CRYSTALLOGRAPHY

AND

PRACTICAL CRYSTAL MEASUREMENT

BY

A. E. H. TUTTON

D.Sc., M.A. (Oxon.), F.R.S., A.R.C.Sc.

PAST PRESIDENT OF THE MINERALOGICAL SOCIETY

IN TWO VOLUMES

VOL. I

FORM AND STRUCTURE

PREFACE TO SECOND EDITION

THE subject of Crystallography has made such remarkable progress since the year 1911, when the first edition of this book was sent to press, that a new edition is urgently called for. The startling discovery of Prof. von Laue, that the planes of atoms in a crystal are capable of reflecting and diffracting X-rays, and thereby of revealing the inner structure of the crystal, was only made in Munich in the year 1912, a year after the book was published; and the masterly development of this mode of attack on crystal structure by Profs. Sir W. H. and W. L. Bragg, together with the contributions of quite a number of other workers attracted to so novel a research, has rendered the last nine years a period of epoch-making progress, in spite of the Great War which has absorbed so much scientific energy. The present is a particularly suitable moment for recording in a second edition the results achieved, and an entire new chapter of considerable length has been added to embody them, besides many other references scattered throughout the book. For a new light has been shed on crystallography by this exceptionally interesting and far-reaching method of investigation, and the most satisfactory fact about it is that X-ray analysis has not only fully confirmed all the main conclusions as to crystal structure which were detailed in the first edition, but has rendered them now incontrovertible. It is most inspiring that the principles which have been established by many years of hard work on the part of crystallographers and geometricians should now receive such absolute confirmation in so unexpected a manner. For not one single conclusion or principle, presented in the first edition, has been shown to be invalid or incorrect.

Our conceptions of the arrangement of the constituent atoms in crystallised solid substances, as occurring on the lines of the 230 types of homogeneous structures based on the fundamental 14 space-lattices, and which are in agreement with all the results of crystal measurements as described in the first edition, are now definitely proved by the X-ray analytical results to represent the truth. The atoms which we knew must be there, and in the positions which we imagined, are now actually located *in situ* and their distances of separation from one another determined in absolute measure. The very dimensions of the space-lattice cells, which in some cases of strictly isomorphous substances we had

ventured to fix in relative measure, are now proved to possess absolute values bearing precisely those relations. Consequently, X-ray analysis has given an immense stimulus and incentive to still further research into the secrets which crystals yet hold in store for the earnest seeker after truth and new knowledge, a fact which is especially cheering to those whose work is thus so happily confirmed.

Besides the new chapter concerning X-rays and crystal structure, four other new chapters have been added, largely in response to many requests. In the anxiety not to render the book too large for a single volume, the scope of the first edition was purposely restricted. But the desirability now, after the lessons taught by the War, of giving to English-speaking students and investigators, in their own language, both in the British Empire and America, as complete and yet concise an account of the subject as possible, has overborne this consideration, and new chapters have been added on (1) Isomorphism, (2) Polymorphism, Isogonism, and Enantiomorphism, (3) the Thermal Properties of Crystals (additional to dilatation which was already fully dealt with), and (4) the Electrical and Magnetic Properties of Crystals. The author cannot express his thanks to his critical and often very helpful reviewers too warmly; besides these new chapters which they recommended it has been found possible to attend to every one of their valid criticisms, to include some account of everything that was specified in the reviews as wanting in the first edition, and to correct every misstatement or slight inaccuracy to which attention was called.

