X-RAY CRYSTALLOGRAPHY

X-ray Crystallography

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To Vera

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[Modern crystallography has] transformed almost out of recognition the knowledge of solids and liquids. In this respect it is as if science had acquired a microscope capable of magnifying 10,000,000-fold, capable of seeing atoms distinctly. As a result science [could] find explanations in terms of atoms and their combinations not only of the phenomena of physics and chemistry but of the behaviour of ordinary things. The beating out of metal under the hammer, the brittleness of glass and the cleavage of mica, the plasticity of clay, the lightness of ice, the greasiness of oil, the elasticity of rubber, the contraction of muscle, the waving of hair, and the hardening of a boiled egg are among the hundreds of phenomena that [have] been completely or partially explained.

J. D. Bernal, "Crystallography," in *Encyclopædia Britannica*,
Chicago: Encyclopædia Britannica, Inc., 1956, vol. 6, p. 828E.

PREFACE AND ACKNOWLEDGMENTS

This textbook was written to achieve two principal goals.

- First, to provide a clearly written exposition of the fundamentals of X-ray crystallography, so that the key concepts can be mastered by graduate students and advanced undergraduate students encountering them for the first time. The text helps readers develop useful mental pictures that aid in understanding the phenomena and mathematics of X-ray crystallography.
- Second, to provide a balanced treatment of symmetry, the diffraction of X-rays by crystals, and the methods to solve and refine X-ray diffraction crystal structures. Many existing textbooks omit or skimp on one or more of these topics, whereas all three are necessary for a full understanding of the beauty and power of X-ray crystallography.

Some notable aspects of the book are as follows. The book opens with a short historical introduction covering both classical and modern crystallography, and then turns to symmetry concepts. Symmetry operations are introduced first, in order to make the construction and classification of lattices based on their symmetries more natural and logical. Two-dimensional lattices and two-dimensional plane groups are presented before the three-dimensional versions of these topics, a progression that makes it easier for the reader to master the material. Step-by-step analyses of the symmetry element diagrams and equivalent positions diagrams are given for selected plane and space groups, which build the skills necessary to interpret the diagrams in the *International Tables*. Throughout this section, symmetry concepts and terms are given precise definitions based on mathematics and are also explained in plain English.

I have coined one new term because I felt a need existed: "travel symmetry operation," which is a collective term for translations, screw operations, and glide operations. To assist in clarity, I have also departed slightly from standard practice by restricting the term "reflection" to mean a diffracted X-ray beam; the symmetry operation often called a reflection is instead referred to consistently in the text as a mirror operation.

The next section of the book begins with a discussion of the generation of X-rays and their use in diffractometers. The interaction of X-rays with a single electron, a single atom, and arrays of scatterers are then analyzed in turn, and subsequent discussions analyze the factors that affect the directions and intensities of X-ray reflections. Two-dimensional diffraction (LEED) is used as an introduction to the corresponding phenomenon in three dimensions.

In the final section of the book, trial-and-error, Patterson, and direct methods for solving and refining crystal structures are discussed in turn, with examples and applications drawn from both small molecule and macromolecular crystallography. Some advanced topics are included that are not always found in textbooks, such as charge flipping, the maximum likelihood method of refinement, disorder, twinning, and powder, neutron, and electron diffraction. A chapter on mistakes and pitfalls provides the reader with case studies of published crystal structures that went wrong, along with hints about how to recognize such errors and thus avoid them.

Throughout the book, problem sets are included that help the reader master the ideas presented in the chapters. In many places, I have discussed questions that might occur to a thoughtful reader, but which are often omitted from standard textbooks. For example, X-rays have both an electric and a magnetic field component, and the present text stops briefly to explain why the magnetic contribution to X-ray scattering can usually be ignored, despite the fact that electrons and many nuclei have magnetic moments. Another discussion explains why it is possible to use complex exponentials to represent electromagnetic waves. Most textbooks never justify the approach (or, worse, leave the impression that the complex exponentials *are* waves, which they are not).

The mathematics behind X-ray crystallography—vector algebra, complex numbers, triple integrals, Fourier analysis, and reciprocal space—can be very intimidating. For this reason, some topics are presented twice but with different mathematical apparatus. For example, X-ray scattering angles are first analyzed by means of trigonometry and then with the use of vectors; similarly, X-ray scattering intensities are first analyzed by means of trigonometry and then with the use of complex structure factors. This dual approach may lack purity of mathematical form, but my experience has been that it promotes better understanding.

I wish to thank Iain Paul, who taught the X-ray crystallography course at Illinois before me and indirectly shaped my own approach to the topic. Holger Hellwig, who taught the course from my lecture notes for three years while I was on an administrative leave, made a few of the notes available to students along with some additions of his own, and thereby created the seed from which this book grew. I am most grateful to the many students, colleagues, and friends—especially Dan Grayson, Ron Stenkamp, Dick Marsh, Ken Raymond, Massimo Nespolo, Marvin Hackert, Bruce Foxman, Art Schultz, Danielle Gray, and Cliff Singer—who provided valuable help and advice.

And finally, I owe my deepest thanks to Vera Mainz for all she has done for this book and for me.

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