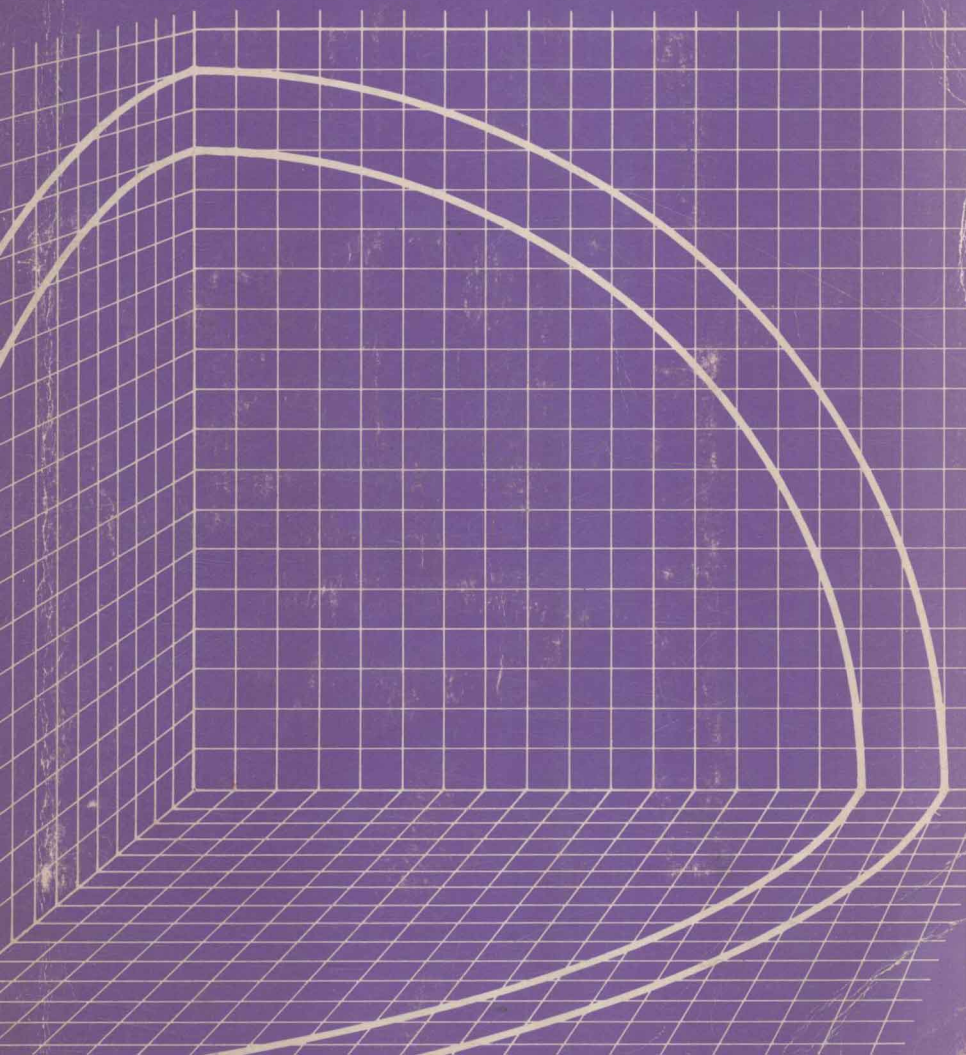# THE SOLID STATE

H.M.Rosenberg

Second Edition

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The solid state

an introduction to the physics of crystals for students of physics, materials science, and engineering

