Disordered Materials

Paolo M. Ossi

Disordered Materials

An Introduction

Second Edition
With 200 Figures

Springer

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Library of Congress Control Number: 2006927569

ISBN-10 3-540-29609-3 Springer Berlin Heidelberg New York
ISBN-13 978-3-540-29609-6 Springer Berlin Heidelberg New York
ISBN 3-540-41328-6 1st ed. Springer-Verlag Berlin Heidelberg New York

Springer is a part of Springer Science+Business Media
springer.com

Printed in Germany

Typesetting: Data prepared by the author using a Springer TEX macro package
Cover design: *design & production* GmbH, Heidelberg
Production and Final processing: LE-TEX Jelonek, Schmidt & Vöckler GbR, Leipzig, Germany

Printed on acid-free paper 57/3100/YL 5 4 3 2 1 0

Teach your tongue to say
"I don't know"
for fear
of inventing things
and then being ensnared.

Berachot, 4a

Preface

The teaching of solid state physics essentially concerns focusing on crystals and their properties. We study crystals and their properties because of the simple and elegant results obtained from the analysis of a spatially periodic system; this is why the analysis can be made considering a small set of atoms that represent the whole system of many particles.

In contrast to the formal neat approach to crystals, the study of structurally disordered condensed systems is somewhat complicated and often leads to relatively imprecise results, not to mention the experimental and computational effort involved. As such, almost all university textbooks, including the advanced course books, only briefly touch on the physics of amorphous systems.

In any case, both the fundamental aspect and the ever wider industrial applications have given structurally disordered matter a role that should not be overlooked. The study of amorphous solids and their structure, stability and properties is a vibrant research branch; it is difficult to imagine how any physicist, chemist or engineer who has to deal with materials could possibly ignore this class of systems.

The author of Disordered Matter – an Introduction uses this course book at the Politecnico in Milan, Italy. Collecting the material for the course proved no mean task, leading him to have to prepare ad hoc didactic material. The continual exchange between teacher and student has led to the present version of the book.

The positive reactions to the first edition of the text have prompted me to prepare this second edition, trying to introduce improvements and corrections where necessary, as well as to include recent relevant experimental and theoretical results.

The goal in preparing this book was to supply a selected range of topics in a way that would allow the reader to understand the various aspects of a highly complicated and many facetted problem, such as the investigation and modelling of the structure of a structurally disordered condensed system.

To this aim Chapter 1 of the book briefly examines the geometry and the symmetries of the platonic solids, taken as constructive elements that can be used to represent atomic structures, even highly complicated ones, by matching them together in various ways.

In Chapter 2 cellular and topological disorders are defined and the entropy approach to describing these kinds of disorder is introduced.

Chapter 3 is devoted to the glass transition, with an emphasis on its kinetic and thermodynamic features, an examination of the material parameters that drive the glass forming ability and an overlook to the current theoretical approaches to the glass transition, including the historical free volume theory and the fundamental mode coupling theory.

Chapter 4 contains an in-depth look at the characteristics and limits of the main experimental techniques used in structural investigations; the various modelling strategies are then examined. Much effort is placed on the ability to geometrically represent the elementary units that, when bonded together, give rise to a structure with local order that is partially similar to the order obtained from experiments on real disordered systems. It is little wonder that an amorphous solid and its corresponding crystal should have a number of structural elements in common. As such we try to study the structure of disordered systems using the very same elements that define the ordered system. An introduction to the collective excitations in liquids and disordered solids is centred on the derivation, the experimental determination and the physical meaning of the dynamic structure factor. Although not simple, this topic helps the reader to understand many features of the mode coupling theory.

Attention is then placed on how the structure of a system evolves with changing its dimensions. Chapter 5 examines how the transition from an atom-molecule to a solid occurs; atomic clusters allow for exploring the role of the surface in the stability of a system and clearly indicate that the structure of small assemblies of atoms is non-crystalline. The analysis of noble-gas clusters offers direct evidence of the problems arising when we realise an extended packing of elementary structural building blocks with icosahedral symmetry. These blocks are made up of only a few atoms and are also locally the most stable. However, it is impossible to endlessly juxtapose them without introducing defects into the structure, which would be destabilised. On the other hand, the evolution of alkali-metal clusters provides a good example of the role of electrons in stabilising the structure of the system. The family of Carbon clusters with a closed-cage structure, Fullerene C_{60} being the prototype, is then described. An introduction to the cluster-assembled nanocrystalline and nanoglassy materials that have recently been synthesised, and that are at the heart of much research activity, is a logical development to cluster physics and is a further relevant step along the path from the atom to the solid.

The quasicrystals are dealt with in Chapter 6: they are a paradigm of extended orientational order but do not have the translational order that is the distinctive feature of usual periodic crystals. The study of these systems, which constitute an intermediate phase between the crystalline phase and topologically disordered matter, leads to a new definition of the concept of the crystal itself. Besides the basic questions about what governs the occurrence and stability of quasicrystals, the features of the amorphous to quasicrystal transformation as well as the reverse one are discussed. Finally, the conditions leading to nano-quasicrystalline phases of technological interest are examined.

Although all topics are treated self consistently, this book is directed at a reader with a reasonable undergraduate background in the physics of crystals. Each chapter is fully supported with a set of figures and completed with references, both general and specialised. Given the plan of the text it is addressed to third, fourth and fifth-year students majoring in physics, materials sciences, chemistry, as well as materials, chemical and electronic engineering. Since the book is the outcome of research work, including very recent research results, it can be used as a reference book for researchers working in the field of structurally disordered condensed systems.

I would like to express my gratitude to several colleagues who helped me with their constructive comments and valuable suggestions at various stages of the preparation of the manuscript. I am indebted to my students, who listened to the lectures, made useful comments and pointed out many mistakes; all remaining errors are my responsibility alone. G. Benedek was the first person to suggest I should prepare an English version of the book. T. Dass made a painstaking translation and provided many suggestions to make reading the book easier. I am grateful to M. Verona for the careful preparation of the figures and to A. Lahee, my editor at Springer, as well as C. Rau, production editor at LE-TEX, for their patience and assistance. Finally I wish to thank the publishers of the journals carrying the papers I refer to throughout the book.

Milano *Paolo M. Ossi*
April, 2006

Contents

1. Platonic Solids: Geometry and Symmetry

It does seem somewhat difficult and artificial to talk about condensed matter with irregular structure without first making some reference to its "non pathological" counterpart, those crystals that made up the entire world of solid state physics up to a few years ago.

When we consider the amorphous metals and the amorphous solidified noble gases we see that both the position of the interstices after high density packing of hard sphere atoms and the structure resulting from the disposition of partially deformable spheres, relaxed in a suitable potential, consist mostly of tetrahedra and octahedra, all distorted to some extent or another. Tetrahedra and octahedra are the very same structural units we find in closely packed crystals. Moreover, the way such simple structural units, with a well defined geometrical shape and composition, are packed lies at the heart of those structural models that have been developed both for covalent glasses and for metals whose stoichiometry depends also on chemical factors and not just on geometric constraints.

As such we shall examine the geometrical and symmetrical properties of certain highly regular solids in order to help us model amorphous solids (see Chap. 4).

A brief introduction will be given to hypersolids in more than three dimensions space and to the techniques to project them onto the usual three-dimensional space. This is particularly relevant in order to study the quasicrystals (see Chap. 5).

