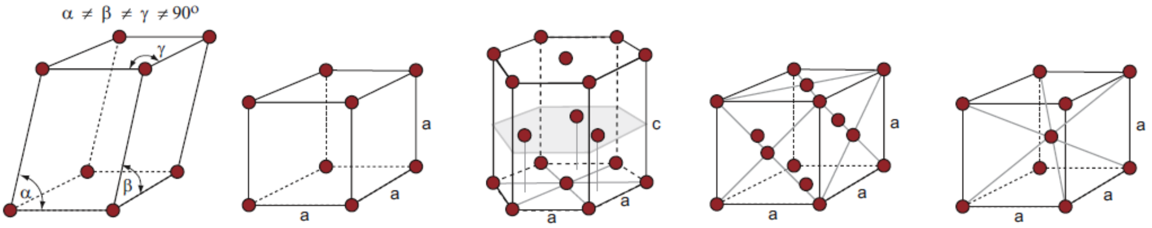
[1] Auguste Bravais (1811—1863), French crystallographer, botanist, and physicist, sought to explain the shapes of mineral crystals by analysing the figures formed by points distributed regularly in space. Others had tried this and had concluded that the number of such 'lattices' distinguishable by their symmetry was finite and small, but it took Bravais to get it right, demonstrating that there are exactly 14.



Triclinic (P) Simple cubic Close-packed hexagonal Face-centered cubic Body-centered cubic

Figure GL1.1 The general triclinic unit cell and the four most important lattices for engineering materials: simple cubic (SC), close-packed hexagonal (CPH), face-centred cubic (FCC), and body-centred cubic (BCC).

The close-packed hexagonal (CPH) structure The CPH structure is usually described by a hexagonal unit cell with an atom at each corner, one at the centre of the hexagonal faces, and three in the middle layer. In this packing, the close-packed layers are clearly seen, and alternate close-packed layers are aligned (as observed for one case in Exercise E.1), giving an ABAB … sequence (Figure GL1.3). Unit cells are often drawn with the atoms reduced in size to show clearly where the centres lie with respect to one another, but in reality atoms will touch in certain *close-packed directions*.

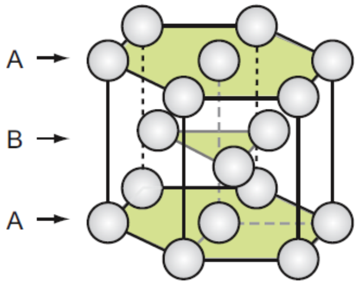


Figure GL1.3 A CPH structure of packed spheres showing ABA stacking.

Of the metallic elements, 30 have the CPH structure, including:

Material	Typical uses of element and its alloys
Zinc	Die-castings, plating
Magnesium	Lightweight structures
Titanium	Light, strong components for airframes and engines; biomedical and chemical engineering
Cobalt	High-temperature superalloys, bone-replacement implants
Beryllium	A light, stiff metal; its use is limited by expense and potential toxicity

CPH metals have the following characteristics:

- They are reasonably ductile, allowing them to be hot forged, but in a more limited way than FCC metals (so they are also commonly cast).
- Their structure makes them more anisotropic than FCC or BCC metals.

The face-centred cubic (FCC) structure The FCC structure is described by a cubic unit cell with one atom at each corner and one at the centre of each face. Atoms touch along the diagonals of the cube faces, and the centre atoms in any pair of adjoining faces also touch one another. The close-packed layers are not so obvious in FCC but can be seen by looking down any diagonal of the cube. Figure GL1.4 shows that the close-packed layers are now stacked in an ABCABC … sequence (the other case in Exercise E.1).

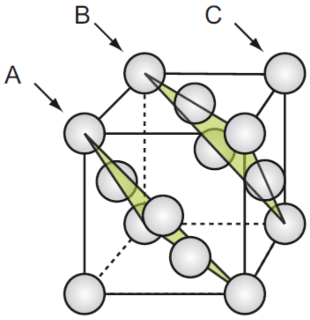


Figure GL1.4 An FCC structure of packed spheres showing the ABC stacking.