Among the more noteworthy additions may be mentioned (1) a very considerable expansion of the chapter on two- and three-circle goniometry, and on the use of the gnomonic projection; (2) an illustrated account, for the benefit especially of workers with X-rays, of each of the 65 regular point-systems of Sohncke, and the evolution therefrom of the remaining 165 of the 230 types of possible crystal structure; (3) a considerable enlargement of the chapter on microscopical methods of dealing with small crystals, whether alone or in rock sections; (4) a summary of the magnificent recent work on the structure of the atom, an account of Moseley's law connecting atomic structure with atomic number, which so wonderfully and logically explains the author's own law of progression of the crystal properties in isomorphous series, an epitome of the latest facts concerning radioactivity and the nature of X-rays, and an account of the remarkable revelation of isotopic forms of many of the chemical elements, including the latest discoveries of Dr. F. W. Aston by means of his positive ray mass spectrograph, all of which are essential to a thorough understanding of the true nature of the perfect solid, a crystal, and of the new avenues of research open to crystallographers.

Other less lengthy additions refer to goniometry at very high and very low temperatures, the luminescence of crystals, their absorption of light including an account of absorption brushes, surface colour, pleochroic haloes, optical anomalies, asterism, crystal viscosity and its relation to the remarkable properties of ice, the foam and pulsation cell theories,

"liquid crystals" and the swarm theory, the determination of the torsion of crystals by an interferometric method, and further crystallographic use of the principles of interferometry, and their application not only in the author's own methods but in those of Michelson and of Fabry and Perot. Five new plates have also been added, bringing the total number of half-tone plates up to eight.

The book is bound in two volumes, the first of which deals with Crystal Form and Structure, and the second with the Physical and Chemical Properties of Crystals. A rearrangement of some of the chapters among themselves has also been effected which, with the additional chapters logically placed, enables the book to be divided into four parts, each more or less complete in itself. These four Parts are: I. Crystal Form and Goniometry; II. Crystal Structure and its X-ray Analysis; III. Crystal Optics and Microscopy; and IV. Crystal Chemistry, Deformational Physics and its Interferometry. *Parts I. and II. constitute the* first volume, and Parts III. and IV. the second volume. It is hoped that by this course the book may attain to a maximum of convenience and usefulness in assisting the study of the subject of Crystallography, now so greatly enhanced in value and importance, and appealing to so much wider a circle of readers and investigators.

The present book also includes the whole of the material and illustrations of the author's monograph *Crystalline Structure and Chemical Constitution*, which is now out of print, and brings the conclusions arrived at in that work right up to date.

The author is especially indebted to Sir William Bragg and to Prof. W. L. Bragg for the quite exceptionally kind manner in which they have supplied the author with their very latest X-ray results, right up to the time of the revision of the final proofs in April 1921, and for full facilities afforded throughout for the effective illustration of their apparatus and results by original figures. The author is also under deep obligation to Lord Rayleigh, Sir Henry Miers, Dr. Arthur Hutchinson, Dr. Herbert Smith, Prof. von Laue of Zurich, Prof. Jaeger of Groningen, Miss Mary Porter, Prof. Bowman, Mr. T. V. Barker of Oxford, Mr. Twyman of Messrs. Hilger, the Royal Society, the Royal Institution, the Royal Society of Arts, Messrs. G. Bell & Sons, and to Messrs. Kegan Paul & Co., the publishers of the author's *Crystals*, for their kindness in supplying electros and materials for illustrations or the text, which have greatly added to the value and interest of the book; and not least to the engraver, Mr. Frank Butterworth, who has taken such infinite pains to render the details of the large number of new figures accurate to the utmost degree. To Messrs. Macmillan, for undertaking the publication of so considerably enhanced a work at a time of peculiar difficulty and expense, the author is indebted more than he can ever express. Their action can only be regarded as a direct contribution to the advancement of Pure Science.

A. E. H. TUTTON.

CORRIGENDA TO VOLUME I

Page 47, in the title of Fig. 29, for "Studnet's" read "Student's."

Page 271, fifth line from foot of table, the symbol "(201)" of r' should be "$(\bar{2}01)$." (Minus sign over the 2 has failed to print.)

Page 279, line 7, the second symbol "$\{hkl\}$" should be "$\{\bar{h}kl\}$." (The minus sign over the h has failed to print.)

