

book reviews

Works intended for this column should be sent direct to the Book-Review Editor, whose address appears in this issue. All reviews are also available from **Crystallography Journals Online**, supplemented where possible with direct links to the publisher's information.

Quasicrystals. The state of the art. (2nd ed.) Edited by D. P. Vincenzo and P. J. Steinhardt. **Series on Directions in Condensed Matter Physics**, Vol. 16. Pp. xi + 618. Singapore: World Scientific, 1999. Price (hardback) USD 113, GBP 71, ISBN 981-02-4155-0; (paperback) USD 55, GBP 34, ISBN 981-02-4156-9.

Twelve years ago, the first edition of this book was published. It served for several years as a very valuable introduction to quasicrystals and as a progress report emphasizing 'critical experimental developments and important theoretical breakthroughs that have occurred in the four years since, subsequent to the initial excitement surrounding the discovery of quasicrystals'. The slightly enlarged second edition appeared in 1999. Two well written chapters had been added to the 15 mostly unchanged previous ones. In one of them, A. I. Goldman and P. A. Thiel review the experimental progress between 1991 and 1998. In the other one, P. J. Steinhardt himself discusses the Gummelt-cluster approach, which allows the structure of decagonal phases to be described in terms of a single overlapping cluster.

Quasicrystals. The state of the art (2nd ed.) is still an interesting book but it no longer reflects the state-of-the art of quasicrystal research. Today the title is misleading. Too many important experimental and theoretical discoveries have been made since 1990/91 when 15 of the 17 chapters of the book were written. This progress is reflected in the number of papers on quasicrystals that have tripled to much more than 6000 since then. New classes of stable ternary and even binary quasicrystals have been discovered, high-temperature/pressure studies have given new insight into stability and phase transformations, huge perfect single-crystalline samples have been grown and structure and physical properties of quasicrystals have been studied in great detail. Even one of the early paradigms that the negative temperature coefficient of electrical resistivity should be an intrinsic property of quasicrystals has recently been questioned by experiments on the new binary quasicrystals.

Quasicrystals. The state of the art (2nd ed.) is definitely 'a must' for everybody who is interested in the early years of quasicrystal research. Some of the theoretical chapters are of lasting value such as the one on *Random tiling models* by C. L. Henley. *Matching rules for quasicrystalline tilings* by K. Ingersent or *Growth rules for quasicrystals* by J. E. S. Socolar are still useful to read. However, if one wants to get an easy general introduction into the field, the textbook by C. Janot, *Quasicrystals: a primer*, 2nd ed. (Clarendon Press, Oxford, 1994), would be a better buy. More detailed insight into structure and properties of quasicrystals is imparted by the useful multiauthor book *Physical properties of quasicrystals*, edited by Z. M. Stadnik (Springer, Berlin, 1999). A more mathematical introduction into the current theory of coverings is given in the excellent book on *Coverings of discrete quasiperiodic sets. Theory and application to quasicrystals*, edited by P. Kramer and Z. Papadopolos (Springer, Berlin, 2003).

Walter Steurer

Laboratory of Crystallography
Department of Materials
ETH Zurich
CH-8092 Zurich
Switzerland
E-mail: steurer@mat.ethz.ch

Linus Pauling selected scientific papers.

Edited by Barclay Kamb, Linda Pauling Kamb, Peter Jeffress Pauling, Alexander Kamb and Linus Pauling Jr. Singapore: World Scientific, 2001. Vols. 1 and 2 set: 1612 pp., USD 114, ISBN 981-02-2784-1; Vol. 1: 864 pp., USD 98, ISBN 981-02-2939-9; Vol. 2: 748 pp., USD 67, ISBN 981-02-2940-2.

Few would dispute that Linus Pauling was the greatest chemist of the 20th century, arguably one of the greatest ever. Imaginative, quantitative, encyclopaedic, selective, omnivorous, lucid, vivid and compelling (in the written and spoken word), he was also a prodigiously hard working and extraordinarily versatile scientist with skills and

knowledge encompassing the crystallographic, mineralogical, mathematical, quantum mechanical, nuclear physical, as well as the chemical, biochemical and biological. In all these fields (along with others such as immunology, anaesthesia and evolution) and particularly at the interfaces between them he made decisive contributions. He was both a deep thinker and a problem solver. Just as the English language owes many of its words and metaphors to Shakespeare, so does the vocabulary and language of modern chemical science owe an enormous debt to Pauling.

