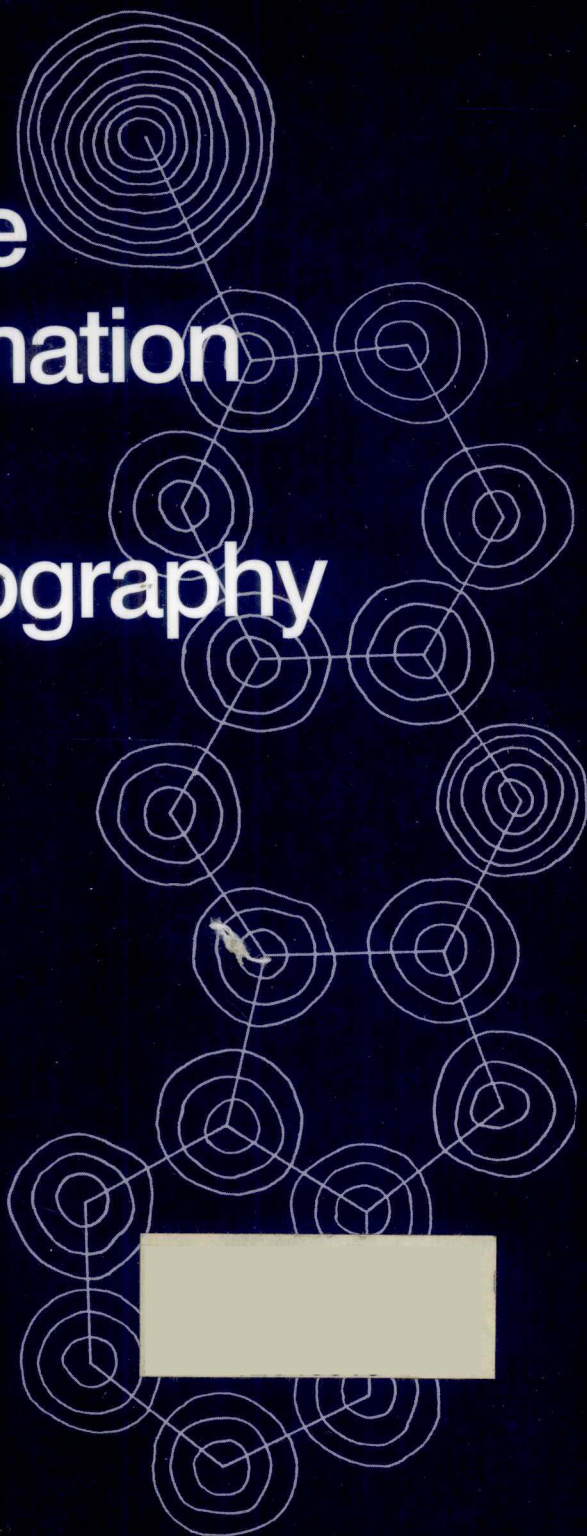


Fourth Edition

Structure Determination by X-ray Crystallography

Mark Ladd
and
Rex Palmer



Structure Determination by X-ray Crystallography

Fourth Edition

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Foreword

I was highly flattered when I was asked by Mark Ladd and Rex Palmer if I would write the Foreword to this Fourth Edition of their book. "Ladd & Palmer" is such a well-known and classic book on the subject of crystal structure determination, one of the standards in the field: I did feel daunted by the prospect, and wondered if I could do justice to it.

The determination of crystal structures by X-ray crystallography has come a long way since the 1912 discoveries of von Laue and the Braggs. In the intervening years great advances have been made, so that today it is almost taken for granted that crystal structures can be determined in which hundreds, if not thousands, of separate atomic positions can be found with apparent ease. In the early years the structures of relatively simple materials, such as the alkali halides, were often argued over and even disputed, whereas today we routinely see published structures of most complex molecular crystals, including the structures of viruses and proteins.

How has this phenomenal development come about? Partly it is the advance in theories of diffraction, particularly made in order to solve the well-known phase problem. If one knows all the phases and amplitudes of the scattered x-rays it is then a straightforward matter to find the positions of the atoms in the crystal: indeed this information tells us everything we need to know. However, because of the absence of suitable lenses for X-rays, one normally only measures the scattered amplitudes and the phase information is lost. The advent of techniques such as the use of direct methods and anomalous scattering measurements has meant that usually reliable estimates of the phases can be made, thus completing the information needed to 'see' the atoms in the structure.

