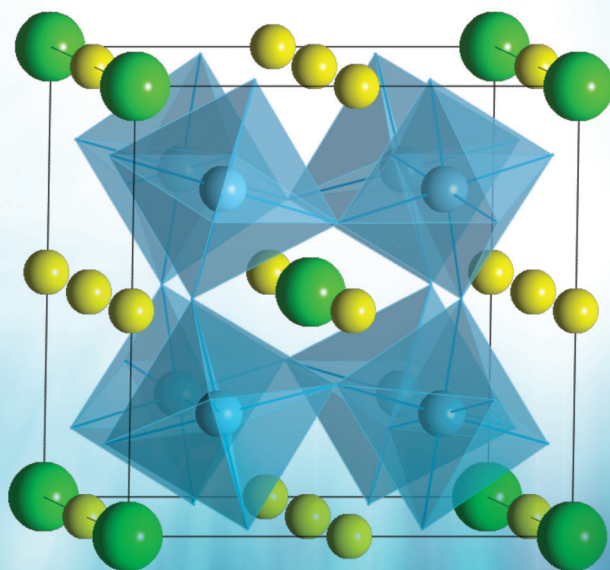


SOLID STATE CHEMISTRY

AND ITS APPLICATIONS

SECOND EDITION

STUDENT EDITION



ANTHONY R. WEST

WILEY

IUPAC Periodic Table of the Elements

1		2		3		4		5		6		7		8		9		10		11		12		13		14		15		16		17		18												
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36											
H hydrogen [1.007; 1.009]	He helium 4.003	Li lithium [6.938; 6.997]	Be beryllium 9.012	B boron [10.80; 10.83]	C carbon [12.00; 12.02]	N nitrogen [14.00; 14.01]	O oxygen [15.99; 16.00]	F fluorine 18.998	Ne neon 20.18	Na sodium 22.99	Mg magnesium 24.31	Al aluminium 26.98	Si silicon [28.08; 28.09]	P phosphorus 30.97	S sulfur [32.05; 32.08]	Cl chlorine [35.44; 35.46]	Ar argon 39.95	K potassium 39.10	Ca calcium 40.08	Sc scandium 44.96	Ti titanium 47.87	V vanadium 50.94	Cr chromium 52.00	Mn manganese 54.94	Fe iron 55.85	Co cobalt 58.93	Ni nickel 58.69	Cu copper 63.55	Zn zinc 65.38(2)	Ga gallium 69.72	Ge germanium 72.63	As arsenic 74.92	Se selenium 78.96(3)	Br bromine 79.90	Kr krypton 83.80											
Rb rubidium 85.47	Sr strontium 87.62	Y yttrium 88.91	Zr zirconium 91.22	Nb niobium 92.91	Mo molybdenum 95.96(2)	Tc technetium	Ru ruthenium 101.1	Rh rhodium 102.9	Pd palladium 106.4	Ag silver 107.9	Cd cadmium 112.4	In indium 114.8	Sn tin 118.7	Sb antimony 121.8	Te tellurium 127.6	I iodine 126.9	Xe xenon 131.3	Cs caesium 132.9	Ba barium 137.3	La lanthanoids	Hf hafnium 178.5	Ta tantalum 180.9	W tungsten 183.8	Os osmium 190.2	Ir iridium 192.2	Pt platinum 195.1	Au gold 197.0	Hg mercury 200.6	Tl thallium [204.3; 204.4]	Pb lead 207.2	Bi bismuth 208.0	Po polonium	At astatine	Rn radon												
Fr francium	Ra radium	actinoids	Rf rutherfordium	Db dubnium	Sg seaborgium	Bh bohrium	Hs hassium	Mt meitnerium	Ds darmstadtium	Rg roentgenium	Cn copernicium	Fl flerovium	Lv livermorium	U uranium 238.0	Np neptunium 237.0	Pu plutonium 244.0	Am americium	Cm curium	Bk berkelium	Cf californium	Es einsteinium	Fm fermium	Md mendelevium	No nobelium	Lr lawrencium																					
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
La lanthanum 138.9	Ce cerium 140.1	Pr praseodymium 140.9	Nd neodymium 144.2	Pm promethium	Sm samarium 150.4	Eu europium 152.0	Gd gadolinium 157.3	Tb terbium 158.9	Dy dysprosium 162.5	Ho holmium 164.9	Er erbium 167.3	Tm thulium 168.9	Yb ytterbium 173.1	Lu lutetium 175.0	Ac actinium	Th thorium 232.0	Pa protactinium 231.0	U uranium 238.0	Np neptunium	Pu plutonium	Am americium	Cm curium	Bk berkelium	Cf californium	Es einsteinium	Fm fermium	Md mendelevium	No nobelium	Lr lawrencium																	

atomic number	Symbol	name	standard atomic weight
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Notes