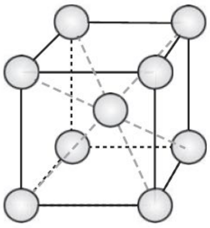


Figure GL1.5 A BCC structure of non-close-packed spheres.

Among the metallic elements, 17 have the FCC structure, including:

Material	Typical uses of element and its alloys
Aluminium	Airframes, and bodies of trains, trucks, cars; beverage cans
Nickel	Turbine blades and disks
Copper	Conductors, bearings
Lead	Batteries, roofing, cladding of buildings
Austenitic stainless steels (based on iron)	Stainless cookware, chemical and nuclear engineering, cryogenic engineering
Silver, gold, platinum	Jewellery, coinage, electrical contacts

FCC metals have the following characteristics:

- They are very ductile when pure, work hardening rapidly but softening again when annealed, allowing them to be shaped by deformation processing (e.g. rolled, forged, or drawn).
- They are generally tough and resistant to crack propagation (as measured by their fracture toughness, K_{1c}).
- They retain their ductility and toughness to absolute zero, something very few other structures allow.

The body-centred cubic (BCC) structure The BCC structure is described by a cubic unit cell with one atom at each corner and one in the middle of the cube (Figure GL1.5). The atoms touch along the internal diagonals of the cube, and this structure is not made up of close-packed planes.

Of the metallic elements, 21 have the BCC structure (most are rare earths), including:

Material	Typical uses of element and its alloys
Iron, mild steel	The most important metal of engineering: construction, cars, cans, and more
Carbon steels, low alloy steels	Engine parts, tools, pipelines, power generation
Tungsten	Lamp filaments
Chromium	Electroplated coatings

BCC metals have the following characteristics:

- They are ductile, particularly when hot, allowing them to be shaped by deformation processing (e.g. rolled, forged, or drawn).
- They are generally tough and resistant to crack propagation (as measured by their fracture toughness, K_{1c}) at and above room temperature.
- They become brittle below a ‘ductile-brittle transition temperature’, limiting their use at low temperatures.
- They can generally be hardened with interstitial solutes.

Atomic packing fraction and theoretical density The density of a crystalline material depends on the mass of the atoms and the way they are packed. We can find the theoretical density of the crystal directly from the mass and volume of the unit cell. An important first step is to be clear how many atoms are fully contained within a given unit cell (since atoms on the boundaries of the unit cell are shared with neighbouring cells). This also allows us to find the *atomic packing fraction* – i.e. the proportion of space occupied by the atoms, represented as solid spheres.

The theoretical density is found as follows. The mass of one atom is given by A/N_A, where A is the atomic mass (in kg) of 1 mol of the element, and $N_A = 6.022 \times 10^{23}$ is Avogadro’s number[2] (the number of atoms per mol). So if the number of atoms per unit cell is n and its volume is V_c, the theoretical density is

$$\rho = \frac{nA}{V_c N_A}$$

Since the atomic mass and the crystal packing are both physically well-defined, this explains why the densities of metals (and ceramics) have narrow ranges, and there is no scope to modify the density of a solid (e.g. by processing a metal differently).

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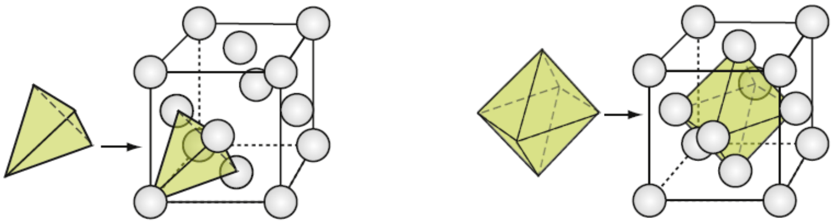
[2] Amedeo Avogadro (1776–1856), Italian professor at the University of Turin, though originally a church lawyer and schoolteacher. The hypothesis and associated constant named after him stem from his essay on the molecular theory of gases, postulating that there are a fixed number of molecules in a given volume of an ideal gas, at constant temperature and pressure. Sacked from his chair for revolutionary activities against the king, the university’s official stance was that he was on leave to concentrate on research, but this particular sabbatical lasted for 10 years before he was reinstated.

