

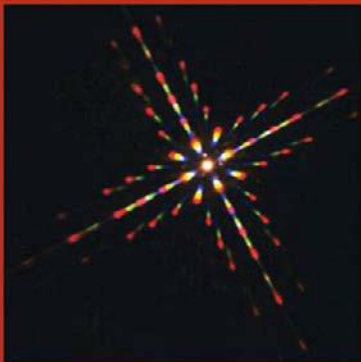
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Crystal Structure Analysis

A Primer

Third Edition

JENNY PICKWORTH GLUSKER
AND KENNETH N. TRUEBLOOD



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Crystal Structure Analysis

A Primer

Third Edition

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*To those who taught us crystallography,
most especially Dorothy Crowfoot Hodgkin,
A. Lindo Patterson, J. H. Sturdivant,
Robert B. Corey, and Verner Schomaker.*

Preface to the third edition

Our aim in this book is to explain how and why the detailed three-dimensional architecture of molecules can be determined from the diffraction patterns produced when X rays or neutrons are scattered by the atoms in single crystals. The diffraction pattern can be analyzed (by the methods described here in this book) to provide molecular structures of the components of the crystal and information on their interactions with each other. In the last 25 years, since the second edition was published, the experimental procedures for achieving molecular structure in this manner have greatly improved and computing facilities (expensive and mostly confined to scientific laboratories in the 1970s and 1980s) are now available to all. Larger and larger molecules can now be investigated at higher and higher resolutions and methods for solving the phase problem (which allow us to convert experimental diffraction data into a map of the material that did the scattering) are now much more efficient. Therefore we thought that it is time for an updated version of this book. We have not changed the overall scheme of the book, merely tried to bring it into the twenty-first century.

Sadly my coauthor, Ken Trueblood, died in May 1998—a big loss to X-ray crystallography. This book was the last scientific item he worked on. He strongly urged me to try hard not to increase the length of the book, and I have tried to comply with this request. It has, however, not been possible with this new edition to make full use of Ken's wisdom and insight. We have had a long history of collaboration since the early days when I was a graduate student in Dorothy Hodgkin's laboratory in Oxford working on the crystal structure of a vitamin B₁₂ derivative, and Ken was at UCLA programming the massive computer, SWAC, for crystallographic programs that tackled large structures. Several teaching examples in this book came from this collaboration across the miles between Los Angeles and Oxford.

This new edition has been improved by generous assistance from Dr. Peter Müller at MIT and Dr. Virginia Pett at the College of Wooster, Ohio. They both read the entire manuscript and made invaluable suggestions for improving it. I also wish to extend sincere thanks to Pat Bateman and Eileen Pytko for typing assistance and to Karen Albert, Carol Brock, Sue Byram, Bud Carrell, Bryan Craven, Dick Dickerson, Dave Duchamp, David Eisenberg, Debra Foster, Bob Hesse, Amy Katz, Bill Stallings, and Karen Trush. The staff at Oxford University Press have been most helpful, and my thanks go to Emma Lonie, April Warman, and Sonke Adlung. The copy-editor Douglas Meekison and the

illustrators at SPi Publishing also deserve thanks. Finally the National Institutes of Health (CA-10925 to JPG and CA-06927 to FCCC) provided the support through the years which made this book possible.

There are numerous additional sources of information now available for students of the subject (see the References and further reading section). These include the IUCr texts and monographs on crystallography listed at the beginning of the book, *International Tables for Crystallography* and the World Wide Web. The latter contains many examples of crystallography courses given at various universities and research organizations throughout the world. They often contain useful illustrations and some are interactive; unfortunately the identifying URLs of the sites of these teaching items do not seem to last with time so it is better for a student to use a search engine and define the specific subject of interest.

Finally my thanks to all of you who have provided me through the years with encouragement, counsel, and advice on the teaching of this subject.

