

Solution of the Phase Problem. I. The Centrosymmetric Crystal. A. C. A. Monograph No. 3. By H. HAUPTMAN and J. KARLE. Pp. xvi +87 with 3 figs. Wilmington: The Letter Shop. Price \$1.50.

The statistical study of the structure factors and intensities of the X-ray reflexions from a crystal during the last few years has shown that more information lies latent within the weighted reciprocal lattice than was at first realized. The extraction of this information has been successfully demonstrated in suitable examples. In this monograph the statistical approach has been used in an attempt to find expressions for the probability that the sign of a structure factor of a centrosymmetric structure is positive or negative. This probability for a single structure factor had already been shown to be symmetrical about a mean value of zero (except for low-order reflexions). These authors, however, demonstrate that the joint probability that several structure factors should have the observed values is no longer symmetrical, and they proceed from these joint probabilities to obtain expressions intended for routine sign determinations.

The problem is approached as one in multivariate statistics, the variates being the contributions made to the structure factor by each group of crystallographically equivalent atoms, and the joint probabilities involve several of the mixed moments of these variates. These mixed moments have non-zero values only for certain groups of reflexions, and the study of these groups occupies a substantial and important part of the monograph. The joint probabilities within each of these groups take on distinct forms, and several of the simpler and more useful are derived and their use is illustrated. Two of the relations suggest that for certain groups of reflexions the signs of one set are deducible from the intensities only of a second set. These may be termed the introductory relations. Although in principle they can always be used, they are only available for finding the signs of reflexions with all indices even. Another relation is analogous to those of Sayre, Cochran and Zachariasen, while the remainder involve both intensities and structure factors. These, therefore, cannot be used until a sufficient number of signs has been determined reliably from the introductory relations.

The central significance of this problem in X-ray structure analysis has caused this monograph and its claims to be scrutinized eagerly by practising crystallographers. They have naturally approached the new relationships with close attention to their structural and geometrical implications, and with varying degrees of success and precision they have reached similar conclusions and have provided physical interpretations for some of the new relations. The introductory relations unfortunately yield comparatively few signs, and these constitute a very shaky foundation upon which to build with the other relations. Furthermore, as Vand & Pepinsky have shown, there is a considerable probability of converging on a solution which is closely akin to the Patterson function. This is a consequence of working with the mixed moments which are very sensitive to correlations between the variates—very much more so than in the statistical theories previously developed. Correlations of a sort are all too common in practice, but the formal analytic procedure adopted in this monograph ignores them and

is so involved and general as to make it almost impossible to discern, even qualitatively, how the relations are likely to be affected by such correlations. It cannot be too strongly emphasized that *all* the information present in the weighted reciprocal lattice goes into the Patterson function, and statistical procedures are only convenient ways of extracting some of the information. No statistical conclusions should ever be drawn in a practical problem without full consideration of the implications of the Patterson function and any structural peculiarities that it reveals.

The fact that later workers have been able to derive the introductory relations (in some cases in more powerful form) by shorter and more direct methods should not detract from the credit due to Hauptman and Karle for their discovery. Their contribution has focused attention on new approaches to the phase problem and cannot fail to stimulate much valuable new work. A careful study has recently been made by Cochran & Woolfson, who conclude that within the limits imposed by the series expansions the analysis in this monograph is correct, but that the interpretation put on the results is not always valid. The circumstances under which the relations are valid, and the practical utility and power of the methods based on them, all remain to be assessed, since the two examples so far adduced, naphthalene and colemanite, are so special that they scarcely reveal the true scope of the methods. Furthermore, where, as here, the structures can be solved by proven direct methods, the practising crystallographer will prefer the latter, and will only resort to new 'blind' methods if it can be proved either that they will solve structures that have hitherto defied solution, or that they are quicker or more reliable than the classical methods. This is a policy of prudence rather than of prejudice; he cannot forget that the road of progress in structure analysis is littered with ingenious ideas which did not live up to the confident claims made for them, usually because when they were applied to real problems they proved to be little or no more powerful than the existing methods. They have added to our insight and, in a more modest way, have had their practical uses. One hopes sincerely that if this is a solution it will be both general and practicable and that the authors' claims will be justified; but even if not, this work will deserve a conspicuous place in the history of our art because of the more intimate understanding of the phase problem we have gained from it.

One conclusion that will disappoint the student of natural products (which are so often optically active) is that if these methods are restricted to a single centric zone the relations reduce to equivalents of the Harker-Kasper inequality and the Sayre-Cochran relation, and so offer nothing new.

The book is reproduced clearly from typescript, and actual misprints are few and unimportant. The reviewers feel, however, that the notation could have been simplified. In places it is unnecessarily confusing: for example, in Chapter 3 m is used to represent both a moment and a variable of enumeration within the same equation.