Another advance has been in the area of instrumentation. For many years after the discovery of X-ray diffraction the usual way in which X-ray diffraction data were collected was by using a photographic film around the crystal and then the intensities of the resulting spots were estimated by eye (As I write this I am startled by the realisation that such crude techniques were widely used even when I was a research student in crystallography back in the 1960's!). Fortunately, this time-consuming and very imprecise method has now been superseded by the development of the commercial diffractometer. Originally such machines had only two circles of movement and then later were replaced by more sophisticated machines

with four circles of movement. These latter diffractometers freed us from having to orient the crystal before collecting data, as they were capable of searching for x-ray spots and working out the orientation, unit cell and symmetry for themselves. More recently, area detectors in the form of image plates and CCD systems have become available so that huge amounts of data can be collected in as little as one hour. There have been advances also in the x-ray sources, with x-ray synchrotrons in several locations around the world providing highly intense and wavelength-tuneable x-rays. And then one must not forget the incredible development of modern computers. When I started in research we were still using Facit calculators (these mechanical devices were capable only of adding, subtracting, multiplying and dividing). Then computers as large as a room came along with storage capacities of just 8K. The first computer that I used is now on exhibit in the Science Museum in London! Today we can do almost everything on a desktop PC. It is perhaps not commonly realised that many of the routines and algorithms that have now become standard on modern computers owe their very existence to the huge computational demands made by crystallographers, since for many years they were just about the only scientists with a need to process very large amounts of data.

Today, we have computer power, automatic diffractometers to collect the data and computer programs that in principle analyse the data and produce for us the crystal structures. Nowadays, there are many scientists around the world using these systems and publishing crystal structures completely automatically. So why do we need Ladd & Palmer? After all, when we drive a car these days, do we generally need to know how the engine works? Is it not case that crystal structure determination has become so automatic that we need only press buttons?

Unfortunately (or fortunately for we crystallographers) it is not so simple. The literature is full of incorrectly determined crystal structures made by people without experience, despite the sophistication of the techniques available to them. For example Richard Marsh in the United States has made a career out of exposing false space groups in lots of published papers. I have seen instances where protein structures have been determined and accepted, but a look through a polarising microscope immediately showed that the crystals were twinned and therefore of lower symmetry than had originally been assumed. And then, there are many, many instances where molecules do not sit in well-defined positions in a crystal, but are disordered over two or more sites. In the last ten or so years there has been a veritable explosion in protein crystal structure determination in which people, mainly with training in biology, but with little or no crystallographic training, have come into the subject. For them it is the molecule that is important and not the crystal per se. For them the crystal is simply a necessary and sometimes annoying way of getting molecules aligned in a regular arrangement, so that diffraction can be used as a means to find out about them. This lack of basic knowledge can be dangerous as it raises questions about the validity of their results.

Crystal structure determination is full of pitfalls to trap the unwary. The International Union of Crystallography several years ago even coined the phrase “Practicing Crystallographic Idiot” or PCI for short, to describe those who treat structure determination as automatic. This is why we need Ladd & Palmer. We need to convert the PCI to a PCE (“Practicing Crystallographic Expert”)! Now there are many books on crystallography and structure determination out there, but Ladd & Palmer is probably unique in being the most thorough treatment you are going to find. The book takes you right through from simple beginnings up to the most recent ideas in macromolecular crystallography. There are lots and lots of worked examples and tutorials, and I see that in this Fourth Edition even computer software has been included. I note with pleasure that now Ladd & Palmer has a chapter on structure determination using powders. The use of powder diffraction took off back in 1969 with the publication of the seminal paper by Hugo Rietveld, in which he showed that it was possible to refine the atomic positions in a structure by fitting the total profile of the powder pattern. As a result, after having languished many years in the crystallographic doldrums, powder diffraction suddenly took off. In recent years the idea of *ab initio* determination of structures using powder methods has become a ‘hot’ topic, and recently success has even been gained in determining structural information about proteins. As there are many instances where single crystals cannot be obtained or where twinning is a severe phenomenon, this opens possibilities of still getting atomic positions. This Fourth Edition is a substantial and scholarly work that deserves to be on the shelves of anyone wishing to determine crystal structures. I am very pleased to have had the opportunity to recommend it to you.

