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New directions in solid state chemistry

Structure, synthesis, properties, reactivity and materials design

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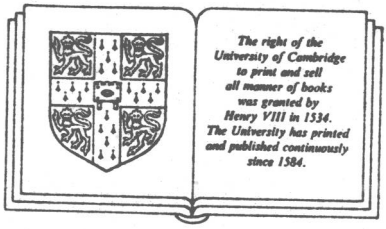

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New directions in solid state chemistry

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Preface

Although solid state science is an area of intense research activity pursued by physicists and materials scientists, the contributions of chemists to this area have a distinct identity. The great skill of chemists in developing novel methods for the synthesis of complex materials, and their understanding of the intricacies of structure and bonding, make their contributions to solid state science unique. At the present time, solid state chemistry is mainly concerned with the development of new methods of synthesis, new ways of identifying and characterizing materials and of describing their structure and above all, with new strategies for tailor-making materials with desired and controllable properties be they electronic, magnetic, dielectric, optical, adsorptive or catalytic. It is heartening that solid state chemistry is increasingly coming to be recognized as an emerging area of chemical science.

In this monograph, we have attempted to present the highlights of modern solid state chemistry and indicate the new directions in a concise manner. In doing so, we have not described the varied principles, properties and techniques that embody this subject at length, but have concerned ourselves with the more important task of bringing out the flavour of the subject to show how it works. We believe that the material covered is up to date, taking the reader to the very frontiers of the subject. We have been careful to include some introductory material for each aspect in order to enable students and beginners to benefit from the book. Instead of dividing the book into the traditional chapters (dealing with crystal chemistry, properties of solids, reactivity and so on) we have tried to present the subject in a style that would reflect the way the subject is growing today. Because of this approach, the lengths of the different chapters have inevitably become somewhat variable.

We hope that the book will be found useful by practitioners of solid state science, especially chemists interested in the study of condensed matter. While the book can certainly be used as a supplementary text in a broad course on solid state science, it could form the basis of a well-planned course in solid state chemistry. We shall be more than rewarded if the book is found useful by students, teachers and practitioners of solid state chemistry.

We have cited important material from the very recent literature including some of the latest references, but in dealing with some of the

new concepts we had to be all too brief in order to limit the size of the book. It is possible that we have not included some references by error of judgement or oversight for which we would like to be excused.

Much of the book was planned and written when one of us (CNRR) was Jawaharlal Nehru Visiting Professor at the University of Cambridge. His thanks are due to Professor J.M. Thomas, FRS., and other colleagues of the Department of Physical Chemistry and to the members of King's College, Cambridge, for their kindness and hospitality.

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June 1985

Contents

1 Structure of solids: old and new facets

1.1 Introduction

Solid state chemistry deals with a variety of solids, inorganic as well as organic; the solids can be crystalline or noncrystalline. A sound knowledge of the structure of solids as well as of the nature of bonding is essential for an appreciation of solid state chemistry since properties of solids are, by and large, determined by the structure. Crystal chemistry of inorganic solids has been reviewed widely in the literature (see, for example, Adams, 1974; Rao, 1974; Wells, 1984), but there has been effort of late to explore new ways of looking at inorganic structures and to

Table 1.1 *Crystal systems and Bravais lattices*

System	Unit cell specification	Essential symmetry[a]	Bravais lattice[b]
Cubic	$a=b=c$ $\alpha=\beta=\gamma=90°$	Four 3s	P, I, F
Tetragonal	$a=b\neq c$ $\alpha=\beta=\gamma=90°$	One 4 or $\bar{4}$	P, I
Orthorhombic	$a\neq b\neq c$ $\alpha=\beta=\gamma=90°$	Three 2s mutually perpendicular or one 2 intersecting with two *m*s	P, I, C, F
Rhombohedral	$a=b=c$ $\alpha=\beta=\gamma\neq 90°$	One 3	R (P)
Hexagonal	$a=b\neq c$ $\alpha=\beta=90°$ $\gamma=120°$	One 6	P
Monoclinic	$a\neq b\neq c$ $\alpha=\gamma=90°\neq\beta$	One 2 or one *m*	P C
Triclinic	$a\neq b\neq c$ $\alpha\neq\beta\neq\gamma$	none	P