Page 302, second line of small print, "$\{hikl\}$" should be "$\{hi\bar{k}l\}$." (The minus sign over the k has failed to print.)

Page 308, line 9, "$\{ki\bar{h}l\}$" should be "$\{ki\bar{h}\bar{l}\}$." Line 6 from foot of page, "$\{h0\bar{h}l\}$" should be "$\{h0\bar{h}\bar{l}\}$." (Minus signs over the h and the second h have failed to print.)

Page 310, line 4 of list of forms, "$\{hik0\}$" should be "$\{hi\bar{k}0\}$." Line 9 of list of forms, "$\{hikl\}$" should be "$\{hi\bar{k}l\}$." (Minus signs over the letters k have failed to print.)

Page 333, Fig. 276; page 334, Fig. 279; page 340, Fig. 286; these three figures are upside down, requiring to be rotated 180°. They have become inverted during the preparation for printing off.

Page 347, line 10 from foot of page, "$\{h0h\bar{l}\}$" should be "$\{h0\bar{h}\bar{l}\}$." (Minus sign over second h has failed to print.)

Page 349, Fig. 301, the dots in the centres of the ring-poles have failed to print.

Page 354, third line from end of small type, "$\{hikl\}$" should be "$\{\bar{h}ikl\}$." (Minus sign over the h has failed to print.)

Page 698, line 18, for "XIV." read "XIII."

Page 736, line 22, "642" should be "641."

PREFACE TO FIRST EDITION

In this book an endeavour has been made to present at the same time both a guide to practical work in crystallography and all the essential theory of the subject, not only as regards crystal morphology but also with respect to the physical properties of crystals. The aim has been to give the main facts unencumbered with obsolete nomenclature, notation, and methods, which confuse and discourage the student or enquiring reader, and occupy time that could with greater advantage be spent in acquiring familiarity with the goniometer and a knowledge of facts of real use in the practical experimental investigation of crystals.

For this reason the notation of Naumann for the labelling of crystal faces is discarded for the more scientifically founded method of Miller, which is in harmony with the important recent development and completion of the geometrical theory of crystal structure, and regards crystals as homogeneous structures built up by the arrangement of their chemical molecules, and the atoms of which they are composed, according to definite schemes of symmetry. For the same reason the conceptions of hemihedrism and tetartohedrism are eliminated in favour of the now well-established principle, that the various classes of the same system of symmetry are different entirely because they possess in a definite manner more or less of the elements of symmetry (planes and axes of symmetry) possible to the system, in various stages and modes of combination, from the class possessing the minimum essential elements of the system to that endowed with the maximum number.

Another feature of the book is that the forbiddingly mathematical aspect of so many works on crystallography has been altogether avoided; the student is shown that there are really no mathematical difficulties involved, but that, on the contrary, all the necessary calculations of crystal angles and elements, as well as of the physical constants, are both simple and straightforward, requiring only an ordinary acquaintance with simple trigonometry and the use of a table of logarithms. Four pages only of mathematical instructions and formulæ, given in Chapter VII., form the key to all the morphological calculations required.

The practical use of the goniometer, which at once clears away all preconceived difficulties, is taught from the very beginning of the book, immediately after the necessary instructions for selecting or preparing

crystals for goniometrical purposes have been given. A typical crystal is measured as early as Chapter IV., and from the actual observations made with it all the salient fundamental facts of crystal morphology are discovered in their natural sequence, thus leading up to their systematic consideration in subsequent chapters.

The method adopted in this succeeding part of the book has then been to give first a chapter on the symmetry of the crystal system under consideration, and to follow it immediately with another in which a characteristic well-formed crystal of a substance crystallising in that system is actually worked through on the goniometer; indeed in the cases of several of the systems two such crystals of substances belonging to different classes of the system are thus employed as practical typical examples. In all cases these are chosen either from readily procurable minerals and such as form small well-developed crystals suitable for goniometry, or from easily prepared chemical salts known to afford good crystals without difficulty. From these practical measurements in each case the symmetry is deduced, the stereographic and clinographic projections of the crystal are accurately drawn, the crystal elements and angles are calculated from the best measured basal angles, and the results are expressed in the approved tabular form, precisely as if for publication.

