



# Essentials of Crystallography

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BLACKWELL SCIENTIFIC PUBLICATIONS  
OXFORD LONDON EDINBURGH  
BOSTON PALO ALTO MENDOZA

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**Editorial offices:**

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**First published 1986**

**Set by Eta Services Ltd, Beccles, Suffolk and printed and bound in Great Britain by Butler & Tanner Ltd, Frome and London**

**DISTRIBUTORS**

**USA and Canada**

**Blackwell Scientific Publications Inc**

**PO Box 50009, Palo Alto**

**California 94303**

**Australia**

**Blackwell Scientific Publications**

**(Australia) Pty Ltd**

**107 Barry Street,**

**Carlton, Victoria 3053**

**British Library**

**Cataloguing in Publication Data**

**Library of Congress**

**Cataloguing in Publication Data**

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## Preface

Some depth of understanding of crystallography and some knowledge of the methods employed in the study of crystalline solids are central to the contemporary study of many of the active areas in chemistry, the earth sciences, materials science, and physics. In this volume we explain the basic concepts of crystallography and discuss the principal modes of study of crystalline solids, the diffraction of X-rays, electrons, and neutrons. In our experience students require a thorough, rather than a superficial, understanding of the basic concepts if they are to make effective progress in the study of crystalline solids and that is what we have set out to provide in this volume. In a subsequent volume we shall discuss the next stage in the study of crystalline solids, crystal chemistry and crystal physics.

This volume stems from the first nine chapters of our *Crystalline Solids* (Nelson, London, and Wiley, New York, 1974). Significant changes in treatment and extensive widening of the scope will be immediately discernible to those who used that book. We have adopted a vector treatment of lattice and diffraction geometry: the elegant methods of spherical trigonometry have been almost totally discarded, albeit with regret, in favour of vector methods which are eminently suitable for computer usage. The reciprocal lattice and the reflecting sphere are now utilized throughout our treatment of diffraction by crystals.

A new chapter on crystal structure determination outlines the contemporary approach to this permanently important aspect of the subject: the chapter is concerned with principles and, by design, no attempt is made to present a detailed account of modern methods of structure determination.

The volume concludes with a new chapter on electron diffraction and microscopy in which we have concentrated on principles and kept technological detail to the minimum. We have deliberately restricted the treatment to the kinematical theory of diffraction and avoided excursions into dynamical theory in order not to overload the chapter with theory. It is our experience that once the student has grasped the essentials of the kinematical theory it is not difficult to make the next step to an understanding of the dynamical theory.

These two new chapters take the reader to direct methods of structure determination and to high resolution electron microscopy of unit-cells. The unifying threads throughout the two volumes are the concepts of lattice, symmetry and structure. They are explored in a way that emphasizes their physical significance for the diffraction of X-rays, electrons, and neutrons. The two volumes are intended to be read together.

We find crystallography a particularly rewarding subject in its essential elegance: we hope to infect some of our readers with our enthusiasm. In the writing of the

volume our enthusiasm has been guided by our experience of teaching all the topics contained in it to students at Cambridge over the past twenty-five years. In our choice of the problems at the end of each chapter we have attempted to provide some interest for the chemist, the geologist, the materials scientist, and the physicist. It is our hope that these problems will provide students with the opportunity to test their understanding of the subject as their reading of the book proceeds.

We owe a debt of gratitude to colleagues from the Department of Metallurgy and Materials Science and from our own Department of Earth Sciences who have been involved in teaching crystallography in Cambridge where the courses we teach are for chemists and physicists as well as for materials scientists and geologists. We are greatly indebted to those who reviewed our preliminary proposals for the revision of the earlier book:

Dr P. Day (Inorganic Chemistry, University of Oxford)

Professor N. L. Paddock (Chemistry, University of British Columbia)

Professor B. Ralph (Metallurgy and Materials Science, University College, Cardiff)

Professor D. W. A. Sharp (Chemistry, University of Glasgow)

Professor J. P. Simons (Physical Chemistry, University of Nottingham)

Professor D. G. W. Smith (Geology, University of Alberta, Edmonton)

Our thanks are also due to our editor, Navin Sullivan, for his continuing interest in our work from the inception of the first edition of *Crystalline Solids*. To Dr Trevor Page (Metallurgy and Materials Science, Cambridge) we are indebted for Fig 10.11 and to Dr Ross Angel (Earth Sciences, Cambridge, and Earth and Space Sciences, Stony Brook, New York) for Figs 10.5 and 10.10. Our debt to Sheila Tuffnell, who converted our manuscript into impeccable typescript, is very special. We are indebted too to Judith Ginifer, who helped in many ways.

