Symmetry and Physical Properties of Crystals

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Symmetry and Physical Properties of Crystals

Springer

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*In memory of Hubert Curien (1924–2005),
Professor at Pierre & Marie Curie University,
Paris, and member of the French Academy of
Sciences. A great administrator, Minister of
Research in the French government, he shared
his enthusiasm for crystallography with his
students through the courses he gave through-
out his career.*

Foreword

Apart from amorphous bodies such as glasses, the arrangement of ions, atoms and molecules in solid matter is regular and presents properties of symmetry. Crystals present both translational and orientational properties of symmetry, which govern their physical properties. It is because of their triple periodicity that crystals grow with a regular habit: quartz prisms, diamond octahedra or garnet rhomb-dodecahedra, and that they present planar cleavage faces, those of the cube for rock-salt, and those of the rhombohedron for Iceland spar. It is this same periodicity that is at the origin of the band structure of solids and conditions the properties of materials used in microelectronics. It is thanks to the redundancy of the information provided by the diffraction in phase of X-rays, neutrons or electrons, by all the molecular groups repeated by the translations of a crystal that one can determine their atomic structure. If one wishes to find the structure of a complex molecule such as a protein or a virus, one should therefore crystallize it. This is done systematically during the elaboration of drugs by the pharmaceutical industry. The orientational symmetry of crystals is present in all their properties, first of all in their external shape. But it is often because a particular element of symmetry is absent that a property may exist. It is because hydrated ammonium tartrate has no centre of symmetry that it is optically active, which Louis Pasteur associated to its external shape, right or left, thus discovering chirality (1848). It is because of symmetry considerations that the Curie brothers, Jacques and Pierre, looked for, and found, piezoelectricity in 1880. If one cools barium titanate below 120°C, its structure is modified. Above, it is cubic holohedral, below, it is tetragonal, with as its only symmetry elements a four-fold axis and mirrors parallel to that axis. It is this symmetry which makes it possible for a spontaneous electric polarisation to appear, and for the crystal to become pyro- and ferroelectric. Generally speaking, the properties associated to structural phase changes depend on the relations between symmetry groups and their subgroups.

The description of the symmetry operations of crystals and of the resulting physical properties is the aim of the present book. These operations are part of a complex system which was not grasped at once. It was a long way from Aristotle's elements to the concept of space lattice. The ancients were always fascinated by the regularity of six-sided prisms of rock-crystal, as noted by

Pliny the Elder in his *Natural History* (77 A.D.). Kepler (1611), followed by Descartes (1637) and Bartholin (1661) tried to interpret the formation of six-cornered snowflakes by the agglomeration of six spherules round a seventh one. Kepler was the first to describe the primitive and face-centred cubic lattices and the hexagonal lattice, although he did not call them that way. Compact pile-ups were considered similarly by Hooke (1665) and Huygens (1678) to explain the shape of quartz and the cleavage rhombohedron of calcite, respectively. The constancy of interfacial angles was established in the seventeenth and the eighteenth centuries by Steno (1669), Carangeot (1780) and Romé de l'Isle (1783). At the end of the eighteenth century, Bergman (1773) for calcite and Haiiy (1784) in a general way, showed that the external shape of crystal may be obtained by a regular and triply periodic pile-up of identical elemental parallelepipeds, now called unit cells, and called *molécules intégrantes* by Haiiy. But Haiiy confused the unit cell with its chemical content and did not accept the notion of isomorphism introduced by Mitscherlich (1819). His classification of crystals was based on their geometrical shape while that of the German School, led by Weiss (1817), was based on systems of symmetry axes. Haiiy's main merit was nevertheless to have introduced the notion of three-dimensional periodicity which defines the crystalline medium and to have established the geometrical properties of lattice planes by means of the law of simple rational intercepts. The relations between symmetry and properties were established in steps all along the nineteenth century: the 7 crystal systems (Mohs, 1822), the notion of point lattice (Seeber, 1824), the 32 crystal classes (Frankenheim, 1826; Hessel, 1830), the notion of hemihedry (Delafosse, 1840), molecular chirality (Pasteur, 1848), the 14 Bravais lattices (1850), groups of motion including helicoidal motions, the 65 chiral groups (Sohncke 1865), and, finally, the 230 space groups (Fedorov, 1890; Schoenflies, 1891; Barlow, 1894).¹

The description of physical properties in their geometrical form requires in general other mathematical tools, such as tensors, which were first introduced in elasticity by Voigt (1899) and Brillouin (1949). If one pulls a rod made of an isotropic material, its length increases and its cross-section decreases. A scalar is insufficient to describe the response of the material to an excitation and two constants are necessary to describe the resulting deformation. Similarly, the polarisation of an anisotropic dielectric can only be expressed by way of a tensor.