Jenny P. Glusker
Philadelphia, Pennsylvania
March 2010

Preface to the second edition

In the thirteen years since the first edition of this book appeared there have been numerous advances in the practice of structural crystallography. Furthermore, many users of the first edition have suggested ways in which the book might have been improved. In this revision, we have endeavored to incorporate those suggestions and to describe the most significant advances in practice. The major changes include a considerable elaboration of the treatment of direct methods, a new chapter on anomalous dispersion and absolute configuration, a more detailed treatment of biological macromolecules, a reorganization and expansion into a separate chapter of the discussion of microcrystalline and non-crystalline materials, enlargement of the section on experimental methods to include discussion of area detectors and synchrotron radiation, and a new appendix on molecular geometry. The bibliography has been expanded by more than 50 percent, and the glossary doubled in length.

Our aim is to explain how and why the detailed three-dimensional architecture of molecules can be determined by an analysis of the diffraction patterns produced when X rays (or neutrons) are scattered by the atoms in single crystals. As with the first edition, the book is intended primarily for those who want to understand the fundamental concepts on which crystal structure determination is based without necessarily themselves becoming specialists in crystallography—an audience that includes advanced undergraduates who have studied some physics and chemistry, as well as graduate students and other research workers.

This book is divided, as before, into three parts; each has been expanded, the last two significantly. Part I, comprising the first four chapters, deals with the nature of the crystalline state, certain relevant facts about diffraction generally and diffraction by crystals in particular, and the experimental procedures used. Part II, consisting of Chapters 5 through 10, examines the problem of converting the experimentally obtained data (directions and intensities of diffracted beams) into a model of the atomic arrangement that scattered these beams—in other words, the problem of determining the approximate structure of this scattering matter, a “trial structure” suitable for refinement. Part III (Chapters 11 through 14) is concerned with techniques for refining this approximate structure to the degree warranted by the experimental

data and with discussions of the structural parameters and other information that can be derived from a careful structure determination. It also includes a discussion of microcrystalline materials and glasses, and an overall summary of the various stages in structure analysis.

We wish to thank those who have helped us in this endeavor, particularly Bill Stallings and John Stezowski, who read through our manuscript and made most helpful comments, and Jack Dunitz who helped us with the glossary. We are also grateful to Margaret J. Adams, Bob Bryan, Bud Carrell, Philip Coppens, Dick Dickerson, Jose Donnay, David Eisenberg, Doris Evans, Setsuo Kashino, Henry Katz, Lisa Keefe, Bill Parrish, Eileen Pytko, Miriam Rossi, Christopher Smart, Verner Schomaker and David Zacharias for their help. One of us (J.P.G.) acknowledges financial support from the National Institutes of Health, U.S.P.H.S. (grant CA-10925).

Finally, we appreciate the help of all of you who have encouraged us through the years with your comments and constructive criticisms.

Philadelphia
Los Angeles
April 1985

J.P.G.
K.N.T.

Preface to the first edition

This book, which developed from a talk to the California Association of Chemistry Teachers at Asilomar in 1966, is designed to serve as an introduction to the principles underlying structure analysis by X-ray diffraction from single crystals. It is intended both for undergraduates who have had some previous chemistry and physics and for graduate students and other research workers who do not intend to become specialists in crystallography but who want to understand the fundamental concepts on which this widely used method of structure determination is based. We have included many illustrations, with legends that form an important part of the text, a rather detailed glossary of common terms, an extensive annotated bibliography, and a list of the symbols used.

Our aim is to explain how and why the detailed three-dimensional architecture of molecules can be determined by an analysis of the diffraction patterns produced when X rays (or neutrons) are scattered by the atoms in single crystals. Part I, consisting of the first four chapters, deals with the nature of the crystalline state, certain relevant facts about diffraction generally and diffraction by crystals in particular, and, briefly the experimental procedures that are used. Part II comprises an examination of the problem of converting the experimentally obtained data (directions and intensities of diffracted beams) into a model of the atomic arrangement that scattered these beams, that is, the problem of determining the approximate structure of this scattering matter. Part III is concerned with techniques for refining this approximate structure to the degree warranted by the experimental data, and also includes a brief discussion of some of the auxiliary information, beyond the geometric details of the structure, that can be learned from modern structure analysis. Most mathematical details have been relegated to several Appendices.

