

X-RAY CRYSTALLOGRAPHY

X-ray Crystallography

Gregory S. Girolami

Professor of Chemistry
University of Illinois at Urbana-Champaign



University Science Books
Mill Valley, California

University Science Books
Mill Valley, California
www.uscibooks.com

Production Manager: *Mark Ong*
Manuscript Editor: *John Murdzek*
Designer: *Yvonne Tsang*
Illustrator: *Lineworks, Inc.*
Compositor: *Wilsted & Taylor Publishing Services*
Printer & Binder: *Marquis*

This book is printed on acid-free paper.

Copyright © 2016 University Science Books

Print ISBN: 978-1-891389-77-1

Cover illustration: M. C. Escher's "Symmetry Drawing E96"
© 2015 The M. C. Escher Company-Holland. All rights reserved.

Reproduction or translation of any part of this work beyond that permitted by Section 107 or 108 of the 1976 United States Copyright Act without the permission of the copyright owner is not permitted. Requests for permission or further information should be addressed to the Permissions Department, University Science Books.

LIBRARY OF CONGRESS CATALOGING-IN-PUBLICATION DATA

Girolami, Gregory S., 1956-
X-ray crystallography / Gregory S. Girolami, professor of chemistry,
University of Illinois at Urbana-Champaign.
pages cm
Includes bibliographical references and index.
ISBN 978-1-891389-77-1 (alk. paper)
1. X-ray crystallography. 2. Crystallography. I. Title.
QD945.G57 2014
548-dc23 2014040789

Printed in Canada

10 9 8 7 6 5 4 3 2 1

To Vera

CONTENTS

Preface and Acknowledgments xi

SECTION 1. Symmetry and Space Groups

<i>Chapter 1.</i> Introduction	3
<i>Chapter 2.</i> Point Symmetry Operations	15
<i>Chapter 3.</i> Point Groups	27
<i>Chapter 4.</i> Periodicity	43
<i>Chapter 5.</i> Travel Symmetry Operations	55
<i>Chapter 6.</i> Two-dimensional Lattices	67
<i>Chapter 7.</i> Three-dimensional Lattices	79
<i>Chapter 8.</i> Two-dimensional Plane Groups	87
<i>Chapter 9.</i> Equivalent Positions	99
<i>Chapter 10.</i> Three-dimensional Space Groups, Part 1	111
<i>Chapter 11.</i> Three-dimensional Space Groups, Part 2	121
<i>Chapter 12.</i> Three-dimensional Space Groups, Part 3	133

SECTION 2. X-rays and Diffraction

<i>Chapter 13.</i> Generation of X-rays	145
<i>Chapter 14.</i> Diffractometers and Data Collection	157
<i>Chapter 15.</i> Data Reduction	167
<i>Chapter 16.</i> Scattering from a Single Electron	179
<i>Chapter 17.</i> Scattering from Atoms	189
<i>Chapter 18.</i> Diffraction from One-dimensional Arrays	199
<i>Chapter 19.</i> Diffraction from Two- and Three-dimensional Arrays	207
<i>Chapter 20.</i> Reciprocal Space and Reflection Indices	219
<i>Chapter 21.</i> Bragg's Law, Scattering Planes, and d -Spacings	225
<i>Chapter 22.</i> The Limiting Sphere, Resolution, and Indexing	235
<i>Chapter 23.</i> Structure Factors and Argand Diagrams	247
<i>Chapter 24.</i> Phases, Friedel's Law, and Laue Classes	255

- Chapter 25.* Centrosymmetry and Chirality 265
- Chapter 26.* Reflection Conditions 277
- Chapter 27.* Determining the Space Group of a Crystal 289

SECTION 3. Solving and Refining Crystal Structures

- Chapter 28.* Fourier Transforms in Crystallography 299
- Chapter 29.* Trial-and-error Methods 309
- Chapter 30.* Charge Flipping 319
- Chapter 31.* The Patterson Method 327
- Chapter 32.* The Heavy Atom Approximation 335
- Chapter 33.* Protein Crystal Structures 349
- Chapter 34.* Direct Methods, Part 1 361
- Chapter 35.* Direct Methods, Part 2 371
- Chapter 36.* Modeling the Electron Density 383
- Chapter 37.* Refining Crystal Structures 395
- Chapter 38.* Twinning 407
- Chapter 39.* Examples of Twinned Crystals 417
- Chapter 40.* Mistakes and Pitfalls 427
- Chapter 41.* Powder X-ray Diffraction 439
- Chapter 42.* Electron and Neutron Diffraction 451

- Appendix A. Vector Tutorial 457
- Appendix B. Complex Number Tutorial 463
- Appendix C. The Ewald Sphere 467
- Appendix D. Atomic Form Factors 473
- Appendix E. The Patterson Function 479
- Appendix F. In-class Demonstration of Diffraction 483

Bibliography 487

Index 491

[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.

Reprinted with permission

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.

Gregory S. Girolami
Urbana, Illinois