The book by Cécile Malgrange, Christian Ricolleau and Michel Schlenker is an extended translation of a first version in French by Cécile Malgrange, Christian Ricolleau and Françoise Lefauchaux. It comprises three parts of roughly equal importance: 1) a first part on crystal symmetry, symmetry operations, crystal lattices, point groups and space groups; 2) a second part on crystal anisotropy and tensors applied to elasticity, propagation of elastic waves in crystals and piezoelectricity; 3) a third one on the optical properties of crystals, polariza-

1. A. Authier, *Early Days of X-Ray Crystallography* (Oxford University Press, Oxford, 2013)

tion, optical activity and electro-optical effects. The various types of chemical bonds are also described in a small chapter between the first and the second parts. Most chapters include an annex on a particular topic related to one of the points developed in the chapter, aimed at exciting the curiosity of the reader, and these complements are a real added value to the book. Exercises are also included, the solutions of which are given at the end of the book. They constitute a very valuable pedagogical tool. The whole of the book is written in a very clear and rigorous way.

The publication of a new, up-to-date, textbook of crystallography and crystal physics will be very welcome at a time when crystallography courses are disappearing in most universities throughout the world, although these disciplines represent basic knowledge compulsory for anyone doing material science, Earth science, biochemistry, solid state physics or chemistry.

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Preface

Crystallography constantly enjoys a new youth, thanks in particular to the spectacular progress in X-ray sources (synchrotron radiation from dedicated facilities and, very recently, free electron X-ray lasers), which make it possible to investigate an extremely broad range of materials. Its contribution is vital in many scientific and technological areas. It makes it possible, for example, to understand, and even to predict the properties of materials as diverse as high- T_c superconductors, high performance magnets, or biological materials such as proteins. The pharmaceutical industry invests large funds to set up data banks of structures, determined in the crystallized state, of molecules which could become medicines, in order to correlate their configuration to their healing action. Crystallography also is very important in nanoscience, since some materials, when prepared in the form of nano-objects, take on crystal structures which do not exist in the bulk and which necessarily affect their physical and chemical properties. Geophysicists obtain major information about the Earth mantle by investigating crystallized materials under extreme temperature and pressure conditions. In technology, we must mention structural wonders such as thin film based artificial crystals (multilayers and superlattices) of semiconductors or magnetic materials. These have for several years been present in the giant or tunnel magnetoresistance read heads of the hard drives in all our computers.

On the other hand, understanding the relation between the structure and the macroscopic properties of crystals opens the way to the use of physical properties with many applications. Thus piezoelectricity, *i.e.* the production of an electrical voltage under the effect of stress, is the basis of our quartz watches and plays a central role in cell phones. Electro-optical effects, the change in refractive indices under the effect of an electric field, entail a change in light propagation in materials.

This book is mostly a translation of *Symétrie et propriétés physiques des cristaux*, published by EDP Sciences, Orsay, France in 2011. It provides the fundamentals underpinning all these research and application areas.

In the first part, it describes in a clear and thorough way the periodicity of crystals and their symmetry, both at the microscopic level (space groups) and at the macroscopic level (point groups). It includes a presentation of the crystallography of two-dimensional systems such as surfaces and interfaces.

The second part is dedicated to various physical properties of crystals. They are described in the tensor formalism which is natural for them, emphasizing their link with crystal symmetry. We show in particular how a given property is allowed or forbidden by various crystal symmetries, and how the coefficients of the characteristic tensor are related for the various point groups. We deal not only with basic properties such as elasticity and birefringence, but also with properties which are less often dealt with, such as piezoelectricity, optical activity or the electro-optical effects.

Each chapter starts with a short presentation of its contents, and almost all chapters are complemented by exercises through which the notions introduced can be concretely applied, and thus mastered. For these exercises to be a real studying tool, the solutions are explicitly given as a final separate Chapter 20.

Many of the chapters also include a brief complement, intended to give a glimpse into an area related to that of the chapter and to whet the reader's scientific appetite, for example on how and what for crystals are grown, with what probes crystal structures can be determined, etc.

