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book reviews

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Mathematical techniques in crystallography and materials science. Third edition. By Edward Prince. Pp. vii + 224. Berlin and Heidelberg: Springer-Verlag, 2004. Price EUR 39.95 (soft cover). ISBN 3-540-21111-X.

The first edition of this book was published about 20 years ago. It is based on the rich experience from the extensive research performed by the author over many years. The carefully selected topics concern common and less familiar mathematical procedures used in structural crystallography. The book is intended to provide a tutorial and a practical guide to novices, and a review to professionals on the theoretical background and on the advantages and disadvantages of the applied numerical procedures.

The book is divided into nine chapters. The first five chapters develop the appropriate mathematical tools related to basic geometrical and algebraic components of structural crystallography. Chapter 1 is devoted to matrices, their definitions and fundamental operations. Chapter 2 treats point-group symmetry while Chapter 3 discusses space-group symmetry. Vectors and tensors including their definitions, algebra and important examples are dealt with in Chapters 4 and 5.

The next several chapters study the mathematics underlying data-fitting problems and modelling. In Chapter 6, the form and the general features of the function of adjustable parameters, whose minimum value corresponds to the best fit of the data, are discussed in greater detail than usually appears in treatments of model fitting. Various fitting algorithms, their robustness and resistance are presented and compared. In the subsequent two chapters, the author considers different methods of evaluating the precision and accuracy in structural experiments. Finally, Chapter 9 focuses on different techniques that may be used to apply constraints to crystal structure refinements.

The book closes with a short bibliography, a subject index and several appendices, the last of which contains Fortran source codes of subroutines including important statistical distribution functions.

The first edition of the book is reviewed in detail by R. Diamond [*Acta Cryst.* (1984), A**40**, 86–87]. The overall estimation of the book is positive apart from the several inconsistencies discussed by the reviewer. However, with one of them I completely disagree. It refers to the character tables of the point groups (Chapter 2) which for the reviewer remain 'the biggest mystery'. Obviously, he has not recognized that the listed data refer to the irreducible representations of the point groups and not to their vector representations which in general are reducible ones.

The slightly enlarged second edition of the book appeared in 1994. The author made corrections and clarified a number of points. Two additional topics were treated: a section on the projection matrix and its use in studying the influence of individual data points, and a new chapter with a very clear presentation of the method of fast Fourier transform. The review of the second edition by Ewa Gałdecka [*Acta Cryst.* (1995), A**51**, 590] concentrates mainly on this new chapter.

The third edition of the book appeared recently. According to the author, it does not represent considerable changes from the contents of the second edition. Apart from the corrections, the author has included further explanations on a few topics, namely, the eigenvalue problem of a 3×3 symmetric matrix and the method of conjugate gradients, which is a variation of the method of steepest descents. It is applied to the search for the minimum of the function of adjustable model parameters. One of the main advantages of such numerical procedures is that it is not necessary to construct and invert the entire Hessian matrix in each iteration. These methods usually use the gradient of the function to be minimized as a search direction in the multidimensional parameter space. However, the method of steepest descents is efficient only when the eigenvalues of the Hessian matrix are of the same order. Otherwise, the method is rather slow and it is not guaranteed to converge to a minimum in a finite number of steps. The inefficiency of the method is due to the fact that the consecutive search lines are always perpendicular to the previous ones but only the current steepest descent direction is used. By contrast, the method of conjugate gradients takes information from previous steps into account. The method is guaranteed to find a minimum of a quadratic function in no more than p steps, where p is the dimension of the parameter space.

In my opinion, one of the main strengths of the book is its clear and pedagogical presentation. The reader benefits from the author's clear grasp of what he wishes to say and care has been taken that the essence of the topic is presented in an educational and concise fashion. Part of the heavy mathematics is truncated or greatly abbreviated since the algebraic details (available elsewhere) can often obscure the salient facts. The author offers the reader a number of illustrative examples and graphical presentations that add a qualitative perspective on the treated problem. Limits in the applications of the numerical procedures are carefully discussed and there are frequent calls for caution in the interpretation of the results.

However, the book is not free from some small imperfections. The text has been composed by the author himself, using LaTeX, resulting in a few typographic errors, although none of them serious.

Further, the user may find some notation confusing as it differs from the usage adopted in *International Tables for Crystallography*, Volume A (hereafter referred to as *IT*A). The author uses a 1×3 column-matrix presentation of the basis vectors in direct space (*e.g.* last section of Chapter 2). A user accustomed to the *IT*A notation (direct-space basis vectors as 1×3 row matrices) should apply transformation matrices transposed to those listed in Appendix *C* in order to generate the superlattices of order two, three and four. Additional misunderstandings could occur as there is no indication that the listed matrices refer to primitive bases only.

Another example of similar nature can be found in Appendix *F* where the elements of specific tensors of rank two, three and four (after imposing the corresponding symmetry restrictions) are given. However, some of the listed data are either incomplete or

could be at least misleading. Two examples: (i) it would be helpful if it were specified that the given form of the third-rank piezoelectric tensor for the point group 2 (and m) refers to a special orientation of the twofold axis (and the plane m), and how the form of the tensor can change for different orientations; (ii) there is only one listed entry for the elasticity fourth-rank tensor for the tetragonal system while one has to distinguish between two tensor forms: one for the point groups $4mm$, $\bar{4}m2$, 422, $4/mmm$, and the other for the point groups 4, $\bar{4}$, $4/m$.

