X-Ray Crystallography

An Introduction to the Investigation of Crystals by Their Diffraction of Monochromatic X-Radiation

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PREFACE

A crystal-structure investigation ordinarily proceeds through two distinct stages. The first consists of an investigation of the general geometry of the repetition or space pattern of the crystal. This leads to a knowledge of the crystal symmetry in the larger sense: the crystal class, the space lattice (its type and dimensions), and the space group. This stage of the structural investigation is a matter of pure geometry. It requires only a crystal and proceeds independently of any data or interpretation of data regarding the chemical constitution or nature of the crystal under investigation. Its results are truly the ultimate goal of the classical crystallographer. These results are easily achieved by employing the phenomenon of x-ray diffraction by the crystal. The science connecting x-ray diffraction and the desired crystallographic results might conveniently be called "x-ray crystallography."

X-ray crystallography is inadequately treated in current reference books. This is partly because the contents of such books usually include a wide selection of material from related fields such as x-ray physics, crystal-symmetry theory, the results of crystal-structure analysis, and crystal chemistry. This leaves the entire subject of the determination of crystal structures to be treated only in outline, and only part of this space can be given to x-ray crystallography. A student wishing to pursue structural studies by means of x-rays cannot learn through the aid of these books but must turn to original literature and possibly to an instructor for personal guidance. There is a definite need for a connected account of the theory and practice of structural investigations for such students.

The present book is intended to fill the x-ray crystallography part of this need. It is restricted in scope. The original intention was to discuss the moving-film methods only, first because they are covered so very superficially in all current books, and, second, because recent developments have shown their great importance and convenience. In order to discuss this phase of x-ray crystallography, it is desirable to develop a number of concepts ordinarily used in other diffraction methods, particularly the rotating-crystal method. It was therefore thought desirable to include chapters on the rotating- and oscillating-crystal methods, which are also ordinarily given all too little space in

current books. The subject matter of this book, therefore, is confined to methods utilizing a single crystal and monochromatic x-rays (in the sense of screened or unscreened characteristic radiation), and the theory necessary to the intelligent use of these methods.

Many users of this book will be those with comparatively little background in the field. For their benefit, several of the elementary topics have been approached in a gradual manner in order to encourage a real understanding of the situation. To this end, subjects such as x-ray diffraction and the reciprocal lattice, which require space geometry, have first been treated in a plane. In this way, all the basic ideas involved can be developed with a minimum of extraneous mathematical fog. Once the basic ideas are grasped, the student's attention may be readily broadened to include the additional dimension of space. In one other direction I have deliberately erred on the side of making things easy for the student who is not already a complete master of the subject. Many textbooks and original papers require the reader to play detective with pencil and paper in an endeavor to find out how the author arrived at equation (2) after leaving equation (1). In this book, an attempt has been made to avoid this by including the important intermediate steps. This procedure will doubtless bore the expert, but I hope the plan will permit the novice to pay more attention to the subject matter, and less to the mystery of arriving at it.

Many crystallographic proofs are customarily given by vector algebraic methods. For the benefit of the reader without training in vector algebra, alternative proofs have been given by geometrical, analytic geometrical, and algebraic methods.

A departure has been made in the usual vector algebra treatment of the reciprocal lattice. The usual treatment has always appeared to me to be a classic example of seeing whether one could achieve an objective by the use of vector methods just because they were vector methods. A little crystallography thrown in here and there eases the understanding of the treatment. Furthermore, the usual treatment of the reciprocal lattice skips over the proof, except by implication, that the points reciprocal to the direct lattice constitute a lattice array, and focuses attention, rather, upon the cumbersome transformation equations connecting triclinic reciprocal and direct cells. This highlights a comparatively unimportant quantitative aspect, of use chiefly in computation. In the present treatment, the lattice aspect and the reciprocity aspect of the polar point system are emphasized first, the quantitative relations between the two point arrays being introduced only subsequently to impressing the more fundamental qualitative matters on the student.

The book contains a good deal of material appearing for the first time, or hitherto inadequately treated. Among such topics are the following:

A method of producing symmetry-true photographs (page 206).

Moving-film photographs taken with the x-ray beam inclined to the layers of the reciprocal lattice.

The Sauter and the Schiebold methods.

The de Jong and Bouman method.†

The choice of setting of a triclinic crystal.

Discussion of Bradley and Jay's absorption error.

Cohen's method extended to the refinement of the lattice constants of single crystals.

