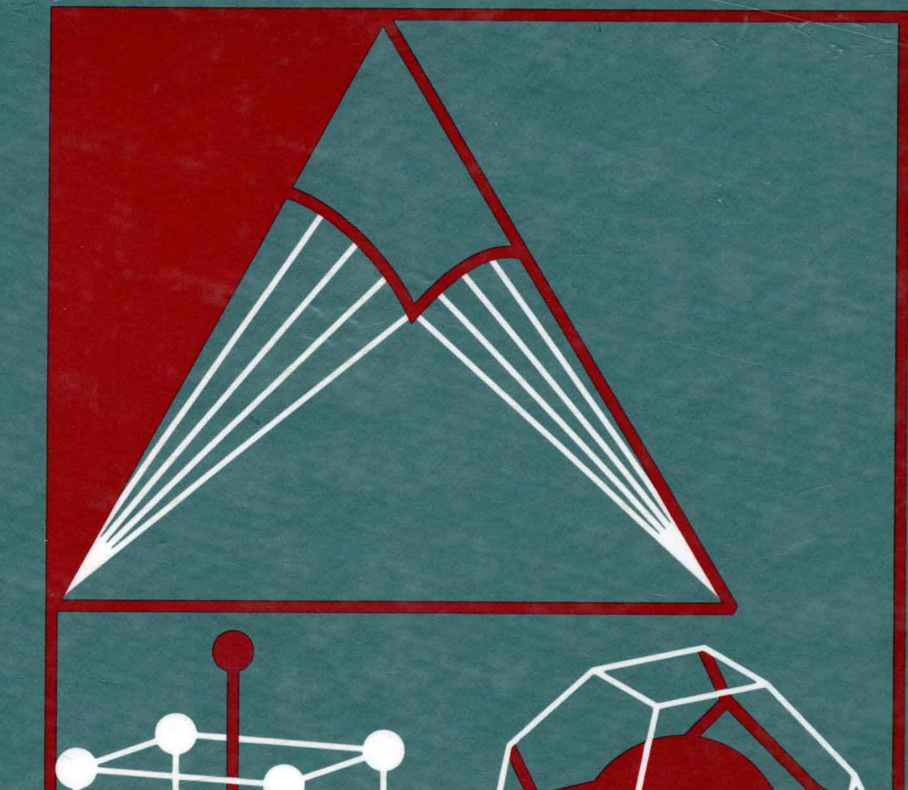
The Physical Chemistry *of* Solids



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Preface

This book was written to encourage the teaching of solid state chemistry in university chemistry and materials science departments. Although a large number, perhaps even a preponderance, of physical chemists find ultimate employment in the realm of solid state science, few have been exposed to the subject during their student years. Perhaps the most widely read book in all of chemistry[†] is subtitled "The Structure of Molecules and Crystals" and devotes considerable space to solids. However, the teaching of solid state chemistry, particularly at the undergraduate level, has never quite caught on. As new technologies continue to emerge, materials science promises to be an expanding field, and physical chemists will have a major stake in the action. An undergraduate or an early post-graduate introduction to the subject will certainly assist in their participation.

The only prerequisite for understanding this text is a reasonable grounding in chemical and elementary statistical thermodynamics plus upper division standing in science or engineering. We have tried to write a self-contained treatise, but suspect the student will find it helpful to keep a modern, advanced physical chemistry text within convenient reach. We have omitted discussion of electron transport properties, magnetism, and optical properties, which seem more properly assigned to solid state physics. Also, mechanical properties and dislocation theory are excluded. We have tried, whenever possible, to use a chemical approach with explanations couched in terms of the chemical bond and thermodynamics.