His published writings number some 1200 in all, of which over 800 are scientific papers and books, produced over the period 1923–1994. His first paper was on the crystal structure of molybdenite (MoS_2). In these two volumes, 144 of his papers are reproduced, preceded by brief introductory assessments of clusters of them that are arranged into four main categories: The Chemical Bond, Crystal and Molecular Structure and Properties, Biomolecular Sciences, and Health and Medicine. The editors, who are his son-in-law, daughter, two surviving sons and grandson, sought the assistance of some notable luminaries (who include Jack Dunitz, Richard Marsh, Harden McConnell, Ray Owen, Alexander Rich and Ahmed Zewail) in deciding which articles to reproduce. The resulting compilation constitutes an intellectual feast. These two volumes are, in effect, an encyclopaedia of modern chemistry, with the important extra quality that it has historical perspective and includes some exhilarating landmark papers which will be consulted for as long as chemistry is taught and pursued.

Soon after the discovery of X-ray diffraction by crystals, the structure of most elements, many simple salts and a small number of complicated substances had been determined by the early 1920s. But the difficulty of finding additional crystalline solids, the structures of which could be completely analysed by the accepted methods (of the Braggs, Wyckoff, Goldschmidt and Pauling himself), was becoming apparent. In 1928, Pauling made a successful attack upon this impasse in his contribution to the *Festschrift* for Sommerfeld (in whose Munich laboratories he learned quantum

mechanics) entitled 'The coordination theory of the structure of ionic crystals' [*Z. Kristallogr.* (1928), **67**, 377] – which, strangely, is not included in this Selection. It is in this paper that Pauling enunciated his famous rules that, by their later brilliant application, enabled him to rationalize and determine the structures of complicated minerals (like mica, $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ or zunyite, $\text{Al}_{13}\text{Si}_4\text{O}_{20}(\text{OH})_{18}\text{Cl}$). Later, Sir Lawrence Bragg (*Atomic Structure of Minerals*, Cornell University Press, 1937, p. 35) said of one of these rules (dealing with electrostatic valence) that it, as well as other principles of coordination theory discovered by Pauling, may be termed the cardinal principle of mineral chemistry. 'It often accounts for the non-existence of certain types of compound, although the formulae of these compounds would be quite possible according to the ordinary laws of valency'. To this day, clay mineralogists and ceramists rely heavily on Pauling's rules and on the principles for isomorphous substitution that emerged from his parallel early crystallographic endeavours.

The selected paper (SP) which, according to the editor, Pauling himself regarded as his best is SP5 'The Nature of the Chemical Bond. Application of Results Obtained from the Quantum Mechanics and from a Theory of Paramagnetic Susceptibility to the Structure of Molecules' [*J. Am. Chem. Soc.* (1931), **53**, 1367]. This was revolutionary. In it the 30 year old Pauling explained the tetrahedral coordination of carbon and the square or octahedral coordination of transition-metal ions on wave mechanical principles. He introduced the concept of hybridization and his rules provided information regarding the relative strength of bonds formed by different atoms, the angles between bonds, free rotation or lack of free rotation about bond axes and a complete theory of the magnetic moments of molecules and complex ions. This paper was published on 6 April 1931. On 7 April, Pauling sent off a one page summary of that paper entitled 'Quantum Mechanics and the Chemical Bond' to *Physical Review*, who published it on 1 May. Such was the confidence, clarity and compelling urgency that animated Pauling in his early days – these qualities never deserted him.

Later papers (reproduced here, e.g. SP1 and SP22) explain how Pauling applied to chemistry the concept of resonance originally introduced by Heisenberg into quantum mechanics: 'It is found that there are many substances whose properties cannot be accounted for by means of a single electronic structure of the valence bond type,

but which can be fitted into the scheme of classical valence theory by the consideration of resonance among two or more structures'. Modern theorists nowadays tend to downgrade Pauling's devotion to resonance. But it must never be forgotten that the α -helix (based on the planarity of the amide bond) and the stereochemistry of carotenoids – to name but two of very many examples – would not have played such a prominent role in molecular biology were it not for this insight by Pauling. (It is relevant to quote what George Wald, the Nobel-Prize-winning biologist once said: 'One of the admirable things about Linus Pauling's thinking is that he pursues it always to the level of numbers. As a result there is usually no doubt of exactly what he means'). In his classic (SP23) 'The Size of Ions and the Structure of Ionic Crystals', the 26 year old Pauling has 19 tables (relating crystallographic data for numerous halides, nitrides, carbides, oxides and other chalcogenides); and in (SP10) 'The Calculation of Resonance Energy in Conjugated Systems', he unites quantum mechanical computation and thermochemical measurements on 12 condensed aromatic hydrocarbons. Elsewhere, as readers of *Acta* know, there are tabulations by Pauling of ionic, covalent and metallic radii – an invaluable source to solid-state and numerous other breeds of chemists.

