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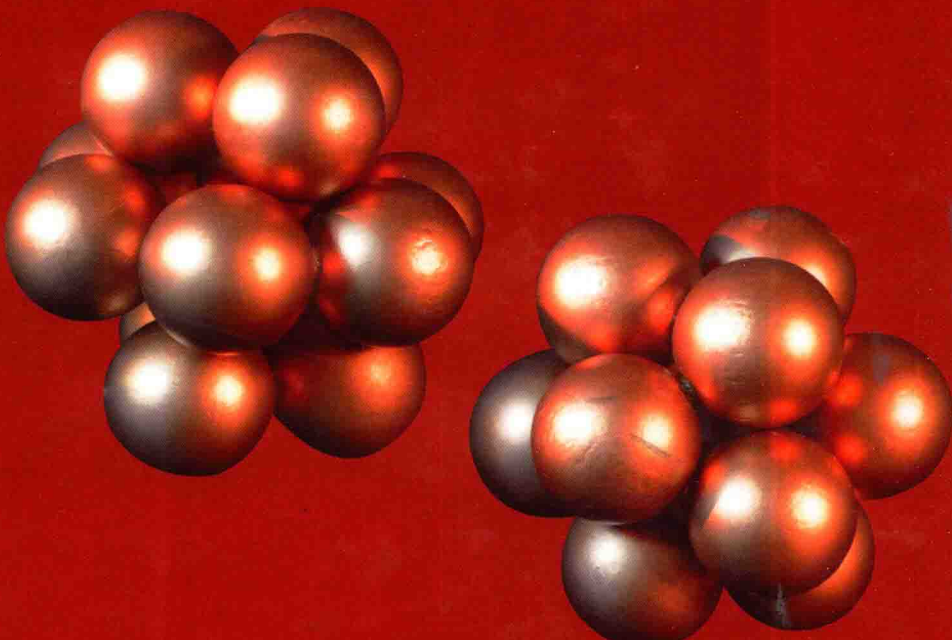
The Basics of Crystallography and Diffraction

Fourth Edition

CHRISTOPHER HAMMOND



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The Basics of Crystallography and Diffraction

Fourth Edition

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Preface to the First Edition (1997)

This book has grown out of my earlier *Introduction to Crystallography* published in the Royal Microscopical Society's Microscopy Handbook Series (Oxford University Press 1990, revised edition 1992). My object then was to show that crystallography is not, as many students suppose, an abstruse and 'difficult' subject, but a subject that is essentially clear and simple and which does not require the assimilation and memorization of a large number of facts. Moreover, a knowledge of crystallography opens the door to a better and clearer understanding of so many other topics in physics and chemistry, earth, materials and textile sciences, and microscopy.

In doing so I tried to show that the ideas of symmetry, structures, lattices and the architecture of crystals should be approached by reference to everyday examples of the things we see around us, and that these ideas were not confined to the pages of textbooks or the models displayed in laboratories.

The subject of diffraction flows naturally from that of crystallography because by its means—and in most cases only by its means—are the structures of materials revealed. And this applies not only to the interpretation of diffraction patterns but also to the interpretation of images in microscopy. Indeed, diffraction patterns of objects ought to be thought of as being as 'real', and as simply understood, as the objects themselves. One is, to use the mathematical expression, simply the transform of the other. Hence, in discussing diffraction, I have tried to emphasize the common aspects of the phenomena with respect to light, X-rays and electrons.

In Chapter 1 (Crystals and crystal structures) I have concentrated on the simplest examples, emphasizing how they are related in terms of the occupancy of atomic sites and how the structures may be changed by faulting. Chapter 2 (Two-dimensional patterns, lattices and symmetry) has been considerably expanded, partly to provide a firm basis for understanding symmetry and lattices in three dimensions (Chapters 3 and 4) but also to address the interests of students involved in two-dimensional design. Similarly in Chapter 4, in discussing point group symmetry, I have emphasized its practical relevance in terms of the physical and optical properties of crystals.

The reciprocal lattice (Chapter 6) provides the key to our understanding of diffraction, but as a *concept* it stands alone. I have therefore introduced it separately from diffraction and hope that in doing so these topics will be more readily understood. In Chapter 7 (The diffraction of light) I have emphasized the geometrical analogy with electron diffraction and have avoided any quantitative analysis of the amplitudes and intensities of diffracted beams. In my experience the (sometimes lengthy) equations which are required cloud students' perceptions of the basic geometrical conditions for constructive and destructive interference—and which are also of far more practical importance with respect, say, to the resolving power of optical instruments.

Chapter 8 describes the historical development of the geometrical interpretation of X-ray diffraction patterns through the work of Laue, the Braggs and Ewald. The diffraction of X-rays and electrons from single crystals is covered in Chapter 9, but only in the case of X-ray diffraction are the intensties of the diffracted beams discussed.

