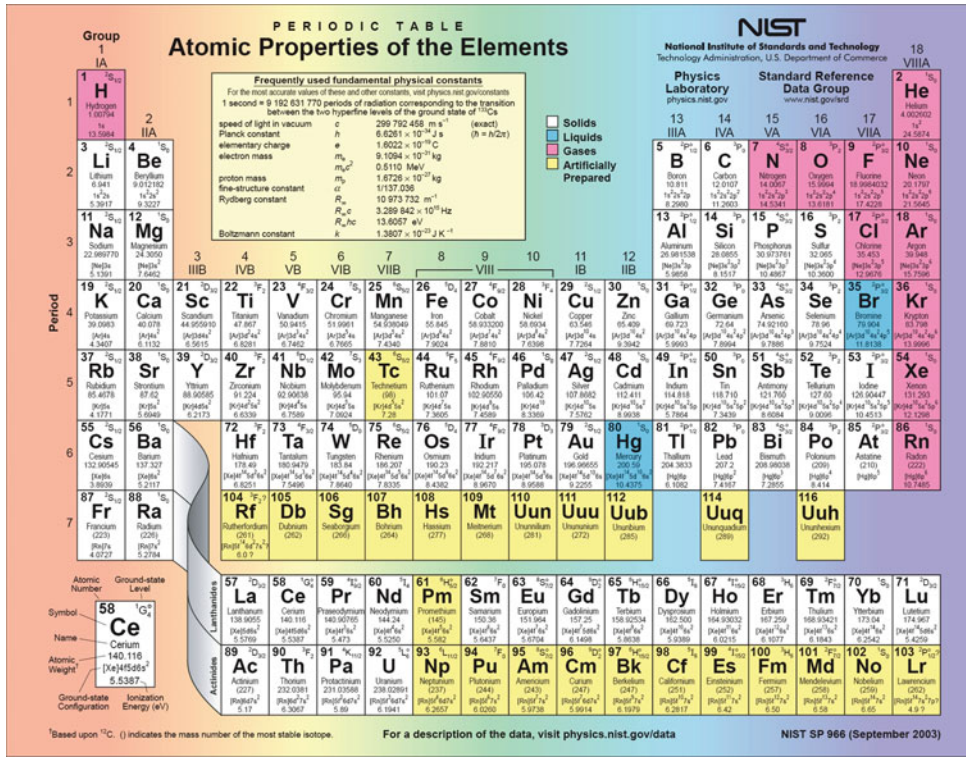
Structure Determination by X-ray Crystallography



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Mark Ladd • Rex Palmer

Structure Determination by X-ray Crystallography

Analysis by X-rays and Neutrons

Fifth Edition

Celebrating the Centenary of X-ray Crystallography

Springer

Mark Ladd
Formerly Head of Chemical Physics
University of Surrey
Guildford, England

Rex Palmer
Reader Emeritus in Structural Crystallography
Birkbeck College, University of London,
London, England

Visiting Professor in X-ray Crystallography
University of Greenwich, England

Senior Visiting Research Fellow
Christ Church University,
Canterbury, England

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When you can measure what you are speaking about and express it in numbers, you know something about it; but when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind; it may be the beginning of knowledge, but you have scarcely in your thoughts advanced to the state of science, whatever the matter may be.

Lord Kelvin

To Valentia and Hilda

Foreword

I am privileged to write the Foreword to this fifth edition of Ladd and Palmer's *Structure Determination by X-ray Crystallography*, a textbook that is now world renowned and that has helped educate two generations of crystallographers in the theory and practice of modern crystallography, myself included. Indeed, a well-worn first edition of this venerable text remains on my shelves today, now somewhat battered and bruised from passage through the hands of successive students who have learned the fundamentals of crystallography from its pages.

This new fifth edition is especially timely, marking as it does a century of discovery in which X-ray diffraction, and diffraction of other radiations, has opened a window to the atomic world. From fundamental knowledge of atomic interactions and chemical bonds in the simplest materials to the atomic resolution analysis of the molecular machines of the cell, crystallographic science underpins much of our understanding of the world we live in today. In recent years, advances in diffraction theory, automated technologies, and computational tools have helped move crystallography from a specialist discipline to a standard laboratory tool across many fields of science. In some fields, these advances have been so spectacularly successful that the solution of the crystal structures of all but the most challenging systems is now considered largely routine. At the same time, the development of a new generation of high powered synchrotron, neutron and, most recently, free electron laser facilities are pushing crystallographic science to new frontiers, aiming to provide diffraction from single molecules, to locate light atoms such as hydrogen in crystal structures, and to move beyond static crystal structures towards time-resolved analyses of structural dynamics at pico-second timescales.