There are three other major features of these volumes that make them such a joy to possess. First, there is the ready access to the numerous seminal innovations (and the context that led to their expression) made by Pauling into the phenomenology of the hydrogen bond; the residual entropy of ice; sickle-cell haemoglobin (a 'molecular disease' as he termed it); chemical paleogenetics (i.e. molecular 'restoration' studies of extinct forms of life) – this work inspired Pauling and Zuckerkandl to propose the existence of an evolutionary clock which ticks at the rate of about one amino acid substitution per hundred residues per 5 million years!; gas-phase electron diffraction, which he initiated with his student L. O. Brockway with a view to retrieving ultra-reliable bond distances in simple molecules; molecular complementarity (with Max Delbruck), which later proved to be the basis of DNA structure and replication; immunology and his ideas on how antibodies might adapt their structures to those of antigens; his insights regarding enzymes, in 1948, the year he produced the α -helix, he said at a Royal Institution Discourse (SP114) 'I think that enzymes are molecules that are complementary in structure to the activated complex of the reactions that they

catalyse, that is intermediate between the reacting substances and the products of the reaction'; and of the hydrogen bond he says in his classic 'The Nature of the Chemical Bond' – his Baker Lectures at Cornell University in 1936, reproduced in part here (SP22) – 'because of its small bond energy and the small activation energy involved in its formation and rupture, the hydrogen bond is especially suited to play a part in reactions occurring at normal temperatures ... (it) restrains proteins to their native configurations and I believe that as the methods of structural chemistry are further applied to physiological problems it will be found that the significance of the hydrogen bond for physiology is greater than that of any other single structural feature' – a remarkable prophecy made long before anything was known about protein structure.

Second, Pauling's style in presenting his science. His opening paragraphs fall into two categories: those that summarize in pellucid terms the centrally important and interesting facts or theories that he is about to present; and those that cite a stirring historical fact which immediately grips the reader. It is instructive to exemplify the second of these two stylistic techniques. Thus, the opening sentence of (SP37) 'The Structure of Chlorine Hydrate' (*Proc. Natl Acad Sci. USA*, 1952) begins 'In 1811 Humphry Davy showed that water is a component of the phase that had earlier been thought to be solidified chlorine, and 12 years later Michael Faraday reported an analysis that corresponds to the formula $\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ '. Pauling's paper with Stundivant (SP17) 'The Structure of Cyameluric Acid, Hydromelonic acid, and Related Substances' (*Proc. Natl Acad Sci. USA*, 1937) begins 'Over a century ago, in 1835, Leopold Gmelin prepared the substance tripotassium hydromelionate by heating potassium ferrocyanide with sulfur; he also made other salts of hydromelonic acid ... he recognised the similarity of the substances to the group of compounds discovered and named by Justus Liebig ...'. And the paper which Max Perutz later claimed had influenced him most, entitled 'The Magnetic Properties and Structure of Hemoglobin Oxyhemoglobin and Carbonmonoxyhemoglobin' (*Proc. Natl Acad Sci. USA*, 1936), opens thus: "Over ninety years ago, on November 8, 1845, Michael Faraday investigated the magnetic properties of dried blood and made a note 'Must try recent fluid blood'".

But, in addition to these memorable historical excursions, there are mellifluous accounts of a wide variety of other subjects,

my own two favourites being the beautifully concise picture he portrays (SP38) of 'The Structure of Water', and his magical introduction (SP123) to 'The Hemoglobin Molecule'. The first was presented at a Royal Society meeting in November, 1957; and J. D. Bernal's comment upon it – in view of the prominence Pauling gave to the centred pentagonal dodecahedron – was that 'this extremely elegant and ingenious theory of water structure, from its very nature, would not be the structure of a liquid at ordinary temperatures ... it may well, however, be the structure of vitreous water at low temperatures'. 'The Hemoglobin Molecule in Health and Disease' (SP123) summarizes a talk he gave to an audience of scientists and non-scientists at the *American Philosophical Society* in Philadelphia, April 1951. The opening paragraph again grips one: 'Hemoglobin is one of the most interesting chemical substances in the world – to me it is the most interesting of all. Each of us carries around with him his own supply, amounting to a pound or two, approximately one per cent of the body weight. This supply is in the red corpuscles of the blood. Hemoglobin is the pigment of the blood: it has a beautiful red colour in arterial blood, and a purple colour in venous blood. It is hemoglobin that gives a pink flush to our skin; we are pale when there is a deficiency of hemoglobin in the skin, either because of a general deficiency of the substance in the body, an anaemia, or because blood is driven from the skin to the interior of the body by the contraction of the blood vessels in the skin'. Was there ever a more enticing opening to a popular lecture?

