An Introduction to
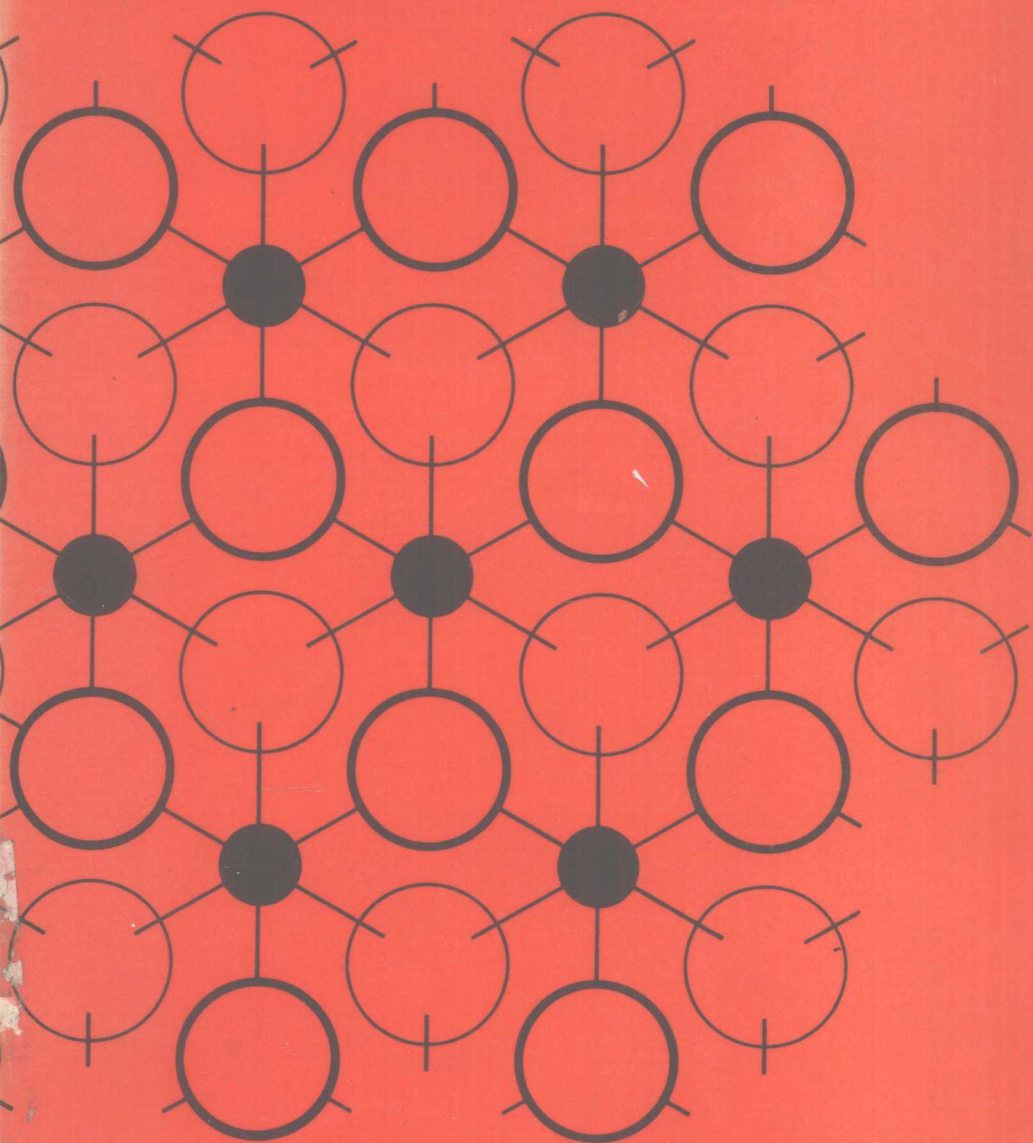# Crystal Chemistry

SECOND EDITION R.C.Evans

AN INTRODUCTION TO
CRYSTAL
CHEMISTRY

BY

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SECOND EDITION

To
my wife

PREFACE

In the years which have elapsed since the first edition of this work was published in 1939 X-ray diffraction has become firmly established as the most powerful tool at our disposal for the study of the solid state. Twenty-five years ago enough structures were known for the general principles of crystal architecture to be understood; to-day the number of known structures has been multiplied many times and these principles have taken their rightful place as an integral part of modern structural chemistry. Even so, it is only at an advanced level that the integration is as yet complete, and it is in any case not only the chemist to whom the study of solids is of interest: the physicist, the metallurgist, the mineralogist and many others must equally be concerned with the relationship between properties of matter and atomic arrangement. For this reason there still remains a need for a presentation of the fundamental principles of crystal chemistry at an elementary level, with the minimum of descriptive detail, and it is this need which the present work seeks to satisfy. Although the new edition has been completely rewritten, and although the structures described have been reinterpreted in terms of more modern ideas of chemical bonding, an attempt has nevertheless been made to avoid undue expansion and to preserve the essentially elementary character of the original. Only those structures have been described which seem best suited to illustrate the principles here advanced, and these principles have been presented in a manner which demands little specialized crystallographic knowledge on the part of the reader.

The value of diagrams as a means of illustrating structural principles needs no emphasis. Much care has therefore been devoted to the preparation of the many figures, all of which have been specially drawn, and it is a pleasure to express my thanks to the artists of the Cambridge University Press for the skill with which they have executed this work. References to original literature have been omitted as no longer appropriate now that the needs of the more advanced student are so admirably met by other works, some of which are cited in the bibliography.

The greater part of the task of preparing this edition was undertaken during a period of leave of absence from Cambridge University generously granted to me by the General Board of the University, the

