Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

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.

Crystal structure analysis. Principles and practice. Edited by William Clegg. IUCr Texts on Crystallography, 6. New York: Oxford University Press/International Union of Crystallography, 2002. Pp. xiv + 265. Price US$ 90.00, GBP 49.50. ISBN 0-19-850618-X.

According to the preface, this textbook was developed from the contents of a biennial Intensive Course in X-ray Structure Analysis, sponsored by the British Crystallographic Association between 1987 and 1999. The editor and the other three contributors (A. J. Blake, R. O. Gould and P. Main) were the principal lecturers in the 1999 course, and the book reflects its origin in extensive course notes, refined over years of use.

The book is very well written, has an excellent organization of material and is filled with many illustrative examples of the subject matter. The subject matter spans all of the basics of small molecule crystallography, from crystal growth and intensity data collection to structure solution, refinement, and derivation and interpretation of results. Only four-circle serial diffractometers and instruments with area detectors are discussed, no photographic methods are covered, and it should be noted that there is essentially no coverage of macromolecular crystallography. An outstanding feature is the inclusion of numerous pertinent problems at the end of most chapters, with answers provided in Appendix 3. Another good aspect is the strong emphasis on structure refinement and the assessment of quality and accuracy of results.

A summary of the book's contents, with brief discussion, follows. An overview of the entire crystallographic structure determination process is presented in Chapter 1. It includes discussions of scattering from electrons, atoms and crystal lattices; structure factor and electron density equations, Bragg's Law, resolution and the phase problem.

The established standard crystal growing and mounting techniques are surveyed in Chapter 2, as well as how to evaluate crystal quality by both microscopic and diffraction examination.

Symmetry operations, point groups, crystal systems, crystal morphology and space groups and their symbols are discussed in Chapter 3, together with space-group determination from systematic absences, $E(hkl)$ values and the statistical distribution of diffraction data. A useful table of the 23 most frequently encountered space groups is provided.

Chapter 4 provides the background for the diffraction process. It includes a derivation of Bragg's Law, the development of the reciprocal lattice, the use and determination of orientation matrices in diffractometry, and the derivation of symmetry from the diffraction pattern. Kappa geometry is briefly discussed, but without diagrams. Data collection using four-circle diffractometers is discussed in Chapter 5. Topics in the first half include choosing the appropriate radiation, the advantages of crystal cooling in data collection, searching for and indexing initial diffractometer reflections, and obtaining a good orientation matrix and accurate cell parameters. The rest of the chapter is devoted to how to collect accurate data, set scan type, width and speed; detector aperture, weak reflections, and checking and reorientation of intensity standards. Two final sections deal with systematic errors in data and possible means for correction. Of course, one feels the need to comment that the methodology in this chapter has been largely supplanted by area detector technology, which is discussed in Chapter 6. That chapter opens with an interesting brief history of area detectors and a comparison of photographic methods with area detector technology. There is a valuable table comparing the advantages and disadvantages of area detectors *versus* conventional serial diffractometers. All the typical area detectors are included: multiwire proportional chambers, phosphors coupled to a TV camera, image plates and charge-coupled devices (CCDs). Characteristics and associated data-correction needs of area detectors in general are outlined, including spatial distortion, nonuniform density response, bad pixels and dark current corrections. A typical area-detector experiment is outlined in the last section.

Fourier syntheses are introduced in Chapter 7, beginning with one- and two-dimensional examples and proceeding to three-dimensional syntheses in Patterson and real space. The basic mathematics of Patterson functions are discussed in Chapter 8, followed by a description, with examples, of the heavy-atom method. The use of Patterson search methods is introduced.

The various constraints on electron density are presented in Chapter 9 as a basis of direct phasing methods. The calculation and statistics of normalized structure factors are discussed. The use of the largest $E(hkl)$ in phase estimation and initial electron density map production is presented. Chapter 10 is a brief but well illustrated presentation of the basic ideas of maximum entropy.

Least-squares fitting of parameters is discussed in Chapter 11, which covers the mathematics and principles involved in refinement of a derived structure: weighted mean, linear regression, variance–covariance, restraints, constraints and the application of non-linear least squares. Practical aspects of structure refinement are covered in Chapter 12. Factors to be considered in finding the best fit of structure model to measured data are presented: (i) use of $|F|$ *versus* F^2, (ii) least-squares weighting schemes, (iii) atomic parameters and scale factors, (iv) treatment of H atoms, (v) constraints–restraints and (vi) thermal displacement parameters. Lastly, disorder, twinning and absolute structure are discussed.

The derivation of results is treated in Chapter 13. The statistical background for structure determination is thoroughly discussed, including distributions, sampling, estimated standard deviations, correlation and covariance, agreement between observed and calculated data, thermal motion. Chapter 14 treats the interpretation of results. The use of statistics is presented: comparison and averaging of geometrical parameters, planarity of groups of atoms, and comparison of different structures. Systematic data errors are considered: absorption, extinction, thermal diffuse scattering, instrument calibration errors. Possible errors in the model are discussed: scattering factors, constraints–restraints, incorrect symmetry, high thermal motion and wrong structures.