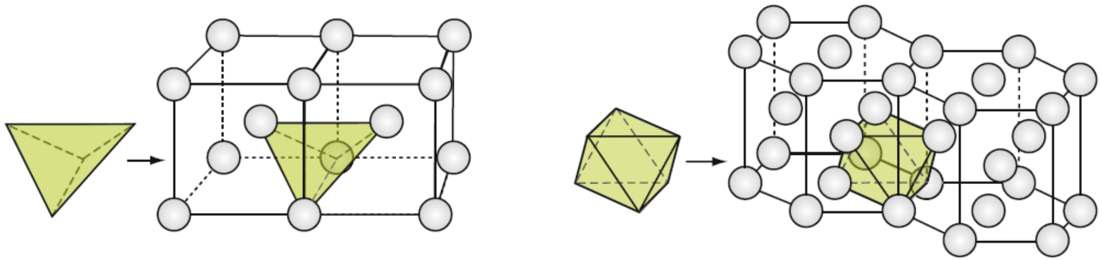
PART 2: Interstitial space

Interstitial space is the unit of space between atoms or molecules. FCC and CPH structures both contain ‘interstitial holes’ of two sorts: *tetrahedral* and *octahedral*; BCC effectively only contains tetrahedral holes. Four examples are shown in Figure GL1.6.



(a) FCC tetrahedral hole

(b) FCC octahedral hole



(c) BCC tetrahedral hole

(d) CPH octahedral hole

Figure GL1.6 (a, b) Two types of interstitial hole in the FCC structure, (c) tetrahedral hole in the BCC structure, and (d) octahedral hole in the CPH structure.

These holes are important because foreign atoms, if small enough, can fit into them. For both FCC and CPH structures, the tetrahedral hole can accommodate, without strain, a sphere with a radius of 0.22 times that of the host. The octahedral holes are larger – you can find out how much in Exercise E.8. In reality atoms are not completely hard, so foreign atoms that are somewhat larger than the holes can be squeezed into the interstitial spaces.

This is particularly important for carbon steel. At room temperature, carbon steel is BCC iron with carbon in some of the interstitial holes. BCC tetrahedral holes can hold a sphere with a radius 0.29 times that of the host without distortion. Carbon goes into these holes, but, because it is too big, it distorts the structure. It is this distortion that gives carbon steels much of their strength.

We encounter interstitial holes in another context later: they provide a way of understanding the structures of many oxides, carbides and nitrides.

PART 3: Describing planes

The properties of crystals depend on *direction*. The elastic modulus of hexagonal titanium (CPH), for example, is greater along the hexagonal axis than normal to it. This difference can be used in engineering design. In making titanium turbine blades, for example, it is helpful to align the hexagonal axis along a turbine blade to use the extra stiffness. Silicon (which also has a cubic structure) oxidises in a more uniform way on the cube faces than on other planes, so silicon 'wafers' are cut with their faces parallel to a cube face. For these and many other reasons, a way of describing planes and directions in crystals is needed. *Miller*[3] *indices* provide it.

DEF. The *Miller indices of a plane* are the *reciprocals* of the intercepts that the plane makes with the three axes defining the edges of the unit cell, reduced to the smallest integers.