Lastly the essential concepts of "classic" crystallography will be recalled; these can be traced back to the recognised crystal perfection and symmetry and supply a simple framework to describe their properties. Indeed, to study disordered solids special reference will be made initially to their corresponding crystals.

1.1 The Platonic Solids and Their Duals

The five platonic solids, tetrahedron, cube, octahedron, dodecahedron and icosahedron, are perfect examples of highly regular and symmetrical structures. Each has the same kind of regular convex polygon faces, whether they

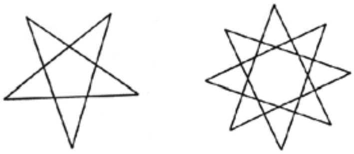

Fig. 1.1. Stellated polygons according to Kepler

be triangle, square or pentagon, and the vertices are all alike. The term polygon means a closed flat region bounded by n straight lines simply connected together. The polygon can be contracted as much as you like and a closed line originally drawn within it will contact accordingly and still within the polygon.

The vertices of a regular polygon, that is equilateral and equiangular, are equally distanced from the centre. As such it is easy to draw a circle around the polygon. The sides are also the same distance from the centre, which means a circle can be drawn inside the polygon that touches each side. A regular polygon $\{n\}$ has n sides and angles.

Apart from studying the regular or primary polygons whose sides do not intersect Kepler was the first to study in a systematic way stellated polygons whose sides are obtained by extending non-adjacent sides of a primary polygon until they intersect, provided that the perimeter is a single line (Fig. 1.1).

A convex polyhedron is said to be regular if its faces are all regular, i.e. the polygons that make up the polyhedron and its solid angles are all regular. For simplicity we shall refer to the term vertex figure rather than solid angle. So, let's consider a vertex V of a polygon: the vertex figure connected to it is the segment enclosed by the centres of the sides that meet at vertex V. For polygon $\{n\}$ whose sides are long L, the length of the vertex figure is given by

$$L_V = L \cos \frac{\pi}{n} \,. \tag{1.1}$$

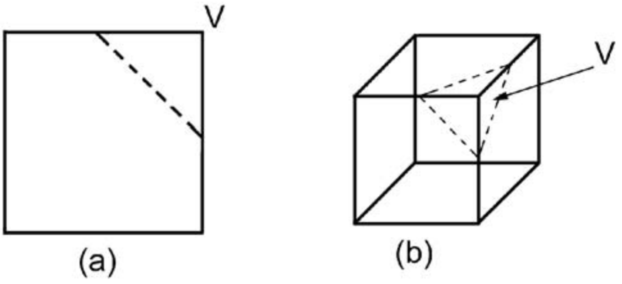

Fig. 1.2. Vertex figure relative to vertex V of a square (**a**) and (dashed-line triangle) at vertex V of a cube (**b**)

Figure 1.2 shows (part a) the vertex figure of a vertex V in a square. The vertex figure of vertex V in a polyhedron is a polygon whose sides are the vertex figures of the faces for V. Figure 1.2 shows (part b) the vertex figure (triangle) of a vertex V of a cube.

The sum of the external angles that make up a polygon is given by 2π, thus each external angle of $\{n\}$ is $2\pi/n$, whereas the corresponding supplementary internal angle is given by $\pi\,(1-2/n)$. Furthermore, the sum of the internal angles is given by $(2n-4)\pi/2$. In a regular convex polyhedron the solid angle of any vertex has r face angles, each of which is $\pi\,(1-2/n)$. The sum of these angles must be less than 2π otherwise we would get re-entrant vertices and not all the vertices would be equal; thus the following would stand:

$$\left(1-\frac{2}{n}\right) < \left(\frac{2}{r}\right) \text{ or } \frac{1}{n}+\frac{1}{r} > \frac{1}{2}, \text{ thus } (n-2)(r-2) < 4\,. \tag{1.2}$$

A platonic solid whose vertex is surrounded by r faces, each face having $\{n\}$ sides, is called a regular polyhedron and is given as $\{n, r\}$.

From (1.2) we can deduce that the only platonic solids are those reported in Table 1.1.

$\{n, r\}$	Faces	Vertices	Edges	Touching faces at each vertex	Name
$\{3, 3\}$	4	4	6	3	Tetrahedron
$\{3, 4\}$	8	6	12	4	Octahedron
$\{4, 3\}$	6	8	12	3	Cube
$\{3, 5\}$	20	12	30	5	Icosahedron
$\{5, 3\}$	12	20	30	3	Dodecahedron

Table 1.1. Features of the platonic solids

It is now possible to obtain the same result by construction. In fact as at least three faces have to meet at each vertex the smallest face angle is $2\pi/3$. This is the value of the angles of a regular hexagon. However, as can be seen from Fig. 1.3, three regular hexagons with a common vertex lie on the same plane and as the value of an angle of a regular polygon increases with the number of sides, the faces of a regular polyhedron can only be a triangle, a square or a pentagon. As the angles of a square are right angles there can be no more than three at any vertex since the sum of the face angles that meet at the vertex must be less than 2π; thus the cube is obtained. By the same analogy there cannot be more than three pentagons at any vertex of a regular polyhedron (dodecahedron); four or more cannot be joined together without there being some overlapping.

If equilateral triangles are joined together then the rule for the sum of the face angles at each vertex is fully met, with three equilateral triangles giving a tetrahedron, four giving a tetrahedron and five giving a icosahedron, whereas if we use six faces we get a hexagon.

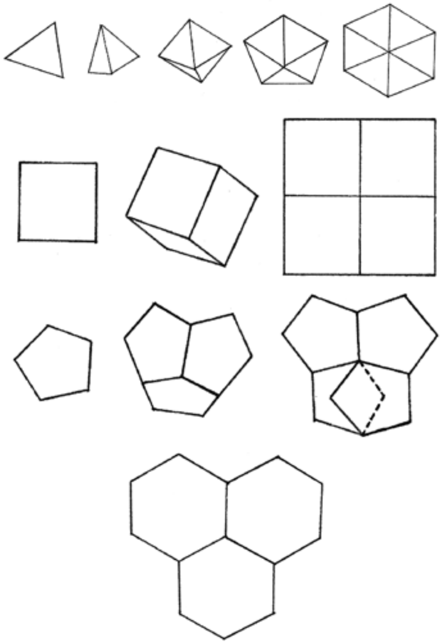

Fig. 1.3. Construction of platonic solids starting from (left side of the figure from top to bottom) an equilateral triangle, a square and a pentagon. The figure also shows how six triangles, four squares, four (overlapping) pentagons and three hexagons with the same vertex lead to a plane figure

Given that all the faces of a regular polyhedron are regular and thus all the edges are the same length L and all the vertex figures are regular, then all the faces must be the same. If, though, two adjacent faces are different, they would have the same vertex V but the vertex figure for V would have different length sides, each given as $L\cos(\pi/n)$ with different values for n. Furthermore, the dihedral angle, between two adjacent faces, must be the same since the faces that meet at a given vertex V are part of a right angled pyramid whose base is the vertex figure. Each lateral face of this pyramid is an isosceles triangle whose sides are $L/2$, $L/2$, $L\cos(\pi/n)$. The number of sides to the base is given by the value of the dihedral angle. This value, r, is the same for all the vertices and the vertex figures must all be the same, too. The regular polyhedron $\{n, r\}$ has polygon faces with n sides each of length L and the vertex figure is a polygon $\{r\}$ whose sides are all: $L\cos(\pi/n)$.

