Siegfried Haussühl
Physical Properties of Crystals

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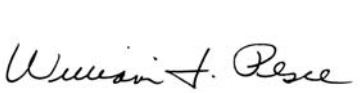

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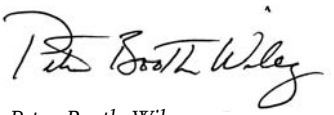

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Physical Properties of Crystals

An Introduction

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Preface

With the discovery of the directional dependence of elastic and optical phenomena in the early 19th century, the special nature of the physical behavior of crystalline bodies entered the consciousness of the natural scientist. The beauty and elegance, especially of the crystal-optical laws, fascinated all outstanding physicists for over a century. For the founders of theoretical physics, such as, for example, Franz Neumann (1798-1895), the observations on crystals opened the door to a hidden world of multifaceted phenomena. F. Pockels (1906) and W. Voigt (1910) created, with their works *Lehrbuch der Kristalloptik* (Textbook of Crystal Optics) and *Lehrbuch der Kristallphysik* (Textbook of Crystal Physics), respectively, the foundation for theoretical and experimental crystal physics. The development of lattice theory by M. Born, presented with other outstanding contributions in Volume XXIV of *Handbuch der Physik* (Handbook of Physics, 1933), gave the impetus for the atomistic and quantum theoretical interpretation of crystal-physical properties. In the shadow of the magnificent success of spectroscopy and structural analysis, further development of crystal physics took place without any major new highlights. The application of tensor calculus and group theory in fields characterized by symmetry properties brought about new ideas and concepts. A certain completion in the theoretical representation of the optical and elastic properties was achieved relatively early. However, a quantitative interpretation from atomistic and structural details is, even today, only realized to a satisfactory extent for crystals with simple structures. The technological application and the further development of crystal physics in this century received decisive impulses through the following three important discoveries: 1. High-frequency techniques with the use of piezoelectric crystals for the construction of frequency determining devices and in ultrasound technology. 2. Semiconductor techniques with the development of transistors and integrated circuits based on crystalline devices with broad applications in high-frequency technology and in the fields of information transmission as well as computer technology. 3. Laser techniques with its many applications, in particular, in the fields of optical measurement techniques, chemical analysis, materials processing, surgery,

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and, not least, the miniaturization of information transmission with optical equipment.

In many other areas, revolutionary advances were made by using crystals, for example, in radiation detectors through the utilization of the pyroelectric effect, in fully automatic chemical analysis based on X-ray fluorescence spectroscopy, in hard materials applications, and in the construction of optical and electronic devices to provide time-delayed signals with the help of surface acoustic waves. Of current interest is the application of crystals for the various possibilities of converting solar energy into electrical energy. It is no wonder that such a spectrum of applications has broken the predominance of pure science in our physics institutes in favor of an engineering-type and practical-oriented research and teaching over the last 20 years. While even up to the middle of the century the field of crystallography-apart from the research centers of metal physics-mainly resided in mineralogical institutes, we now have the situation where crystallographic disciplines have been largely consumed by physics, chemistry, and physical chemistry. In conjunction with this was a tumultuous upsurge in crystal physics on a scale which had not been seen before. With an over 100-fold growth potential in personnel and equipment, crystal physics today, compared with the situation around 1950, has an entirely different status in scientific research and also in the economic importance of the technological advances arising from it. What is the current state of knowledge, and what do the future possibilities of crystal physics hold? First of all some numerical facts: of the approximately 45,000 currently known crystallized substances with defined chemical constituents and known structure, we only have a very small number (a few hundred) of crystal types whose physical properties may largely be considered as completely known. Many properties, such as, for example, the higher electric and magnetic effects, the behaviour under extreme temperature and pressure conditions and the simultaneous interplay of several effects, have until now-if at all-only been studied on very few crystal types. Apart from working on data of long known substances, the prospective material scientist can expect highly interesting work over the next few decades with regard to the search for new crystal types with extreme and novel properties. The book *Kristallphysik* (Crystal Physics) is intended to provide the ground work for the understanding of the distinctiveness of crystalline substances, to bring closer the phenomenological aspects under the influence of symmetry and also to highlight practical considerations for the observation and measurement of the properties. Knowledge of simple physical definitions and laws is presumed as well as certain crystallographic fundamentals, as found, for example, in the books *Kristallgeometrie* (Crystal Geometry) and *Kristallstrukturbestimmung* (Crystal Structure Determination). The enormous amount of material in the realm of crystal physics can, of course, only be covered here in an exemplary way by making certain