A. M. Glazer
Clarendon Laboratory
Oxford University

Preface to the Fourth Edition

There have been many advances in x-ray crystallography since the production of the third edition of this book, and we have endeavoured to introduce a number of them into this new edition. The overall plan of the book and the important additions to the previous two editions have been maintained because we believe that they have been well received in the academic community, but substantial revisions have now been carried out and new material and chapters added.

In particular, we have extended the discussion of the theory of x-ray diffraction and added new chapters on structure determination from powder data, on macromolecular crystallography and on computational procedures in x-ray crystallography. We consider that x-ray crystallography is a universal tool for studying molecular structure, a view upheld by the pioneers in the subject, notably W. H. & W. L. Bragg, J. D. Bernal, Dorothy Hodgkin (néé Crowfoot), Kathleen Lonsdale (néé Yardley) and Linus Pauling, so that the broadening of the scope of the text in this way is fully justified.

We have maintained the practice of devising problems to illustrate the work of each chapter, and have provided detailed, tutorial solutions. The appendices contain mostly mathematical procedures related to the material of the main text.

This edition is accompanied by a suite of computer programs on a compact disc. The programs are available also at the web address <www.wkap.nl/subjects/crystallography> from which they can be downloaded, and which, except for ESPOIR, ITO12 and LEPAGE, may be amended from time to time. The first set will be labelled Version 1, dated 1 April 2003.

These programs enable the reader to participate fully in many of the aspects of x-ray crystallography discussed in the book. In particular, the program system XRAY* is interactive, and enables the reader to follow through, at the monitor screen, computational techniques involved in single-crystal structure determination, albeit in two dimensions. Several sets of x-ray data are provided for practice with this system.

The text, particularly the later chapters, refers to a number of programs that are essential in current structure analysis, by both single-crystal and powder

methods. Abbreviated references to these programs are listed in Appendix 10, where authors' names and Journal and/or Internet addresses are provided, so that through the goodwill of the authors they may be obtained from the appropriate sources. In order to distinguish between these programs and those in the CD suite with the book, the latter are marked with an asterisk, as in XRAY*.

We have listed appropriate bibliographic references at the end of each chapter. Although it leads to duplication in some cases, we feel that it is most useful to have these references close to the material to which they are relevant. In addition, we call attention to the International Union of Crystallography, which publishes journals, books and other information of importance to crystallographers. A convenient reference to this material is <<http://www.iucr.ac.uk>>

Our first acknowledgement is to Professor A. M. Glazer of the Clarendon Laboratory, Oxford who kindly wrote the Foreword to this book. We are grateful also to the various copyright holders for permission to reproduce those figures that carry appropriate acknowledgements; a number of figures, particularly in Chapters 7 and 10, has been prepared by Effective Graphics U.K. The original program which formed the basis of the XRAY* package included with the CD suite was prepared by Dr. Neil Bailey of the University of Sheffield and his colleagues, and we are grateful to him for permission to use it in the present context. It has been modified (M.F.C.L.) for PC operation and several enhancements made, including the contouring of Fourier maps on the monitor screen. We thank Dr. Jan Visser of the Technisch Physische Dienst, Delft for permission to include the powder indexing program IT012*; Dr. Armel Le Bail of Laboratoire des Fluorures, Université du Maine, Le Mans for permission to include the program ESPOIR*; Dr. A. L. Spek of the University of Utrecht for making available the program LEPAOE*; Dr. Lynne McCusker of the Department of Physics, ETH Zurich for reading the chapter on powder methods and for helpful comments; Mr. Robin Shirley of the Department of Psychology, University of Surrey for helpful discussions on aspects of powder indexing; and also Dr. Lachlan Cranswick and Dr. Jeremy Cockcroft of the School of Crystallography, Birkbeck College, London for further useful comments. Finally, we thank Kluwer Academic/Plenum Publishers for inviting this edition and for bringing it to a state of completion.