We are indebted to D. Adzei Bekoe, Helen Berman, Herbert Bernstein, Carol Ann Casciato, Anne Chomyn, Joyce Dargay, David Eisenberg, Emily Maverick, Walter Orehowsky, Jr., Joel Sussman, and David E. Zacharias for their help in suggesting revisions of earlier drafts, and to all those writers on crystallography whose ideas and illustrations we have included here.

One of us (J.P.G.) acknowledges financial support from the National Institutes of Health, U.S.P.H.S. (grants CA-10925, CA-06927 and RR-05539), and an appropriation from the Commonwealth of

Pennsylvania. This book is Contribution No. 2609 from the Department of Chemistry, University of California, Los Angeles.

Finally, we want to express our gratitude to Miss Doris E. Emmott for her patient, painstaking, and precise typing of the manuscript and to Miss Leona Capeless of Oxford University Press for her help through the stages of publication.

Philadelphia
Los Angeles
April 1971

J.P.G.
K.N.T.

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Symbols used in this book

A	Amplitude of a wave.
$A, B, A(hkl),$ $B(hkl), A_j B_j$	Values of $ F \cos \alpha$ and $ F \sin \alpha$, respectively; that is, the components of a structure factor $F = A + iB$. The subscript j denotes the atom j .
$A', B', A'', B'', A_d,$ B_d	Values of A and B taking into account f' (to give A' and B'), f' and f'' (to give A'' and B''), and the anomalously scattering atom (A_d and B_d).
Abs	Absorption factor.
a	The width of each of a series of (or single) diffracting slits.
a, b, c	Unit-cell axial lengths.
$\mathbf{a}, \mathbf{b}, \mathbf{c}$	Unit-cell vectors of the direct lattice.
a^*, b^*, c^*	Lengths of the unit-cell edges of the reciprocal lattice.
$\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$	Unit-cell vectors in reciprocal space.
a, b, c, n, d, g	Glide planes. The row parallel to the translation is designated; it is the side of the net (a , b , or c) or its diagonal (n in a primitive net, d in a centered net). In two dimensions, a glide-reflection line is represented by g .
B_{iso}, B	Isotropic atomic displacement (or temperature or vibration) parameter.
$b^{11}, b^{22}, b^{33}, b^{12},$ $b^{23}, b^{31}, b_{ij}, b_{11j}$	Six anisotropic vibration parameters representing anisotropic temperature motion; a third subscript j denotes the atom j .
c_i, c_1, c_2, c_r	Wave amplitudes (see Chapter 5).
d	The distance between two diffracting slits.
d_{hkl}, d	The spacing between the lattice planes (hkl) in the crystal.
$d_{\text{A-B}}$	Bond distance between atoms A and B.
E, E_{hkl}, E_H	Values of F corrected to remove thermal-motion and scattering-factor effects. These are called "normalized structure factors."
F	Face-centered lattice.
$F(hkl), F, F(000)$	The structure factor for the unit cell, for the reflection hkl . It is the ratio of the amplitude of the wave scattered by the entire contents of the unit cell to that scattered by a single electron. A phase angle for the scattered wave is also involved. $F(000)$ is thus equal to the total number of electrons in the unit cell.
$ F(hkl) , F $	The amplitude of the structure factor for hkl with no phase implied.
$ F_o , F_c $	Amplitudes of structure factors observed ($ F_o $), that is, derived from measurements of the intensity of the diffracted beam, and calculated ($ F_c $) from a postulated trial structure.

