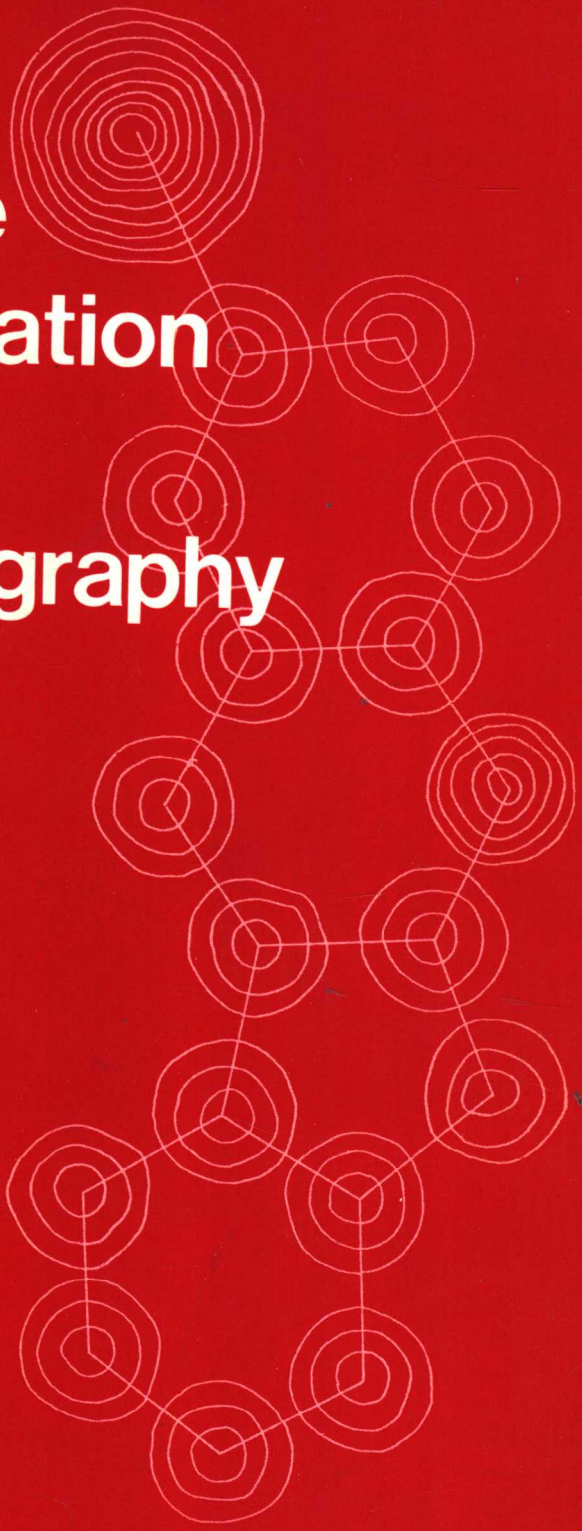
Second Edition

Structure Determination by X-Ray Crystallography



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Structure Determination by X-Ray Crystallography

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Plenum Press · New York and London

Library of Congress Cataloging in Publication Data

Ladd, M. F. C. (Marcus Frederick Charles).
Structure determination by X-ray crystallography.

Includes bibliographies and index.
1. X-ray crystallography. I. Palmer, R. A. (Rex Alfred), 1936- . II. Title.
QD945.L32 1985 548'.83 84-24811
ISBN 0-306-42295-6 (pbk.)

A Division of Plenum Publishing Corporation
233 Spring Street, New York, N.Y. 10013

Printed in the United States of America

Foreword

X-ray crystallography provides us with the most accurate picture we can get of atomic and molecular structures in crystals. It provides a hard bedrock of structural results in chemistry and in mineralogy. In biology, where the structures are not fully crystalline, it can still provide valuable results and, indeed, the impact here has been revolutionary. It is still an immense field for young workers, and no doubt will provide yet more striking developments of a major character. It does, however, require a wide range of intellectual application, and a considerable ability in many fields.