This is largely because structure factors are important but also because the derivation of the interference conditions between the atoms in the motif can be represented as nothing more than an extension of Bragg's law. Finally, the important X-ray and electron diffraction techniques from polycrystalline materials are covered in Chapter 10.

The Appendices cover material that, for ease of reference, is not covered in the text. Appendix 1 gives a list of items which are useful in making up crystal models and provides the names and addresses of suppliers. A rapidly increasing number of crystallography programs are becoming available for use in personal computers and in Appendix 2 I have listed those which involve, to a greater or lesser degree, some 'self learning' element. If it is the case that the computer program will replace the book, then one might expect that books on crystallography would be the first to go! That day, however, has yet to arrive. Appendix 3 gives brief biographical details of crystallographers and scientists whose names are asterisked in the text. Appendix 4 lists some useful geometrical relationships.

Throughout the book the mathematical level has been maintained at a very simple level and with few minor exceptions all the equations have been derived from first principles. In my view, students learn nothing from, and are invariably dismayed and perplexed by, phrases such as 'it can be shown that'—without any indication or guidance of *how* it can be shown. Appendix 5 sets out all the mathematics which are needed.

Finally, it is my belief that students appreciate a subject far more if it is presented to them not simply as a given body of knowledge but as one which has been gained by the exertions and insight of men and women perhaps not much older than themselves. This therefore shows that scientific discovery is an activity in which they, now or in the future, can participate. Hence the justification for the historical references, which, to return to my first point, also help to show that science progresses, not by being made more complicated, but by individuals piecing together facts and ideas, and seeing relationships where vagueness and uncertainty existed before.

Preface to the Fourth Edition (2015)

The successive editions of this book have incorporated a wider range of subject matter, some of which is of a rather more 'advanced' nature. However, I hope that I have adhered throughout to my original objective of showing that crystallography (and diffraction) is not an 'abstruse and difficult subject'. And as the book has expanded I hope that it will serve a further function, namely that of providing a reader with a greater confidence in tackling the more advanced and mathematically sophisticated texts included in Further Reading.

To this end I have used the simplest possible figures (both the drawings and photographs of crystal models) that a student is able to reproduce for himself or herself and which, I hope, will complement and aid an understanding of, the beautiful but invariably more complex computer-generated images of crystal structures that are now so widely available.

Each Chapter and Appendix is largely self-contained, and the Contents and Index have been made sufficiently detailed such that the reader should be able to locate, at a glance, those pages that contain the information which she or he requires.

Finally, there are it seems to me, two 'landmark' X-ray diffraction photographs: Laue's 1912 photograph of zinc blende and Franklin's 1952 photograph of DNA and in view of which I have placed these 'by way of symmetry' at the beginning of this book.

Acknowledgements

In the preparation of the successive editions of this book, I have greatly benefited from the advice and encouragement of present and former colleagues in the University of Leeds who have appraised and discussed draft chapters or who have materially assisted in the preparation of the figures. In particular, I wish to mention Dr Andrew Brown, Professor Rik Brydson, Dr Tim Comyn, Dr Andrew Scott, and Mr David Wright (Institute for Materials Research); Dr Jenny Cousens and Professor Michael Hann (School of Design); Dr Peter Evennett (formerly of the Department of Pure and Applied Biology); Dr John Lydon (School of Biological Sciences); Professor Anthony North (Emeritus Professor of Biophysics); the late Dr John Robertson (former Chairman of the IUCr, Book Series Committee), and the late Dr Roy Shuttleworth (formerly of the Department of Metallurgy).

Dr Pam Champness (formerly of the Department of Earth Sciences, University of Manchester) read and advised me on much of the early draft manuscript; Mrs Kate Crennell (formerly Education Officer of the BCA) prepared several of the figures in Chapter 2; Professor István Hargittai (of the Budapest University of Technology and Economics) advised me on the work, and sought out biographical material on A.I. Kitaigorodskii; Professor Amand Lucas (of the University of Namur and Belgian Royal Academy) allowed me to use his optical simulation of the structure of DNA; Dr Keith Rogers (of Cranfield University) advised me on the Rietveld method; Professor Shigeru Ohba (of Keio University, Japan) kindly drew my attention to a number of errors and misprints overlooked in earlier editions; Dr David Watkin (University of Oxford) instructed me on direct and charge-flipping methods and Professor Michael Glazer (Universities of Oxford and Warwick) advised me on space groups and group theory.

Ms Hema Latha of Integra Software Services, Pondicherry, India, Ms Ania Wronski and Dr Sonke Adlung of the Academic Division, Oxford University Press, have guided me in the overall preparation and submission of the manuscript.