Faculty Board of Geography and Geology, and the Governing Body of St Catharine's College. Part of the time was spent at the National Bureau of Standards in Washington, and it is a pleasure to express my thanks to Dr I. C. Schoonover, Mr H. S. Peiser and their many colleagues for all that they did to make my visit a most stimulating and memorable experience. I am equally indebted to Professor H. G. F. Winkler for his hospitality and for the facilities he placed at my disposal during the months which I spent at his laboratory in the University of Marburg.

No reader of this book can fail to recognize how much I owe to others who have written in this field. To the authors of the works quoted in the bibliography, and not least to the selfless editors of the reference works, I express my warm thanks. I am also indebted to many friends (too numerous to mention individually) whose counsels I sought and whose opinions and advice, so generously given, have largely determined the scope and character of what I have written.

Finally, but above all, I am indebted to my wife, but for whose encouragement this book might never have been written. From the day we first discussed the project (at sea off the coast of California) I have been sustained by her interest and support and by her acceptance, with characteristic cheerfulness, of the sacrifices involved. As a token of what I owe to her inspiration this work is dedicated to her with love.

R. C. E.

CAMBRIDGE
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PART I

GENERAL PRINCIPLES
OF CRYSTAL ARCHITECTURE

1 INTRODUCTION

EARLY HISTORY

1.01. Crystals have been known to man from the earliest times, for, as we now realize, the rocks of the Earth's crust, the sands of the desert and, indeed, almost all forms of solid matter are crystalline in character. The Egyptians who operated turquoise mines in the Sinai peninsula, possibly as early as the sixth millenium before Christ, must have been aware of the beauty and geometrical perfection of many naturally occurring minerals, and Theophrastus, in his treatise *On Stones* published in the fourth century B.C., describes the angular shape and regular form of crystals of garnet. Rock crystal or quartz from India was studied by the geographer Strabo (b. 64 B.C.), who, impressed by its resemblance to ice, applied to it the term κρύσταλλος from which our 'crystal' is derived, and the same mineral was later described by the elder Pliny (A.D. 23–79) in his *Natural History*. References to diamond, sapphire and many other gem stones are numerous throughout the Bible, and by the first century of the Christian era jewels were so prized that we find contemporary Egyptian writers giving recipes for the preparation of artificial stones.