Empirical or semiempirical methods are presented in detail when they have a useful predictive value. Unfortunately, much, if not most, of modern solid state theory is

[†] *The Nature of the Chemical Bond*, Linus Pauling.

beyond the level of this text. Our task would have been much easier if watered-down versions of such advanced treatments could be presented in a way that would prove enlightening to the student and provide a better tool for making numerical estimates; such is seldom the situation. Rightly or wrongly, we have consciously avoided abbreviated presentations of complex theories, thinking that this leads more frequently to confusion rather than understanding.

Finally, we suggest that a student planning a career in solid state chemistry will profit from additional courses in solid state physics and physical metallurgy. Such course work will furnish a review of some of the material that is in this book, as well as an introduction to much important material that is not.

The authors wish to acknowledge the friendly criticism of several friends and colleagues. In particular we want to thank Professor Lawrence M. Slifkin, who has advised us on every chapter. Selected chapters were critiqued by Drs. Richard van Konynenburg, Arthur C. Damask, Malcolm H. MacGregor, Laurence Passel, Donald Hildenbrand, and James C. Selser. In addition, we give our heartfelt thanks to the careful efforts of Mrs. Diane L. Governor and Ms. Sue E. Garber, whose contributions far exceed mere typing of the manuscript. Most of the illustrations were prepared by Steven M. Wright, whose artistic and graphics capabilities enhance the text. The cover was designed by Mrs. Ellen L. Baldwin. We also wish to thank our technical editor Ms. B. Jane Ellis of Academic Press for her help and, above all, her patience.

Contents

Don't think there are no crocodiles just because the water is calm.
-Sam Wyche, Coach, Cincinnati Bengals

Crystallography and Structure of the Elements

The most distinguishing feature of crystals is the very long range periodic order of the atoms, leading to a high degree of macroscopic symmetry, which, in turn, reflects the symmetry of the crystal's physical properties. Of course, not all inorganic solids are crystalline, glass being a prominent exception, and most liquids exhibit at least some short-range molecular order; in fact, that class of substances known as liquid crystals provides a spectacular example of rather long-range order in the fluid state. Nevertheless, it was the obvious macroscopic symmetry that first attracted man's attention to crystals and continues to do so for esthetic, as well as scientific, reasons. Many of the common substances that we encounter daily are crystalline without appearing to be. The soil under our feet is composed mostly of tiny crystals of various minerals. Solid metals, regardless of the shapes into which they have been fabricated, are made up of crystallites. Because the realm of inorganic solids consists mainly of crystalline, rather than amorphous, substances we can adduce that maximum thermodynamic stability is achieved by the creation of the spatial periodicity of the atoms.

The external symmetry of a crystal directly or indirectly reflects the nature of the bonding between the constituent atoms, ions, or molecules. Indeed, there are fundamental qualitative differences between ionic, covalent, and metallic chemical bonds that dictate the symmetry of the resultant crystal structure. In addition to crystals that are held together by strong bonds, such as the aforementioned, there are molecular crystals in which the fundamental building blocks are molecules bonded through weaker dipolar forces. Crystals of solidified rare gases are bonded via very weak induced dipolar forces, whereas crystals such as graphite and MoS_2

have both covalent and dipolar bonds. In all cases the symmetry, on the atomic scale, is manifest in the overall symmetry of the crystal structure, though it need not be the same.

Before delving into the physical and chemical behavior of solids, we need the vocabulary and concepts necessary to describe the geometry of the atomic arrangements in crystals. It will not be necessary to review in detail a great deal of classical crystallography in order to understand solid state chemistry, but it will be helpful to have in mind some of the more important ideas and terminology.

1. Symmetry

The geometric relationships between the planar faces determined the macroscopic symmetry by which crystals were first grouped and cataloged. Niels Stensen, professor of anatomy at Copenhagen, noted in 1669 that the angles between corresponding planes were always the same in a collection of quartz crystals. His observation has been duly generalized to include all crystals under the fitting title of "Steno's Law," sometimes called the first law of crystallography. The degree and type of symmetry possessed by any object is determined by certain symmetry operations, e.g., rotation, translation, and reflection. A symmetry operation is defined by the particular manipulation that brings the object into congruence with itself.