$F_P, F_{PH1}, F_{PH2},$ $F_{H1}, F_{H2}, F_M,$ $F_{M'}, F_R, F_T, F_{T'}$	Structure factors for a given value of hkl for a protein (P), two heavy-atom derivatives ($PH1$ and $PH2$), the parts of F due to certain atoms ($M, M', H1$ and $H2$) and the rest of the molecule (R), and for the total structure (T and T').
F	Structure factor when represented as a vector.
F_{novib}	Value of F for a structure containing only nonvibrating atoms.
F_+, F_-	Values of $F(hkl)$ and $F(\bar{h}\bar{k}\bar{l})$ when anomalous-dispersion effects are measurable.
$f(hkl), f, f_j$	Atomic scattering factor, also called atomic form factor, for the hkl reflection relative to the scattering by a single electron. The subscript j denotes atom j .
f', f''	When an anomalous scatterer is present the value of f is replaced by $(f + f') + if''$.
$G(r)$	Radial distribution function.
G, H	Values of A and B with the scattering factor contribution $(f + f' + f'')$ removed (see Chapter 10).
H	Reciprocal lattice vector.
H, K	Indices of two Bragg reflections. $H = h, k, l$; $K = h', k', l'$.
$hkl, -h, -k, -l,$ $\bar{h}\bar{k}\bar{l}, hki$	Indices of the Bragg reflection from a set of parallel planes; also the coordinates of a reciprocal lattice point. If h, k , or l are negative they are represented as $-h, -k, -l$ or $\bar{h}\bar{k}\bar{l}$. In hexagonal systems a fourth index, $i = -(h + k)$, may be used (see Appendix 2).
(hkl)	Indices of a crystal face, or of a single plane, or of a set of parallel planes.
I	Body-centered lattice.
$I(hkl), I$	Intensity (on an arbitrary scale) for each reflection.
I_{corr}	Value of I corrected for Lp and Abs.
i	An "imaginary number," $i = \sqrt{-1}$
i, j	Any integers.
Lp	Lorentz and polarization factors. These are factors that are used to correct values of I for the geometric conditions of their measurement
l	The distance between two points in the unit cell (e.g., bond length).
l	A direction cosine.
M	Molecular weight of a compound.
M_1, M_2, M, M'	Atoms or groups of atoms that are interchanged during the preparation of an isomorphous pair of crystals. Heavy atoms substituted in a protein, P .
m	Mirror planes.
N	The number of X-ray reflections observed for a structure.
$N_{\text{Avog.}}$	Avogadro's number. The number of molecules in the molecular weight in grams, 6.02×10^{23} .
n	Any integer. Used for n -fold rotation axes. Also used as a general constant.
n_r	Screw axis designations, where n and r are integers (2, 3, 4, 6 and 1, ..., $(n - 1)$, respectively).
$P, PH1, PH2$	Protein (P), also heavy-atom derivatives $PH1$ and $PH2$.
$P(uvw), P,$ $P_s(uvw)$	The Patterson function, evaluated at points of u, v, w in the unit cell. The $P_s(uvw)$ function is used with anomalous-dispersion data (see Chapter 10).