Figure GL1.8 illustrates how the Miller indices of a plane are found. Draw the plane in the unit cell so that it does *not* contain the origin – if it does, displace it along one axis until it doesn't. Find where the plane intersects the axes and measure the three intercepts, taking one unit as the cell edge-length, and take the reciprocals. (If the plane is *parallel* to an axis, its intercept is at infinity and the reciprocal is zero.) Reduce the result to the smallest set of integers by multiplying or dividing through by a constant to get rid of fractions or common factors. The Miller indices of a plane are always written in *round* brackets: (100), (111), and so on. Note that the plane intercepts may be negative; e.g. $x = y = 1, z = -1$: the indices are then written as $(11\overline{1})$. Work through the examples in the figure to check that you get the same indices. Note that there are many planes of the 111-type; two are shown in Figure GL1.8. The complete *family* of planes is described by putting the indices in curly brackets:

$$\{111\} = (111), (11\overline{1}), (1\overline{1}1), (\overline{1}11)$$

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[3] William Hallowes Miller (1801–1880), British mineralogist, devised his index system (the 'Millerian system') in 1839. He also discovered a mineral which he named – wait for it – Millerite.

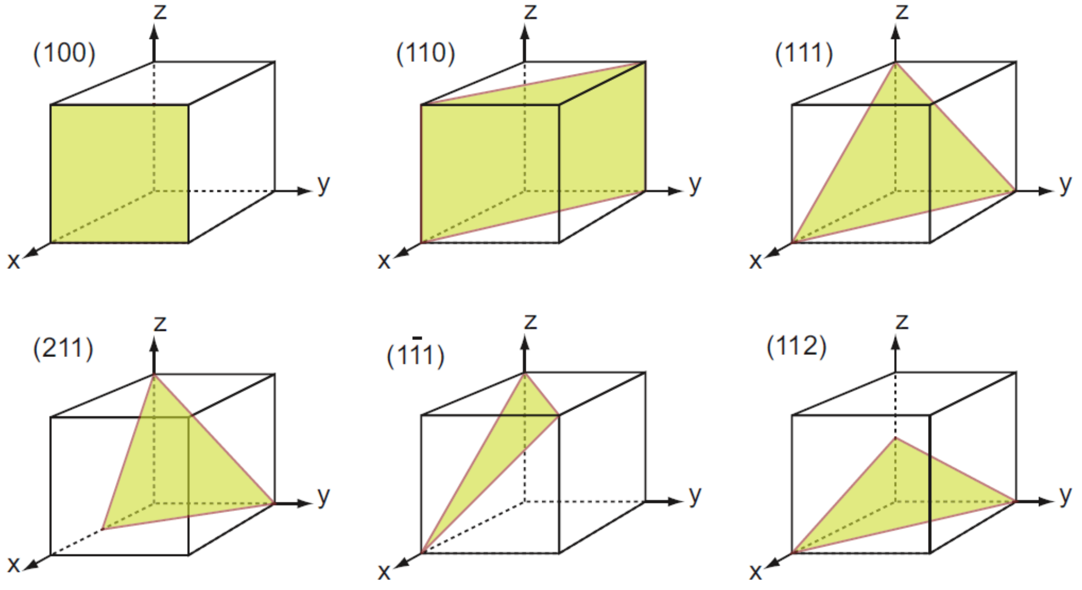

Figure GL1.8 Miller Indices of planes from four common families.

PART 4: Describing directions

DEF. The *Miller indices of a direction* are the components of a vector parallel to that direction, starting from the origin, reduced to the smallest integer values (but *not* in this case taking reciprocals).

Figure GL1.10 shows how to find the Miller indices of a direction. Draw a line from the origin, parallel to the direction, extending it until it hits an edge or face of the unit cell. Read off the coordinates of the point of intersection. Get rid of any fractions by multiplying all the components by the same constant. Check that you agree with the direction indices in the figure. The notation $\bar{1}$ simply means an intersection point is -1. The Miller indices of a direction are always written in *square* brackets – e.g. [100] – and as with planes, there are several directions of the 100-type. The complete *family* of directions is described by putting the indices in angle-brackets:

