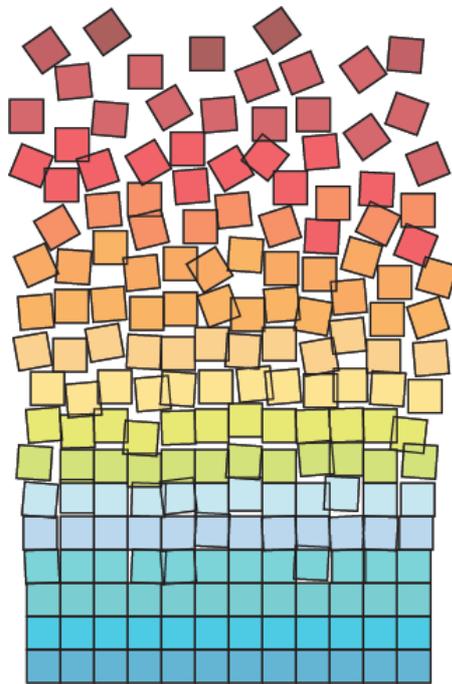


# Teach yourself Crystallography

*5<sup>th</sup> Edition, Mike Ashby, Cambridge, March 2009*



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# Teach yourself Crystallography

## Introduction and synopsis

Though they lacked the means to prove it, the ancient Greeks suspected that solids were made of discrete atoms that packed in a regular, orderly way to give crystals. Today, with the 20th century techniques of X-ray and electron diffraction and lattice-resolution microscopy available to us, we know that all solids are indeed made up of atoms, and that most (but not all) are crystalline. The common engineering metals and ceramics are made up of many small crystals, or *grains*, stuck together at *grain boundaries* to make *polycrystalline aggregates*. The properties of the material - its strength, stiffness, toughness, conductivity and so forth - are strongly influenced by the underlying crystallinity. So it is important to be able to describe it.

Crystallography is a sort of language for describing the 3-dimensional packing of atoms or molecules in crystals. Much of the language can be illustrated by 2-dimensional packings, and they are far easier to draw. So we start with those. If you work through this course, doing the exercises, you will get a working knowledge of crystallography at a sufficient level to deal with most engineering problems, and to understand what people mean when they speak of "the diamond-cubic structure" or of "the (111) plane of the f.c.c. lattice" or "mirror symmetry". Don't rush it. Learn the definitions and ponder a little over the 3-dimensional structures to make sure you understand the geometry. Some parts (the definitions, for instance) are terse and concentrated. Others, (some of the exercises, perhaps) may strike you as trivial. That is inevitable in a "teach yourself" course that has to accommodate students with differing backgrounds. Do them anyway.

The course is in three parts, each of which will take about an hour. Each part contains Exercises, most with one-word or one-line answers or the requirement of a simple sketch. There are answers at the end of each part, but *don't* look at them until you have done all the Exercises in a given set, and then only when you have made every effort to get them right. The three parts are:

**PART 1:** 2-dimensional crystal structures, packing and symmetry

**PART 2:** 3-dimensional crystal structures, planes and directions

**PART 3:** The structures of common engineering materials.

Parts 1 and 2 introduce the basics – the ideas of symmetry, lattices and structures. Part 3 takes us back to practicalities, focussing on the crystal structures of common engineering materials.

The Teach Yourself Unit ends with an Appendix listing the 14 Bravais lattices and the structures and lattice parameters of commonly used elements.

## PART 1: 2-dimensional crystal structures, packings and symmetry

### 1.1 Packing of spheres in 2 - dimensions

If you try to pack spheres together in a plane, you find that there are three topologically different arrangements - that is, three packings which differ in their symmetry. They are shown in Figure C1, called *square*, *oblique*, and *hexagonal*. Each can be extended indefinitely by adding more spheres along the rows defined by those already there. All three satisfy the definition of a crystal.

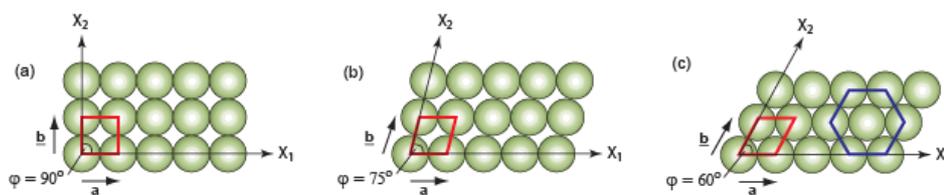


Figure C1. The three 2-dimensional packings of circles: (a) square, (b) oblique and (c) hexagonal. The primitive cell is shown in red on each figure. The blue hexagonal unit cell at (c) is non-primitive.

**DEF.** A *crystal* is a regularly-repeating pattern of atoms (our spheres) in 2 or 3 dimensions which can be extended, without change of pattern, indefinitely.

Each of the three structures is made up of rows of spheres that touch; they are the *close-packed directions* (the  $X_1$  and  $X_2$  directions on Figure C1). Of the three, the hexagonal arrangement shown at (c) has a higher *packing density* than the others; in fact it is the highest possible. The hexagonal arrangement is a *close-packed plane*, that is, it is the arrangement which minimises the area-per-sphere. The other two arrangements are *non-close-packed*, even though they contain close packed directions.

Each of the structures is made up of a unit which repeats itself, 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 regularly, builds up the entire structure. The *primitive unit cell* is the smallest such cell.

Primitive unit cells are marked in red on Figure C1. The primitive cell, in these structures, contains just one atom. Often we choose the primitive unit cell to describe the structure, but not always. If a larger cell has greater symmetry (discussed in a moment) then it helps to choose it instead. A larger, hexagonal, unit cell containing 3 atoms, is drawn on Figure C1 (c).

### 1.2 Interstitial Space

The cusp-shaped spaces between the spheres (or atoms) is called the interstitial space.

**DEF.** The *interstitial space* is the unit of space between packed atoms or molecules.

The unit of interstitial space in each of the three structures is shown in black in Figure C2. In the square lattice it is a cuspy square; in the oblique lattice it is a dog-bone; and in the hexagonal structure it is a cuspy triangle. Interstitial space is important because, in some alloys and in many compounds, smaller atoms fit into the interstitial space between the larger ones. The alloy or compound can only

exist if the *interstice* (a name for the unit of interstitial space) is large enough to hold the smaller atom without undue distortion.

Now some Exercises. Don't go on until you have answered these; and if you can't, go back over the material so far. It is *essential* in a teach-yourself course that you only turn to the answers when you have thought through the problem in depth and believe you have it right. And if, when you look it up, you find that you were wrong, it is even more *essential* that you figure out why. These

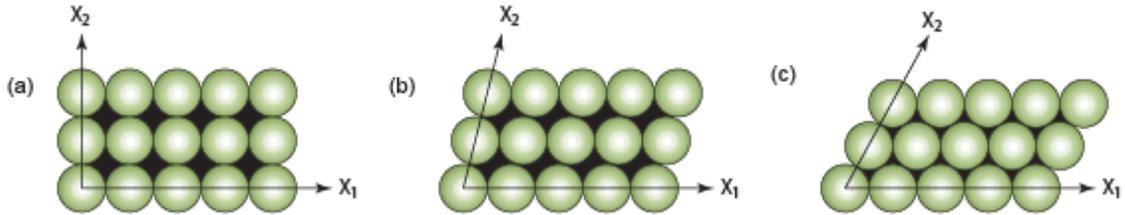


Figure C2. The interstitial spaces, or "interstices", are shown in black for (a) the square, (b) the oblique and (c) the hexagonal packing of circles.

first Exercises are easy. Later, they get harder. Answers are given at the end of Part 1. No peeping till you've done them all.

### Exercises

**E1.** Identify each of the six structures shown in Figure C3. (Is it oblique, square, hexagonal?). Use the shape of the interstices to help you.

**E2.** Draw the primitive unit cells onto copies of the structures shown in Figure C3.

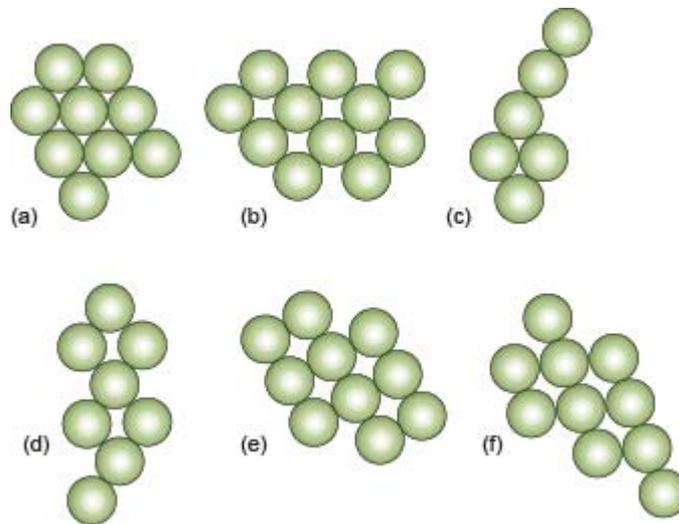


Figure C3. Six segments of arrays of packed circles.

**E3.** Calculate the area-per-sphere in the square, the oblique and the hexagonal structure taking the diameter of a sphere to be  $a$ . Express that for the oblique structure in terms of the angle  $\phi$ , shown in Figure C1

**E4.** How many nearest neighbours (neighbours that actually touch a given sphere) does a sphere have in each of the three structures of Figure C1 ?

**E5.** How many interstices are there per atom in each of the three structures?

**(c) Packing of non-spherical units**

So far we have thought of atoms as spheres. The simplest crystals, such as aluminium, copper or nickel, are made up of one sort of atom, and it is a good approximation to think of them as spherical. But in many solids the unit which packs together is not a single atom, but a grouping of atoms (as in alumina,  $Al_2O_3$ , or polyethylene  $CH_3-(CH_2)_n-CH_3$ ). The grouping is not spherical, so the spacing,  $a$ , of the centre of the group along the  $X_1$  axis, is not the same as the spacing,  $b$ , along the  $X_2$  axis. When  $a$  and  $b$  are not equal, two (and only two) more structures become possible, making five in all. We will describe them in a moment. First we introduce the idea of a *lattice*.

**(d) The lattice**

We describe all crystals in terms of a periodic *lattice*, with an identical group of atoms attached to each lattice point, as shown in Figure C4. The group of atoms is called the *basis*; the basis is repeated in space to form the crystal.

**DEF.** Lattice + Basis = Crystal Structure

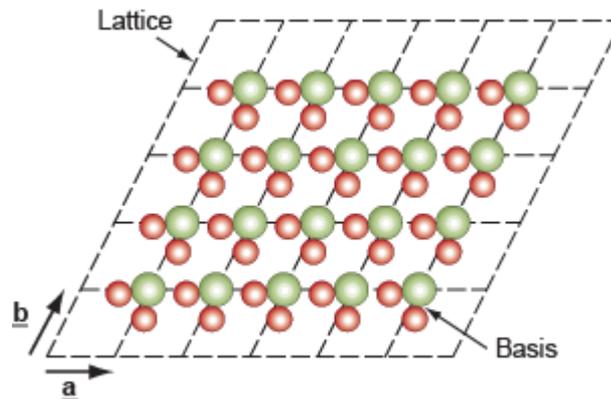


Figure C4. An oblique lattice (the grid) partly filled with a basis consisting of a group of 3 atoms, identically arranged at each lattice point.

The lattice is like a regular scaffolding or space-frame. The basis is like a cluster of balloons. You create the crystal by tying an identical balloon-cluster to each intersection of the scaffolding such that each cluster has an identical arrangement at every intersection.

**DEF.** The *lattice* is defined by the fundamental translation vectors  $\underline{a}$  and  $\underline{b}$  (or in 3-dimensions,  $\underline{a}$ ,  $\underline{b}$ , and  $\underline{c}$ ) such that the atomic arrangement looks identical when observed from each lattice point. One lattice point is carried to any other by the translation

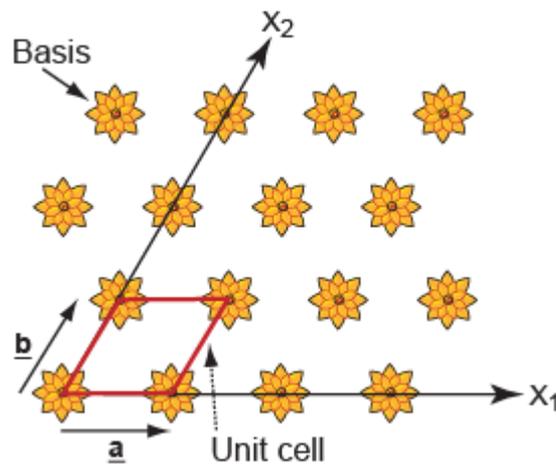
$$T = n_1\underline{a} + n_2\underline{b} \quad (+ n_3\underline{c}) \quad (\text{C.1})$$

Where  $n_1$ ,  $n_2$  (and  $n_3$ ) are integers.