I am deeply grateful to the editor and publishers of the *Zeitschrift für Kristallographie*, not only for permission to reproduce, in slightly modified form, some of my articles which originally appeared there, but also for having had the kindness to permit reproduction of many of the illustrations. These include Figs. 136, 138, 142, 144, 147, 148, 155, 156, 221, 222, 223, 224, 225, 226, 227, 228, 229, 230, 231, 232, 233, 234, 236, 240, 243, 244, 245, 247, 252, and 253.

The editor of the *American Mineralogist* has also kindly permitted me to reproduce Figs. 1, 113, 214, 248, 249, 250, and 251. The plane-group patterns inside the covers are from blocks released to me by the *Technology Review*.

I am also indebted to the *Zeitschrift für Kristallographie* and to Dr. E. Schiebold for permission to reproduce Fig. 174; to the *Zeitschrift für Kristallographie* and to Dr. Linus Pauling for permission to reproduce Fig. 31; to Dr. Erwin Sauter for permission to reproduce Figs. 166 and 172; to the Royal Society of London and to Prof. J. D. Bernal for permission to reproduce Figs. 79, 80, and 86; and to Dr. I. Fankuchen for Fig. 105.

With the exception of the cuts acknowledged above, the illustrations have been prepared especially for this book. I am indebted to several assistants, particularly Mr. Howard Brooke Hindle, Jr., Mr. Herman William Ahrenholz, Jr., Mr. W. H. Dennen, and Mr. Joseph W. Mills, for transforming some of my pencil sketches of illustrations into draftings. Mr. Frank G. Chesley executed Fig. 60. I am indebted to my wife and to Miss Edna Howley for taking charge of transforming the most complicated parts of the manuscript into typescript.

† The chapter on the de Jong and Bouman method was written just after the first paper by these authors appeared. Their subsequent papers have covered ground almost identical with the material in Chapter 17.

My thanks are especially due to Dr. I. Fankuchen and to Mr. Joseph S. Lukesh who kindly offered to read the proof. Because of their efforts many misprints have been eliminated and not a few inaccuracies corrected.

I also wish to take this opportunity to thank the administration of the Massachusetts Institute of Technology as well as Dr. Warren J. Mead, Head of the Department of Geology, for their liberal policy of encouraging and providing facilities for undertaking work of the kind discussed in this book.

I hope that this account of x-ray crystallography will encourage the use of moving-film methods and level analysis methods not only among those who wish to employ them as a step in the complete determination of crystal structure, but also among those engaged in systematic crystallography.

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CHAPTER 1

INTRODUCTION

From a certain point of view, a crystal structure (Fig. 1) is like a wallpaper pattern, except that it is three-dimensional and therefore more complex. In a wallpaper pattern (or in fact in any extended plane pattern such as is found, for example, in textile weaves, linoleums, tiling, etc.), the pattern as a whole has two aspects:

(1) a motif, such as a picture of a flower or other figure, a tile, or group of tiles, and

(2) a mechanism or scheme of repetition of this motif.

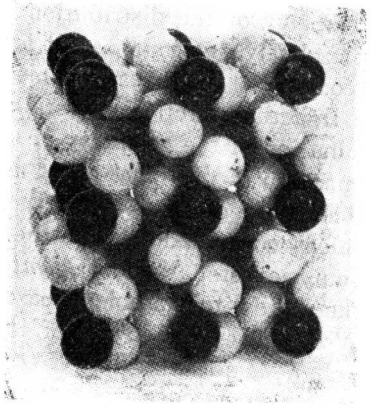

FIG. 1. The space pattern of atoms in a crystal of marcasite, orthorhombic FeS_2. Dark balls represent iron atoms, light balls sulfur atoms.

In a crystal structure, the same two general aspects can be recognized, only they occur in three dimensions, and they apply specifically to the packing of atoms. The motif is a cluster of atoms, which may or may not be a chemical molecule. (Molecules occur chiefly in crystals of organic material and, for the most part, cannot be recognized in the patterns of crystals of inorganic substances.) This motif cluster is repeated by a mechanism or scheme of repetition in three dimensions, the entire resulting pattern being the crystal structure.

In anticipation, it can be said that such a three-dimensional pattern acts as a diffraction grating to light having wavelengths of the same order of magnitude as the translation repeat period of the pattern. This period is of the order of 1×10^{-8} cm., and light having wavelengths of this order is x-radiation. In other words, x-rays may be used to explore the nature of crystal patterns through the phenomenon of diffraction by the crystal pattern. The discovery of this fact was made by von Laue and his collaborators. The technique of investigating this effect was quickly improved by Bragg, and subsequently by many others.