SECOND EDITION

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Editor's Foreword

T HE extension of our understanding of the properties of solids at a micro-scopic level is one of the important achievements of physics in this century, and a study of solid state physics is now an essential ingredient of all under-graduate courses in physics, materials science, metallurgy, electrical engineer-ing, and related topics. Dr. Rosenberg's book in this field succeeds in capturing the spirit of the stimulating lecture course that Oxford undergraduates have enjoyed for many years. It may be used as a text for a first course in solid state physics or as a follow up to a qualitative survey of the nature of condensed matter in the manner of Jennings and Morris's *Atoms in contact* (OPS 5). Dr. Rosenberg's book requires only a fairly basic background in mechanics, electricity and magnetism, and atomic physics along with relatively intuitive ideas in quantum physics, but from such a modest platform of knowledge he is able to develop a remarkably mature perspective of the solid state. All the usual aspects are considered, but dislocations receive a particularly lucid treatment. By emphasizing the simple case and by avoiding complicated mathematical derivations, Dr. Rosenberg gives insights which many much larger and more expensive books in this area fail to provide.

The solid state is a second-level book in the integrated structure of the Oxford Physics Series. Core texts in this series cover material usually treated in the first year of Honours Courses in English universities or in the second year in Scottish Honours Courses. The core texts include *Radiation and quantum physics, D.c. and a.c. circuits, Mechanics and motion, Interactions of particles, Atoms in contact,* and *Electromagnetism.* The typical length of books in the series is 100 pages, but for Dr. Rosenberg's book an exception has been made, so that this double volume gives sufficient range for it to be considered as the single basic text for typical solid state physics courses in universities all over the world. *The solid state* complements other second-level texts in the series, and paves the way for more advanced texts in special areas such as *Surface physics* (OPS 11).

J.A.D.M.

Preface

YET another book on solid state physics requires some explanation and excuse. Most solid state texts are fat and encyclopaedic. My aim was to write a thin volume and the result, whilst inevitably thicker than I had anticipated, is still reasonably slim. The treatment is intended for second-year undergraduates of physics, materials science, and engineering and it is an attempt to describe the basic elements of the physics of solids with as much continuity as is possible. Particular emphasis has been placed in the early chapters on the properties of waves in a periodic structure since this is the only basis on which to build a proper appreciation of diffraction, lattice vibrations, and electrons in metals and semiconductors.

Since the book is meant as an introductory text complicated proofs and points of detail have been omitted, although certain interesting topics which are not discussed or are not developed in the chapters are treated in the problems.

In this second edition I have, in response to several requests, written a chapter on superconductivity which covers, but only too briefly, most of the major topics associated with that remarkable phenomenon. I have also included the answers to the numerical problems, although I view the ensuing correspondence with some trepidation.

A book like this can lay little claim to originality. I owe a great debt to the standard texts by Dekker, Kittel, and Wert and Thomson, as well as to several of the other books quoted in the bibliography.

I am most grateful to the many people who have made suggestions for improvements in the text and who have pointed out errors in the first edition.

I should also like to thank many of my colleagues for reading and criticizing certain chapters. In particular these include S. L. Altmann, J. W. Christian, A. H. Cooke, G. Garton, W. Hayes, R. W. Hill, J. W. Hodby, F. N. H. Robinson, A. C. Rose-Innes, and C. E. Webb.

I am very grateful to all those who kindly supplied me with photographs for the figures, to Mrs. B. Wanklyn and to Dr. D. Double who provided specimens for microphotography, and to Mr. A. G. King who gave valuable help in taking many of the micrographs.

Acknowledgement is also made to the Delegates of the Oxford University Press for permission to use some questions set in examinations of the University of Oxford.

Oxford   H. M. ROSENBERG
April 1978

Contents

1. Atoms in crystals

NEARLY all the materials which we use today are crystals—collections of atoms or molecules assembled in some characteristic regular pattern. For an easy life physicists have nearly always limited their work to explanations of the properties of simple regular patterns of atoms—who can blame them—for even these can be extremely complex; so they have been concerned with the behaviour of a piece of rocksalt, or a diamond, or perhaps a single crystal of silicon or sodium. It is with the basic properties of such systems that we too must begin. But like life, most materials are neither regular nor simple. A piece of metal is rarely a single crystal, it is usually an agglomerate of small crystallites packed together. The lattice structure of such small crystallites, or even of large crystals, is rarely perfect. There will be regions where atoms are wrongly placed, or perhaps missing; impurities, accidental as well as intentional, will be present. In some cases the regularity of atomic arrangement extends over such a short distance that the material can hardly be considered to have any crystalline structure—it is a glass. Finally in the higher stages of complication and confusion we have very important structural materials of a composite nature such as wood and fibre-glass. Clearly a full understanding of their properties is a formidable problem.

