

(except for the intrusion of a chapter on twinning) is devoted to chapters of more specifically mineralogical or geological interest: mineral formation in nature, mineral synthesis, crystal growth (but without any reference to the important recent work on this subject), gem stones, colour, luminescence and fluorescence, the core of the Earth, the occurrence of gold, platinum and iron in the Earth's crust (twice as much space is devoted to this topic as to crystal optics), meteorites, and methods of mineral identification.

In spite of its title and the recommendations on the wrapper, the book gives a distorted picture of the field of modern crystallography. There is no mention at all of the structures of metals or molecular compounds, and the general reader might well be excused if he formed the impression that crystals are to be found only in the mineral kingdom and that their study has been almost exclusively confined to German-speaking scientists.

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### The Statistical Approach to X-ray Analysis.

By V. VAND and R. PEPINSKY. Pp. xvi+98. State College: X-ray and Crystal Analysis Laboratory of the Pennsylvania State University. 1953. Price \$1.50.

The solution of the phase problem is the rainbow's end which those interested in the theory of crystal-structure analysis have been pursuing for a long time now. The statistical approach of Vand & Pepinsky represents an important step in the right direction. They sensibly refrain from claiming that they have found a pot of gold; in fact an important part of their book is devoted to showing that all is not gold that is published by the American Crystallographic Association. The present research monograph will be read with interest and profit by all concerned with research on crystal structures. It is certain to stimulate further work: in fact the authors suggest enough undeveloped lines of exploration to keep us all busy for a long time.

Part I examines the Hauptman & Karle probability distribution function for interatomic vectors but concludes that the new representation gives little more information than a Patterson function. Parts II, IV and VI demonstrate, both theoretically and by means of numerical examples well illustrated with X.R.A.C. maps, that the Hauptman & Karle method of obtaining signs from the intensity distribution alone, depends, in effect, on equating a crystal structure to a modification of its Patterson function, or the square of the latter, or a section through it. The limitations of this procedure are clearly demonstrated.

Parts III and VIII show how the distribution of  $U_h$  and of  $U_{2h}$  can be found by a semi-empirical method when the unit cell contains  $N$  equal atoms distributed at random. The results presented are most interesting and unexpected; for example for a given value of  $U_h$  there is a range of values which  $U_{2h}$  cannot assume, quite apart from the well-known restriction imposed by

Harker-Kasper inequalities. The way in which Fig. 2 can be obtained from Fig. 1 is unfortunately described in rather a cryptic fashion.

In the remaining sections (there are eleven in all) the authors develop the connection between the 'statistical approach' and the Patterson function, and derive formulae which give the probability that the sign of a structure factor is positive, or that it is equal to the product of the signs of two related structure factors. This is done in some detail for a number of commonly occurring space groups and some very interesting results emerge. Their relation to those obtained by Hauptman & Karle is discussed. A suggestion is made for increasing the usefulness of the conventional Patterson-Harker section.

The text is free from small random errors (apart from a few noted on an errata sheet) and the general style is clear. The same cannot be said of many of the mathematical derivations, however. The authors always treat the mean and the root-mean-square of a function as if they were equivalent. This leads them to make some quite incorrect assumptions. For example, the following objections can be made to the derivation of  $P_+(U_{2h})$  on p. 46. (1) The distribution of values of  $(U_{2h} - NU_h^2 + 1)$  is far from gaussian, since  $U_h$  has itself a gaussian distribution. (2) The distribution function

$$P = \exp \left[ -\frac{1}{4}(U_{2h} - NU_h^2 + 1)^2 \right]$$

cannot in any case give the distribution of values of  $U_{2h}$  for a fixed value of  $U_h^2$ , as is tacitly assumed. To prove this, it is only necessary to put  $U_h^2 = 0$ , when the distribution  $P$  predicts a most probable value for  $U_{2h}$  of  $-1$ , a value which is contradicted both by experience and the authors' Fig. 2. Nevertheless, the reviewer considers that, by a cancellation of errors, the final expression for  $P_+(U_{2h})$  is correct, as after a severe tussle he was able to derive it in another way. The authors have not been so lucky on p. 71. In this case a similarly incorrect derivation has led to an incorrect result, equation (11). A revision of many of the derivations would enhance the value of what is already an excellent piece of work.

