PHYSICAL PROPERTIES OF CRYSTALS

THEIR REPRESENTATION BY TENSORS AND MATRICES

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PREFACE TO FIRST EDITION

THE purpose of this textbook is to formulate the physical properties of crystals systematically in tensor notation—to explain what the tensors are, and how they are used. The book is not concerned with the explanation of particular crystal properties in terms of structure; it aims rather at a unified presentation of the tensor properties in terms of two themes: the common mathematical basis of the properties, and the thermodynamical relations between them.

The plan has been to start with the mathematical groundwork, treating at first tensors up to the second rank only—this forms Part 1—and then to show how the various properties in turn find their places within the tensor scheme. Tensors of higher rank than the second, and matrix methods, are introduced later as natural developments of the theory. This mathematical arrangement of the properties goes hand in hand with a threefold division on a thermodynamical and optical basis represented by Parts 2, 3, and 4.

The book originated in a course in crystal physics given by the author at Cambridge to second-year undergraduates reading crystallography (as part of the main subject Mineralogy and Crystallography) in Part I of the Natural Sciences Tripos. The level of treatment is, for the most part, well within the grasp of honours students in physics in their second or later years; but the author has also had in mind the post-graduate student, and the research worker in solid-state physics or metallurgy who needs an introductory text on the use of tensors and matrices in his subject. The mathematics has been kept as simple as possible, particularly in the early chapters where the tensor notation and the formal manipulations are explained in detail. The reader who already knows something of crystal symmetry will be at an advantage, but the essential symmetry theory needed for following the argument is summarized in an appendix. The chapter on thermoelectricity may be found a little more difficult than the others; it was not possible to give a satisfactory treatment of thermoelectricity at the level of the rest of the book—and yet the property fits so naturally into the systematic development that it seemed right to include it.

The references to published work are not intended to be complete: they are simply pointers to further reading and acknowledgements of sources.

The rationalized metre-kilogram-second system of units is used

throughout. It was chosen primarily because it is a rationalized system, and thereby avoids the awkward factors of 4π which otherwise spoil the simplicity of many of the electrical and magnetic formulae. Any rationalized system would have served, but the well-known special advantages of the m.k.s. system, and its growing acceptance by physicists, made it an obvious choice.

I have the pleasant task of expressing my gratitude to Dr. R. C. Evans and Dr. N. F. M. Henry, of the Department of Mineralogy and Petrology at Cambridge, for encouraging me to write this book, and for criticizing in detail the first drafts of all the chapters. Their advice has been of the greatest assistance at all times. I have also to thank the other friends and colleagues who have read and commented upon the manuscript: Professor F. C. Frank, F.R.S. (for reading Chapters I to X), Professor K. Lonsdale, F.R.S. (for reading the first drafts of Chapters I, II, III, VIII and IX), and Sir Edward Bullard, F.R.S. Dr. D. Polder has helped me with Chapter XII and Dr. F. G. Fumi with Chapter XIV. The book was begun while I was on the staff of Bell Telephone Laboratories, Murray Hill, New Jersey, and I appreciate very much the generous co-operation I received there. Three colleagues at Murray Hill gave me particular help: Mr. W. L. Bond, who showed me his unpublished 'least-squares octagonal-disc' method and supplied the numerical illustrations of matrix methods in § 7 of Chapter IX; Dr. A. N. Holden, who likewise gave me the use of unpublished work, reproduced in the *résumé* on pp. 181–2, and who read Chapter X; and Dr. Conyers Herring, who helped me with the troublesome subject of magnetic and electrical energy.

The dot-and-ring notation used for showing the form of the crystal-property matrices in the thirty-two crystal classes is taken, with slight variations, from the unpublished *Manual of Piezoelectric Data* by K. S. Van Dyke and G. D. Gordon, by kind permission of the authors.

Some of the exercises distributed through the book have been taken or adapted, by permission, from the collections used by the teaching staff of the Department of Mineralogy and Petrology at Cambridge, to whom I tender my thanks.