This book will provide much help. It is a very straightforward and thorough guide to every aspect of the subject. The authors are experienced both as research workers themselves and as teachers of standing, and this is shown in their clarity of exposition. There are plenty of illustrations and worked examples to aid the student to obtain a real grasp of the subject. The practical side is encouraged by the very clarity of the theory. The examples chosen as illustrations cover the various branches of chemistry and there is useful guidance even as far as the protein field. In the later chapters dealing with the really tricky area of "getting the structure out," the treatment is well balanced, and this should help even an experienced worker to choose the most likely approach in each particular case. We seem to have passed beyond the stage at which one method is favored to the neglect of the others, and the book seems to mark a "coming of age" of X-ray crystallography.

I wish the book the great success it undoubtedly deserves.

University of Edinburgh C. A. Beevers

Preface to the Second Edition

We have not changed the original plan and scope of this book because the first edition was, in general, well received. Additional space has been allocated to certain topics, notably experimental techniques, direct methods of phasing, and least-squares refinement. We have tried to respond to the helpful comments that we have received from reviewers and readers, and we are grateful for the interest that has been accorded to the first edition. In particular, we wish to acknowledge the kindness of Dr. C. A. Beevers for writing the Foreword to this edition.

University of Surrey M. F. C. Ladd
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Preface to the First Edition

Crystallography may be described as the science of the structure of materials, using this word in its widest sense, and its ramifications are apparent over a broad front of current scientific endeavor. It is not surprising, therefore, to find that most universities offer some aspects of crystallography in their undergraduate courses in the physical sciences. It is the principal aim of this book to present an introduction to structure determination by X-ray crystallography that is appropriate mainly to both final-year undergraduate studies in crystallography, chemistry, and chemical physics, and introductory postgraduate work in this area of crystallography. We believe that the book will be of interest in other disciplines, such as physics, metallurgy, biochemistry, and geology, where crystallography has an important part to play.

In the space of one book, it is not possible either to cover all aspects of crystallography or to treat all the subject matter completely rigorously. In particular, certain mathematical results are assumed in order that their applications may be discussed. At the end of each chapter, a short bibliography is given, which may be used to extend the scope of the treatment given here. In addition, reference is made in the text to specific sources of information.

We have chosen not to discuss experimental methods extensively, as we consider that this aspect of crystallography is best learned through practical experience, but an attempt has been made to simulate the interpretive side of experimental crystallography in both examples and exercises.

During the preparation of this book, we have tried to keep in mind that students meeting crystallography for the first time are encountering a new discipline, and not merely extending a subject studied previously. In consequence, we have treated the geometry of crystals a little more fully than is usual at this level, for it is our experience that some of the difficulties which

students meet in introductory crystallography lie in the unfamiliarity of its three-dimensional character.

We have limited the structure-determining techniques to the three that are used most extensively in present-day research, and we have described them in depth, particularly from a practical point of view. We hope that this treatment will indicate our belief that crystallographic methods can reasonably form part of the structural chemist's repertoire, like quantum mechanics and nmr spectroscopy.

Each chapter is provided with a set of problems, for which answers and notes are given. We recommend the reader to tackle these problems; they will provide a practical involvement which should be helpful to the understanding of the subject matter of the book. From experience in teaching this subject, the authors are aware of many of the difficulties encountered by students of crystallography, and have attempted to anticipate them in both these problems and the text. For any reader who has access to crystallographic computing facilities, the authors can supply copies of the data used to solve the structures described in Chapters 6 and 8. Certain problems have been marked with an asterisk. They are a little more difficult than the others and may be omitted at a first reading.