In one of these cases—the measurement of copper sulphate as an example of triclinic symmetry in Chapter XX.—the whole chapter is really a record of an original investigation now published for the first time; for the existing data concerning the crystallography of copper sulphate are so confused that a reinvestigation was imperative. The student is thus enabled to follow an actual piece of research through all its stages.

The fact that no two crystals are ever alike entirely saves this method from being a cut-and-dried one, affording no opportunity for original thought and treatment. For the crystals of suitable small size and perfection, purchased from the mineral dealer, or grown in the laboratory by the student personally, with the object of repeating the measurements here detailed and working through the chapter practically with the goniometer, while being similar can never be copies, and will generally afford some additional or different faces, or be deficient in others, compared with those exhibited by the crystal described in this book as typical of the substance.

A special endeavour has been made in Chapter IX. to give a full but concise account of the important work on the geometrical theory of homogeneous crystal structures, and in Chapter XXXI. of the development of the fruitful idea of molecular distance ratios, the dimensions along the three axial directions in space of the elementary cell (the habitat of a molecule) of the space-lattice of the crystal structure, our nearest approach to the determination of the molecular dimensions. Practical guidance is also given in the succeeding chapter for the determination of the density of crystals, now in consequence rendered so very important.

The illustrations are almost entirely original and of two kinds, namely, (1) direct reproductions of the author's own drawings, which include all

the figures of crystals, and (2) wood-cut engravings; the latter are used to illustrate every instrument and piece of apparatus referred to in the text, a large number of which are in the author's own laboratory. The drawings of crystals have all been constructed to scale and according to the axial ratios and angular elements of actual substances, the very few copies of crystal forms being taken with full references and acknowledgments from the memoirs of original authors. Besides the essential instruction in clinographic projection given in Chapter XXV., the great utility of the stereographic projection, on the lines indicated by Penfield, as an important aid to the drawing of crystals, has been emphasised. The illustrations of interference figures afforded by crystal plates in convergent polarised light are almost exclusively reproductions of actual photographs taken by the author.

An attempt has been made to render the optical portion of the book a special feature. So little practical aid has hitherto been forthcoming for the student in this domain of crystal optics, that it is no wonder the optical details are usually so meagre in the published descriptions of the crystals of new substances. The optical part of a crystallographic investigation is frequently of exceeding interest and often of prime importance, and it is hoped that a really practical guide to this branch of the work will be found in the book. Moreover, the science of optics has been undergoing such remarkable changes of recent years, owing to the rapid succession of discoveries of the first rank, that an introductory chapter (XXXIV.) has been given in which the present position of the theory of light is briefly presented, as a definite basis on which to rest the subsequent chapters applied to crystal optics.

The chapters on the microscope include a full account of the important new methods introduced by Becke and von Fedorow, and it is hoped that they will be a help in presenting the difficultly accessible work of these investigators to English readers. The chapters on the thermal expansion and elasticity of crystals are also of a fully practical character, and the instruments employed, which are mostly original, illustrated.

The last chapter (LV.) includes a brief account of the liquid crystals discovered by Lehmann, with instructions for their study by observation or screen projection.

The author desires to record his indebtedness to Principal Miers, F.R.S., for much kindly help and criticism, which has materially enhanced the value of the book, and for his permission to illustrate by new wood engravings the whole of the instruments designed by him. Also to his successor at Oxford, Professor Bowman, for similar facilities concerning his additions to the Oxford instruments. To Dr. Herbert Smith of the Mineralogical Department of the British Museum (Natural History) at South Kensington the author's best thanks are due, for like privileges in connection with the two three-circle goniometers with which he has enriched the science, as well as with respect to the total refractometer and other attributes of goniometrical-optical research on crystals which he has devised, and for the permission to redraw certain illustrations of his memoir concerning the gnomonic projection of crystals. To Dr.