Artificially prepared crystals were formed in many of the processes of alchemy, and Libavius in 1597 was the first to recognize that the geometrical habit of these crystals was often characteristic of the salts concerned. In the next century crystals were described by Boyle, Leeuwenhoek and others, but it was Steno, distinguished also as a physiologist and later as Bishop of Titiopolis, who made the most important contribution by remarking in 1669 that quartz crystals, whatever their origin or habit, always preserved the same characteristic interfacial angles. This observation was extended to other crystals by Guglielmini during the period 1688–1705, and was further extended by de l'Isle in 1772. A few years later, the invention of the contact goniometer by Carangeot in 1780 provided the means for a more precise study of crystal form than had previously been possible, and in the years immediately following this invention a great mass of crystallographic data appeared. As early as 1783 de l'Isle published four volumes incorporating his observations on over four hundred mineral specimens, observation which added precision to his earlier studies and enabled him to formulate the law of constancy of interfacial angle. A year later, in

1784, Haüy enunciated the laws governing crystal symmetry, and paved the way for his later discovery of the law of rational indices, which, in 1801, he substantiated by a comprehensive survey of the mineral kingdom. Thus by the first year of the nineteenth century the fundamental laws of morphological crystallography had been established.

1.02. The researches of de l'Isle and Haüy may well be said to have laid the foundations of modern crystallography, but it was not until the invention of the reflecting goniometer by Wollaston in 1809 that further progress was possible. The contact goniometer had served to provide the data for early researches on crystal symmetry, but an instrument of an altogether different order of accuracy was required before crystallography could claim the title of an exact science. The application of the reflecting goniometer to crystallographic research resulted in the rapid accumulation of a great wealth of exact experimental data not only on naturally occurring minerals but also on artificial crystals of chemical importance, and it was these data which provided the material for Mitscherlich's discovery of isomorphism in 1819 and of polymorphism in 1822. The work of Mitscherlich at once directed attention to the chemical significance of crystal form and habit, and from 1820 onwards crystallographic research for nearly a hundred years was concerned primarily with the relationship of crystalline form to chemical constitution. Here we can mention only a few of the more important contributions. Pre-eminent stands the work of Pasteur on the enantiomorphism of tartaric acid, of the greatest significance in the later developments of chemical theory. Other researches were concerned with the physical and crystallographic properties of substances chemically closely related, and as early as 1840 Kopp observed that the tendency to form mixed crystals increased with increasing similarity in molecular volume. Later in the century Hiortdahl and Groth showed that in a series of organic compounds systematic substitution brought about a progressive change in crystal form, while important observations on the physical properties of substances chemically closely related are associated with the names Retgers, Liebisch, Gossner, Barker and Tutton. The great volume of crystallographic data on both inorganic and organic compounds which accumulated during the period was tabulated in Groth's monumental *Chemische Krystallographie*. This work, published in the years 1906–19, records morphological, optical and other properties of over 7000 crystalline substances.

1.03.   Although the work of the second half of the nineteenth century provided many data which have been of the greatest value to subsequent investigators, it cannot be said to have led to developments in any way comparable in importance with the discoveries of Mitscherlich and Pasteur in the first half of the century. In particular, little progress was made in studying the internal constitution and structure of a crystal, although it was recognized that the regularity of external form must have its origin in some more deep-seated regularity of internal arrangement, and that this, in its turn, must determine other properties of crystals. In the final decade of the century Fedorov, Schoenflies, and Barlow did, indeed, independently and almost simultaneously develop the abstract theory of the internal symmetry of crystals, and this work (which attracted little attention at the time) laid the foundations on which the X-ray crystallographer later and so successfully built. But at the time no means were available for the experimental study of internal structure.

This is not to say that speculations on the internal architecture of crystals had not taken place. In 1611 Kepler suggested that the characteristic hexagonal symmetry of snowflakes was due to a regular packing of the constituent particles. This idea was also developed by Descartes in 1637 and by Hooke, who in 1665 remarked in his *Micrographia* that all the crystal forms which he had studied could be simulated by building piles of 'bullets or globules'. A century later, Bergman in 1773 and Haüy in 1784, as a consequence of studies on cleavage, envisaged calcite crystals, of whatever habit, as built up by the packing together of 'constituent molecules' in the form of minute rhombohedral units. In this way Haüy was able to account for the law of rational indices, to which we have already referred above; but such a viewpoint was soon shown to be an essentially artificial one by the consideration that many crystals have no well developed cleavages, while others have cleavage forms (such as the octahedron) which cannot be assembled to fill space. It was not until the present century that Barlow and Pope (1906–7) gave precision to the ideas of crystal structure by assuming the constituent units to be *atoms* and by regarding a crystal as an essentially geometrical entity formed by the packing of spherical atoms, each of a definite and characteristic size. These speculations, as we shall see later, were extraordinarily close to the truth; but still the means were lacking for their experimental confirmation.