If we take the shortest vectors  $\underline{a}$ ,  $\underline{b}$  (and  $\underline{c}$ ) that satisfy the "looks identical" criterion, the unit cell contains only one molecule or structural unit, and the vectors  $\underline{a}$ ,  $\underline{b}$  (and  $\underline{c}$ ) are primitive.

All regularly repeating patterns can be described by a lattice and a basis. Consider the flower-crystal shown in Figure C5. To identify the lattice, the unit cell and the basis, we proceed as follows.

- (i) Identify some point in the pattern - the centre of the flower, say - and mark all such points that have identical surroundings. They are the lattice points.
- (ii) Link the lattice points to give a lattice: it is hexagonal.
- (iii) Mark in the primitive unit cell: it is the smallest unit which packs to fill space and which completely characterises the structure. The red parallelogram does this.
- (iv) The basis is the contents of a primitive unit cell. It is the unit of the pattern - one of the little flowers (the segments of flower inside one cell add up to one complete flower exactly).



*Figure C5. A flower-crystal. Any point on the flower could be taken as a lattice point, provided all others are chosen in the same way. Then an observer at any lattice point would see exactly the same surroundings.*

In 2-dimensions there exist five, and only five, distinguishable lattices. To understand why, we must look at symmetry.

**(e) Symmetry**

In describing a crystal structure, there are four important questions to answer:

- (i) What is its lattice?
- (ii) What unit translation vectors  $\underline{a}$  and  $\underline{b}$  describe it?
- (iii) What is the basis?
- (iv) What symmetry operations carry the structure into itself?

We have dealt with the first three. Now for the fourth.

**DEF.** The *symmetry operations* that carry the crystal structure into itself are

- 1. Translation (as defined by equation C.1)
- 2. Rotation
- 3. Reflection.

All crystals have *translational symmetry* – if they hadn't, they wouldn't be crystals. Sometimes that is all they have got. Look again at Figure C5. A rotation of  $\pi/3$  about an axis through any of the lattice points carries the structure into itself. In a total rotation of  $2\pi$  the structure is carried into itself 6 times: the structure has an axis of *6-fold rotational symmetry*. It is given the symbol  $\blacklozenge$ . A rotation of  $\pi$  that carries the crystal into itself is called a 2-fold rotation axis and gives the symbol  $\blacklozenge$ . Axes with 2, 3, 4 and 6-fold symmetry (but not, normally, 5 or 7 or higher) are found in crystals.

**DEF.** Axes of rotational symmetry are identified by the number of times, in a total rotation of  $2\pi$ , the structure is carried identically into itself.

<i>Axis</i>	<i>Symbol</i>
2-fold rotation axis (diad)	$\blacklozenge$
3-fold rotation axis (triad)	$\blacktriangle$
4-fold rotation axis (tetrad)	$\blacksquare$
6-fold rotation axis (hexad)	$\blacklozenge$

The reason that 5 and 7-fold axis won't give crystals is shown in Figure C6. The unit of a crystal must pack together to fill space in a regularly repeating way (see DEF of a crystal). Pentagons and heptagons don't pack to fill space. Parallelograms, triangles, squares and hexagons do.

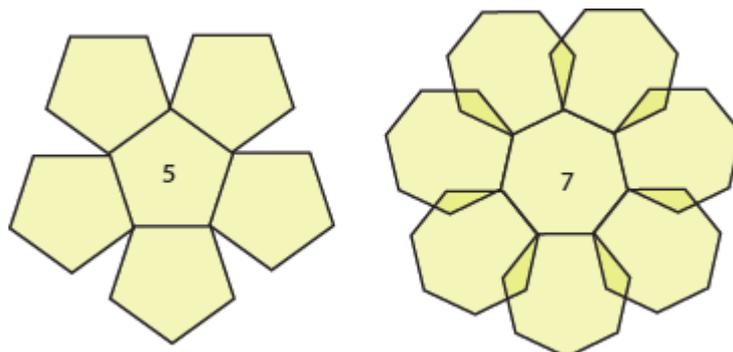


Figure C6. Regular five and seven-sided figures do not pack to fill space. So the unit cell cannot have this shape (see definition of unit cell), and the crystal cannot have 5 or 7-fold rotational symmetry.

The final operation is that of *reflection*.

**DEF.** If the structure on one side of a plane drawn through a lattice point is the reflection of that on the other side, the structure has a *mirror plane*, symbol **m**.

Figure C7(a) shows a lattice with the minimum symmetry: it has translational symmetry associated with the two vectors shown plus a 2-fold rotation axis marked by the symbol  $\blacklozenge$ . The lattice of Figure C7 (b) is more symmetric: it has a 2-fold axis and 2 mirror planes; it is called  $2mm$ . The lattice of Figure C7(c) has a four-fold rotation axis and two mirror planes: it is called  $4mm$ . The hexagonal lattice of Figure C7(d) is  $6mm$ . You may be able to find more mirror planes, but they are related to the first by the rotational symmetry specified for the lattice, so the nomenclature  $6mm$  (or one of the others) already includes them.

The *point-group symmetry* (so called because the rotation axes and the mirror planes must be chosen to pass through a lattice point) gives the *minimum* number of elements which completely describe the symmetry of the structure.

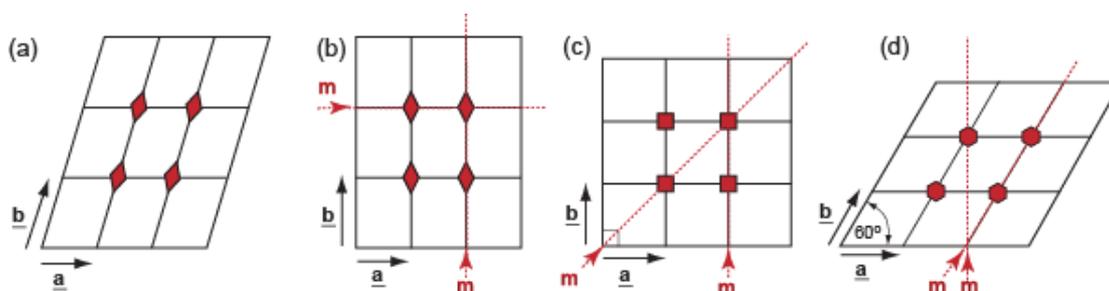


Figure C7. Lattices with increasing levels of symmetry: (a) 2, (b)  $2mm$ , (c)  $4mm$ , (d)  $6mm$ .

### (f) The five 2-dimensional lattices

When we discussed sphere-packing, we identified three lattices: the oblique lattice (with a variable inter-axis angle  $\varphi$ ), and two special cases of it: the square and the hexagonal lattices. We could have distinguished these by their point symmetry. The oblique lattice has a two-fold (diad) axis; the square lattice is the special case of the oblique lattice which has a four-fold (tetrad) axis; the hexagonal lattice is the special case with a six-fold (hexad) axis. The hexagonal lattice is distinguished from the oblique lattice by its extra symmetry elements.

If we pack non-spherical units (molecules instead of atoms), then the vectors  $\underline{a}$  and  $\underline{b}$  no longer have the same length. The *general oblique lattice*, then, has  $a \neq b$  and  $\varphi \neq 90^\circ$  (Figure C8 (a)). The square and the hexagonal lattice still exist as special cases of it (Figures C8, (b) and (c)). And there are two, and only two, more. If the axes are unequal but orthogonal, we have the rectangular lattice (Figure C8(d)) and if the primitive axes are at the special angle, not  $90^\circ$ , which still gives a mirror plane, **m**, then we have the *centred rectangular lattice* (Figure C8 (e)). The five distinct lattices are distinguished by their symmetry, summarised below.

**DEF.** The five 2-dimensional lattice types.

<i>Lattice</i>	<i>Cell edge-length and angle</i>	<i>Point group*symmetry of lattice</i>
Oblique	$a \neq b, \quad \varphi \neq 90$	2
Square	$a = b, \quad \varphi = 90$	4 <b>mm</b>
Hexagonal	$a = b, \quad \varphi = 120$	6 <b>mm</b>
Primitive rectangular	$a \neq b, \quad \varphi = 90$	2 <b>mm</b>
Centred rectangular	$a \neq b, \quad \varphi \neq 90$	2 <b>mm</b>

\* The Point Group is the symmetry of the *lattice* about a lattice point: it tells you the rotational and reflection symmetry of the lattice.

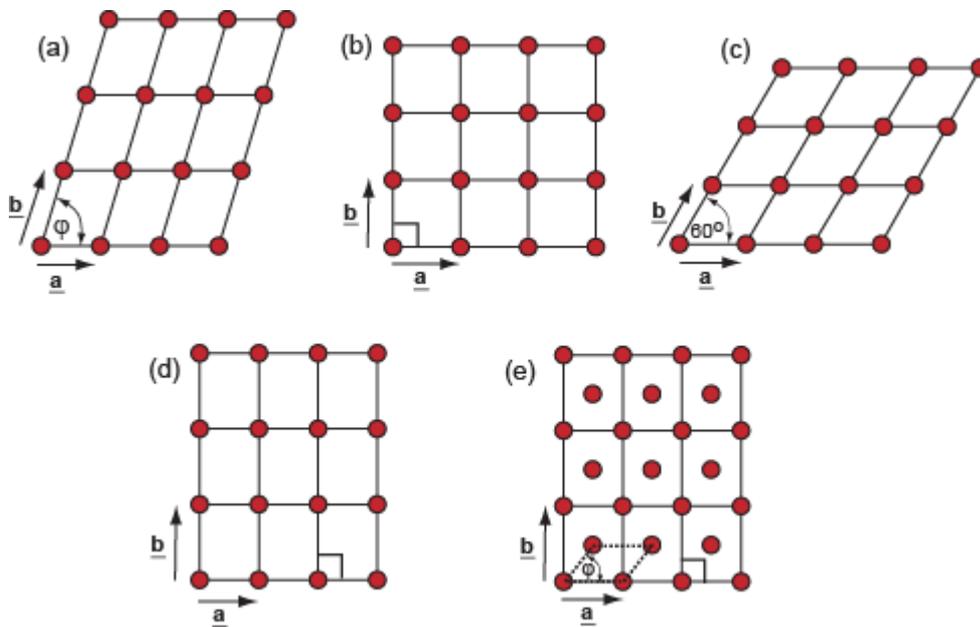


Figure C8 The five 2-dimensional lattices.

**(g) The symmetry of the crystal structure**

The crystal structure may not be as symmetric as its lattice. If the basis has high symmetry (it is a sphere, for instance) than the symmetry of the structure is the same as that of its lattice. But when the basis is less symmetric (shaped like a sausage, for example), the low symmetry of the basis reduces that of the structure.

And now some more Exercises. Still easy.

**Exercises** (Answers at the end of the Section).

**E6.** Think of the worried Professor in Figure C9 as a big sad molecule. Identify the lattice on which he has crystallized by taking a point on his face (the mid-point of his specs, for instance) as a lattice point and linking it to other points with identical surroundings.

- What is the professor's lattice ?
- What is the point group symmetry of his lattice ?
- What is the symmetry of his structure (that of the lattice plus basis)?

**E7.** Miss Monroe has been crystallized by Andy Warhol in Figure C10. What is her lattice? What is its point group? Has her structure got as much symmetry as her point group?

**E8.** The two images in Figure C11 are 2-dimensional patterns by M.C. Escher.

Construct the lattice by joining points with identical surroundings. Identify the lattice. Indicate the primitive unit cell and identify the point group symmetry of the lattice. Identify the basis (remember it has to be a complete unit of the design, so it must include a white and a colored shape). Do the structures have the same symmetry as their lattice?

**E9.** Figure C12 is a tile pattern. What is the lattice? What is the point-group symmetry of the lattice? What are the symmetry elements of the structure?

**E10.** What is meant by

- (a) The lattice of a crystal structure?
- (b) The basis associated with a structure?
- (c) Primitive axes?
- (d) The unit cell of a structure?
- (f) The primitive unit cell?

**E11.** Why are the rectangular and the centred-rectangular lattices distinct?

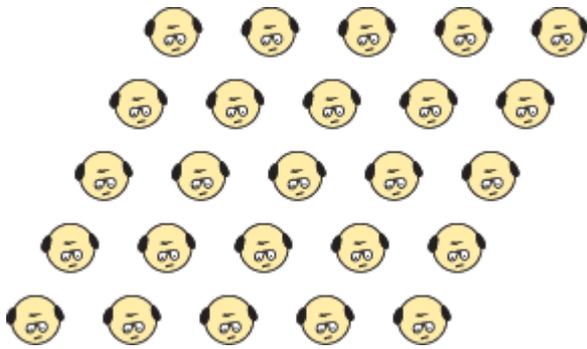


Figure C9. A professor-crystal.