It must be admitted at the outset that the only materials whose properties we can understand and explain in depth are single crystals of high purity. On the basis of this understanding we must then use our judgment and what knowledge we have to see how best we can account for the properties of more complicated structures.

1.1. Atoms in crystals

The regular arrangement of atoms in a material is, of course, the distinguishing feature of a crystal as compared with an amorphous substance. However, many scientists, particularly physicists, tend to disregard the details of the atomic arrangement and they often represent a small volume of a crystal as a simple cubic array, as shown in Fig. 1.1. Some even seem to regard the actual details of the atomic arrangement as being rather *earthy*, and perhaps best left to metallurgists and engineers who can cope with such irrelevant complexities.

Although only one element (polonium) is known to crystallize in the simple cubic form this structure does have the virtue that it is easy to draw; but
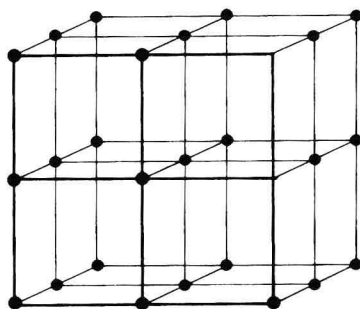
FIG. 1.1. The simple cubic structure.

as we shall see, many of the important properties of solids can be explained only if details of the structure of atoms in crystals are taken into account. We shall therefore give a brief description of the crystal structures of some of the more common simple materials. In a stable configuration of atoms the interatomic separation is usually between 0·2 nm and 0·3 nm (2–3 Å). The precise arrangement depends largely on the form of the electron clouds which surround the central positive nucleus of every atom. In many cases the crystal structure of a solid changes at certain temperatures and the examples which we give below are those which are stable at room temperature.

1.2. Cubic structures

Atoms do not arrange themselves on a simple cubic pattern because this is a very open structure. There are many empty spaces, and as a rule atoms tend to pack together more closely. If we examine the simple cubic arrangement to see how it might accommodate more atoms, the most obvious empty space is that at the centre of the cube. If this is filled we have the body-centred-cubic (b.c.c.) structure (Fig. 1.2(a)). Note that it can be considered as being two interlinked simple cubic lattices which are displaced with respect to one another along the body-diagonal of one cube by half the length of the diagonal (Fig. 1.2(b)). Many metals have a b.c.c. structure. The most important is iron, but in addition there are Cr, Mo, W, and also the alkali metals Li, K, Na, Rb, and Cs.

Certain simple binary compounds have what is essentially the b.c.c. arrangement in which the centre of the cube is occupied by one type of atoms and the corner sites are occupied by the others. This is usually called the caesium chloride structure.

We should here differentiate between the terms 'structure' and 'lattice' which are often used synonymously. By 'structure' we mean the actual pattern of the arrangement of atoms in space. The term 'lattice', although loosely used to denote the atoms in a crystal, should be reserved to describe that
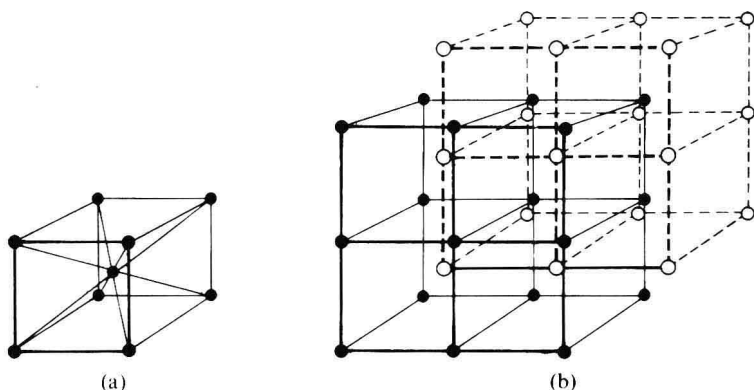
FIG. 1.2. (a) The body-centred cubic structure. (b) The body-centred cubic structure may be considered to be two interlinked simple cubic arrays.