Many other colleagues at Leeds and elsewhere, have permitted me to reproduce figures from their own publications, as have the copyright holders of books and journals. Individual acknowledgements are given in the figure captions.

I would like to thank Miss Susan Toon and Miss Claire McConnell for word processing the manuscript and for attending to my constant modifications to it and to Mr David Horner and Dr Peter Evennett for their careful photographic work.

Finally, I recall with gratitude the great influence of my former teachers, in particular Dr P.M. Kelly and Dr N.F.M. Henry.

C.H.

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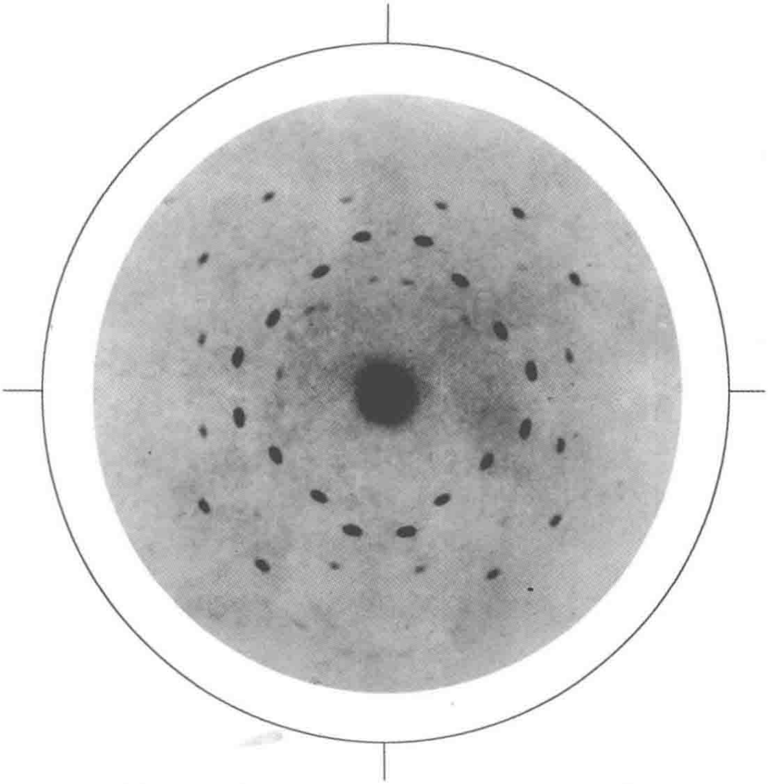
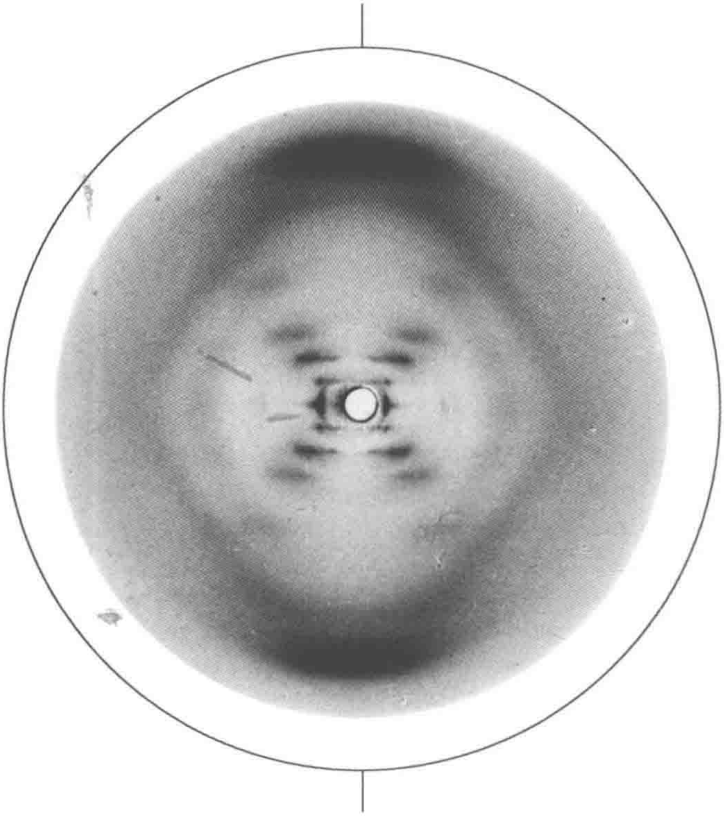


X-ray photograph of zinc blende

One of the eleven 'Laue Diagrams' in the paper submitted by Walter Friedrich, Paul Knipping and Max von Laue to the Bavarian Academy of Sciences and presented at its Meeting held on June 8th 1912—the paper which demonstrated the existence of internal atomic regularity in crystals and its relationship to the external symmetry.