Figure C10. Miss Monroe, crystallized.

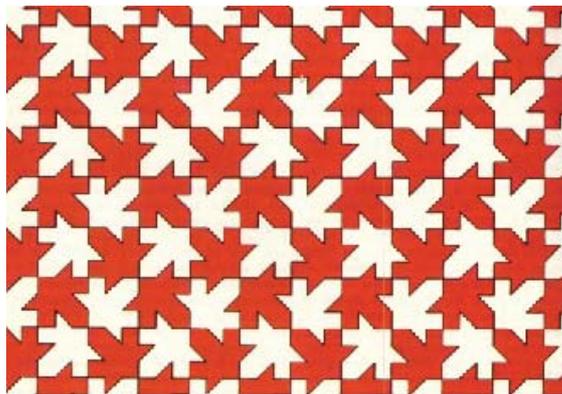


Figure C11. Two patterns by the Dutch artist, M.C. Escher.

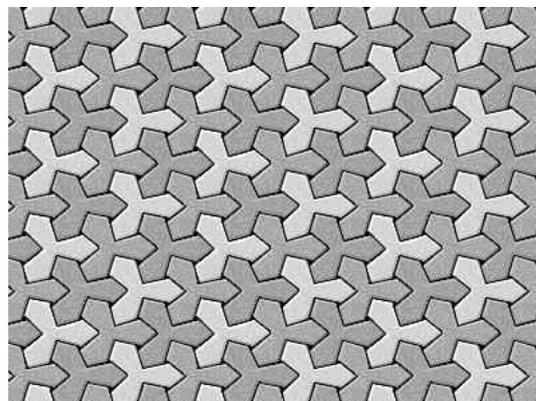


Figure C12. A pattern of grey and white tiles.

## Answers to the Exercises of Part I

**E1.** The structures are

- |               |            |               |
|---------------|------------|---------------|
| (a) hexagonal | (b) square | (c) hexagonal |
| (d) oblique   | (e) square | (f) oblique   |

**E2.** The unit cells are shown. That for the hexagonal structure is not a hexagonal. The *smallest* repeating unit is the parallelogram shown in Figure C13.

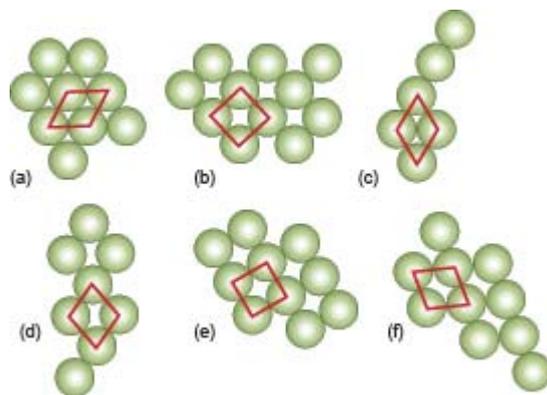


Figure C13. The primitive unit cells of the lattice fragments.

**E3.** The best method is to note that the unit cell has the same area as that associated with each "atom". This area, for the oblique lattice is  $a^2 \sin \varphi$ . The square and hexagonal lattices are special cases for  $\varphi = \pi/2$  and  $\varphi = \pi/3$ . Thus the areas per atom are

Square: $a^2$	Oblique: $a^2 \sin \varphi$	Hexagonal: $\sqrt{3}/2 a^2$
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**E4.** The numbers of nearest neighbours are

Square: 4	Oblique: 4	Hexagonal: 6
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**E5.** The number of interstices per atom is

Square: 1	Oblique: 1	Hexagonal: 2
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**E7.** The Professor has crystallised onto an oblique lattice with symmetry 2. His structure has translational symmetry Figure C14 (a).

**E7.** Miss Monroe has chosen a rectangular lattice with point group symmetry  $2mm$ . Her structure, however, has no mirror planes because of her asymmetric basis (Figure C14(b)).

**E8.** The Escher leaf-pattern has a square lattice with point group symmetry  $4mm$ . The basis is made up of 4 leaves, two white and two red. The asymmetry of the basis gives the structure only one mirror plane instead of two (Figure C15(a)). The Escher birds fly on an oblique lattice with a point group symmetry of 2 (Figure C15(b)).

**E9.** The tile has a hexagonal lattice with point group symmetry  $6mm$ , The basis has only 3-fold (trid) symmetry, reducing the symmetry elements of the structure to  $3m$  (Figure C15(c)).

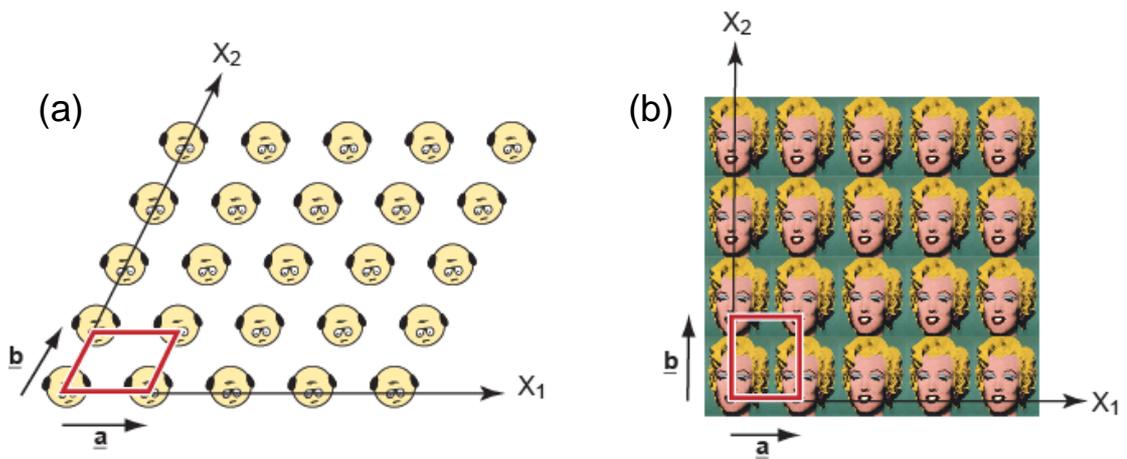


Figure C14. The translation vectors and primitive unit cells of the Professor and Miss Monroe.

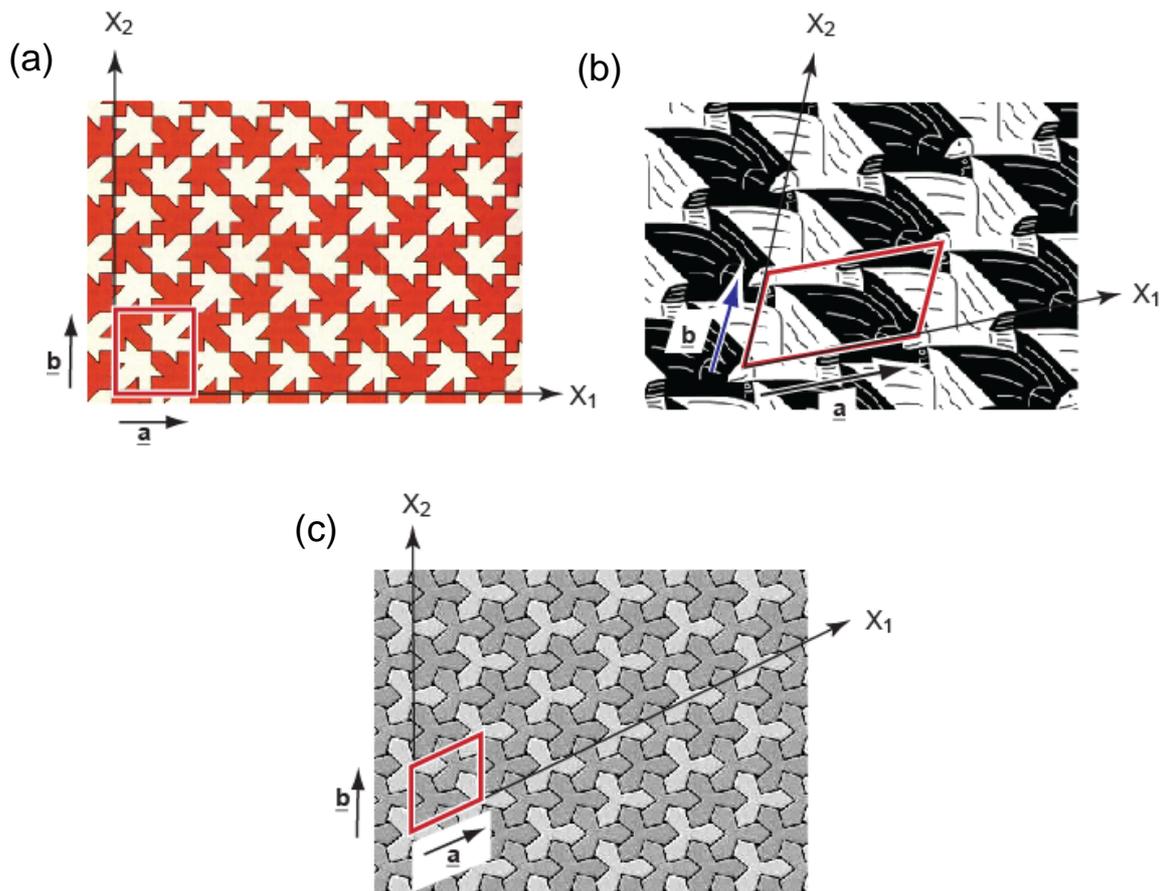


Figure C15. The translation vectors and primitive unit cells of the three patterns.

**E10.** (a) The lattice is the regular "scaffolding" of the structure. Each lattice point (in 2-dimensions) can be reached from the origin by a translation

$$\underline{\mathbf{T}} = n_1 \underline{\mathbf{a}} + n_2 \underline{\mathbf{b}}$$

where  $\underline{\mathbf{a}}$  and  $\underline{\mathbf{b}}$  are the primitive lattice translation vectors and  $n_1$  and  $n_2$  are integers.

- (b) The basis is the identical group of atoms which, when attached identically to each lattice point, creates the crystal structure.
- (c) Primitive axes are the shortest set of translation vectors which will reproduce the structure.
- (d) The unit cell is the unit which stacks to fill space and reproduce the structure, chosen by convention to illustrate the symmetry of the structure.
- (e) The primitive unit cell is the smallest such unit, and contains only one basis.

**E11.** The rectangular lattice has orthogonal primitive axes. The centred rectangular lattice does not. But it is still special because it has a mirror plane.



## PART 2: 3-dimensional crystal structures, planes and directions

Three-dimensional crystals are harder to draw than those in two dimensions, but the ideas and language used to describe them are the same. The extra dimension means that there are 14 distinguishable lattices instead of 5. All have translational symmetry, of course – they wouldn't be crystals if they did not. Some have axes of 2, 3, 4 or 6-fold rotation (symbols  $\blacklozenge$ ,  $\blacktriangle$ ,  $\blacksquare$  and  $\blacklozenge$ ) and up to three mirror planes (**mmm**). If you are a crystallographer you need to know all about all of them. But engineering materials, for the most part, have simple structures. We shall concentrate on these.

### (a) Lattice and symmetry

In 2-dimensions, the oblique lattice was the general one; the other four were special cases of it. In 3-dimensions, the *triclinic* lattice is the general one. Figure C15 shows the unit cell; the lattice is built up by translating the cell in steps of the unit cell edge vectors  $\underline{a}$ ,  $\underline{b}$  and  $\underline{c}$ . The edge lengths  $a$ ,  $b$ , and  $c$  are all different and none of the angles is  $90^\circ$ : The other thirteen space (or *Bravais*<sup>1</sup>) lattices are special cases of this one. For completeness they are shown in the Appendix at the end of Part 3 of this course, but don't try to memorise them.

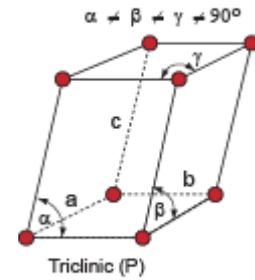


Figure C15. The triclinic unit cell

Four lattices are particularly important to us, and these you should memorise.

**SUMMARY.** The important 3-dimensional lattices for engineering materials (Figure C16) are

1. The simple cubic or SC lattice ( $a = b = c$ ; all angles  $90^\circ$ ),
2. The body-centered cubic or BCC lattice
3. The face-centered cubic or FCC lattice
4. The hexagonal close packed or HCP (sometimes CPH) lattice.

They are shown in Figure C16.