One should note that a perpendicular line passing through the centre of a face will meet the perpendicular line passing through the centre of a vertex figure at a point O, which is the centre of the circumsphere (touching all the vertices) and of the midsphere, touching all the edges, as well as being the centre of the insphere which touches all the faces.

The platonic solids are nothing but simply connected polyhedra and show the property (just like simply connected polygons) that any simple closed curve drawn onto the surface of a polyhedron can be shrunk until it is a dot, still remaining on the surface of the polyhedron. Alternatively we can see that any region bounded by edges of the polyhedron is made up of one or more faces of the solid.

For those polyhedra that are simply connected, Eulero's formula stands. This formula defines the number of faces N_f, vertices N_v and edges N_e as

$$N_\mathrm{f} + N_\mathrm{v} = N_\mathrm{e} + 2\,. \tag{1.3}$$

Equation (1.3) is an important result from Eulero's research on polyhedra and was mentioned in his letter to his friend Goldbach dated November 1750. The formula expresses how the number of different elements that make up the surface of a polyhedron are related to each other. The really new aspect is the distinction between the edges (lines on the surface of the polyhedron) and the sides (lines that define the perimeter on its faces). Given that each edge has two sides, the number N_s of sides is given by

$$N_\mathrm{e} = \frac{1}{2} N_\mathrm{s} \tag{1.4}$$

where N_s is even. Furthermore, as each face of the polyhedron has at least three sides,

$$2N_\mathrm{e} \geq 3N_\mathrm{f} \tag{1.5}$$

and as at least 3 faces are required to define a solid angle, then

$$2N_\mathrm{e} \geq 3N_\mathrm{v}\,. \tag{1.6}$$

As such (1.3) is fully met both by the platonic solids (see Table 1.1) and by the pyramids and prisms. If the base of a pyramid has n sides then there are $(n+1)$ faces, the same number of solid angles and $2n$ edges. At the same time a prism with n sides to the base will have $(n+2)$ faces, $2n$ solid angles and $3n$ edges.

Using formulas (1.3), (1.5) and (1.6) we get new conditions for N_f and N_v as given by

$$2N_\mathrm{v} + 2N_\mathrm{f} = 2N_\mathrm{e} + 4 \geq 3N_\mathrm{v} + 4$$

and get

$$2N_\mathrm{f} - 4 \geq N_\mathrm{v}\,. \tag{1.7}$$

If, on the other hand, we say

$$2N_\mathrm{v} + 2N_\mathrm{f} = 2N_\mathrm{e} + 4 \geq 3N_\mathrm{f} + 4$$

from which

$$2N_\mathrm{v} - 4 \geq N_\mathrm{f}$$

we can deduce that

$$N_{\mathrm{v}} \geq \frac{1}{2} N_{\mathrm{f}} + 2\,. \tag{1.8}$$

The proof of (1.3), as drawn up by Eulero, assumed that polyhedra were convex, given that at the time polyhedra and convex solids were synonyms.

Later on exceptions to the formula were found. One, for example, is a polyhedron made up of two tetrahedra meeting at one common edge or vertex. For a polyhedron to meet the requirements of Eulero's formula it must consist of a definite number of polygons where any two vertices are connected by edges and each closed curve on the surface divides the polyhedron into two parts.

The term polygon means a plane surrounded by straight segments that are topologically equivalent to a disc which, in turn, is any flat surface that is homeomorphic to a circle.

To demonstrate (1.3) we shall divide the edges of the polyhedron into two groups, each with a given colour. For simplicity let's take a cube and colour one edge red. The two vertices must thus also be red. The next edge to colour is chosen according to the rule that it must have a red vertex (there are only two options). If we continue to colour all the edges of the cube following the above rule in the end all the vertices will be coloured red and the edges, whether coloured or not, will have red vertices.

The cube will have eight red vertices and seven red edges; there will usually be one red edge $N_{\mathrm{e,r}}$ less than the number of red vertices. The number of red vertices is, though, equal to the number of vertices in the polyhedron, N_{v}. Let us now colour all the faces yellow leaving the red edges intact. You will get $N_{\mathrm{e,y}}$ yellow edges (five for the cube), one less than the number of faces (yellow) N_{f} (six in the cube). The relation between the number of edges, vertices and faces is

$$N_{\mathrm{e,r}} = N_{\mathrm{v}} - 1 \quad ; \quad N_{\mathrm{e,y}} = N_{\mathrm{f}} - 1.$$

Since the number of edges of the polyhedron is N_{e} and

$$N_{\mathrm{e}} = N_{\mathrm{e,r}} + N_{\mathrm{e,y}} = (N_{\mathrm{v}} - 1) + (N_{\mathrm{f}} - 1) = N_{\mathrm{v}} + N_{\mathrm{f}} - 2$$

then

$$N_{\mathrm{e}} + 2 = N_{\mathrm{v}} + N_{\mathrm{f}}\,.$$

In this example the polyhedron is divided into two parts, red and yellow. Both parts are topologically connected and have the same contour, the line where the two colours meet. As such each part can be deformed to give a disc. The surface obtained by joining two discs together by way of the perimeter is a sphere, so the polyhedron can be deformed uniformly to obtain a sphere. Thus, for Eulero's formula to be valid the polyhedron musty be "spherical" or otherwise defined as simple.

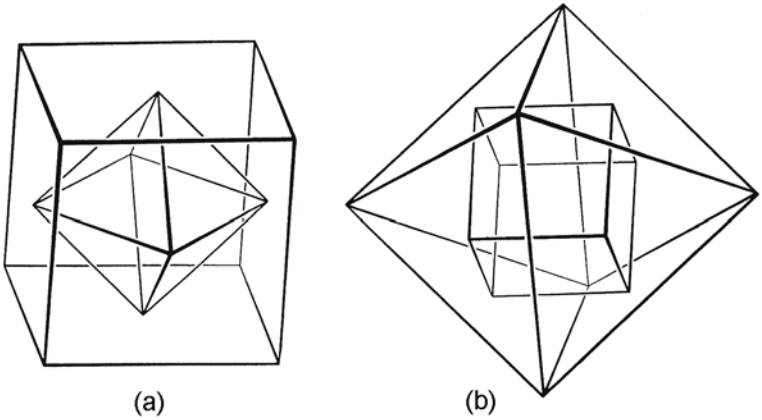

Fig. 1.4. Cube-octahedron duality

For the circumsphere of a given platonic solid, i.e. the sphere touching all the polyhedron vertices, we defined a set of non continuous rotations in space such that the vertices of the polyhedron form a set of equivalent points under the mentioned rotations and as such the polyhedron is brought into self-coincidence. The tangent planes to the circumsphere at the vertices of the polyhedron outline another regular polyhedron which, in turn, is brought into self-coincidence when the original circumsphere undergoes the same set of rotations.

This construction establishes that there is a relation between pairs of platonic solids: when applied to a octahedron, for example, it becomes a cube and vice versa the octahedron can circumscribe a cube as shown in Fig. 1.4. The two polyhedra are defined *dual* to each other. The group of rotations is called the octahedral group. There is a similar dual relation between the icosahedron and the (pentagonal) dodecahedron: the pertinent group of rotations is called the icosahedral group.

Duality has nothing to do with the fact that the platonic solids are made up of regular polygons. The principle holds because there is a relation between the number of faces and vertices for pairs of regular polyhedra. As can be seen in Table 1.1 the construction of dual solids consists in exchanging vertices and faces: where there is a face we substitute it with a vertex. The eight vertices and six faces of a cube become six vertices and eight faces of an octahedron. Likewise, the twenty vertices and the twelve faces of a dodecahedron become the twelve vertices and the twenty faces of the icosahedron. The tetrahedron, with its four vertices and four faces, is self-dual.