- IUPAC 2009 Standard atomic weights abridged to four significant digits (Table 4 published in *Pure Appl. Chem.* 83, 359-396 (2011)); doi: 10.1351/PAC-REP-10-09-14). The uncertainty in the last digit of the standard atomic weight value is listed in parentheses following the value. In the absence of parentheses, the uncertainty is one in that last digit. An interval in square brackets provides the lower and upper bounds of the standard atomic weight for that element. No values are listed for elements which lack isotopes with a characteristic isotopic abundance in natural terrestrial samples. See PAC for more details.
 - "Aluminium" and "caesium" are commonly used alternative spellings for "aluminum" and "caesium".
 - Claims for the discovery of all the remaining elements in the last row of the Table, namely elements with atomic numbers 113, 115, 117 and 118, and for which no assignments have yet been made, are being considered by a IUPAC and IUPAP Joint Working Party.
- For updates to this table, see iupac.org/reports/periodic_table/. This version is dated 1 June 2012.
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INTERNATIONAL UNION OF
PURE AND APPLIED CHEMISTRY

**Solid State Chemistry
and its Applications**

Second Edition

Solid State Chemistry and its Applications

Second Edition

Student Edition

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Department of Materials Science and Engineering,
University of Sheffield, UK

WILEY

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For Sheena, Isla, Graeme, Jenny and Susie

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Preface

This book is a slimmed down, student edition of ‘Solid State Chemistry and its Applications’ whose second edition is scheduled for publication in 2015/6. It is modelled on the authors’ ‘Basic Solid State Chemistry’, but has been completely rewritten with about 40% new material added and all the diagrams drawn professionally, in full colour. The nine chapters in ‘Basic’ have become ten in this new edition since ‘Magnetic and Optical Properties’ is split into separate chapters.

In the period since the second edition of ‘Basic’ was published in 1999, we have witnessed many major new discoveries and developments in the solid state chemistry of inorganic materials with topics such as colossal magnetoresistance, multiferroics, light emitting diodes and graphene. New materials synthesis techniques have evolved such as mechanosynthesis, microwave-hydrothermal synthesis and atomic layer deposition and of course, there have been many improvements in the techniques used to characterise solids including use of synchrotrons for diffraction and spectroscopy as well as high resolution scanning transmission electron microscopy permitting atomic-level identification and structural imaging. It was felt that an updated version of both ‘Basic’ and ‘Solid State Chemistry and its Applications’ was long overdue, therefore.

A major feature of this new edition is the extensive coverage of the crystal structures of important families of inorganic solids. Purchasers of the book will be able to download, free, a bespoke and easy-to-use CrystalMaker[®] viewer program. The CrystalViewer software is accompanied by more than 100 crystal structure models which users will be able to view on their computers with the facility to rotate the structures, view them from different orientations and either highlight or hide different structural features. CrystalViewer and the accompanying structure files can be downloaded from the companion website at <http://www.wiley.com/go/west/solidstatechemistrystudent>.

Many people have helped and encouraged me in preparing this new edition. Special thanks are due to: John McCallum who produced many of the crystal structure drawings and files, Frances Kirk who prepared the whole manuscript, in electronic format, and Wiley staff Sarah Hall and Sarah Tilley for their enthusiastic encouragement and involvement: in particular, Sarah Hall was instrumental in making the CrystalMaker[®] arrangements and Sarah Tilley oversaw all the artwork preparations.