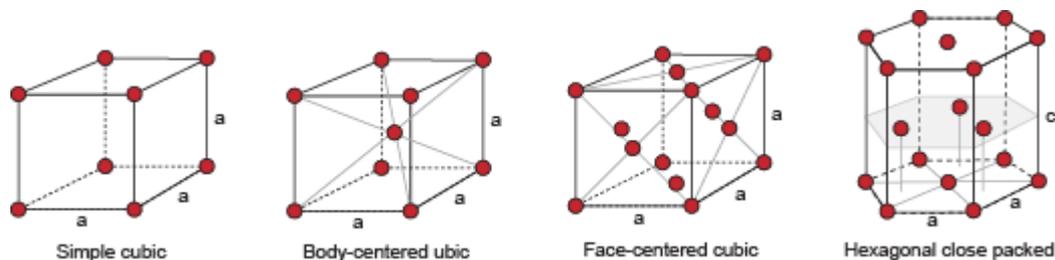


Figure C16 The four important lattices: simple cubic (SC), body-centred cubic (BCC), face-centred cubic (FCC) and hexagonal close packed (HCP).

<sup>1</sup> 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.

All three cubic lattices have primitive axes that are equal in length. Only in the simple cubic lattice are they orthogonal. The next two, (like the centered rectangular lattice of Part I) are special because they have extra mirror planes. This symmetry means that a non-primitive cell (one with more than one lattice point per cell) can be found that is a cube; hence the word "cubic" in the name. The primitive cell of the close-packed hexagonal lattice is a rhombus; but because it has a 6-fold rotation axis, it can be described by a non-primitive, hexagonal-prismatic unit cell, and this is mostly used.

Any structure that is close packed (as the FCC and HCP are) can be made by packing spheres together as tightly as possible. To understand them, we must examine sphere packing in 3-dimensions.

**(b) Packing of spheres in 3-dimensions**

If you try to pack spheres to form a *close-packed pyramid* (like oranges in a fruit market) you find that two different arrangements are possible. You start with a close-packed plane like that in Figure C17(a). The next layer nests into the first so that each sphere touches three in the layer below, as shown in Figure C17(b). The third layer nests in the second, again positioned so that each sphere drops into the seat formed by three below. But with this third layer two positions are possible: it can sit so that its spheres do not lie above those in the first layer (as in Figure C17(c)), or so that they do (Figure C17(d)).

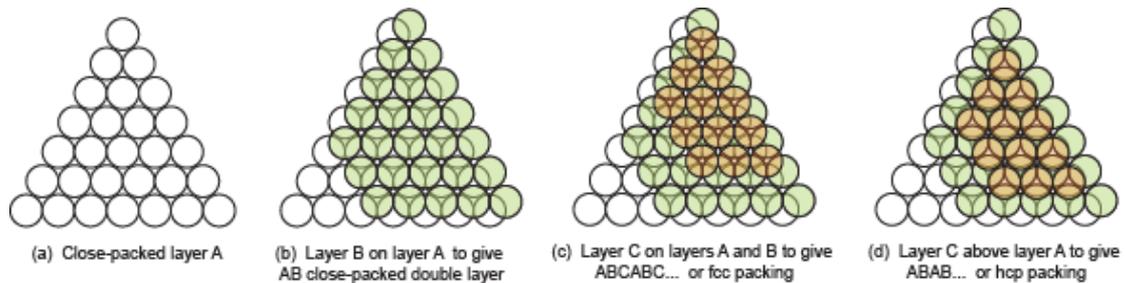


Figure C17. (a) A close-packed (cp) plane. (b) Two nested cp planes. (c) Three nested cp planes in ABC stacking. (d) Three nested planes in ABA stacking.

The two arrangements are equally dense (both are close-packed in 3-dimensions) but they differ in their symmetry and thus in the shape of the primitive unit cell which describes them. The first is described by the stacking sequence of

$$A B C A B C A B C \dots$$

and is in fact *face-centered cubic (FCC)*, though it may not at first look it. The other is described by the repeated stacking

$$A B A B A B \dots$$

and is - surprise! - *close-packed hexagonal (HCP)*, though with four atoms per unit cell.

<b>SUMMARY. Close packing</b>		
<i>Structure</i>	<i>Stacking sequence</i>	<i>Examples</i>
Face-centered cubic (FCC)	ABCABC...	Aluminum, Nickel, Copper
Close-packed hexagonal (HCP)	ABABAB...	Titanium, Magnesium, Zinc

Figure C18 shows the unit cell of each lattice with the stacking sequence of close-packed planes identified. An observer with his eye in the position shown would see the arrangements of Figures C17(c) and C17(d). So the FCC and HCP structures are made up by stacking close-packed planes. Each plane contains three close-packed directions along which the spheres touch, just as in 2-dimensions.

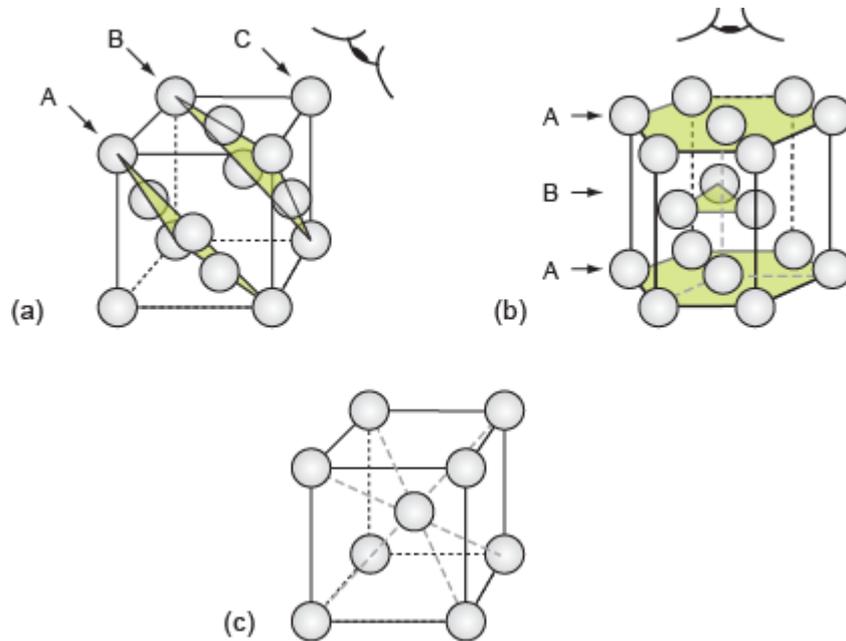


Figure C18. (a) An FCC structure of packed spheres showing the ABC stacking. (b) An HCP structure of packed spheres showing the ABA stacking. (c) A BCC structure of non-close-packed spheres.

The other two structures can be made by gluing spheres together, but they are not close-packed so the fraction of space filled by the spheres is less. The *simple cubic (sc)* packing of spheres gives a unit cell with a sphere at each corner; the *body-centered cubic packing* has one at each corner and one in the middle of the cube. It is shown in Figure C18(c).

That defines the four lattices which matter to us. Now recall:

**DEF.**

Lattice + Basis = Crystal Structure

Most engineering metals have one of three lattices - FCC, HCP or BCC - with a basis of one atom on each lattice point, exactly like the spheres in Figure C18. Most engineering ceramics, too, have one of these lattices, but with a basis of 2 or more atoms per lattice point. Sodium chloride, for instance, is FCC with a basis of one  $\text{Na}^+$  and one  $\text{Cl}^-$  hung on each lattice point. We will come back to these in Section III.

And now for the moment of truth: three Exercises.

**Exercises.** (Answers at the end of the section.)

**E11.** The symmetry of the hexagonal lattice about a lattice point is  $6mm$ . Identify the 6-fold axis and the three mirror planes on the unit cell of the hexagonal lattice shown in Figure C19. (The mirror planes must not rotate into superposition by the operation of the rotation axis - if they do, the description contains redundant information.)

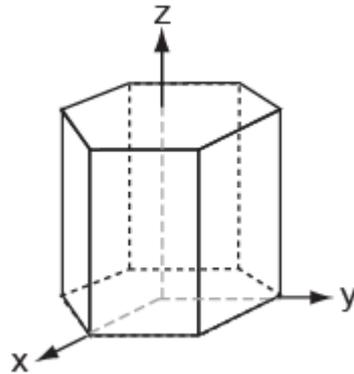


Figure C19. Hexagonal unit cell

**E12.** Copper has an FCC structure. Draw the third layer on the Figure C20 shown below, left, to make it. There is an axis of symmetry normal to the plane of the figure. What is it?

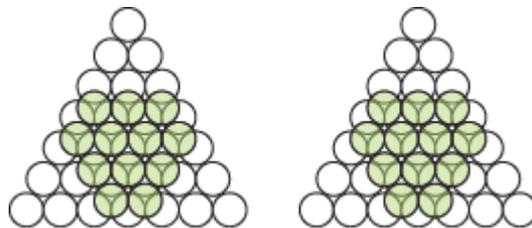


Figure C20. Two layers of close-packed planes.

**E13.** Magnesium has the HCP structure. Draw the third layer on the figure shown above, right, to create this structure. There is an axis of symmetry normal to the plane of the figure. Why is it not a hexad (6-fold) axis?

### (c) Interstitial space

As in 2-dimensions, the *interstitial space* is the unit of space between the atoms of molecules. The FCC and HCP structures both contain interstitial holes of two sorts: *tetrahedral* and *octahedral*. They are shown for the FCC structure in Figure C21(a) and (b).

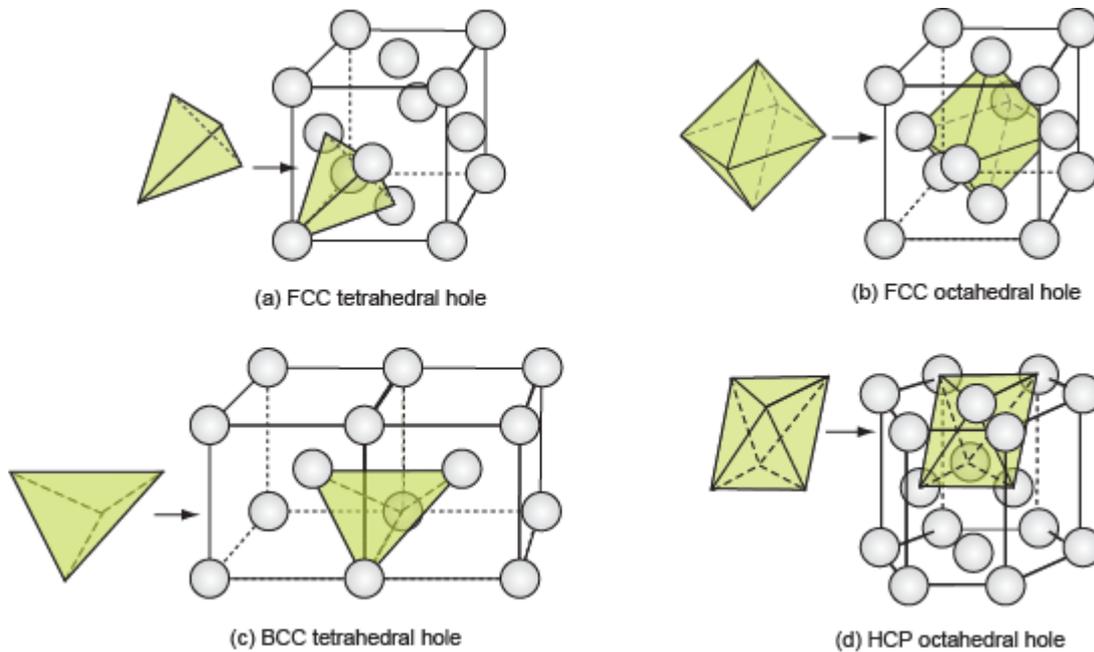


Figure C21. (a) and (b) The two types of interstitial hole in the FCC structure, (c) the tetrahedral hole of the BCC structure and (d) the octahedral hole in the HCP structure.

The holes are important because foreign atoms, if small enough, can fit into them. For both structures, the tetrahedral hole can accommodate, without strain, a sphere with a radius of 0.22 of that of the host. The octahedral holes are larger: they can hold a sphere that is... but wait, that is Exercise E14. The atoms of which crystals are made are, in reality, slightly squashy, so that foreign atoms which are larger than the holes can be squeezed into the interstitial space.

Nowhere is this more important than for carbon steel. Carbon steel is iron with carbon in some of the interstitial holes. Iron is BCC, and, like the FCC structure, it contains holes (Figure C21(c)). They are tetrahedral. They 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.

The HCP structure, like the FCC, has both octahedral and tetrahedral interstitial holes. The larger of the two, the octahedral hole, is shown in Figure C21 (d). The holes have the same sizes as those in the FCC structure. We shall encounter these interstitial holes in another context in Part 3. They give a way of understanding the structures of many oxides, carbides and nitrides.