network of points which show the simple translation vectors on which the structure is based. Thus Fe (b.c.c. structure) also has a b.c.c. *lattice* since a translation of an atom from the corner of the cube to the various points on that lattice is necessary in order to describe the atomic arrangement. The CsCl structure described above, however, has as its basis a simple cubic *lattice*, composed of pairs of Cs and Cl ions. It does *not* have a b.c.c. lattice because a translation from the corner of a cube to the body centre would not result in the correct structure since the atoms at those two sites are different.[†]

1.3. Close-packed structures

If we consider the atoms as hard spheres then the most efficient packing in one plane is the close-packed arrangement shown in Fig. 1.3. There are two simple ways in which such planes can be layered on top of one another to form a three-dimensional structure. In the layer which is illustrated the atoms are all at positions A and a second layer could nest above the A layer by being either in the spaces marked B or in those marked C. Let us suppose that the second layer is in the B spaces. Where can the succeeding layers be placed? There are two possible arrangements each of which is a very important type of structure.

1.4. Hexagonal close-packed structure

The simplest arrangement is for the third layer to be laid down in positions A, i.e. immediately above the atoms in the first layer, and the fourth to be at

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[†] It might be thought by this argument that Fe also has a simple cubic lattice composed of pairs of Fe ions. However, since the ions are now identical the full symmetry of the structure would not be covered by this description.
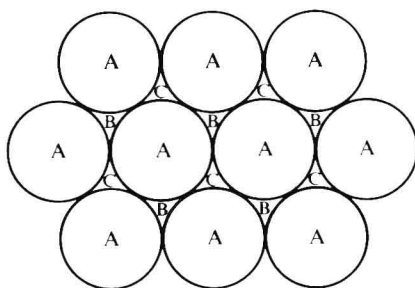
FIG. 1.3. The close-packed array of spheres. Note the three different possible positions, A, B, and C for the successive layers.

B and so on. This gives a layering of the type ABABAB... (or, of course, we could have ACAC...). This arrangement, in which the pattern is repeated at every alternate layer, is called the hexagonal close-packed (h.c.p.) structure. The hexagonal form of the arrangement is clearly seen from Fig. 1.4. Note that the basal planes of the hexagon (i.e. the planes parallel to the page in Fig. 1.4(a)) are unique. There are no other planes in other directions which are equivalent, i.e. which have the same close-packed pattern. The *hexagonal axis* is normal to the basal plane. Many metals have the h.c.p. structure. Among them are Mg, Zn, Cd, Ti, and Ni.
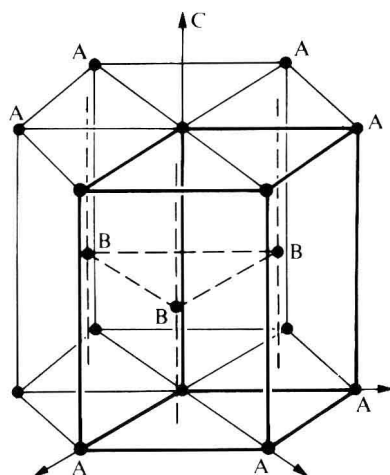
1.5. Face-centred cubic structure

There is another way in which successive close-packed planes of the type shown in Fig. 1.3 can be stacked. The first and second layers can be in positions A and B as before, but the third layer, instead of reverting to the A positions as in the h.c.p. arrangement, can be placed above the C positions. The fourth layer is then put in the A positions which are immediately above the atoms in the lowest plane, and so the pattern continues as ABCABC... with the pattern repeating at every third layer (Fig. 1.5(a)).