From the construction of dual solids we can see that the vertices of an inscribed solid coincide with the centres of the faces of its dual. If we examine pairs of dual solids whose edges are the same length we will see that in the dual construction the edge of the first solid lies perpendicular to the edge of its dual and they intersect at the centres. As such every two edges form a

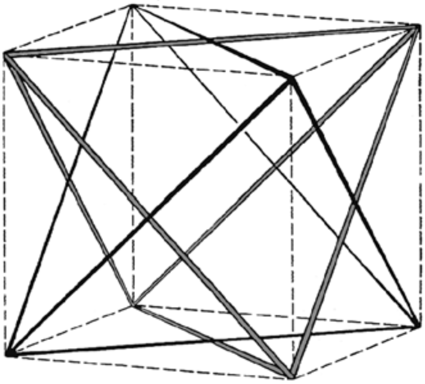

Fig. 1.5. Inscribing a tetrahedron inside a cube where the vertices of the two solids coincide. The double lines and the lines in bold show the two possible dispositions of the tetrahedron

pair of perpendicular bisectors; it is clear that one solid will have the same number of edges as its dual.

That the tetrahedron is self-dual may be related to the property, shared by all other platonic solids, that they are symmetrical to their centres; the vertices, faces and edges make up symmetrical pairs around the centre of the polyhedron. As such, for example, the straight line that connects the centre point of an edge of a cube to the cube centre intersects another edge at its centre point. However, the tetrahedron is not centrosymmetric; the straight line that connects a vertex with the centre of the polyhedron intersects the tetrahedron in the centre of a face. A tetrahedron can be inscribed into a cube in two different ways; in both cases the vertices of the two solids will coincide and the edges of the tetrahedron will make up the diagonals of faces of the cube, as shown in Fig. 1.5. This construction is possible because the tetrahedral group is a subgroup of the octahedral group. Similarly, we will see

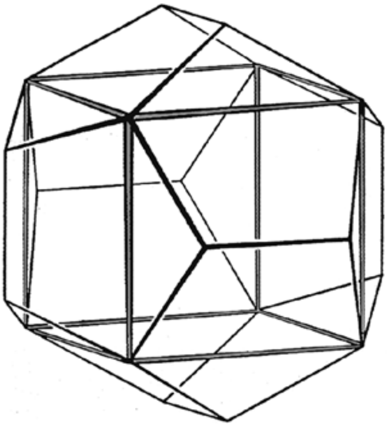

Fig. 1.6. One of the possible dispositions of a cube inscribed in a dodecahedron. Each edge of the cube lies on a face of the dodecahedron

that the octahedral group is a subgroup of the icosahedral group and as such a cube can be inscribed into a dodecahedron in the same way a tetrahedron can be inscribed into a cube. Figure 1.6 shows one of the five dispositions of a cube inscribed into a dodecahedron; each edge of the cube lies on a face of the dodecahedron, and two cubes meet at each vertex of the dodecahedron.

1.2 Elements of Symmetry in Space

The platonic solids are highly symmetrical. If we examine a cube's axes of rotational symmetry we will see (Fig. 1.7) three fourfold rotation axes, each of which intersects with the centre of two opposite faces, four threefold axes that extend from opposite vertices, and six twofold axes, each of which intersects with the centre of pairs of opposite edges. Since the octahedron is dual with the cube it has the same number of rotation axes as the cube with the three fourfold rotation axes passing through pairs of opposite vertices, the four threefold axes intersecting the centres of pairs of opposite faces, and the six twofold axes must lie as in the cube.

In the case of the dodecahedron-icosahedron dual solids (Fig. 1.8) fifteen twofold axes intersect with the centres of opposite edges, ten threefold axes intersect with the centres of opposite faces (icosahedron) and pass through pairs of opposite vertices (dodecahedron), six fivefold axes pass through pairs of opposite vertices (icosahedron) and intersect with the centres of opposite faces (dodecahedron). The tetrahedron (Fig. 1.9), on the other hand, has four threefold axes and three twofold axes. The three twofold axes intersect with the centres of pairs of opposite edges whereas each threefold axis passes through a vertex and intersects with the centre of the opposite face.

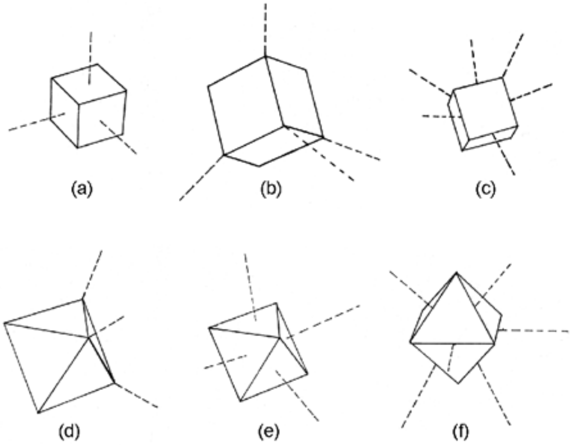

Fig. 1.7. Cube rotation axes: (**a**) fourfold; (**b**) threefold; (**c**) twofold. Octahedron rotation axes: (**d**) fourfold; (**e**) threefold; (**f**) twofold

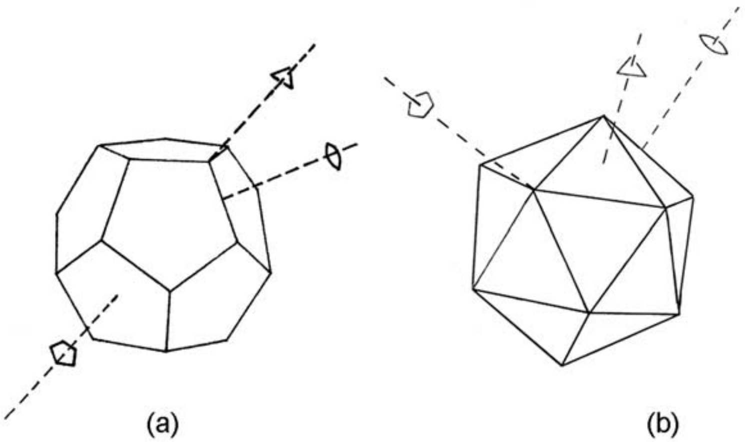

Fig. 1.8. (**a**) Twofold (15, about the centre of the opposite edges), threefold (10, about pairs of opposite vertices), fivefold (6, about centres of opposite faces) rotation axes of dodecahedron. (**b**) Analogous scheme for the icosahedron; the number of axes of each order is the same as the corresponding axes in the dodecahedron. The figure shows only one axis of each kind

Apart from rotation the platonic solids have important reflection symmetries. If we divide a cube into two with the plane intersecting the centre of two opposite faces and we imagine we have put one of the cut surfaces onto a mirror we will see a cube where one half of the cube is real and the other half is its reflection in the mirror. Whenever a plane cuts a solid into two, so that when it is put onto a mirror the reflected image gives us the original

