Dongcai Liang

Fundamentals of X-Ray Crystallography

Second Edition

X射线晶体学基础

（第二版）

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Alpha Science International Ltd.
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Foreword to the 2nd Edition

The Fundamentals of X-ray Crystallography has been republished.

Fifteen years ago, in response to the urgent needs of crystallographers (especially protein crystallographers in China), this book was published as a fundamental textbook and reference book. In the subsequent 15 years, crystallography and its related fields have experienced rapid development. In particular, life sciences research urgently demands information about the structure of the microscopic world that is composed of molecules and atoms. As the main research approach of structural biology, the methods of X-ray crystal structure analysis have become more established and efficient, and they are understood and used by more and more researchers in relevant fields. However, as Mr. Lu Jiaxi emphasized in the preface of the first edition of this book, "The basic problem of crystallography hasn't changed." Thus a thorough understanding of the symmetry principles and the diffraction principles of microscopic space remains necessary fundamental knowledge and a component of basic skills for researchers devoted to this field. The readers (including many previous postgraduate students of Professor Dongcai Liang) of *The Fundamentals of X-ray Crystallography* benefitted from reading this book so much that they have recommended it to their colleagues and students. Many readers, including scholars overseas who understand Chinese, have tried to order this book. The exclusive purpose for the republication of this book is to meet those demands, especially the needs of biological macromolecular crystallographers.

The symmetry principle and the diffraction principle of microscopic space are invisible, untouchable, and abstract concepts. An in-depth understanding of the fundamental principles of crystallography has enabled Professor Dongcai Liang to use simple and easily understood concepts to illustrate geometric crystallography, X-ray crystallography, and the fundamental principles and concepts of real space and reciprocal space. This is the most distinctive and characteristic difference between this book and other crystallography books. The imaginary thinking and ability to think 3-dimensionally are the keys for understanding this book. I believe that the republication of this book will satisfy the expectation of its readers. Before republicating book, the author reviewed its content and carried out necessary revisions.

Wenrui Chang
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Professor of the Institute of Biophysics
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Zihe Rao
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Foreword to the 1st Edition

The development of crystallography can be traced to the past century. Since the 1920s, crystallography has been the foundation of chemistry, physics, mineralogy, metallurgy, and other sciences and technologies. In the past 20 to 30 years, the necessity of crystallography in the application of biology has been realized. However, the fundamental problems of crystallography have not changed, and biological macromolecular crystallography should follow the symmetry principle and the diffraction principle of microscopic space. During a long career of research and teaching (especially with respect to young scholars), the author of *The Fundamentals of X-ray Crystallography*, Professor Dongcai Liang, realized that having a thorough understanding of the symmetry principle of microscopic space is extremely important and that many misconceptions or errors in practice result from a vague understanding of that principle. A thorough understanding of that subject is based on the ability to think 3-dimensionally. Therefore in this book, the author did not use the group theory or any other advanced mathematical methods and tools to illustrate that principle, instead, he used simple geometric concepts and methods to explain the fundamental principle of crystallography intuitively.

During his early studies in the Soviet Union, Professor Dongcai Liang analyzed and characterized complex symmetry principles. A very unique system of thinking, deducing, and teaching crystallography was formed during his 30 years of experience in teaching and research in crystallography. The uniqueness of his system is based on treating microscopic symmetry as a combination of macroscopic symmetry and 3 types of translations. The consistency principle between the symmetrical distribution of general symmetry equivalent points and spatial symmetry is used in a profound analysis and illustration of the nature of crystal symmetry. Professor Liang's method of deducing this symmetry is intuitive and easily understood. Because of the unique features of this book, its illustrations, and the arrangement of its content, this book is suitable for researchers, teachers, and undergraduate and graduate students. It will serve as an excellent crystallography reference book as well. I believe that the publication of this book will promote the research and teaching of crystallography (especially biological macromolecule crystallography) in China.