This type of array is called the face-centred cubic (f.c.c.) structure. At first sight there seems to be nothing cubic about it. This is because the close-packed layers which we have been discussing do not correspond to the ordinary faces of a cube. A face-centred cubic unit cell drawn with conventional cube axes as the basis is shown in Fig. 1.5(b). As its name implies the structure is the same as the ordinary simple cubic lattice (Fig. 1.1) with the addition of an extra atom at the centre of each cube face. The close-packed layers which we discussed in the previous paragraph are the body diagonal planes of the cube and one of these is shown in Fig. 1.5(c). The f.c.c. structure has a very important property which the h.c.p. arrangement does not possess—there are four equivalent close-packed planes as can be seen from a study of Fig. 1.5(c).
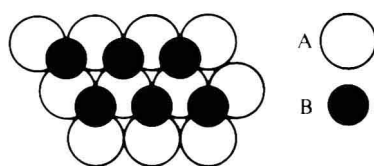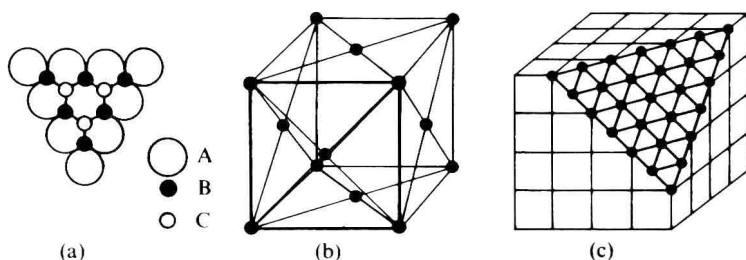
(a)

(b)

FIG. 1.4. Hexagonal close-packing. (a) The layering sequence ABABA... (b) The three-dimensional arrangement of the atoms which shows the hexagonal pattern more clearly.

(a)   (b)   (c)

FIG. 1.5. The face-centred cubic structure. (a) The layering sequence ABCABCA... (b) The unit cell based on a cube. (c) The close-packed planes of (a) are the body-diagonal planes of the cube. (After D. Hull, *Introduction to Dislocations*, Pergamon Press, Oxford.)

It should nevertheless be noted that although in the h.c.p. structure the basal plane is the only one which is close-packed, the actual fraction of space filled in h.c.p. is the same as in f.c.c.

Face-centred cubic structures are typical of many metallic elements, e.g. Cu, Ag, Au, Al, Ni, Pd, and Pt.

1.6. The diamond structure

The crystal structure of diamond can be derived from the f.c.c. lattice although it is not itself a close-packed arrangement. Formally it may be described as being built up from two interpenetrating f.c.c. lattices which are offset with respect to one another along the body-diagonal of the cube by one quarter of its length (Fig. 1.6(a)). Whilst this definition accurately describes the position of the atoms, it is not very useful when one tries to envisage the positions of the atoms relative to one another. A more useful model is to consider each atom to be at the centre of a tetrahedron with its four nearest neighbours at the four corners of that tetrahedron (Fig. 1.6(b)). From Fig. 1.6(a) it can be seen that if the 'central' atom of the tetrahedron is on one f.c.c. sub-lattice then the four 'corner' atoms are all on the other sub-lattice. It should also be noted that since all the atoms are equivalent *each* of them can be thought of as being the centre atom of a tetrahedron, although it would require a rather extended diagram to show this.