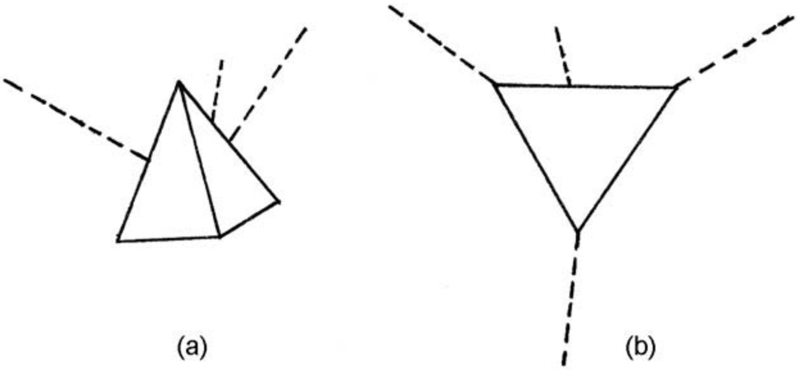

Fig. 1.9. Twofold (**a**) and threefold (**b**) rotation axes of a tetrahedron

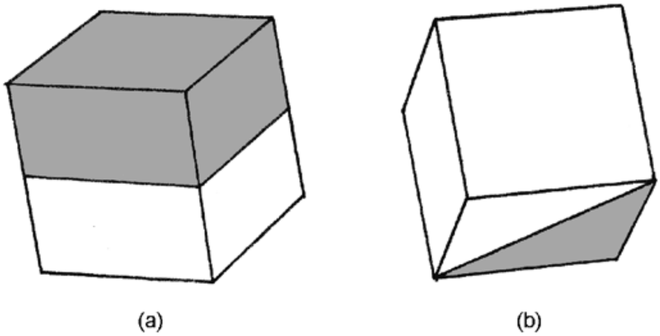

Fig. 1.10. Reflection planes lying normal to a fourfold rotation axis (**a**) and to a twofold rotation axis (**b**) of a cube

solid again, we have identified a reflection plane. All reflection planes have a common point, i.e. the centre of the platonic solid we are examining.

Since a cube has three pairs of parallel opposite faces, we have three reflection planes (Fig. 1.10) each of which lies normally to one of the three fourfold rotation axes. Furthermore, each plane, (six all together) that intersects with the diagonals of one face and its opposite face, i.e. it passes through pairs of opposite edges (Fig. 1.10) is in turn a reflection plane and lies normally to a twofold rotation axis. In the end we can count nine reflection planes.

Since the octahedron is dual with the cube it too has nine reflection planes which lie the same way as the reflection planes of the cube (Fig. 1.11).

The number of reflection planes of a tetrahedron can easily be deduced, provided we remember how the tetrahedron is inscribed into a cube. The tetrahedron has six reflection planes: each plane contains an edge and cuts

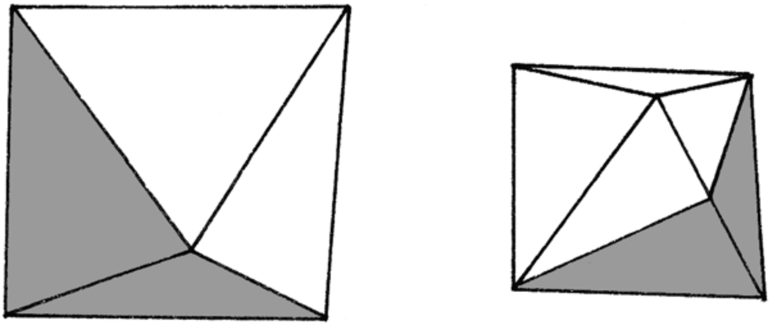

Fig. 1.11. Reflection planes of an octahedron. Notice that the disposition of the reflection planes of the cube is the same. This is due to the duality between the two solids

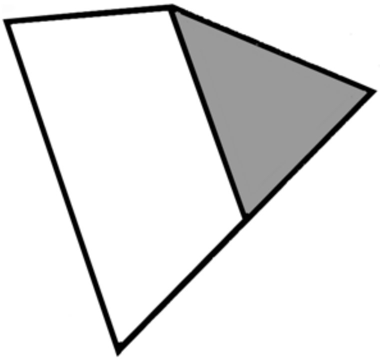

Fig. 1.12. Each reflection plane of a tetrahedron contains one edge and cuts the opposite edge in half

the opposite edge into two (Fig. 1.12). These planes coincide with the same number of reflection planes of the cube the tetrahedron is inscribed into.

It is quite easy to see the reflection planes of a dodecahedron and a icosahedron, which are dual to each other (Fig. 1.13). Each reflection plane intersects with a pair of opposite edges, cuts another two opposite edges into half and is perpendicular to one of the fifteen twofold rotation axes. There are also fifteen reflection planes.

Let us now consider a pair of dual platonic solids: the construction method used to define duality makes the vertices of one of the two solids coincide with the centres of the same number of faces of the other solid. This way all the rotation axes and the reflection planes of the two solids coincide, and thus are also symmetry elements of the compound solid.

The method used to find the reflection planes of a tetrahedron, by way of inscribing it into a cube, where the cube is not dual to the tetrahedron, consists in making all four threefold axes of the two solids coincide with each

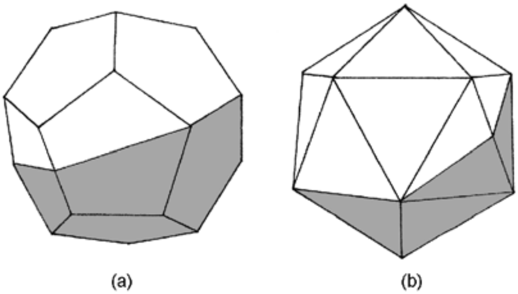

Fig. 1.13. Each reflection plane of dodecahedron (**a**) and icosahedron (**b**) passes through a pair of opposite edges, cuts another two opposite edges into half and is perpendicular to a twofold rotational axis

other and then expanding or shrinking the tetrahedron until its four vertices fall on four of the cube vertices. This method can be pursued systematically every time a platonic solid can be inscribed into a different one by identifying the symmetry elements that are common to both solids. These constitute the symmetry elements of the compound solid. Where a tetrahedron is inscribed into a octahedron, which is dual to a cube, the procedure is just the same as the above explanation.

If, though, we want to inscribe a tetrahedron into a dodecahedron using the same method to inscribe it into a cube, making the vertices of the tetrahedron coincide with the same number of vertices of the dodecahedron so that there are four common threefold axes, we will see that the three twofold axes of the tetrahedron coincide with the same number of twofold axes of the dodecahedron. However, all similarity with the tetrahedron in a cube ends here because the edges of the tetrahedron do not lie on the faces of the dodecahedron and the six reflection planes of the tetrahedron do not correspond to any reflection plane of the dodecahedron. The compound solid has no reflection planes.

When a tetrahedron is inscribed into a icosahedron, which is dual to the dodecahedron, the vertices coincide with four face centres of the icosahedron, thus each of the four opposite faces of the icosahedron is parallel to one face of the tetrahedron.

As we have seen we can inscribe a cube into a dodecahedron or into its dual icosahedron. In this way if we make the threefold axes of the cube coincide with the same number of threefold axes of the icosahedron, the vertices of the cube will fall on the centre of the faces of the icosahedron parallel to those of a octahedron. However, each face of the cube will be parallel to one of the edges of the icosahedron or of the circumscribed dodecahedron. Three reflection planes of the cube and the icosahedron (dodecahedron) will coincide and make up the reflection planes of the compound solid.