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Mark Ladd
Rex Palmer

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 A3. 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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Every effort has been made to ensure the correct functioning of the software associated with this book. However, the reader planning to use the software should note that, from the legal point of view, there is no warranty, expressed or implied, that the programs are free from error or will prove suitable for a particular application; by using the software the reader accepts full responsibility for all the results produced, and the authors and publisher disclaim all liability from any consequences arising from the use of the software. The software should not be relied upon for solving a problem, the incorrect solution of which could result in injury to a person or loss of property. If you do use the programs in such a manner, it is at your own risk. The authors and publisher disclaim all liability for direct or consequential damages resulting from your use of the programs.

Physical Constants and Other Numerical Data

Atomic mass unit	u	1.6605×10^{-27} kg
Avogadro constant	L	6.0221×10^{23} C mol ⁻¹
Bohr radius for hydrogen	a_0	5.2918×10^{-11} m
Elementary charge	e	1.6021×10^{-19} C
Planck constant	h	6.6261×10^{-34} J Hz ⁻¹
Rest mass of the electron	m_e	9.1094×10^{-31} kg
Rest mass of the neutron	m_n	1.6750×10^{-27} kg
Speed of light in a vacuum	c	2.9979×10^8 ms ⁻¹

Conversions

1 eV (electron-volt) = 1.6021×10^{-19} J

1 Å (Ångström unit) = 10^{-10} m = 0.1 nm

Prefixes to Units

femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga
f	p	n	μ	m	c	d	k	M	G
10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^3	10^6	10^9

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
\AA	Ångström unit
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 j th atom
C	C -face-centered unit cell
\nless	"Not constrained by symmetry to equal"

c	Speed of light; as a subscript: calculated, as in $ F_c $
D_m	Experimentally measured crystal density
D_c, D_x	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 hkl th reciprocal lattice point
Da	Dalton; equivalent to u
$E, E(hkl)$	Normalized structure factor (centrosymmetric crystals)
$\mathcal{E}(hkl)$	Total energy of the hkl th diffracted beam from one unit cell
e	Electron charge
e, \exp	Exponential function
$F(hkl)$	Structure factor for the hkl th spectrum referred to one unit cell
$F^*(hkl)$	Conjugate of $F(hkl)$
$ F $	Modulus, or amplitude, of the structure factor $F(hkl)$
f	Atomic scattering factor
$f_{j,\theta}, f_j$	Atomic scattering factor for the j th atom
g	Glide line in two-dimensional space groups
g_j	Atomic scattering factor for the j th 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 <i>after</i> 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
I	Body-centered unit cell; intensity of reflection
$I(hkl)$	Intensity of reflection from the (hkl) planes referred to one unit cell
\mathcal{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 (counterclockwise) sense
$J(hkl)$	Integrated reflection
K	Scale factor for $ F_o(hkl) $ data
L	Lorentz correction factor
M_r	Relative molecular mass ('weight')
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 (several R parameters exist)
\bar{R}	Inversion axis
\mathcal{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 j th atom
$[UVW]$	Zone or direction symbol
$\langle UVW \rangle$	Form of zone axes or directions
u	Atomic mass unit
(u, v, w)	Components of a vector in Patterson space
\bar{U}^2	Mean-square amplitude of vibration
v_n	Spacing between the zeroth- and n th-layer lines
V	Volume
V_c	Volume of a unit cell
w	Weight factor
x, y, u, z	Crystallographic reference axes descriptors
X, Y, Z	Spatial coordinates, in absolute measure, of a point, parallel to the x, y , 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 j th 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
$\pm\{x, y, z; \dots\}$	$x, y, z; \bar{x}, \bar{y}, \bar{z}; \dots$
Z	Number of formula entities of mass M_r per unit cell
Z_j	Atomic number of the j th 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 (epsilon factor)
ε, ω	Principal refractive indices for a uniaxial crystal
θ	Bragg angle

κ	Reciprocal space constant
λ	Wavelength
μ	Linear absorption coefficient
ν	Frequency
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
$\bar{X}, \langle X \rangle$	Average value of X

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