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### The Crystalline State. III. The Determination of Crystal Structures.

By H. LIPSON and W. COCHRAN. Pp. ix+345 with 305 figs. and 9 plates. London: Bell. 1953. Price 50s.\*

This book is the third, and probably the final, volume in the series edited by Sir Lawrence Bragg and entitled *The Crystalline State*. It is a worthy companion to its two excellent predecessors in the series: *A General Survey* by Sir Lawrence Bragg, and *The Optical Principles of the Diffraction of X-rays* by R. W. James.

The authors assume that the X-ray diffraction data have been collected, corrected and tabulated, and direct their attention solely to the problems that arise in at-

\*Contribution No. 1910 from the Gates and Crellin Laboratories.

tempting to find the structure corresponding to the data. Although in Chapter I they do give a very brief survey of diffraction theory, it is chiefly for the purpose of recording concepts and mathematical relationships needed in the subsequent discussion and, quite properly, the reader is constantly referred to various portions of the earlier volumes of the series for detailed discussions of these fundamentals.

In Chapters II–IV a discussion is given of methods of calculation which are of a straightforward nature and some of which are always required in the solution of any crystal-structure problem. The subjects include the determination of space group both by extinctions and by statistical methods, the calculation of structure factors and the summation of Fourier series.

Then in Chapters V–VIII the authors discuss the heart of their problem: the achievement of a satisfactory trial structure. The reviewer does not pretend to have made an exhaustive survey of the literature, but it is his impression that in these pages the authors have probably made reference to every method or consideration that possesses any degree of generality and that had been shown, by actual application prior to the publication of the book, to be effective in deducing trial structures. The more important methods are described in considerable detail and are usually illustrated by examples. The latter often are given in pairs; first a very simple one to illustrate clearly the principle involved, and then a second taken from an actual research problem. The last of these chapters discusses the so-called 'direct methods', and although this field is currently undergoing very active development the authors have included progress down to early 1953.

Methods for refining trial structures and the errors to be expected in the final results are discussed in the last chapter. There have been extensive advances in this field in recent years and old-timers who have not kept up with them will be surprised to learn to what lengths a modern research student can go in reducing the probable errors of atomic coordinates if he has access to a high-speed digital computer, or even only to a battery of punched-card machines.

There is a curious contradiction on p. 120, where cyanite is said to be cubic after it had been correctly characterized as triclinic on p. 112. The error to be expected when applying Wilson's averaging method to two-dimensional data is given incorrectly: the observed structure factors are often made too small compared to  $F_{000}$  rather than the reverse, which is stated at the top of p. 137. The discussions given of 'generalized projections', pp. 175 and 221–4, apply only when the projection axis is perpendicular to the other two axes of the crystal. If this condition does not hold, then  $f_n(hkL)$  is not equal to  $f_n(\overline{hk}L)$  and the generalized projection of a spherically symmetrical atom is never circularly symmetrical and the maximum or minimum in its projection does not in general correspond to its true coordinates. A similar error occurs in non-orthogonal bounded projections when an atom does not lie entirely within the slice of structure being projected.

The reviewer and his colleagues have been able to discover no other points worthy of criticism here. This is a book which can be recommended to new research students with considerable confidence in its accuracy, its completeness and its clarity, and with the expectation that they can learn from it not only the theory of any particular operation but also how to carry it out in practice.

An innovation in the make-up of the book deserves notice. Figures, tables and equations are not numbered serially but instead bear the number of the page on which they occur. Thus any of these items can be referred to at points in the text remote from its actual location without causing the reader any difficulty in finding it. Otherwise the general format follows that of Volume II of the series. The paper and binding are good and the printing is excellent. There seem to be remarkably few typographical errors.

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