Preface

This book presents the fundamentals of crystallography to university and college students in biology, chemistry, physics, materials science, geological sciences, or engineering. It is also appropriate for scientists who want to teach themselves. Computers are an essential part of crystallography, and appropriate computer-based exercises are integrated into this book.

The mathematics prerequisite for this book is an introductory knowledge of linear algebra, including matrices and determinants. The computing requirement is a familiarity with an advanced computer language like MATLAB®. The linear algebra allows exploitation of the power of the metric matrix. The metric matrix incorporates the information for the lattice—namely, the lattice constants a, b, c, α, β, and γ—into a single matrix. All the crystal systems from triclinic to cubic are accommodated. This allows easy computation of important crystallographic quantities such as bond lengths, bond angles, unit cell volumes, reciprocal lattice constants, interplanar angles, and d-spacings in all the crystal systems. The three-dimensional unit cell is constructed by the advanced computer language. Later, that cell is populated with atoms. Starter programs are given, as this is not a programming course.

Two model crystal examples are used throughout the book. The first crystal is hexamethylbenzene, $C_6(CH_3)_6$ (HMB). This crystal is chosen because

- there is one molecule per unit cell
- the carbon atoms lie in a plane, conveniently chosen as the (001) plane
- the benzene ring is easy to see
- the structure is of historical importance, having proved that the six carbon atoms of the benzene ring lie in a plane
- the crystal structure is triclinic

Every other crystal structure can be handled by the programs developed for HMB. It is a small organic structure that can be considered to be a model polymer with both covalent and Van der Waals bonds. The crystal is centrosymmetric.

My second crystal is anhydrous alum, $KAl(SO_4)_2$ (AA), which is a noncentrosymmetric framework structure typical of ceramics and metals. AA is a ceramic. It is trigonal and there is one formula unit to the unit cell. In Chapter 4, the structure of AA is used to explain how the symmetry operators work in a crystal. For example, the sulfur atoms are on threefold axes. Also, the SO bond lengths are not all equal; that is, they are not all crystallographically equivalent. From the structure, the student can see that the environment of the oxygens near the Al^{+3} ions is different from the environment near the K^{+} ions.

In my course, I have each student select a third crystal structure of personal interest. This is called YC, *your crystal*. Students have chosen a wide range of crystals, including superconductors, polymers, ceramics, gems, metals, and biologically important organic materials. The graduate students pick crystals related to their theses. The YC exercises are indicated in the exercises for each chapter. The book is designed so that an instructor may (1) allow each student complete freedom in selecting a crystal, (2) assign a crystal from a selection of worked-out examples made available in the instructor's notes, (3) divide the class into groups and assign a crystal structure for each group, or (4) ignore the third crystal entirely. The exercises related to YC are *only* in the problems at the end of each chapter.

The material in the book is given in a logical order with the goal of understanding not only how atoms are arranged in crystals but also how crystal systems are related to each other. Examples of this are the point group and space group trees. The ideas proceed from simple to complex. The theoretical material is developed extensively in two dimensions.

The book is organized into seven chapters and an introduction. The introduction starts out with a figure showing a red flag with a snowflake on it. Chapter 1 is on lattices and includes a starter program transforming nonorthogonal coordinates to Cartesian coordinates. A three-dimensional computer graphic model of a unit cell is constructed. The model is rotated and projections are examined with MATLAB® doing all the work. Already the idea of going from general to specific is in place, since once the triclinic cell is drawn, the student can then go to the literature and construct any unit cell. I like to bring in practical examples as early as possible, so at the end of the lattice chapter, I include temperature and pressure variations in lattice parameters.

Chapter 2 forms the mathematical basis for the rest of the book. The metric matrix is introduced in the derivation of the magnitude of a vector in the unit cell. From now on the metric matrix is used in the calculation of the interatomic distances, interatomic angles, and volumes of the unit cells. Unit cell transformations are derived. The MATLAB® project for this chapter is the two-dimensional construction of a unit cell of HMB, populated with carbon atoms. Note that the concepts of symmetry have not been introduced. This powerful exercise is a foretaste of what is to come in Chapter 4, when an arbitrary cell is populated. HMB was chosen because all 12 of its carbon atoms lie in the *xy* plane.

Chapter 3 begins the study of symmetry. The task here is not only to understand the individual symmetry elements that make up individual point groups, but also to take a holistic approach to all 10 point groups and how they are constructed and related. This

relationship is seen in the point group tree and in the relatively increasing size of the multiplication tables as the order of the point groups increases. After a thorough description of the two-dimensional point groups, the rotoinversion operations are added and the three-dimensional point groups and their point group tree are discussed. The computer exercise for this chapter is the construction of multiplication tables, first in two dimensions and then extended to three dimensions by a starter program. The largest point group has a 48 by 48 multiplication table. All the notation in this chapter is consistent with the **International Tables for Crystallography** in preparation for Chapter 4.

Chapter 4 is where the Bravais lattices are combined with the point groups to produce the space groups in both two and three dimensions. The main computer exercise is a three-dimensional graphics model of AA, which is populated with atoms using the symmetries from the Wyckoff positions. The two-dimensional projections have the symmetries of the 17 planar space groups. The students are encouraged to do calculations on a crystal of their own choosing.

Chapter 5 is devoted to the reciprocal lattice. The computer exercise is to superimpose the reciprocal unit cell on the unit cell in direct space. The reciprocal lattice parameters, $\mathbf{G}^*$, V^*, $\mathbf{H}(hkl)$ are calculated and the interfacial angles are derived using $\mathbf{G}^*$. The relationship of the reciprocal lattice to the diffraction pattern is explored.

Chapter 6 introduces the experimental side of crystallography, including the discovery of x-rays, properties of waves, the first x-ray diffraction picture, and the identification of materials by powder diffraction.

Chapter 7, the final chapter, discusses how the contents of the unit cell influence the intensity of the diffraction maxima. Scattering by a single electron, by a single atom, and, finally, by the whole crystal is discussed. The structure factors are calculated from the positions and atomic scattering curves for several crystals. The structure factors are proportional to the amplitudes of the Fourier series used to calculate the electron density map on the cover of the book.

This book makes frequent reference to the **International Tables for Crystallography, Volume A**. All eight volumes of the **International Tables for Crystallography** are available online at http://it.iucr.org. Readers may find that their institution has access to the full content of this site and they will therefore be able to find all the information they need there. If not, a *Brief Teaching Edition of Volume A* is available in paperback; this contains a subset of the information in Volume A at a very reasonable price and makes an ideal companion to the present book. Course organizers who are interested in placing a bulk order for copies of the *Brief Teaching Edition of Volume A* to accompany the present book should contact the International Union of Crystallography (execsec@iucr.org).

The author would like to hear from readers of this book. Please contact her at Maureen.Julian@taylorandfrancis.com with comments, suggestions, or corrections. For additional student and instructor materials associated with this book, please see foundations-of-crystallography.com