Third, the Selection contains many papers on some unrelated subjects that, together with orthomolecular medicine, occupied much of Pauling's research time in the later years of his long and fertile life. One of these was his effort to model the atomic nucleus as a close-packed cluster of spherons (α -particles) and to account for nuclear properties, including fission (SP77), with this model. This was largely ignored by physicists, as was his model of superconductivity (SP78, SP79), based on the resonating valence bond theory of metals (SP31). As the editors rightly state (p. 459), in the controversy over quasicrystals, discovered by Shechtman *et al.*, Pauling took on, ironically, the role of the conservative, defending (SP80, SP81) classic crystallographic thinking against the radical ideas of the quasicrystal advocates who ultimately carried the day. Even to the last, he had the knack of choosing a gripping title and writing a tantalizing summary, as evidenced by the *Physical Review Letters*

paper (SP81), written in his 86th year, entitled 'So-called Icosahedral and Decagonal Quasicrystals are Twins of an 820-Atom Cubic Crystal'.

I commend this Selection unreservedly.

John Meurig Thomas

Davy Faraday Research Laboratory
The Royal Institution of Great Britain
London W1S 4BS
and
Department of Materials Science
University of Cambridge
Cambridge CB2 3QZ
England

Sir John Meurig Thomas is a recent winner of the Linus Pauling Gold Medal.

On quaternions and octonions: their geometry, arithmetic and symmetry. By John H. Conway and Derek A. Smith. Natick, MA: A. K. Peters Ltd, 2003. Price USD 29.00. ISBN 1-56881-134-9

This book consists of three chapters of increasing length, dealing with complex numbers, quaternions and octonions, respectively. I shall concentrate my review on the first two chapters, where the connection with concepts familiar to crystallographers is made.

In the introductory chapter on complex numbers, the authors show that the complex units correspond to rotations in two-dimensional space and they determine the finite subgroups of the special and general orthogonal group in two dimensions. Then they discuss definitions of complex integers with unique factorization into products of primes, the simplest of which, Gaussian and Eisenstein integers, correspond to the square and hexagonal lattice, respectively. Finally, they reproduce Polyá's famous illustration of the 17 types of two-dimensional space groups. Instead of the usual symbols for these groups, 'orbifold symbols' are given, of which only a summary definition appears in the book.

Whereas for complex numbers the terms norm, unit and complex conjugate are defined, they are taken for granted in the case of quaternions. It is shown that there exists a 2-to-1 homomorphism from the group of unit quaternions to the group SO_3 of rotations in 3-dimensional space. The finite subgroups of SO_3 are derived using spherical trigonometry, similar to that done

in the book *Geometric Symmetry* by Lockwood & Macmillan (Cambridge University Press, 1978). The transition to the finite subgroups of the group of unit quaternions is mentioned only briefly. More space is devoted to the derivation and listing of the finite subgroups of the general orthogonal group GO_3 . These are the well known (generally non-crystallographic) point groups listed also in Volume A of *International Tables for Crystallography*. Various kinds of symbols are used to denote these point groups, one resembles the Schoenflies notation whereas the orbifold symbols resemble the Hermann-Mauguin notation.

It is then shown that a 2-to-1 homomorphism exists between ordered pairs of unit quaternions and SO_4 . Names characterizing the finite subgroups of SO_4 are introduced; in the case of polyhedral groups, also modified Coxeter symbols are given. The authors claim that they have for the first time given unique names to all finite subgroups of SO_4 . They explain the various types of chirality shown by subgroups of SO_4 . Finally, Hurwitz and Lipschitz integral quaternions are defined and their factorization into products of primes is discussed.

The book has been written by two mathematicians. A great advantage is that it is written in a style that makes it easily accessible also to other scientists. The main messages are clearly stated, not buried under technical details. The book is carefully written; I noted only few misprints: In Figure 2.1, z_0^3 and zz_0^2 are shown instead of z_0^2 and zz_0 ; the orbifold symbols 3^*2 and $*332$ are exchanged in Table 3.1; the alternative symbols for 2^*12 and 2^*30 have wrong subscripts in Table 3.2: $\bar{v}qv$ should be replaced by $\bar{q}vq$ in the title of the Appendix on page 40.

The authors do not state for what readership they have written the book. Although it cannot serve as a basic text for crystallographers, I enjoyed reading it and added Hermann-Mauguin symbols to many tables and figures. Looking at the title of the book, I had hoped that it might also discuss the use of quaternions to derive the coincidence misorientations of cubic lattices, which is not the case. Instead it gives the 17 types of two-dimensional space groups and the finite subgroups of GO_3 , which seem to me less closely related to quaternions.

Hans Grimmer

Laboratory for Neutron Scattering
ETH Zürich and Paul Scherrer Institut
CH-5232 Villigen PSI
Switzerland
E-mail: hans.grimmer@psi.ch