$$\langle 100\rangle = [100], [010], [001]$$

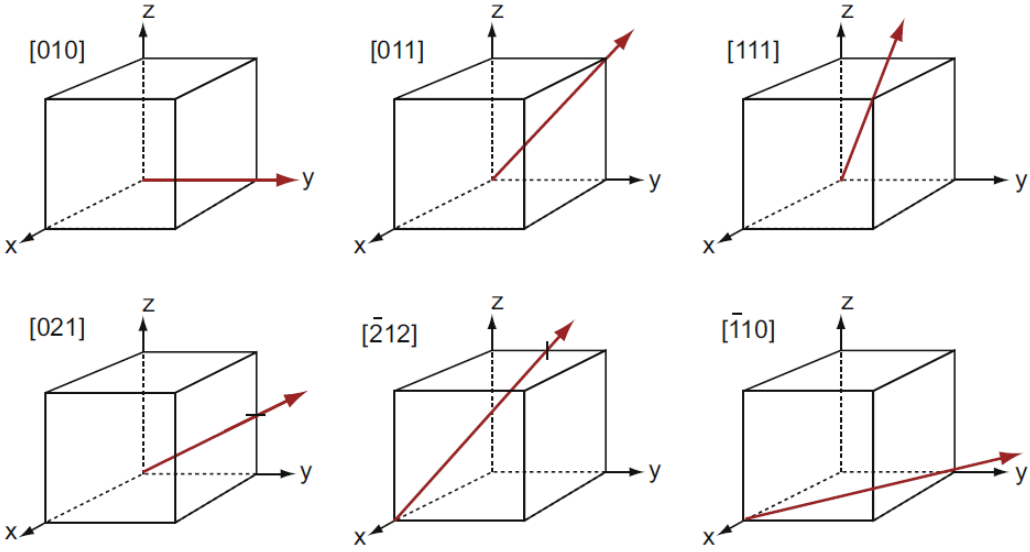

Figure GL1.10 Miller indices of direction. Always translate the vector so that it starts at the origin.

PART 5: Ceramic crystals

Technical ceramics give us the hardest, most refractory materials of engineering. Those of greatest economic importance include:

- alumina, Al_2O_3 (spark plug insulators, substrates for microelectronic devices).
- magnesia, MgO (refractories).
- zirconia, ZrO_2 (thermal barrier coatings, ceramic cutting tools).
- uranium dioxide, UO_2 (nuclear fuels).
- silicon carbide, SiC (abrasives, cutting tools).
- diamond, C (abrasives, cutting tools, dies, bearings).

The ceramic family also gives us many functional materials – those that are semiconductors, are ferromagnetic, show piezo-electric behaviour, and so on. Their structures often look complicated but can usually be made comprehensible by reading them as atoms of one type arranged on a simple FCC, CPH, or BCC lattice with the atoms of the second type (and sometimes three or more) inserted into the interstitial spaces of the first.

The diamond-cubic (DC) structure We start with the hardest ceramic of the lot – diamond – of major engineering importance for cutting tools, abrasives, polishes, and scratch-resistant coatings, and at the same time as a valued gemstone for jewellery. Silicon and germanium, the foundation of semiconductor technology, have the same structure.

Figure GL1.12 shows the unit cell. Think of it as an FCC lattice with an additional atom in four of its eight tetrahedral interstices, labelled 1, 2, 3, and 4 in the figure. The tetrahedral hole is far too small to accommodate a full-sized atom, so the others are pushed farther apart, lowering the density. The tetrahedral structure is a result of the covalent nature of the bonding in carbon, silicon, and germanium atoms – they are happy only when each has four nearest neighbours symmetrically placed around it (Chapter 4).

Silicon carbide, like diamond, is very hard, and it too is widely used for abrasives and cutting tools. The structures of the two materials are closely related. Carbon lies directly above silicon in the periodic table. Both have the same crystal structure and are chemically similar. So it comes as no surprise that a compound of the two with the formula SiC has a structure like that of diamond, with half the carbon atoms replaced by silicon, as in Figure GL1.13 (the atoms marked 1, 2, 3, and 4 in Figure GL1.12 are the ones replaced).