Cambridge,  
December 1985

Duncan McKie  
Christine McKie

# 1

## Crystal Lattices

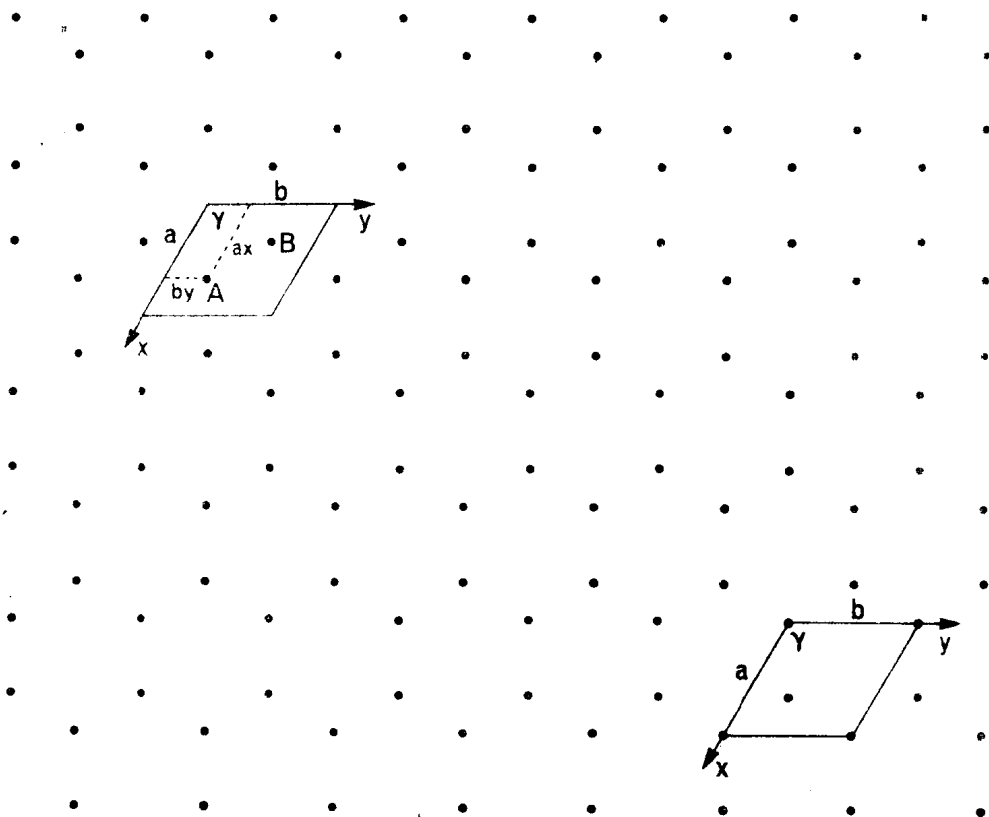
A crystalline solid is essentially a solid whose atoms are disposed in regular three-dimensional array. The atoms in a solid are not static: each atom possesses thermal energy and vibrates about its mean position. It is the mean positions of the constituent atoms that are regularly arranged in space in a crystalline solid. Such regularity of mean atomic positions corresponds to a state of minimum free energy and is the fundamental characteristic of the crystalline state.

In its early development crystallography was confined to the study of *single crystals*, that is solid bodies bounded by natural plane faces within which the mean positions of all the constituent atoms are related to a single regular three-dimensional array of points. But there are in addition many other solid crystalline substances which can never, or only with difficulty, be obtained in single crystal form; such are the common metals, brass and steel, which are aggregates of interlocking randomly oriented crystals of varying shape and size. Such *polycrystalline* substances belong just as surely to the crystalline state as do the single crystals which exclusively formed the subject of the science of crystallography in its early days. Not all solids are crystalline however; glasses and other amorphous solids have, like liquids, only severely localized volumes of atomic order involving merely hundreds or thousands of atoms. Examples of solids with two-dimensional or one-dimensional atomic periodicity are known and are regarded as special cases within the crystalline state.

In this first chapter we develop the principles of geometrical crystallography by consideration of *perfect single crystals*. For a perfect single crystal, the regular arrangement of atoms in the crystal can be completely described by definition of a fundamental *repeat unit* coupled with a statement of the translations necessary to build the crystal from the repeat unit. For geometrical simplicity we exemplify this basic crystallographic concept first by consideration of a two-dimensional case.

The arrangement of atoms in a layer of graphite (the crystalline form of carbon stable at room temperature and atmospheric pressure) is shown in Fig 1.1. The carbon atoms, represented as small solid circles in the figure, are in a honeycomb pattern. The distance between the centres of adjacent hexagons of the 'honeycomb' is  $2.46 \text{ \AA}$  so that a layer of area about  $1 \text{ mm}^2$  will contain about  $(4 \cdot 10^6)^2 = 1.6 \cdot 10^{13}$  hexagons; the array of atoms in a layer of this size is thus effectively infinite. The repeat unit of the two-dimensional structure, containing two carbon atoms, is shown in the top left-hand corner of the figure enclosed in a parallelogram whose corners lie at the





**Fig 1.1** The arrangement of carbon atoms in one layer of the graphite structure. Each carbon atom is represented by a small solid circle. Two reasonable unit-meshes are outlined and labelled with the axial vectors  $a$ ,  $b$ , and the inter-axial angle  $\gamma$ .

centres of four adjacent hexagons. The atomic pattern of the layer can be reconstructed by repeating this parallelogram in a regular manner so as to fill the plane of the atomic layer completely. The parallelogram, known as the *unit-mesh* of the layer, is completely specified by designating two of its sides as the reference axes  $x$  and  $y$ , stating the interaxial angle, and specifying the lengths of its edges. It is conventional to denote the lengths of the edges of the unit-mesh parallel to the  $x$  and  $y$  axes as  $a$  and  $b$  respectively and to denote the angle between the  $x$  and  $y$  axes as  $\gamma$ . In graphite the unit-mesh has  $a = b = 2.46 \text{ \AA}$ ,  $\gamma = 120^\circ$ . A variety of parallelograms, all of the same area, could have been chosen as the unit-mesh of a graphite layer; but it is in general conventional and convenient to select a unit-mesh with  $a$  and  $b$  as short as possible and the angle  $\geq 90^\circ$ . It is immaterial where the corners of the unit-mesh are placed in relation to the atoms of the graphite layer; the shape of the conventional unit-mesh is controlled by the atomic pattern to be constructed from it, a change of origin merely affecting the coordinates of the atoms within the unit-mesh. For the purpose of defining the positions of the atoms of the repeat unit within the unit-mesh we employ a coordinate system which has the edges of the unit-mesh as axes, the unit of length along each axis being taken as the length of the corresponding edge; atomic coordinates are thus given as fractions of the lengths of the edges of the unit-mesh referred conventionally to an origin at the top left-hand corner of the unit-mesh. The origin of each of the unit-meshes in Fig 1.1 is differently disposed