By way of illustrating this procedure, let us first consider a sphere, the most symmetrical of all shapes. Rotation of a perfect sphere about any of the infinite number of axes passing through its center leaves the object unchanged with reference to any arbitrary set of external coordinates. There is, in fact, no symmetry operation about the center of the symmetry of a sphere that does not leave it congruent with its previous position. Let us now examine the two-dimensional constructs shown in Fig. 1.1. One should imagine a single axis emerging from the center of each figure, which is perpendicular to the plane of the page. The symmetry operation will be

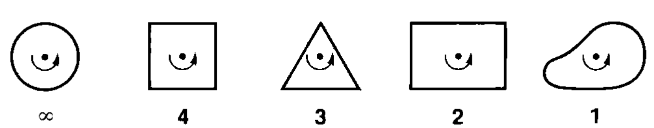


Figure 1.1.

Planar objects with varying degrees of symmetry categorized by the number of positions of congruence attained during a single complete rotation.

simple rotation about this imaginary axis, as indicated by an arrow, and the number of positions of congruence is listed beneath each figure. The central three figures possess, respectively from left to right, fourfold, threefold, and twofold axes of rotation. The last figure on the right, although geometrically quite regular, has no elements of rotational symmetry but the trivial identity element.

The symmetry operations of reflection, translation, and inversion are illustrated in Fig. 1.2.

A mirror-of-reflection plane has an identical set of points equidistant from it on both sides. Translation is the reproduction of the initial configuration at another place in space by simple linear motion. The rotation-inversion operation, Fig. 1.2, is equivalent to having a mirror plane, *m*, between the initial and final positions. Crystals can have two-, three-, four-, and sixfold rotation and rotation-inversion axes, but no five- or sevenfold. A pseudo-fivefold symmetry exists for substances called quasicrystals, but it would be inappropriate to take up this phenomenon so early in our treatise. The nonexistence of five- and sevenfold axes stems from the fact that objects with this symmetry are inherently unable to fill all space, as is illustrated in Fig. 1.3. The difficulty results from the requirement that the rotational and translational symmetries be commensurate, which they clearly are not. That is to say, one cannot perform both the translational repetition of the pentagon and the rotational operation in a way that maintains the postulated fivefold symmetry and yet leaves no voids.

We can recognize, simply by inspection, the maximum number of planes of symmetry and axes of rotation possessed by a simple cube, as shown in Fig. 1.4.

One should not conclude from this that all cubic structures are described by a simple cube possessing all possible symmetry elements. There are innumerable complex cubic structures, such as the spinels (e.g., Fe_3O_4, $MgFeO_4$, $HgK_2(CN)_4$ or

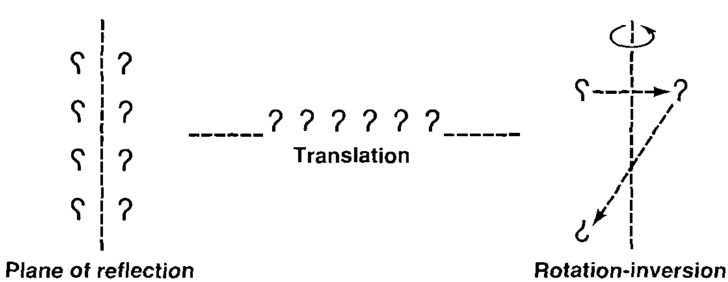


Figure 1.2.

Symmetry operations, reflection, translation, and rotation-inversion.