Now more Exercises. Conveniently, there is an interstitial space before the next sub-section. It will just hold three Exercises.

**Exercises** (Answers at the end of this Section).

**E14.** Calculate the diameter of the largest sphere which will fit into the octahedral hole in the FCC structure. Take the diameter of the host-spheres to be unity.

**E15.** What is the ratio of the number of tetrahedral to the number of octahedral holes in the FCC structure?

**E16.** The HCP structure contains tetrahedral interstitial holes as well as octahedral ones. Identify a tetrahedral hole on the BCC lattice of Figure C22.

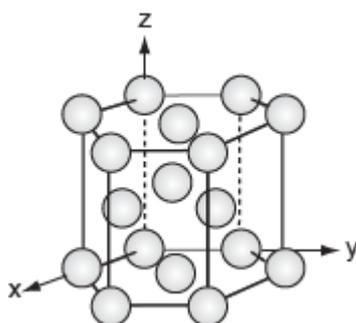


Figure C22. The HCP structure.

#### (d) Describing planes

The properties of crystals depend on *direction*. The elastic modulus of hexagonal titanium (HCP), 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) oxidizes 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 indices*<sup>2</sup> provide it.

First, describing planes.

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

Figure C23 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. Extend the plane until it intersects the axes. Measure the intercepts, in units of 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 through to get rid of fractions or dividing to remove common factors. The six little sketches show, in order, the (100), the (110), the (111), the (211), the ( $\bar{1}\bar{1}$ ) and the (112) planes; the  $\bar{1}$  means that the plane intercepts the y-axis at the point -1. Check that you get the same indices.

<sup>2</sup> William Hallows 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.

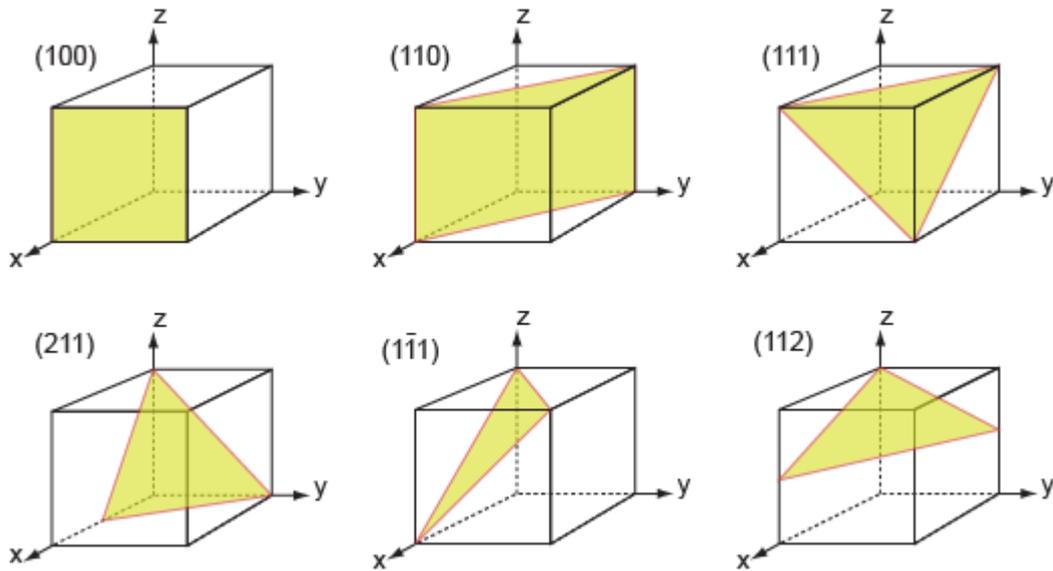


Figure C23. The procedure for finding the Miller Indices of a plane. The indices of four common planes are shown on the right.

The Miller indices of a plane are always written in *round* brackets: (111). But there are many planes of the 111-type. The *complete family* is described by putting the indices in curly brackets, thus:

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

Before going on, confirm your total mastery of the last bit by answering the following Exercises.

**Exercises.** (Answers at the end of the Section)

**E17.** What are the Miller Indices of the planes shown in the six sketches of Figure C24 (a), (b) and (c)? (Remember that, to get the indices, the plane must not pass through the origin, and remember, too, to get rid of fractions or common factors).

**E18.** Why does the complete  $\{111\}$  family, listed above, not include the  $(\bar{1}\bar{1}1)$  plane or the  $(\bar{1}\bar{1}\bar{1})$  plane?

**E19.** When iron is cold it cleaves (fractures in a brittle way) on the (100) planes. What will be the angle between cleavage facets?

**E20.** Mark, on the cell of Figure 24 (d), (e) and (f) below, the following planes:  $(\bar{1}11)$ , (120),  $(\bar{1}\bar{1}2)$

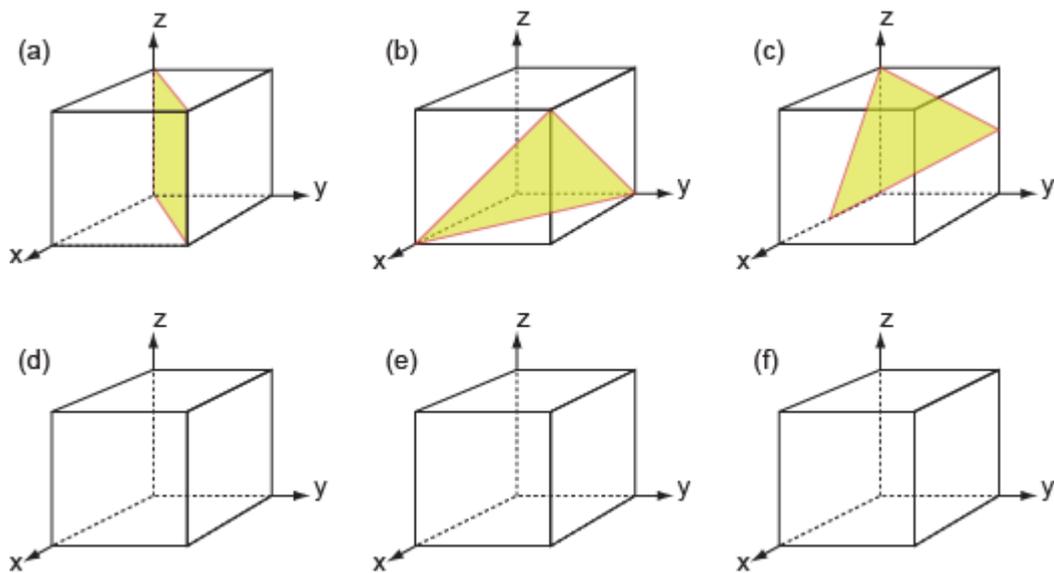


Figure C24. Identify the planes shown in the upper three figures. Draw those required in the question in the lower three.

### (e) Describing directions

Now for directions.

**DEF.** The *Miller Indices of a direction* are the components of a vector (**not** reciprocals) which starts from the origin, along the direction, reduced to the smallest integer set.

Figure C25 shows how to find the indices of a direction. Draw a line from the origin, parallel to the direction, extending it until it hits a cell edge or face. Read off the coordinates of the point of intersection. Get rid of any fraction or common factor by multiplying all the components by the same constant. The six sketches show the [010], the [011], the [111], the [021], the  $\bar{2}$ 12 and the  $\bar{1}$ 10 directions. The  $\bar{1}$  means that the y-coordinate of the intersection point is -1.

The Miller indices of a direction are always written in *square* brackets: [100]. As with planes, there are several directions of the 100-type. The *complete family* is described by putting the indices in angle-brackets, thus:

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

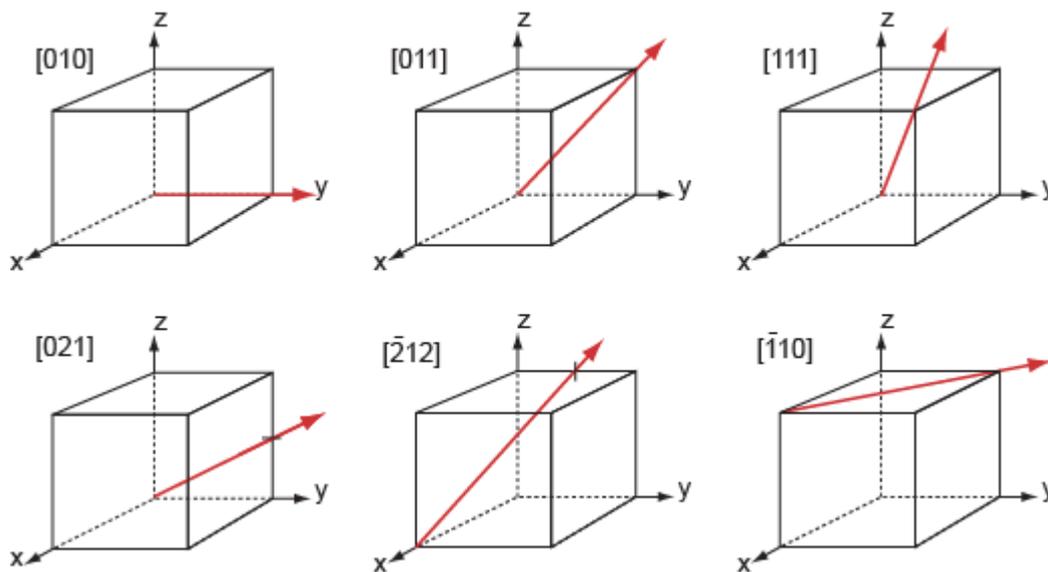


Figure C25. Miller indices of directions. Always translate the direction so that it starts at the origin.

**Exercises.** (Answers at the end of the Section).

**E21.** Identify the Miller indices of the three directions shown in Figure C26 (a), (b) and (c).

**E22.** Why does the family of  $\langle 100 \rangle$  directions listed above not include  $[\bar{1}00]$ ?

**E23.** Show, in any way you like, that the  $[111]$  direction is normal to the  $(111)$  plane in a cubic crystal.

**E24.** Mark, on the cells of Figure C26 (d), (e) and (f) the following directions:  $[\bar{1}\bar{1}1]$ ,  $[210]$  and  $[2\bar{2}1]$

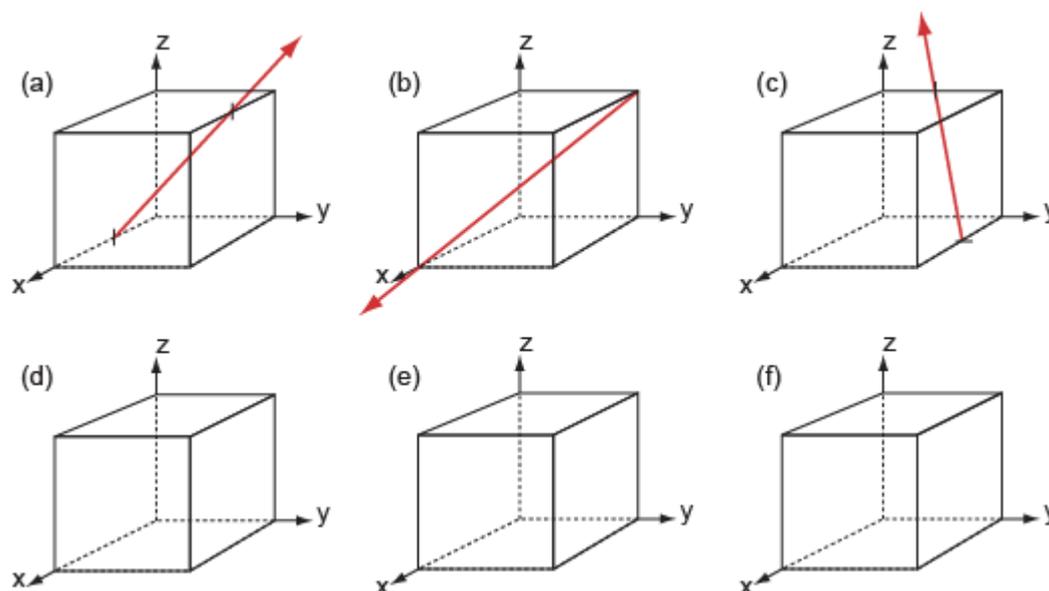


Figure C26. Identify the directions shown in the upper three figures. Draw those required in the question in the lower three. Remember that, to get indices, the direction must start at the origin.

## Answers for the Exercises of Part 2

**E11.** The hexagonal axis and the mirror planes are shown in Figure C27.

**E12.** The FCC packing of copper is shown in Figure C28, left. There is a 3-fold axis normal the drawing.

**E13.** The packing in magnesium is shown in Figure C28, right. There is a 3-fold axis normal to the drawing. The 6-fold axis of the 2-D hexagonal layer A is destroyed by placing the layer B in the position shown, leaving 3-fold symmetry.