with respect to the atomic array, but the reference axes are parallel and the area is the same in each case. The unit-mesh on the left of the figure contains an atom A with coordinates  $\frac{2}{3}, \frac{1}{3}$  and an atom B with coordinates  $\frac{1}{3}, \frac{2}{3}$ . The periodic nature of the atomic arrangement naturally implies that an atom situated at a point with coordinates  $x, y$ , that is at a vector distance  $xa + yb$  from the origin, will be repeated at vector distances  $(m+x)a + (n+y)b$  from the origin, where  $m$  and  $n$  are integers; in this case the atom A at  $\frac{2}{3}, \frac{1}{3}$  is repeated at  $(m+\frac{2}{3})a, (n+\frac{1}{3})b$  and the atom B at  $(m+\frac{1}{3})a, (n+\frac{2}{3})b$ . The presence of an atom at the origin of the unit-mesh on the right of the figure implies the presence of other atoms of the same element at points with coordinates 1, 0; 0, 1; 1, 1; 2, 1; and so on: a statement of any one such pair of coordinates is sufficient for reconstruction of the structure. In the unit-mesh on the left of the figure the atom B has coordinates  $\frac{1}{3}, \frac{2}{3}$  and there will be necessarily an equivalent atom with coordinates  $-1+\frac{1}{3}, -1+\frac{2}{3}$ , i.e.  $-\frac{2}{3}, -\frac{1}{3}$ , corresponding to the coordinates of the atom A in this unit-mesh with change of sign. The positions of the two carbon atoms in unit-mesh I can thus be neatly specified as  $\pm(\frac{2}{3}, \frac{1}{3})$ . In terms of this unit-mesh the structure of a layer of graphite can be completely specified by stating the dimensions of the unit-mesh,  $a = b = 2.46 \text{ \AA}$ ,  $\gamma = 120^\circ$ , and the coordinates of the carbon atoms within it,  $\pm(\frac{2}{3}, \frac{1}{3})$ ; the atomic layer can then be reconstructed by repetition of the unit-mesh in two non-parallel directions.

We now pass on to the next stage of complexity and consider in general terms a three-dimensional structure. Here the repeat unit can always be enclosed within a parallelepiped, known as the *unit-cell*, and the effectively infinite structure can be built up by repetition of the unit-cell in three non-coplanar directions which are conventionally taken as the reference axes  $x, y$ , and  $z$ . The lengths of the unit-cell edges parallel to the  $x, y$ , and  $z$  axes are respectively denoted  $a, b$ , and  $c$ . It is conventional also to take the positive directions of the reference axes so that the axial system is right-handed and the interaxial angles  $\alpha = y \wedge z$ ,  $\beta = z \wedge x$ ,  $\gamma = x \wedge y$  are all three  $\geq 90^\circ$  as exemplified in Fig 1.2.<sup>1</sup> As in the two-dimensional example considered earlier the coordinates of atomic positions are conventionally stated as fractions of the unit-cell edges.

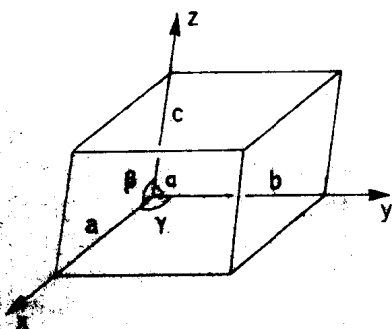
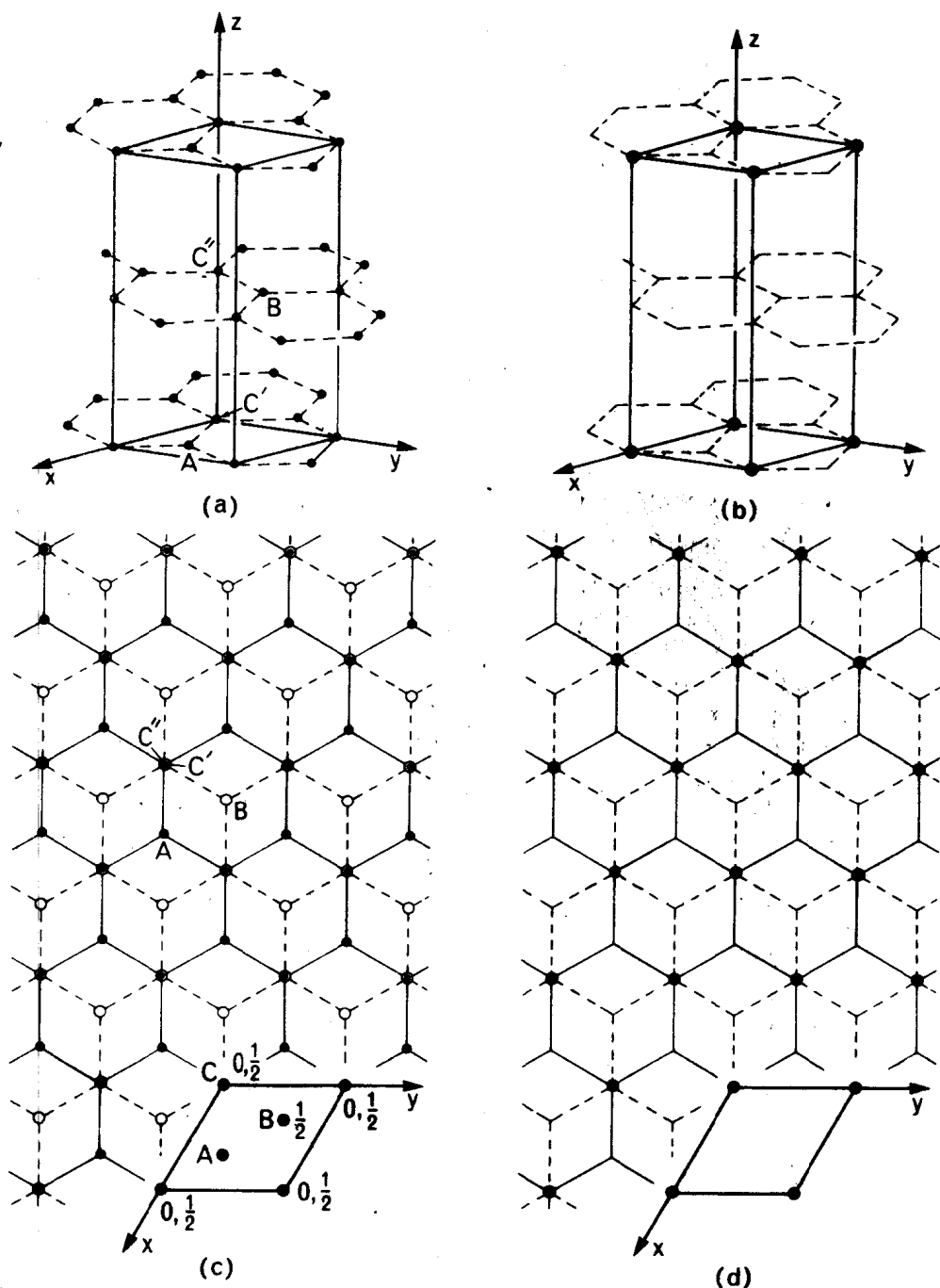