Hutchinson of Cambridge the author is also indebted for the kind loan of the beautifully prepared copper engraving of his stereographic net, and of the blocks illustrating his stereographic protractor and his universal apparatus. Also the author's sincere thanks are due to Mr. T. V. Barker for most kind assistance in presenting the work of Professor von Fedorow, with whom he studied in St. Petersburg, adequately before the readers of this book. For much kindly help and many valuable suggestions in connection with the geometrical theory of crystal structure (Chapter IX.), and with the valency theory of Pope and Barlow (Chapter XXXIII.), the author is deeply indebted to Mr. W. Barlow, F.R.S. The author also desires to record his hearty thanks to the firm of Carl Zeiss, for kindly placing at his disposal for experimental demonstration their beautiful apparatus for the study of liquid crystals, together with facilities for preparing a wood engraving of the heating microscope employed. Similarly, to Messrs. Swift for the loan of electros of certain attributes of the Dick microscope, and for facilities for illustrating this beautiful instrument in its absolutely latest form with a new wood engraving. Also the author is particularly desirous of recording his thanks to the firm of Steeg and Reuter of Homburg, for very kind help in obtaining suitable sections of mineral crystals for the preparation of the photographs of interference figures, and for the loan of electros of their well-known sectioning apparatus.

The author cannot conclude without paying a tribute to the careful work of the engraver, Mr. Frank Butterworth, to whose personal skill and draughtsmanship it is due that the wood engravings of this book are such faithful representations to the last details of the most recent form of crystallographic instruments. The author also wishes to express in conclusion his gratitude to Messrs. Macmillan for their unfailing kindness and consideration during the production of the book, and particularly for their public-spirited expenditure on a work of this kind, which can scarcely hope for a very wide circulation in the early days of this growing science of crystallography, when its value is only just beginning to be realised. That there is a great future before this subject, the science of the organised and perfect solid, is assured, however, and that the book may help forward the progress of crystallography by enabling it to be more widely studied, and its value to be more fully appreciated, and especially that there may be attracted to it an increasing number of earnest spirits seeking for a field of fascinating and richly rewarding research, is the author's chief aim and desire concerning it.

A. E. H. TUTTON.

The Chapters referred to in this Preface to the First Edition as IX., XX., XXXIII., XXXIV., and LV. are now in this Second Edition Chapters XXX., XIX., XXXIV., XXXV., and LX. respectively.

CONTENTS

PART I

CRYSTAL FORM AND GONIOMETRY

CHAPTER I

CHAPTER II

CHAPTER III

CHAPTER IV

CHAPTER V

CHAPTER VI

CHAPTER VII

CHAPTER VIII

CHAPTER IX

CHAPTER X

CHAPTER XI

CHAPTER XII

CHAPTER XIII

CHAPTER XIV

CHAPTER XV

CHAPTER XXV

CHAPTER XXVI

CHAPTER XXVII

PART II

CRYSTAL STRUCTURE AND ITS X-RAY ANALYSIS

CHAPTER XXVIII

CHAPTER XXIX

CHAPTER XXX

CHAPTER XXXI

CHAPTER XXXII

CHAPTER XXXIII

CHAPTER XXXIV

CONTENTS

PART III

CRYSTAL OPTICS AND MICROSCOPY

CHAPTER XXXV

CHAPTER XXXVI

CHAPTER XXXVII

CHAPTER XXXVIII

CHAPTER XXXIX

CHAPTER XL

CHAPTER XLI

CHAPTER XLII

CHAPTER XLIII

CHAPTER XLIV

CHAPTER XLV

CHAPTER XLVI

CHAPTER XLVII

CHAPTER XLVIII