Jiaxi Lu

May 1990 in Chinese Academy of Sciences

Preface of the 1st Edition

X-ray crystal structure analysis is an important tool used to study the spatial structure of minerals, metals, inorganic compounds, organic compounds and the 3-dimensional structure and conformation changes in biological macromolecules such as proteins, nucleic acids, viruses, etc. X-ray crystallography is the foundation of crystal structure analysis. And therefore it is very important to understand the principle of X-ray diffraction by crystals. Crystal symmetry principles (especially symmetry principles in microscopic space) are applied during the entire process of crystal structure analysis. Our object of structure analysis is 3-dimensional, so the keys to understanding and skillfully applying the symmetry principles of crystals are essential to establish vivid spatial concepts and to think and image 3-dimensionally.

In early 1950s, it was my honor to pursue a postgraduate degree under the guidance of Professor А. И. Китагороски and Professor Ю. Т. Стучков in the Soviet Union. I am grateful for the enlightenment and education provided by my mentors, who directed me step by step toward the fields of X-ray crystallography and structure analysis and helped me to obtain a solid foundation in those fields. In my later research career, I benefitted from the knowledge of many pioneers in the field of crystallography and then gradually formed my own understanding and application methods for the symmetry principle and the diffraction principle of crystal. I used primarily geometric concepts and methods to establish the spatial concept, which is the key to understanding, mastering, and applying crystallography. In 1963 and 1964, when I taught crystallography as part of a solid state physics course at the University of Science and Technology of China, I had the opportunity to prepare a primitive summary of the above concepts and application methods. The success of this attempt intensified my thinking and understanding. Twenty years later, I taught geometric crystallography and X-ray crystallography from 1983 to 1989 at the University of Science and Technology of China as an adjunct professor. During that time, I developed a systematic summary of the understanding and derivation of the crystal symmetry principle with geometric concepts and methods, and I integrated that summary into my teaching material. This book is based on that lecture material, which has been revised and supplemented three times. I hope that this book will benefit young scholars in this field. There may be imperfections in this book, and any criticisms and suggestions are sincerely welcome.

During the formation and compilation of this book, the main references included: *Principle of Crystallography* written by E. E. Ф линт (Translated by Yang Chaoliang and et al. The Commercial Press, 1954); Volume I of *Essential Course on Roentgen-ray Structure Analysis* written by T. B. Ъоки and M. A. П ороКош ищ (Translated by Shi Shiyuan and et al., Higher Education Press, 1958); *X-ray Structure Analysis* written by A. N. Китагороски (Translated by Gong Raogui and et al. Science Press, 1958); *Prodromes to X-ray Crystallography* written by M. M. Woolfson (Translated by Crystal Structure Analysis Group of Biophysics Institute of Chinese Academy of Science, Science Press, 1981); *Crystal Structure Determination* written by Zhou Gongdu (Science Press, 1981); *The Precession Method in X-ray Crystallography* written by M. J. Buerger (Wiley, 1964); *International Tables for X-ray Crystallography* written by K. Lonsdale (ed.) (Vol. I, Kynoch, 1952), etc.

I thank Professor Jiaxi Lu for his passionate encouragement and support during the development of this book and Mr Zhong Ren for proofreading the content and preparations for the publication of this book. The Scientific Publishing Fund of the Chinese Academy of Science provided financial support for the publication of this book. I am grateful for all the assistance.

Dongcai Liang
Beijing, April 1990

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Section I

Fundamental Principles of Geometric Crystallography

Chapter 1 Principal Characteristics of Crystalline Solids

1.1.1 Periodicity of internal crystal structure

Crystals, as one form of solid matter, are different from other noncrystalline solids because they have an internal structure that consists of a regular periodic arrangement. The internal repeating units of the crystal, also called as structural elements(eg, atoms, ions, molecules), have strictly periodic arrangements in 3-dimensional space. This is the major difference between crystals and other forms of solids and is also the fundamental reason behind the diverse properties of crystals.