Fig 1.2 Unit-cell nomenclature. The reference axes  $x, y, z$  are right-handed, the length of the unit-cell edge parallel to each reference axis is respectively  $a, b, c$ , and the interaxial angles are denoted  $\alpha, \beta, \gamma$ .

It is difficult to make easily intelligible perspective drawings of three-dimensional structures unless they are very simple and the task is virtually impossible for really complicated structures. It has consequently become common practice to use structural plans where the three-dimensional structure is projected down one of the reference

<sup>1</sup> Only very occasionally is it convenient to modify this simple convention.



**Fig 1.3** The structure of graphite. (a) and (b) are perspective drawings to show how identical two-dimensional layers are stacked to make the three-dimensional structure; in (a) the positions of carbon atoms are shown as small solid circles and  $C_6$  rings are outlined; in (b) the  $C_6$  rings are again outlined and lattice points are shown as large solid circles; in both (a) and (b) the unit-cell is outlined. The coordinates of the carbon atoms in the graphite unit-cell, are  $0, 0, 0$ ;  $0, 0, \frac{1}{2}$ ;  $\frac{1}{3}, \frac{1}{3}, 0$ ;  $\frac{1}{3}, \frac{1}{3}, \frac{1}{2}$ . (c) and (d) are projections down the z-axis on to the xy plane; in (c) the carbon atoms with  $z = 0$  are shown as small solid circles and the  $C_6$  rings of this layer are outlined with solid lines while the carbon atoms of the superimposed layer at  $z = \frac{1}{2}$  are shown as open circles and their linkage into  $C_6$  rings is indicated by broken lines; in (d) the  $C_6$  rings of the  $z = 0$  and  $z = \frac{1}{2}$  layers are similarly represented and lattice points are shown as large solid circles; in the lower right-hand corners of both (c) and (d) the unit-cell is shown in projection.

axes on to the plane containing the other two axes, which may or may not be perpendicular to the axis of projection. Atomic coordinates in the direction of the axis of projection are marked on the plan beside the symbol representing the atomic position. In Fig 1.3(a) and (c) a perspective drawing and a plan of the three-dimensional graphite structure are shown. The atom labelled A lies in the  $x, y$  plane and at distances  $mc$ , where  $m$  is a positive or negative integer, above or below the plane. When the coordinate parallel to the axis of projection of an atom, such as A, is zero it is customary to omit the coordinate from the plan of the structure; an atom with no coordinate written beside it is to be taken as lying in the plane of projection. The atom labelled B lies at  $\frac{1}{2}c$  above the plane of projection and this is indicated by writing  $\frac{1}{2}$  next to the symbol for the atom on the plan. At C, and related positions, two atoms, C' and C'', are superimposed in projection, one with  $z = 0$  and the other with  $z = \frac{1}{2}$ ; in such a case it is customary to write both coordinates beside the symbol for the atom as  $0, \frac{1}{2}$ .

## Lattices

Some crystal properties of interest and importance are dependent only on the shape of the unit-cell, that is to say they depend only on the way in which repeat units are related to one another. It is consequently useful to have a simple way of describing the periodicity of a crystal structure and for this purpose the concept of the *lattice* is introduced. The way in which the crystal structure is built up by repetition of the repeat unit can be completely, and very simply, described by replacing each repeat unit by a *lattice point* placed at an exactly equivalent point in each and every repeat unit. All such lattice points have the same environment in the same orientation and are indistinguishable from one another. We return to two dimensions to exemplify this matter in the first instance and again take as our example a layer of the graphite structure (Fig 1.4). Figure 1.4a shows a layer of the graphite structure with carbon atoms labelled A, B, C, . . . , a, b, c, . . . and a conventional unit-mesh outlined. The lattice of this structure can be constructed by placing a lattice point at the carbon atom A and at all equivalent points, that is at B, C, D, E, F, G, H, I, etc. The resultant two-dimensional lattice is shown in Fig 1.4(b). If a lattice point is placed at A, then it is not permissible to place a lattice point at a because, although A and a both represent carbon atoms they are not identically situated; both lie at the centroid of a triangle formed by their three nearest neighbours, but the triangles about A and a are disposed at  $60^\circ$  to each other so that although both atoms have identical environments, their environments are not similarly oriented. Either the carbon atoms at A, B, C, . . . or the atoms at a, b, c, . . . , but not both sets of atoms, may be taken as lattice points.