[a] 3, 4 etc. are the rotation axes; $\bar{3}$, $\bar{4}$ etc. are the inversion axes; *m* is mirror plane.
[b] P = primitive lattice containing lattice points at the corners of the unit cell; F = face-centred lattice; I = body-centred lattice.

understand their stabilities. In this chapter, we shall briefly review the highlights of inorganic crystal chemistry after summarizing some of the basic information related to crystals and the different types of bonding found in them. We shall also discuss polytypism, organic crystal structures and related topics before finally presenting the models employed to understand the structures of noncrystalline or amorphous solids.

1.2 Description of crystals

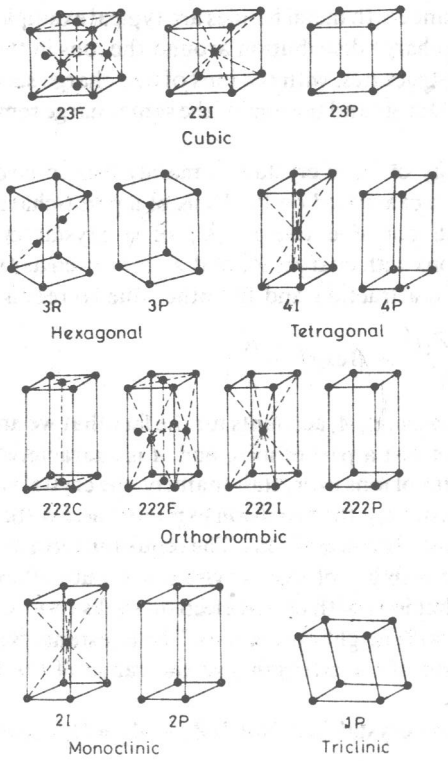
A regular crystal consists of an infinite array of constituent units in three dimensions. Since the nature of the constituent unit does not affect translational periodicity, the periodicity is generally represented by replacing the repeating unit by a point, the resulting array of such points in space being called a lattice. In a *space lattice*, the translation vectors a, b and c in the three crystallographic directions define a parallelepiped called a *primitive cell.* A primitive cell or a suitable combination thereof, chosen as the repeating unit of the lattice, is called the *unit cell.* In order to define a crystallographic unit cell in three dimensions, we require the three translation vectors and the interaxial angles α, β and γ. We can define seven *crystal systems* based on the six lattice parameters (Table 1.1). There are fourteen independent ways of arranging points in space (in three dimensions) giving rise to the 14 *Bravais lattices* (Fig. 1.1) listed in Table 1.1. In two dimensions, five plane lattices are possible, whereas in one dimension there is only one way of arranging points, in the line lattice.

Based on extensive studies of the symmetry in crystals, it is found that crystals possess one or more of the ten basic symmetry elements (five proper rotation axes 1, 2, 3, 4, 6 and five inversion or improper axes, $\bar{1}$ = centre of inversion i, $\bar{2}$ = mirror plane m, $\bar{3}$, $\bar{4}$ and $\bar{6}$). A set of symmetry elements intersecting at a common point within a crystal is called the *point group.* The 10 basic symmetry elements along with their 22 possible combinations constitute the 32 *crystal classes.* There are two additional symmetry elements, *screw axis* and *glide plane,* which arise in crystals but have no counterpart in molecular symmetry. A combination of these elements involving translation with the point group symmetry is called a *space group.* For a triclinic system, for example, there are only two possible space groups P1 and P$\bar{1}$ while for a monoclinic system there are thirteen possible space groups arising from the two possible Bravais lattices P and C and three point groups 2, m and $2/m$. In all, there are 230 possible space groups.