For the interdisciplinary students of today seeking a thorough and detailed understanding of the principles and methods of modern crystallography, Ladd and Palmer remains as essential and relevant today as when it first appeared some 35 years ago. Building from the fundamental concepts of crystallography, through crystal symmetry to the mathematical formalism of diffraction and on to the principle and practice of structure determination, the text provides an excellent introduction to the techniques and applications of crystallography, illustrated throughout by applications to real world problems. The fifth edition is expanded and enhanced with updated examples and description of recent technical developments and achievements in X-ray crystallography and benefits from a completely new chapter that describes

the application of neutron crystallography in structural science. This is an important addition. Neutrons are scattered by atomic nuclei and have a magnetic moment. Hence, neutron diffraction can be used to determine accurate atomic and magnetic structures of materials. With a new generation of neutron sources and instruments now coming on-line, these properties will be increasingly exploited in fundamental studies of new inorganic, organic, and biological systems, of superconducting and magnetic materials, and for structure-function analysis of hydrogen atoms in macromolecules.

Extending the scope of this classic text beyond the purely X-ray Crystallography of its title to include diffraction of other radiations acknowledges some of the new frontiers and ever-increasing impact of crystallographic analysis in structural sciences. As has been the case for the last 35 years, Ladd and Palmer is set to educate and equip the students of today to drive and inspire the developments of tomorrow!

Neutron Sciences Directorate
Oak Ridge National Laboratory, TN, USA Dean A.A. Myles

Preface to the Fifth Edition

We were honoured to be asked by Springer, New York to prepare a fifth edition of *Structure Determination by X-ray Crystallography*. First published in 1977 under the Plenum imprint, this book has received wide acclaim in both teaching and research in X-ray crystallography because of its extensive and detailed coverage of all aspects of the subject.

As we prepare this new edition, we are entering the centenary of the discovery of X-ray diffraction in 1912, the beginning of X-ray crystallography as a science in its own right. Today, X-ray crystallography and the complementary technique of neutron diffraction together provide the most powerful tools for the investigation and elucidation of crystal and molecular structures. X-ray and neutron crystallography may be described as the science of the structure of materials, in the widest sense of the phrase, and their ramifications are evident across a broad spectrum of scientific endeavour.

The power of computers and available software has unleashed an unprecedented ability to carry out with speed the complicated calculations involved in crystal structure determination on a desktop PC. This is paralleled by the availability of powerful X-ray and neutron sources and low temperature devices for facilitating measurements at liquid nitrogen temperature or lower, which provide ever higher precision in the determination of crystal structures. However, a detailed knowledge of the theory underlying the process of crystal structure determination is still required in order both to ensure that the literature contains correct well-determined structures and to understand the complexities introduced by features such as disorder and twinning in crystals. There are many pitfalls in crystal structure determination to trap the unwary.

In this new edition, we have continued the approach that has been well reviewed in its earlier editions. We have always kept in mind that students meeting X-ray crystallography for the first time are encountering a new discipline, and not merely extending the range of a subject already studied. In consequence, we have chosen, for example, to discuss the geometry and symmetry of crystals in rather more detail than is found in other books on this subject, for it is our experience that some of the difficulties that students meet in introductory X-ray crystallography lie in their unfamiliarity with a three-dimensional concept, whether they be final-year undergraduate or post-graduate students in chemistry, biochemistry, materials science, geology, bioinformatics, information technology, or physics. Both low molecular weight (small molecules) and macromolecular methods (proteins) are covered in detail.

As well as retaining and thoroughly revising the overall contents of the earlier editions, we have added a significant chapter on neutron diffraction studies, and sections introducing Molecular Modelling and Structure Prediction. In order to maintain a workable size for the book, a number of elaborations of mainly mathematical argument have been stored as Web Appendices on the website http://extras.springer.com.

Although several novel methods have been added to the armoury of crystal structure determination, we limit our discussion principally to Patterson interpretation, Direct Methods, Isomorphous and Molecular Replacement and Powder Crystallography, and developments from them. The basic problem remains the determination of the phases of X-ray reflections, and this problem is addressed in these techniques discussed herein. In order to simulate the actual process of structure determination, we are fortunate to be able to include the XRAY program package prepared by Dr. Neil Bailey and colleagues of the University of Sheffield, and we are grateful to him for permission to use it in the present context. It has been modified (M.L.) for PC operation and several enhancements made, including the presentation of Fourier contour maps on the monitor. Although this package uses two-dimensional data, much valuable insight into X-ray structure determination can be gained, and a number of sets of X-ray data are included.