1.3 Polytopes in the Four Dimensional Space and Their Projections onto the Physical Space

We can imagine the transformation of polyhedra into hyper-solids in Euclidean space having more than three dimensions by repeating the procedure by which we can transform the figure defined in a low dimension space into a figure in progressively higher dimension space.

In space of null dimension the only figure is a point P_0. In space of one dimension there can be any number of points and two of these points will bound a line-segment P_1 which can be constructed by joining point P_0 to another point. If we join P_1 to a third non collinear point we will get a triangle, the simplest polygon, P_2, on a plane; if we then join this triangle to a fourth point outside its plane we will construct a tetrahedron, the simplest form of

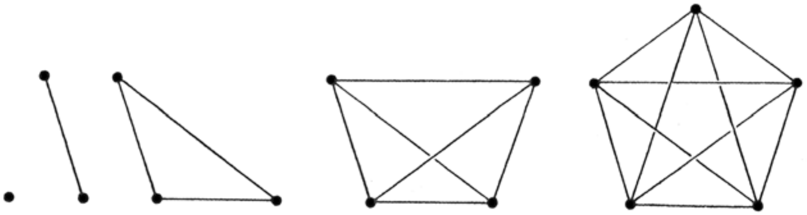

Fig. 1.14. Constructive scheme of pentatope P_4

polyhedron, P_3. If we now join a fifth point to the polyhedron outside the three dimensional space we will construct a pentatope, the simplest element P_4. This succession is exhibited in Fig. 1.14 where the equilateral triangle has the same faces as the tetrahedron.

In general any set of $(r+1)$ points that do not lie in a $(r-1)$ space are the vertices of the r-dimensional simplest figure, the so-called simplex, whose elements are simplexes formed by subsets of the $(r+1)$ points, namely the vertices themselves, $\binom{r+1}{2}$ edges, $\binom{r+1}{3}$ triangles, $\binom{r+1}{4}$ tetrahedra, $(r+1)$ *cells*: in a single relation,

$$R_l = \binom{r+1}{l+1} = \binom{r}{l+1}\binom{r}{l} \, . \tag{1.9}$$

A line-segment is bounded by two points, a triangle by three line-segments (sides), a tetrahedron by four planes (faces) and a pentatope by five three-dimensional regions (tetrahedral cells). In general a simplex is a finite region of r-dimensional space enclosed by $(r+1)$ hyper-planes. If all the $\frac{1}{2}r(r+1)$ edges are equal then we obtain a regular simplex, as shown in Fig. 1.14.

If we limit ourselves to the 4-dimensional space the regular polytopes are those whose cells are regular polyhedra. These polytopes are called r-cells if they are bounded by only r polyhedra. One fundamental property of Euclidean r-dimensional space is that we can draw r mutually perpendicular lines through any point O; r points equidistant from O along these lines will thus make the vertices of a regular simplex $(r-1)$ whereas all the lines together constitute a set of r cartesian reference axes.

If all the centre points of the edges that extend from a given vertex V of P_r lie in one single hyper-plane (e.g. if there are r edges) then these centre points are the vertices of a $(r-1)$-dimensional polytope called the vertex figure of V in P_r. Since the cells of the vertex figure are themselves the vertex figures of cells then a regular polytope P_4, whose cells are $\{n, r\}$, must have $\{r, s\}$ vertex figures where s is the number of cells that surround an edge. This polytope is $\{n, r, s\}$. Thus in four dimensions the formula

$$\sin\frac{\pi}{n}\sin\frac{\pi}{s} \geq \cos\frac{\pi}{r} \tag{1.10}$$

Polytope P_4	Equivalent polyhedron	Number & kind of limit polyhedra	Number of vertices	Duality
$\{3,3,3\}$; 5-cell	Tetrahedron	5 Tetrahedra	5	Self-dual
$\{4,3,3\}$; 8-cell	Cube	8 Cubes	16	Dual of $\{3,4,3\}$
$\{3,4,3\}$; 16-cell	Octahedron	16 Octahedra	8	Dual of $\{4,3,3\}$
$\{3,3,4\}$; 24-cell	-	24 Tetrahedra	24	Self-dual
$\{5,3,3\}$; 120-cell	Dodecahedron	120 Dodecahedra	600	Dual of $\{3,3,5\}$
$\{3,3,5\}$; 600-cell	Icosahedron	600 Tetrahedra	120	Dual of $\{5,3,3\}$

Table 1.2. Features of the P_4 polytopes

holds; this means that $2\pi/s$ is greater than or equal to the dihedral angle $(\pi - 2\phi)$ of $\{n, r\}$. As such we can place s polyhedra $\{n, r\}$ around a common edge. The 4-dimensional Schläfli symbol $\{n, r, s\}$, gives a polytope where $\{n, r\}$ and $\{r, s\}$ must belong to the platonic solids

$$\{3,3\}, \{3,4\}, \{4,3\}, \{3,5\}, \{5,3\}\,.$$

The criterion in (1.10) limits the number of possible polytopes to six, as shown in Table 1.2.

The polytope $\{3, 3, 4\}$ is the only one with no equivalent polyhedron. Apart from being self-dual this polytope is also centrosymmetric whereas $\{3, 3, 3\}$, like the tetrahedron, has no centre of symmetry.

From Table 1.2 duality relations can be inferred when we consider that, in four dimensional space, points correspond dually to three-dimensional lines and the lines to three-dimensional planes.

The study of the projections of polytopes P_4 into three dimensional space is simplified by first considering an analogous, but easier to visualise, case where a polyhedron is projected onto a plane. Among the various possible projections, which are based on the choice of the centre of projection and the choice of the image plane, a usual one is the parallel projection with the centre at an ideal point and whose parallel lines represent parallel lines. However, there is the disadvantage that the projected faces partially overlap. This limitation can be overcome by moving the centre of projection to a point very close to one of the polyhedron faces; we usually prefer the centre of the face and to project onto the plane of that face. The projections of the platonic solids obtained this way are shown in Fig. 1.15; this is what we see when we remove one face of the polyhedron and look at the interior through the hole.

Parallel projection is not the correct method when projecting polytopes P_4 since the polyhedra that bound the polytope are represented in three-dimensional space by polyhedra that intersect with each other and partially

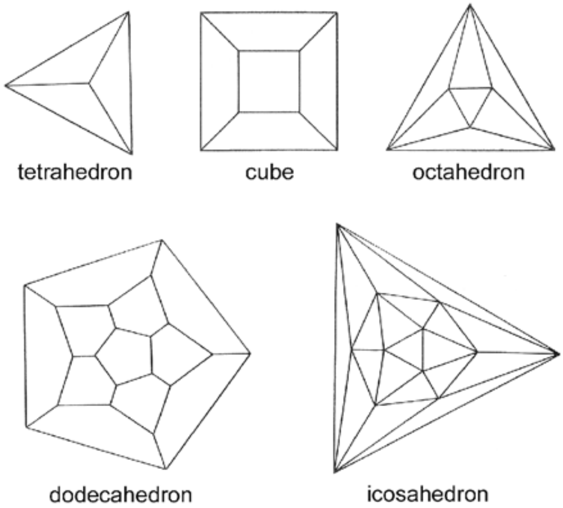

Fig. 1.15. Projections onto the plane of the five platonic solids

overlap, thus giving a distorted image. The very best results are obtained when we project from a point very close to a hyper-surface; in so doing the boundary polyhedra of the polytope P_4 are represented by sets of polyhedra in three-dimensional space, one of which has a very special role and is filled up in a simple way by the others. If we project further onto the plane we will achieve the images as seen in Fig. 1.16 for polytopes $\{3,3,3\}$, $\{4,3,3\}$, $\{3,4,3\}$ and $\{3,3,4\}$. It is noticeable that the last projection is a large octahedron filled by