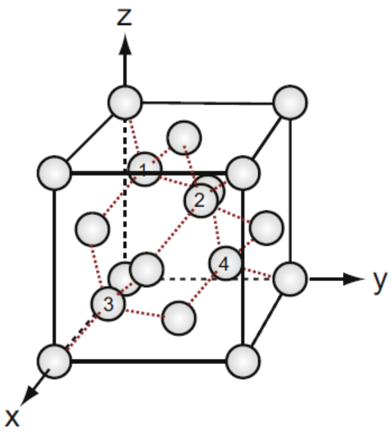

Figure GL1.12 The diamond-cubic (DC) structure.

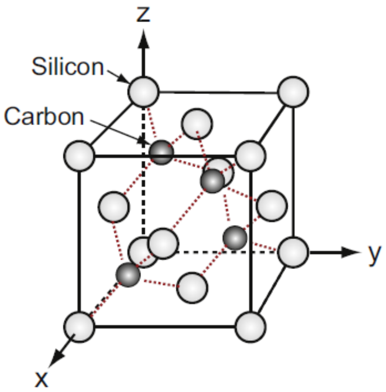

Figure GL1.13 The structure of silicon carbide.

Materials with the diamond-cubic structure	Comment
Carbon, as diamond	Cutting and grinding tools, jewellery
Silicon, germanium	Semiconductors
Silicon carbide	Abrasives, cutting tools

Ceramics with the rocksalt (halite) structure Several important oxides have the formula MO, where M is a metal ion. Oxygen ions are large, usually bigger than those of the metal. When this is so, the oxygen packs in an FCC structure, with metal atoms occupying the octahedral holes in this lattice – an example, MgO, is shown in Figure GL1.14. This is known as the rocksalt (or halite) structure because it is that of sodium chloride, NaCl, with chlorine replacing oxygen and sodium replacing magnesium in the figure. Sodium chloride (common salt) itself is a material of engineering importance. It has been used for roadbeds and buildings, there are plans to bury nuclear waste in rocksalt deposits, and large single crystals of rocksalt are used for the windows of high-powered lasers.

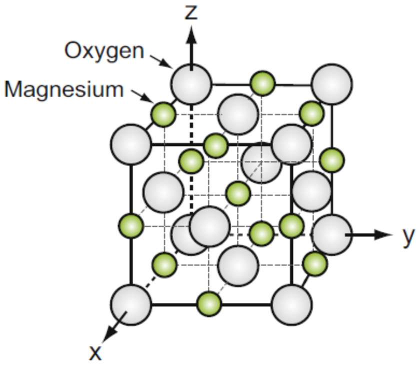

Figure GL1.14 The halite structure of MgO, typical of many simple oxides.

Materials with the rocksalt structure	Comment
Magnesia, MgO	A refractory ceramic with useful strength
Ferrous oxide, FeO	One of several oxides of iron
Nickel oxide, NiO	Ceramic superconductors
All alkali halides, including salt, NaCl	Feedstock for chemical industry, nuclear waste storage

Oxides with the corundum structure A number of oxides have the formula M_2O_3, among them alumina (Al_2O_3). The oxygen ions, the larger of the two, are arranged in a CPH-like stacking. The M ions occupy two-thirds of the octahedral holes in this lattice, one of which is shown for alumina, filled by an Al ion, in Figure GL1.15. The hole is not big enough to accommodate the aluminium ion, and the oxygen lattice is pushed slightly apart – so it is not actually close-packed, but the atom centres fit the CPH structure. It is also the case that in this instance the hexagonal unit of Figure GL1.15 is not a unit cell. A larger and more complicated unit cell is needed, so that when these are stacked to form the lattice, the metal ions also fall into a regular pattern of hexagons, occupying the correct proportion of holes. This need not concern us further here.