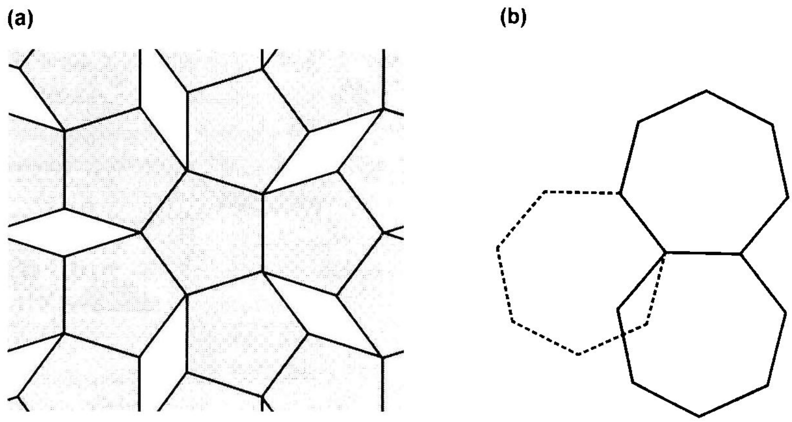


Figure 1.3

(a) A fivefold axis of symmetry does not exist in a lattice because it is impossible to fill all space with a connected array of pentagons. (b) Kepler's original demonstration that no lattice can possess a sevenfold axis of symmetry. (After C. Kittel, *Introduction to Solid State Physics*, Wiley, New York, p. 2, 1967.)

intermetallic compounds, including examples such as $CuCd_5$, that are complex cubic and contain only a minimum number of the symmetry elements shown in Fig. 1.4.

There are two commonly used sets of symbols that stand for the symmetry elements, viz. the Schoenflies and the Hermann-Mauguin; the latter are listed in Table 1.1, and we shall not elaborate the former because it is not commonly used. Although this system of symbols provides a convenient and efficient way of cataloging crystal types according to their symmetry elements, they are infrequently applied in the study of solid state chemistry where attention is focused on the atomic structure of the unit cell. This brings us to the subject of crystal lattices.

Table 1.1. The international symbols for the symmetry elements of crystals.

Identity element (no symmetry)	1	Fourfold rotation axis (rotor)	4
Mirror plane of symmetry	m $(=\bar{2})$	Fourfold rotatory inverter	$\bar{4}$
Twofold rotation axis (rotor)	2	Sixfold rotation axis (rotor)	6
Threefold rotation axis (rotor)	3	Sixfold rotatory inverter	$\bar{6}$
Threefold rotatory inverter	$\bar{3}$	Center of symmetry (inverter)	$\bar{1}$

