Crystalline Symmetries

AN INFORMAL MATHEMATICAL INTRODUCTION

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Adam Hilger

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An Informal Mathematical Introduction

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This book is dedicated to the memory of my father

Abraham Wikler

1910–1981

Preface

Von Laue's discovery of the diffraction of x-rays by crystals, in 1912, was the key to the solid state revolution of our times, a revolution which has led to the development of powerful techniques for the determination of structure on the molecular and atomic scale. In the ensuing 78 years, crystallography has branched into a large number of subspecialties, and its tools have become central to a large number of fields. Not only mineralogy and crystallography, but also physics, chemistry, biology, materials science, medicine and other branches of science have been fundamentally changed by the availability and power of crystallographic techniques.

Most of the conceptual tools for the classification of crystal structure—the theory of lattices and space groups—had been developed in the nineteenth century, but in the absence of any obvious use for them they were put on the shelf to await their time should it ever come. By 1915 the need for those tools was evident, and so was the need to present them in a form useful to practioners of the new art. Thus was born the series of volumes which became the *International Tables for X-Ray Crystallography*. Over the years, the International Union of Crystallography has revised the *Tables* to keep pace with the needs of workers in a growing number of fields whose scientific backgrounds are less and less coherent. This has meant that not only must more data be supplied, but also more detailed discussions of interpretation of these data are necessary. The most recent edition of these tables is a multi-volume set, of which only volume A, on crystal symmetry, has appeared so far. This volume alone is over 700 pages long.

Unfortunately, despite the extensive discussions of interpretation that they contain, there is an inverse relation between the size of the *Tables* and the ease of deciphering them. Several companion volumes have been written which explain how to use the tables, but

there is no volume devoted solely to the simple and elegant mathematical ideas which underly them. As the computer increasingly comes to dominate the practice of crystallography, these simple ideas are in danger of being forgotten, or never even being learned, by the crystallographic community.

For many years I have lamented this gap, especially when asked by mathematicians and scientists to recommend an introductory account of mathematical crystallography. An invitation in 1988 from Dan Shechtman of the Department of Materials Engineering of the Technion, in Haifa, Israel to give a series of six lectures on this subject (including a lesson on how to decipher the *Tables*) gave me an opportunity to try to remedy this situation. At the same time, it was an opportunity to explain some of the ways in which new developments in crystallography, such as the discovery of quasicrystals by Shechtman, are stimulating a reexamination of the mathematical foundations on which the *Tables* rest.

In trying to transform these lectures to the printed word, I have resisted the temptation (never very strong) to write a textbook with proofs and exercises. Detailed, rigorous and sometimes excellent accounts of most of the topics I discuss can be found in the literature; what is missing is an overview. My intent has been to write an account of this overview for the armchair reader, not the reader at a desk with pencil and paper and maybe a copy of the *Tables* too. I doubt that I have succeeded in making it as simple as that, but at least I have avoided giving proofs unless they are especially instructive, and have avoided assigning exercises unless they really look like fun (answers can be found in Appendix 2). Armchair mathematics is like armchair travelling. It is not the real thing, but it can be enjoyable, and it can help you decide if you want to go there to see for yourself. Just as the articles in the New York Times Sunday Travel Section contain a coda entitled 'Getting There' with lists of air service, hotels, and so forth, this book concludes with an annotated bibliography for further study.

The basic ideas of the classical theory are quite simple. The situation is much like trigonometry: despite the plethora of tables, formulas, and graphs, all of trigonometry is really an elaboration of the Pythagorean theorem, and once you appreciate this fact, the main ideas of the subject are very easy to grasp. Nevertheless, as I learned long ago when I tried unsuccessfuly to teach trigonometry to my younger brother in one hour (to save him from failing a

calculus course), some mathematical sophistication is necessary in order to comprehend and make use of this simplicity. Thus I will assume that the reader has taken an introductory course in linear algebra. I do not assume prior acquaintance with the idea of a group.

My choice of topics has been guided primarily by the goal of making the *Tables* intelligible in the span of a few lectures. I have also presented some material that is especially beautiful as well as useful but which is not easy to find elsewhere, including Klein's enumeration of the finite rotation groups of the sphere, Delone's derivation of the Voronoï cells of the three-dimensional lattices, and de Bruijn's construction of the Penrose tiles.

Mathematical crystallography has a rich and interesting history that deserves a book of its own. Historical remarks are clustered in several places throughout this book; all the people who appear in them are identified in Appendix 1.