P, A, B, C, F, I	Lattice symbols. Primitive (P), centered on one set of faces (A, B, C), or all faces (F) of the unit cell, or body-centered (I).
P_+	Probability that a triple product is positive (see Eqns. 8.6 and 8.7).
p, q	Path differences.
Q	The quantity minimized in a least-squares calculation.
R	Discrepancy index $R = \frac{\sum(F_o - F_c)}{ F_o }$. Also called R factor, R value, or residual.
R/S	System of Cahn and Ingold for describing the absolute configuration of a chiral molecule.
r	The distance on a radial distribution function.
$s(hkl)$	The sign of the reflection hkl for a centrosymmetric structure.
t	Crystal thickness.
U^{11}, U^{ii}, U^{ij}	Anisotropic vibration parameters.
$\langle u^2 \rangle$	Mean square amplitude of atomic vibration.
u, v, w	The coordinates of any one of a series of systematically spaced points, expressed as fractions of a, b , and c , in the unit cell for a Patterson (or similar) function.
V_c, V, V^*	The unit-cell volume in direct and reciprocal space.
V_M	Matthews coefficient, volume on \AA^3 per dalton of protein.
$w(hkl)$	The weight of an observation in a least-squares refinement.
X, Y, Z	Cartesian coordinates for atomic positions.
$x, y, z; x_j, y_j, z_j;$ x, y, z, u	Atomic coordinates as fractions of a, b , and c . The subscript j denotes the atom under consideration. If the system is hexagonal a fourth coordinate, u , may be added (see Appendix 2).
x_1, x_2, x_j, x_r	Displacements of a wave at a given point. The waves are each designated 1, 2, j ; r is the resultant wave from the summation of several waves.
x, y, z	Coordinates of any one of a series of systematically spaced points, expressed as fractions of a, b, c filling the unit cell at regular intervals.
Z	Number of molecules in a unit cell.
Z_i, Z_j	The atomic number (total number of diffracting electrons) of atoms i and j .
α, β, γ	Interaxial angles between \mathbf{b} and \mathbf{c} , \mathbf{a} and \mathbf{c} , and \mathbf{a} and \mathbf{b} , respectively (alpha, beta, gamma).
$\alpha^*, \beta^*, \gamma^*$	Interaxial angles in reciprocal space.
$a(hkl), a, a_M, a_P,$ a_H	Phase angle of the structure factor for the reflection hkl . $a = \tan^{-1}(B/A)$.
$\alpha_1, \alpha_2, \alpha_j, \alpha_r$	Phases of waves 1, 2, j , and r , the resultant of the summation of waves, relative to an arbitrary origin.
$\Delta F $	The difference in the amplitudes of the observed and calculated structure factors, $ F_o - F_c $ (delta $ F $).
$\Delta\rho$	Difference electron density.
δ	Interbond angle.
δ_{ij}	An index that is 1 when $i = j$ and 0 elsewhere; i and j are integers (delta).

ε	Epsilon factor used in calculating normalized structure factors (see Glossary).
θ, θ_{hkl}	The glancing angle (complement of the angle of incidence) of the X-ray beam to the "reflecting plane." 2θ is the deviation of the diffracted beam from the direct X-ray beam (two theta).
κ	A device for aligning the crystal and detector in a diffractometer that utilizes κ geometry (Figure 4.12) (kappa).
λ	Wavelength, usually that of the radiation used in the diffraction experiment (lambda).
μ/ρ	Mass absorption coefficient. μ , linear absorption coefficient; ρ , density.
$\rho(xyz), \rho_{\text{obs}}, \rho_{\text{calc}}$	Electron density, expressed as number of electrons per unit volume, at the point x, y, z in the unit cell (rho).
Σ	Summation sign (sigma).
Σ_1, Σ_2	Listing of triple products of normalized structure factors (see Chapter 8).
τ	Torsion angle.
ϕ	An angular variable, proportional to the time, for a traveling wave. It is of the form $2\pi\nu t$, where ν is a frequency and t is the time (phi).
ϕ	Angle on spindle axis of goniometer head. See diffractometer (Figure 4.12).
ϕ_H	The phase angle of the structure factor of the Bragg reflection H .
χ	Angle between ϕ axis and diffractometer axis (see Figure 4.12) (chi).
ψ	Angle incident beam makes with lattice rows (see Appendix 4) (psi).
ω	Angle between diffraction vector and plane of χ circle on diffractometer (Figure 4.12) (omega).
$\langle \rangle$	The mean value of a quantity.
$1, 2, 3, 4, 6$	Rotation axes.
$\bar{1}, \bar{2}, \bar{3}, \bar{4}, \bar{6}$	Rotatory-inversion axes.
$2_1, 4_1, 4_2, 4_3$	Screw axes n_r .