The Hermann–Mauguin system of symmetry notation is used in crystallography, but, unfortunately, this notation is not common to other disciplines. Consequently, we have written the Schoenflies symbols for point groups on some of the figures that depict point-group and molecular symmetry in three dimensions, in addition to the Hermann–Mauguin symbols. The Schoenflies notation is described in Appendix 3. General symbols and constants are listed in the Notation section.

We wish to acknowledge our colleague, Dr. P. F. Lindley, of Birkbeck College, London, who undertook a careful and critical reading of the manuscript and made many valuable suggestions. We acknowledge an unknown number of past students who have worked through many of the problems given in this book, to our advantage and, we hope, also to theirs. We are grateful to the various copyright holders for permission to reproduce those figures that carry appropriate acknowledgments. Finally, we thank the Plenum Publishing Company for both their interest in this book and their ready cooperation in bringing it to completion.

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Notation

These notes provide a key to the main symbols and constants used throughout the book. Inevitably, some symbols have more than one use. This feature arises partly from general usage in crystallography, and partly from a desire to preserve a mnemonic character in the notation wherever possible. It is our belief that, in context, no confusion will arise. Where several symbols are closely linked, they are listed together under the first member of the set.

$A'(hkl), B'(hkl)$.	Components of the structure factor, measured along the real and imaginary axes, respectively, in the complex plane (Argand diagram)
$A(hkl), B(hkl)$.	Components of the geometric structure factor, measured along the real and imaginary axes, respectively, in the complex plane
A	A-face-centered unit cell; absorption correction factor
Å	Angstrom unit; $1\ \text{Å} = 10^{-8}\ \text{cm} = 10^{-10}\ \text{m}$
a, b, c	Unit-cell edges parallel to the x, y, and z axes, respectively, of a crystal; intercepts made by the parametral plane on the x, y, and z axes, respectively; glide planes with translational components of $a/2$, $b/2$, and $c/2$, respectively
$\mathbf{a}, \mathbf{b}, \mathbf{c}$	Unit-cell edge vectors parallel to the x, y, and z axes, respectively
a^*, b^*, c^* . . .	Edges in the reciprocal unit cell associated with the x^*, y^*, and z^* axes, respectively
$\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$ . . .	Reciprocal unit-cell vectors associated with the x^*, y^*, and z^* axes, respectively
B	B-face-centered unit cell; overall isotropic temperature factor
B_j	Isotropic temperature factor for the jth atom
C	C-face-centered unit cell
$\mathcal{C}$	"Not constrained by symmetry to equal"

c	Velocity of light (2.9979×10^{-8} m s^{-1}); as a subscript: calculated, as in $\lvert F_c \rvert$
D_m	Experimentally measured crystal density
D_c	Calculated crystal density
d	Interplanar spacing
$d(hkl)$	Interplanar spacing of the (hkl) family of planes
d^*	Distance in reciprocal space
$d^*(hkl)$ . . .	Distance from the origin to the hklth reciprocal lattice point
$E, E(hkl)$ . . .	Normalized structure factor (centrosymmetric crystals)
$\mathscr{E}(hkl)$	Total energy of the hklth diffracted beam from one unit cell
e	Electron charge (1.6021×10^{-19}C); exponential factor
$\mathbf{F}(hkl)$	Structure factor for the hklth spectrum referred to one unit cell
$\mathbf{F}^*(hkl)$ . . .	Conjugate vector of $\mathbf{F}(hkl)$.
$\lvert F \rvert$	Modulus, or amplitude, of any vector $\mathbf{F}$
f	Atomic scattering factor
$f_{j,\theta}, f_j$	Atomic scattering factor for the jth atom
g	Glide line in two-dimensional space groups
g_j	Atomic scattering factor for the jth atom, in a crystal, corrected for thermal vibrations
H	Hexagonal (triply primitive) unit cell
$(hkl), (hkil)$ . .	Miller, Miller–Bravais indices associated with the x, y, and z axes or the x, y, u, and z axes, respectively; any single index containing two digits has a comma placed *after* such an index
$\{hkl\}$	Form of (hkl) planes
hkl	Reciprocal lattice point corresponding to the (hkl) family of planes
$\mathbf{h}$	Vector with components h, k, l in reciprocal space.
h	Planck's constant (6.6256×10^{-34} J s)
I	Body-centered unit cell; intensity of reflection
$I(hkl)$	Intensity of reflection from the (hkl) planes referred to one unit cell
$\mathscr{I}$	Imaginary axis in the complex plane
i	$\sqrt{-1}$; an operator that rotates a vector in the complex plane through 90° in a right-handed (anticlockwise) sense