Chapter 15 is an extensive discussion of graphical and tabular presentation of struc-

tural results. It's last section discusses archiving of final results. Chapter 16 gives an excellent introduction to the preparation and use of the CIF and Chapter 17 lists the various crystallographic databases with primary emphasis on the Cambridge Structural Database. Chapter 18 deals with twinning, anomalous dispersion and X-ray sources.

Three appendices present mathematics and formulae, a crystallographic dictionary, and answers to exercises.

This textbook should definitely be considered for use in introductory courses in X-ray structure determination as it provides a good framework for course organization. The concise treatment of the material (all of small-molecule X-ray crystallography in 265 pages) will work well when supplemented with lectures and additional class discussions.

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Perovskites modern and ancient. By Roger H. Mitchell. Thunder Bay, Ontario: Almaz Press, 2002. Price USD 70.00. ISBN 0-9689411-0-9

Perovskites, whose general formula is given by ABX_3, where A and B are cations and X is an anion, form a very important class of inorganic crystals whose physical properties are extensively used in many technological applications. These generally arise from the large range of pseudosymmetrically related crystal structures. The basic, so-called aristotype structure, consists of an infinite array of corner-linked anion octahedra, with the A cations in the spaces between the octahedra and a B cation at the centre of each octahedron. This structure can then be altered by allowing the cations to move away from their central positions, either together, in which case one has polar structures, or antiparallel. In addition, the octahedra can tilt about different directions, giving rise to multiple unit cells, and they can be distorted. For the crystallographer they are a delight as the vast range of structures can furnish a lifetime of study.

What is surprising is that, apart from one text published by F. S. Galasso many years ago, no-one until now has put together a complete account in English on this intriguing family of structures. There was a good treatment written in Russian by K. S. Aleksandrov and B. V. Beznosikov in 1997, but as far as I know it was not translated into English. This new book by Roger Mitchell addresses this gap in a such a splendid manner. The book is dedicated to my old boss, Dr Helen D. Megaw, who pioneered so much of our knowledge of the perovskite structure: personally, I feel that the author could not have chosen a better person. This is the book that I wish I had written!

So what about the book itself? The first thing that strikes one is the quality of the production. This is a book in which colour has been used to considerable good effect – almost a work of art. It is, put simply, a beautiful book, and the author has obviously worked extremely hard to present his subject in as clear and as eye-catching manner as possible. But I should emphasize that it is not just a matter of presentation that makes this book so worthwhile. Roger Mitchell has in fact produced such a thorough, well researched description of all aspects of the perovskite structure that I believe it will become a classic in this field. It is stuffed full of factual material, lavishly illustrated and informative. However, having waxed lyrical about this book, I hope the author will forgive me one gripe. There is no subject index, the author preferring instead to point to an extended table of contents. This is a pity as it makes it hard to look up particular items. For instance, I had difficulty in trying to locate a discussion of incommensurability in these structures.

The book consists of ten chapters in a nice logical sequence. It begins with a description of the ideal structure and related compounds, and then proceeds to describe how this structure can be altered, using geometric and structural principles. The author makes much use of the concept of octahedral tilting to explain the many structural types as well as the effect of cation displacements. A really nice feature is the inclusion of many powder diffraction diagrams to illustrate how one can distinguish between the types, including close-ups of particular diffraction peaks to illustrate splittings distinguishing symmetries. Chapter 3 considers what happens on mixing perovskite compounds to form solid solutions, and Chapter 4 discusses cation ordering, both at the A and B sites. Following this, non-stoichiometric perovskites, *i.e.* those with vacancies and defects, are described.

Subsequent chapters cover related materials, such as hexagonal perovskites, layered perovskites, including those familiar to scientists working on high-T_c superconducting phases. Finally the effect of high pressure on silicate perovskites and naturally occurring perovskites are dealt with. These last two chapters will be of prime interest to earth scientists, since perovskites such as $MgSiO_3$ form large parts of the earth's mantle.

Summarizing then, this book should be read by everyone interested in perovskites, or for that matter, inorganic structures in general. It is bang up-to-date, and as such it is a vital reference in the field. I am delighted to have a copy and it will occupy pride of place on my bookshelf for a very long time.

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books received

The following books have been received by the Editor. Brief and generally uncritical notices are given of works of marginal crystallographic interest; occasionally, a book of fundamental interest is included under this heading because of difficulty in finding a suitable reviewer without great delay.

Fundamentals of solid-state phase transitions, ferromagnetism and ferroelectricity. By Yuri Mnyukh. Bloomington, IN: 1st Books Library, 2002. Price USD 23.95 (hardback), USD 18.95 (paperback), USD 16.95 (electronic book 8350k). ISBN 0-75960-219-0. Theory and experiments on solid-state phase transitions, especially relating to ferromagnetism and ferroelectricity, have a very long history. They are documented and discussed in substantial books and a voluminous literature. This review of the subject, following a Critical Survey, has chapters on the Molecular mechanism of solid-state phase transitions, 'Lambda-anomalies' and other apparent anomalies, and Fundamentals of ferromagnetism and ferroelectricity. Throughout the text there are conventional and alternative descriptions offered of these phenomena as well as six appendices describing earlier debates.