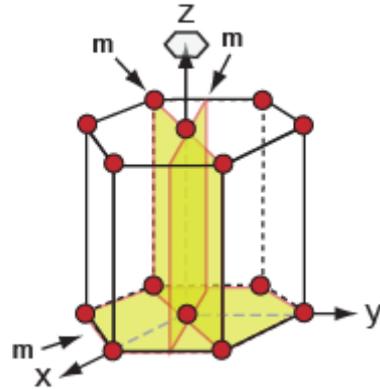


Figure C27. Answer to exercise E11.

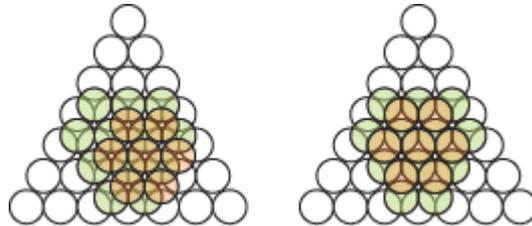


Figure C28. FCC (ABCABC) and HCP (ABAB) stacking of close-packed layers.

**E14.** Figure C29 shows how to calculate the octahedral hole size in the FCC structure. The face diagonals are close packed directions, so the atom spacing along the diagonal is 1 unit. The cell edge thus has length  $\sqrt{2} = 1.414$  units. That is also the separation of the centers of the atoms at opposite corners of the octahedral hole. The atoms occupy 1 unit of this, leaving a hole that will just contain a sphere of diameter 0.414 units without distortion.

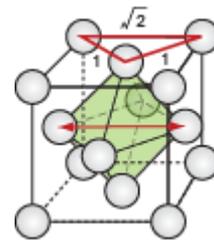


Figure C29. The calculation of the interstitial hole size in the FCC lattice

**E15.** There are 2 tetrahedral interstitial holes per octahedral hole in the FCC lattice.

**E16.** A tetrahedral hole of the HCP structure is sketched in Figure C30.

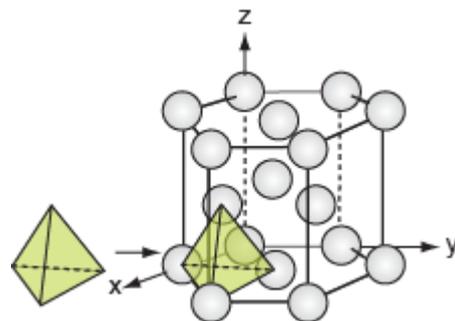


Figure C30. One of the tetrahedral holes of the HCP structure.

**E17.** The indices of the planes are (a)  $(\bar{1}22)$ , (b)  $(\bar{1}\bar{1}1)$ , (c)  $(142)$ ,

**E18.** The  $(\bar{1}\bar{1}\bar{1})$  plane is parallel to (and thus indistinguishable from) the  $(\bar{1}11)$  plane. Similarly, the  $(\bar{1}\bar{1}\bar{1})$  and the  $(111)$  planes are indistinguishable.

**E19.** The cleavage facets will meet at  $90^\circ$ .

**E20.** Figure C31 shows the planes.

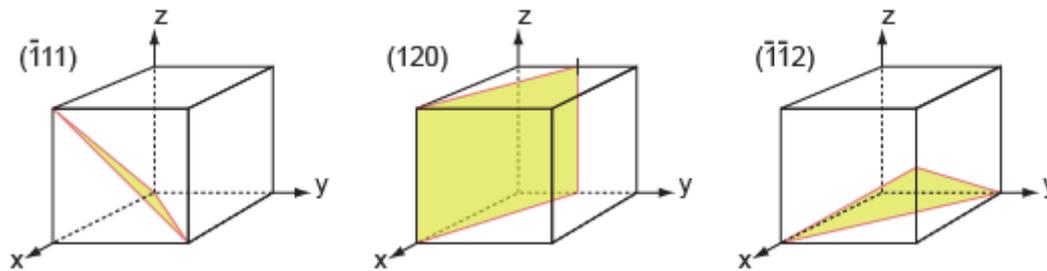


Figure C31. The planes of exercise E20

**E21.** The directions are (a)  $[011]$ , (b)  $[111]$  (or, equivalently,  $[\bar{1}\bar{1}\bar{1}]$ ), (c)  $[\bar{1}\bar{1}2]$ ,

**E22.** The  $[100]$  and the  $[\bar{1}00]$  directions are the same (only the sense is different).

**E23.** Two close packed directions in the  $(111)$  plane are the  $[\bar{1}01]$  and the  $[0\bar{1}1]$ . The dot product of either of these with the vector  $[111]$  is zero. So the  $[111]$  direction lies normal to the  $(111)$  plane.

**E24.** Figure C32 shows the directions..

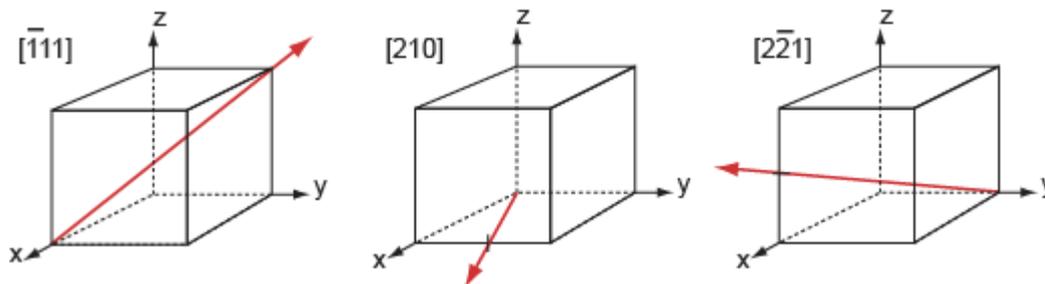


Figure C32. The directions of exercise E24



## PART 3: The structures of common engineering materials

This last Part of the course summarizes, extends and tests your knowledge of the important crystal structures of engineering materials. The great majority of the 92 stable elements are *metallic*, and of these, the majority (68 in all) have one of the three simple structures we have examined already: face-centered cubic (FCC), body-centered cubic (BCC) and hexagonal close packed (HCP). We start by revisiting them briefly. There is another good reason for a second look: many of the engineering compounds we use in the greatest quantities – oxides (such as alumina  $Al_2O_3$ ), carbides and nitrides (such as titanium nitride, TiN) – can be thought of as atoms of one type arranged in one of these simple structures with the atoms of the second type inserted into the interstices of the first.

### 3.1 Metals

#### *The Face-centered cubic (FCC) structure*

DEF. The FCC structure is described by a non-primitive, cubic, unit cell with one lattice point at each corner and one at the centre of each face; the basis is a single atom located at each lattice point. From a packing viewpoint, it consists of close-packed planes stacked in an A-B-C-A-B-C....sequence.

Among the metallic elements, 17 have the FCC structure. Engineering materials with this structure include the following.

Material	Typical uses
Aluminum and its alloys	Airframes, space frames and bodies of trains, trucks, cars, drink cans
Nickel and its alloys	Turbine blades and disks
Copper and $\alpha$ - brass	Conductors, bearings
Lead	Batteries, roofing, cladding of buildings
Austenitic stainless steels	Stainless cook-ware, chemical and nuclear engineering, cryogenic engineering
Silver, gold, platinum	Jewelry, 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 rolled, forged, drawn or otherwise shaped by deformation processing.
- They are generally tough, resistant to crack propagation (as measured by their fracture toughness,  $K_{Ic}$ )
- They retain their ductility and toughness to absolute zero, something few other structures allow.

**Exercises** (Answers - should you need them – at the end of the section)

- E25.** (a) How many atoms are there in the FCC unit cell?  
 (b) Is the [100] direction a close-packed direction?  
 (c) Is the [110] direction a close-packed direction?

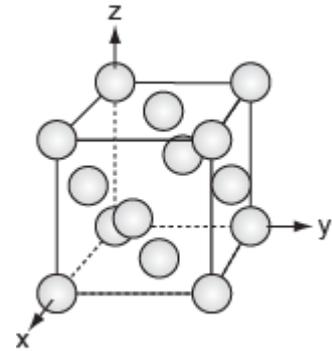


Figure C33. The FCC unit cell.

**E26.** The sketch of Figure C33 shows the FCC unit cell, the structure of copper, nickel and aluminum.

- (a) The slip planes in the f.c.c. structure (the ones on which dislocations glide) are the {111} planes. Outline and shade one of them.  
 (b) The slip directions are the  $\langle 110 \rangle$  directions. Mark two of these on the slip plane you have shaded

**E27.** Determine the packing factor (the fractional volume occupied) for an FCC structure, assuming that the atoms behave as hard spheres.

**E28.** (a) The atomic diameter of an atom of nickel is 0.2492 nm. Calculate the lattice constant (the edge-length of the unit cell) of FCC nickel.

- (b) The atomic weight of nickel is 58.71 kg/kmol. Calculate the density of nickel.

### The body-centered cubic (BCC) structure

DEF. The BCC structure is described by a non-primitive unit cell with one lattice point at each corner and one in the middle of the cube; the basis is a single atom located at each lattice point.

Of the metallic elements, 21 have this structure (most are rare earths). They include the following.

Material	Typical uses
Iron, mild steel	The most important metal of engineering: construction, cars, cans
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 rolled, forged, drawn or

otherwise shaped by deformation processing.

- They are generally tough, resistant to crack propagation (as measured by their fracture toughness,  $K_{Ic}$ ) at and above room temperature.
- They become brittle at low temperatures. The change happens at the “ductile-brittle transition temperature”, limiting their use below this.
- Their strength depends on temperature, even at low temperatures
- They can generally be hardened with interstitial solutes.

### Exercises (Answers: end of section)

**E29.** (a) Is the BCC structure close-packed?

(b) How many atoms are there in the unit cell?

**E30.** Figure C34 is a sketch the BCC unit cell, the structure of iron and mild steel

(a) Draw the  $[1\bar{1}1]$  direction.

(b) Outline and shade all the (001) planes which contain one or more atoms

(c) Mark a diad axis of the structure.

(d) Mark the close-packed direction in the BCC structure.

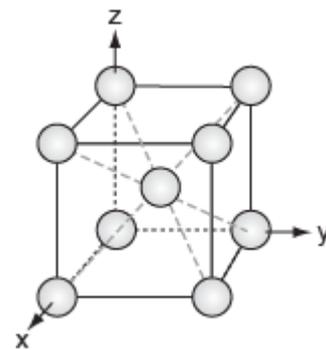


Figure C34. The BCC unit cell.

**E31.** The slip planes of BCC iron and steel are the  $\{110\}$  planes; the slip directions are the  $\langle 111 \rangle$  directions. Sketch a projection of a slip plane in the plane of the paper, identify the lengths of its sides, and mark the slip directions onto it.

**E32.** (a) The atomic diameter of an atom of iron is 0.2482 nm. Calculate the lattice constant of BCC iron.

(b) The atomic weight of iron is 55.85 kg/kmol. Calculate the density of iron.

**The close-packed hexagonal (HCP) structure**

DEF. The HCP structure is usually described by a non-primitive, hexagonal-prismatic unit cell with a lattice point at each corner, and one at the centre of the hexagonal faces. The basis consists of two atoms (one at 0,0,0, and the other at  $2/3, 1/3, 1/2$ ). From a packing viewpoint, it consists of close-packed planes stacked in an A-B-A-B....sequence.

Of the metallic elements, 30 have this structure. They include the following.

Material	Typical uses
Zinc	Die-castings, plating
Magnesium	Light-weight structures, an alloying element in aluminum
Titanium	Light, strong components for airframes and engines, biomedical and chemical engineering
Cobalt	High temperature superalloys, bone-replacement implants.
Beryllium	The lightest of the light metals. Its use is limited by expense and potential toxicity.

HCP metals have the following characteristics.

- They are ductile, allowing them to be forged, rolled, and drawn, but in a more limited way than FCC metals,
- Their structure makes them more anisotropic than FCC or BCC metals.
- They deform both by slip and by twinning.

**Exercises** (Answers at end of section).

**E33.** (a) The cleavage-plane (the plane of easy fracture) in the HCP structure is the (001) plane. Mark it on Figure C35.

(b) Diffusion in the HCP structure is faster in some directions than in others (that is, diffusion is anisotropic in the HCP structure). Using the symmetry of the structure to guide you, mark two directions in which the difference might be expected to be great.

(c) Young's modulus for a titanium crystal is 16% greater along the [001] than along the [100] or [010] directions. Mark these directions on the figure.