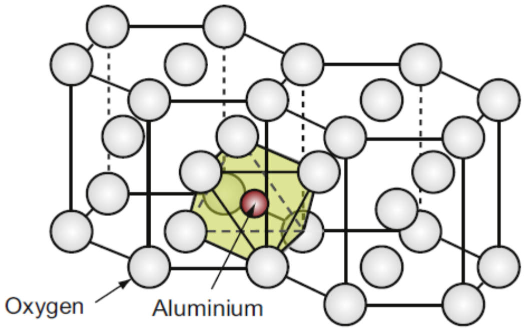

Figure GL1.15 The M atoms of the corundum structure lie in the octahedral holes of a CPH oxygen lattice, of which one is shown. Two adjacent cells are needed to show an octahedral hole.

Materials with the corundum structure	Comment
Alumina, Al_2O_3	The most widely used technical ceramic
Iron oxide, Fe_2O_3	The oxide from which iron is extracted
Chromium oxide, Cr_2O_3	The oxide that gives chromium its protective coating
Titanium oxide, Ti_2O_3	The oxide that gives titanium its protective coating

Oxides with the fluorite structure The metal atoms in the important technical ceramic zirconium dioxide, ZrO_2, and the nuclear fuel uranium dioxide, UO_2, being far down in the periodic table, are large in size. Unlike the oxides described earlier, the M in MO_2 is now larger than the O. So it is the M atoms that form an FCC-like structure with the oxygen atoms in the eight tetrahedral holes – one such site in ZrO_2 is shown in Figure GL1.16.

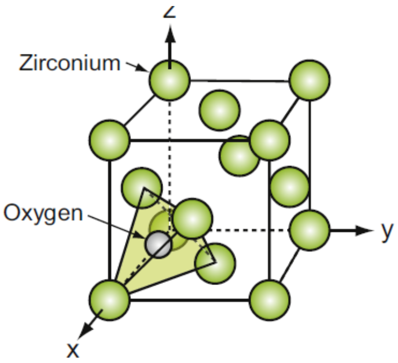

Figure GL1.16 The M atoms of fluorite-structured oxides like ZrO_2 pack in an FCC array, with oxygen in the eight tetrahedral holes (one of which is shown).

Materials with the fluorite structure	Comment
Zirconia, ZrO_2 (slightly distorted fluorite)	The toughest refractory ceramic
Urania, UO_2	Nuclear fuel
Thoria, ThO_2	Nuclear fuel
Plutonia, PuO_2	A product of nuclear fuel reprocessing, a fuel in itself

PART 6: Polymer crystals

Many polymers crystallise, if their chains are sufficiently regular. The long chains line up and pack to give an ordered, repeating structure, just like any other crystal. The low symmetry of the individual molecules means that the choice of lattice is limited. Figure GL1.17 is a typical example; it is polyethylene.

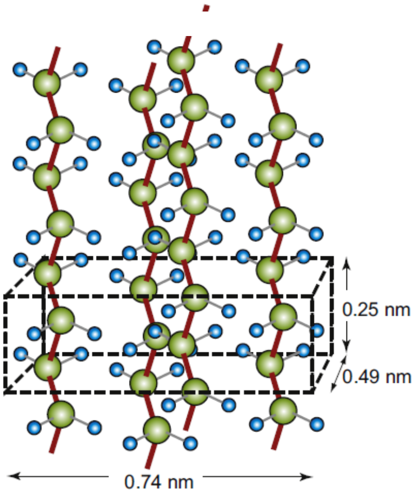

Figure GL1.17 The structure of a crystalline polyethylene.

Few engineering polymers are completely crystalline, but many have as much as 90% crystallinity. Among those of engineering importance are:

Material (crystallinity)	Typical uses
Polyethylene, PE (65–90%)	Bags, tubes, bottles
Nylon, PA (65%)	High-quality parts, gears, catches
Polypropylene, PP (75%)	Mouldings, rope