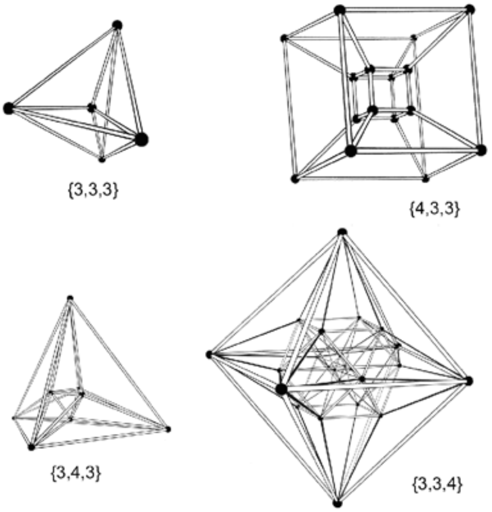

Fig. 1.16. Projections onto the plane of polytopes P_4 $\{3,3,3\}$, $\{4,3,3\}$, $\{3,4,3\}$, $\{3,3,4\}$

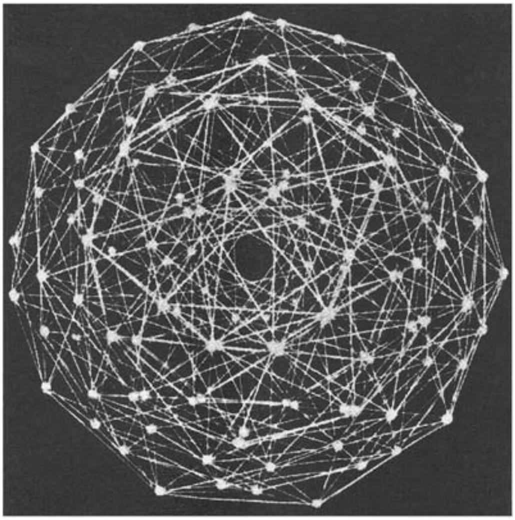

Fig. 1.17. One of the possible projections onto the plane of polytope $\{3,3,5\}$

23 smaller octahedra, with four different possible forms, making 24 polyhedra in all.

Projections of $\{5,3,3\}$ and $\{3,3,5\}$ are much more complicated; Figure 1.17 shows a possible projection of $\{3,3,5\}$.

Our main interest on the polytopes P_4 is given by the observation that $\{3,3,5\}$ is a packing of tetrahedra where every five have a common edge. This packing represents an excellent model of the highly dense physical structures with local icosahedral coordination such as the Frank–Kasper metallic phases and the quasicrystals. In these structures the local coordination polyhedra coincide with the icosahedral coordination polyhedron, which is typical of the atoms arranged at the vertices of the $\{3,3,5\}$ polytope. On the other hand the four-dimensional space has positive curvature whereas the three-dimensional space is flat. The idea of representing a physical structure (three-dimensional) using an ideal four-dimensional crystal will allow us to use the normal techniques adopted to analyse the properties of three-dimensional crystals, but it requires defects, particularly disclinations, being introduced just when the projection is made, in order to obtain, on average, a flat plane. Thus the local interaction between atoms will lead to a local icosahedral configuration that is ideal to obtain an efficient packing of metallic atoms with isotropic interaction. This configuration is however partially incompatible with the requirement to fill the three-dimensional space with matter; this is possible without altering the icosahedral coordination *only* with an energy cost to introduce disclinations (see Chap. 5). This will be discussed in further depth in the following chapters.

1.4 Elements of Crystallography

In order to specifically study the degree of structural order of extended systems, as seen from the position in the physical three dimensional space $\boldsymbol{R}$ of the atoms, or molecules, we must start by examining how regular an ideal, defect free crystal with no surfaces is. In order to discuss the regularity of atomic arrangement in a crystal we have to refer to the idea of a crystal lattice. This is a mathematical construction made of an infinite three-dimensional array of points distributed periodically in space. Each point has identical first neighbours and is equal to every other lattice point. Thus the crystal lattice is said to have perfect *translational symmetry.*

The position $\boldsymbol{r}$ of any lattice site in relation to an arbitrary origin is defined by a vector:

$$\boldsymbol{r} \equiv n_1\boldsymbol{x}_1 + n_2\boldsymbol{x}_2 + n_3\boldsymbol{x}_3 \,. \tag{1.11}$$

Equation (1.11) defines the set of lattice vectors called *lattice translations* or *primitive translations.*

A translation vector, also called lattice vector $\boldsymbol{T}$, joins equivalent points on the lattice

$$\boldsymbol{T} = \boldsymbol{r}_i - \boldsymbol{r}_j \,. \tag{1.12}$$

Equation (1.12) is true of any of the indices i, j.

In (1.11), n_i are *integers* and the non-coplanar vectors, called *basis vectors*, $\boldsymbol{x}_1$, $\boldsymbol{x}_2$, $\boldsymbol{x}_3$, are the fundamental units of translation symmetry. The volume enclosed by the three integers $(\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{x}_3)$ defines the so called *primitive cell.* Referring to a given lattice there is not a single choice of basis vectors, as shown in Fig. 1.18 for a two-dimensional square lattice. It is usual to choose the two shortest basis vectors (top left) but each choice of $(\boldsymbol{x}_1, \boldsymbol{x}_2)$ allows us to reach any point of the square lattice.

If the system is elemental, namely it is made up of a single kind of atoms, then these atoms can be placed directly onto the lattice sites so that each

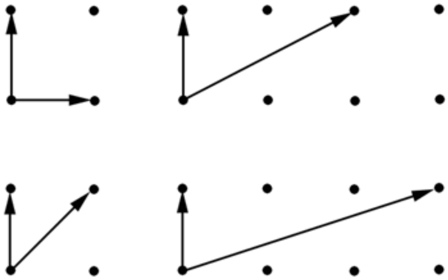

Fig. 1.18. Possible choices for the basis vectors for a two-dimensional square lattice

lattice vector coincides with the position of one atom. More frequently we will find that each lattice site is associated with a set of atoms. In this case we speak about a lattice with a *basis* and the three vectors $(\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{x}_3)$ will define a parallelepiped unit-cell (not necessarily the cell with the minimum volume). Repetition of this unit-cell in space generates the whole crystal with the associated periodicity. The unit-cell with the minimum volume is called the primitive unit cell and it contains one atom.