Anthony R. West
Sheffield
July 2013

Chemistry – Solid State Chemistry – Materials Chemistry – Materials Science and Engineering

Chemistry is an evolving subject! Traditionally, there have been three branches of chemistry: organic, physical and inorganic, with some arguments in favour of including analytical as a fourth branch. An alternative, fairly new classification (favoured by the author!) divides chemistry into two broad areas: molecular (which includes liquids and gases) and non-molecular (or solid state). The ways in which we think about, make, analyse and use molecular and non-molecular substances are completely different, as shown by a comparison of one ‘simple’ substance in each category, toluene and aluminium oxide:

Comparison of the chemistries of molecular and non-molecular materials

Characteristic	Toluene	Aluminium oxide
Formula	Fixed, $C_6H_5CH_3$	Usually fixed, Al_2O_3 , but for other oxides may be variable, e.g. $Fe_{1-x}O$
Are defects present?	Not allowed: missing or mis-placed atoms give rise to different molecules	Unavoidable: small concentration of vacancies, interstitials and dislocations are always present
Doping possibilities	Not possible without producing a different molecule	Doping or solid solution formation allows control and optimisation of properties, e.g. ruby is Cr-doped Al_2O_3
Structure and its determination	Molecular structure can be determined spectroscopically: NMR/Mass Spec/IR. Determine packing arrangement, bond lengths and angles, by single crystal X-ray diffraction. Usually, structural information is then complete.	Full characterisation of a solid requires structural and compositional information across the length scales from local, to unit cell, nano and microscales. Many diffraction, spectroscopic and microscopic techniques are needed for full characterisation.
Properties and applications	Controlled by molecular formula and configuration; cannot be modified by doping. Some properties (e.g. pharmaceutical activity) may depend on molecular packing arrangements in crystals.	Properties/applications depend on crystal structure, defects, dopants, surface structure, particle size and whether the material is a powder, single crystal, film, etc. Consider the diverse applications of Al_2O_3 : films and ceramics used as insulators; powders used as abrasive; with Cr^{3+} dopants, ruby is used for lasers; porous solids used as catalyst supports.

Thus, for toluene, once its formula and molecular structure had been determined there were few remaining issues to be resolved other than, perhaps, the detailed packing arrangement of molecules in crystalline toluene at low temperatures or the possible discovery and evaluation, even today, of as-yet unknown chemical, biological or pharmaceutical properties of pure toluene.

Alumina, by contrast, is a highly complex material; its properties, and therefore potential applications, depend on different aspects of its structure (bulk, defect, surface, nano), the methods needed to fabricate it in different forms and shapes, the possibility of doping to modify its properties and the characterisation or determination of its structure (and its composition, whether homogeneous or heterogeneous, if doped) across all length scales. This is solid state chemistry!

The biggest contrast between molecular and non-molecular materials is that the latter can be doped, allowing modification and control of properties such as magnetism, superconductivity and colour/optical band gap. By contrast, attempts to dope molecules are inevitably frustrated since replacing one atom in the molecule by another, or creating defects such as missing atoms, lead to entirely different molecules.

In recent decades, *materials chemistry* has emerged as a distinct branch of chemistry which covers both non-molecular, solid state materials (oxides, halides, etc.) and many molecular materials (especially, functional polymers and organic solids with potentially useful physical properties). Materials chemistry cuts across the traditional disciplines of chemistry but also includes something extra which is an interest in the physical properties of compounds and materials. In the past, solid state physics and materials science have been the usual ‘home’ for physical properties; but now, they are an intrinsic part of solid state and materials chemistry.

The distinction between *materials chemistry* and *materials science* is often unclear but can be summarised broadly as follows:

Materials chemistry

Synthesis – structure determination – physical properties – new materials

Materials science

Processing and fabrication – characterisation – optimisation of properties and testing – improved/new materials for engineering applications in products or devices.