$J(hkl)$	Integrated reflection
K	Reciprocal lattice constant; scale factor for $\|F_o(hkl)\|$ data
L	Lorentz correction factor
M_r	Relative molecular weight (mass)
m	Mirror plane
N	Number of atoms per unit cell
n	Glide plane, with translational component of $(a+b)/2$, $(b+c)/2$, or $(c+a)/2$
n_1, n_2, n_3 . . .	Principal refractive indices in a biaxial crystal
o	subscript: observed, as in $\|F_o(hkl)\|$
P	Probability; Patterson function
$P(u, v, w)$ . . .	Patterson function at the fractional coordinates u, v, w in the unit cell
p	Polarization correction factor
R	Rhombohedral unit cell; rotation axis (of degree R); reliability factor
$\bar{R}$	Inversion axis
$\mathscr{R}$	Real axis in the complex plane
RU	Reciprocal lattice unit
s, $s(hkl)$, $s(\mathbf{h})$.	Sign of a centric reflection
$T_{j,\theta}$	Thermal vibration parameter for the jth atom
$[UVW]$ . . .	Zone or direction symbol
$\langle UVW \rangle$ . . .	Form of zone axes or directions
u	Atomic mass unit (1.66057×10^{-27} kg)
(u, v, w) . . .	Components of a vector in Patterson space
$\overline{U^2}$	Mean square amplitude of vibration
V_c	Volume of a unit cell
w	Weight factor
x, y, z; x, y, u, z . .	Spatial coordinates, in absolute measure, of a point, parallel to the x, y, (u), and z axes, respectively
x, y, z	Spatial fractional coordinates in a unit cell
x_j, y_j, z_j . . .	Spatial fractional coordinates of the jth atom in a unit cell
$[x, \beta, \gamma]$ . . .	Line parallel to the x axis and intersecting the y and z axes at β and γ, respectively
(x, y, γ) . . .	Plane normal to the z axis and intersecting it at γ
$\pm\{x, y, z; \ldots\}$.	$x, y, z; \bar{z}, \bar{y}, \bar{z}; \ldots$
Z	Number of formula-entities of weight M_r per unit cell

Z_j	Atomic number of the jth atom in a unit cell
α, β, γ	Angles between the pairs of unit-cell edges bc, ca, and ab, respectively
$\alpha^*, \beta^*, \gamma^*$ . . .	Angles between the pairs of reciprocal unit-cell edges b^*c^*, c^*a^*, and a^*b^*, respectively
δ	Path difference
$\varepsilon, \varepsilon(hkl)$ . . .	Statistical weight of a reflection
ε, ω	Principal refractive indices for a uniaxial crystal
θ	Bragg angle
λ	Wavelength
μ	Linear absorption coefficient
ν	Frequency
ν_n	Spacing between the zeroth- and nth-layer lines
ρ	Radius of stereographic projection
$\rho(x, y, z)$ . . .	Electron density at the point x, y, z
Φ	Interfacial (internormal) angle
$\phi(hkl), \phi(h), \varphi$.	Phase angle associated with a structure factor
χ, ψ, ω	$(\cos\chi, \cos\psi, \cos\omega)$ direction cosines of a line with respect to the x, y, and z axes
ω	Angular frequency
Ω	Azimuthal angle in experimental methods

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