It is a pleasure to thank the faculty and staff of the Department of Materials Engineering of the Technion for their hospitality. I am also indebted to the members of the Mathematics Department of the University of the Philippines at Diliman, Quezon City, for their hospitality and interest in mathematical crystallography; it was there, in 1987, that the need for a monograph like the present one first became clear to me. I am grateful to Richard Roth, Peter Engel, Louis Michel, Ray Streater, Doris Schattschneider and Richard Ghez for their very helpful comments on the manuscript. Thanks also are due to Richard Ghez and Jim Revill for their enthusiasm and encouragement, and to Jen Halford for her skilful editing and her patience.

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Marjorie Senechal
August 1990

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Chapter 1

Mathematical Crystals

1.1 What is mathematical crystallography?

Many branches of the science of crystals make extensive use of mathematics. For example, mathematical analysis is central to the study of crystal optics and to the interpretation of diffraction patterns. However, for rather obscure historical reasons, *mathematical crystallography* usually means the study of spatial patterns that have properties that make them appropriate models for crystal structure; it has sought to classify both atomic patterns and external forms, to show how they are related to one another, and to predict some of the properties that crystals with these patterns and forms must have.

By 1980, this program seemed to have been achieved. During the nineteenth century, a theory of crystal structure as a modular, repeating pattern had slowly emerged; by 1890 the corresponding catalogue of basic crystalline atomic patterns was complete. Within 25 years, this catalogue, in the form of tables, was widely used in the new field of x-ray crystallography; by the early 1980's, the underlying mathematical ideas had been reformulated and reinterpreted in many different ways and the results stored in large computers. The relation of these patterns to the shapes and properties of ideal crystals was, by that time, also fairly clear. Although many intriguing problems remained unsolved on the theoretical level, it was not anticipated that their solutions would bring with them any major surprises.

But in science there are always surprises. The discovery, in 1984, of crystals which break the symmetry 'rules' of crystallography has prompted a reexamination of the role of crystallography's

most treasured theoretical support, the symmetry group. This will proceed whatever structure quasicrystals are eventually determined to have (as of this writing, August 1990, their structure has not yet been completely deciphered). One direction this reexamination is taking is intensive research in the theory of nonperiodic patterns. If this theory continues to develop along useful lines, the mathematical crystallography of tomorrow may be very different from today's.

Before we try to see where the subject is going, however, it is helpful to see what it is now and where it has been. Our approach to history is inspired by the *Guides Michelin*.

1.2   Un peu d'histoire

In his thoughtful and influential monograph 'Order and Life', J Needham pointed out that 'form is simply a short time-slice of a single spatio-temporal entity'. Needham was speaking of biological form, but the remark is equally applicable to the conceptual forms, or paradigms, which guide our scientific thinking. For example, if you open any contemporary textbook on crystallography, you will find a sentence something like this (see Figure 1.1):

> *The regular shape of crystals suggests that within a crystal atomic building units, congruent to each other, are regularly arranged.*
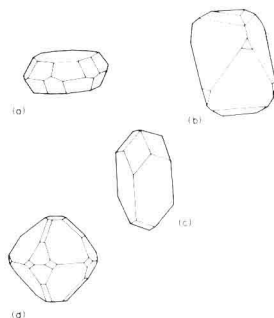

Figure 1.1. What sort of structure do these regular shapes suggest?

However, even a casual study of the history of crystallography shows that the shapes of crystals did not necessarily suggest anything of the sort to our early predecessors. True, Plato had postulated geometric units as the basic forms of the four elements, earth, air, fire and water: to these elements he assigned the cube, the regular octahedron, the regular tetrahedron, and the regular icosahedron (Figure 1.2). These assignments were not entirely arbitrary. In the first place, the octahedron, tetrahedron, and icosahedron are made of identical, equilateral triangles; Plato envisioned that these triangles could be disassociated and regrouped. This would explain, for example, the transition from liquid to steam that water undergoes when it receives a sufficiently large dose of fire. And the assignment of shapes also made some sense: the cube was appropriate for earth particles, since earth sits solidly; the tetrahedron, which has the sharpest corners of the four, was appropriate for fire particles. The octahedron, nice and light, was a good choice for air, while the icosahedron, which is almost spherical, was just the particle for fluids. (Even today it is argued that icosahedral groupings of molecules are fundamental for the structure of liquids and their solid state counterparts, the glasses.)
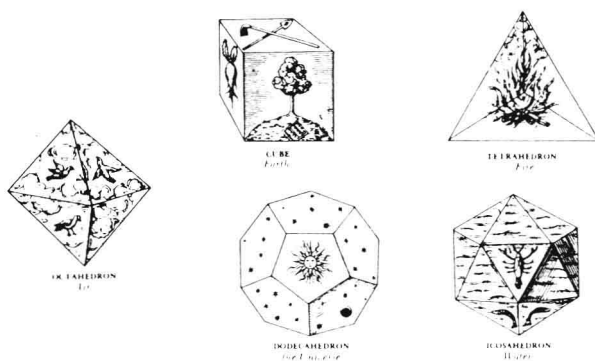
Figure 1.2. Plato assumed that the basic particles of earth, air, fire and water had the forms of regular polyhedra. From Beck, Bleicher, and Crowe, *Excursions into Mathematics*, 1969. Reproduced by permission of Worth Publishers, New York.