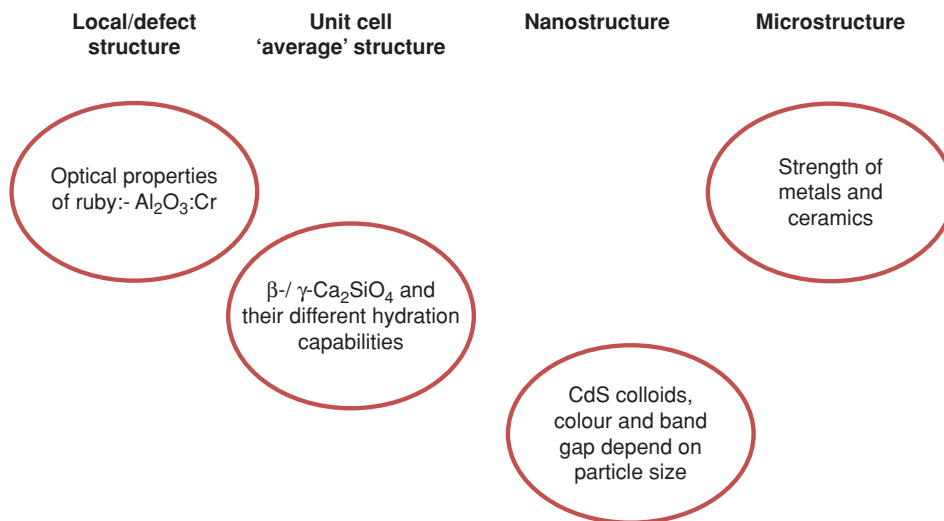
Materials science focuses on materials that are already known to be useful or have the potential to be developed for applications, either by compositional control to optimise properties or by fabrication into desired forms, shapes or products. Materials science therefore includes whatever aspects of chemistry, physics and engineering that are necessary to achieve the desired aims.

Materials chemistry is much more than just a subset of materials science, however, since it is freed from the constraint of a focus on specific applications; materials chemists love to synthesise new materials and measure their properties, some of which may turn out to be useful and contribute to the development of new industries, but they do this within an overarching interest in new chemistry, new structures and improved understanding of structure – composition – property relationships.

A curious fact is that, in the early days of chemistry, inorganic chemistry had as its main focus, the elements of the periodic table and their naturally occurring or easy-to-make compounds such as oxides and halides. Inorganic chemistry subsequently diversified to include organometallic chemistry and coordination chemistry but interestingly, many traditional inorganic materials have returned to centre-stage and are now at the heart of solid state materials science. Examples include: Cr-doped Al_2O_3 for lasers; doped Si semiconductors

for microelectronics; doped ZrO_2 as the solid electrolyte in solid oxide fuel cells; BaTiO_3 as the basis of the capacitor industry with a total annual production worldwide exceeding 10^{12} units; copper oxide-based materials for superconductor applications; and many, many more. The scope for developing new solid state materials/applications is infinite, judging by the ‘simple’ example of Al_2O_3 described above. Most such materials tend not to suffer from problems such as volatilisation, degradation and atmospheric attack, which are often a drawback of molecular materials, and can be used safely in the environment.

It is important to recognise also that physical properties of inorganic solids often depend on structure at different length scales, as shown by the following examples:



Thus in the case of ruby, which is a natural gemstone and was the first material in which LASER action – light amplification by stimulated emission of radiation – was demonstrated, two structural aspects are important. One is the host crystal structure of corundum, α - Al_2O_3 and the other is the Cr^{3+} dopant which substitutes at random for about 1% of the Al^{3+} ions in the corundum lattice: the Cr-O bond lengths and the octahedral site symmetry are controlled by the host structure; the two together combine to give the red ruby colour by means of d-d transitions within the Cr chromophore and the possibility of accessing the long-lived excited states that are necessary for LASER action.

A remarkable example of the effect of crystal structure details at the unit cell scale on properties is shown by dicalcium silicate, Ca_2SiO_4 which is readily prepared in two polymorphic forms at room temperature. One, the β -polymorph, reacts with water to give a semicrystalline calcium silicate hydrate which sets rock-solid and is a main constituent of concrete; the other polymorph, γ - Ca_2SiO_4 , does not react with water. Just think, the entire construction industry rests on the detailed polymorphism of dicalcium silicate! It is not sufficient that one of the key components of cement has the right composition, Ca_2SiO_4 ; in addition, the precise manner in which ions are packed together in the solid state is critical to its hydration properties and whether or not it turns into concrete.

At the nanoscale, crystalline particles may contain many hundreds of unit cells but often their properties are different from powders, ceramics or single crystals of the same material with larger-sized grains simply because of the influence of surface energies. In small nanoparticles, surface free energies and structures

increasingly dominate the total free energy of a material, as shown by the colour, and associated band gap, of CdS nanoparticles (or colloids in older terminology) which can be fine-tuned by controlling the particle size.