There are now numerous computer packages available for the many aspects of crystallography that are in current use. We have referred to them freely within the text, and they have been collected in an appendix together with a reference to a source for each so that they become readily available to the practising crystallographer. There are numerous references to each chapter including website addresses for topics of crystallographic importance. References among the text are given as "Sect. 1.2.3," which refers to that section in Chap. 1, or as "(3.4)" which refers to that equation in Chap. 3.

Each chapter contains a set of problems designed to assist the reader in the understanding of the textual material, and detailed tutorial solutions are provided. Some of these problems require computer assistance, and a set of programs has been designed and included with the Web material and dated 1 January 2013 (Version 5.1). In this context, we are grateful to Dr. Jan Vissser of the Technisch Physische Dienst, Delft, Professor Armel Le Bail of Laboratoire Fluorures, Université du Main, Le Mans, and Professor A L Spek of the University of Utrecht for the continued incorporation of the programs ITO12, ESPOIR, and LEPAGE, respectively, in the Program Suite for this book. Finally we thank Springer Science + Business Media for inviting this edition and bringing it to a state of completion.

University of Surrey
Guildford, England — Mark Ladd

Birkbeck College
London, England — Rex Palmer

Disclaimer

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Physical Constants and Other Numerical Data

Atomic mass unit	m_u	1.6605×10^{-27} kg
Avogadro constant	L	6.0221×10^{23} mol^{-1}
Bohr radius for hydrogen	a_0	5.2918×10^{-11} m
Boltzmann constant	k	1.3806×10^{-23} J K^{-1}
Elementary charge	e	1.6022×10^{-19} C
Permittivity of a vacuum	ε	8.8542×10^{-12} F m^{-1}
Planck constant	h	6.6261×10^{-34} J s
Rest mass of the electron	m_e	9.1094×10^{-31} kg
Rest mass of the neutron	m_n	1.6749×10^{-27} kg
Rest mass of the proton	m_p	1.6726×10^{-27} kg
Speed of light in a vacuum	c	2.9979×10^{8} m s^{-1}

Conversions

1 eV (electron-volt) $= 1.6022 \times 10^{-19}$ 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^{-5}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}

Projected Revision of SI Units

The year 1960 saw the publication of *Le Système international d'unités* (the SI) as a rational and coherent system of units for scientific research and communication. A projected revised SI aims to eliminate certain infelicities in the current system, particularly in relation to the kilogram, kelvin, mole, and ampere. The standard kilogram, a Pt–Ir alloy, was adopted as a standard in 1889, but has very slowly lost material over the intervening years. In the case of the kelvin, the purity and isotopic composition of water need to be defined for a complete specification of its triple point, which is used in fixing the kelvin.

The new SI scheme will define the values of certain constants exactly. Thus, it begins with the speed of light (c), which was set exactly as 2.99792458×10^8 m s^{-1} in 1983. A re-definition of the other fundamental SI units can then be projected. For example, the kilogram will be defined such that the Planck constant (h) is exactly $6.6260693 \times 10^{-34}$ J s, then the kilogram will be fixed, since $h\nu = E = mc^2$ and the metre and second have defined values.

The metre is defined in terms of the speed of light, and the second as the distance travelled by light in a vacuum in $1/(2.99792458 \times 10^8)$ s. The second was given originally as $1/(8.6400 \times 10^4)$ of the mean solar day, but in 1967 it was re-defined as the duration of 9.192631770×10^9 periods of the radiation corresponding to the transition between two hyperfine levels in the ground state of ^{133}Cs at 0°K; these two units will be unaltered.

The mole hitherto based on the molar mass of ^{12}C will be revised to that mass of the isotope which makes the Avogadro constant exactly 6.0221415×10^{23} per mole. Changes have also been proposed for the ampere, but the candela remains unaltered.

Notwithstanding the value of the SI, certain traditional units are still in common use. Thus the Ångström ($1\ \text{Å} = 10^{-10}$ m) remains a very convenient unit in crystallography for quoting interatomic distances and wavelengths. Detailed accounts of the history, revisions, and proposed changes of the fundamental units in the system may be found in the published literature[1,2]. These changes in the fundamental units will not affect the numerical values involved in the text of this book or in its set problems.

[1] http://physics.nist.gov/cuu/Units/

[2] Mills IM, Mohr PJ, Quinn TJ, Taylon BN, Williams ER (2011) Phil Trans Roy Soc. 369:3907ff

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 X-ray 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. Two or more applications of one and the same symbol are separated by a semicolon.