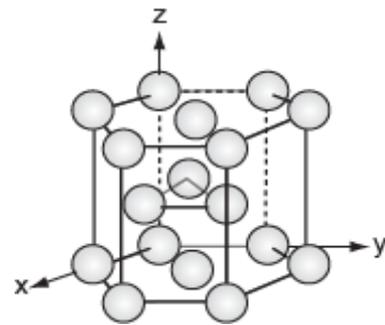


Figure C35. The HCP unit cell.

**E34.** Magnesium has an HCP structure and a density of  $1.74 \text{ Mg/m}^3$  and an atomic weight of  $24.312 \text{ kg/kmol}$ .

- (a) Assuming that the atoms can be represented as hard spheres, what is the packing factor (the fraction of space filled by the atoms)?
- (b) Calculate the dimensions of the unit cell.

### 3.2 Ceramics

Technical ceramics give us the hardest, most refractory (heat-resistant) materials of engineering. Those of greatest economic importance include

- Alumina,  $\text{Al}_2\text{O}_3$  (spark plug insulators, substrates for microelectronic devices)
- Magnesia,  $\text{MgO}$  (refractories)
- Zirconia,  $\text{ZrO}_2$  (thermal barrier coatings, ceramic cutting tools)
- Uranium dioxide,  $\text{UO}_2$  (nuclear fuels)
- Silicon carbide,  $\text{SiC}$  (abrasives, cutting tools), and, of course,
- Diamond,  $\text{C}$  (abrasives, cutting tools, dies, bearings).

The ceramic family also gives us many of the functional materials – those that are semiconductors, are ferromagnetic, show piezo-electric behavior, etc. Their structures often look complicated, but when deconstructed, so to speak, a large number turn out to be comprehensible (and for good reasons) as atoms of one type arranged on a simple FCC, HCP or BCC lattice with the atoms of the second type (and sometimes a third) inserted into the interstices of the structure of the first.

#### *The diamond cubic (DC) structure and DC-like structures*

We start with hardest ceramic of the lot – diamond – of major importance for cutting tools, abrasives, polishes and scratch-resistant coatings. Silicon and germanium, the foundation of semiconductor technology, have the same structure.

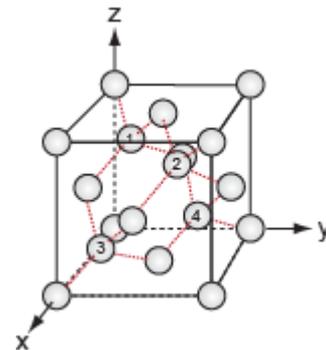


Figure C36. The diamond-cubic (DC) structure.

DEF. The Diamond Cubic structure is a face-centered cubic lattice with a basis of 2 atoms (at 0,0,0 and 1/4,1/4,1/4) associated with each lattice point.

Figure C36 shows the unit cell. Think of it as an FCC lattice with an additional atom in half of its tetrahedral interstices (see Part 2). They are labeled 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 further apart, lowering the density. The underlying cause is the 4-valent nature of the carbon, silicon and germanium atoms – they are happy only when each has 4 nearest neighbors, symmetrically placed around them. That is what this structure does.

Material	Typical uses
Silicon	Semiconductors
Germanium	Semiconductors
Carbon as diamond	Cutting and grinding tools, jewelry
(Silicon carbide)	Abrasives, cutting tools

Silicon carbide, like diamond, is very hard. The structure of the two materials are 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 C37 (it is the atoms marked 1, 2, 3 and 4 of Figure C36 that are replaced).

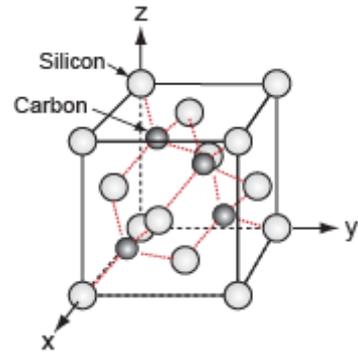


Figure C37. The structure of silicon carbide.

**Exercises** (Answers at the end of the section)

- E35.** (a) Is the DC structure close-packed?  
 (b) Now many atoms are there in the DC unit cell?
- E36.** Dislocations in silicon (DC) lie on  $\{111\}$  planes and tend to align themselves along  $\langle 110 \rangle$  directions. What is the angle between dislocations on a given (111) plane?
- E37.** (a) How many carbon atoms are there in the unit cell of silicon carbide? How many silicon atoms?  
 (b) The lattice parameter of cubic silicon carbide is  $a = 0.436\text{nm}$ . The atomic weight of silicon is 28.09 kg/kmol, and that of carbon is 12.01 kg/kmol. What is the density of silicon carbide?

**Oxides with the Rocksalt (Halite) structure**

These oxides all 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; the metal atoms occupy the octahedral holes in this lattice. The resulting structure is sketched in Figure C38. This is known as the Rocksalt (or Halite) structure because it is that of Sodium chloride, NaCl with chlorine where the oxygens are and sodium where the magnesiums are in the figure.

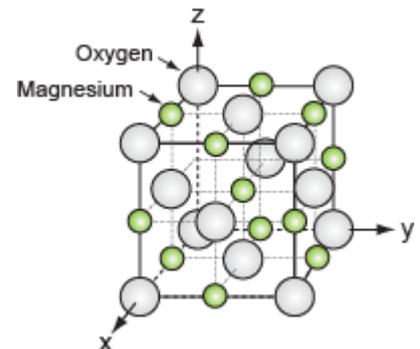


Figure C38 The structure of MgO, typical of many simple oxides.

Sodium chloride (common salt) itself is a material of engineering importance. It has been used for road beds 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.

Materials with the Rocksalt structure	Comment
Magnesia, MgO	A refractory, and 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, the larger of the two ions, are close-packed, in an HCP stacking. The M atoms occupy two thirds of the octahedral holes in this lattice, one of which is shown for alumina, filled, in Figure C39. Locating the rest is the subject of Exercise E38, below.

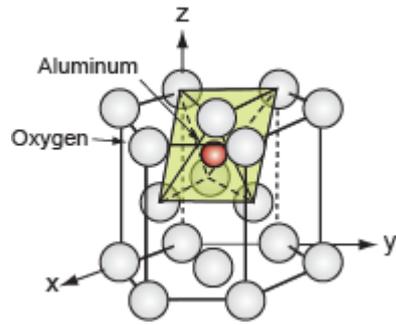


Figure C39. The M atoms of the corundum structure lie in the octahedral holes of a HCP oxygen lattice.

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,  $UO_2$ . Zirconium and Uranium lie far down in the periodic table and are large in size – larger than the Oxygen. In these it is the Zr or U atoms that form a close packed FCC structure and it is the oxygens that fit into the tetrahedral interstices in it, as shown in Figure C40.

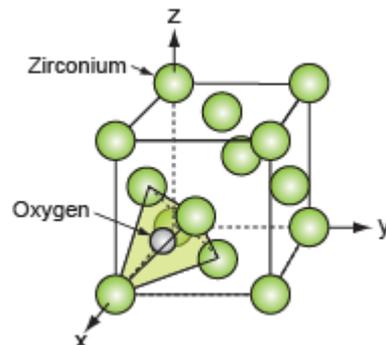


Figure C40. The M atoms of fluorite-structured oxides pack in an FCC array, with oxygen in the tetrahedral interstices.

Materials with the Fluorite structure	Comment
Zirconia, $ZrO_2$ (slightly distorted fluorite)	The toughest high-temperature ceramic
Urania, $UO_2$	Nuclear fuel
Thoria, $ThO_2$	Nuclear fuel
Plutonia, $Pu_2O_3$	A product of nuclear fuel reprocessing, a fuel in itself

**Exercises** (Answers at end of section)

- E38.** The symmetry elements of the HCP structure are  $3m$ . Use this information to infer how many octahedral holes are contained in the HCP unit cell of Figure C39. If all were occupied by M atoms, what would the formula of the oxide be?
- E38.** Use the symmetry of the structure to infer how many tetrahedral holes there are in the FCC unit cell of Figure C40.
- E40.** Sketch the unit cell of uranium dioxide,  $UO_2$ . If the uranium ions in this structure are close-packed and behave like hard spheres of diameter 0.276 nm, what is the lattice parameter of  $UO_2$ ?

**The structure of crystalline polymers**

Many polymers crystallize to some extent. 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 lattice is usually *triclinic*, which just means that the three unit vectors  $\underline{a}$ ,  $\underline{b}$ , and  $\underline{c}$  are of different lengths and do not meet at 90. Figure C41 shows a typical example; it is polyethylene. The unit cell is sketched.

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

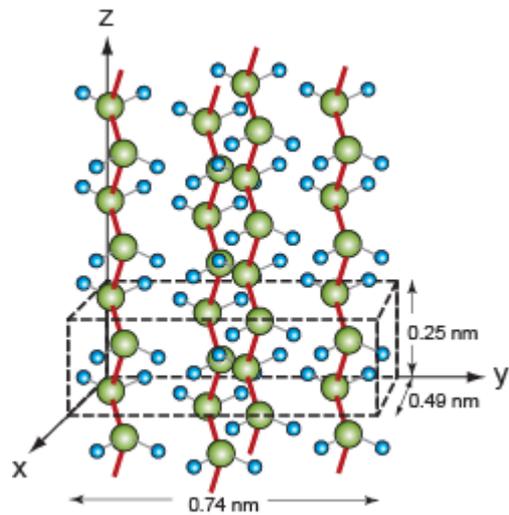


Figure C41. The structure of crystalline polyethylene.

Material	Typical uses
Polyethylene, PE, 65-90%	Bags, tubes, bottles.
Nylon, PA, 65%	High quality parts, gears, catches.
Polypropylene, PP, 75%	Moldings, rope.

**Exercises**

- E41.** Polymer crystals are very stiff and strong in the direction of molecular alignment. What are the indices of this direction in Figure C41?

### Answers to the Exercises of Part 3

- E25.** (a) The FCC unit cell contains 4 atoms.  
 (b) The [100] direction is not close-packed.  
 (c) The [110] direction is close packed.

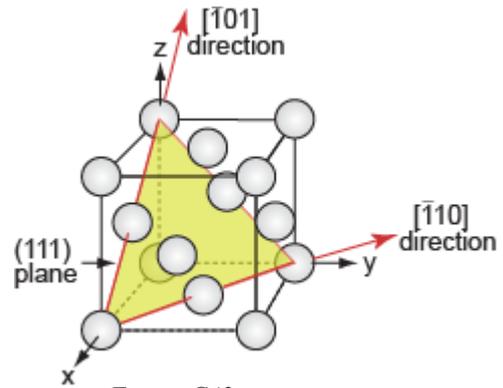


Figure C42.

- E26.** The planes and directions are shown on Figure C42.
- E27.** The diagonal of a face of the FCC structure (a  $\langle 110 \rangle$  direction) is a close packed direction. Atoms touch along this direction, so the length of a face diagonal is  $4r$  where  $r$  is the radius of an atom. Thus the edge-length  $a$  of the unit cube is given by noting that

$$2a^2 = (4r)^2$$

Thus  $a = 2.83r$  and the cell volume is  $a^3 = 22.7r^3$ . There are 4 atoms per unit cell, so the occupied volume is  $4\left(\frac{4\pi r^3}{3}\right) = 16.8r^3$ . Taking the ratio of these two volumes gives the packing fraction for the FCC structure: it is 0.74.

- E28.** (a) The relationship between atom radius  $r$  and lattice parameter  $a$  in the FCC structure was derived in the previous answer: it is  $a = 2.83r$ . The question gives the atom diameter  $a = 2.83r$  from which the lattice constant of nickel is calculated as 0.352 nm.

(b) The lattice parameter of nickel, from part (a) of the question, is 0.352 nm. The structure is face-centered cubic, so the volume of the unit cube of nickel is

$$a^3 = (0.352 \times 10^{-9})^3 \text{ m}^3 = 4.36 \times 10^{-29} \text{ m}^3.$$

The unit cell has 4 atoms associated with it. The mass of one of these atoms is the molecular weight 58.76 kg/kmol divided by Avogadro's Number ( $6.022 \times 10^{26}$  atoms/kmol) =  $9.75 \times 10^{-26}$  kg. The density is the mass of the unit cell divided by its volume, giving, for nickel a density of 8940 kg/m<sup>3</sup>.

- E29.** (a) The BCC structure is not close packed.  
 (b) There are 2 atoms per unit cell in the BCC structure.