Some properties are determined by structure at the micron ($1\ \mu\text{m} = 10^3\ \text{nm} = 10^4\ \text{\AA} = 10^{-3}\ \text{mm}$) scale and this is the reason why ‘microstructure’ features strongly in the characterisation of metals and ceramics, primarily using optical and electron microscopy techniques. Frequently, impurities/dopants may precipitate at grain boundaries and surfaces and these can have a dramatic influence on for instance, the mechanical properties.

These examples illustrate the awesome challenges that must be met before an inorganic solid can be regarded as fully characterised across the length scales. This, coupled with the enormous number of inorganic crystal structures that are known, and the possibility to introduce dopants which modify properties, underlines why solid state chemistry is a central subject to many areas of physical science, engineering and technology.

This book concerns solid state chemistry and focuses on inorganic solids: their crystal structures, defect structures and bonding; the methods used to synthesise them and determine their structures; their physical properties and applications. Organic and other molecular materials are included in the coverage if their properties in the solid state complement, or relate to, those of inorganic solids. Physical properties are an intrinsic part of solid state chemistry since the whole area of structure–property relations requires the insights and input of chemistry to synthesise and characterise materials, as well as a good understanding of physical properties and the factors that control them.

Companion Website

This textbook is supported by a website which contains a variety of supplementary resources:

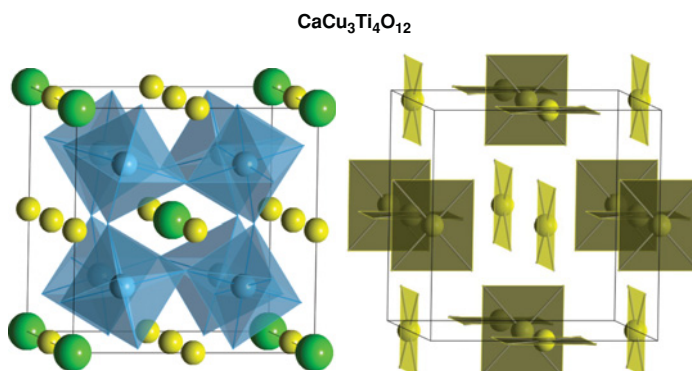
<http://www.wiley.com/go/west/solidstatechemistrystudent>

Online you will find PowerPoint slides of all figures from the book, as well as solutions to the set of questions. The website also gives you access to a CrystalMaker[®] viewer program. The CrystalViewer software is available for Windows and Mac, and is accompanied by a broad array of crystal structures for you to view and manipulate.

CrystalViewer

CrystalViewer is a visualisation program for displaying and manipulating crystal structures. The CrystalViewer software facilitates the exploration of crystal structures from the book in three dimensions, allowing users to view the structures in different orientations, and highlight/hide different structural features so as to aid the interpretation of complex crystal structures. The CrystalViewer program is accompanied by over 100 crystal structure files; many of these structures relate directly to illustrations from the book, identified by their figure numbers, and a variety of additional structures are provided to complement the concepts and applications discussed in the text.

The CrystalViewer software and accompanying structure files can be downloaded from the companion website at <http://www.wiley.com/go/west/solidstatechemistrystudent>



CrystalMaker[®] CrystalMaker Software Ltd. www.crystalmaker.com

An example of how a crystal structure can appear very different, depending on which aspects are emphasised, is shown here for $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, in which the two diagrams highlight either the TiO_6 octahedra or the CuO_4 square planar units.

Crystal Structure Library

A Crystal Structure Library is available on the companion website containing >100 structures which can be examined in detail using the CrystalViewer Software. The structures which correspond directly to figures in the book are listed below, with the relevant figure number noted in parentheses. Many more crystal structures are available online, including minerals and other inorganic structures. Further structures may be added from time to time.