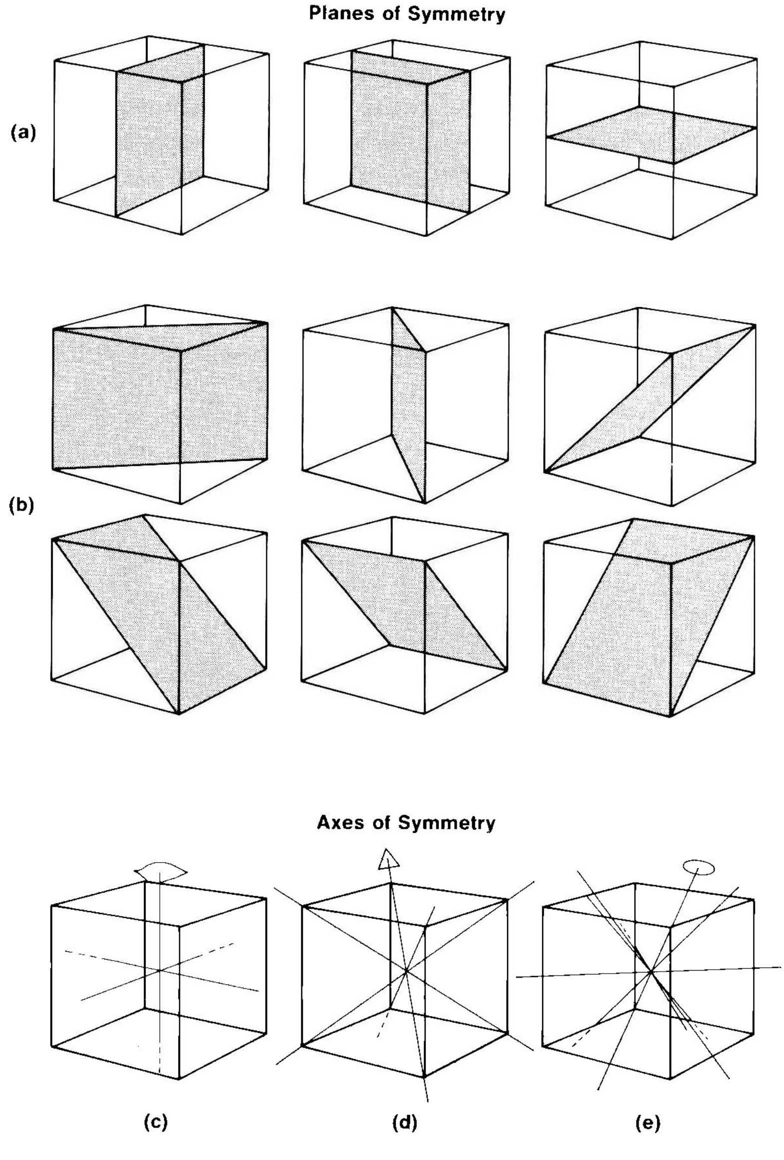


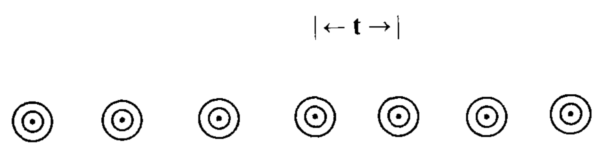
Figure 1.4.

Major planes and axes in the cubic system: (a) the three symmetry planes parallel to the cube faces, (b) the six diagonal mirror planes, (c) the three fourfold rotation axes ◇, (d) the four threefold axes △, and (e) the six twofold axes of rotation ○.

2. Lattices

Although all crystal structures can be described in terms of their respective symmetry elements, they are more easily visualized as the actual three-dimensional arrays of ions or atoms. Such periodic structures, in turn, are most conveniently depicted by their appropriate three-dimensional lattices. Strictly speaking, a lattice is a theoretical symmetrical array of structureless points, a purely mathematical concept not to be interchanged with the term "crystal structure." This rigorous differentiation is largely ignored in common practice, and we will conform to popular usage.

Lattices are constructed by combining the symmetry operations described in Fig. 1.1. The simplest lattice is a row of equally spaced dots separated by the translational vector **t** such as



An example of a two-dimensional lattice is the planar array shown in Fig. 1.5. All points in this figure can be reached by the straightforward addition of the conjugate translations $\mathbf{t}_1$ and $\mathbf{t}_2$. Together these vectors can be combined to form a variety of unit cells, three examples of which are shown in Fig. 1.5. The symbol P stands for

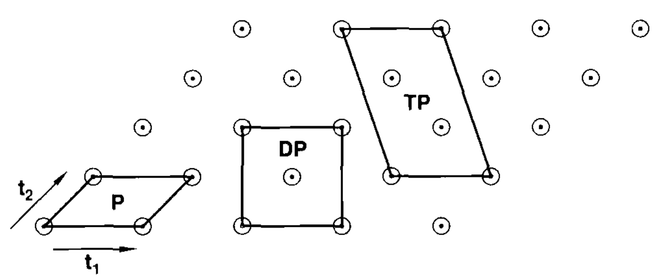


Figure 1.5.

All points are connected by a linear combination of the primitive translation vectors $\mathbf{t}_1$ and $\mathbf{t}_2$. P, DP, and TP designate the outlined primitive, doubly primitive, and triply primitive two-dimensional unit cells.