Nevertheless, Plato's intriguing hypothesis was persuasively refuted by Aristotle on the grounds that not all of these units could fill space. According to Aristotle, a particulate theory of matter

could only be valid if the units of which matter was composed filled all of space without gaps, because vacua do not exist. This argument, together with the apparent inability of any space-filling model to explain motion, contributed to the demise of this early, more or less atomic, theory of matter.

For centuries thereafter, atomic theory lay dormant, for religious as well as scientific reasons. Instead of focusing on shape, subsequent classification schemes for crystals (until the seventeenth century) included 'virtues' such as talismanic and healing powers, and the imagined 'imitative' characteristics of surface markings. The annals of seventeenth century science are replete with debates about the origin of crystals and fossils (which were not always distinguished). Were they 'sports of nature'? Were they permanently frozen ice? Some argued that crystals were of organic origin. The fact that crystals grow, and in some cases have visible 'veins', was seen by many as evidence that crystal structure is analogous to the structure of plants. As late as the eighteenth century, the great botanist C Linnaeus attempted to extend his successful classification scheme for plants to the mineral kingdom. His distinction between mother and father stones strikes our ears as somewhat curious.

The idea that crystals are modular structures—that is, that they can be represented by aggregations of spheres or polyhedral building blocks (the word *polyhedron* means 'many sides'), was proposed early in the seventeenth century by J Kepler, and again some years later by R Hooke (Figure 1.3) and by N Steno.

Their ideas finally came to fruition early in the nineteenth century in the work of R-J Haüy; perhaps not coincidentally, this was also the time of the rebirth of atomic theory. A highly debatable legend has it that this French abbé accidentally dropped a calcite specimen belonging to a friend; to his dismay, the crystal shattered into tiny pieces. But genius turned disaster into triumph: Haüy noted that the tiny pieces all had the same shape, perfect, identical rhombohedra or groupings of these rhombohedra. This suggested to him that crystals are arrays of subvisible blocks whose shapes were specific to the type of crystal (Figure 1.4).

Haüy showed how the same blocks could be used to construct different shapes; in this way he was able to account for the puzzling fact that crystals of the same substance sometimes have different external forms (Figure 1.5).
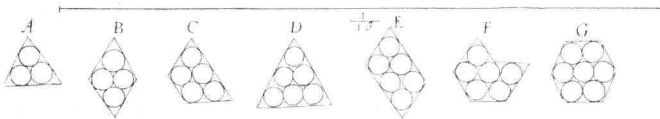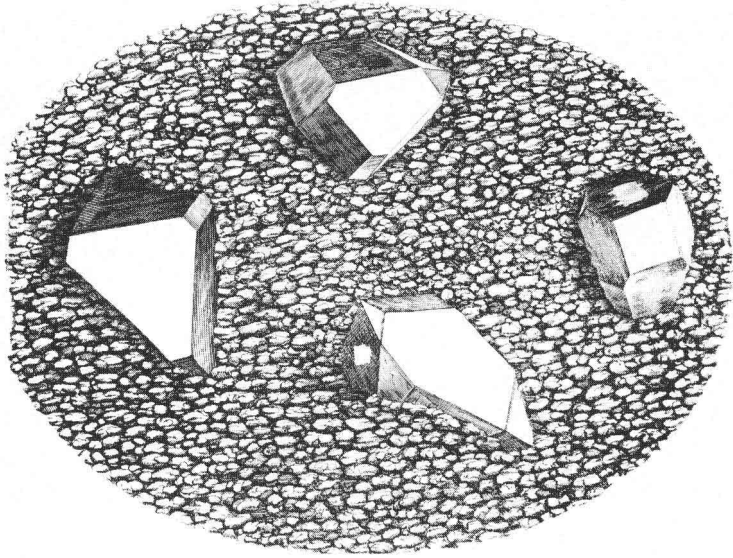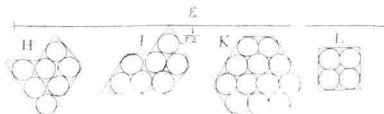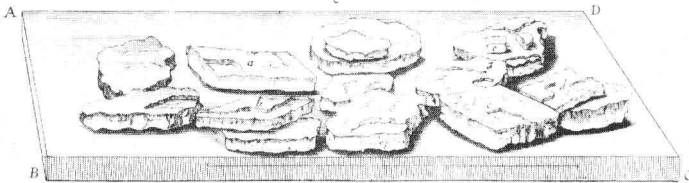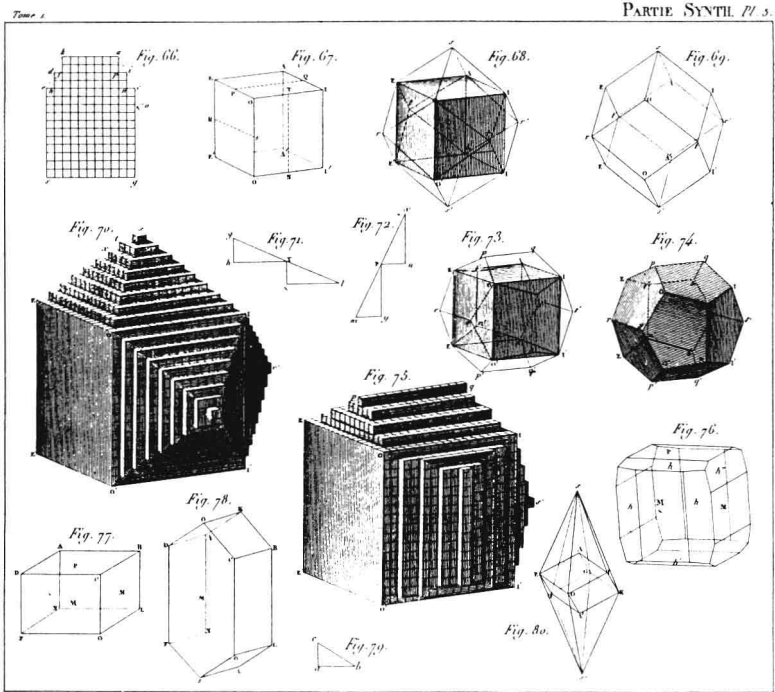
Figure 1.3. 'Had I time and opportunity, I could make probable, that all these regular Figures ... arise onely from three or four several positions of Globular particles.'—Hooke, *Micrographia*, 1665.