The tetrahedral arrangement in the diamond crystal in which each atom has four equally-spaced nearest-neighbours is a consequence of the special type of electron sharing (covalent bonding) which occurs in these structures. This is described in a later section of this chapter.
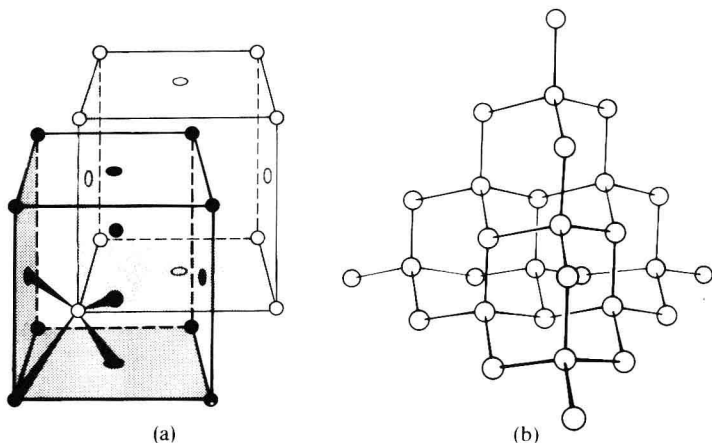

FIG. 1.6. The diamond lattice showing (a) how it is formed from two interpenetrating f.c.c. lattices, (b) the tetrahedral arrangement of the atoms.

Apart from diamond, the other elements which have the same structure are also tetravalent—germanium and silicon. Tin also has a diamond-structure allotrope 'grey tin' which is stable below about − 40 °C.

If the two interpenetrating lattices are of two different elements the atoms on different sub-lattices are of course no longer equivalent although they will still yield a similar tetrahedral arrangement. This is then called the zincblende (ZnS) structure and it is typical of the 3–5 semiconducting crystals such as InSb, GaAs, and GaP.

The structures which we have discussed in the preceding sections are the simplest types which occur, although of course a whole hierarchy of structures of increasing complexity may be found, particularly in biological materials. But even though many materials do not crystallize precisely in the form of the simple lattices which have been described, some are quite close to them. For example, some materials are nearly cubic, but the sides of the 'cube' are not all equal, or in other cases the sides may be equal but the angles of the 'cube' are not exactly right angles. It should also be emphasized, as has already been remarked, that some materials change their crystal structure at certain temperatures. For instance, from among the examples we have given, iron becomes f.c.c. and nickel becomes h.c.p. at high temperatures, whereas at very low temperatures (about 30 K) sodium transforms to a complex mixed structure.

1.7. The unit cell

An entire single crystal is produced by a process of repeating the simple atomic patterns such as those which we have just described. Each of these elementary building blocks (e.g. the body-centred cube in Fig. 1.2(a)) is called a unit cell.

It is often possible to break down the unit cells into smaller simpler arrangements which contain fewer atoms and which, when repeated, will also make up the crystal lattice. These are called primitive cells. The choice of primitive cell or unit cell is purely a matter of geometrical convenience.

Since unit cells often contain more than one atom, the size of the unit cell is usually larger than the nearest-neighbour interatomic spacing in a crystal and care must be taken not to confuse the unit cell dimensions with the atomic spacing.

1.8. The nomenclature for directions and for planes in crystals

Although a single crystal is formed by a regularly repeated pattern of atoms, the material can still exhibit anisotropy, i.e. certain properties, such as the electrical conductivity or the velocity of sound might have different values along different crystallographic *directions*. Or again, if we deform the crystal, say, in tension, then this deformation proceeds as certain preferred *planes*

of atoms slide over one another. In order to discuss the properties of crystals we therefore need a simple way of labelling unambiguously the directions and planes within a crystal. On first reading the systems might seem to be unduly pedantic but they have the advantage that they can be used, not merely for the simple types of structure which we have been discussing, but also for more complicated arrangements and in particular for lattices which do not have cubic symmetry. We shall, however, only give examples for crystals with cubic symmetry. The nomenclature we shall describe is also particularly well adapted to be used in the mathematical theory of the diffraction of waves in crystals.