Figure 1.4(c) represents a layer of the structure of boron nitride, BN, boron atoms being represented by solid circles and nitrogen atoms by open circles. The two-dimensional lattices of graphite and BN are evidently identical except for the small difference in their unit-mesh dimensions: for graphite  $a = b = 2.46 \text{ \AA}$ , while for BN  $a = b = 2.51 \text{ \AA}$ . The repeat unit in graphite however consists of two carbon atoms, while in boron nitride it consists of one boron and one nitrogen atom.

In a lattice every repeat unit of the structure is represented by a lattice point. A graphite layer, for instance, can be built up by placing the repeat unit of two carbon atoms in the same orientation at each lattice point in such a manner that the corresponding point of every repeat unit is placed at a lattice point. It is of no consequence which point of the repeat unit is sited at the lattice point so long as it is

the same point for every repeat unit. The lattice thus has, in two dimensions, the same unit-mesh as the structure to which it refers and is completely specified by a statement of the repeat lengths  $a$  and  $b$  parallel to its  $x$  and  $y$  axes and its interaxial angle  $\gamma$ .

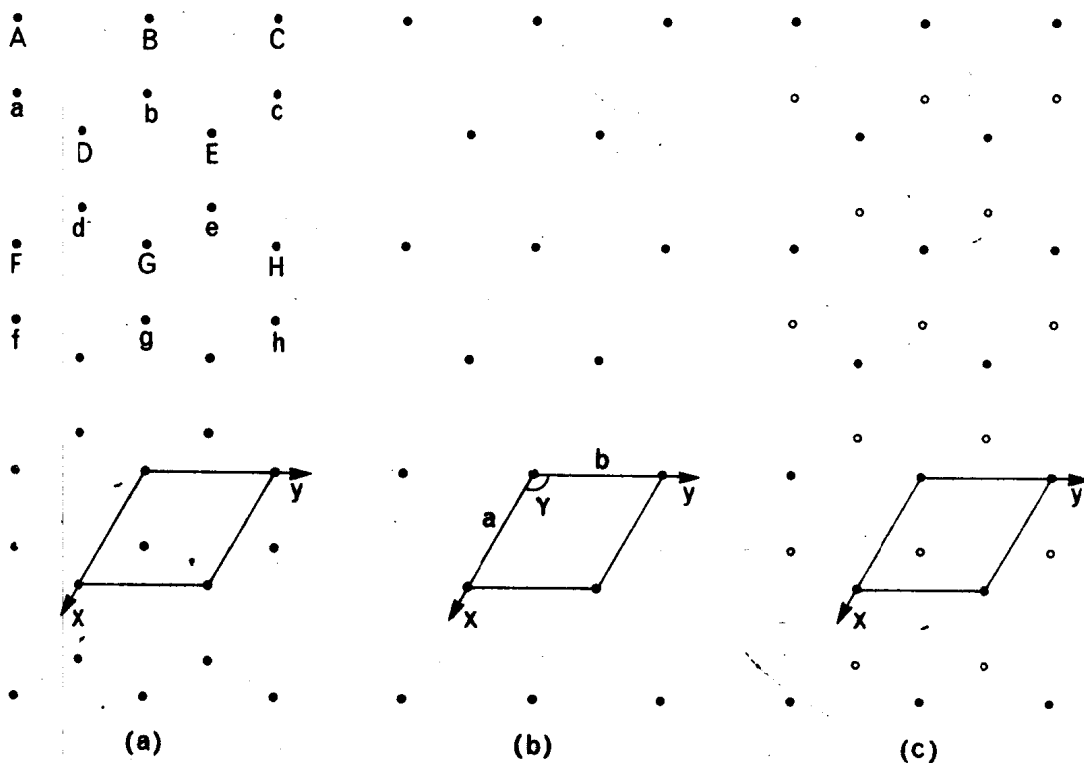


Fig 1.4 The two-dimensional lattice of a graphite layer. (a) shows the arrangement of carbon atoms (solid circles) in one layer of the graphite structure (Figs 1.1, 1.3); identically situated carbon atoms are labelled A, B, C, D, ...; the carbon atoms labelled a, b, c, d, ... have a differently oriented environment but are each identically situated; the unit-mesh is outlined and it is apparent that the repeat unit consists of two carbon atoms, such as A and a. (b) shows the corresponding two-dimensional lattice with the dimensions  $a = b$ ,  $\gamma$  of the unit-mesh indicated. (c) shows the structure of a layer of boron nitride, BN, which has the same lattice with  $\gamma = 120^\circ$  and  $a = b$ , but  $a$  is slightly different from  $a$  for graphite, the difference being too small to show on the diagram; boron and nitrogen atoms are represented respectively as solid and open circles.