Major Inorganic Structure Types (and relevant book diagrams)

β -alumina, NaAl ₁₁ O ₁₇ (8.23 and 8.24)	Li ₃ N (8.32)
BaTiO ₃ (8.40)	LiCoO ₂ / α -NaFeO ₂ (8.35)
<i>bcc</i> metal (2.12)	LiNbO ₃ (1.46)
Brass, ZnCu (2.11)	Magnetoplumbite (9.14)
Brownmillerite, Ca ₂ (Fe,Al) ₂ O ₅ (1.42)	MgB ₂ (1.51)
CaC ₂ (1.10)	Nasicon, NaZr ₂ (PO ₄) ₃ (8.27)
CaCu ₃ Ti ₄ O ₁₂ (1.42)	Nickel arsenide, NiAs (1.35)
CdCl ₂ (1.40)	Olivine, LiFePO ₄ (1.45)
CdI ₂ (1.39)	PbFCl, matlockite (8.6)
Chevreil Phase, BaMo ₆ S ₈ (8.6)	PbO (3.14)
Corundum, α -Al ₂ O ₃ (1.46)	Perovskite, SrTiO ₃ (1.41)
CsCl (1.36)	Pyrochlore (1.48)
Diamond (1.33)	Rock salt, NaCl (1.2, 1.29 and 1.31)
<i>fcc</i> metal (1.20)	Rutile, TiO ₂ (1.37)
Fluorite/antifluorite, CaF ₂ (1.29, 1.30 and 1.34)	Spinel (1.44)
Garnet, Y ₃ Fe ₅ O ₁₂ (1.49)	Tetragonal tungsten bronze (1.43)
GdFeO ₃ (1.41)	Wurtzite, ZnS (1.35)
<i>hcp</i> metal (1.21)	YBa ₂ Cu ₃ O ₆ (8.8)
Hollandite (8.27)	YBa ₂ Cu ₃ O ₇ (8.8)
Ilmenite, FeTiO ₃ (1.46)	Zinc blende/sphalerite, ZnS (1.29 and 1.33)
K ₂ NiF ₄ (1.50)	ZrCuSiAs (8.6)
Layered double hydroxides (4.11)	

Biography

Tony West obtained his BSc degree in Chemistry at University College Swansea and his PhD at the University of Aberdeen, where he worked with Professor F. P. Glasser on silicate chemistry. He was appointed as a Lecturer in Aberdeen in 1971 and developed a lifetime interest in the then-emerging field of solid state chemistry with special interest in the synthesis of new oxide materials, their crystal structures and electrical properties. He was awarded a DSc from Aberdeen in 1984 and rose through the ranks to become Professor of Chemistry in 1989 before moving to the University of Sheffield, Department of Materials Science and Engineering, as Head of Department in 1999, a post he held until 2007.

Tony was founding editor of the *Journal of Materials Chemistry* and subsequently established the Materials Chemistry Forum, which has now become the Materials Chemistry Division of the Royal Society of Chemistry. He organised the First International Conference on Materials Chemistry, MCI, in Aberdeen, 1993, and co-organised the first Materials Discussion, MDI, in Bordeaux, 1998. He also served as President of the Inorganic Chemistry Division of IUPAC, 2004–2007.

Tony is a Fellow of the Royal Society of Chemistry, the Institute of Physics, the Institute of Materials, Minerals and Mining (IOM³), and the Royal Society of Edinburgh. Over the years he has received several awards, including an Industrial Award in Solid State Chemistry from the RSC (1996), the Griffiths Medal and Prize from the IOM³ (2008), the Epsilon de Oro Award from the Spanish Society of Glass and Ceramics (2007) and the Chemical Record Lectureship from the Chemical Societies of Japan (2007). He has been awarded the 2013 John B. Goodenough Award in Materials Chemistry by the RSC, a lifetime award which recognises exceptional and sustained contributions to the field of materials chemistry.

1

Crystal Structures and Crystal Chemistry

Solid state chemistry is concerned mainly with crystalline inorganic materials, their synthesis, structures, properties and applications. A good place to begin is with *crystal structures* and *crystal chemistry*. All necessary crystal structure information is contained in data on unit cells, their dimensions and the positions or atomic coordinates of atoms inside the unit cell. Crystal chemistry combines this basic structural information with information about the elements, their principal oxidation states, ionic radii, coordination requirements and preferences for ionic/covalent/metallic bonding. A working knowledge of the Periodic Table and the properties of elements is, of course, invaluable to be able appreciate crystal chemistry, but conversely, knowledge of crystal structures and especially crystal chemistry provides a very useful way to gain increased understanding of the elements and their compounds.