The publishing of original research contributions in monograph form rather than in the usual journals is perhaps understandable in this case, in view of the length and importance of the material. It is, however, to be deprecated, partly because such a format lends an aura of finality and proven worth to what is in fact a research

contribution offered for general discussion and assessment by practising crystallographers, partly because it bypasses the usual safeguards of impartial refereeing, but chiefly because such format requires a review.

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X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials. By H. P. KLUG and L. E. ALEXANDER. Pp. xiii+716 with 325 figs., 94 tables and 9 appendices. New York: Wiley; London: Chapman and Hall. 1954. Price \$15.00; £6.

In step with the spectacular growth of X-ray crystallography, a number of valuable books have recently been written. It remains, however, a rare event for a book to appear which is new in scope and which can be recommended to numerous readers with diverse interests. Both these attributes apply to this volume. The reviewer indeed supports the authors' contention that the book should appeal to those who must acquire crystallographic knowledge and skills through their own efforts. It should interest industrial plant technologists (the reviewer's interpretation of 'plant workers'), science graduate students, research scientists, as well as group leaders and research directors in industry.

Let us examine how individual chapters will appeal to this wide range of readers. The first 160 pages consist of three introductory chapters: 1 'Elementary Crystallography', 2 'The Production and Properties of X-rays', and 3 'Fundamental Principles of X-ray Diffraction'. For plant technologists they are rather formidable, and science graduates and research workers should turn first to other text-books such as those referred to by the authors. Perhaps these chapters are best suited to group leaders and research directors for whom they would probably supply revision of university curricula.

Chapter 4 on 'Photographic Powder Techniques' is written for the experimental research worker, who might in places welcome even more detail, such as on high-temperature and micro-cameras. Summaries of this and other chapters would have added to the usefulness of the book.

Chapter 5 'Spectrometric Powder Technique' (the internationally agreed word 'diffractometric' would be preferable) is one of the most valuable of the book. Again it is addressed primarily to the practising research scientist for whom fuller discussion of some topics, notably proportional counters, seems desirable.

Chapter 6 'The Interpretation of Powder Diffraction Data' will appeal to all readers. Plant technologists and research directors may wish to omit some details such as on indexing methods. This very subject, however, could have been more fully treated for the research worker. It would be instructive to set some representative problems

on indexing to two teams working competitively and using respectively methods described in the book and those only referred to. If the latter team were to win, as the reviewer suspects, a change of emphasis would be indicated.

Chapters 7 'Qualitative and Quantitative Analysis of Crystalline Powders', 8 'The Precision Determination of Lattice Constants from Powder Photographs' and 9 'Crystallite-Size Determination from Line Broadening' strictly speaking still fall under the title of Chapter 6. They, too, are admirable accounts of these most important topics and will be appreciated by all readers.

Chapter 10 'Further Applications of Polycrystalline Diffraction' really deals with stress determinations (not 'measurement') and preferred orientation. The applications to the industrially important high-polymer field would have deserved fuller description.

Chapters 11 'Diffraction Studies of Non-Crystalline Materials' and 12 'Small-Angle X-ray Scattering' are self-contained summaries of these fields, which very properly fit into this volume because they refer to the X-ray crystallographic study of materials that at first sight do not lend themselves to the experimental procedures discussed elsewhere in the book.

The appendices are helpful though not intended to replace the use of the *International Tables for X-ray Crystallography*. The subject index is adequate when used in conjunction with the table of contents. Printing and paper are superb, but they necessarily make the volume rather heavy. Considering that this is a first edition of a novel and large text-book, it is great credit to the authors that errors and misprints are revealed only on close study. The reviewer singled out the author index for fairly close scrutiny and noticed that the initials of Arndt, Prins and Rinn are wrong, that the spellings of Matthews, Müller, Schäfer, Waite and Zernike are incorrect, and that Cox appears in the wrong alphabetic order.

The achievements of the authors overshadow all criticism. They have written the first comprehensive and up-to-date text-book dealing with those crystallographic subjects on which the great majority of technological applications depend. It is no secret that another group of crystallographers—of whom the reviewer is one—has been independently engaged in writing a similar text-book. The present authors must be congratulated on their priority of publication and the conviction might here be expressed that the two volumes will find complementary rather than competitive use.

The price of the present volume might be excessive to individuals but not to libraries in industrial and academic establishments; for, just as chemical analytical methods have established themselves during the past fifty years as indispensable to virtually all research investigations, so it will soon be unthinkable for major research projects to be embarked on without the aid of the crystallographic methods described in this book.

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