Each unit cell contains the same number of atoms, usually a small number, in a fixed position. Thus if the cell contains p atoms, and if we suppose that this cell is centred on the origin O, the atomic coordinates being ξ_p $(\xi = 0, 1, 2,\ldots, p-1)$, the distribution of the atoms in the crystal is given by the (microscopic) density $\varrho(\boldsymbol{x})$ as

$$\varrho(\boldsymbol{x}) = \sum_{\boldsymbol{r}} \sum_{\xi=0}^{p-1} \delta(\boldsymbol{x} - \boldsymbol{r} - \xi_p) \tag{1.13}$$

to which is associated the periodicity property

$$\varrho(\boldsymbol{x} + \boldsymbol{r}) = \varrho(\boldsymbol{x}) \,. \tag{1.14}$$

Since each basis is positioned and oriented the same way with respect to its lattice site then the resulting atomic structure is a *perfect crystal.* Some very complicated structures have even been found where the unit cells have up to a few thousand atoms. All the $\boldsymbol{r}$ vectors defined by (1.11) have greater or equal modules to the module of the shortest vector connecting two vertices of the unit primitive cell. The set of lattice translation vectors $\boldsymbol{T}$ is closed with respect to the sum and product. Thus, if we take two lattice vectors $\boldsymbol{T}_1$ and $\boldsymbol{T}_2$ then $\mp\boldsymbol{T}_1$, $\mp\boldsymbol{T}_2$, $(\boldsymbol{T}_1 \mp \boldsymbol{T}_2)$, $\mp(\boldsymbol{T}_1 + \boldsymbol{T}_2)$ are also lattice vectors.

It is often quite useful to substitute one parallelepiped unit-cell with another unit cell, the so-called *Wigner–Seitz* cell.

Taking any point of the lattice as the centre of the cell to be constructed, we join such a centre to all its closest lattice sites, bisecting them and making the bisector planes intersect with each other. The obtained (two dimensional) regular polygon or (three-dimensional) regular polyhedron is the Wigner–Seitz cell. Like the primitive cell the Wigner–Seitz cell contains *one* lattice site; this lies at the centre of the cell whereas each of the eight lattice sites at the vertices of the primitive cell is common to eight adjacent cells. If we represent the atoms as hard spheres on the sites of the various lattices then the crystal will look like a box where the hard spheres are packed in different arrays, depending on the structure, to obtain the highest packing efficiency in the space.

The planes defining the faces of the three-dimensional Wigner–Seitz cell are given by the equation:

$$(\boldsymbol{r} + \boldsymbol{x})^2 = \boldsymbol{x}^2 \,. \tag{1.15}$$

This means that such planes are defined by the intersection of spheres of equal radii centred around adjacent lattice sites. This is another example of the periodicity property of functions associated with the distribution of atoms on the lattice sites.

When we examine elemental metals the most frequent structures found are the simple cubic, sc, the body-centred cubic, bcc, and the face-centred cubic, fcc (see Fig. 1.19). In the first case there are eight atoms on the vertices of the unit cubic cell, whose edge l is called the *lattice parameter*. $\frac{1}{8}$ of the total volume of each atom goes to fill volume l^3 of the cell, which thus contains one atom. The volume available for each atom is $V = \frac{4}{3}\pi\left(\frac{l}{2}\right)^3$ and the packing efficiency is given as

$$f = \frac{V}{l^3} = \frac{\pi}{6} = 52.36\% \,. \tag{1.16}$$

The body-centred cubic structure not only has atoms at the vertices of the cube, it also has an atom at the centre of the cube. The unit cell contains two atoms; the radius of the hard sphere is thus given as $r = l\frac{\sqrt{3}}{2}\frac{1}{2} = \frac{\sqrt{3}}{4}l$

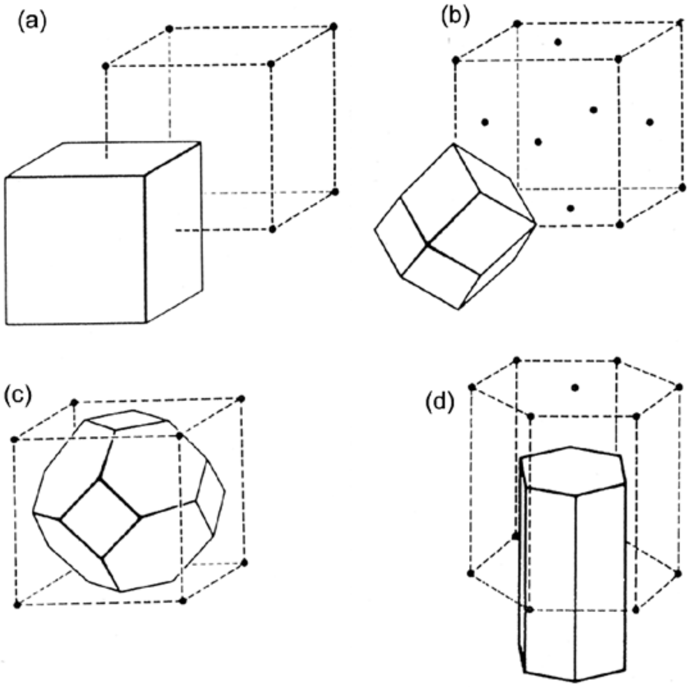

Fig. 1.19. Wigner–Seitz cell for the most common lattices: (**a**) simple cubic structure; (**b**) face-centred cubic structure; (**c**), body-centred cubic structure; (**d**), hexagonal structure

and the packing efficiency is:

$$f = \frac{2\frac{4}{3}\pi\left(l\frac{\sqrt{3}}{4}\right)^3}{l^3} = 68.02\% \,. \tag{1.17}$$

The face-centred cubic structure, on the other hand, still has eight atoms at the cube vertices as well as an atom at the centre of each face; thus the cell contains four atoms. The radius of the hard sphere is given by $r = \frac{1}{2}\frac{l}{2}\sqrt{2} = l\frac{\sqrt{2}}{4}$ and the packing efficiency is:

$$f = \frac{4\frac{4}{3}\pi\left(l\frac{\sqrt{2}}{4}\right)^3}{l^3} = 74.05\% \,. \tag{1.18}$$

This is the most efficient extended three dimensional packing of hard spheres. The hexagonal close-packed structure, hcp, is in turn often found in pure metals and has the same packing efficiency as the fcc. If we examine an fcc crystal and an hcp crystal from the same angle (Fig. 1.20) we will see that the sequence of planes in the hcp crystal is ABAB…, whereas in the fcc crystal the sequence is ABCABC….

The geometric problem to realise the most efficient packing of hard spheres, simple in the case of elemental structures, becomes more complicated when we try to achieve highly compact structures using two different kinds of atoms of different sizes. One typical example is given by the Laves phases AB_2 where the prototype is $MgCu_2$. This is an intermetallic compound whose stability depends not only on electronic factors but especially on geometric factors such as the greatest possible symmetry, the most dense

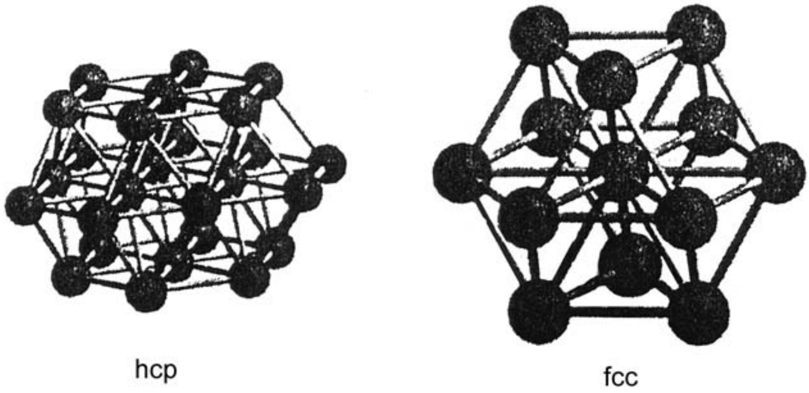

Fig. 1.20. Stereographic models of the hcp and fcc lattices seen from the same angle. In the hcp structure the plane sequence is ABAB…, whereas in the fcc structure the sequence is ABCABC…