THE TWENTIETH CENTURY

1.04. In 1912 Friedrich, Knipping and Laue discovered the diffraction of X-rays by a crystal, thus *proving* for the first time the regular and periodic arrangement of the atoms in a crystal structure. At first the interest of these experiments lay in the light which they threw on the nature of X-rays, but it soon became clear that they were of even greater importance in providing a means not only of establishing the regularity of atomic arrangement in a crystal but also of actually determining just exactly what that arrangement was. Furthermore, as subsequent X-ray studies have shown, this regularity of internal arrangement is a characteristic not only of substances which occur as well-formed crystals but also of metals and many other solids seemingly amorphous in external form. In fact, with very few exceptions, *all* solids are crystalline in this sense, so that on the discovery of X-ray diffraction crystallography may be said to have become the science of the solid state.

If the importance of a discovery is to be measured by the consequences to which it has given rise, that of Friedrich, Knipping and Laue must be ranked as one of the most important in the whole history of science, for it has provided a means of investigating the solid state of a power altogether transcending any previously available. Prior to the development of X-ray methods, the solid state was the least tractable of all the states of matter, and the internal structure of a solid could be deduced only by argument from its physical properties or from its chemical properties in the liquid or gaseous form. X-ray analysis has removed the determination of crystal structure and molecular configuration from the sphere of speculation to that of measurement, and it is not difficult to see that the consequences of such an advance must be of the greatest significance in all branches of chemical theory.

The year following the discovery of X-ray diffraction saw the publication of the first crystal analysis, that of sodium chloride by W. H. and W. L. Bragg, and within a short time many other simple structures had been elucidated. Concurrently, the theory of the diffraction of radiation by a three-dimensional grating was developed, and improved apparatus and new experimental techniques were introduced. By 1926 the number of known structures was sufficiently large for Goldschmidt to be able to formulate the general principles governing the structural architecture of the crystals of simple inorganic compounds: he showed that such structures were the result of the packing together of spherical atoms (or

more commonly ions), each of a constant size characteristic of the element concerned, in a manner determined by geometrical considerations, thus confirming the speculations of Barlow and Pope of twenty years before. It was not, however, only inorganic compounds which were studied. The crystal structures of metallic elements and alloys and of many organic compounds were also elucidated, and by the beginning of the Second World War, when the first edition of this book was published, the general principles underlying the structural characteristics of all known types of solid matter had become clear.

Recent progress

1.05. In the years following the war advances in the science of X-ray crystallography have been both numerous and rapid. Experimental equipment has been improved, important developments have taken place in the theory of structure determination, many more workers have interested themselves in this field, several learned journals devoted exclusively to structural studies have been founded, and many more structures, often of great complexity, have been determined. It is true to say, however, that with few exceptions the numerous new structures elucidated have not added notably to the number of known structural types: for the most part they have been further examples of the basic types already well established. But this is not to belittle the work of the modern structural crystallographer. By determining more and more structures with ever higher precision he has demonstrated that in X-ray crystal analysis we have by far the most powerful and precise tool yet available for the study of the solid state. Nevertheless, this tool, powerful though it is, is but one of many available for this study, and the X-ray crystallographer, if he is interested in anything more than the technique of the X-ray method, must also be something of a chemist, a physicist, a metallurgist or a mineralogist. The chemist, to single out but one field of study, is interested in solving his problems by any means at his disposal, and in this connexion the very phrase 'crystal chemistry' is something of an anachronism, implying, as it does, a division of interest where none should exist. We do not speak of 'gas chemistry' or 'liquid chemistry', being quite prepared to absorb the results of studies of these phases into our conspectus of chemistry as a whole. The same should be true of the study of crystal structures; but historically this has not been the case. In the past, the results of X-ray studies have been assimilated but slowly into chemical thought, perhaps