Coloured symmetry. In discussing the symmetry of point groups and

space groups, we assigned to every point in the lattice a set of spatial coordinates (x, y, z) and studied the effect of various symmetry operations on the points. Shubnikov suggested that, in addition to the three spatial coordinates, a fourth coordinate, s, may be added to each point. This coordinate s is allowed to take one of two possible values at a time; s may refer to the spin of a particle, in which case the two allowed values are spin-up and spin-down. In abstract terms, they may correspond to two colours, black and white. A new symmetry operation, called operation of antisymmetry R, is introduced to reverse the value of s from black to white or from spin-up to spin-down. If this operation is considered in conjunction with all the other symmetry operations of point groups and space groups, the total number of possible crystallographic point groups and space groups swells to 122 and 1651 respectively. These enlarged numbers of groups are often referred to as

Figure 1.1 The fourteen Bravais lattices. The numbers 2, 3 etc. designate the symmetry axes and the letters P, F, I and C designate the lattice type.



magnetic groups or *coloured groups* and are of use in describing the symmetry of magnetically ordered crystalline solids (Cracknell, 1975).

1.3 Bonding in crystals

A classification of crystals based on bonding is useful in understanding structure–property relations in solids. Five types of solids are readily defined on bonding considerations: ionic, covalent, metallic and molecular (van der Waals) and hydrogen-bonded. In Table 1.2, the important characteristics of the five types of solids are presented. In real situations, however, solids may exhibit features of more than one type of bonding.

Ionic crystals. Ionic crystals are formed between highly electropositive and highly electronegative elements when electron transfer from the former to the latter occurs, resulting in oppositely charged ions with closed shell electronic configuration. X-ray diffraction studies of ionic crystals reveal an essentially spherical charge distribution around the ions. Alkali and alkaline earth metal halides are typical examples of ionic solids. The spherical charge distribution around the ions in these solids results in symmetric structures, with the ions of one charge surrounding those of the opposite charge and the ions of the same charge remaining as far apart as possible.

The cohesive energy of ionic crystals is mainly due to electrostatic interaction and can be calculated on the basis of a point-charge model. Following Born, the cohesive energy (U) of a crystal containing oppositely charged ions with charges Z_1 and Z_2 is written as the sum of two terms, one due to attraction and the other due to repulsion:

$$U = -\frac{AZ_1Z_2e^2}{R} + B\exp\left(-\frac{R}{\rho}\right) \tag{1.1}$$

Here, the *Madelung constant*, A, accounts for the fact that we are dealing with a crystal and not just a pair of ions, and A is characteristic of the geometric arrangement of ions in crystals (namely, the crystal structure); B is the repulsion constant, ρ the repulsion exponent and R the distance between the two oppositely charged ions. The repulsion term in equation (1.1) accounts for the stability of ionic crystals without collapsing and arises from the fact that ions with closed electron shells resist overlap of their electron clouds with neighbouring ions. The constants B and ρ are respectively a measure of the strength and the range of the repulsive interaction.

For a uni–univalent crystal like NaCl ($Z_1 = Z_2 = 1$), equation (1.1)

Table 1.2 *Types of solids*

Type	Units present	Characteristics	Examples	Approximate cohesive energy, kJ mol^{-1}
Ionic	Positive and negative ions	Brittle, insulating and fairly high melting	NaCl LiF	795 1010
Covalent	Atoms (bonded to one another)	Hard, high melting and nonconducting (when pure)	Diamond SiC	715 1010
Metallic	Positive ions embedded in a collection of electron 'gas'	High conductivity	Na Fe	110 395
van der Waals (Molecular)	Molecules or atoms	Soft, low melting, volatile and insulating	Argon CH_4	7.6 10
Hydrogen-bonded	Molecules held together by hydrogen bonds	Low melting insulators	H_2O (ice) HF	50 30

becomes

$$U = -\frac{Ae^2}{R} + B\exp\left(-\frac{R}{\rho}\right) \tag{1.2}$$

B can be evaluated from the fact that the potential energy U is a minimum at the equilibrium separation, R_e, between a pair of oppositely charged ions,

$$\left(\frac{dU}{dR}\right)_{R=R_e} = 0 = \frac{Ae^2}{R_e^2} - \frac{B}{\rho}\exp\left(-\frac{R_e}{\rho}\right) \tag{1.3}$$