In referring to the department of which I was formerly a member, I should like to acknowledge my particular debt to Dr. W. A. Wooster, for the present book is an outcome of the interest aroused by the course which he initiated there.

J. F. N.

Bristol
July 1955

PREFACE TO THE 1985 EDITION

SINCE the first edition of this book artificial crystals of many more substances have been successfully grown, and study of their physical properties has produced a formidably extensive literature. For example, Landolt-Börnstein lists some 4700 references on the properties of the elastic dielectric alone, and that was six years ago. There has been great progress on the atomistic and experimental sides, but amidst all this activity the principles of the macroscopic continuum treatment of the subject have remained the same, and that is why it now seems worthwhile to produce this new edition.

The only change in the main text worth special note concerns the role of body-torques in the formulation of elasticity and related properties, the confusion that previously surrounded this topic having now cleared away. At the same time I have taken the opportunity of adding at the end of the book an up-to-date bibliography with notes, which I hope may serve as an indication of the main new developments that have taken place in the subject. I thank Dr. J. W. Steeds and Professor F. G. Fumi for their ready help in guiding me to relevant literature.

J. F. N.

Physics Department
University of Bristol
April 1984

NOTATION

ORDINARY letters in bold-face type, $\mathbf{P}$, $\mathbf{h}$, etc., denote vectors.

Bold sans serif letters, P, h, etc., and bold Greek letters, $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$, etc., denote matrices.

The range of values of all letter suffixes is 1, 2, 3 unless some other range is specified.

INTRODUCTION

THE physical properties of crystals are defined by relations between measurable quantities. Density, for example, is defined from a relation between mass and volume. Now both mass and volume may be measured without reference to direction, and, accordingly, density is a property that does not depend on direction. On the other hand, a crystal property such as electrical conductivity is defined as a relation between two measurable quantities (the electric field and the current density) both of which have to be specified in direction as well as in magnitude. We therefore have to allow for the possibility that a physical property of this sort will depend upon the direction in which it is measured—and, as an experimental fact, the electrical conductivity of many crystals does indeed vary with direction. In such cases the crystals are said to be *anisotropic* for the property in question.

The problem then arises of how to specify the value of a crystal property that can depend upon direction—clearly, a single number will not suffice. There is also the problem of how the specification, when we have it, is related to the symmetry of the crystal. The answers to these two questions, and some of their implications, form the subject of this book.

Electrical conductivity is one of many crystal properties that can depend upon the direction of measurement. A few further examples are: the flow of heat produced by a temperature gradient (thermal conductivity); the polarization produced in a dielectric by an electric field (dielectric susceptibility); the polarization of a crystal that may be produced by mechanical stress (piezoelectricity); the deformation caused by a mechanical stress (elasticity); and the birefringence that can be set up by an electric field (electro-optical effect) or by a stress (photoelastic effect).

For a few properties, such as density, all crystals are isotropic. Cubic crystals happen to be isotropic for certain other properties as well, such as conductivity and refractive index, and this sometimes leads to the misconception that they are isotropic for all properties. Nevertheless, the symmetry elements of a cubic crystal are not the same as those of a completely isotropic body, and, in fact, cubic crystals are anisotropic, often markedly so, for elasticity, photoelasticity, and certain other properties. We must therefore regard cubic crystals as

potentially anisotropic, and then we can go on to prove that, for *certain* properties, they are isotropic. All crystals are anisotropic for some of their properties.

In this book, then, we study how to specify the physical properties of crystals; a large number of the properties are represented by mathematical quantities called *tensors*, and only these properties will concern us. A list of them is given in Appendix C; to help put the subject in proper perspective a further list is given there of some other properties that are not directly represented by tensors. It is, of course, part of the task of physics to explain the values of these tensors for any particular crystal in terms of its atomic and crystalline structure. That is, in a sense, the next stage. Here we are less ambitious; we concern ourselves more with the form and general significance of the tensors than with their actual numerical values. For our purpose it will be sufficient to regard a crystal as simply an anisotropic continuum, without structure, having certain properties of symmetry. Moreover, except in dealing with one property, namely thermoelectricity, we shall assume *homogeneity*: that the properties of a crystal are the same at all points.