1.9. Designation of directions

Let the sides of the unit cell have lengths and directions given by the vectors a, b, and c. In the cubic system these will of course be mutually perpendicular to one another and equal in length, but in the general case this will not be so. We wish to label a certain direction in the crystal lattice. This is indicated in Fig. 1.7 by the direction of the vector z which passes through the origin, O,
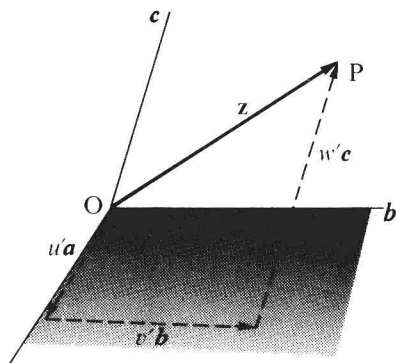

FIG. 1.7. The designation of directions. The direction of the vector z is given in terms of its projections on the unit-cell axes as described in the text.

of the axes of the unit cell. We proceed by starting at O and we go a distance $u'a$ along the a axis, $v'b$ parallel to the b axis and $w'c$ parallel to the c axis so that with a suitable choice of u', v', and w' we finally end up somewhere along the vector z, say at P. $u'a$, $v'b$, and $w'c$ are, of course, the projections of OP on to the three axes. The three numbers u', v', and w' are then reduced to the set of simplest integers u, v, w, and the direction of z is labelled as $[uvw]$ using square brackets. If a negative direction was used to reach z then this is indicated by a bar over the appropriate letter, e.g. $\bar{v}$. The complete set of equivalent directions in a crystal is denoted, using angular brackets, by $\langle uvw \rangle$. In the cubic system u, v, and w are proportional to the direction cosines of the vector z

As examples, the cube edge direction **a** in Fig. 1.7 would be denoted by [100], that of direction **b** by [010] and the negative direction of **a** would be [$\bar{1}$00]. The general set of all the cube edge directions would be ⟨100⟩. The face-diagonals of the cube are ⟨110⟩ and the body-diagonals are ⟨111⟩. These are the only important directions which need be remembered.

1.10. Designation of atomic planes—Miller indices

The planes are labelled in a similar way to the directions. Let the plane in which we are interested cut the three axes of the unit cell (Fig. 1.8) at $u'a$,
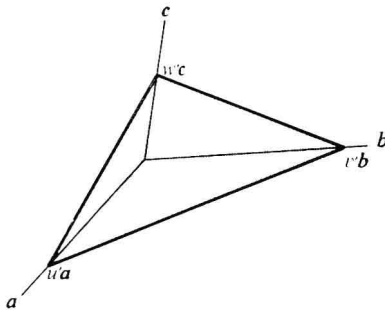

Fig. 1.8. Miller indices. The shaded plane is described in terms of the reciprocals of its intercepts with the unit-cell axes as described in the text.

$v'b$, and $w'c$ respectively. We then reduce the *reciprocals*, $1/u'$, $1/v'$, $1/w'$ to the simplest integers h, k, l, and the plane is labelled as (hkl), using round brackets. These are called the Miller indices of the plane. Once again a bar is used for a negative direction. The general set of planes of a particular type is placed within curly brackets $\{hkl\}$.

In the cubic system the Miller indices of a plane are just the reciprocals of the intercepts of that plane on each of the three axes, reduced to the simplest integers. For example, the set of all cube faces is $\{100\}$; the planes which pass through the face-diagonals of two parallel sides are $\{110\}$ and those which pass through three face diagonals on adjacent sides are $\{111\}$. These are shown in Fig. 1.9.

The Miller index system enables the spacings between adjacent planes to be calculated very easily. For example, in the cubic system with a unit cell dimension of a, the spacing d between the $\{hkl\}$ planes is

$$d = a/(h^2 + k^2 + l^2)^{\frac{1}{2}}.$$

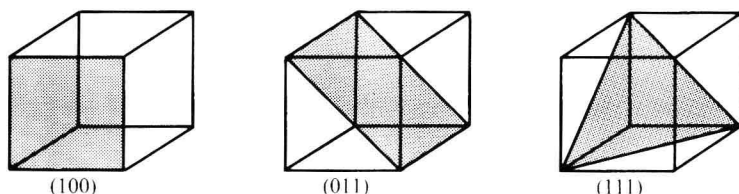(100)   (011)   (111)

FIG. 1.9. The most important planes in a cubic system.