Figure 1.4. Haüy's idea of crystal structure. From *Traité de Crystallographie*, 1822.

A good theory restricts: it must explain why, among all possible phenomena, only a certain few occur. Not every polyhedron occurs as a crystal form; it is necessary to explain why the others do not. Haüy realized that his building-block theory had implications for crystal symmetry as the overall shape of a crystal cannot have symmetry which is impossible for its pattern of constituent parts. Like Plato, though for different reasons, Haüy too believed that it is possible to group the basic particles of a crystal into shapes that fill space. This is a severe restriction. For example, among the regular polygons only triangles, squares, and hexagons fill the plane (Figure 1.6); pentagons and polygons with more than six sides do not. In particular, it follows that a repeating pattern of congruent blocks (e.g., a crystal) cannot have five-fold symmetry.
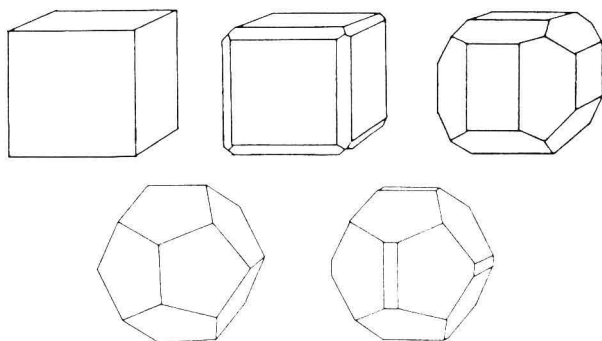
Figure 1.5. Five drawings of pyrite crystals. From V Goldschmidt, *Atlas der Kristallformen*, Carl Winters Universitätsbuchhandlung, Heidelberg, 1913.

(A more rigourous argument will be given later in this chapter.) In three dimensions, the regular icosahedron and dodecahedron have five-fold symmetry; thus Haüy's theory predicts that no crystal can have these shapes. Notice that the dodecahedron in Figure 1.5 is not regular. The 32 classes of symmetry that crystals *can* have were first enumerated in 1826 by M Frankenheim.
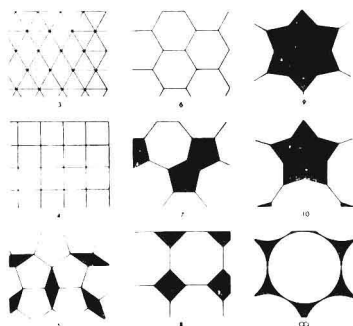
Figure 1.6. Among the regular polygons only triangles, squares, and hexagons fill the plane.

Only after Haüy did it become 'evident' that the regularity of crystal form 'suggests' the regularity of crystal structure. This suggestion generated a great deal of research on 'regular systems of