A three-dimensional lattice can be derived in an exactly analogous manner. For instance, the three-dimensional structure of graphite has a repeat unit containing four carbon atoms (Fig 1.3(a) and (c)). The lattice of this structure may be simply obtained by placing lattice points at the site of the carbon atom C' (Figs 1.3(a) and (c)) and at all equivalent points. Inspection of the figure shows that the atom B cannot be related to the atom C' by a lattice translation; both atoms have identical environments in their own layer, but their environments in adjacent layers are different. The unit-cell of the graphite lattice has dimensions  $a = b = 2.46 \text{ \AA}$ ,  $c = 6.80 \text{ \AA}$ ,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ . The lattice of the graphite structure is shown in perspective and in plan in Figs 1.3(b) and (d) respectively.

Having exemplified a crystal lattice, we are now ready to make a formal definition of a lattice as an array of points in space such that each lattice point has exactly the

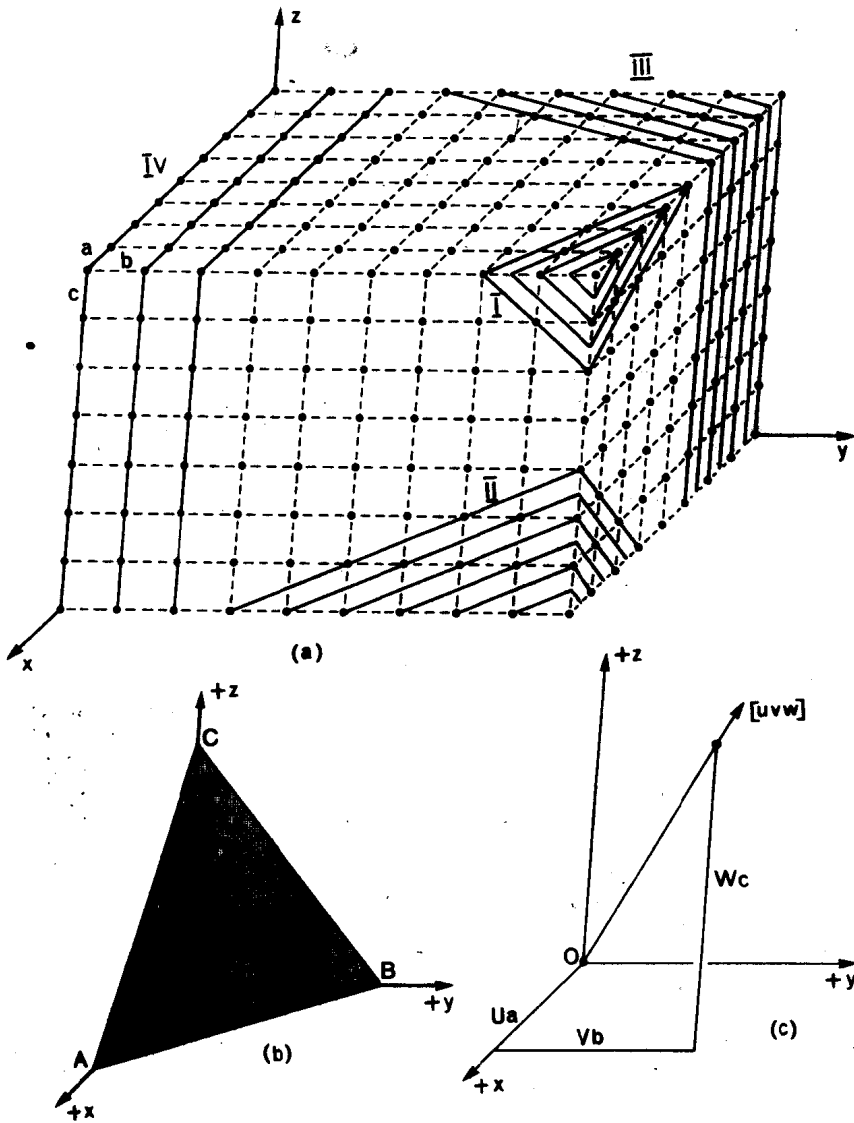
same environment in the same orientation. It follows immediately that any lattice point is related to any other by a simple lattice translation.

A plane passing through three non-colinear lattice points is known as a *lattice plane*. Since all lattice points are equivalent there will be equivalent parallel planes passing through all the other points of the lattice. Such a set of planes is known as a *set of lattice planes*; several sets are illustrated in Fig 1.5. A set of lattice planes divides each edge of the unit-cell into an integral number of equal parts; this property forms the basis of the very useful system of indexing of lattice planes developed by W. H. Miller, Professor of Mineralogy in the University of Cambridge from 1832 to 1880. If the lattice repeats along the  $x, y, z$  axes are respectively  $a, b, c$  and if the first plane out from the origin (at a lattice point) of a set of lattice planes makes intercepts  $a/h, b/k, c/l$ , where  $h, k, l$  are integers, on the  $x, y, z$  axes respectively, then the *Miller indices* of this set of lattice planes are  $(hkl)$ , the three factors  $h, k, l$  being conventionally enclosed in round brackets. A set of lattice planes  $(hkl)$  thus divides  $a$  into  $|h|$  parts,  $b$  into  $|k|$  parts, and  $c$  into  $|l|$  parts. The set of lattice planes labelled I in Fig 1.5 has Miller indices (122).

The equations to a set of lattice planes can be written in intercept form as  $(hx/a) + (ky/b) + (lz/c) = n$ , where  $n$  is an integer. If  $n$  is zero the lattice plane passes through the origin; if  $n = 1$  the plane of the set makes intercepts  $a/h, b/k, c/l$  on the  $x, y, z$  axes respectively; if  $n = 2$  the intercepts are  $2a/h, 2b/k, 2c/l$ ; and if  $n = -1$  the intercepts are  $-a/h, -b/k, -c/l$ . Thus the set of lattice planes  $(hkl)$  includes the plane with indices  $(\bar{h}\bar{k}\bar{l})$ , which makes intercepts  $-a/h, -b/k, -c/l$  on the reference axes and is commonly spoken of as the ' $\bar{h}, \bar{k}, \bar{l}$ ' plane.