The X-ray beam (central black spot) is incident along one of the cubic crystal axes of the (face-centred cubic) ZnS structure and consequently the diffraction spots show the four-fold symmetry of the atomic arrangement about the axis. But notice also that the spots are not circular in shape—they are elliptical; the short axes of the ellipses all lying in radial directions. William Lawrence Bragg realized the great importance of this seemingly small observation: he had noticed that slightly divergent beams of light (of circular cross-section) reflected from mirrors also gave reflected spots of just these elliptical shapes. Hence he went on to formulate the Law of Reflection of X-Ray Beams which unlocked the door to the structural analysis of crystals.



X-ray photograph of deoxyribonucleic acid

The photograph of the 'B' form of DNA taken by Rosalind Franklin and Raymond Gosling in May 1952 and published, together with the two papers by J. D. Watson and F. H. C. Crick and M. H. F. Wilkins, A. R. Stokes and H. R. Wilson, in the 25 April issue of *Nature,* 1953, under the heading 'Molecular Structure of Nucleic Acids'.

The specimen is a fibre (axis vertical) containing millions of DNA strands roughly aligned parallel to the fibre axis and separated by the high water content of the fibre; this is the form adopted by the DNA in living cells. The X-ray beam is normal to the fibre and the diffraction pattern is characterised by four lozenges or diamond-shapes outlined by fuzzy diffraction haloes and separated by two rows or arms of spots radiating outwards from the centre. These two arms are characteristic of helical structures and the angle between them is a measure of the ratio between the width of the molecule and the repeat-distance of the helix. But notice also the sequence of spots along each arm; there is a void where the fourth spot should be and this 'missing fourth spot' not only indicates that there are two helices intertwined but also the separation of the helices along the chain. Finally, notice that there are faint diffraction spots in the two side lozenges, but not in those above and below, an observation which shows that the sugar-phosphate 'backbones' are on the outside, and the bases on the inside, of the molecule.

This photograph provided the crucial experimental evidence for the correctness of Watson and Crick's structural model of DNA—a model not just of a crystal structure but one which shows its inbuilt power of replication and which thus unlocked the door to an understanding of the mechanism of transmission of the gene and of the evolution of life itself.

Contents

1

Crystals and crystal structures

1.1 The nature of the crystalline state

The beautiful hexagonal patterns of snowflakes, the plane faces and hard faceted shapes of minerals and the bright cleavage fracture surfaces of brittle iron have long been recognized as external evidence of an internal order—evidence, that is, of the patterns or arrangements of the underlying building blocks. However, the nature of this internal order, or the form and scale of the building blocks, was unknown.

The first attempt to relate the external form or shape of a crystal to its underlying structure was made by Johannes Kepler* who, in 1611, wrote perhaps the first treatise on geometrical crystallography, with the delightful title, 'A New Year's Gift or the Six-Cornered Snowflake' (*Strena Seu de Nive Sexangula*).[1] In this he speculates on the question as to why snowflakes always have six corners, never five or seven. He suggests that snowflakes are composed of tiny spheres or globules of ice and shows, in consequence, how the close-packing of these spheres gives rise to a six-sided figure. It is indeed a simple experiment that children now do with pennies at school. Kepler was not able to solve the problem as to why the six corners extend and branch to give many patterns (a problem not fully resolved to this day), nor did he extend his ideas to other crystals. The first to do so, and to consider the structure of crystals as a general problem, was Robert Hooke* who, with remarkable insight, suggested that the different shapes of crystals which occur—rhombs, trapezia, hexagons, etc.—could arise from the packing together of spheres or globules. Figure 1.1 is 'Scheme VII' from his book *Micrographia,* first published in 1665. The upper part (Fig. 1) is his drawing, from the microscope, of 'Crystalline or Adamantine bodies' occurring on the surface of a cavity in a piece of broken flint and the lower part (Fig. 2) is of 'sand or gravel' crystallized out of urine, which consist of 'Slats or such-like plated Stones … their sides shaped into **Rhombs, Rhomboeids** and sometimes into **Rectangles** and **Squares**'. He goes on to show how these various shapes can arise from the packing together of 'a company of bullets' as shown in the inset sketches A–L, which represent pictures of crystal structures which have been repeated in innumerable books, with very little variation, ever since. Also implicit in Hooke's sketches is the *Law of the Constancy of Interfacial Angles*; notice that the solid lines which outline the crystal faces are (except for the last sketch, L) all at 60° or 120° angles which clearly arise from the close-packing of the spheres. This law was first stated by Nicolaus Steno,* a near contemporary of Robert

* Denotes biographical notes available in Appendix 3.

[1] *The Six-Cornered Snowflake*, reprinted with English translation and commentary. Classic Texts in the Physical Science Oxford University Press, Oxford, 2014.

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