This book originates in courses we gave at Paris Diderot University and at Grenoble Institute of Technology, France. It is aimed, with no special prerequisite, at students in crystallography, physics and engineering (especially materials science and electrical engineering) curricula, and at PhD students. It should also be a reference book for researchers and engineers involved, in their daily activity, in the properties of crystals.

The authors sincerely thank the five members of the Advisory Editorial Committee for their very valuable suggestions, the vast majority of which were followed. They are also very grateful to Professor André Authier for writing the Foreword, which actually is a very informative chapter on the history of crystallography.

The authors intend to correct the mistakes and typos which will, in spite of their efforts, have remained in this first edition. Errata sheets will be provided at

<https://grenoble-sciences.ujf-grenoble.fr/ouvrage/symmetry-crystals>

Comments from readers are very welcome. Please write to

symmetry-book@imPMC.upmc.fr

Cécile Malgrange,
Christian Ricolleau,
Michel Schlenker.

Table of symbols

$\mathbf{a}, \mathbf{b}, \mathbf{c}$	Basis vectors of the unit cell in direct space
a, b, c	Lengths of the basis vectors of the unit cell in direct space
$\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$	Basis vectors of the reciprocal unit cell
a^*, b^*, c^*	Lengths of the basis vectors of the reciprocal unit cell
v_0	Volume of the direct unit cell
v_0^*	Volume of the reciprocal unit cell
$[uvw]$	Lattice row parallel to the vector $u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$
$\langle uvw \rangle$	Set of lattice rows equivalent to $[uvw]$ through all the symmetry operations of the crystal group
(hkl)	Family of lattice planes with Miller indices h, k and l
$(hkil)$	Family of lattice planes with Miller indices h, k, i and l for a hexagonal lattice
$\{hkl\}$	Set of lattice planes equivalent to (hkl) through the symmetry operations of the crystal group
$\{hkil\}$	Set of lattice planes equivalent to $(hkil)$ through the symmetry operations of the crystal group, for a hexagonal lattice
d_{hkl}	Distance between two neighboring (hkl) lattice planes, <i>i.e.</i> the lattice spacing of family (hkl)
$\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$	Basis vectors of an orthonormal frame
$\{M_{ij}\}$	The matrix for which M_{ij} is the coefficient located on the i -th row and the j -th column
$\{a_{ij}\} = A$	Transition matrix for going over from an orthonormal frame to another one
$\mathbf{V}$	Polar vector
$\mathbf{\hat{V}}$	Axial vector
$[T]$	Tensor
T_{ij}	Components, in a given orthonormal axis system, of a rank-2 tensor $[T]$. The associated matrix is noted T .
T_{ijk}	Components, in a given orthonormal axis system, of a rank-3 tensor $[T]$

e_{ij}	Components of the tensor of displacement gradients, or distortion tensor, $[e]$
T	The set of the crystal lattice translations
G_s	Space group
G_p	Point group
$[S], S_{ij}$	Strain tensor, and its components
$[T], T_{ij}$	Stress tensor, and its components
S_α, T_α	Contracted notation (Voigt's notation) for the tensors $[S]$ and $[T]$. α ranges from 1 to 6, so that the components of these tensors form column vectors with 6 rows.
$[s], s_{ijkl}$	Compliance tensor, and its components
$[c], c_{ijkl}$	Stiffness tensor, and its components
Θ	Temperature
S	Entropy
$\mathbf{E}$	Electric field
$\mathbf{D}$	Electric induction
$\mathbf{P}$	Polarization
$[\varepsilon], \varepsilon_{ij}$	Relative permittivity (or dielectric constant) tensor, and its components
ε_0	Permittivity (or dielectric constant) of vacuum
$[\eta], \eta_{ij}$	Electric impermeability tensor, and its components
δ_{ij}	Kronecker symbol
δ_{ijk}	Levi-Civita, or permutation, tensor
$[G], G_{ij}$	Gyration tensor, and its components
$[d], d_{ijk}$	Piezoelectric tensor, and its components
$[r], r_{ijk}$	Linear electro-optic tensor, or Pockels tensor, and its components
$[z], z_{ijkl}$	Quadratic electro-optic tensor, or Kerr tensor, and its components
$[p], p_{ijkl}$	Elasto-optic tensor and its components
$[\pi], \pi_{ijkl}$	Piezo-optic tensor and its components

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