Common salt(NaCl) can be used as an example to illustrate the properties of crystals. An analysis of crystal structure shows that the NaCl salt is formed by a 3-dimensional arrangement of sodium ions(Na^+) and chloride ions (Cl^-) according to geometric principles. Sodium ions (Na^+) and chloride ions (Cl^-) are arranged alternately in 3 dimensions(X, Y, and Z) that are perpendicular to each other. As shown in Figure 1-1-1, The shortest distance between the 2 closest sodium ions(Na^+) and between the 2 closest chloride ions(Cl^-) is 5. 628Å(1Å$=1\times10^{-8}$cm).

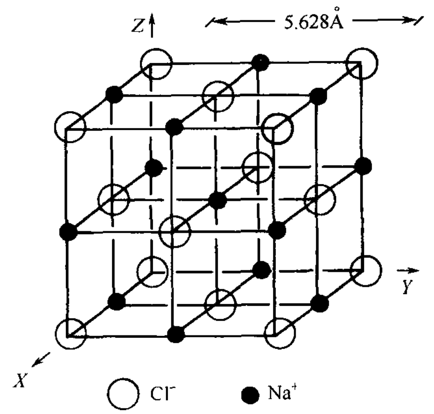

Figure 1-1-1 The internal structure of sodium chloride crystals.

Natural and artificial salt crystals can form perfect, colourless, transparent cubes in a favorable growth environment. Cubes are finite closed spaces formed by 6 smooth cubic planes that are connected to each other. Each plane on the surface of a crystal is called a *crystal face*. The straight line that links 2 crystal faces is called a *crystal edge*. The finite obturator that is composed of many crystal faces is called a *crystal polyhedron*, In the following chapters, we shall see that the shape of the crystal polyhedron(its crystal faces and crystal edges) is closely related to the internal structure of the crystal and particularly to the periodicity of the internal structure of the crystal. If a crystal is affected by various conditions(for example, being limited by the ambient mediums) during the growth process, it may not grow into a perfect polyhedron and may not even be in the shape of a polyhedron, however, as long as the internal structure is arranged in a regular and periodic manner, the definition of crystal still applies.

Many beautiful natural crystals with regular geometric shapes have been discovered in natural minerals. Thus solids with regular geometric polyhedral shapes have been referred to as *crystals*. However, the definition of a crystal is not precise because some solids with natural and regular polyhedral shapes are not crystals. For example, allanite has undergone noncrystalline metamorphosis and its interior has even been transformed into a noncrystalline solid, but it retains the natural polyhedral shape of the original crystal. Crystal growth can be restricted by external conditions, and not all crystals form complete and regular polyhedral shapes. Both feldspar and quartz, which are the main minerals from which granite is formed, are crystals, but they do not have a regular polyhedral shape. In fact, very few crystals in nature have a complete and regular polyhedral shape.

If a crystal grain that has an irregular shape or has been polished into a round shape is placed into a growth liquid, it continues to grow freely under appropriate conditions and will finally form a regular polyhedral shape. This demonstrates that even though the crystal does not grow into a complete regular polyhedron under a given set of conditions, it retains the innate potential to spontaneously grow into a regular geometric polyhedron. It is clear that the nature of a crystal is restricted by the principle of its internal structure. The external polyhedral shape of a crystal is simply a reflection of the internal structure of that crystal.

The characteristics of crystals should, therefore, not be limited to external properties such as their shape or physical or chemical properties but should include their internal structure. The fundamental characteristic of a crystal is the periodicity of its internal structure, and the fundamental difference between crystals and other noncrystalline solids is the periodic arrangement of crystal structural elements in 3-dimensional space.

Max Von Laue, a German physicist, first demonstrated crystal periodicity in an experiment in 1912. Laue treated the 3-dimensional lattice formed from periodically arranged structural elements as a natural optical grating. Röntgen, another German physicist, discovered in 1885 that such optical gratings could cause X-ray interference. Laue's great achievement demonstrated the fundamental characteristics of crystals and opened a new era for crystallography.

1.1.2 Space lattice and crystal lattice

A crystal, then, is solid matter that is formed by periodically arranged structural elements such as the atom, ion and molecule, in 3-dimensional space. In a crystal, the structural elements are periodically arranged in space, and after a cer-