The angle ϕ between two planes (or directions) in a cubic system with indices $h_1k_1l_1$ and $h_2k_2l_2$ is given by

$$\cos \phi = \frac{h_1h_2 + k_1k_2 + l_1l_2}{(h_1^2 + k_1^2 + l_1^2)^{\frac{1}{2}}(h_2^2 + k_2^2 + l_2^2)^{\frac{1}{2}}}$$

The most important planes are those with low index numbers and these are the ones which are the most widely spaced.

Note also that in the cubic system the $[hkl]$ vector is perpendicular to the (hkl) plane.

For the hexagonal crystal lattice four indices are used $(hkil)$. These are derived by using the intercepts on four axes a,b,c,d, three in the basal plane at 120° to each other, and the fourth one normal to the basal plane (Fig. 1.10).
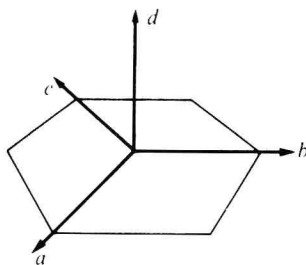

FIG. 1.10. Miller indices for the hexagonal lattice. The intercepts of the plane on three basal axes a,b,c and the one hexagonal axis d are used to derive the indices.

The reciprocals of these intercepts are then reduced to simple integers as before, and the third index is chosen to be minus the sum of the first two. Although, of course, one of these indices must be redundant, the four-figure system is a more convenient one to use for the hexagonal lattice. Thus the basal plane is (0001) and $\{10\bar{1}0\}$ designates the set of hexagonal faces. An analogous system is used for designating directions.

1.11. Binding forces in crystals

What holds the atoms together so that they form a crystal? There must be an attractive force between atoms, because otherwise solids would not be formed; but there must also be a repulsive force which prevents the atoms from getting too close together. In general terms the stability of the crystal lattice depends on a balance between this repulsive force, which is dominant when the atoms are very close, and the attractive force which remains important when they are slightly farther apart.

The stable position for the atoms is most satisfactorily understood by considering how the potential energy of a pair of atoms varies with their separation. The repulsive force gives rise to a positive potential energy since under its influence work has to be done on the system in order to bring the atoms closer together. We shall assume that this energy varies as some inverse power of the atomic separation, r, say as A/r^n, although it is sometimes written in the form $A \exp(-r/\alpha)$. The attractive force gives a negative potential energy of the form $-B/r^m$. This tends to zero when the atoms are far apart and it increases negatively as they approach one another. Curves for these two contributions to the potential energy, as a function of the interatomic spacing are shown in Fig. 1.11, together with that for the total potential energy $A/r^n - B/r^m$. It can be seen that, as drawn, the total potential energy passes through a minimum. The atomic separation r_0 at which this minimum potential energy occurs is, of course, the stable spacing for the pair of atoms. It is at this separation that the negative and positive forces annul one another. It should be noted that a minimum in the potential energy (and hence a position of *stable* equilibrium) can only arise if the power n in the repulsive term is greater than m in the attractive term. If $m > n$ an unstable situation would develop and bonding would not occur under these conditions.

1.12. The dissociation energy

The zero of energy (which is of course quite arbitrary) used in Fig. 1.11 is taken to be the energy which the two atoms have when they are far apart. The depth of the energy minimum at the equilibrium spacing is a measure of the work which must be done to remove an atom, originally stably bound in the lattice, right away from the crystal. This is called the dissociation energy or the cohesive energy and it may be determined experimentally by calorimetric measurements.

1.13. The repulsive force

Let us now consider the physical mechanisms which give rise to the forces between atoms.

The repulsive force is most quickly dealt with. When atoms are brought very close together the electron clouds around neighbouring atoms are made to overlap. There is a mutual repulsion between like charges and so the electron