I would add that it is a pity that in the present third edition the author has not used the opportunity to update the presentation of *IT*A (Chapter 3) in accordance with the new fifth edition of the tables or to improve the quality of some of the figures (*e.g.* Fig. 2.1).

Leaving these defects aside, I believe that the book will be useful both to graduate students in physics, chemistry and engineering who have an interest in structural crystallography and to experts seeking a review of numerical methods and implementation strategies. A great advantage of the book is that it is written in a style that makes it accessible also to material scientists whose background does not include structural crystallography. The main messages are clearly stated and not buried beneath technical details.

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Crystal structure determination. Second edition. By Werner Massa. Pp. xi + 210. Translated into English by Robert O. Gould. Berlin: Springer, 2004. Price EUR 44.95, USD 49.95. ISBN 3-540-20644-2.

This textbook, *Crystal structure determination*, is a translation by Robert O. Gould based on the third German edition of *Kristallstrukturbestimmung* by Werner Massa of the University of Marburg, Germany, published in 2002. This new edition in English has been updated from previous editions, particularly in the chapter on experimental methods. It is an excellent teaching text, highly recommended, particularly for those interested in the general principles of this experimental technique and its application to small-molecule crystallography (although the general principles described here are similar for all sizes of molecules). The chapters are short and to the point (179 pages, plus a worked example). The translation is excellent and I understand that the translator worked with the author in order to clarify certain portions of the text. Different students have different needs for the amounts of mathematics used in a textbook of this kind. I recommend they try this text as it contains a medium amount of mathematics.

Initially, we are introduced to crystals and crystal lattices. It seems that not enough emphasis is given to examining the symmetry of the crystal when determining which crystal system it belongs to, although the problem of β near 90° in a monoclinic crystal (which could be mistaken for orthorhombic) is discussed. The descriptions of centered, hexagonal, trigonal, rhombohedral and reduced unit cells, however, are excellent. Then the geometry of X-ray diffraction is described. The reason the characteristic spectral lines are obtained plus a background of white radiation is explained, as is how to select and collimate one component only (usually $K\alpha$). Diffraction is then described, starting with a one-dimensional lattice and proceeding to the Laue equations and the indexing of lattice planes, and finally presenting the Bragg equation and how to calculate scattering angles of diffracted beams if the unit-cell dimensions are known. Then follows a description of the reciprocal lattice that the student should find very helpful. I found this chapter particularly clear. In the chapter on structure factors, I particularly liked the description of what happens to the diffraction pattern as more and more atoms are added to the unit cell.

In the chapter on symmetry, the essentials are described clearly with some fine figures to illustrate each topic. Interestingly (and successfully), the author starts with space groups and then proceeds to Bravais lattices and crystal classes (although the two latter were also mentioned earlier in Chapter 2). I thought the section on space-group determination was very helpful, but the section on group–subgroup relationships was somewhat hard to follow and could have been expanded, for example, by a more comprehensive figure.

The newly expanded chapter on experimental methods will be of great use to students. Some useful recipes for crystallizing small molecules are given. Advice on crystal size, choice of radiation and what to do if the crystal is unstable is given for small molecules only. The various useful film methods are described – again I would have liked more information in the figure captions. There is a good section on reflection profiles and scan types (as seen with the four-circle diffractometer). This involves a discussion of mosaic structure and which portion of reciprocal space needs to be measured (thereby teaching again about symmetry). While nothing is written about the crystallization of macromolecules, the section on area detectors (used now also for small molecules) is highly recommended for all crystallographers. Charge-coupled-device (CCD) systems and image plates are nicely described. The photographs of diffraction and equipment are good. Neutron diffraction is also touched on. There is an excellent treatment of accuracy and estimated standard deviations and absorption coefficients.

The chapter on structure determination begins with the Patterson function. The extension to macromolecules is briefly mentioned, including the multiple isomorphous replacement (MIR) and multiwavelength anomalous dispersion (MAD) methods. Again the diagrams need more explanation. It is nice to see Harker–Kasper inequalities (Section 8.3.1) and the Sayre equation (Section 8.3.3) given prominence. Then follows the work of Karle and Hauptman for which the 1985 Nobel Prize was awarded. I am not sure that the left side of Fig. 8.4*b* is correct. There is a good description of strategies of phase determination. The author gives information on the programs available and also describes what all the terms derived in these programs are. So there is a good mixture of theory and practice in this chapter, which should help students.

In the chapter on structure refinement, it is stressed that there are errors in both the model and the data and this is an excellent fact to stress. It is pointed out how important the advances in computing power have been for X-ray crystallographic research, especially structure refinement. Problems with hydrogen atoms (bond lengths, isotropic refinement only) are also touched on. The refinement of rigid groups is described, as is Rietveld refinement of powder diffraction data.

In a chapter entitled *Additional topics*, the author tackles disorder in crystals. This was most interesting to me. He describes how to refine such a model with disorder, *e.g.* orientational disorder, and also the problem of dynamic and static disorder. He also mentions the crystal defects that occur on increasing the temperature, together with one- and two-dimensional disorder, modu-