$A'(hkl)$ $B'(hkl)$	Components of the structure factor, measured along the real and imaginary axes of an Argand diagram
$A(hkl)$ $B(hkl)$	Components of the geometrical structure factor, measured along the real and imaginary axes of an Argand diagram
A	A-face-centred unit cell; absorption correction factor
Å	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^*	Reciprocal unit-cell edges 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-centred unit cell; overall isotropic temperature factor
B_j	Isotropic temperature factor for the jth atom
C	C-face-centred unit cell
$\not C$	Not constrained by symmetry to equal
c	Speed of light; 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 chosen origin of the reciprocal lattice to the hklth reciprocal lattice point
Da	Dalton; equivalent to m_u
E	Normalized structure factor (E value), including phase
$\lvert E \rvert$	Amplitude of normalized structure factor, E (an "observed" value)
E, $E(hkl)$	Normalized structure factor in centrosymmetric crystals (an "observed" value)
E_c	Normalized structure factor calculated from the atomic positions in the unit cell
$\mathcal{E}$	Total energy of the hklth diffracted beam from one unit cell
e	Electron charge
e, exp	Exponential function
esd	Estimated standard deviation

(continued)

F(*hkl*)	Structure factor for the *hkl* spectrum referred to one unit cell, including phase
$F^*(hkl)$	Conjugate of F(*hkl*), including phase
|F| or *F*	Modulus, or amplitude, of the structure factor F (excluding phase); $\|F\|$ is superfluous notation, but frequently used informally
F_o	Observed structure "factor" (only ever an amplitude); $\|F_o\|$ is superfluous notation, but frequently used informally
f/f_j	Atomic scattering factor / for the *j*th atom
$f_{j,\theta}$	Atomic scattering factor for the *j*th atom at a given sin θ/λ
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 (of planes) 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
h	Vector with components *h*, *k*, *l* in reciprocal space
h	Miller index parallel to the *x* axis; Planck's constant
I	Body-centred unit cell; intensity of reflection
$I_o(hkl)$	Observed intensity of reflection from the (*hkl*) planes referred to one unit cell
$\mathscr{I}$	Imaginary axis on an Argand diagram
i	$\sqrt{-1}$; an operator that rotates a quantity on an Argand diagram through 90° in a right-handed (counterclockwise) sense from the real axis
K	Scale factor for $F_o(hkl)$ data
k	Miller index parallel to the *y* axis; Boltzmann constant
l	Miller index parallel to the *z* axis
L	Lorentz correction factor
m_u	Atomic mass unit
M_r	Relative molecular mass (molecular "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 $\|F_o(hkl)\|$
o	Superscript, as in 25°C
P	Probability; Patterson function; Polarization correction factor
P(*uvw*)	Patterson function at the fractional coordinates *u*, *v*, *w* in the unit cell
p	Polarization correction factor
p_i	Probability of the *i*th state of a system
R	Rhombohedral unit cell; rotation axis of degree *R*; reliability factor (several *R* parameters are in current use)
$\overline{R}$	Inversion axis of degree *R*
$\mathscr{R}$	Real axis on an Argand diagram
rms	Root mean square
RU	Reciprocal lattice unit
S	Statistical distribution parameter; $2 \sin\theta/\lambda$
s, *s*(*hkl*), *s*(**h**)	Sign of a centric reflection, |F| or |E|

(continued)

$T_{j,\theta}$	Thermal vibration parameter for the *j*th atom at a given sin θ/λ
$[U\ V\ W]$	Zone or direction symbol
$<U\ V\ W>$	Form of zone axes or directions
(uvw)	Components of a vector in Patterson space
$\overline{U^2}$	Mean-square amplitude of vibration
V	Volume
V_c	Volume of a unit cell
W	Probability or number of arrangements of a system
w	Weight factor
x, y, u, z	Crystallographic reference axes descriptors
X, Y, Z	Spatial coordinates, in absolute measure, of a point with respect to the x, y, and z axes
x, y, z	Spatial fractional coordinates in a unit cell parallel to x, y, z, respectively
x_j, y_j, z_j	Spatial fractional coordinates of the *j*th atom in a unit cell parallel to x, y, z, respectively
$[x, \beta, \gamma]$	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
$\pm\{x, y, z;\ \ldots\}$	$x, y, z;\ \overline{x}, \overline{y}, \overline{z} \ldots$
Z	Number of formula entities of mass M_{rr} 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
$\rho(xyz)$	Electron density at the point x, y, z (units are length^{-3})
Φ	Interfacial (internormal) angle
$\varphi(hkl), \varphi(h), \varphi$	Phase angle associated with a structure factor
χ, Ψ, ω	(cos χ, cos Ψ, cos ω) direction cosines of a line with respect to the x, y, and z axes
ω	Angular frequency
Ω	Azimuthal angle in experimental methods; ohm
$\overline{X}, <X>$	Average value of X