Plan of the book

Tensors are classified by their *rank*. Chapter I introduces the concept of a tensor and shows how tensors of zero, first and second rank may be used for studying crystal properties. Chapter II continues the mathematical development. In Chapters III to VI the tensor method is applied to various physical properties in turn; then, in Chapters VII and VIII, tensors of the third and fourth rank are introduced and are used for representing piezoelectricity and elasticity. Chapter IX describes the alternative method of representing crystal properties by matrices, a technique which is particularly useful for carrying out numerical calculations. All the properties dealt with up to this point are describable by reference to equilibrium states and thermodynamically reversible changes; a unified treatment of the properties and their thermodynamical inter-relations is given in Chapter X. In Chapters XI and XII we pass on to conduction and thermoelectricity; these are treated after the equilibrium properties, because, being transport phenomena, they are irreversible and their thermodynamics needs special consideration. The two final chapters, XIII and XIV, are devoted to crystal optics, and especially to the electro-optical effect, photoelasticity and optical activity.

Selection for first reading

For a first reading of the book the following selection, which is more or less self-contained, is suggested.

Chapter I.	The groundwork of crystal physics
Chapter III.	Paramagnetic and diamagnetic susceptibility
Chapter IV.	Electric polarization
Chapter V.	The stress tensor
Chapter VI.	The strain tensor and thermal expansion
Chapter VII.	Piezoelectricity. Third-rank tensors
Chapter VIII.	Elasticity. Fourth-rank tensors
Chapter XI.	Thermal and electrical conductivity (up to the end of § 4)

CONTENTS

NOTE

FIG. 13.7 is reproduced, by permission, from Hartshorne and Stuart's *Crystals and the polarising microscope* (Edward Arnold (Publishers) Ltd.).

PART 1

GENERAL PRINCIPLES

I

THE GROUNDWORK OF CRYSTAL PHYSICS

1. Scalars, vectors and tensors of the second rank

(i) *Scalars.* In physics we are accustomed to dealing with certain quantities, such as the density or the temperature of a body, which are not connected in any way with direction. With the usual definitions of density and temperature it is meaningless to speak of measuring these quantities in any particular direction. Such non-directional physical quantities are called *scalars*, and we note that the value of a scalar is completely specified by giving a single number. For a reason that will appear later, a scalar is also called a *tensor of zero rank.*

(ii) *Vectors.* In contrast to scalars there are physical quantities of a different type, called *vectors*, which can only be defined with reference to directions. Mechanical force is a well-known example. To specify completely a force acting at a point we need to give both its magnitude and its direction. It may be conveniently represented by an arrow of definite length and direction. Other examples of vectors are: the strength of an electric field at a point, the moment of a magnetic dipole, and the temperature gradient at a point. In this book we denote vectors by bold-face type: thus $\mathbf{E}$ denotes the strength of an electric field at a point. The magnitude, or length, of a vector $\mathbf{p}$ is denoted by p.

As an alternative to specifying a vector by giving its magnitude and direction we may, instead, choose three mutually perpendicular axes Ox_1, Ox_2, Ox_3 and give the *components* of the vector along them. The components are simply the projections of the vector on the axes. If the components of $\mathbf{E}$ are E_1, E_2, E_3, we write

$$\mathbf{E} = [E_1, E_2, E_3].$$

Thus, when the axes of reference have been chosen, a vector is completely specified by giving the values of its three components along the axes. For a reason that will appear later, a vector is also called a *tensor of the first rank.*

The methods of manipulation of vectors form the subject of *vector analysis.* We shall not have to use this much in what follows, but we shall occasionally draw on it. It will be assumed that the reader is already familiar with the notions of scalar and vector product, the