Of course some sets of lattice planes will make intercepts that are not all positive or all negative: for instance the first plane out from the origin (taken as the front lower right-hand corner) of the set labelled II in Fig 1.5 makes intercepts  $-a/2, -b, c/2$  on the  $x, y, z$  axes respectively so that the indices of this set are  $(\bar{2}\bar{1}2)$ . If a plane is parallel to one of the reference axes, its intercept on that axis is at infinity and the corresponding Miller index is zero; thus set III in Fig 1.5 being parallel to the  $z$ -axis has  $c/l$  infinite so that  $l$  must be zero and the Miller indices of the set are  $(\bar{2}10)$ . The set of planes labelled IV in Fig 1.5 is parallel to the  $x$  and  $z$  axes so that  $h = l = 0$ ; since the intercept of the first plane out from the origin on the  $y$ -axis is  $b$ , the indices of the set are  $(010)$ . In terms of Miller indices the unit-cell can be described as the parallelepiped bounded by adjacent lattice planes of the sets  $(100), (010), (001)$ .

The line of intersection of any two non-parallel lattice planes is the row of lattice points common to both planes. The intersections of two sets of lattice planes will thus be a set of parallel rows of lattice points; for instance sets III and IV in Fig 1.5 intersect in lines parallel to the  $z$ -axis. It is convenient to index such rows by reference to the parallel row through the origin, which is itself the intersection of the lattice planes through the origin belonging to each of the two sets. The coordinates of the lattice points in such a row are  $0, 0, 0$  for the lattice point at the origin;  $Ua, Vb, Wc$ , where  $U, V, W$  are integers with no common factor other than unity, for the next lattice point out from the origin; and  $nUa, nVb, nWc$ , where  $n$  is an integer, for the other lattice points of the row. Such a row of lattice points is completely specified by the three integers  $U, V, W$ , which are conventionally enclosed in square brackets as  $[UVW]$  in order to distinguish them from Miller indices for lattice planes, conventionally enclosed in round brackets as  $(hkl)$ . The symbol  $[UVW]$  represents not only the lattice point row passing through the origin and through the lattice point with coordinates  $Ua, Vb, Wc$  but all parallel lattice point rows; the



**Fig 1.5** Lattice planes and zone axes. The array of lattice points exposed on the three visible faces of a parallelepiped whose edges are parallel to those of the unit-cell is displayed in (a) with solid circles to represent lattice points and thin broken lines parallel to axial directions. Four sets of lattice planes are indicated by thick solid lines representing the intersection of lattice planes with the visible faces of the parallelepiped; their Miller indices are I (122), II (212), III (210), IV (010). In (b) the definition of Miller indices is illustrated: the shaded plane ( $hkl$ ) makes intercepts  $a/h$ ,  $b/k$ ,  $c/l$  on the  $x$ ,  $y$ ,  $z$  axes,  $a$ ,  $b$ ,  $c$  being the lattice repeat along each axis and  $h$ ,  $k$ ,  $l$  being integers. In (c) the definition of the zone axis symbol is illustrated:  $[UVW]$  is the direction parallel to the line through the origin and the point  $Ua$ ,  $Vb$ ,  $Wc$ .

lattice direction  $[UVW]$  is thus parallel to the lattice vector  $U\mathbf{a} + V\mathbf{b} + W\mathbf{c}$ , where  $U, V, W$  are integers and  $\mathbf{a}, \mathbf{b}, \mathbf{c}$  are the base vectors of the lattice.

It is necessary for us to explore further the geometry and notation of lattice planes and rows because a thorough understanding of these matters is essential not only for the description of the external shape of single crystals but also, and more importantly, for the interpretation of the diffraction of X-radiation by crystals (chapter 6). In both these fields it is only the angular disposition of lattice planes and rows with respect to the reference axes of the unit-cell that is significant; the actual position in space of a given plane or row is of no consequence. For this reason the Miller indices  $(hkl)$  may be taken to represent a set of parallel lattice planes and the lattice vector  $[UVW]$  to represent a set of parallel lattice point rows (the alternative description of  $[UVW]$  as the zone axis symbol must await the definition of the term 'zone' on p. 13). The symbol  $(hkl)$  thus denotes any plane of the set of lattice planes which satisfy the equation  $(hx/a) + (ky/b) + (lz/c) = n$ , where  $n$  is integral, with one qualification which enables a distinction to be made between planes of the set which lie on opposite sides of the origin. If it is desired to make this distinction, as is often the case, the symbol  $(hkl)$  is reserved for those planes of the set which make intercepts on the same side of the origin as the plane whose intercepts on the  $x, y, z$  axes are respectively  $a/h, b/k, c/l$  and the symbol  $(\bar{h}\bar{k}\bar{l})$  is used to denote those planes of the set which make intercepts on the same side of the origin as the plane whose intercepts on the  $x, y, z$  axes are respectively  $-a/h, -b/k, -c/l$ . The plane  $(\bar{h}\bar{k}\bar{l})$  is said to be the *opposite* of  $(hkl)$ , the superscript 'bar' representing, as is usual in crystallography, a minus sign. In a precisely analogous way the zone axis symbol  $[UVW]$  represents all directions parallel to the vector from the origin to the lattice point with coordinates  $Ua, Vb, Wc$ , with the proviso that opposite directions may be distinguished as  $[UVW]$  and  $[\bar{U}\bar{V}\bar{W}]$ ;  $[UVW]$  is taken to be in the same sense as the vector from the origin to  $Ua, Vb, Wc$  and  $[\bar{U}\bar{V}\bar{W}]$  in the same sense as the vector from the origin to the lattice point at  $-Ua, -Vb, -Wc$ . In general, of course, the indices in the symbols  $(hkl)$  or  $[UVW]$  need not all be of the same sign.