choices. Fields in which the crystal-specific anisotropy effects remain in the background, such as, for example, the semiconductors and superconductors, are not considered in this book. A sufficient amount of literature already exists for these topics. Also the issue of inhomogeneous crystalline preparations and the inhomogeneous external effects could not be discussed here. Boundary properties as well as the influence of defects connected with growth mechanisms will be first discussed in the volume *Kristallwachstum* (Crystal Growth). The approaches to the structural interpretation of crystal properties based on lattice theory were only touched on in this book. The necessary space for this subject is provided in the volume *Kristallchemie* (Crystal Chemistry) as well as thermodynamic and crystal-chemical aspects of stability. A chapter on methods of preparation is presented at the beginning, which is intended to introduce the experimenter to practical work with crystals. We clearly focus on the problem of orientation with the introduction of a fixed "crystal-physical" reference system in the crystal. For years a well-established teaching method of separating the physical quantities into inducing and induced quantities has been taken over. The connection between these allows a clear definition of the notion of "property." The properties are classified according to the categories "tensorial" and "nontensorial, " whereby such properties which can be directly calculated from tensorial properties, such as, for example, light or sound velocity, can be classified as "derived tensorial" properties. A large amount of space is devoted to the introduction of tensor calculus as far as it is required for the treatment of crystal-physical problems. Important properties of tensors are made accessible to measurement with the intuitive concepts of "longitudinal effect" and "transverse effect." The treatment of group theoretical methods is mainly directed towards a few typical applications, in order to demonstrate the attractiveness and the efficiency of this wonderful tool and thus to arouse interest for further studies. The reader is strongly recommended to work through the exercises. The annex presents tables of proven standard values for a number of properties of selected crystal types. References to tables and further literature are intended to broaden and consolidate the fields treated in this book as well as helping in locating available data. My special thanks go to Dr. P. Preu for his careful and critical reading of the complete text and his untiring help in the production of the figures. A. Möws through her exemplary service on the typewriter was of great support in completion of the manuscript. Finally, I would also like to express my thanks to the people of Chemie Verlag, especially Dr. G. Giesler, for their understanding and pleasant cooperation.

Cologne, summer 1983 *S. Haussühl*

Preface to the English Edition

In the first edition of *Kristallphysik* it was assumed that the reader possessed basic knowledge of crystallography and was familiar with the mathematical tools as well as with simple optical and X-ray methods. The books *Kristallgeometrie* (Crystal Geometry) and *Kristallstrukturbestimmung* (Crystal Structure Determination), both of which have as yet only been published in German, provided the required introduction. The terms and symbols used in these texts have been adopted in Crystal Physics. In order to present to the reader of the English translation the necessary background, a chapter on the basics of crystallography has been prefixed to the former text. The detailed proofs found in Kristallgeometrie (Crystal Geometry) and Kristallstrukturbestimmung (Crystal Structure Determination) were not repeated. Of course, other books on crystallography are available which provide an introduction to the subject matter. Incidentally, may I refer to the preface of the first edition. The present text emerges from a revised and many times amended new formulation. Some proofs where I have given the reader a little help have been made more accessible by additional references. Furthermore, I have included some short sections on new developments, such as, for example, the resonant ultrasound spectroscopy (RUS) method as well as some sections on the interpretation of physical properties. This last measure seemed to make sense because I decided not to bring to print the volumes *Kristallchemie* (Crystal Chemistry) and *Kristallzüchtung* (Crystal Growth) announced in the first edition, although their preparations were at an advanced stage. An important aspect for this decision was that in the meantime several comprehensive and attractive expositions of both subjects appeared and there was therefore no reason, alone from the scope of the work, to publish an equivalent exposition in the form of a book. In addition, the requirement to actualize and evaluate anew the rapid increase in crystallographic data in ever shorter time intervals played a decisive role in my decision. The same applies to the experimental and theoretical areas of crystal growth. Hence, the long-term benefit of an all too condensed representation of these subjects is questionable. In contrast, it is hoped that the fundamentals treated in the three books published so far will provide a sufficient basis for crystallographic training for a long time to come. I thank Dr. Jürgen Schreuer, Frankfurt, for his many stimulating suggestions with respect to the new formulation of the text. In particular, he compiled the electronic text for which I owe him my deepest gratitude. Finally, I wish to thank Vera Palmer of Wiley-VCH for her cooperation in the publishing of this book.

Siegfried Haussühl