Many of the properties and applications of crystalline inorganic materials revolve around a surprisingly small number of structure types. In this chapter, the main families of inorganic structures are reviewed, especially those which have interesting properties; more details of the vast array of structures may be found in the encyclopaedic text by Wells and also in the Wyckoff *Crystal Structures* book series. First, however, we must consider some basic concepts of crystallography.

1.1 Unit Cells and Crystal Systems

Crystals are built up of regular arrangements of atoms in three dimensions; these arrangements can be represented by a repeat unit or motif called the *unit cell*. The unit cell is defined as *the smallest repeating unit which shows the full symmetry of the crystal structure*. Let us see exactly what this means, first in two dimensions. A section through the NaCl structure is shown in Fig. 1.1(a); possible repeat units are given in (b) to (e). In each, the repeat unit is a square and adjacent squares share edges and corners. Adjacent squares are identical, as they must be by definition; thus, all the squares in (b) have Cl^- ions at their corners and centres. The repeat units in (b), (c) and (d) are all of the same size and, in fact, differ only in their relative position. The choice of origin of the repeat unit is to some extent a matter of personal taste, even though its size, shape and orientation are fixed. The repeat unit of NaCl is usually chosen as (b) or (c) rather than (d) because it is easier to draw and visualise the structure as a whole if the repeat unit contains atoms or ions at special positions such as corners and edge centres. Another guideline is that usually the origin is chosen so that the symmetry of the structure is evident (next section).

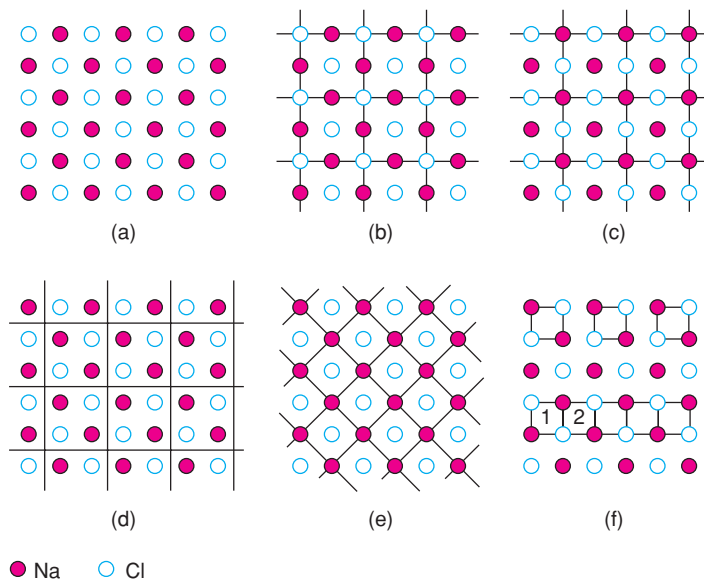


Figure 1.1 (a) Section through the NaCl structure, showing (b) to (e) possible repeat units and (f) incorrect units.

In the hypothetical case that two-dimensional (2D) crystals of NaCl could form, the repeat unit shown in (e), or its equivalent with Cl at the corners and Na in the middle, would be the correct unit. Comparing (e) and, for example, (c), both repeat units are square and show the 2D symmetry of the structure; as the units in (e) are half the size of those in (c), (e) would be preferred according to the above definition of the unit cell. In three dimensions, however, the unit cell of NaCl is based on (b) or (c), rather than (e) because only they show the cubic symmetry of the structure (see later).

In (f) are shown two examples of what is *not* a repeat unit. The top part of the diagram contains isolated squares whose area is one-quarter of the squares in (c). It is true that each square in (f) is identical but it is not permissible to isolate unit cells or areas from each other, as happens here. The bottom part of the diagram contains units that are not identical; thus square 1 has Na in its top right corner whereas 2 has Cl in this position.

The unit cell of NaCl in three dimensions is shown in Fig. 1.2; it contains Na at the corner and face centre positions with Cl at the edge centres and body centre. Each face of the unit cell looks like the unit area shown

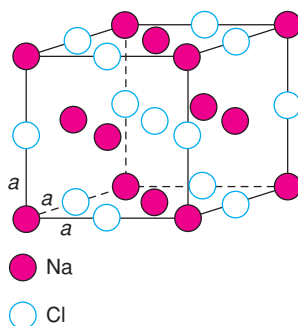


Figure 1.2 Cubic unit cell of NaCl, $a = b = c$.