The condition for the lattice vector  $[UVW]$  to be parallel to a plane  $(hkl)$  can be derived by reference to Fig. 1.5(b). Any vector  $\mathbf{r}$  parallel to the set of planes  $(hkl)$  will be given by

$$\mathbf{r} = \lambda \mathbf{AB} + \mu \mathbf{AC},$$

where  $\lambda$  and  $\mu$  are scalars

Since  $\mathbf{AB} = -\frac{1}{h}\mathbf{a} + \frac{1}{k}\mathbf{b}$

and  $\mathbf{AC} = -\frac{1}{h}\mathbf{a} + \frac{1}{l}\mathbf{c},$

$$\mathbf{r} = -\frac{1}{h}(\lambda + \mu)\mathbf{a} + \frac{\lambda}{k}\mathbf{b} + \frac{\mu}{l}\mathbf{c}.$$

So, for the lattice vector  $[UVW]$  to be parallel to the set of planes  $(hkl)$

$$U\mathbf{a} + V\mathbf{b} + W\mathbf{c} = -\frac{1}{h}(\lambda + \mu)\mathbf{a} + \frac{\lambda}{k}\mathbf{b} + \frac{\mu}{l}\mathbf{c},$$

i.e.  $hU = -(\lambda + \mu), \quad kV = \lambda, \quad \text{and} \quad lW = \mu,$

whence  $hU + kV + lW = 0.$



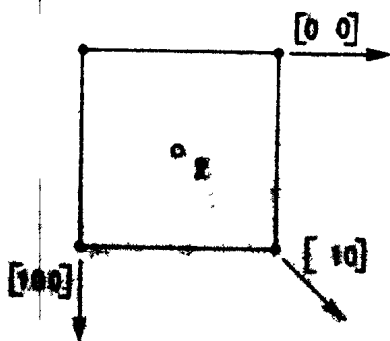


Fig. 6. The structure of CsCl shown in plan are the direct and are the reciprocal lattice vectors. The open circles are the Cs atoms and the solid circles are the Cl atoms.

This equation  $hU + kV + lW = 0$  is known as the zone equation for reasons which will be discussed in the next section; it is simply a statement of the condition that the planes  $(hkl)$  are parallel to the lattice vector  $[UVW]$ .

### The external shape of crystals

The regular nature of the spatial arrangement of the atoms within a crystal, whether simple or complicated, leads directly to the consequence that different directions in the crystal may not be equivalent. We take a very simple example, the structure of calcium chloride, illustrated in Fig. 1. The unit cell of calcium chloride is a cube and the axes  $a, b, c$  are equal,  $a = b = c$ . The calcium atoms are situated at the corners of the cube, and the chlorine atoms are at the centers of the edges. The direction parallel to the  $a$ -axis,  $[100]$ , is evidently equivalent to the direction parallel to the  $b$ -axis,  $[010]$ , and neither of these in any way corresponds to the direction parallel to the  $c$ -axis,  $[001]$ . The apparent reason why any directional property of a crystal is different in these three directions is that the density of the lattice points is different in these three directions.

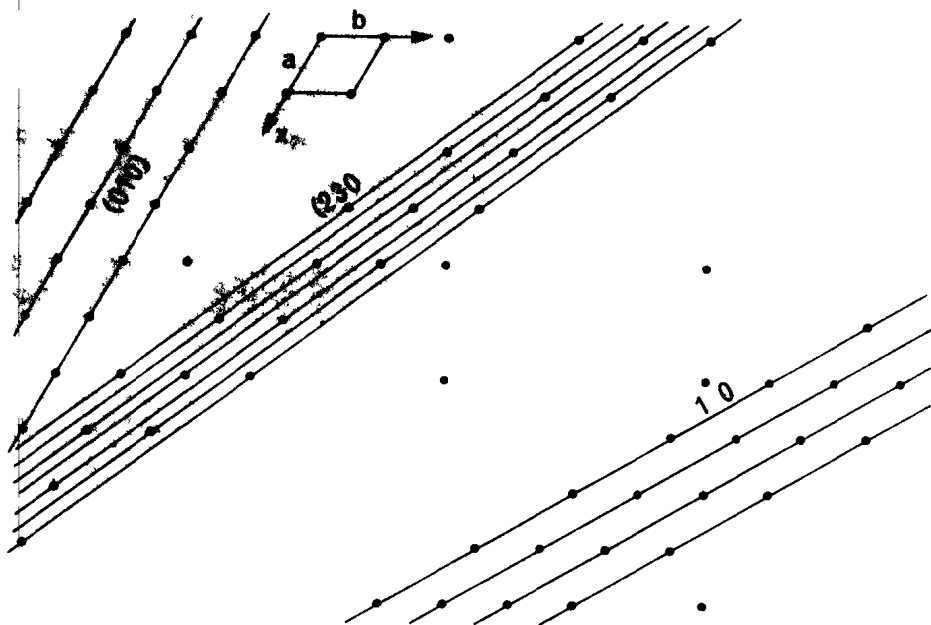


Fig. 1. Projection of the decrease in the density of the lattice points in the  $(230)$  plane.

The density of the lattice points in the  $(230)$  plane is different from the density of the lattice points in the  $(100)$  plane. The density of the lattice points in the  $(230)$  plane is higher than the density of the lattice points in the  $(100)$  plane.