Accordingly,

$$U = -\frac{Ae^2}{R_e}\left(1 - \frac{\rho}{R_e}\right) \tag{1.4}$$

Equation (1.4) is an expression for the lattice energy of an ionic solid like NaCl, first derived by Born and Mayer. The equation can be used directly for the calculation of cohesive energy of ionic solids provided we know A and ρ.

In the early work on cohesion of ionic solids, the repulsion energy was assumed to vary as an inverse power of the distance between the ions, (B/R^n). Both n and ρ are obtained from the compressibility of solids, the compressibility at zero Kelvin being given by

$$\frac{1}{K_0} = V_0\left(\frac{d^2U}{dV^2}\right)_{V=V_e} \tag{1.5}$$

where V_e is the volume of the crystal corresponding to R_e. Values of B and ρ for various alkali halides are given in Table 1.3. Pauling (1960) has suggested the following n values for various closed shell electronic configurations: He, 5; Ne, 7; Ar, 9; Kr, 10; Xe, 12. The value of n for an alkali halide is taken as the average between the values for the two ions. For example, n for NaCl according to this method is 8.

The Madelung constant, A, is a function of crystal structure and can, therefore, be computed from the geometrical arrangement of ions in the crystal. Thus the Madelung constant for the NaCl structure can be written as a summation series,

$$A = \frac{6}{1} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \cdots$$

which converges to a value of 1.74756. The series is, however, only conditionally convergent because the summation can be stopped at any finite point. The value obtained at a finite point is characteristic of a finite crystal. The value of A quoted above for the NaCl structure is obtained for a nearly infinite crystal. Cohesive energies of alkali halides calculated using equation (1.4) are given in Table 1.3. These values refer to a static crystal and do not include the contribution from van der Waals forces and the correction for zero-point energy. These are, however, minor terms, accounting for a small percentage of the total lattice energy. A modified expression for the lattice energy of a solid MX incorporating all the four terms reads as

$$U_c = -\frac{Ae^2}{R_e} + B\exp\left(-\frac{R_e}{\rho}\right) - \left(\frac{C}{R_e^6} + \frac{D}{R_e^8}\right) + \frac{9}{4}h\nu_{max} \qquad (1.6)$$

where the terms on the right-hand side represent respectively the Madelung energy, the repulsion energy, the van der Waals contribution and the zero-point correction, ν_{max} being the highest frequency of the lattice vibrational mode. In the van der Waals term, the R_e^{-6} and R_e^{-8} terms represent dipole–dipole and dipole–quadrupole interactions respectively. Cohesive energies of ionic solids have been extensively reviewed in the literature (Tosi, 1964). Experimental lattice energies of ionic solids are obtained from thermodynamic data using the Born–Haber cycle. The agreement between the experimental and theoretical values of lattice energies is good, thereby lending support to the ionic model for alkali halides and such solids. The ionic model is, however, a poor approximation for crystals containing large anions and small cations, where the covalent contribution to bonding becomes significant. In addition, cohesive energy calculations cannot be used a priori to predict the structure of an ionic compound for the reason that the method makes use of experimental interatomic distances in conjunction

Table 1.3 *Cohesive energy parameters of some alkali halides with NaCl structure*

Crystal	R_e(Å)	$B(10^{-8}$ erg)	ρ(Å)	U(kJ mol^{-1})
NaCl	2.820	1.05	0.321	795
NaBr	2.989	1.33	0.328	757
KCl	3.147	2.05	0.326	724
KBr	3.298	2.30	0.336	695
RbCl	3.291	3.19	0.323	695
RbBr	3.445	3.03	0.338	673