**E30.** The planes and directions are in Figure C43.

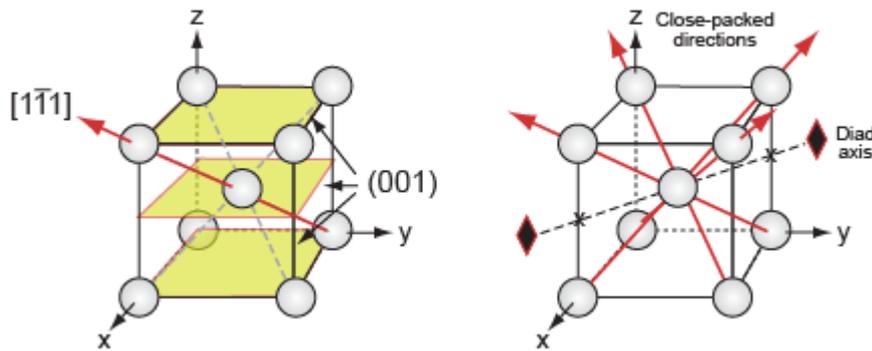


Figure C43.

**E31.** The slip plane and direction are shown in Figure C44.

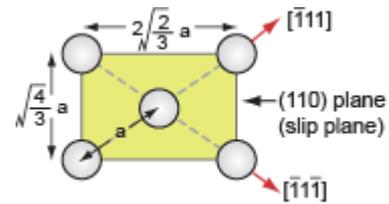


Figure C44.

**E32.** (a) The diagonal of the unit cube of the BCC structure ( $\langle 110 \rangle$  direction) is a close packed direction. Atoms touch along this direction, so the length of a face diagonal is  $4r$  where  $r$  is the radius of an atom. Thus the edge-length of the unit cube is  $a = 2.31r$  and its volume is  $a^3 = 12.3r^3$ . The lattice constant  $a$  of BCC iron is thus  $0.287 \text{ nm}$ .

(b) The lattice parameter of iron, from part (a) of the question, is  $0.287 \text{ nm}$ . The structure is body-centered cubic, so the volume of the unit cube of iron is

$$a^3 = (0.287 \times 10^{-9})^3 \text{ m}^3 = 2.364 \times 10^{-29} \text{ m}^3.$$

The unit cell has 2 atoms associated with it. The mass of one of these atoms is the molecular weight  $55.85 \text{ kg/kmol}$  divided by Avogadro's Number ( $6.022 \times 10^{26} \text{ atoms/kmol}$ ) =  $9.274 \times 10^{-26} \text{ kg}$ . The density is the mass of the unit cell divided by its volume, giving, for iron a density of  $7850 \text{ kg/m}^3$ .

**E33.** (a) The cleavage plane is shaded on Figure C45.

(b) One might expect a large difference between the diffusion in a close-packed direction and any direction normal to it.

(c) The (001) planes and the [001] direction are shown on Figure C45.

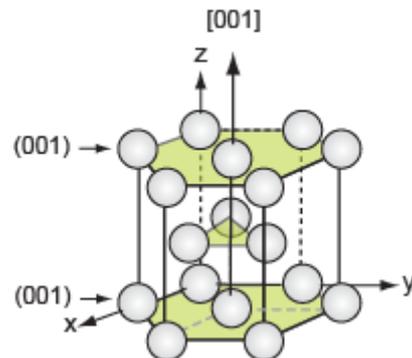


Figure C45.

**E34.** (a) The packing factor of the HCP structure is the same as that for the FCC: 0.74 (both are close-packed).

(b) The cell dimensions are  $a = 0.320 \text{ nm}$ ;  $c = 0.523 \text{ nm}$ .

**E35.** (a) The diamond-cubic structure is not close-packed.

(b) There are 8 atoms per unit cell.

**E36.** The angle between dislocations is  $60^\circ$  or  $120^\circ$ .

**E37.** (a) There are 4 silicon and 4 carbon atoms per unit cell.

(b) The density of silicon carbide, calculated in the way laid out in the solution to E28 and E32, is  $3200 \text{ kg/m}^3$ .

**E38.** The HCP lattice has a triad axis normal to the close packed planes. Rotation about this axis thus returns the lattice to itself 3 times per full revolution. This means there are three octahedral holes like that in Figure C39. The lattice also has a mirror plane – it is the close-packed plane. Reflecting about this plane creates three more octahedral holes. Thus the unit cell contains six octahedral holes.

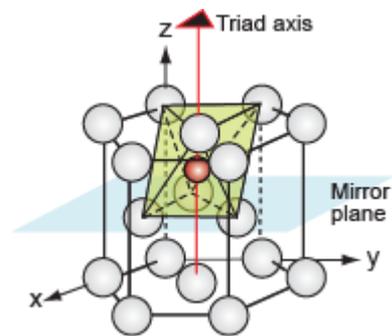


Figure C46

**E39.** The FCC lattice has a tetrad axis parallel to each of the three axes, plus mirror planes which reproduce the lattice in the same way. Rotation about the marked tetrad axis returns the lattice to itself 4 times per full revolution. This means there are four tetrahedral holes like that marked on the figure. The lattice also has a mirror plane – it is the cube face. Reflecting about this plane creates four more tetrahedral holes. Thus the unit cell contains eight tetrahedral holes.

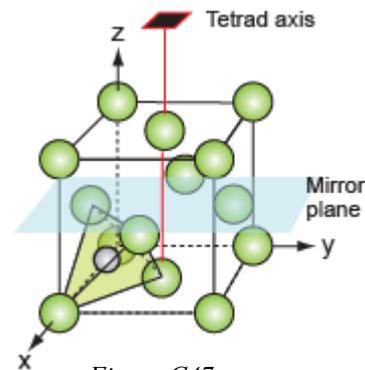


Figure C47

**E40.** The uranium dioxide structure looks like Figure C48.

The relationship between atom radius  $r$  and lattice parameter  $a$  in the FCC structure was derived in the previous answer: its is  $a = 2.83r$ . The question gives the atom diameter from which the lattice constant of nickel is calculated as  $0.391 \text{ nm}$ .

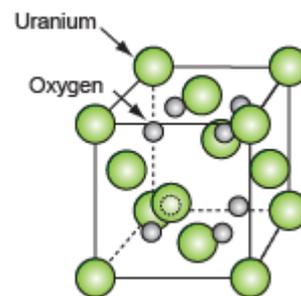


Figure C48

**E41.** The stiff direction is the  $[001]$  direction.

APPENDIX: The 14 Bravais lattices and the crystal structure of selected elements

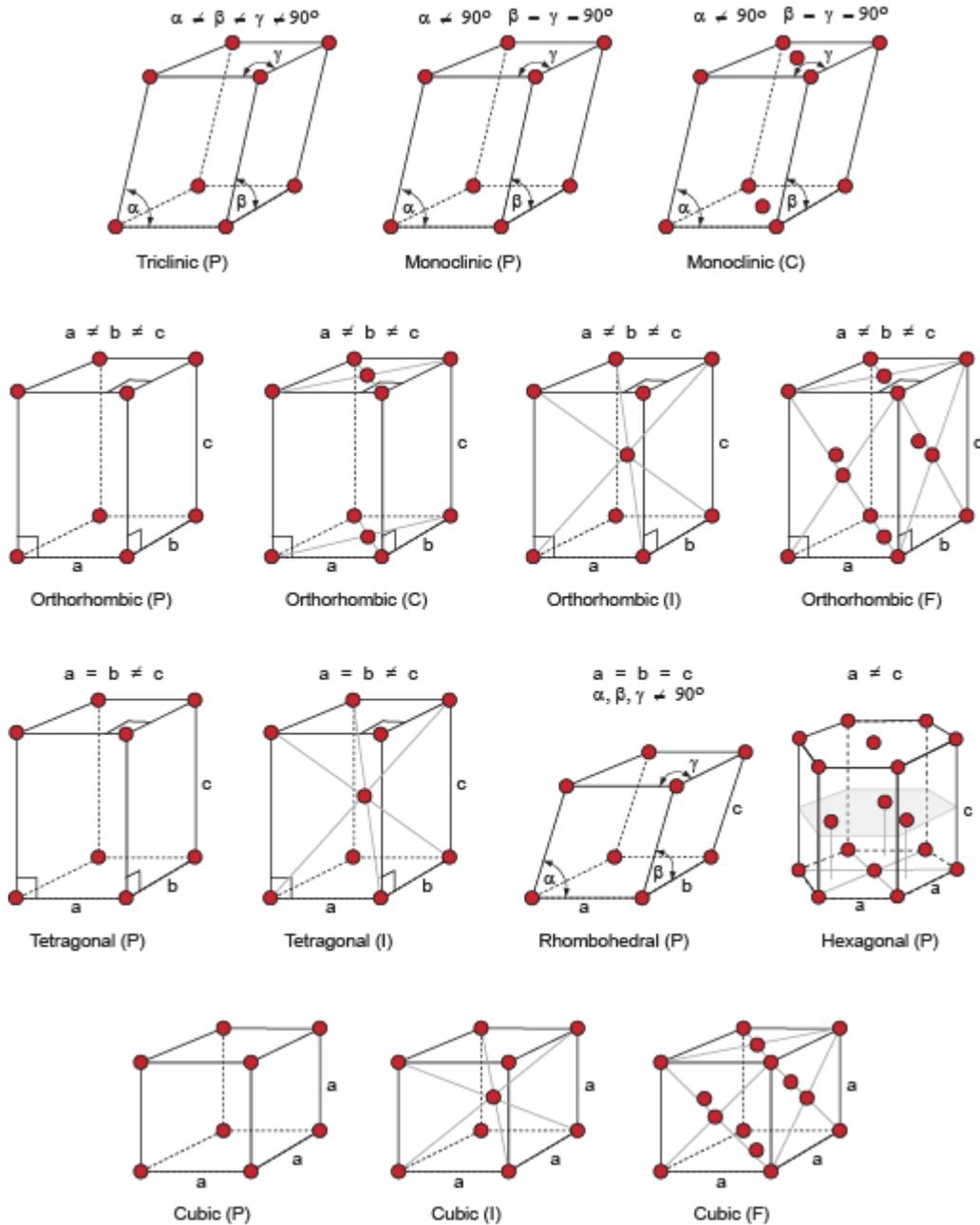


Figure C49. There are 14, and only 14, possible lattices in 3-dimensions. They are shown here; the red dots are the lattice points. The triclinic lattice is the general one; it has no rotational symmetry and no mirror planes. The others are special cases of it with 2, 3, 4 or 6-fold axes of rotational symmetry and one or more mirror planes. Here (P) means Primitive, (I) means Body-centered, (C) means Centered on one face, (F) means Face centered.

The crystal structure and parameters of selected elements

<b>Element</b>	<b>Structure at 20° C</b>	<b>Density at 20° C (Mg/m<sup>3</sup>)</b>	<b>a, (nm)</b>	<b>c, (nm)</b>	<b>Atomic volume (x10<sup>-3</sup>m<sup>3</sup>)</b>	<b>Nearest neighbor distance,(nm)</b>
Aluminium	FCC	2.70	0.404		1.66	0.286
Barium	BCC	3.5	0.501		60.48	0.434
Beryllium	HCP	1.82	0.227	0.359	0.82	0.222
Cadmium	HCP	8.65	0.297	0.561	2.16	0.297
Calcium	FCC	1.55	0.556		4.3	0.393
Carbon	DC	3.51	0.356		0.57	0.154
Cerium	FCC	6.9	0.514		3.32	0.364
Chromium	BCC	7.19	0.288		1.20	0.249
Cobalt	HCP	8.9	0.251	0.407	1.10	0.250
Copper	FCC	8.96	0.361		1.18	0.255
Gadolinium	HCP	7.95	0.362	0.575	3.27	0.355
Germanium	DC	5.36	0.565		2.24	0.244
Gold	FCC	19.32	0.407		1.69	0.288
Iron	BCC	7.87	0.286		1.18	0.248
Lanthanum	FCC	6.15	0.529		3.74	0.373
Lead	FCC	11.34	0.494		3.03	0.349
Lithium	BCC	0.53	0.350		2.16	0.303
Magnesium	HCP	1.74	0.320	0.520	2.32	0.319
Molybdenum	BCC	10.2	0.314		1.56	0.272
Nickel	FCC	8.90	0.352		1.09	0.249
Niobium	BCC	8.57	0.329		1.79	0.285
Palladium	FCC	12.0	0.388		1.48	0.274
Platinum	FCC	21.45	0.392		1.51	0.277
Potassium	BCC	0.86	0.533		7.47	0.462
Silicon	DC	2.33	0.543		1.99	0.235
Silver	FCC	10.49	0.408		1.71	0.288
Sodium	BCC	0.97	0.428		3.99	0.371
Strontium	FCC	2.6	0.605		5.65	0.430
Tantalum	BCC	16.6	0.330		1.81	0.285
Tin (gray)	DC	5.75	0.646		3.35	0.280
Titanium	HCP	4.54	0.295	0.473	1.76	0.291
Tungsten	BCC	19.3	0.316		1.58	0.273
Uranium	complex	18.7			2.11	0.276
Vanadium	BCC	6.0	0.303		1.41	0.263
Zinc	HCP	7.13	0.266	0.494	1.52	0.266